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Thermally/Mechanically Responsive Polymeric Composites with Shape Memory/Self-Healing Properties

Hossein Birjandi Nejad
Syracuse University

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Thermally/Mechanically Responsive Polymeric Composites with Shape Memory/Self-Healing Properties

Abstract

By

Hossein Birjandi Nejad

Smart materials with the ability to respond to external stimulus have attracted tremendous attention in both academic institutions and industry\(^1\). Such unique aspect of these materials make them great candidates to address current challenges in the world of Materials Science including those that no human intervention is a necessity. The objective of this dissertation is to employ different techniques to develop novel thermally and mechanically responsive polymeric composites for several industrial applications.

In Chapter 2, the curing kinetics and polymerization induced phase separation (PIPS) of an epoxy matrix with and without a semicrystalline thermoplastic was investigated. Same PIPS technique studied in this chapter was utilized in the following chapters to develop composites featuring triple shape memory and self-healing properties as we now describe.

In Chapter 3, we report an investigation into the preparation and characterization of shape memory assisted self-healing (SMASH) coatings utilizing shape memory (SM) response of a glassy amorphous epoxy matrix and rebonding the crack by a low melt-viscosity thermoplastic. Note that same materials and polymerization induced phase separation (PIPS) technique as in Chapter 2 was employed in this chapter.

Seeking to develop a simpler method to fabricate composites featuring SMASH, we successfully designed a setup for dual-electrospinning two immiscible polymers in Chapter 5. Specifically
Poly(vinyl acetate) (PVAc) and poly(ε-caprolactone) (PCL) solutions were dual-electrospun to fabricate composites featuring shape memory assisted self-healing (SMASH) and SM properties. The resulting material was capable of restoring its shape and mechanical properties with a simple thermal trigger.

Continuing on the subject of “Self-Healing”, fiber reinforced composites (FRCs) in which the healing agent was encapsulated in polymeric fibers and released upon fracture were developed and studied in Chapter 4. Unique core-sheath fibers featuring stiff polyacrylonitrile (PAN) in the sheath and epoxy based self-healing agents in the core were fabricated by coaxial electrospinning. Upon damage, fibers break and the healing agent would flow to the damage site and polymerize to restore the mechanical properties of the composites. The proposed FRCs will lead to a cost-effective and much more durable composite structure capable of withstanding loads that would otherwise fail due to lack of proper reinforcement.

Chapter 6 then represents a novel strategy exploiting organic based layered double hydroxides (LDHs) to enhance mechanical and barrier properties of tire rubber-LDH composites. Pneumatic tires are composite structures inflated with pressurized gas to provide weight support, shock absorbance and traction transmission for an automotive. Therefore, developing tires that can hold inflation pressure for an extensive period of time is of great interest in auto industry. This was achieved by nano-exfoliation of the organic based LDHs in tire rubber. The relationship between microstructure and mechanical properties of such composites were investigated in this chapter.

In the case of “Shape Memory”, Chapter 7 will focus on fabrication of triple shape memory composites featuring a semicrystalline thermoplastic and an amorphous epoxy. Such composites utilize polymerization induced phase separation (PIPS) (introduced in Chapter 2) and exhibit two distinct transition temperatures required for triple shape memory behavior. This study explores the
relationships between the morphology of triple shape memory polymers and their shape memory characteristics.

Finally, Chapter 8 explores for the first time design, preparation, and characterization of triple shape memory polymeric foams that is open cell in nature and features a two phase, crosslinked SMP with a glass transition temperature of one phase at a temperature lower than a melting transition of the second phase. The soft materials were observed to feature high fidelity, repeatable triple shape behavior, characterized in compression and demonstrated for complex deployment by fixing a combination of foam compression and bending. We further explored the wettability of the foams, revealing composition-dependent behavior favorable for future work in biomedical investigations.

It is noteworthy that all the aforementioned materials and methods exhibit great potential for industrial applications considering their simplicity and low manufacturing costs. Beside, future work is required for each project some of which are listed at the end of each chapter.

References

Thermally/Mechanically Responsive Polymeric Composites with Shape Memory/Self-Healing Properties

By

Hossein Birjandi Nejad

B.S. Tehran University, 2010

DISSERTATION

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May 2015
To my Parents, Mohammadali & Ehteram,

Without whom none of my achievements would be possible
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Triple Shape Memory Foams (Chapter 8) and Triple Shape Memory Films (Chapter 7), respectively. I am grateful of all the present and past members of MRG particularly Dr. Ryan Tappel, Dr. Eric Finkesltein (SBI facility lab manager), Dr. Erika Rodrigues and my dear friend, Chris Iversen. I would also like to thank undergraduate researchers who have significantly contributed to this work: Katie Garrison, James Sutton, Arman Shahriar, Sarah McCandless and Danny Rich. Thank you for your collaborations, support and brainstorming.

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Table 7-1. Summary of thermal properties determined from DSC experiments. Melting transitions were determined as the middle point of the transitions of the second heating runs.

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**Table 8-2.** Fixing and recovery ratios calculated using one-step and two-step shape memory cycles to demonstrate the triple-shape memory. --: Not applicable.

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**Scheme 1-1.** Classification of polymers based on their structure and mechanical properties. Crosslinked polymers are generally amorphous and recognized as elastomers, those that are rubbery or thermosets, those that are rigid at ambient conditions. Thermoplastics (linear polymers) can be amorphous or semicrystalline and typically are considered tough (high strain to failure and higher modulus than elastomers) above their glass transition temperature and below melting transition.

**Scheme 1-2.** Schematic illustration of the self-healing process introduced by White and colleagues. (A) The self-healing agent is encapsulated in microcapsules embedded in a matrix containing catalyst. Note that the self-healing agent and catalyst polymerize upon contact at RT. (B) Damage ruptures the microcapsule allowing the self-healing agent to flow out of the microcapsule, into the damage site. (C) The self-healing agent polymerizes at the site of damage in the presence of catalyst to recover the mechanical properties of the composite. Adopted with permission from [White, S. R.; Sottos, N.; Geubelle, P.; Moore, J.; Kessler, M. R.; Sriram, S.; Brown, E.; Viswanathan, S.; *Nature* 2001, 409, 794-797.].

**Scheme 1-3.** Schematic illustration for preparation of PCL/Sylgard composite. PCL fibers were first electrospun to fabricate a porous nano-scale fiber mat. The fiber mat was then imbedded in an uncured Sylgard resin where Sylgard infiltrated into PCL fibers under vacuum. The PCL/Sylgard composite was then cured to yield a composite featuring 3 separate transitions attributed to the glass transition of Sylgard, glass transition of PCL and melting transition of PCL. Adopted with permission from [Luo, X.; Mather P.T.; *Macromolecules* 2009, 42, 7251-7253.].

**Scheme 1-4.** Schematic illustration of a two-step method to characterize TSMPs. To deform the first temporary shape, the material is heated above its higher transition temperature ($T_{H}$), deformed and then cooled below its $T_{H}$ to fix the first temporary shape. The sample is then heated above the
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Scheme 6-1. Schematic illustration of multi-stack nano structure of LDHs. Adopted with permission from [David G. Evans, Journal Chemical Communications, 2006, 45,485-496]. LDHs
are composed of positively charged layers with interlayer anions. (Anion Clays) resembling brucite structure.

**Scheme 6-2.** Schematic illustration of preparing PCO-LDH Ricinoleate composite using solvent mixing method. First, (A) PCO and (B) LDH Ricinoleate were separately dissolved in excessive amount of THF and stirred for 72 h at RT until completely dissolved. (C) Two solutions were then combined and stirred for another 24 h. (D) The solution was then solvent casted and dried at RT for 24 h followed by vacuum oven at RT for 24 h and finally 50 °C for 8 h.

**Scheme 6-3.** Schematic structure of a modern tubeless tire innerliner whose main responsibility is to withstand air pressure is the innermost layer of the tire. It is a thin layer of rubber laminated to the inside of a pneumatic tire that serves as a barrier layer to the pressurized internal gas. Scheme was taken from [http://www.changemytyre.com/](http://www.changemytyre.com/).

**Scheme 6-4.** Schematic illustration of polymer-LDH composites morphologies showing (A) separated (microstructure), (B) intercalated (nanostructure) and (C) exfoliated nanostructure. When phase separated, LDH has low affinity to the polymer and LDH layers remains tightly bound to each other in the composite. As a result, the intensity and 2θ (basal spacing) values of LDH in the composite remain almost identical to that of pure LDH. When intercalated, LDH retains its layered structure but basal spacing increases and as result, 2θ values shift to the left in XRD patterns. If the LDH is highly compatible with the polymer, the layers would fully exfoliate and completely lose their stacking order. The basal diffraction peaks would disappear in the XRD profile. For our application, an exfoliated or at least intercalated morphology is desired given that the interfacial area and consequently load transfer and barrier properties are maximized in both cases.

**Scheme 7-1.** The chemical structures of (A) diglycidyl ether of bisphenol-A (DGEBA), (B) neopentyl glycol diglycidyl ether (NGDE), (C) Jeffamine D230, (D) Jeffamine ED2000, and (E) poly(ε-caprolactone) for preparation of (I) PPG-EP/PCL and (II) PEO-EP/PCL.

**Scheme 8-1.** Step-by-step illustration for preparing the triple shape memory composites. Epoxy monomers and PCL were first mixed at 75 °C for 20 min until a clear, homogenous blends was achieved (A). Then the blend was cooled down to room temperature (RT) after which the crosslinker (JD230) was added (B). The blend was mixed again for another 2-3 min. The product,
a low viscosity blend was then poured into a salt template (C) and was kept at ambient for 10 min followed by pulling light vacuum for an additional 10 min in to allow the blend to completely diffuse into the salt template and replace the air. The product was then cured at RT for 24 h followed by curing at 40 °C for 3 days after which the salt was distracted. After drying, the product was a porous interconnected foam (G).

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Figure 1-1. Typical distribution of molecular weight in a polymer. Two polymers that have the same average molecular weight but different distributions. Polymer A exhibits a narrow distribution whereas polymer B exhibits a wider distribution covering a wider range of molecular weights. Reproduced with permission of Sperling, L. H., *Introduction of Physical Polymer Science*. 4th Edition ed.; John Wiley and Sons Inc.: Hoboken, New Jersey, 2006; p 7.]

Figure 1-2. Hypothetical stress-strain curve of rigid plastic, flexible plastic and elastomer. Below glass transition temperature, rigid plastics require high tensile stress to be stretched to only a few percent before they break indicating high Modulus and brittleness. Elastomers that are above glass transition temperature at RT are highly elastic and are typically elongated to above 500 %. Tough plastic exhibit an intermediate behaviour compared to rigid plastics and elastomers with moderate tensile strength and strain to failure. A semicrystalline thermoplastic with its amorphous region above glass transition is an example of tough plastic. Reproduced with permission of Sperling, L. H., *Introduction of Physical Polymer Science*. 4th Edition ed.; John Wiley and Sons Inc.: Hoboken, New Jersey, 2006; p 7.]

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While PAN doesn’t degrade or sublime at 200 °C for 1 h, most of DMF and Ancamine was evaporated in less than 10 minutes. The weight loss of PAN/Ancamine/DMF was about 35 % corresponding to Ancamine assuming that all of DMF evaporates during the electrospinning step.

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**Figure 4-27.** Optical micrographs of electrospun PAN/DGEBA/DMF co-solution as core and pure DMF as sheath with flow rates of: (A) 2.0, (B) 1.5, (C) 1.0 and (D) 0.5 ml h⁻¹. The core solution flow rate (PAN/DGEBA/DMF) was kept consistent at 1.0 ml h⁻¹. Presence of DMF as the sheath even at its lowest flow rate (0.5 ml h⁻¹) evidently prevented beads to form indicating that all the core solution was successfully encapsulated in the sheath. As core flow rate increases, the electrospinning conditions became more stable and more beads-on-string structure was observed. The best results was accomplished when sheath flow rate was at 1.5 ml h⁻¹ given that the beads on string density was maximized. Scale bar represents 50 μm.

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**Figure 4-41.** Photographs of “Epoxy Roll” preparation process. Ancamine and DGEBA were first pipetted on two separate rectangular pieces of PAN fiber mat (A,B). (C) The embedded PAN fiber mats were then placed and rolled on the top of each other.

**Figure 4-42.** SEM micrographs of the epoxy roll cross section at different magnifications. Top and bottom rows represent cut with a fresh razor blade and cryofractured samples at different magnifications, respectively. Note that the entire sample was cured at RT for at least 1 week prior to the experiment.

**Figure 5-1.** SEM micrographs of (A) an as spun and (B) a heated PVAc60:PCL40 fiber mat. During heating, the PVAc polymers chains reconfigure to a relaxed state and the semicrystalline self-healing fibers melt and form a film resulting in significant fiber mat shrinkage.

**Figure 5-2.** SEM micrographs of (A) as spun PCL (B) heated PCL, (C) as spun PVAc and (D) heated PVAc fiber mats. During heating, PVAc polymers chains reconfigure to a relaxed state and the semicrystalline self-healing fibers melt and form a film resulting in significant fiber mat shrinkage. Scale bar represents 50 µm.

**Figure 5-3.** (I) Photographs of (A) PVAc60:PCL40, (B) PVAc and (C) PCL fiber mat. Left and right columns represent as spun samples and corresponding heated samples, respectively. During heating, PVAc polymers chains reconfigure to a relaxed state and the semicrystalline self-healing fibers melt and form a film resulting in significant fiber mat shrinkage. Such reduction in size was quantified by heating 1 cm$^2$ square pieces of the PVAc60:PCL40 fiber mats at 80 ºC for 20 min. The shrinkage was calculated using the following equation:
\[ Shrinkage\% = \left(1 - \frac{A_{\text{Film}}}{A_{\text{Fiber}}}\right) \times 100 \]

where \( A_{\text{Film}} \) and \( A_{\text{Fiber}} \) correspond to surface area values of the fiber mat after heating (film) and as spun, respectively. **(II)** Quantitative characterization of fiber mat shrinkage showing average fiber mat sizes and shrinkage percentages for PVAc60:PCL40, PVAc and PCL (n=5). Results showed that the dual-electrospun sample (PVAc60:PCL40) has an intermediate shrinkage \% value compared to the two controls (PCL and PVAc fiber mats).

**Figure 5-4.** Representative optical micrographs showing (A) bright field, (B) fluorescent and (C) overlaid (combined (A) and (B)) images of the dual-electrospun PVAc60:PCL40 fibers. Blue and pink colors correspond to PCL and PVAc, respectively. To take the images, the fibers were electrospun on a thin glass slide for ~10 s. Note that the PVAc solution contained ~0.5 wt. \% of Rhodamine B. Scale bar represents 100 µm.

**Figure 5-5.** Micrographs of (A) PCL and (B) PVAc fibers. The top and bottom rows represent the bright field and fluorescent micrographs of such fibers, respectively. To take the images, the fibers were electrospun on a thin glass slide for ~10 s. Note that PVAc solution contained ~0.5 wt. \% of Rhodamine B. PCL solution however, did not contain any Rhodamine B (fluorescent dye) and did not appear under fluorescent light. Scale bar represents 100 µm.

**Figure 5-6.** DSC thermograms (2nd heating cycle) of (i) PVAc, (ii) PVAc80:PCL20, (iii) PVAc60:PCL40 and (iv) PCL composites. The temperature was ramped at 10 °C min\(^{-1}\) and 5 °C min\(^{-1}\) for heating and cooling, respectively.

**Figure 5-7.** DSC thermograms (2nd heating cycle) of (i) hydrated PVAc and (ii) hydrated PVAc80:PCL20 composite. Heating rates were 10 °C min\(^{-1}\) and 5 °C min\(^{-1}\) for heating and cooling, respectively.

**Figure 5-8.** Storage modulus (\( E' \)) traces of (-) PVAc60:PCL40 film, (-) PVAc80:PCL20 film, and (-) PVAc film.

**Figure 5-9.** Tan (\( \delta \)) traces (-) PVAc60:PCL40 film, (-) PVAc80:PCL20 film and (-) PVAc film. The loss tangent (tan(\( \delta \))) profiles for PVAc60:PCL40 and PVAc80:PCL20 showed double peaks indicative of both PVAc \( T_g \) and PCL \( T_m \) transitions.
Figure 5-10. Wide angle Xray scattering (WAXS) patterns of (A) PVAc60:PCL40, (B) PVAc, (C) PCL. The Top and bottom rows represent films and fiber mats, respectively. Shown in (D) are the overlaid patterns of PVAc (B) and PCL (C), which is in good agreement with PVAc60PCL40 results. The Xray wavelength ($\lambda$) is 1.5405 Å.

Figure 5-11. Intensity vs. $2\theta$ profiles of (i) PVAc60:PCL40 film, (ii) PVAc60:PCL40 fibers, (iii) PVAc film, (iv) PVAc fibers, (v) PCL film and (vi) PCL fibers. The Xray wavelength ($\lambda$) is 1.5405 Å.

Figure 5-12. Photographs of PVAc60:PCL40 composite showing (A) scratched and (B) thermally mended (75 °C for 10 min) sample. Scale bars denote 1 mm.

Figure 5-13. Schematic illustration of the crack opening method. The surface of the sample was first cleaved by a fresh razor blade. The sample was then bent on a cylindrical rod to propagate the crack. Shown in (B) and (C) are the photographs of the damaged and self-healed sample, respectively. Insets present the zoomed in stereo micrographs of the damaged and self-healed sample, respectively. All scale bars denote 1 mm.

Figure 5-14. (I) Optical microscope images of PVAc60:PCL40 composite showing: (A) notched sample, (B) crack propagated sample and (C) thermally mended sample (75 °C for 10 min). Sample was first notched using a custom-made dogbone cutting die (A). The damage was then controllably propagated by stretching the notched sample (B). The damaged sample was then “self-healed” by heating isothermally at 75 °C for 10 min. Scale bar denotes 1 mm. (II) Force vs displacement curves for the virgin, notched damaged and healed state of a PVAc60:PCL40 film. The healed sample shows a profile almost identical to the virgin sample indicating complete recovery of mechanical properties.

Figure 5-15. Force vs displacement curves for the virgin, damaged and healed state of a PVAc film.

Figure 5-16. (A) Stress vs. strain profiles for PVAc and PVAc80:PCL20 in both dry and hydrated state. Samples were stretched at 50 $\mu$m.s$^{-1}$ at RT. Both composites showed stiff characteristics with low strain to failure and high modulus at RT. Upon hydration though, they become elastomeric with low modulus and high strain to failure as PVAc plasticizes. (B) Photograph of a hydrated
PVAc80:PCL20 dogbone sample pre and post stretching to 500 % on Linkam. Hydrated samples were immersed in water for at least 24 prior to the experiment. Sample was kept hydrated during the experiment by constantly pipetting water onto it.

**Figure 5-17.** Dual shape memory demonstration of PVAc80:PCL20 composite showing (A) permanent shape at RT, (B) a temporary spiral shape, which was deformed at 80 °C and fixed by quenching at -17 °C and (D) the recovered shape. Scale bar represents 1 cm.

**Figure 5-18.** Triple Shape memory demonstration of hydrated PVAc80PCL20 composite showing (A) the permanent shape at RT, (B) temporary shape 1, a curled “C” shape, which was deformed in an 80 °C water bath and fixed by immersing in ice/water bath, (C) temporary shape 2, a rolled shape which was deformed in a water bath at RT and fixed by immersing in ice/water bath, (D) recovered temporary shape 1, obtained by submerging in a water bath at RT for 10 min and (E) recovered permanent shape obtained by heating at 80 °C in water. All scale bars represent 1 cm.

**Figure 6-1.** Photograph of a co-rotating twin-screw mini-extruder (DACA Instruments). Binary blends of PCO and LDH were prepared by feeding the pre mixed appropriate amount of PCO and LDH into extruder funnel and subsequently extruded at 160 °F (zone 1), 175 °F (zone 2), 185 °F (zone 3) and 185 °F (zone 4). The extruded composites were molded into discs or strands and then hot pressed at 1.5 mTons and 100 °C to form films. Shown in (B) and (C) are photograph of an extruded and hot pressed film, respectively. Scale bars represent 1 cm.

**Figure 6-2.** Photographs of (A) a TST350 Linkam Tensile Stress Testing Stage (Linkam Scientific Instruments, Ltd.) with a 20 N load cell and (B) a dogbone sample (ASTM D63-Type IV, scaled down by a factor of 4). Scale bar represents 5 mm.

**Figure 6-3.** Thermogram traces of (i) Perkalite LD, (ii) Pural MG70 (from Sasol), (iii) LDHRicinoleate, (iv) LDHAcetate, (v) Perkalite A100, (vi) Perkalite F100 and (vii) LDHSB250. The remaining weight in all LDHs correspond to the inorganic portion of the material. Commercially available LDHs such as Perkalite-LD (from AkzoNobel) or normally are substantially free of organic constituents. Therefore, these materials exhibit higher weight % remaining at 800 °C. The LDHs prepared by the enzymatic process such as LDHSFBA however show much lower weight fraction compared to their inorganic counterparts.
Figure 6-4. SEM micrographs of (A) Perkalite LD, an inorganic Mg/Al LDH with inter-layer anions being predominantly OH⁻ (a commercial product of AkzoNobel), (B) Perkalite F100, an Mg/Al LDH functionalized with hydrogenated fatty acid (a commercial product from AkzoNobel), (C) Perkalite A100, an Mg/Al LDH functionalized with rosin (a commercial product from AkzoNobel), (D) LDHacetate, acetate functionalized LDH prepared by adding acetic acid to Perkalite LD (LDH-OH; dispersed in water) until pH reaches 8, (E) LDH Ricinoleate, Ricinoleate functionalized LDH prepared by ion exchanging LDHacetate with potassium Ricinoleate at 60 °C for 4 h, (F) LDHSB: LDH functionalized with soybean (SB) (mixed fatty acids from soybean oil, primarily oleic (20-30%) and linoleic (50-60%) acid) and (G) Pural MG70: a LDHCO3 from Sasol with nominal Mg/Al of 70/30.

Figure 6-5. TGA profiles of (i) PCO, (ii) PCO-LDH Ricinoleate (10 %) and (iii) PCO-LDH Ricinoleate (50 %). The nominal and actual weight fractions of the LDH in the composite calculated from eqn. (6-1) are provided in the table. Results indicate that the actual weight fraction of the LDH is close but slightly lower than the nominal value.

Figure 6-6. 2D WAXS patterns of (A) PCO, (B), (C) extruded PCO-LDH Ricinoleate (10 %) and (D) extruded PCO-LDH Ricinoleate (50 LDHRicinoleate %). Sample to IP collector distance was 142.7 mm and exposure time was 30 min.

Figure 6-7. (A) Normalized WAXS profiles of (i) PCO, (ii) PCO-LDH Ricinoleate (10 %), (iii) PCO-LDH Ricinoleate (50 %) and (iv) LDHRicinoleate. Sample to IP collector distance was 142.7 mm and exposure time was 30 min. Corresponding X-ray diffraction (XRD) profiles of LDHRicinoleate in both PCO-LDH Ricinoleate (10 %) and PCO-LDH Ricinoleate (50 %) stayed almost identical to the LDH before blending indicating low affinity of the LDH to mixing with the polymer. Interestingly, the crystalline peaks corresponding to PCO phase substantially attenuated after mixing with LDH Ricinoleate. We postulate this is due to interrupted crystalline structure of PCO in the presence of LDH.

Figure 6-8. Stereo microscope micrographs of a PCO-LDH Ricinoleate (50 %) during tensile testing by Linkam showing a dogbone sample (A) before stretching, (B) right before failure and (C) after failure. During extrusion, LDH was not uniformly dispersed in PCO and LDH regions were macroscopically visible in the film (highlighted by red circles). As a results, these regions...
did not hold stress, acted as defects within which the crack was initiated and propagated (shown by arrow). Scale bar denotes 1 mm.

**Figure 6-9.** 2D WAXS pattern and (B) WAXS profiles of extruded PCO-LDHRicinoleate-Promix (10 %, LDHRicinoleate: Promix weight ratio: 2:1) which shows complete exfoliation of LDH. The very sharp peak at low 2θ is due to Xray beam.

**Figure 6-10.** TGA results for five different regions of PCO- LDHRicinoleate-Promix (10 %, LDHRicinoleate: Promix weight ratio: 2:1) film. All 5 samples show almost identical degradation profile indicative of homogenous dispersion.

**Figure 6-11.** (I) Stress vs. strain profiles of Tensile tests of extruded (A) PCO, (B) PCO-LDHRicinoleate and (C) PCO-LDHRicinoleate-Promix (10 %, LDHRicinoleate: Promix weight ratio: 2:1) and (II) Average Young Modulus values estimated from the slope of linear portion of stress-strain curve for each sample (n=3). All samples were hot pressed and then cut to a dogbone shape prior to tensile testing. All the experiments were conducted at 25 °C. The samples were stretched at 200 µm s⁻¹. PCO showed elastomeric behaviour with an average Modulus of 96.9 MPa and strain to failure of >300 %. Both Young Modulus (62.2) and strain to failure (<250 %) of the PCO-LDH Ricinoleate was lower than neat PCO due to heterogeneous dispersion of LDH within PCO in the extrusion process indicating low affinity of the LDH to polymer. This is in agreement with WAXS results where LDH layers remained tightly bound to each other in the composite and consequently, intensity and 2θ (basal spacing) values of LDH in the composite remained almost identical to that of pure LDH. Better dispersion of LDH was achieved in the presence of Promix resulting improvement in both average Young Modulus and strain to failure results in the PCO-LDHRicinoleate-Promix (10 %) composite given that Promix exfoliates and entirely disrupts the layered structure of LDH as evidenced in Figure 6-9.

**Figure 6-12.** WAXS patterns for (A) PCO, (B) LDHRicinoleate and (C) PCO-LDH composite prepared by solvent mixing method.

**Figure 6-13.** (A) Normalized WAXS profiles of (i) PCO, (ii) PCO-LDHRicinoleate (10 %) prepared by solvent mixing method, (iii) LDHRicinoleate, (iv) zoomed in LDHRicinoleate and (B) d-spacing/2θ values of the WAXS profiles peaks of both LDHRicinoleate and PCO-LDHRicinoleate (10 %) prepared by solvent mixing method. Sample to IP collector distance was
142.7 mm and exposure time was 30 min. Corresponding X-ray diffraction (XRD) profile of LDHRicinoleate in PCO-LDHRicinoleate (10 %) stayed almost identical to the LDH before blending indicating low affinity of the LDH to mixing with the polymer. In other words, d-spacing and 2θ values of WAXS profile peaks remain almost intact in PCO-LDHRicinoleate composite compared to neat LDHRicinoleate.

Figure 6-14. WAXS results for (A) neat Bromobutyl, (B) LDHSB250, (C) Bromobutyl-LDHSB250 (2.5 Phr), (D) Bromobutyl –LDHSB250 (5.0 Phr) and (E) Bromobutyl-LDHSB250 (10 Phr).

Figure 6-15. WAXS results for (i) Neat Bromobutyl, (ii) Bromobutyl-LDHSB250 (2.5 Phr), (iii) Bromobutyl-LDHSB250 (5.0 Phr), (iv) Bromobutyl-LDHSB250 (10 Phr) and (v) neat LDHSB250.

Figure 6-16. (A) TGA thermograms and (B) final residual weight remaining of (i) neat cured Bromobutyl, (ii) Bromobutyl- LDHSB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1), (iii) Bromobutyl-LDHSB50-Promix (15 Phr, LDHSB50:Promix weight ratio: 2:1), (iv) Promix, (v) LDHSB50 and (vi) Bromobutyl-Promix (10 Phr) (overlaps with (ii) and (iii)).

Figure 6-17. 2D WAXS patterns of (A) Neat Promix, (B) premixed LDHSB50-Promix (weight ratio: 2:1) and (C) LDHSB50. Sample to IP collector distance was 142.7 mm and exposure time was 30 min.

Figure 6-18. (A) Normalized WAXS profiles of (A) Neat Promix, (B) LDHSB50 and (C) premixed LDHSB50-Promix (weight ratio: 2:1). Sample to IP collector distance was 142.7 mm and exposure time was 30 min. Intensity (A.U.) axis is in log-scale to reduce data noise and amplify peaks. Clearly, LDHSB50 lost its layered structure when mixed with Promix indicating exfoliation of LDH by Promix.

Figure 6-19. 2D WAXS patterns of (A) neat Bromobutyl, (B) Bromobutyl-LDHSB50 (10 Phr, with no Promix) and (C) Bromobutyl-LDHSB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1). Sample to IP collector distance was 142.7 mm and exposure time was 30 min.

Figure 6-20. (I) Normalized WAXS profiles and (II) corresponding 2θ and d-spacing values of (A) neat Bromobutyl, (B) Bromobutyl-LDHSB50 (10 Phr) and (C) Bromobutyl-LDHSB50-
Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1). Sample to IP collector distance was 142.7 mm and exposure time was 30 min. When Bromobutyl was mixed with LDHSB50 the 2θ values shifted to lower values indicating partial intercalation. After adding Promix to the composite however, the basal spacing peaks disappeared indicating successful exfoliation (II).

**Figure 6-21.** (A) 1st and (B) 2nd DSC cycles of neat Bromobutyl, Promix, Bromobutyl-Promix (10 Phr) and Bromobutyl-LDHSB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1). All samples except for neat Promix showed single glass transition temperature at ~ 63 °C as highlighted by black vertical lines.

**Figure 6-22.** Tensile storage modulus (E’) traces of Bromobutyl-Promix (10 Phr) replicated 3 times to assure reproducibility. All composites (neat Bromobutyl, Bromobutyl-Promix (10 Phr) and Bromobutyl-LDHSB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1) showed a single glass transition temperature at ~ 63 °C, glassy modulus > 2 GPa and rubbery modulus < 1.0 MPa at -90 and 50 °C, respectively. Summary of thermomechanical properties of all the composites are provided in Table 6-1.

**Figure 6-23.** (I) Stress vs. strain profiles of Tensile tests of (A) Bromobutyl , (B) Bromobutyl-Promix (10 Phr) and (C) Bromobuytl-Promix-LDHSB50 (10 Phr, LDHSB50:Promix weight ratio: 2:1) and (II) average Ultimate Stress values estimated from for each sample (n=3). All samples were cut to a dogbone shape prior to tensile testing. All the experiments were conducted at 25 °C. The samples were stretched at 200 µm s⁻¹. Incorporation of Promix and LDH yielded Better dispersion of LDH was achieved improvement in both average ultimate stress and strain to failure results.

**Figure 6-24.** 2D WAXS patterns for enzymatic LDHSB synthesized from (A) 50, (B) 100 and (C) 250 g of soybean oil.

**Figure 6-25.** Normalized WAXS results for enzymatic LDHSB synthesized from (A) 250 g, (B) (100) g, and (C) 50 g of soybean oil.

**Figure 6-26.** (A) TGA results for enzymatic LDHSB produced from (i) 50 g, (ii) 100 g and (iii) 250 g of soybean oil mixed with LDH-OH. (B) Results show that with increase in initial soybean
oil used, more functionalization occurs and consequently less weight remaining at high temperatures due to degradation of functionalized moieties.

**Figure 7-1.** DSC thermograms of 1st cooling and 2nd heating for: (I) PPG-EP/PCL and (II) PEO-EP/PCL. Heating rate of 10 °C/min was used for cooling and heating of both samples.

**Figure 7-2.** (I) PPG-EP/PCL and (II) PEO-EP/PCL exhibit: (A) Photographs of samples before curing, (B) photographs of samples after curing, and (C) POM images of cured samples under crossed polarizers. The scale bars for (A) and (B) represents 2 mm. The scale bars for (C) represents 100 µm.

**Figure 7-3.** POM images under crossed polarizers at room temperature exhibited by: (A) PPG-EP, (B) PEO-EP, and (C) PCL. The scale bar represents 200 µm.

**Figure 7-4.** Intensity value at λ= 550 nm plots for epoxyPCL(10) blend for isothermal at 80 °C (▼), isothermal at 100 °C (■) and ramped up from 80 °C to 120 °C at 0.2 °C min⁻¹ (●). Temperature profile for (C) is shown in red.

**Figure 7-5.** Tensile storage modulus (E’) and loss tangent (tan δ) trace of (I) PPG-EP/PCL and (II) PEO-EP/PCL. Dashed lines separate different thermomechanical regions for each composite.

**Figure 7-6.** DMA loss tangent (tan δ) trace of (I) PPG-EP/PCL and (II) PEO-EP/PCL in log scale demonstrating all three transition temperatures. Red lines show the transition temperatures of each composite.

**Figure 7-7.** The triple-shape memory cycle of (A) PPG-EP/PCL and (B) PEO-EP/PCL using one-step fixing. The beginning of the cycles are marked by the asterisk. Samples were loaded, cooled to -10 °C and unloaded (fixing), followed by continuous heating to 75 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) fixing, (3) unloading, and (4) recovery.

**Figure 7-8.** The triple-shape memory cycle of (A) PPG-EP/PCL and (B) PEO-EP/PCL (b) using two-step fixing. The beginning of the cycles are marked by the asterisk. Samples were loaded at 75 °C, cooled to 10 °C and unloaded (1st fixing), heated to an intermediate temperature and loaded again, cooled to -10 °C (2nd fixing), followed by continuous heating to 75 °C (recovery). The
arrows denote the various stages, specifically (1) deformation, (2) 1st fixing, (3) 1st unloading, (4) 2nd fixing, (5) 2nd unloading, and (6 and 7) recovery.

**Figure 7-9.** (I) Schematic Illustration of Triple Shape memory demonstration experiment showing sample shapes: (A) at RT, below the 1st transition temperature with two ends fixed, (B) at intermediate temperature of 40 °C with left end fixed and right end recovered, and (C) at 75 °C, above the 2nd transition temperature (completely recovered); Photographs showing dual shape recovery of fixed (II) PPG-EP/PCL, and (III) PEO-EP/PCL samples from R.T. (A) to two different temperatures of 40 °C (B) and 75 °C (C). All scale bars represent 1 cm.

**Figure 7-10.** DSC thermograms of 1st cooling (dashed line) and 2nd heating (solid line) for: (I) PPG-EP, (II) PPG-EP/10%-PCL, (III) PEO/EP, (IV) PEO-EP/10%-PCL, and (V) PCL. Heating rate of 10 °C/min was used for cooling and heating of both samples. It is noted that the heat flow magnitude of the DSC thermogram for PCL was reduced by half for scaling purposes.

**Figure 7-11.** (a) Tensile storage modulus (E’) and (b) loss tangent (tan δ) trace of PEO-EP/PCL with different PCL content in comparison with neat epoxy PEO-EP, measured by DMA. (i) PEO-EP and (ii) PEO-EP/10%PCL.

**Figure 7-12.** The triple-shape memory cycle of PEO-EP/PCL with (a) 0% and (b) 10% PCL content using one-step fixing. The beginning of the cycles are marked by the asterisk. Samples were loaded to a tensile strain of 20%, cooled to -10 °C and unloaded (fixing), followed by continuous heating to 75 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) fixing, (3) unloading, and (4) recovery.

**Figure 7-13.** (I) Schematic of a thermomechanical triple shape memory cycle. At T_H the material is initially embossed with circular pattern. The temperature is then decreased to T_0 to fix one temporary shape (1). The sample is then stretched at T_L and cooled down to T_0 to fix the second temporary shape (2). The sample then material recovers into its first temporary shape by heating to T_L and the permanent shape is reached by heating to T_H. (II) Micrographs of sample showing (A) fixed temporary shape 1, (B) temporary shape (2) and (C) permanent flat shape. Blue mark indicates exactly the same spot on the sample. Scale bar represents 1 mm.
Figure 7-14. (I) Schematic of a thermomechanical triple shape memory cycle. At $T_H$ the material is initially embossed with circular pattern. The temperature is then decreased to $T_0$ to fix one temporary shape (1). The sample is then embossed with parallel stripes at $T_L$ and cooled down to $T_0$ to fix the second temporary shape (2). The sample then material recovers into its first temporary shape by heating to $T_L$ and the permanent shape is reached by heating to $T_H$. (II) Micrographs of sample showing (A) fixed temporary shape (1), (B) temporary shape (2) and (C) permanent flat shape. Blue mark indicates exactly the same spot on the sample. Scale bar represents 1 mm.

Figure 7-15. Demonstration of reversibility of adhesion showing (A) stainless steel bonded specimen, (B) bonded specimen withstanding the stainless steel substrate weight, (C) debonded specimen after heating up to 80 °C and (D) metal substrate surface indicating some PCL residue (highlighted).

Figure 8-1. SEM micrographs of NaCl templates used to fabricate the foams. To improve pore interconnectivity, salt was fused prior to polymer synthesis, as we now describe. About 6 g of salt with 150-300 μm diameter was added to a 20 ml high density polyethylene (HDPE) vial. The vial was then placed in a Styrofoam box (9.25 x 6.25 x 8.25 in) with the lid off in which a 2 L water at 40 °C was placed to provide a humidity saturated environment. The salt was kept in Styrofoam for 24 h during which the humidity of this chamber facilitates the fusion of the salt. The salt was then dried under light vacuum at RT for 24 h. Dashed lines represent some of the regions where salt crystals were welded together. Scale bar is 500 μm.

Figure 8-2. Optical micrograph and SEM micrograph of cryofractured (A, B) $N_2J_1PCL10$ and (C) $D_1N_2J_{1.5}PCL10$ foam cross section. Both foams have an interconnected porous architecture that is cuboidal in morphology. This cuboidal morphology is dictated by the cuboidal structure of the salt particles (See Figure 8-1). Scale bars represent 1.0 mm.

Figure 8-3. Representative MicroCT image of a triple shape memory foam. Such high porosity enables high compressibility and shape change capability of the foams. To obtain the image, a 6.0 mm diameter and 9.0 mm thick disc was scanned using a Scanco Medical μCT40 scanner at voltage of 45 kV and current of 177 μA. Scanning parameters led to a nominal voxel resolution of 12 μm. Porosity of the foam was obtained to be about 73%. Scale bar represents 1.0 mm.
Figure 8-4. Thermogram traces of (-) D1N2J1.5PCL10 film, (-) D1N2J1.5PCL10 foam, (-) N2J1PCL10 film and (-) N2J1PCL10 foam. The remaining weight % of each film and foam group are almost identical indicating successful extraction of salt.

Figure 8-5. Thermogram traces of (-) D1N2J1.5 film, (-) N2J1 film, (-) PCL and (-) NaCl template. The salt thermograms stays at 100 % indicating its stability over the temperature monitoring range.

Figure 8-6. DSC thermograms (2nd heating cycle) of (i) D1N2J1.5PCL10 film, (ii) D1N2J1.5PCL10 foam, (iii) N2J1PCL10 film and (iv) N2J1PCL10 foam. Both compositions showed two well-separated transitions: a step-like transition at lower temperature followed by a sharp peak at higher temperature which correspond to the T_g of the epoxy-rich phase and the melting transition of the semi-crystalline PCL phase, respectively. Heating rates were 10 °C min^{-1} and 5 °C min^{-1} for heating and cooling, respectively.

Figure 8-7. DSC thermograms (2nd heating cycle) of (i) D1N2J1.5 film, (ii) N2J1 film and (iii) PCL. It is noted that the heat flow magnitude of the DSC thermogram for PCL was scaled down 5 times. Heating rates were 10 °C min^{-1} and 5 °C min^{-1} for heating and cooling, respectively.

Figure 8-8. Tensile storage modulus (E’) traces of (i) D1N2J1.5PCL10 film, (ii) D1N2J1.5PCL10 foam, (iii) N2J1PCL10 film and (iv) N2J1PCL10 foam. Both foams (traces ii and iv) and films (traces i and iii) exhibited high modulus plateaus at low temperature, followed by an intermediate plateau between the epoxy T_g and the PCL melting transition and finally a third rubbery plateau above the PCL Tm, where the material exists as an epoxy rubber with an encapsulated liquid PCL phase.

Figure 8-9. Tan Delta traces of (i) D1N2J1.5PCL10 film, (ii) D1N2J1.5PCL10 foam, (iii) N2J1PCL10 film and (iv) N2J1PCL10 foam.

Figure 8-10. Tensile storage modulus (E’) traces of (-) D1N2J1.5 film and (-) N2J1 film. Samples go through only one transition temperature in the absence of PCL.

Figure 8-11. Representative contact angle micrographs (and average contact angle ) of (A) D1N2J1.5PCL10 film, (B) D1N2J1.5 film, (C) D1N2J1.5PCL10 foam, (D) N2J1PCL10 film, (E) N2J1 film and, (F) N2J1PCL10 foam. Water permeated into N1J2PCL10 foam in less than 30 s.

XLVI
Figure 8-12. Representative contact angle micrograph of (A) D₁N₂J₁.₃PCL₁₀ foam at RT, (B) D₁N₂J₁.₅PCL₁₀ foam at 45 °C and (C) D₁N₂J₁.₅PCL₁₀ foam after 20 min at 45 °C. Even when heated above the Tᵣ of the epoxy phase at 45 °C, water did not permeate into the rubbery D₁N₂J₁.₅PCL₁₀ foam within our observation time of 20 min indicating hydrophobic characteristics of composites arising from higher hydrophobicity of chemical components rather than different mechanical properties of the foams. Scale bar represents 1.0 mm.

Figure 8-13. Triple shape memory characterization of (A) D₁N₂J₁.₅PCL₁₀ foam, (B) D₁N₂J₁.₅PCL₁₀ film, (C) N₂J₁PCL₁₀ foam and (D) N₂J₁PCL₁₀ film using one-step fixing method. The beginning of the cycles are marked by the asterisk (*) symbol. Samples were deformed at 65 °C (deformation), cooled to -20 °C and unloaded (fixing), followed by continuous heating to 80 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) fixing, (3) unloading, and (4) recovery.

Figure 8-14. Triple shape memory characterization of (A) D₁N₂J₁ film and (B) N₂J₁ film using one-step fixing. The beginning of the cycles are marked by the asterisk. Samples were deformed at 65 °C (deformation), cooled to -20 °C and unloaded (fixing), followed by continuous heating to 80 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) fixing, (3) unloading, and (4) recovery. One step recovery of both samples indicate dual shape memory behavior.

Figure 8-15. Triple shape memory characterization of (A) D₁N₂J₁.₅PCL₁₀ foam, (B) D₁N₂J₁.₅PCL₁₀ film, (C) N₂J₁PCL₁₀ foam and (D) N₂J₁PCL₁₀ film using a two-step fixing method. Samples were deformed at 65 °C, cooled to -20 °C and unloaded (1ˢᵗ fixing), heated to an intermediate temperature and deformed again, cooled to -10 °C (2ⁿᵈ fixing), followed by continuous heating to 85 °C (recovery). The beginning of the cycles are marked by the asterisk (*) symbol. The arrows denote the various stages of a shape memory cycle; specifically (1) deformation, (2) 1ˢᵗ fixing, (3) 1ˢᵗ unloading, (4) 2ⁿᵈ fixing, (5) 2ⁿᵈ unloading, and (6 and 7) recovery.

Figure 8-16. Triple shape memory characterization of (A) D₁N₂J₁.₅ film and (B) N₂J₁ film using a two-step fixing method. Samples were deformed at 65 °C, cooled to -20 °C and unloaded (1ˢᵗ fixing), heated to an intermediate temperature and deformed again, cooled to -10 °C (2ⁿᵈ fixing),
followed by continuous heating to 85 °C (recovery). The beginning of the cycles are marked by the asterisk. The arrows denote the various stages of a shape memory cycle; specifically (1) deformation, (2) 1st fixing, (3) 1st unloading, (4) 2nd fixing, (5) 2nd unloading, and (6 and 7) recovery. In both cases, sample completely recovered after heating to an intermediate temperature indicating dual shape memory properties of epoxy films.

**Figure 8-17.** Triple Shape memory demonstration experiment showing: (A) permanent shape at RT, (B) compressed to 75% at 80 °C strain and fixed (C) curled to a “C” shape at 40 °C and fixed, (D) recovered at 40 °C and, (E) recovered at 80 °C. Top and bottom rows show top and side views, respectively. All scale bars represent 1 cm.
Chapter 1: Introduction

1.1 Polymers

Polymers are defined as long chain molecules primarily consisting of Carbon, Oxygen and Hydrogen atoms. The building blocks of polymers are referred to as monomers that are covalently bonded to each other through a chemical reaction known as polymerization\textsuperscript{1,2}. The molecular weight of polymers typically falls in the range of thousands to millions. As such, polymers are also known as “macromolecules” given their high molecular weight\textsuperscript{2,3}. There are several methods to synthesize polymers which can be categorized to 2 major methods: chain polymerization and step-growth polymerization. The most common chain polymerization and step-growth polymerization are free radical polymerization and condensation polymerization, respectively\textsuperscript{1,4,5}.

1.2 Molecular Weight Distribution

One of the unique characteristics of polymers that distinguish them from simple low molecular weight molecules is their molecular weight distribution. All synthetic polymers and most natural polymers molecular weight (except for proteins) follow a distribution of molecular weight\textsuperscript{2}. That is, in one single batch of a polymer, molecules with different chain lengths (i.e. molecular weight) are synthesized. This is primarily because termination of chain growth in a polymerization reaction occurs entirely by random events and is often very difficult to control\textsuperscript{5}. Figure 1-1 shows two polymers that have the same average molecular weight but different distributions. Polymer A exhibits a narrow distribution whereas polymer B exhibits a wider distribution covering a wider range of molecular weights. Therefore, molecular weight is usually reported in averages:
\[ \langle M \rangle_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \]  

(1-1)

\[ \langle M \rangle_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} \]  

(1-2)

where \( N_i \) is the number of species \( i \) molecules with a molecular weight of \( M \).

\( M_n \) and \( M_w \) are number average molecular weight and weight average molecular weight of the polymer. Statistically, \( M_n \) is the first moment and \( M_w \) is the ratio of the second to first moment in the distribution\(^5\). The breadth of distribution is typically reported by polydispersity:

\[ PDI = \frac{M_w}{M_n} \]  

(1-3)

Note that proteins are the only polymers with absolutely identical chain length and therefore a polydispersity index of 1. Most synthesized polymers have a polydispersity of around 2 and to this date no successful polymer reaction resulting to a polydispersity of 1 has been reported\(^2\).

1.3 Classification of Polymers

Polymers are the most common compound molecules on earth. From human cells, to any transportation industry and personal home care products, synthetic or naturally occurring polymers are so prevalent that cannot be avoid in our daily lives. Without polymeric products, human modern life would not be as convenient as it is nowadays. For instance, consider your phone, car and clothes; they all contain polymers or polymeric composites. Considering the vast diversity of polymers, they are deservedly considered as the essence of our life. Polymers are typically categorized from different points of view such as their mechanical properties which are briefly discussed in what follows.
1.4 Mechanical Properties of Polymers

Countless polymers with a wider range of properties now exist. Based on mechanical appearance and Modulus, the polymers can be categorized into 3 major classes: Rigid plastic, tough plastic and elastomers. A hypothetical stress-strain curve of rigid plastic, flexible plastic and elastomer is provided in Figure 1-2. Below glass transition temperature, rigid plastics require high tensile stress to be stretched to only a few percent before they break indicating high Modulus and brittleness. Elastomers that are above glass transition temperature at RT are highly elastic and are typically elongated to above 500%. Tough plastics exhibit an intermediate behaviour compared to rigid plastics and elastomers with moderate tensile strength and strain to failure. A semicrystalline thermoplastic with its amorphous region above glass transition is an example of tough plastic. It is important to note that mechanical properties of the polymers strongly depend on several factors including molecular weight, crystallinity, and temperature which are discussed next.

1.4.1 Molecular Weight

Molecular weight of a polymer can greatly influence its mechanical properties. As a rule of thumb, the tensile strength (defined as the stress at the point of material failure during tensile testing) increases with molecular weight. The effect of molecular weight on tensile strength is depicted in Figure 1-3. At very low molecular weight, the tensile strength is negligible, meaning that polymer chains cannot hold any stress as in wax. However, above a critical molecular weight (shown with asterisk), the tensile strength drastically increases as molecular weight increases until it reaches a definitive value at infinite molecular weight. Molecular weight-tensile strength relationship can be simplified into the following equation:
\[ \sigma_b = A - \frac{B}{M_n} \]  

(1-4)

where \( \sigma_b \) and \( M_n \) represent tensile strength and number average molecular weight of the polymer and A, B are constants. [note: this introduction chapter is very rudimentary – unclear why you went so basic?]

1.4.1 Crystallinity

The mechanical properties of a polymer significantly vary depending on the physical state of the polymer. For crosslinked amorphous polymers, the linear viscoelasticity theory applies. However, this is no longer true for semicrystalline polymers. Linear polymers can undergo crystallization process encompassing arrangement of polymer chains. Degree of crystallinity of polymers depend on both molecular weight and thermal history of the polymer\(^5\).\(^6\). Shown in Figure 1-4 is the influence of molecular weight and crystallinity on the mechanical appearance of poly-ethylene as an example\(^6\). At a constant crystallinity, polyethylene transforms from a soft wax, to tough wax and eventually a hard plastic as highlighted by blue dashed line. At a constant molecular weight, polyethylene transforms from a grease to a soft wax and eventually to a brittle wax as crystallinity increase as highlighted by red dashed line.

1.4.3 Effect of Temperature on Polymer Properties

Temperature can significantly affect the mechanical properties of the polymers. Polymers storage Modulus significantly drop as they go through glass transition temperature or melting temperature for amorphous and semicrystalline polymers, respectively. Theoretical Young Modulus profile of a polymer as function of temperature is represented in Figure 1-5\(^2\). Below glass transition temperature, the chain molecules are immobilized and can only vibrate.
Therefore, the polymer is stiff or glassy with high Young Modulus (region 1). If sufficient energy is provided, the amorphous portion of polymer start to mobilize and Modulus drops 3 orders of magnitude (region 2). This transition is known as glass transition temperature. Elastomers glass transition temperature is lower than room temperature making them rubbery at ambient conditions (region 3). Besides, the Modulus of the polymer above glass transition temperature is in direct relationship with crosslinking density:

\[ E = nRT \]  

(1-5)

Where \( E \), \( n \) and \( T \) are Young Modulus, the number of crosslinks and absolute temperature, respectively. \( R \) is the universal gas constant. Note that some polymers such as crosslinked networks are commonly amorphous and exhibit only one transition being glass transition. Semi-crystalline polymers such as thermoplastics though feature both glass transition and melt transition corresponding to softening the amorphous phase and transition of polymer from solid to liquid (region 5). Classification of polymers based on their structure and mechanical properties is provided in Scheme 1-1. Crosslinked polymers are generally amorphous and recognized as elastomers-those that are rubbery- or thermosets-those that are rigid- at ambient conditions. Thermoplastics (linear polymers) can be amorphous or semicrystalline and typically are considered tough (high strain to failure and higher modulus than elastomers) above their glass transition temperature and below melting transition.

1.5 Smart Polymers

Smart polymers are defined as the materials that have the ability to undergo a change in any form (i.e. shape, mechanical and chemical change) in response to an external stimuli\(^7\). Two relatively young but fascinating classes of smart polymers are “Self-Healing” and “Shape Memory”
polymers which this dissertation focuses on. In what follows, both topics are briefly introduced and reviewed.

1.5.1 Self-healing Polymers

Mechanical or environmental elements constantly situate polymeric materials under stress causing damage and eventually failure. The repair and in some cases, the detection of such damage is often costly\(^8,9\). More importantly, original properties of polymeric materials can decay over time as a result of such damage(s). Inspired by biological systems, “self-healing (SH)” materials were introduced with ability to restore their mechanical strength and functionality using the resources inherently available to them such as heat or light\(^9-11\). Researchers have reported various strategies to develop SH materials with a wide range of properties geared towards different applications. One categorization groups SH materials based on the particular stimulus responsible for triggering the healing mechanism, such as mechanical\(^12-16\) and thermal\(^17-20\) which are briefly elaborated on in what follows.

1.5.1.1 Mechanically activated Self-Healing Composites

Self-healing composites were first introduced by White et al. by incorporating a microencapsulated healing agent and a chemical catalyst in a polymeric host\(^12,14\). The self-healing agent is encapsulated in microcapsules embedded in a matrix containing catalyst as shown in **Scheme 1-2**. Damage ruptures the microcapsule allowing the self-healing agent to flow out of the microcapsule, into the damage site. The self-healing agent (dicyclopentadiene (DCPD)) polymerizes via ring-opening metathesis polymerization (ROMP) initiated by Ruthenium-based Grubbs' catalyst at the site of damage. The formation of the crosslinked
network at ambient conditions contributes to recover the mechanical properties of the composite\textsuperscript{12,14}.

Recently core-sheath fibers prepared by coaxial electrospinning\textsuperscript{21-27} has attracted tremendous attention in several fields of research from tissue engineering\textsuperscript{28-30} to self-healing\textsuperscript{22,31,32}. As opposed to encapsulating the self-healing agent in microcapsules, Wu and co-workers recently reported on multiply reinforced composites with self-healing core-sheath nanofibers prepared by coaxial electrospinning. The self-healing agent ((DCPD) was enwrapped into polyacrylonitrile (PAN) forming core-sheath fibers as shown in Figure 1-6\textsuperscript{31}. Upon damage, the fibers would rupture, the self-healing agent flows to the damaged area and polymerizes in the presence of Grubb’s catalyst. After polymerization, the composite followed the same flexural stress-strain profiles as the virgin sample indicating complete recovery of mechanical properties(Figure 1-7)\textsuperscript{31}. The most substantial advantage of the mechanically activated self-healing systems lays on the fact that they do not require any external stimulus and damage itself triggers the SH mechanism. However, a disadvantage of this method is the limited amount of available SH agent. Besides, the ruptured microcapsule itself may act as a defect in the material structure, compromising the material.

1.5.1.2 Shape Memory Assisted Self-Healing

A unique approach introduced by our group, utilizes shape memory\textsuperscript{33,34} (SM) phenomenon (For details, see Section 1.5.2.) to prepare novel SH polymers that are capable of simultaneously closing and rebonding cracks with a simple thermal trigger\textsuperscript{18,19}. This strategy, termed “shape memory assisted self-healing (SMASH)”, was first demonstrated in a blend system consisting of a cross-linked poly(\(\varepsilon\)-caprolactone) network (n-PCL) with interpenetrating linear poly(\(\varepsilon\)-
caprolactone) (I-PCL) as shown in Figure 1-8(A). Both materials were compatible with each other and formed a homogenous composite given their similar chemical structure. Such unique chemistry exhibited the SM response from the network component and a SH capacity from the linear recovering the mechanical properties to “as new” with a single heating step (Figure 1-8(B))\textsuperscript{19}.

1.5.2 Shape Memory Polymers

Shape memory polymers (SMPs) are a class of smart materials that can be designed to undergo programmed changes in shape or mechanical properties including stiffness in response to an external stimulus, such as heat\textsuperscript{35-39}, light\textsuperscript{40-43}, electrical current\textsuperscript{44,45}, solvent\textsuperscript{46-48}, magnetic field\textsuperscript{49-51} and pH\textsuperscript{52-54}. To achieve such unique shape changing behaviour, two requisites are needed. First, material are to feature a stable low entropy permanent shape which is typically governed by physical or chemical crosslinking. Besides, the material should be able to undergo a controllable shape change. To do so, SMP is usually heated above its characteristics transition temperature and deformed to a desired shape. Upon chain immobilization (crystallization for semicrystalline polymers or vitrification for amorphous polymers), the program shape is then fixed\textsuperscript{33,34}. When heated above its transition temperature, polymer chains are remobilized providing drive force to revert back to permanent shape (i.e. Polymer remembers its permanent shape).\textsuperscript{34,55} This shape changing cycle, referred to as “shape memory” cycle is illustrated in Figure 1-9\textsuperscript{56}. Starting from the asterisk, the polymer is deformed above its transition temperature (deformation). The polymer is then cooled sown while holding the stress to fix the strained polymer chains (cooling/fixing) followed by unloading the stress (unloading). Upon heating the material goes back to its low entropy state and recovers to its permanent shape.
1.5.2.1 Shape memory elastomeric composites

To fix their temporary shape, SMPs have to undergo a vitrification or crystallization process making them generally stiff at RT. A popular demand exists for materials that are soft and resilient at RT with mechanical properties mimicking those of human tissues. Our group has previously introduced a shape memory composite that is rubbery and soft, and yet, has the ability to fix a temporary shape. A shape memory elastomeric composite (SMEC) was prepared in a two-step method illustrated in Scheme 1-3. First poly(ε-caprolactone) (PCL) fibers were electrospun to fabricate a porous nano-scale fiber mat. The fiber mat was then imbedded in an uncured Sylgard resin. The PCL/Sylgard composite was then cured to yield a composite featuring 3 separate transitions attributed to the glass transition of Sylgard, the glass transition of PCL and the melting transition of PCL (60 °C). Note that the composite exhibited elastomeric properties given that glass transition temperatures of both PCL and Sylgard phases are well below RT. Besides, the composite was deformed at 80 °C and fixed to a temporary shape by crystallizing the PCL phase. Upon heating, the composite sharply recovered to its permanent shape by heating above the PCL melting transition indicating excellent shape memory properties as shown in Figure 1-10.

1.5.2.2 Triple Shape Memory Polymers

Shape memory polymers are limited to two shapes commonly referred to as permanent and temporary shapes. The permanent shape is the polymer cross-linked equilibrated shape which cannot be programmed or altered. Therefore, a need exists to develop polymers featuring two programmable shapes besides to the permanent shape. Given that these materials have the ability to exhibit 3 shapes (two programmed shapes and one permanent shape), they have been
dubbed triple shape memory polymers (TSMPs). TSMPs can successively switch from temporary shape (A) to temporary shape (B) and eventually to permanent shape (C), all upon external stimulation. To achieve such properties, two distinct thermal transitions (e.g., glass transition and melting transition) should be built into the material to occur within the temperature range appropriate for an intended application. TSMPs Storage Modulus profile would then feature two step drops corresponding to each transition and 3 rubbery plateaus (Figure 1-11).

In our group, we developed a two-step fixing method to characterize triple shape memory properties as schematically illustrated in Scheme 1-4. To deform the first temporary shape, the material is heated above its higher transition temperature ($T_H$), deformed and then cooled below its $T_H$ to fix the first temporary shape. The sample is then heated above the lower transition temperature ($T_L$) but lower than $T_H$, deformed and then cooled below $T_L$ to fix the second temporary shape. Upon heating, the material sequentially recover from the second temporary shape to the first temporary shape and to permanent shape as it goes through $T_L$ and $T_H$. Several different approaches have been reported in literature so far to develop triple shape memory polymers. Generally, these approaches can be categorized in to two classes:

1.5.2.2.1 Molecular Approach

In this approach, a polymer with two building blocks each having a distinct transition temperatures is synthesized. Bellin et al. first developed two polymer network structures featuring triple shape memory properties shown in Figure 1-12. The first network contained poly($\varepsilon$-caprolactone) (PCL) and poly(cyclohexyl methacrylate) (PCHMA) with two transition temperature at ~60 °C and ~140 °C, respectively. In the second system, PCL segments were grafted with poly(ethylene glycol) (PEG) as side chains with two transitions at ~60 °C and
17-39 °C corresponding to PCL and PEG blocks, respectively. Synthesis techniques to develop polymer chains featuring two separate transition temperatures are often time consuming and require several processing steps. In our group, we took relatively simpler route where a composite with two separate phases and consequently two separate transitions were developed as we now explain.

1.5.2.2.2 Composite Approach

In this approach, a composite consisting of two phase separated polymers are fabricated. In our group, we developed a composite featuring triple shape memory properties following a similar two-step method explained in Section 1.5.2.1. Briefly, PCL fibers were imbedded in an epoxy resin and cured yielding a composite featuring two separate transition temperatures above RT corresponding to glass transition temperature of amorphous epoxy phase and melting transition of semicrystalline PCL phase. There, the sample was heated above PCL melting transition, deformed to programmed shape (B) and fixed by crystalizing the PCL phase. The second temporary shape was programmed by heating above the epoxy phase, deforming to programmed shape and fixed by vitrifying the epoxy phase (A). Upon heating, the sample sequentially recovered from shape (A) to shape (B) to permanent shape (C) demonstrating triple shape memory characteristics as shown in Figure 1-13.

1.5.2.3 Shape Memory Foams

Recently, shape memory functionality has been married with the high compressibility and low density of porous materials to develop SMP foams. While some studies have reported on closed-cell SMP foams, most studies to-date have focused on open-cell foams based on polyurethane or epoxy chemistries. These foams are well-suited for applications
where large expansion ratios are required from a light-weight, compact packaged state. For instance, Solowski and colleagues developed cold-hibernated elastic memory foams (CHEM) for deployable space aircraft structures. Polyurethane based SMP foams have also recently received increased attention for biomedical applications. For instance, our group recently developed a poly(ε-caprolactone)-co-poly(ethylene glycol) SMP foam that can be used for cell mechanobiology studies. SMP foams were elastomeric at ambient conditions with high compressibility capable of expanding once hydrated at 37 °C as shown in Figure 1-14.

1.6 Scope of Dissertation

The aim of this dissertation is to employ different techniques to develop mechanically or thermally responsive polymeric composites. It is important to note that our strategy throughout this dissertation was to develop relatively simple and industrially scalable methods using commercially available-inexpensive materials, as we now explain.

1.6.1 Self-Healing Polymers

First, development and characterization of self-healing systems was studied. In Chapter 2, a blending approach to develop bi-component composite was introduced and studied in details. Results showed that the two phases undergo polymerization induced phase separation (PIPS) yielding a variety morphologies which vary significantly with temperature, viscosity and molecular weight of the components. The same blending approach was then employed in Chapter 3 to fabricate an epoxy based coating capable of self-healing on metallic surfaces to prevent corrosion. The coatings exhibited shape memory assisted self-healing (SMASH) properties where not only the crack was closed but only the corrosion resistance properties of the coating was successfully restored.
Current self-healing systems are often rubbery and require mechanical support. We introduced in **Chapter 5** a one-step dual electrospinning method to develop stiff, interwoven polymer composites featuring SMASH properties. The dual electrospinning approach allowed us to develop composites from polymers that are otherwise immiscible with precisely controlled compositions. The development of dual electrospinning amenable to stiff self-healing films with potential applications in packaging or building envelopes was introduced for the first time. Seeking to develop an autonomous self-healing system, a coaxial electrospinning approach was then presented in **Chapter 4**. The key objective of this chapter was to develop and characterize core-sheath fibers with a thin layer of a stiff polymer in sheath capsuling an epoxy based self-healing blend.

### 1.6.2 Nano-LDH/Rubber Composites

In **Chapter 6**, organic layered double hydroxides (LDHs) were introduced and incorporated in a polymer host. The goal of this work was to study the effect of LDHs on barrier/mechanical properties of tire compounds as high performance additives that are formulated into tire innerliner compounds.

### 1.6.3 Triple Shape Memory Composites

Field of shape memory has attracted a lot of attraction and has moved towards more complex patterns such as triple or multiple shapes. The proposed methods to develop multiple shape memory systems are, however, complicated and are not marketable from industrial point of view. To address this gap in the field, a thermoset/thermoset composite featuring triple shape memory properties was developed in **Chapter 7** following the same blending approach as in **Chapter 2**. Inspired by successful development of triple shape memory composites and shape memory
foams in our group, we report for the first time in Chapter 8 on the design, preparation, and characterization of a triple shape memory polymeric foams that are open cell in nature and features triple shape memory properties.

Finally, proposed future directions to further develop and dive in to deeper details of materials and methods introduced in each chapter are outlined at the end of each chapter.

1.7 References


**Figure 1-1.** Typical distribution of molecular weight in a polymer. Two polymers that have the same average molecular weight but different distributions. Polymer A exhibits a narrow distribution whereas polymer B exhibits a wider distribution covering a wider range of molecular weights. Reproduced with permission of Sperling, L. H., *Introduction of Physical Polymer Science*. 4th Edition ed.; John Wiley and Sons Inc.: Hoboken, New Jersey, 2006; p 7.]
Figure 1-2. Hypothetical stress-strain curve of rigid plastic, flexible plastic and elastomer. Below glass transition temperature, rigid plastics require high tensile stress to be stretched to only a few percent before they break indicating high Modulus and brittleness. Elastomers that are above glass transition temperature at RT are highly elastic and are typically elongated to above 500%. Tough plastics exhibit an intermediate behaviour compared to rigid plastics and elastomers with moderate tensile strength and strain to failure. A semicrystalline thermoplastic with its amorphous region above glass transition is an example of tough plastic. Reproduced with permission of Sperling, L. H., *Introduction of Physical Polymer Science*. 4th Edition ed.; John Wiley and Sons Inc.: Hoboken, New Jersey, 2006; p 7.)
Figure 1-3. Theoretical tensile strength of a polymer as a function of its molecular weight. At very low molecular weight, the tensile strength approaches zero. However, above a critical molecular weight (shown with asterisk), the tensile strength drastically increases as molecular weight increases until it reaches a definitive value (A) at infinite molecular weight. Reproduced with permission of Sperling, L. H., *Introduction of Physical Polymer Science*. 4th Edition ed.; John Wiley and Sons Inc.: Hoboken, New Jersey, 2006; p 7.}
Figure 1-4. Effect of molecular weight and crystallinity on mechanical properties of polyethylene. At a constant crystallinity, polyethylene transforms from a soft wax, to tough wax and eventually a hard plastic as highlighted by blue dashed line. At a constant molecular weight, polyethylene transforms from a grease to a soft wax and eventually to a brittle wax as crystallinity increase as highlighted by red dashed line. Adopted with permission from [Richards, R.; Journal of Applied Chemistry 1951, 1, 370-376.].
Figure 1-5. Theoretical Young Modulus profile of a polymer as a functional of temperature. Below glass transition temperature, the chain molecules are immobilized and can only vibrate (region 1). Therefore, the polymer is stiff or glassy with high Young Modulus. If sufficient energy is provided, the amorphous portion of polymer starts to mobilize and Modulus drops 3 orders of magnitude (region 2). This transition is known as glass transition temperature. Elastomers glass transition temperature is lower than room temperature making them rubbery at ambient conditions (region 3). Besides, the Modulus of the polymer above glass transition temperature is in direct relationship with crosslinking density (E=nRT). Semi-crystalline polymers such as thermoplastics feature both glass transition and melt transition corresponding to softening the amorphous phase and transition of polymer from solid to liquid (region 5). Reproduced with permission from [Sperling, L. H., *Introduction of Physical Polymer Science*. 4th Edition ed.; John Wiley and Sons Inc.: Hoboken, New Jersey, 2006; p 7.].
Scheme 1-1. Classification of polymers based on their structure and mechanical properties. Crosslinked polymers are generally amorphous and recognized as elastomers, those that are rubbery or thermosets, those that are rigid at ambient conditions. Thermoplastics (linear polymers) can be amorphous or semicrystalline and typically are considered tough (high strain to failure and higher modulus than elastomers) above their glass transition temperature and below melting transition.
Scheme 1-2. Schematic illustration of the self-healing process introduced by White and colleagues. (A) The self-healing agent is encapsulated in microcapsules embedded in a matrix containing catalyst. Note that the self-healing agent and catalyst polymerize upon contact at RT. (B) Damage ruptures the microcapsule allowing the self-healing agent to flow out of the microcapsule, into the damage site. (C) The self-healing agent polymerizes at the site of damage in the presence of catalyst to recover the mechanical properties of the composite. Adopted with permission from [White, S. R.; Sottos, N.; Geubelle, P.; Moore, J.; Kessler, M. R.; Sriram, S.; Brown, E.; Viswanathan, S.; Nature 2001, 409, 794-797].
Figure 1-7. Load-displacement curves of a virgin (red) and a self-healed composite (blue) subjected to three-point bending loads. The multiply composites were reinforced at the interface with core-sheath fibers containing self-healing agent in the core. Upon damage, the fibers rupture and the self-healing agent flows to the damaged area and polymerized in the presence of Grubb’s catalyst. Upon self-healing, the composite followed the same flexural stress-strain profiles as the virgin sample indicating complete recovery of mechanical properties. Adopted with permission from [Wu, X. F.; Rahman, A.; Zhou, Z.; Pelot, D. D.; Sinha-Ray, S.; Chen, B.; Payne, S.; Yarin, A. L.; Journal of Applied Polymer Science 2013, 129, 1383-1393.].
Figure 1-8. (A) Chemical structure of shape memory assisted self-healing composites containing a cross-linked poly(ε-caprolactone) network (shape memory network) with interpenetrating linear poly(ε-caprolactone) (self-healing agent). (B) Mechanical properties of the damaged composite was recovered upon heating through a two-step mechanism: SM response from the network first closed the crack and the self-healing agent rebonded two crack surfaces together. Adopted with permission from [Rodriguez, E. D.; Luo, X.; Mather, P. T.; *ACS applied materials & interfaces* 2011, 3, 152-161.].
Figure 1-9. A typical Shape memory Cycle. Starting from the asterisk, the polymer is deformed above its transition temperature (deformation). The polymer is then cooled down while holding the stress to fix the strained polymer chains (cooling/fixing) followed by unloading the stress (unloading). Upon heating the material goes back to its low entropy state and recovers to its permanent shape. Adopted with permission from [Chung, T.; Romo-Uribe, A.; Mather, P. T.; Macromolecules 2008, 41, 184-192.].
Scheme 1-3. Schematic illustration for preparation of PCL/Sylgard composite. PCL fibers were first electrospun to fabricate a porous nano-scale fiber mat. The fiber mat was then imbedded in an uncured Sylgard resin where Sylgard infiltrated into PCL fibers under vacuum. The PCL/Sylgard composite was then cured to yield a composite featuring 3 separate transitions attributed to the glass transition of Sylgard, glass transition of PCL and melting transition of PCL. Adopted with permission from [Luo, X.; Mather P.T.; Macromolecules 2009, 42, 7251-7253.].
**Figure 1-10.** Photographs of Sylgard/PCL composite showing the recovery from a fixed temporary shape to permanent flat shape on a temperature-controlled plate at 80 °C. For fixing, the sample was heated to 80 °C, deformed to a spiral shape and fixed by cooling below the PCL melting transition. Adopted with permission from [Luo, X.; Mather P.T.; *Macromolecules* **2009**, *42*, 7251-7253.].
Figure 1-11. Theoretical Storage Modulus profile of a TSMP as a function of temperature showing two distinct thermal transitions (e.g., glass transition and melting transition). TSMPs Storage Modulus profile would then feature two step drops corresponding to each transition and 3 rubbery plateaus. Each rubbery plateau corresponds to one shape in the shape changing process.
**Scheme 1-4.** Schematic illustration of a two-step method to characterize TSMPs. To deform the first temporary shape, the material is heated above its higher transition temperature ($T_H$), deformed and then cooled below its $T_H$ to fix the first temporary shape. The sample is then heated above the lower transition temperature ($T_L$) but lower than $T_H$, deformed and then cooled below $T_L$ to fix the second temporary shape. Upon heating, the material sequentially recover from the second temporary shape to the first temporary shape and to permanent shape as it goes through $T_L$ and $T_H$. 
Figure 1-12. Triple Shape Memory Polymer networks prepared by molecular approach. (A) The first network contained poly(ε-caprolactone) (PCL) and poly(cyclohexyl methacrylate) (PCHMA) in which first transition is a melting (crystallizable PCL $T_m=50$-$60^\circ C$) and second transition is a glass transition (amorphous PCHMA $T_g=140^\circ C$). (B) PCL segments were grafted with poly(ethylene glycol) (PEG) as side chains having one dangling end and PCL segments connect two net points. In this network, both transitions are melting points (crystallizable PCL, $T_m=50$-$60^\circ C$) and (crystallizable PEG $T_m=17$-$39^\circ C$). Adopted with Permission from [Bellin, I.; Kelch, S.; Langer, R.; Lendlein, A; *Proceedings of the National Academy of Sciences* **2006, 103**, 18043-18047].
Figure 1-13. Photographs of a triple shape memory composite (TSMC) film sequentially recovering from temporary shape (A) to temporary shape (B) to permanent shape (C). Sample was heated above PCL melting transition, deformed to programmed shape (B) and fixed by crystalizing the PCL phase. The second temporary shape was fixed by heating above the epoxy phase, deforming to programmed shape (A) and fixed by vitrifying the epoxy phase. Upon heating, the sample sequentially recovered from shape (A) to shape (B) to permanent shape demonstrating triple shape memory characteristics. Adopted with permission from [Luo, X.; Mather, P. T.; *Advanced Functional Materials* **2010**, *20*, 2649-2656].
Figure 1-14. Optical micrographs (left) and SEM images (right) of poly(ε-caprolactone)-co-poly(ethylene glycol) SMP foam cross-section (top), temporary compressed shape (middle), and after recovery (bottom) indicating high compressibility and shape memory characteristics of the scaffold. Adopted with permission from [Baker, R. M.; Henderson, J. H.; Mather, P. T.; *Journal of Materials Chemistry B* **2013**, *1*, 4916-4920.].
Chapter 2: Analysis of Polymerization Induced Phase Separation (PIPS) in a Thermoplastic/Thermoset Blend

2.1 Synopsis

In this chapter, the curing kinetics and morphology evolution of an epoxy matrix with and without a semicrystalline thermoplastic was investigated. This was done in order to better understand the principles of the blending of such materials which was exploited for different applications later in this dissertation. Utilizing differential scanning calorimetry (DSC), in dynamic mode, degree of cure as a function of temperature, cure range and enthalpy of cure were investigated and compared. In the isothermal mode, degree of cure as a function of time was investigated for a range of temperatures. Chemorheology experiments were also conducted to investigate polymerization induced phase separation (PIPS) that occurs during cure of the epoxy blended with an initially miscible thermoplastic. Time profiles of linear viscoelastic material functions enabled establishment of both the onset of phase separation and the gelation point of the blend at different isothermal cure temperatures. For the conditions used, the observed morphology evolution observed by microscopy and viscosity-time profiles indicate that the PIPS transition precedes gelation. The methods developed should be applicable to a range of other curing systems.

2.2 Introduction: Polymerization Induced Phase Separation (PIPS)

2.2.1 Overview of PIPS

Seeking to achieve improved performance in polymeric composites, the idea of mixing two or more different polymers featuring combined attributes of all components has engrossed a lot of
attraction. Polymerization induced phase separation (PIPS) (also known as reaction induced phase separation (RIPS)) is extensively used to fabricate bi-component composites containing two polymers which are otherwise immiscible with each other\textsuperscript{1-8}. As we know polymers are not generally miscible with each other. However, one polymer can be miscible with a monomer or a pre-polymer especially at elevated temperatures as we now explain.

When two liquids or a liquid and a polymer are mixed with each other, the combinational entropy favors a one-phase homogenous blend. Such behaviour can be explained by Flory-Huggins theory. Mixing $N_1$ molecules of pre-polymer A with $N_2$ molecules of pre-polymer B takes place in a hypothetical lattice with $N_1 + N_2$ cells. Note that in Flory-Huggins theory all the molecules are considered to have approximately the same size for the sake of simplicity and so are the lattice cells\textsuperscript{9-12}. The total number of possible arrangements in which all these molecules can be place on the lattice can be calculated with the following equation\textsuperscript{9}:

$$\Omega = \frac{(N_1 + N_2)!}{N_1!N_2!}$$  \hspace{1cm} (2-1)

For simplicity, consider a 10 X 10 lattice containing 100 different spots for each molecule. The number of possible different arrangements to take place with 50 units of A molecules and 50 units of B molecules is approximately $\Omega = 10^{30}$ as shown in Scheme 2-1. Now if units of A and units of B are connected to each other (i.e. both A and B now have 10 building blocks) the number of possible different arrangements dramatically decreases to about $\Omega = 10^{3}$. As a result, the entropy of mixing decreases as the molecular weight of any of the components decrease.

In PIPS, the system consists initially of a miscible homogeneous blend of a polymer and monomer (or pre-polymer). The low molecular weight of pre-polymer gives a high number of possible
arrangements in the lattice (and in reality) and therefore, high entropy of mixing. Upon polymerization of the pre-polymer, the miscibility of the two components decrease:

$$\Delta S_M = -R(N_A \ln \phi_A + N_B \ln \phi_B)$$

(2-2)

where $\Delta S_M$, $R$, $N_i$ and $\phi_i$ are the enthalpy of mixing, gas constant, mole number, and volume fraction of the components, respectively.

Consequently, at a certain point, the Gibbs free energy becomes positive considering that enthalpy of mixing in PIPS ($\Delta H_M$) remains constant and the two components phase separate from each other:

$$\Delta G_M = \Delta H_M - T\Delta S_M$$

(2-3)

$\Delta G_M$, $\Delta H_M$ and $\Delta S_M$ correspond to Gibbs free energy of mixing, enthalpy of mixing and entropy of mixing, respectively. Note that a homogenous one-phase blend is only achieved when $\Delta G_M < 0$.

2.2.2 Phase Diagram

Flory-Huggins theory predicts the phase diagram of two liquid phases whether both phases contain polymers or one/two phases are solvents. Again such two components become homogenous only when $\Delta G_M$ is negative or in other words, when Gibbs free energy of mixing is less than Gibbs free energy of any individual components. It’s important to note that all these energy factors are strongly temperature dependent. Generally, the miscibility of a two polymer or a polymer/solvent system that are immiscible at ambient conditions are higher as temperature increases and above a critical temperature (known as Upper-Critical-Solution-Temperature (UCST)), a one phase solution forms. Above UCST, two components are miscible with each other regardless of their volume fractions. In some cases however, the miscibility of the two components heavily depend on the enthalpy of melting ($\Delta H_M$) which is usually endothermic. In those cases, Gibbs free energy
of mixing ($\Delta G_M$) becomes positive as temperature increases resulting in phase separation. Such unusual behaviour is associated with lower critical solution temperature (LCST) systems. The phase diagram of binary polymer blends with both UCST and LCST is illustrated in Scheme 2-2.

In binary polymer blend phase diagrams, different regions can be identified: (A) a stable region when a one homogenous phase is formed, (B) a metastable region located between bimodal and spinodal lines and (C) an unstable region located inside the spinodal lines as shown in Scheme 2-3 for a system showing UCST behaviour. During PIPS, as the monomer starts to polymerize, the phase diagram shifts up to higher temperatures until eventually the blend transforms the blend from region (A) to either region (B) or (C) resulting in phase separation\textsuperscript{13}. In the unstable region, phase separation occurs by spinodal decomposition (SD) whereas in the metastable region, phase separation occurs by nucleation and growth mechanism. The morphology of the blends constantly evolves as PIPS proceeds and depends on several factors such as reaction rate, phase separation kinetics and temperature which can result to a variety of morphologies. Generally, NG and SD lead to formation of particle/matrix and co-continuous morphologies, respectively. Such time and temperature dependent morphology evolution can be tailored by different techniques such Small Angle Light Scattering (SALS)\textsuperscript{14} and Optical Microscopy (OM)\textsuperscript{6}.

2.2.3 PIPS in Epoxy/PCL Systems

PIPS in such epoxy/PCL systems has long been of interest to many researchers\textsuperscript{15-25}. As an example, Luo et al. studied PIPS processes of DDS cured epoxy/PCL blends with different PCL contents, The morphology and viscoelastic evolution of the blend were monitored using optical, microscopic and rheological techniques to develop rigid reversible adhesion composites\textsuperscript{26}. The epoxy matrix in
their system had relatively high glass transition temperature (T<sub>g</sub>) which could not be altered. In this Chapter, we investigate PIPS in a tri-component epoxy matrix in the presence of PCL. Such composite featuring epoxy matrix with tunable T<sub>g</sub>, will be utilized to develop self-healing coatings and triple shape memory composites in Chapters 3 and 7, respectively.

2.3 Experimental Section

2.3.1 Materials

Poly(ε-caprolactone) (PCL) (Mn ≈ 70,000-90,000 g/mol), neopentyl glycol diglycidyl ether (NGDE), diglycidyl ether of bisphenol A (DGEBA), and poly(propylene glycol) and bis(2-aminopropyl ether) (Jeffamine® D-230) were purchased from Sigma-Aldrich. All materials were used as received. The chemical structures of all the components and the hypothesized epoxy network consisting of randomly distributed DGEBA, NGDE and Jeffamine® D-230 are provided in Scheme 2-4.

2.3.2 Blend Preparation

Thermoplastics (generally linear polymers) have been extensively incorporated in epoxy resins to achieve more desirable properties such as toughening brittle epoxy resins. However, thermal and rheological properties (such as curing kinetics) of epoxy systems substantially differ in the presence of such a thermoplastic. Here, the curing kinetics of a thermoset epoxy system in the presence of PCL, a semicrystalline thermoplastic was investigated. The curing kinetics of the blend was then compared with that of neat epoxy to determine the effect of added PCL. To do so, two sets of materials (with and without PCL) were prepared:
1. To prepare the epoxy resin, equimolar mix of DGEBA, NDGEA and Jeffamine® D-230 were mixed and hand-stirred at room temperature until a clear, homogeneous and low-viscosity solution was obtained (the molar ratio of DGEBA:NGDE:Jeffamine® D-230 was 1:1:1). This formulation is called epoxyPCL₀ hereafter, indicating that no PCL was used.

2. To prepare the thermoplastic/thermoset blend, 10 wt. % PCL with an equimolar mixture of DGEBA, NGDE and PCL were combined in a three-neck round bottom flask, heated at 90 °C in a hot-oil bath, and vigorously mixed with a high power stirrer (Arrow Engineering Co., Model 6000) for 1-2 hours or until a homogenous clear solution was achieved. To avoid air bubbles formation, vacuum was applied during this process. Once uniform consistency was achieved, the flask was removed from the heat source and let cool to RT. Jeffamine® D-230 was then added and stirred for 2-5 minutes. Note that the combined weight fraction of DGEBA, NGDE and Jeffamine® D-230 is 90 % and the molar ratio of them is 1:1:1. As the epoxy polymerizes, the initial miscible mixture becomes unstable and starts to phase separate. This process is called Polymerization Induced Phase Separation (PIPS) and is extensively investigated in literature.⁸,²⁶,³⁴ This formulation is called epoxyPCL₁₀ hereafter, indicating PCL weight fraction in the blend of 10%. Step-by-step preparation protocol of the epoxyPCL₁₀ blend is provided in Scheme 2-5.

2.3.3 Hot-stage Optical Microscopy

Generally speaking optical microscopy (OM) is the simplest and most direct way to observe the change of morphology during cure⁶. To track morphology evolution of the epoxy blend and polymerization induced phase separation, an Olympus BX51 optical microscope was used with a
hot-stage (Instec HCS402) for temperature control. In principle, for each experiment, a bubble free, uncured blend was first sandwiched between a glass slide and a cover slip and then quickly placed on the hot stage with a stable isothermal temperature. Micrographs were taken at different time points using a CCD camera to monitor blend morphology of blend during cure.

2.3.4 Thermal Characterization

Thermal properties and PCL content of coatings were characterized using Differential Scanning Calorimetry (DSC). DSC experiments were conducted using a Q200 (TA Instrument) equipped with a refrigerated cooling system (RCS). 3-5 mg of the epoxy components (DGEBA, NGDE, Jeffamine® 230), PCL, epoxy blend and completely cured epoxy was heated from -80 °C to 120 °C, cooled back to -80 °C, and finally heated to 120 °C. All heating were conducted at the rate of 10 °C min\(^{-1}\) and all cooling rates were 5 °C min\(^{-1}\).

2.3.5 Curing Kinetics Investigation by DSC Measurements

Curing was conducted using the same Q200 (TA Instruments) differential scanning calorimeter (DSC) equipped with a refrigerated cooling system (RCS).

2.3.5.1 Dynamic Cure

In dynamic mode, as-mixed blends were equilibrated at -80 °C and then ramped to 200 °C at 5, 10, 15 and 20 °C min\(^{-1}\). Degree of cure as a function of temperature, cure range and enthalpy of cure were investigated and compared for different epoxyPCL compositions. Activation energies of cure were then estimated using Kissinger and Ozawa models.
2.3.5.2 Isothermal Cure

In isothermal mode, the as-mixed blends were equilibrated in the DSC at 60 °C or 80 °C and held isothermally for 4 h. Degree of cure as a function of time was investigated for a range of temperatures. An autocatalytic model was then used to describe the curing process.

2.3.6 Chemorheology

Chemorheology experiments were conducted to further investigate PIPS of the epoxyPCL10 blend. A TA ARG2 stress-controlled rotational rheometer with parallel-plate geometry (disposable aluminum plates; the diameter was either 25 mm or 40 mm) was used to track the complex viscosity profile of the blend as it cures, including gelation isothermally at 60, 80, 100 and 140 °C.

2.4 Results and Discussion

2.4.1 Evolution of Morphology during PIPS

Morphology evolution of the blend over time at various isothermal temperatures were monitored using OM (For blend preparation details, refer to Experimental section). Figure 2-1 shows Optical microscope images displaying the morphological evolutions of PIPS blend at 60 °C, 80 °C and 100 °C. In all cases, the as mixed blend showed a homogenous, one-phase mixture with no observable features. However, over time, the mixture started to become cloudier and turned turbid over time indicating PIPS. (Figure 2-1). The onset of phase separation (defined as the point which domains start to form) occurred sooner at higher temperatures indicating faster cure and phase separation kinetics. More interestingly, at 60 and 80 °C, formed domains were small at first but coarsened over time. This phenomenon did not occur at 100 °C which is attributed to very fast
kinetics of cure that froze the domains right after formation and ceased their growth. Morphology evolution of epoxyPCL_{10} is also evident in 2D FFT patterns of such micrographs (Figure 2-2).

### 2.4.2 Thermal Characterization

Shown in Figure 2-3 are the DSC results of DGEBA, NGDE and Jeffamine® D-230 epoxy monomers. DGEBA had a T_g around -20 °C indicating amorphous structure whereas NGDE and Jeffamine® D-230 did not show any transition temperature in our observation range (-80 to -40 °C). Semi-crystalline PCL showed a melting transition at 55 °C and amorphous cured epoxy showed at glass transition temperature at 46 °C as shown in Figure 2-4. The as mixed epoxyPCL_{10}, however, showed one single transition at 24.1 °C which indicated that the blend was homogenous and in one phase. The fully cured epoxyPCL_{10} sample (cured isothermally at RT for 24 h followed by 40 °C for 72 h) showed two transitions at 34 °C and 55 °C. This result was in agreement with optical microscopy results that showed epoxy and PCL are in one phase but as epoxy polymerization progress, PIPS occurred. However, epoxy T_g in cured PIPS sample (Figure 2-4(iv)) was about 10 °C lower than that of neat epoxy in cured state indicating that some portion of PCL remained in one phase with PCL due to high viscosity of the blend or thermodynamics of the UCST curve that yields some PCL in same phase with epoxy.

### 2.4.3 Curing Kinetics Investigation by DSC Measurements

#### 2.4.3.1 Dynamic Cure

Figure 2-5 shows the DSC thermograms of the epoxyPCL blends with different PCL weight fractions. An exothermic peak was observed for all blends, indicating the occurrence of exothermic
cure reactions. Table 2-1 summarizes the curing characteristics of the resin systems with different PCL weight fractions. For all DSC traces, as the heating rates increased, the onset temperature (T_o), peak temperature (T_p), off-set temperature (T_f), and curing range (T_f - T_o) increased. In the presence of PCL, the heat-flow profiles were shifted to higher temperatures. The cure range also increased for a particular heating rate but the area under the curve (enthalpy of cure) decreased. The cumulative enthalpy of reaction was then determined by the “Run Integral” application in the range of T_o to T_f in the TA Universal Analysis 2000 software. Normalizing the result by enthalpy of melting of the “as mixed” blends, the conversion (%) profiles of epoxyPCL blends were calculated for different PCL weight fractions (Figure 2-6) as a function of temperature.

To better understand cure, several models have been used in literature. For dynamic cure, the Kissinger and Ozawa models are among the most extensively cited models. In Kissinger Model\textsuperscript{35}, an nth order equation is assumed for the reaction rate:

\[
q \frac{dq}{dT} = A(\exp(-\frac{E}{RT})(1 - \alpha^n)) \tag{2-4}
\]

where q is the reaction rate, \(\alpha\) is the conversion (%), \(E\) is activation energy and \(T\) is absolute temperature. Assuming that maximum conversion rate occurs at the peak temperature, differentiating with respect to time and equating with zero gives:

\[
q \frac{E}{RT_p} = An(1 - \alpha)^{n-1}\exp(-\frac{E}{RT}) \tag{2-5}
\]
Therefore, the peak temperature is independent of heating rate and by plotting \( \ln\left(\frac{q}{T_p^2}\right) \) vs. \( \frac{1}{T_p} \) the activation energy can be estimated. In Ozawa’s model\(^{36}\), the relationship between the heating rate and peak temperature is as follows:

\[
\log q = -0.457\left(\frac{E}{RT_p}\right) + A' 
\]

where \( E \) is activation energy, \( T_p \) is peak temperature, \( R \) is the gas constant, and \( A' \) is constant. Therefore the slope of \( \log q \) vs. \( \frac{1}{T_p} \) can be used to calculate activation energy (For calculations, refer to Table 2-3).

### 2.4.3.2 Isothermal Cure

In isothermal cure mode, the blend was kept at an isothermal temperature and the heat flow profile of the blend with respect to reference was monitored over time. Figure 2-7 shows the DSC thermograms of epoxyPCL\(_{10}\) isothermal runs. The heat flow profiles are associated with an exothermic peak that corresponds to a cure reaction that levels off over time.

An autocatalytic model \(^{37}\) was then implemented to further analyze the isothermal data. Amine-crosslinked systems have been shown previously to display an autocatalytic mechanism due to the creation of secondary hydroxyls during opening of the epoxide ring, which then catalyze further ring opening. The model therefore includes two reaction rates, where one corresponds to early stage cure \((k_1)\) and the other to later stages \((k_2)\):

\[
\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^n)(1 - \alpha)^n 
\]
Here, $\alpha$ is the conversion, while $k_1$ and $m$ are the rate constant and reaction order related to base cure rate without changes in accelerant levels and $k_2$ and $n$ are the rate constant and reaction order related to auto-accelerated cure, respectively.

To analyze the data, a custom program in Matlab was written that automatically imports the Universal Analysis software data and estimates the autocatalytic model parameters. What follows is a summary of program protocol. Heat flow versus time was imported into the program and normalized by subtracting the final heat flow data (assuming that after 4 h cure is complete) to provide a zero baseline. Then the cumulative area under the peak of the heat flow vs. time (total enthalpy of reaction) was calculated using a numerical trapezoid integration method. On this data set, the conversion for each time step is calculated as the normalized heat flow (cumulative heat flow at time t divided by total enthalpy of reaction.). Then the conversion rate ($\%$) $\left(\frac{d\alpha}{dt}\right)$ was calculated as the ratio of incremental heat to total heat and conversion rate was plotted vs. time.

Having the conversion ($\%$) ($\alpha$) and conversion rate $\left(\frac{d\alpha}{dt}\right)$ profiles as a function of time, we were able to plot conversion rate vs. conversion. It is important to note that the real data did not fit the autocatalytic data at early times due to thermal equilibration and at late times processes such as vitrification prevent the kinetics from being described solely from chemical kinetics. This noted, a curve-fitting program was utilized to estimate the model parameters in the autocatalytic model following previous work in our group$^{38}$. Data was interpolated for even spacing in cure (not time) so that the weighting is linear with degree of cure. This is necessary since the slowing of cure on the time axis leads to a significant increase in density of data points along the degree of cure axis towards later degrees of cure and time. Uncorrected, this would lead the fitting algorithm to focus
primarily on late stages of cure. Table 2-2 shows the calculated autocatalytic model constants. As temperature increased, n and m remained constant indicating that reaction order did not change as a function of temperature but rate constants (k_1 and k_2) increased by approximately two orders of magnitude indicating higher cure reaction rates which was expected.

2.4.5 Chemorheology

Figure 2-8 shows the real and complex viscosity profiles of epoxyPCL_{10} blend held isothermal at 60 °C. The plot begins at the point where the data comes within the detectable range of the rheometer; i.e. at low viscosity, storage modulus is below detection limits of the rheometer. The plot showed two transitions (pointed with arrows) which correspond to onset of phase separation and the gelation point of the blend, respectively. It is noteworthy that the time profiles of linear viscoelastic material functions enabled establishment of both the onset of phase separation and the gelation point of the blend at different isothermal cure temperatures. For the conditions used, the observed time profiles indicated that the PIPS transition precedes gelation and both transition times decreased with increasing temperature. Such a “double gel-point” phenomenon has been reported before in a variety of PIPS systems.\(^{39,40}\)

The gelation point can be loosely identified as the crossover between the storage and loss moduli indicating that sample has transferred from “liquid” “solid” in character. (Rigorously it is the point of frequency-invariance of loss tangent\(^{41}\)) By constructing an Arrhenious plot of inverse in gelation time, an Arrhenius\(^{42}\) dependence between activation energy and gelation time can be evaluated:

\[
\ln(k) = \ln\left(\frac{1}{t_{gel}}\right) = \ln(A) - \frac{E}{RT}
\]  

\[(1-8)\]
where \( k \) is the rate constant, \( t_{gel} \) is the gelation point, \( A \) is the pre-exponential constant, \( E \) is the activation energy and \( T \) is cure temperature (60, 80, 100 and 140 °C). Plotting the natural log of inverse time to gelation against the inverse cure temperature allowed estimation of the activation energy. Table 2-3 shows the calculated activation energies for the epoxy-PCL blends using Kissinger, Ozawa and Arrhenius models. All models yielded activation energy within the same range. With the incorporation of PCL, the activation energy slightly decreased which was expected since dynamic DSC results showed that for a particular heating rate, the total enthalpy of the reaction decreased in the presence of PCL.

2.5 Conclusions

Curing kinetics of an epoxy-based thermoset, with and without a semicrystalline thermoplastic, were investigated using differential scanning calorimetry (DSC) in both dynamic and isothermal modes. Several models were utilized to further investigate the cure mechanism. Our results showed that incorporation of PCL lowered the activation energy of cure reaction. Chemorheology experiments were also conducted to investigate the viscoelastic behavior of the blend as a function of cure temperature. Time profiles of the storage and loss moduli enabled the establishment of both the onset of phase separation and the gelation point of the blend at different isothermal cure temperatures. For the conditions used, the observed time profiles indicate that PIPS preceded gelation and that they both occurred faster as the cure temperature increased. Same PIPS technique studied in this chapters will be utilized in the next chapters to develop composites featuring triple shape memory (Chapter 7) and self-healing (Chapter 3) properties.
2.6 References


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Scheme 2-1. Schematic illustration of arrangement of molecules on a 10 X 10 lattice in Flory Huggins Theory. (A) Lattice with 50 units of ○ and 50 units of ■ placed on a lattice and (B) same lattice with 5 polymers with 10 ○ building blocks and 5 polymers with 10 ■ building blocks. The number of possible arrangements plunges dramatically from (A) to (B) reducing enthalpy of mixing. Scheme was adopted with permission from [Cowie, J. M. G.; Arrighi, V.: Polymers: chemistry and physics of modern materials; CRC Press, 2007, p. 220.].
Scheme 2-2. Schematic illustration of a binary polymer blends phase diagram showing (A) lower critical solutions temperature (LCST) and (B) upper critical solution temperature (UCST) with single-phase regions lying in between the two. Adopted with permission from [Cowie, J. M. G.; Arrighi, V.: Polymers: chemistry and physics of modern materials; CRC Press, 2007, p. 213.].
Scheme 2-3. Schematic illustration of a binary polymer blend phase diagram with upper critical solution temperature (UCST) behaviour. Stable, metastable and unstable regions territories are highlighted in the diagram. Green and red lines indicate bimodal and spinodal liners respectively. The convergence of these two lines is the UCST. Scheme was adopted with permission from [Cowie, J. M. G.; Arrighi, V.: Polymers: chemistry and physics of modern materials; CRC Press, 2007, p. 207.].
Scheme 2-4. The chemical structures of (A) diglycidyl ether of bisphenol-A (DGEBA), (B) neopentyl glycol diglycidyl ether (NGDE), (C) Jeffamine D230, (D) poly(ε-caprolactone) and (E) proposed epoxy matrix.
Scheme 2-5. Experimental procedure for the melt blending of DGEBA, NGDE, PCL and JD230. As phase separation progresses, a homogenous transparent blend changes to a translucent blend indicating polymerization induced phase separation (PIPS).
Figure 2-1. Optical microscopy (OM) images showing the morphological evolutions of PIPS blend at (A) 60 °C, (B) 80 °C and (C) 100 °C. Scale bar denotes 100 µm.
Figure 2-2. 2D FFT patterns of morphology evolution of PIPS blend (Figure 2-1) isothermally (A) 60 °C, (B) 80 °C and (C) 100 °C.
Figure 2-3. DSC thermograms of (i) Jeffamine® D-230, (ii) NGDE and (iii) DGEBA. Samples were heated only to 40 °C to avoid degradation of monomers. DSC did not detect any transition temperature for Jeffamine® D-230 and NGDE in our observation range. DGEBA though has a $T_g$ at round -20 °C.
Figure 2-4. DSC thermograms (2nd heating) of (i) PCL, (ii) cured EpoxyPCL₀, (iii) uncured EpoxyPCL₁₀ and (iv) cured EpoxyPCL₁₀ composite.
Figure 2-5. DSC 1st heating cycle (exo up) thermograms of as mixed (A) EpoxyPCL$_0$ and (B) EpoxyPCL$_{10}$ blends at different heating rates: (−) 5 °C/min, (−) 10 °C/min, (−) 15 °C/min and, (−) 20 °C/min. Scale bar represents 1 W/g.
Figure 2-6. Calculated Conversion (%) profiles for as mixed (A)EpoxyPCL$_0$ and (B) EpoxyPCL$_{10}$ blends at different heating rates: (−) 5 °C/min, (−) 10 °C/min, (−) 15 °C/min and, (−) 20 °C/min.
Table 2-1. Dynamic Curing Characteristics of EpoxyPCL\textsubscript{10} and EpoxyPCL\textsubscript{0} blends evaluated from Figure 2-5. To: the onset temperature, Tp: Peak Temperature and Tf: off-set temperature.

<table>
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<th>Composition</th>
<th>Heating Rate (°C min\textsuperscript{-1})</th>
<th>T\textsubscript{o} (°C)</th>
<th>T\textsubscript{p} (°C)</th>
<th>T\textsubscript{f} (°C)</th>
<th>Curing Range (°C)</th>
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</table>
Figure 2-7. Isothermal DSC traces of EpoxyPCL$_{10}$ blend at (i) 60 °C and (ii) 80 °C. The scale bar represents 0.02 W/g.
Table 2-2. Calculated autocatalytic constant for epoxyPCL$_{10}$ isothermal DSC at 60 and 80 °C.

<table>
<thead>
<tr>
<th>Cure Temperature (°C)</th>
<th>$k_1$ (10$^{-6}$ s$^{-1}$)</th>
<th>$k_2$ (10$^{-6}$ s$^{-1}$)</th>
<th>n</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1.71</td>
<td>3.80</td>
<td>1.088</td>
<td>0.353</td>
</tr>
<tr>
<td>80</td>
<td>17.4</td>
<td>38</td>
<td>1.088</td>
<td>0.353</td>
</tr>
</tbody>
</table>
**Figure 2-8.** Complex morphology profile for EpoxyPCL$_{10}$ as function of time showing (−) Real Viscosity and (−) Imaginary viscosity. Experiment was conducted at 60 °C. Arrows indicate (A) onset of phase separation and (B) gelation point.
**Table 2-3.** Calculated activation energy for epoxyPCL blends with different PCL weight fractions using Kissinger, Ozawa and Arrhenius models.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$E_{\text{Kissinger}}$ (kJ/mol)</th>
<th>$E_{\text{Ozawa}}$ (kJ/mol)</th>
<th>$E_{\text{Arrhenius}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EpoxyPCL$_0$</td>
<td>53.5</td>
<td>57.1</td>
<td></td>
</tr>
<tr>
<td>EpoxyPCL$_{10}$</td>
<td>50.3</td>
<td>54.4</td>
<td>47.1</td>
</tr>
</tbody>
</table>
Chapter 3: Thermally Triggered Self-Healing Coatings

3.1 Synopsis

Self-healing materials exhibit the ability to repair and to recover their functionality upon damage. Here, we report on an investigation into the preparation and characterization of shape memory assisted self-healing (SMASH) coatings. We built on past work in which poly(ε-caprolactone) (PCL) electrospun fibers were infiltrated with a shape memory epoxy matrix and delve into fabricating and characterizing a coating with the same materials, but employing a blending approach, polymerization induced phase separation (PIPS). Controlled damage was induced to both types of coatings and the ability to achieve crack closure and corrosion resistance restoration was investigated and compared. In both methods, coatings showed excellent healability though we consider the latter method more suitable to be industrialized due to simplicity and feasibility for widespread applications, including naval, as a self-healing corrosion barrier.

3.2 Introduction

Corrosion of metallic surfaces has been a major problem for the industry within the United States and globally for years. Particularly, the US Department of Defense (DOD) in its July 2009 report, *DOD Annual Cost of Corrosion*, stated that corrosion alone costs the military services an estimated $22 billion per year or 3.3% of the military’s total spending budget\(^1\,^2\). This estimate includes maintenance, repairs and replacement of corroded surfaces which can impose negative effects on military equipment, costs, readiness and safety. Corrosion in this context is defined as destruction of a material due to its interactions with the environment. Thus, there is a demand for coatings that can (1) protect metallic surfaces from corrosive elements such as mineral buildup, UV light exposure and rusting and, (2) avoid organic decay or degradation from exposure to harsh
environments. One of the most extensively used approaches to address such problems is to apply an organic barrier, usually polymeric coatings on a metal surface. In “Chapter 2: Self-Healing Anticorrosion Coatings” from Self-Healing Anticorrosion Coatings, this class of corrosion protection is considered the most economically feasible. Polymers and structural composites have been included in a variety of applications such as transport vehicles (cars, airplanes, trains), civil engineering, electronics and of course, corrosion prevention. However, these materials are susceptible to damage and failure under harsh environmental conditions. This could lead to formation of microcracks within the material that are very difficult if not impossible to detect and repair. Over time, microcracks propagate to form macrocracks and eventually lead to material failure. As such, there has been tremendous demand on developing biomimetic self-healing materials. Self-healing materials exhibit the ability to repair themselves and to recover functionality using the resources inherently available to them upon damage. There are a variety of ways to classify self-healing materials. One is to sort them based on the particular self-healing trigger such as mechanical, thermal and electrical.

Recently, shape memory materials have been extensively employed to further automate the self-healing process as we now explain. Shape memory materials have the built-in capacity to be deformed to a temporary shape and stored in that form until recovered to original shape under programed condition. This phenomenon can be utilized in self-healing process by providing a mechanism to partially or fully close the crack. Such novel concept has been demonstrated in at least two approaches. In the first approach, shape memory alloys (SMA) wires or shape memory polymers (SMPs) are locally positioned in the damaged area. Upon activation, they exert a contractual force that pulls the crack surfaces closer. The second approach utilizes “bulk shape memory effect to close the crack. Nji et al. fabricated a composite with thermoplastic
particles (copolyester) dispersed in a shape memory matrix (Veriflex polystyrene)\textsuperscript{27}. The concluded that shape recovery of the shape memory matrix governed sealing the cracks and the thermoplastic particles provided molecular-length scale healing. Results showed that over 65\% of the peak bending load recovered and the structural-length scale damage (notch) is healed at molecular-length scale. Our group has reported a poly(\(\varepsilon\)-caprolactone) based molecular composite consisting a thiol-ene crosslinked PCL (n-PCL) and a high molecular weight (\(M_w\)) linear PCL (l-PCL)\textsuperscript{28}. The crosslinked PCL network demonstrated reversible plasticity; a form of shape memory where large plastic deformation at room temperature is fully recoverable upon heating. Followed by crack closure, l-PCL chains rebond the crack surfaces by diffusion to the free surface and ultimately across the area of damage during the same heating step as used for SM. This process, dubbed as shape memory assisted self-healing (SMASH) revealed that damage imparted in the sample was well-healed when the samples were heated. Inspired by the concept of SMASH, we here report on two strategies to develop thermally triggered self-healing coatings. The first approach was based on our previous experience with the processing of “SMASH coating” in which electrospun fibers of a thermoplastic polymer were infiltrated with an epoxy network\textsuperscript{29}. Our second approach utilized polymerization induced phase separation (PIPS)\textsuperscript{30-38} of epoxy and PCL yielding a unique morphology amenable for self-healing. For both methods, structural self-healing (crack closure) and functional self-healing (corrosion resistance restoration) were investigated.

3.3 Experimental Section

3.3.1 Materials

Poly(\(\varepsilon\)-caprolactone) (PCL) (\(M_n \approx 70,000-90,000 \text{ g mol}^{-1}\)), neopentyl glycol diglycidyl ether (NGDE), diglycidyl ether of bisphenol A (DGEBA), and poly(propylene glycol) bis(2-
aminopropyl ether) (Jeffamine® D-230), dimethylformamide (DMF) and chloroform were purchased from Sigma-Aldrich. All materials were used as received. All coatings were applied on general purpose 1074/1075 spring steel panels purchased from McMaster-Carr. The stainless steel substrates were first cut into rectangular (15.1 mm width x 30.0 mm length x 0.6 mm thickness) pieces and then carefully sanded at the surface to remove any corrosion prior to the experiments.

3.3.2 Fabrication of Coatings

Two different methods were employed to apply coatings on the metal substrate. In the first method, PCL was electrospun onto the metal substrate. The PCL fiber mat was then infiltrated with epoxy resin using spin coater. Hereafter, these samples are referred to as Espun Coating. In the second method, PCL was mixed with epoxy monomers first followed by addition of crosslinker to the blend yielding polymerization induced (PIPS) phase separation. Such samples are dubbed PIPS Coating hereafter. Details of both methods are explained below.

3.3.2.1 Espun Coating

The Espun coating was fabricated following the method developed in our group29. In what follows, the two-step process for fabricating the coatings are explained.

3.3.2.1.1 Electrospinning

PCL solution was prepared from 2.0 g of PCL dissolved in 8 ml of chloroform and 2 ml dimethylformamide by volume to achieve a 20 % (weight/volume) solution. The solution was then mixed overnight at room temperature (RT) until a clear, homogenous solution was obtained. The solution was then electro sprayed onto a steel substrate at a flow rate of 1.0 mL·h⁻¹, working distance
of 15 cm, voltage of 12.0 kV and no rotation or translation for 20 minutes. The schematic illustration of the setup is provided in Scheme 3-1.

3.3.2.1.2 Spin Coating

To prepare the epoxy resin, equimolar mix of DGEBA, NGDE and Jeffamine® D-230 were mixed and hand-stirred at room temperature until a clear, homogeneous and low-viscosity solution was obtained (Molar ratio of DGEBA:NGDE:Jeffamine® D-230 was 1:1:1). 1.5 mL of this mixture was then spin coated to the electrosprayed substrate using a Laurell Technologies Corporation instrument. This process does not swell or dissolve PCL and removed any excess liquid epoxide on the surface of the sample. The samples were then cured at RT for 24 hours, heated in isothermally at 40 °C for 48 hours, then 60 °C for 24 hours. Note that epoxy phase not only permeated through the fibers, but also formed a strong adhesion to the metal substrate upon cure.

3.3.2.2 PIPS Coating

Coatings were also prepared following the same method introduced in Section 2.3.2. Briefly, coatings were prepared by mixing 9 wt. % PCL with a combined 91 wt. % equimolar mixture of DGEBA, NGDE and Jeffamine® D-230. Note that for comparison, PCL weight fraction here is the same as that of Espun coating (See Results and Discussions). PCL, DGEBA and NGDE were first combined in a three-neck round bottom flask, heated at 90 °C in a hot-oil bath, and vigorously mixed with a high power stirrer (Arrow Engineering Co., Model 6000) for 1-2 hours or until a homogenous clear blend was achieved. To avoid air bubbles formation, vacuum was applied during this process. Once uniform consistency was achieved, the flask was removed from the heat source and allowed to cool to RT. Jeffamine® D-230 was then added and the entire blend was stirred for another 2-5 min.
The blend consisting of PCL and uncured epoxy formulation was then poured and spread onto stainless steel substrates to achieve a uniform thickness on par with that of the Espun coating (Figure 3-1). The samples were then cured using the same procedure followed for Espun coating; 24 hours at RT, 48 hours at isothermal 40 °C then 24 hours at isothermal 60 °C. As the epoxy polymerized, the initial miscible mixture became less stable and eventually phase separated from PCL phase. This process is called polymerization induced phase separation (PIPS) and is largely reviewed in literature and by our group\textsuperscript{30-36}. For details of PIPS process, refer to Chapter 2.

### 3.3.3 Thermal Characterization of the Coatings

Thermal properties and PCL content of coatings were characterized using Differential Scanning Calorimetry (DSC), expecting relatedness to self-healing behavior studied later. DSC experiments were conducted using a Q200 (TA Instrument) equipped with a refrigerated cooling system (RCS). 3-5 mg of each coating was scratched off from the metal substrate surface and was encapsulated in a Tzero aluminum pan. Samples were then heated from -80 °C to 120 °C, cooled back to -80 °C, and finally heated to 120 °C. All heating were conducted at the rate of 10 °C min\textsuperscript{-1} and all cooling rate were 5 °C min\textsuperscript{-1}. Glass transition temperature (T\textsubscript{g}) and melting transition (T\textsubscript{m}) of the samples were determined as the middle point of the step transition and the melting peak transition of the DSC second heating runs, respectively.

### 3.3.4 Damage Application

A custom made scratch machine was designed and employed to apply reproducible and controllable scratches to the coatings. The scratch machine was exploited in order to standardize the force applied to the sample and keep scratches relatively uniform from sample to sample. Photographs and a schematic illustration of the scratch machine is provided in Scheme 3-2. In
order to apply scratch onto the sample, a sample was placed in the sample holder and the sample holder was screwed into place in the machine. The sample holder was then secured within the sample car and the overhang was lowered with the blade resting on the sample. By adding additional weight (100 or 1000 g) to the mass holder, the applied pressure on the sample was controllably altered. The set up was powered by an external power source (2 A Regulated DC Power Supply, 12 V applied) which initiated motion of the sample car towards the right at approximately 0.8 cm s⁻¹; scratching the sample. For each experiment, a fresh industrial blade (GEM Stainless Steel, uncoated) was screwed in and positioned at approximately a 45° angle to the sample (Scheme 3-2(C)). In order to compare self-healing capability of the coatings under various types of damage, 3 different types of scratches were induced onto the coatings by adding additional weight (100 or 1000 g) to the mass holder: single scratch line with a 100 g weight in the mass holder, single scratch line with a 1000 g weight and, two perpendicular scratch lines to form a cross-shape scar with additional 1000 g. Note that by adding the weight in mass holder (from 100 to 1000 g), higher stress is applied from tip of the blade onto the coating surface resulting in more severe damage. Hereafter, the samples scratched using the aforementioned 3 methods are called “mildly”, “severely” and “obliquely” damaged coatings, respectively.

3.3.5 Self-Healing Characterization-Microscopy

The ability of the coatings to close the “crack”, i.e. structural self-healing was studied primarily using microscopy techniques. To monitor this process, mildly and severely damaged coatings were placed on an Instec HCS-402 hot-stage and heated from 25 to 95 °C at a constant heating rate of 2 °C min⁻¹ followed by holding isothermally at 95 °C for 10 min. A Zeiss Discovery V8 stereo microscope equipped with a QImaging CCD camera was used to monitor the structural changes at the damaged site during heating. Images were taken every 2 minutes during the experiment.
In the second method, mildly, severely and obliquely damaged coatings were quickly heated and held isothermally at 80 °C for 1 h during which changes at the damaged area was monitored using a JEOL JSM-5600 scanning electron microscope (SEM) to examine the damaged site and crack closure process at higher magnifications. Finally, seeking to simulate a more practical method to close a crack, only the surface of a severely damaged coatings were heated using a heat gun (Windmere Salon Mate 1250). The distance of the gun from the sample was set to achieve a temperature of approximately 80 °C at the surface of the coating over the specified period of time (1 h). The temperature was measured using a thermocouple (Fluke Corporation, S1 II Thermometer) for 20 min after turning the gun on every 2 min for 1 h to assure the initial temperature gradient is minimized and temperature remains consistent prior to the experiment. The set-up scheme is displayed in Scheme 3-3. Same JEOL SEM instrument was utilized to study crack closure of a severely damaged coating pre and post heating only at the surface with a heat gun. Note that these experiments were conducted on both Espun and PIPS coatings to compare their functional self-healing.

**3.3.6 Multiscratch Testing**

In an effort to examine the ability of both the Espun and PIPS coatings to heal after repeated damage cycles, we attempted to investigate crack closure ability of the sample after recovering from several damages located at the same location, to the best of our precision in sample mounting. To do so, damaged coatings were thermally mended at 80 °C for 1 h in the 1st cycle. Then coatings were scratched at the same location as in the 1st cycle using the scratch machine and heated at 80 °C for 1 h to complete the 2nd cycle. This cycle was repeated 5 times and damaged recovery was monitored using the same Zeiss Discovery V8 stereo microscope.
### 3.3.7 Voltammetry

Linear sweep voltammetry was performed to directly characterize the ability of the coatings to prevent corrosion (functional self-healing). Rebonding of the crack is difficult to visualize yet can be quantified by characterizing restoration of corrosion resistance of the coatings. To do so, a three-electrode setup with an electrochemical cell specifically designed for plate geometries and a Bio-Logic SP-50 potentiostat were used for all the experiments (For details refer to our group previous report\(^{29}\)). A severely damaged coating was then exposed to a 5 wt. % NaCl electrolyte solution. Only the portion of the crack within the O-ring (inner diameter = 8 mm) was in actual contact with the electrolyte. The working, counter and reference electrodes were the coating substrate, Pt and Ag/AgCl in 3M KCl solution, respectively. The open circuit potential (OCP) was first monitored until it became stable versus time (Generally, the OCP profile reached a plateau within 1 h). The voltage (relative to the reference electrode) was then linearly scanned from -0.8 V to 1 V at a constant rate of 20 mV s\(^{-1}\) while recording the electrical current data\(^{39-41}\). The measured current (I (mA)) would indicate the corrosion resistance of the coating since the rate of corrosion is proportional to the current density. For an ideal coating with good barrier properties (either undamaged or completely self-healed), the coating would be a perfect isolator and subsequently the measured current would be negligible. Therefore, if self-healing is complete; i.e. crack closure occurred followed by rebonding of the crack surfaces, the measured current ideally would approach zero. To compare the corrosion resistance, the average maximum current of a healed coating (heated isothermally at 80 °C) observed in the linear sweep voltammetry experiments were compared to that of the severely damaged coating for both PIPS and Espun coatings (n=3). A student \(t\)-test was used to compare the damaged and healed groups. To investigate the effect of PCL on the self-healing process, the average maximum current of both
healed PIPS and Espun coatings were compared with Epoxy coating (with no PCL) as the control (n=3). Note that Epoxy coating was applied onto a stainless steel substrate using the same protocol for applying the PIPS blend (See Section 3.3.2.2). The student t-test was performed using the Sigmaplot software with 95% confidence interval and 0.05 P-value to reject. All the experiments were conducted at ambient conditions.

3.4 Results and Discussion

3.4.1 Thermal Characterization

Thermal properties of the coatings were characterized using Differential Scanning Calorimetry (DSC) expecting relevance to self-healing behaviour studied later. DSC traces of as received PCL, PCL fibers, cured neat epoxy, cured Espun coating, uncured PIPS blend and PIPS coating are shown in Figure 3-2. Semi-crystalline PCL fibers showed \( T_m = 55 \, ^\circ C \) and amorphous cured epoxy showed at \( T_g = 46 \, ^\circ C \). For self-healing purposes it is essential to heat the coating above both of these transitions to completely utilize shape memory response of the epoxy matrix and also capillary flow of PCL to the damaged area.

The Espun coating showed two distinct transitions at 43 \( ^\circ C \) and 55 \( ^\circ C \) resulting from \( T_g \) of amorphous epoxy phase and \( T_m \) of semicrystalline PCL phases, respectively. In Espun coating, transition temperature of each phase remained approximately equal to each individual component transition temperature in pure state indicating that the two phases were completely separated from each other. The weight fraction of the epoxy and PCL phases were gravimetrically measured to be 91 and 9 \%, respectively. Note that average PCL enthalpy of melting was calculated by averaging the magnitude of melting for each group (DSC traces of 3 different PIPS and Espun coatings are provided in Figure 3-3). The weight fraction of phase separated PCL was then calculated
gravimetrically to be c.a. 9 % by dividing latent heat of fusion for PCL in the coatings to that of pure PCL.

The as mixed PIPS blend, showed one single transition at 24.1 °C which indicated that the blend was homogenous and in one phase. The glass transition value was higher than what we expected. We attribute this to some cure that took place in the 3-5 min window that is normally required after adding the crosslinker to the blend to prepare DSC pans and start the DSC experiment. Nonetheless, the cured PIPS coating showed two transitions at 34 °C and 55 °C corresponding to epoxy and PCL phases, respectively. This result was in agreement with optical microscopy results (Figure 2-1) where the epoxy and PCL were initially in one phase showing one transition temperature but as epoxy polymerization progress, PIPS occurred resulting in two separate transitions. Curing, phase separation kinetics and chemorheology analysis of such blend, with and without PCL is reported in Chapter 2. Fully cured PIPS coatings also showed one glass and one melting transition similar to Espun coating. However, the epoxy T_g in the cured PIPS coating was about 10 °C lower than that of cured epoxy indicating that some portion of PCL remained in one phase with PCL probably due to high viscosity of the blend and acted as plasticizer. This is in good accordance with PCL T_m in the PIPS coating showing that final weight percentage of PCL that is separated from the matrix is only 5.7 %, less than the, 9 %, total weight percentage of PCL in the PIPS coating. Thermal properties of both PIPS and Espun coatings (n=3) are summarized in Table 3-1.
3.4.2 Coatings Morphology

Shown in Figure 3-4 are SEM micrographs and photographs of electrosprayed PCL fiber mat, Espun coating and PIPS coating. Results indicate that PCL fibers are randomly oriented with an average fiber diameter of 2.69 μm ± 0.33 (measured by image analysis using ImageJ software, Number of measurements: 100) (Figure 3-4(A)). Upon spin coating, the epoxy mixture (DGEBA, NGDE and Jeffamine® D-230) easily permeated into and wetted the PCL fiber mat due to its highly porous structure turning the white PCL fibers to translucent. It’s important to note that spin coating was conducted at high speeds (1000 rpm for 20 s; 3) 2000 rpm for 20 s; and finally (4) 3000 rpm for 20 s) which removed any excess epoxy on the surface of the PCL fiber mat. Therefore, the final thickness of the Espun coating is dictated by the thickness of PCL fiber mat and in fact, some of the PCL fiber are sticking out of the coating as evident in Figure 3-4(B). The final average thickness of the given coatings were measured to be 410 μm ± 132 (n=100 with an average PCL weight fraction of ca. 9 % which was measured gravimetrically (For more details in thermal properties of fabricated coatings, refer to Table 3-1.). The PIPS coatings were much smoother in the surface compared to Espun Coatings given that they were applied on stainless steel substrates using a precision film applicator (Figure 3-4(C)). It’s important to note that average final thickness and PCL content of PIPS coating were purposefully set to be consistent with that of the Espun coating in order to avoid effects of coating thickness and PCL content on healability (The average final thickness of these samples was 450 μm (± 118)). Additionally, the epoxy based thermosets formed strong adhesion to several substrates including stainless steel in both types of coatings with minimal water absorption in both Espun and PIPS coatings42-44. Though the strength of epoxy adhesion to metallic substrate was not quantified, we qualitatively observed that such adhesion was noticeably strong and it was impossible to manually debond the coatings from the substrate.
3.4.3 Structural Self-healing

Structural recovery (crack closure capability) of the prepared coatings was visualized using microscopy. Figure 3-5 shows SEM micrographs of mildly, severely and obliquely damaged Espun coatings after 2 min and 1 h of heating isothermally at 80°C. The mild damage induced minimal material removal and mostly plastic deformation (Figure 3-5(A)). After 2 min, reversible plasticity shape memory recovery\textsuperscript{36} of the epoxy matrix pulled crack surfaces in spatial proximity and the crack was completely closed. However, a remaining scar was still visible. This is due to the fact that upon damage, the two edges of the crack bow upwards (Figure 3-6) and during recovery, the two edges of crack did not return to their precise original location leading to formation of scar in the recovered area. After 1 h the scar was also faded however not completely removed. In the severely damaged coating, there was evidence of material removal and the crack was wider relative to the previous case (Figure 3-5(B)). After 2 min, the crack width reduced significantly but it was not completely closed. However, after 1 h, complete crack closure was achieved and only a scar on the surface remained. Snapshots of crack closure for mildly and severely damaged Espun coatings heated from 25 to 80 °C at 2 °C min\textsuperscript{-1} are provided in Figure 3-7 and Figure 3-8, respectively. To quantify crack closure, the widths of cracks in the SEM micrographs were measured for severely damaged, healed after 2 min and healed after 1 h coatings using ImageJ software. The self-healing efficiency was calculated using the following equation:

\[
Healing\% = \left(1 - \frac{W_{Healed}}{W_{Damaged}}\right) \times 100 \tag{3-1}
\]

where \(W_{Healed}\) is the crack width of the healed sample and \(W_{Damaged}\) is the crack width of the damaged sample. The experiments were repeated 3 times. The crack width were 80.57 ± 1.265 μm; 21.35 ± 0.524 (73.5 %) and 2.39± 0.371 μm (corresponding to 97.0 % self-healing efficiency).
for severely damaged Espun coating, mended at 80 °C for 2 min and 1 h, respectively. Results indicate excellent crack-closure ability which is attributed to shape memory properties of epoxy matrix\textsuperscript{45}. In the obliquely damaged coating, the second damage deformed the first damage line into a curve (Figure 3-5(C)). This was interesting to study since in ideal self-healing scenario, the deformed line would revert back to straight followed by complete crack closure. In this case, the total damaged area at the intersection was larger than singular damage, thus the self-healing efficiency was lower and the crack was not completely closed even after 1 h despite the fact that same amount of force was applied to induce the damage. In addition, some compress lines were observed around the damaged area in all Espun coatings, highlighted with arrows in Figure 3-5(C). We attribute this to glassy characteristics of epoxy at RT when the damaged was induced (Epoxy $T_g = 46 \, ^\circ\text{C} > \text{RT}$, for more details, see Table 3-1). Interestingly, all these compress lines disappeared upon initiation of self-healing. Moreover, these compress lines were not observed in PIPS coating due to the fact that epoxy $T_g$ was lower than that of Espun coating. We speculate that portion of PCL that was in one phase with epoxy contributed to more ductile behavior of the PIPS coating. In the last case, when only the surface of the Espun coating was heated at 80 °C, even after 1 h the crack was not closed completely designating that thermal conduction to the coating was not adequate to release the stored energy of the coating and the crack was not completely closed (Figure 3-5(D)).

Same experiments were conducted on the PIPS coating to compare the healing behaviour of the two coatings as provided in Figure 3-9. Both mildly and severely damaged PIPS coatings showed complete crack closure upon damage (figure 3-9(A) and 3-9(B)). Results showed that the crack width were $45.59 \pm 0.648 \, \mu\text{m}$, $21.08 \pm 0.736 \, (53.76\%)$ and 0 (corresponding to self-healing efficiency of 100 %) for the severely damaged PIPS coating, mended 80 °C for 2 min and 1 h,
respectively. Snapshots of crack closure for mildly and severely damaged PIPS coatings as temperature increases are provided in Figure 3-10 and Figure 3-11, respectively. After 1 h, the crack was completely closed with only a scar evident at the surface indicating comparable crack-closure ability compared to that of Espun coating. The extent of deformation in the obliquely deformed coating led to incomplete recovery after 1 h as shown in Figure 3-9(C). In the last case, the surface treated severely damaged coating was completely healed after 1 h demonstrating better crack closure than Espun coating (Figure 3-9(D)). We speculate this is due to the fact that $T_g$ of epoxy phase in the PIPS coating was about 10 °C lower than Espun coating and consequently reversible plasticity shape memory effect triggered at lower temperatures. Had we selected an epoxy with higher $T_g$, the recovery would occur at higher temperatures. However, we opted to keep the epoxy matrix chemistry consistent for both Espun and PIPS coatings. It’s noteworthy that different morphologies of the PIPS and Espun coatings could also affect the shape memory response of the coatings which requires further investigation in future studies. Note that morphology of the Espun coating is fixed but final morphology of the PIPS coating can be controlled as function of temperature and blend viscosity yielding a variety if phase domain shape and sizes.

### 3.4.4 Multi scratch Testing

In realistic environments, coatings undergo damage several times. Therefore, self-healing systems that would recover from damage multiple times are desirable. To investigate this important characteristic of the coatings, both coatings were severely damaged, heated at 80 °C for 1 h and then damaged again at the same location. This cycle was repeated 5 times for both PIPS and Espun coatings. Figure 3-12 shows optical micrographs of the first damaged and 5 consecutive healed coatings. Results showed that both PIPS and Espun coatings showed good crack closure even after
being damaged for 5 times. For Espun coating, a scar remained, but the PIPS coating showed nearly prefect healing even after 5 cycles. To our knowledge, this is one of the highest numbers of self-healing cycles requiring no human intervention reported in literature so far.

3.4.5 Functional Self-healing

The functional recovery (corrosion resistance restoration) of the coatings was also studied using linear sweep voltammetry technique. Severely damaged Espun and PIPS coatings were exposed to a 5 wt. % NaCl electrolyte solution while monitoring the current and voltage. The solution OCP was first monitored until it became stable over time. A typical OCP profile decays until it reaches an equilibrium value within 1 h as illustrated in Figure 3-13. The voltage (relative to the reference electrode) was then linearly scanned from -0.8 V to 1 V at a constant rate of 20 mV.s⁻¹ while recording the electrical current data. The voltage (V) vs. current (I) results for PIPS and Espun coatings are presented in Figure 3-14(A). Electrical current profiles of both Espun and PIPS damaged coatings showed an increase at first, reached a maximum and then decreased. We speculate this was attributed to formation of iron(III) oxides Fe₂O₃·nH₂O and iron(III) oxide-hydroxide (FeO(OH), Fe(OH)₃) that are produced by reaction of metallic substrate in and around the damaged area which macroscopically are green in color and act as isolators themselves⁴⁶. This decrease in current was not observed for self-healed samples due to the fact that corrosion-induced formation of such components was minimal, indicating complete self-healing. The average maximum current observed in voltammetry experiment for Espun and PIPS coatings at damaged and healed states are provided in Figure 3-14(B) (n=3). Results showed a significant difference between the damaged and self-healed coatings. Maximum current for self-healed samples were about 3 orders of magnitude lower than damaged samples indicating excellent recovery of corrosion resistance properties of the coatings (Figure 3-14(B)). Without PCL, the neat epoxy
coating also showed high corrosion resistance restoration (low current) after healing as shown in Figure 3-15(A). However, in presence of PCL the maximum current decreased another order of magnitude for healed coatings (both PIPS and Espun Coating) compared to control (neat epoxy coating) indicating successful rebonding of the crack surfaces in the presence of PCL (Figure 3-15(B)).

3.5 Conclusions

Corrosion resistant coatings featuring shape memory assisted self-healing\textsuperscript{28,29} properties were fabricated using two different methods: first electrospun fibers were infiltrated with a shape memory epoxy matrix whereas in the second approach, coatings were prepared using polymerization induced phase separation (PIPS) technique. By keeping composition and thickness relatively constant, the ability of the two coating groups to close the crack and recover their initial corrosion resistant properties were compared from an engineering standpoint. Both coatings revealed excellent and comparable structural (crack closure) and functional (corrosion resistance restoration).

3.6 Future Work

3.6.1 Self-Healing Agent Weight Fraction

Advantages of coatings prepared by PIPS technique include but are not limited to flexibility in varying coating thickness or self-healing agent (PCL) weight fraction which require further investigation. The control on the volume fraction of PCL in the Espun coating however is difficult if not impossible. We hypothesize that as PCL weight fraction increases, it plasticizes epoxy phase further and consequently suppresses epoxy $T_g$ to lower temperatures. The rebonding of the crack surfaces would be stronger given that volume fraction of PCL is higher. Lastly, PCL acts as a
viscosity thickener in the blend and increase in volume fraction of PCL can significantly increase the viscosity of the blend retarding both epoxy curing and phase separation kinetics.

3.6.2 Incorporation of Corrosion Inhibitor in PIPS Coatings

Incorporation of corrosion inhibitors\textsuperscript{47,48} in the fibers or the mixed blend that are released upon damage further minimizing the corrosion, also remains the subject of future work. Given the simplicity of fabrication of coatings and their impressive self-healing properties, we envision mass product of them for several applications such as naval.

3.7 References


(45) Xie, T.; Rousseau, I. A. Facile tailoring of thermal transition temperatures of epoxy shape memory polymers. Polymer 2009, 50, 1852-1856.


Scheme 3-1. (A) Schematic illustration and (B) photograph of the custom-made electrospaying apparatus for coating the steel substrate with PCL fiber mat. PCL solution was pumped (i) through tubing (ii) to a needle on the top of the collecting drum. The solution was charged using a high voltage power supply at the tip of the needle (iii). As the polymer solution within the syringe becomes charged, a “Taylor” cone forms at the tip of the syringe needle due to like-charge electrostatic repulsion. At a critical point, a charged jet of the polymer solution forms and is gunned towards the grounded drum covering the entire metallic substrate surface as shown by arrows. Before reaching the collecting plate (iv) which is electrically grounded (v), the electrostatic force overcomes the solvent surface tension force resulting in solvent evaporation. Dry polymer fibers are then collected on the stainless steel substrate (vi). Fiber properties such as diameter and orientation can be controlled by adjustment of electrospinning parameters such as voltage (iii), flow rate (i) and tip of the needle to collector distance (vii). (C) and (D) show photographs of a stainless steel substrate before and after electrospraying covering it with white PCL fibers, respectively.
Figure 3-1. Photographs of the film applicator, (A) top view and (B) front view with coated stainless steel substrate. A PIPS blend as thick as Espun coating was applied onto the substrate. The blend was then cured to fabricate PIPS coating approximately as thick as the Espun coating.
Scheme 3-2. (A) Schematic of custom-made scratch machine. Samples (i) were loaded in the sample holder (ii) and secured within the sample car (iii). The overhang (iv) was lowered with the blade (v) resting on the sample. A mass (vi), either 100 g or 1000 g was placed with in mass holder (vii) and the power was turned on which initiated motion of the sample car towards the right (viii) at approximately 0.8 cm s⁻¹; scratching the sample. Top and side view photographs of the custom made scratch machine are provided in (B) and (D), respectively. (C) For each experiment, a fresh industrial blade (GEM Stainless Steel, uncoated) was screwed in and positioned at approximately a 45° angle to the sample.
Scheme 3-3. Schematic illustration of surface heating of the samples with a heat gun. Several heat-gun to sample distances were examined to find one which yielded a surface temperature of approximately 80 °C making it comparable to the samples healed at isothermal 80 °C in the oven. Blue arrow indicates heat gun to substrate surface distance.
Figure 3-2. DSC thermograms (2\textsuperscript{nd} heating) of (i) PCL, (ii) PCL fiber, (iii) neat epoxy, (iv) Espun coating, (v) uncured PIPS blend and (vi) cured PIPS coating. Heating and cooling rates for all samples were 10 and °C min\textsuperscript{-1}, respectively.
Figure 3-3. DSC thermograms (2nd heating) of Espun coatings (solid lines) and PIPS coatings (dashed lines) for 3 samples in each group. Heating and cooling rates for all samples were 10 and 5 °C·min⁻¹, respectively. Average PCL enthalpy of melting was calculated by averaging the magnitude of melting for each group (PIPS or Espun). Weight fraction of phase separated PCL was then calculated by latent heat of fusion for PCL in the coatings divided by that of pure PCL. Epoxy phase glass transition temperature in the cured PIPS coating was about 10 °C lower than that of cured neat epoxy which indicated that some portion of PCL remained in one phase with PCL probably due to high viscosity of the blend and acted as plasticizer. This is in good accordance with PCL melting transition in the PIPS coating that indicates final weight fraction of PCL that is separated from the matrix is only 5.7 %, less than 9 % in the Espun Coating.
Table 3-1: Summary of thermal properties determined from DSC experiments. Melting transitions were determined as the peak of transitions of the second heating runs. Glass Transitions were determined as the middle point of transitions. Enthalpy of coating is reported as average of 3 DSC runs for each group (See Figure 3-2 and 3-3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_g (°C)</th>
<th>T_m (°C)</th>
<th>(\Delta H_{m,PCL}) (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>-</td>
<td>56.3</td>
<td>51.2</td>
</tr>
<tr>
<td>PCL Fiber</td>
<td>-</td>
<td>54.9</td>
<td>54.9</td>
</tr>
<tr>
<td>Epoxy</td>
<td>46.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Espun Coating</td>
<td>43.2</td>
<td>55.6</td>
<td>5.0± 0.2</td>
</tr>
<tr>
<td>PIPS blend</td>
<td>24.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PIPS Coating</td>
<td>34.0</td>
<td>55.9</td>
<td>2.9± 0.1</td>
</tr>
</tbody>
</table>
**Figure 3-4.** Scanning electron micrographs and photographs of (A) PCL electrospun fiber mat, (B) Espun coating and (C) PIPS coating. Scale bars for SEM micrographs and photographs are 100 µm and 1 mm, respectively.
Figure 3-5. Scanning electron micrographs of damaged and respective healed Espun coatings showing (A) mildly, (B) severely, (C) obliquely and (D) severely damaged coating that was heated only at the surface. Left, middle and right columns represent damaged, healed after heating for 2 min and healed after heating for 1 h at 80 °C samples, respectively. Note that in (A), (B) and (C), the entire coating was heated at 80 °C whereas in (D) only the surface of the coating was heated at 80 °C. Scale bare represents 100 µm. Arrows show the compresslines around the damaged area.
Figure 3-6. Surface of a scratched coating topography obtained with a KLA-Tencor P15 Surface Profiler plotting the height, $z$, versus position on the surface. Surface profilometry shows that scratch induced deforming the side crack walls upwards. Dashed circle highlights the scratched area.
Figure 3-7. Stereo microscope micrographs showing structural self-healing of mildly damaged Espun coating. The damaged coating was heated from 25 to 95 °C at 2 °C·min⁻¹ and then kept isothermally at 95 °C for 10 min. The scale bar represents 200 μm.
**Figure 3-8.** Stereo microscope micrographs showing structural self-healing of severely damaged Espun coating. The damaged coating was heated from 25 to 95 °C at 2 °C·min⁻¹ and then kept isothermally at 95 °C for 10 min. The scale bar represents 200 μm.
**Figure 3-9.** Scanning electron micrographs of damaged and respective healed PIPS coatings showing (A) mildly, (B) severely, (C) obliquely and (D) severely damaged coating that was heated only at the surface. Left, middle and right columns represent damaged, healed after heating for 2 min and healed after heating for 1 h at 80 °C samples, respectively. Note that in (A), (B) and (C), the entire coating was heated at 80 °C whereas in (D) only the surface of the coating was heated at 80 °C. Scale bare represents 100 µm.
Figure 3-10. Stereo microscope micrographs showing structural self-healing of mildly damaged PIPS coating. The damaged coating was heated from 25 to 95 °C at 2 °C·min⁻¹ and then kept isothermally at 95 °C for 10 min. The scale bar represents 200 μm.
Figure 3-11. Stereo microscope micrographs showing structural self-healing of severely damaged PIPS coating. The damaged coating was heated from 25 to 95 °C at 2 °C min⁻¹ and then kept isothermally at 95 °C for 10 min. The scale bar represents 200 μm.
Figure 3-12. Optical micrographs showing (A) damaged Espun coating and 4 consecutive healed Espun coatings, (B) damaged PIPS coating and 4 consecutive healed PIPS coatings. The scale bar represents 200 μm. Both coatings exhibited good crack closure event after being damaged 4 consecutive times at the same location.
**Figure 3-13.** A typical pen circuit potential (OCP) profile which decays until it reaches an equilibrium value within 1 h.
Figure 3-14. (A) Linear sweep voltammetry experiment showing I (mA) vs. V (v) plots for (i) bare stainless steel, (ii) damaged Espun, (iii) damaged PIPS, (iv) healed Espun and (v) healed PIPS coatings after 1 h at 80 °C. (B) The average maximum current observed in voltammetry experiments for Espun and PIPS coatings at damaged and healed states (n=3). The difference in the mean values of the damaged and healed samples for both Espun and PIPS coatings are greater than would be expected by chance; thus there is a statistically significant difference between the input groups (P < 0.001).
Figure 3-15. (A) Linear sweep voltammetry experiment. $I$ (mA) vs. $V$ (v) plots for epoxy coating without any PCL (as a control) (i) damaged and (ii) healed after 1 h at 80 °C. (B) Average maximum current measured for (1) Espun coating, (2) PIPS coating and (3) epoxy coating without any PCL (as a control) in both damaged and healed states ($n=3$). The difference in the mean values of the damaged and healed groups is greater than would be expected by chance; there is a statistically significant difference between the input groups. The * and ** indicate $p<0.001$ and $p<0.05$ in the $t$-test.
Chapter 4: Fabrication and Characterization of Core-Sheath Fibers: Toward Mechanically Activated Self-Healing Composites

4.1 Synopsis

In order to prolong life-time of polymeric materials, researchers have been seeking to develop self-healing materials. In this chapter we report on a novel approach to fabricate core-sheath fibers where a healing agent is encapsulated in polymeric fibers through the use of a coaxial electrospinning technique. Upon fracture of a composite bearing such fibers, the healing agents would be released, flow to the damaged area and crosslink to the self-healed form. This chapter highlights characterization of our new core-sheath fibers for self-healing materials including curing kinetics of the core material (self-healing agent) at RT and structural investigation of the fibers. We then introduce a new concept fiber structure termed “beads-on-string” and report on progress made to achieve such properties.

4.2 Introduction

Polymeric composites are ordinarily subjected to under mechanical stress and harsh environmental conditions during their use which can lead to the formation of microcracks and eventually material failure. The induced damage is challenging to detect which makes it even more difficult, if not impossible to repair\textsuperscript{1,2}. Consequently, the mechanical proprieties of polymeric materials can be excessively compromised over time. Reinforcing specific critical areas in Polymer Matrix Composites (PMCs), also known as Fiber Reinforced Composites (FRCs)\textsuperscript{3-6}, is the most advantageous method to prolong structural durability. FRCs offer several advantages over other load bearing materials including high strength-to-weight ratio, mechanical properties that can be tailored to specific applications, and fatigue resistance. Since poly(acrylonitrile) (PAN) fibers (and the carbon nanotubes (CNTs) made from them)\textsuperscript{7-10} have admirably high tensile strength, they can
be used as a functional additive to enhance the mechanical properties of FRCs. Therefore, well-dispersed and well-aligned PAN fibers in conjunction with a self-healing technology in order to fabricate FRCs improves mechanical properties of the composite that will self-heal damaged regions of the FRCs, in particular at the interlaminar interface of the resin matrix and the PAN fibers. Such multi-functionality will enable enhanced mechanical, thermal and electrical properties not otherwise achievable. In addition, the self-healing property would enable a damaged FRC component to be healed to a restored condition. Note that self-healing materials are defined as those that exhibit the ability to recover functionality using the resources inherently available to them upon damage\textsuperscript{1,2,11-13}. In this chapter, we report on a unique strategy to introduce the self-healability feature to nanofibers that can be eventually used in self-healing FRCs.

The specific objective of this chapter is to develop core-sheath fibers consisting of thin PAN sheath containing within a core solution. Separate solutions of the self-healing components (epoxy resin and hardener) will separately form the cores of the two core-sheath microfiber populations. Cross sectional views of the core-sheath fibers are provided in Scheme 4-1. We hypothesized that the encapsulated crosslinker and liquid epoxide flow to the damaged area and cure at RT after contact with each other which recovers the original properties of the mat upon self-healing. In order to achieve this goal, the following requirements were to be established:

1. The liquid epoxide and hardener must polymerize (cure) in ambient conditions in less than 6 h upon contact.
2. Successful encapsulation of core during the coaxial electrospinning process must be achieved. Besides, higher overall volume fraction of the core in the fiber leads to higher self-healing extent.
3. In order for self-healing to occur, the core liquid should flow to the damaged area and polymerize to recover the initial mechanical properties, upon damage.

Different strategies to meet the aforementioned requirements is provided in what follows.

**4.3 Experimental Section**

**4.3.1 Materials**

Poly(acrylonitrile) (PAN) (Mn ≈ 150,000 g mol⁻¹), diglycidyl ether of bisphenol A (DGEBA), Rhodamine B, Dimethylformamide (DMF), and chloroform were purchased from Sigma-Aldrich. Ancamine 2072 (crosslinker, product of Air Products, referred to as Ancamine hereafter) and Heloxy™ modifier (viscosity reducing agent, product of Momentive) were received from NEI Corporation. PAN solution was prepared by dissolving 1.0 g of the polymer in 10 ml of DMF. Two core solutions were prepared by dissolving DGEBA/Heloxy and Ancamine in DMF. Specifically, 4 g of DGEBA and 1 g of Heloxy were dissolved in 5 ml of DMF and 5 ml of Ancamine was mixed with 5 ml of DMF. Note DGEBA was heated at 80 ºC until all its crystallites melt to form a viscous liquid prior to mixing with DMF. All solutions were mixed at RT overnight until a homogenous, one phase solution was achieved. N,N-benzylidimethylamine (BMDA), aminoethylpiperazine (AEP) and Al POMs were used as curing accelerators. Al POMS was purchased from Plastic Hybrids whereas BMDA and AEP were purchased from Sigma-Aldrich.

**4.3.2 Kinetic Analysis of Curing Behavior of the Epoxy System**

As mentioned earlier, one of the goals of this project was to develop epoxy-based self-healing system which can polymerize (cure) at RT in less than 6 h. Differential Scanning Calorimetry (DSC) was used to determine degree of cure of the mixed epoxy blends at room temperature (RT)
as a function of time. Our strategy was to incubate samples at RT for different times, post-mixing, at RT and interrogate the state of cure by a “dynamic” heating experiment that reveals both glass transition temperature ($T_g$) (increasing) and residual cure exotherm (decreasing) as cure advances. Thus, DSC experiments were conducted using a Q200 (TA Instrument) equipped with a refrigerated cooling system (RCS). Epoxy blends were prepared by mixing 1.66 g of DGEBA and Heloxy (DGEBA:Heloxy weight ratio was 80:20, as recommended by NEI) with 1.0 g of Ancamine. To further reduce the curing time, 3 curing accelerators, BMDA, AEP and Al POMS were elected to be mixed with the epoxy blend. 0.16 g of BMDA, 0.16 g of AEP or 0.03 g of Al POMS was separately mixed with DGEBA/Heloxy/Ancamine mixtures. Samples with masses of 3-5 mg were encapsulated in Tzero aluminum pans and were then heated from -80 °C to 180 °C to determine the total energy required to complete the cure reaction, cooled back to -80 °C, and finally heated to 180 °C. All heating rates were 10 °C min$^{-1}$ and all cooling rates were 5 °C min$^{-1}$. Enthalpy of reaction were calculated as area under the curve (AUC) of exothermic peak. Conversion degree was then calculated using the following equation:

$$Conversion\% = (1 - \frac{AUC_t}{AUC_0}) \times 100$$

(4-1)

where $AUC_t$ [J g$^{-1}$] is area under the curve of sample that is cured at RT for $t$ h and $AUC_0$ [J g$^{-1}$] is area under the curve for blend as mixed. Schematic illustration of such curing kinetics analysis is provided in Scheme 4-2. Thermal stability of epoxy matrix is also another indicator of reaction progress. Thermogravimetric analysis was conducted using a TA Q500 TGA instrument under a constant nitrogen purge. For all samples, a small amount of material ranging from 5-10 mg was loaded on the TGA pan and heated at a fixed rate of 10 °C min$^{-1}$ to 600 °C while recording the sample mass as a function of temperature.
Thermomechanical properties of fully cured epoxy blends were characterized using a Q800 Dynamic Mechanical Analysis (DMA) (TA Instrument). Dogbone samples (ASTM D638 Type IV), scaled down by a factor of 4) were loaded under tension and oscillatory deformation with an amplitude of 15 µm, a frequency of 1 Hz and a “force track” (ratio of static to dynamic force) of 108 % was applied. To determine transition temperatures and rubbery plateaus of the composite, the samples were equilibrated and held isothermally at -100 °C for 10 min, then heated to 100 °C at 2 °C min⁻¹. T_g was measured as the middle point of step transition and the onset of modulus drop in DSC and DMA, respectively.

4.3.3 Coaxial Electrospinning

Photographs of the coaxial electrospinning setup and a custom-made coaxial spinneret are provided in Figure 4-1. The polymer solution and the core solution were pumped through the outer and the inner diameter of a custom made spinneret using a Fischer Scientific pump, respectively. Flow rates varied to achieve stable electrospinning, but were typically 1.0 ml h⁻¹ for the sheath solution and 0.1 mL h⁻¹ for the core solution. The tip to collector distance was 14 cm for all tests. Exact voltages and thus field strengths varied slightly from test to test, but the needle was typically at 13 kV and the collector (a mandrel rotating at 400 RPM) was at -500 V.

4.3.4 Core-Sheath Fiber Structure Investigation

4.3.4.1 Scanning Electron Microscopy

In order to observe microscopic structure of electrospun fibers, a JEOL JSM-5600 scanning electron microscope was used. Samples were dried and sputter coated with gold for 45 s prior to the experiment.
4.3.4.2 Fluorescent Microscopy

In order to characterize the presence of core material in fibers, the core material was dyed with ~1 wt. % of Rhodamine B (Sigma Aldrich), simplifying visual observation of the Taylor cone and permitting fluorescent observation of the encapsulated core material. Note that only core material contained Rhodamine B which emits under fluorescent light. In other words, sheath material (PAN) should not appear under fluorescent light. Bright Field and fluorescent images of electrospun fibers were then taken using a Leica DMI 4000B inverted microscope with a Leica DFC 340FX camera using a 5x/0.130 NA oil objective with Zeiss Immersol 518 F immersion oil. To further analyzing the structure of the fibers, the images were then overlaid on the top of each other using ImageJ software. Finally, by converting grey level microscopy images (from fluorescent microscopy) to black and white images using Threshold application in ImageJ, we determined the number of pixels that fibers occupy in both bright field and fluorescent images. This enabled estimation of the weight fraction of fibers which contained core material.

4.3.5 PAN Wetting Behaviour

For self-healing, it is important that the healing agent(s) have favorable wetting characteristics along the PAN fibers countering them. As such, we sought to measure the pertinent contact angles, a low angle indicating wetting. Static contact angle measurements of Ancamine and DGEBA/Helox on a PAN substrate (fiber or film) were studied with a Rame-Hart 250-F1 standard goniometer. A droplet of DGEBA (as the prominent component in the DGEBA/Helox blend) or Ancamine was placed on a clean, dry surface of a PAN substrate and the contact angle was immediately measured. PAN films were prepared by dissolving 3.0 g of PAN in 30 ml of DMF followed by solvent casting and drying at RT.
4.3.6 Core Material Tracking

As mentioned in the Introduction section, for the self-healing to occur, the crosslinker and liquid epoxide should flow out of the fibers, to the damaged area and cure at RT at the site of damage. Again, the core material was mixed with Rhodamine B, a fluorescent dye allowing to observe and track the core solution upon breakage under fluorescent microscopy. Core-sheath fibers were electrospun for about 30 s (For electrospinning conditions, see Section 4.3.3) on a glass slide. The fibers were then cut with a fresh razor blade and heated at 80 º for 12 h. Heating the fibers at elevated temperature further accelerates this process given that thermal expansion coefficient of solid materials are much higher than liquids\textsuperscript{21}. Ideally, the core liquid would autonomously flow out of the fibers at RT as illustrated in Scheme 4-3 upon breakage.

4.3.7 Coelectrospinning

Xu and colleagues developed core-sheath fibers by electrospinning a water-in-oil emulsion in which the aqueous phase consists of a poly(ethylene oxide) (PEO) solution in water and the oily phase is a chloroform solution of an amphiphilic poly(ethylene glycol)-poly(L-lactic acid) (PEGPLA) diblock copolymer\textsuperscript{22}. As such, we aimed to mix PAN with the epoxy components (DGEBA/Heloxy or Ancamine) with the intention to yield a two-phase emulsion. 0.5 g of materials containing PAN and epoxy (DGEBA/Helox or Ancamine) with different ratios (PAN:Epoxy weight ratios: 2:1, 1:1 and 1:2) were poured in to 5 ml of DMF and stirred overnight at RT (dubbed PAN/Ancamine/DMF and PAN/DGEBA/DMF co-solutions, hereafter). The solutions were then electrospun followed by examination of morphology on an Olympus BX51 microscope. For electrospinning, the tip to collector distance was 14 cm for all tests. The needle was typically at 16 kV and the collector (a mandrel rotating at 400 RPM) was at -500 V.
4.3.8 Isothermal Degradation

Here, we sought to estimate the overall weight fraction of epoxy components in co-electrospinning. PAN is known to be a very stable polymer even at elevated temperatures\(^{23,24}\). On the other hand, given the liquid state of the core materials (DGEBA/Heloxy or Ancamine), they are expected to eventually evaporate when heated. Thus the weight loss in the fiber mat when heated above degradation temperature of the epoxy components, corresponds to weight fraction of the epoxy in the fiber mat. To determine such intermediate temperature at which PAN fibers remain intact whereas core materials completely degrade; PAN fibers, Ancamine, DGEBA and Heloxy were first heated at a fixed rate of 10 °C min\(^{-1}\) to 600 °C while recording the sample mass as a function of temperature. As such, intermediate temperature where PAN does not degrade or sublime whereas both Ancamine and DGEBA completely degrade overtime, was determined to be 200 °C (For details, see Results and Discussions section). Then PAN fibers, Ancamine and electrospun PAN/Ancamine/DMF co-solutions were heated isothermally at 200 °C. The weight loss of the fiber during the isothermal step at 200 °C corresponds to the weight fraction of the core materials within the PAN fibers allowing us to determine the overall weight fraction of core solution in the fibers mats. The effect of such isothermal heating on fiber structure was also investigated by acquiring optical micrographs of exactly the same region of electrospun cosolution fibers pre and post heating (at 200 °C for 1 h in the isothermal using an Olympus BX51 microscope.

4.3.9 Coaxial Electrospinning with Solvent as the Sheath

Co-electrospinning (electrospinning in PAN and DGEBA in the same DMF solution) DGEBA and PAN resulted in formation of droplets present in the fiber mat (For details, refer to Section 4.4.5.2). To improve the electrospinning conditions for the PAN/DGEBA/DMF co-solution, we used such
solution in a coaxial electrospinning setup where it was surrounded by a pure DMF stream as the sheath and the PAN/DGEBA/DMF in the core expecting that DMF stabilizes the electrospinning conditions. To determine optimal operating conditions, flow rate of the core, was kept consistent at 1.0 ml h\(^{-1}\) while the sheath flow rate was dialed up from 0.5 to 2.0 ml h\(^{-1}\) with 0.5 increments. For electrospinning, the tip to collector distance was 14 cm for all tests. The needle was at maintained 16 kV and the collector (a mandrel rotating at 400 RPM) was maintained at -500 V. In a separate experiment, the core and sheath flow rates were kept consistent at 1.0 and 1.5 ml h\(^{-1}\) while the needle voltage was dialed up from 7.0 to 16.0 kV with 3 kV increments. All other electrospinning conditions were kept the same. The fibers were electrospun on a glass slide for ~30 s, after which their optical micrographs were taken using an Olympus BX51 microscope.

4.3.10 PAN Fiber Diameter Measurements

In order to maximize self-healing efficiency of core-sheath fibers, the volume fraction of core should be as high as possible relative to sheath. Therefore, higher sheath (PAN) fiber diameter combined with small sheath thickness, providing adequate space for the encapsulated core is desirable. Our first approach to increase PAN fibers overall size was to increase PAN concentration in the electrospinning solution. 0.5, 1.0, 1.5, 2.0 and 3.0 g of PAN were mixed with 10 ml of DMF and stirred at RT overnight. Those solutions that were mixed completely and did not undergo gelation (See Results and Discussions) were electrospun with consistent conditions:

- Needle Voltage: 13.5 kV
- Frame Voltage: -500 V
- Flow Rate: 1 ml h\(^{-1}\)
- Tip of needle to collector distance: 7 cm
- Drum rotation speed: 400 RPM-Translation On
In the second approach, the solution flow rate was varied from 0.5 to 4.0 ml h\(^{-1}\) while the PAN concentration was kept constant at 0.1 g ml\(^{-1}\). In both cases, a standard 22-gauge needle with a nominal inner diameter of 0.41 mm was used. All other parameters were held constant (see above). SEM micrographs of these fiber mats were then taken with a JEOL JSM-5600 scanning electron microscope at different magnifications. ImageJ software was then employed to measure the average fiber diameter of all samples. For each sample, SEM micrographs at a magnification of x2000 were taken and the fiber diameter of 50 randomly selected fiber strands in the micrograph was measured using the “Measure” tool in the ImageJ software. Histogram of fiber diameter distribution for all samples were plotted to determine the effect of solution flow rate and concentration on fiber diameter.

4.3.11 Epoxy Hardener Interface

In order to further investigate the diffusion of epoxy (DGEBA) and hardener (Ancamine) phase, we took a reverse approach than before as we now explain. PAN fibers were imbedded with liquid epoxide matrix as opposed to before where liquid epoxide was encapsulated by PAN fibers. Ancamine and DGEBA were first pipetted onto separate rectangular pieces of PAN fiber after which the excess liquid was carefully removed from the surface of PAN fibers\(^{25}\). The embedded PAN fiber mats were then placed on the top of each other as illustrated in Scheme 4-4. This sample in which the liquids only wet the PAN fibers, is dubbed “sandwich A” hereafter. For comparison, a second sample was prepared by layering the two pieces of PAN fiber pipetted with excessive amount of DGEBA and Heloxy (dubbed “Sandwich B”, hereafter). To fabricate a multilayer embedded PAN composite consisting of alternating PAN layers embedded with DGEBA and Heloxy, two embedded fiber mats were then carefully rolled on the top of each other. We dub this sample “Epoxy Roll” hereafter. All samples were cured at ambient conditions for 1 week. The
cross section structure of both sandwich A, sandwich B and Epoxy Roll were then studied using a JEOL JSM-5600 scanning electron microscope. Samples were cut with a razor blade and then sputter coated at the cross section for 45 s prior to the experiment.

4.4 Results and Discussion

4.4.1 Kinetic Analysis of Curing Behavior of the Epoxy System

In the core-sheath fiber, healing is induced by curing reaction of liquid epoxide and hardener upon damage. Therefore, understanding curing kinetics of DGEBA/Heloxy (liquid epoxide) and Ancamine (hardener) is of great importance. One target to attain is a fast cure of the epoxy system during the self-healing process. In order to achieve optimal self-healing properties, the blend should achieve full cure within several hours instead of several days using a prescribed curing accelerator agent. Thermal stability of samples as a function of temperature is shown in Figure 4-2. Results showed that degradation temperature of blend increased as sample was curing and overall sample stability was high. Figure 4-3 shows the first DSC heating cycle of epoxy (DGEBA/Heloxy/Ancamine) blends as mixed (t=0) and after 2, 4, 6, 12, 24, 48, 72 and 96 h of incubation at RT. By measuring the area under the peak of 1st heating cycle exothermic peak (Figure 4-3(A)), the conversion % over time was calculated. It is important to note that all 2nd heating cycles showed a Tg around 25 °C indicating complete cure as shown in Figure 4-3(B). This was attributed to the fact that sample was heated up to elevated temperature (150 °C) in the 1st heating cycle which provides adequate energy to achieve 100 % cure. Results showed that complete cure (where no exothermic peak was observed anymore) was achieved within 96 h. However, ideally this curing reaction (i.e. self-healing) should occur within 6 h as mentioned before. Therefore BMDA, AEP and Al POMS were separately added to the blend chemistry as
accelerating agents. Chemical structures of such curing accelerator agents are provided in Figure 4-4. (A) 1st and (B) 2nd heating cycle DSC traces of the epoxy blend (DGEBA/Heloxy and Ancamine) in the presence of AEP, BMDA and Al POMS are provided in Figures 4-5, 4-6 and 4-7, respectively. The same protocol was repeated to calculate conversion % of epoxy in presence of AEP, BMDA and AL POMS. Shown in Figure 4-8 are curing profiles of the epoxy blend (DGEBA/Heloxy and Ancamine) with and without curing accelerators; Al POMS, BMDA and AEP. All curing accelerators reduced the curing time to about the same extent to less than 12 h (After 6 h, conversion was higher than 80 % and by 12 h it was 100 %.) satisfying the requirement to cure (self-heal) at RT in several hours.

Thermomechanical testing was also conducted to understand how the viscoelastic properties of the cured epoxy depended on temperature. This set of testing is important to provide context for mechanical behavior of cured epoxy as a function of temperature. Tensile storage modulus (E’) and tan (δ) as a function of temperature are reported in Figure 4-9. The epoxy showed a broad T_g (storage modulus drop) onsetting of 35 °C. This result was in agreement with DSC results showing comparable T_g. We note that despite having a relatively low T_g, the epoxy was very brittle and difficult to handle at RT which should be taken into consideration for manufacturing purposes.

4.4.2. Core-Sheath Fiber Structure Investigation

4.4.2.1 Scanning Electron Microscopy

SEM was used to study coaxially electrospun fibers structure. Representative images of: (A) PAN fibers (electrospun via singular needle) as a control, (B) coaxially electrospun fibers with PAN in the sheath and DGEBA/Heloxy solution in the core and (C) PAN in the sheath and Ancamine solution in the core are provided in Figure 4-10. Quite interestingly, morphology of fibers in image
(B) is different compared to image (C), the latter showing a beads-on-string morphology. We postulate this is due to different viscosity of two core solutions and different surface tension between the core and sheath solution. The presence of oval beads for the coaxially electrospun fiber with Ancamine implied the presence of core material. For the coaxially electrospun fibers with DGEBA however, it was not clear whether the fibers were impregnated or not. Histograms of fiber distribution for coaxially electrospun fibers with PAN in the sheath and DGEBA/Heloxy in the core and control (PAN fibers) are provided in Figure 4-11. The coaxially electrospun fibers were cylindrical fibers with higher average diameter relative to PAN. Interestingly, the fiber size for coaxially electrospun fibers showed a double peak distribution which we tentatively attribute to fibers with and without core material. The impregnation of PAN fibers by DGEBA/Heloxy blend was further investigated by fluorescent microscopy as we now describe.

4.4.2.2 Fluorescent Microscopy

In order to examine the presence of core material in fibers, the core material was dyed through incorporation of Rhodamine B (Sigma Aldrich). This simplified visual observation of the Taylor cone and allowed fluorescent observation of the encapsulated core material. Rhodamine B is a dye that is commonly used as a tracer within water (or other commonly used solutions) given that it can be detected easily and inexpensively with fluorescent microscopes. Chemical structure and photographs of Rhodamine B as received and in a DMF solution are provided in Figure 4-12.

The resulting fluorescent microscopy images of a coaxially electrospun fiber mat are shown in Figure 4-13. Two images of the same area of the slide were obtained. One was obtained under visible light (Figure 4-13(A)) and one under ultraviolet light using a fluorescent filter (Figure 4-13(B)). Then the bright field and fluorescent images were overlaid using ImageJ software as
illustrated in Figure 4-13(C). Using threshold application in Image J, the grey level image was converted to a black and white image by which number of pixels that fibers occupy in the image were estimated. Step by step illustration of image analysis is provided in Figure 4-14. By dividing the number of pixels occupied in fluorescent image by that of bright field image, the weight fraction of fibers that contain core material was calculated to be ~70% (Figure 4-15). Therefore, most of the fibers did in fact contain core material. In what follows, PAN fibers wetting behaviour and tracking procedure of core liquid flow upon fiber breakage is discussed.

4.4.3 PAN Wetting Behaviour

We utilized the contact angle technique to investigate the wetting characteristics of self-healing agents (DGEBA and Heloxy) on the PAN fibers. Figure 4-16 shows the representative contact angle micrographs of (A) Ancamine droplet and (B) DGEBA droplet on a PAN film. Both Ancamine and DGEBA have relatively low contact angles on a PAN film and permeated into a PAN fiber mat in less than 1 min indicating favorable wetting characteristics. These results suggest that the contact angle and surface tension of both systems are relatively close to each other and favorable for wetting. Note that PAN film was prepared by dissolving 1.0 g of PAN in 10 ml of DMF followed by casting in a Teflon® mold for several days at RT and drying in a vacuum oven at RT for 2 d. We note that the resulting film was very brittle, difficult to handle and curled on the sides during the solvent casting process.

4.4.4 Core Material Tracking

Considering the high wetting characteristics (low contact angle) of both DGEBA and Ancamine on PAN fibers, we aimed to track the fluorescent stained core material upon breakage under fluorescent microscope. Since thermal expansion coefficient of liquids are much higher than
solids, we hypothesized that heating the liquid impregnated PAN fibers would drive the liquid material out of the fiber mat. Bright field and fluorescent images of a coaxially electrospun fiber mat after heating isothermally at 80 °C for 1, 3 and 12 h are provided in Figure 4-17. Results showed no evidence of core material squeezing out of the fibers even after 12 h. We attribute this to high mechanical strength of PAN fibers which withstand the inner pressure induced by the core material preventing it from diffusing out of the fiber. In a second experiment, a coaxially electrospun fiber mat was chopped several times with a fresh razor blade, heated to 80 °C and kept isothermal at 80 °C for 12 h. Bright field (A) and fluorescent (B) images of such co-axially electrospun fiber mat is shown in Figure 4-18. The blade trace showing the regions of the fibers that were damaged are evident in the image. However, no evidence of core material flowing out of the fibers even after 12 h was detected despite the fact that both Ancamine and DGEBA showed favorable wetting characteristics towards PAN fibers mat as discussed earlier. We postulate such results is due to high surface tension of the liquid material in nano scale tube-like fibers (Average fiber diameter of PAN fibers is 500 nm as shown in Figure 4-11). Such characteristics can be quantitatively measured by a dimensionless factor known as Bond Number:

$$Bo = \frac{\rho \times g \times D^2}{\sigma}$$ \hspace{1cm} (4-2)

where $\rho$, $g$, $D$ and $\sigma$ are the density, gravitational acceleration, fiber diameter and surface tension of liquid in the fiber, respectively. Assuming that $\rho = 1000 \frac{kg}{m^3}$, $g = 9.8 \frac{m}{s^2}$, $D = 1$ nm, and $\sigma = 5 \times 10^{-3} \frac{J}{m^2}$, gives us a bond number of $Bo = 2 \times 10^{-6}$, indicating significant dominance of surface energy over gravity which is in agreement with common experience. “Leaking out” of a tube requires air to be pulled back, a phenomenon commonly observed when lifting water out of a
glass by closing one end. A vacuum forms in the air space that is enough to pull back the weight of liquid even in that extreme case. For this reason, healing from tubes will require multiple breaks or some other means (like thermal expansion) to drive the liquid out. In addition, at the small diameter of the containing fibers, surface energy dominates over gravitational forces, so our intuition needs to focus on the relative contact angle of healing agent on crack surface versus contact angle of healing agent on surface of containing tube. The crack surface needs to “win” so that the core materials leaks out which doesn’t occur in our case due to relatively low Bond number. Thus, the volume fraction of the core material, its encapsulating tube size along with its inner diameter should significantly increase. We discuss our strategy to achieve this goal in what follows.

4.4.5 Beads-On-String Structure

The volume fraction of the core material in the PAN fibers are generally low due to small size of the PAN fibers (< 1 μm). Therefore, the nano-fibers simply do not provide any room for the core material to be encapsulated in leading to substantially small Bond numbers as conversed earlier. In the beads on string structure however, the beads containing a thin layer of sheath outside and self-healing agent inside are at least one order of magnitude higher than fiber mat diameter allowing to increase the overall self-healing agent volume fraction (Scheme 4-5). Our strategy to increase the amount of core material in the electrospinning process is to fabricate fibers with “Beads on String” structures26-29. We took several different approach to achieve this goal as we now explain.
4.4.5.1 Beads-on-String Structure, Coaxial Electrospinning

Seeking to fabricate fibers with beads-on-string structure, we first opted to tweak the coaxial electrospinning parameters. Shown in Figure 4-19 are fluorescent microscopy micrographs of coaxially electrospun fiber mats with PAN and DGEBA/Heloxy as the sheath and core at: (A) (13.5) and (B) 16.0 kV. All fibers were observed to contain core material however there were sparse beads present in the fiber mat with a relatively small size. The density of the beads were much higher in the case of Ancamine/DMF core solution as shown in Figure 4-20. Higher viscosity of the Ancamine solution led to formation of regular oval beads with up to 8 μm in diameter observed in the resulting fiber mats. Such promising result requires further investigation to determine the overall amount of Ancamine in the fiber mat. However, optimizing the coaxial electrospinning parameters is often time-consuming and therefore, we attempted a relatively simpler approach as we now explain.

4.4.5.2 Beads on String Structure, Coelectrospinning

Xu and colleagues developed core-sheath fibers by electrospinning a hydrophilic poly(ethylene oxide) solution in water phase and a more hydrophobic amphiphilic poly(ethylene glycol)-poly(L-lactic acid) (PEGPLA) diblock copolymer in oil phase in the form of a water-in-oil emulsion\textsuperscript{22}. They hypothesized that it is this viscosity difference between the elliptical droplets and their matrix, and this viscosity gradient from the outer layer to the inner layer that results in the inward movement of the emulsion droplets resulting in forming core-sheath structure. By staining the PEO in water phase with fluorescein isothiocyanate, the authors confirmed the core-sheath structure of the fibers under fluorescent microscopy. In a similar fashion, we also aimed to investigate whether or not an emulsion forms when PAN and Ancamine (or DGEBA/Heloxy) are mixed together in a
DMF solution. Figure 4-21 shows the photographs of (A) 5 ml of 10 % PAN/DMF solution in 0.5 g of Ancamine and (B) 5 ml of 10 % PAN/DMF solution in 0.5 g of DGEBA. Both solutions became clear after stirring overnight at RT designating homogeneity. Table 4-1 summarizes compatibility of PAN and epoxy monomers (DGEBA, Ancamine) in a DMF solution with respect to PAN:epoxy weight ratios. At higher ratios of epoxy (Ancamine or DGEBA/Heloxy), the solutions did not become homogenous and a solid lump remained segregated in the solution. Such observation requires further investigation. Although we were unable to form an emulsion at this point, the electrospinning results showed that coelectrospinning can indeed lead to the formation of beads on string structure fiber mat as shown in Figure 4-22. In the case of coelectrospinning DGEBA and PAN, there were some droplets present in the fiber mat resulting from incomplete encapsulation of core material. In the case of coelectrospinning Ancamine and PAN, however, there were no beads present in the resulting fiber mat. To prove that Ancamine was unquestionably encapsulated in the fiber mat, the fibers were subsequently heated on a glass substrate isothermally at 200 ºC for 1 h. Should Ancamine be surrounded by a thin PAN sheath, the fiber morphology remains intact even at temperatures at which Ancamine degrades. Optical micrographs of exactly the same location pre and post heating was then taken as shown in Figure 4-23. Given that the morphology and the density of fibers remain intact after heating, we postulate that Ancamine was protected by an outer sheath of PAN though such postulation required further quantitative investigation. Benefiting from the fact that at 200 ºC, PAN doesn’t degrade whereas Ancamine will boil or degrade completely (Figure 4-24), we were able to gravimetrically quantify the weight fraction of Ancamine in the PAN/Ancamine/DMF coelectrospun fibers by isothermally heating the sample at 200 ºC for 1 h. The weight loss percentage of the sample was about 35 % corresponding to Ancamine as illustrated in Figure 4-25 assuming that all of the DMF evaporated
during the electrospinning process. We then aimed to tailor the flow of Ancamine out of PAN fibers by heating the fiber mat isothermally at 55 ºC for 30 min. Note that 55 ºC is slightly below degradation temperature of Ancamine at 65 ºC, measured by TGA shown in Figure 4-24 (Degradation temperature being defined here as the temperature where material mass remaining begins to drop with a threshold of 100 to 99.5 %). As thermal expansion coefficient of liquids like Ancamine are much higher than solids like PAN, we expected that the heating step forces all the encapsulated liquid material to flow out of the fiber mat upon heating. Photographs and SEM micrographs of the coelectrospun PAN/Ancamine/DMF fiber mat before and after heating isothermally at 55 ºC for 30 min are provided in Figure 4-26. Results showed no evidence of core material forced out of the fibers even after 12 h, although a strong Ancamine odor was evident specially after heating the fiber mat. We postulate that PAN fibers were able to withstand the inner pressure induced by the core material during heating preventing it from flowing out of the fiber, at least by the desired fluid flow mechanism.

4.4.5.3 Coaxial Electrospinning with Solvent as the Sheath

As discussed in the previous section, coelectrospinning DGEBA and PAN resulted in formation of droplets present in the fiber mat attributable to incomplete encapsulation of core material. In order to prove the electrospinning condition to prevent formation of droplets, we electrospun the same PAN/DGEBA/DMF co-solution as the core surrounded by a stream of pure DMF as the sheath in a coaxial electrospinning setup (Scheme 4-6). The presence of a high surface tension solvent as the sheath in the coaxial electrospinning setup is known to improve the electrospinning conditions\(^{14,16}\). To determine optimal electrospinning conditions, the flow rate of the core, was kept consistent at 1.0 ml h\(^{-1}\) while the sheath flow rate was dialed up from 0.5 to 2.0 ml h\(^{-1}\) with 0.5 increments. See Experimental Section for the rest of electrospinning parameters. Figure 4-27
shows the micrographs of the resulting fibers. Presence of DMF as the sheath even at its lowest flow rate (0.5 ml h⁻¹) evidently prevented beads to form indicating that all the core solution was successfully encapsulated in the PAN. As the core flow rate was increased, the electrospinning conditions became more stable and more beads-on-string structure was observed. The optimum results were accomplished when sheath flow rate was at 1.5 ml h⁻¹ given that the beads on string density was maximized. In order to further improve the electrospinning conditions, the core and sheath flow rates were kept consistent at 1.0 and 1.5 ml h⁻¹ while the needle voltage was increased from 7.0 to 16.0 kV with 3 kV increments. Micrographs of such fiber mats are shown Figure 4-28. At 7.0 kV, no Taylor cone was formed at the tip of spinneret demonstrating that the electrostatic force did not adequately charge solvent molecules. Therefore, we were unable to collect any fibers on the drum at such low voltage. At 10.0 kV, the Taylor cone was formed but the core and sheath phases quickly segregated as the latter was drooling from the spinneret and the former was sporadically being collected on the drum. Therefore, no core sheath fibers was formed and no beads on string structure was observed in the micrograph. It is important to note that for a given electrospinning setup, a small range of “working” applied voltage exists in which a stable compound Taylor cone can form. Such working range varies with the polymer, polymer solution, flow rate and other operating conditions and can only be determined by trial and error. Voltage values below the working range leads to droplets and intermittent jet from the sheath with an occasional incorporation of the core as observed at 10.0 kV in our case. At 13.0 kV, a stable Taylor cone was formed without presence of non-encapsulated beads indicating successful encapsulation of core. At 16.0 kV though, no beads on string structure was observed. This is attributed to the fact that above the working range, the strength of the electric field exceeds that required for the given material and the processing conditions. As such, Taylor cone tends to withdraw the originating jet
inside the spinneret capillaries resulting into separate jets from the sheath and core solutions\textsuperscript{19}. We conclude that the working applied voltage for this specific system is around 13.0 kV. Determining the optimized electrospinning conditions allowed us to steadily electrospin fibers with beads-on-string structure containing DGEBA as the core surrounded by a thin layer of PAN as the sheath. The weight fraction of DGEBA in the resulting fibers could be measured by isothermal TGA as explained earlier for coelectrospun PAN/Ancamine/DMF which remains subject of future work.

4.4.6 PAN Fiber Diameter

4.4.6.1 Effect of Concentration

The overall weight fraction of the core material in the coaxial electrospinning process can be increased by utilizing larger sheath fibers. This is simply due to the fact that larger hollow fibers may feature larger volume fraction for the core material to be encapsulated for a given sheath fiber thickness. It is well known that fiber diameter monotonically increase with flow rate and concentration of polymer solution\textsuperscript{30,31}. PAN solutions with different concentrations were prepared by dissolving 0.5, 1.0, 1.5, 2.0 and 3.0 g of PAN (corresponding to concentrations of 0.05, 0.1, 0.15, 2.0 and 3.0 g ml\textsuperscript{-1}, respectively) separately in 10 mL of DMF as shown in Figure 4-29. For the highest concentration (0.3 g ml\textsuperscript{-1}), the polymer did not dissolve completely in DMF. In other words, the solubility limit of PAN in DMF is less than 0.3 g ml\textsuperscript{-1}. 2.0 g of PAN dissolved in 10 ml DMF but it was not electrospinnable due to its extremely high viscosity. Figure 4-30 shows SEM micrographs of PAN fiber mats electrospun from 0.05, 0.1, 0.15, 2.0 and 3.0 g ml\textsuperscript{-1} solutions. Macroscopically all fiber mats were white. Shown in Figure 4-31 are the fiber diameter distribution for all of these samples. Average fiber diameter for 0.05, 0.1 and 0.15 g ml\textsuperscript{-1} solution were 0.19±0.49, 0.58±0.12 and 1.77 ±0.37, respectively. The dependence of fiber diameter on
PAN concentration is shown in Figure 4-32. Our results show that fiber diameter increased monotonically with polymer concentration. For the 0.05 g·ml⁻¹ solution, many beads were also present in the fiber mat which is due to the natural Rayleigh instability that was not entirely suppressed by viscosity or gelation at this particular concentration. Besides, polymer entanglements do not occur below a critical concentration in polymeric solutions. Such critical concentration for electrospinning can be estimated by the following equation:

\[ Be = [\eta] \times C \]  \hspace{1cm} (4-3)

Where \([\eta]\) and \(C\) are the inherent viscosity and concentration of the solution, respectively. In particular, when \(Be = [\eta] \times C > 5\) electrospinning will yield fibers instead of droplets. Therefore, \(\sim [\eta]^{-1}\) is approximately the concentration at which polymer chains overlap. Approximately 5 times of this value \(\left(\frac{5}{[\eta]}\right)\) will indicate an entangled polymer solution with the proper rheology for electrospinning\(^{26,32-35}\).

### 4.4.6.2 Effect of Flow Rate

Another important variable that can affect fiber diameter is flow rate. Figure 4-33 shows SEM micrographs of fiber mats at different flow rates 0.5, 1.0, 2.0 and 4.0 ml·h⁻¹ (for 0.1 g·ml⁻¹ concentration) Shown in Figure 4-34 are the fiber diameter distribution for all of these samples. Average fiber diameter for fibers matt electrospun at 0.5, 1.0, 2.0 and 4.0 ml·h⁻¹ were 0.55±0.17, 0.58±0.12, 0.67±0.16 and 0.86±0.30 µm, respectively indicating that fiber diameter increased monotonically, indeed linearly as polymer solution increases in the electrospinning process (See Figure 4-35). Besides, all the histograms roughly follow Gaussian (normal) distribution except for the one corresponding to 0.5 ml·h⁻¹. This is due to the fact that formation of beads in the
electrospinning process disrupts the stable electrospinning conditions leading to deviance from normal distribution (Normal distribution states that mean that tells the probability that any real observation will fall between any two real limits or real numbers, as the curve approaches zero on either side physical quantities that are expected to be the sum of many independent processes often have a distribution very close to the normal.) We then conclude that higher flow rate along with higher concentration led to thicker fiber mat which can be considered as a useful element to fabricate larger fibers and reduce electrospinning time.

4.4.7 Epoxy-Hardener Interface

For the self-healing to occur both epoxy (DGEBA) and hardener (Ancamine) phases should autonomously flow to the vicinity of each other, mix by diffusion and then polymerize. The polymerization will slow down or even cease if the rate of flow is small or the diffusion distance is large. In order to further investigate the diffusion of epoxy (DGEBA) and hardener (Ancamine) phase, we took a different approach than before as we now explain. The PAN fibers in this case were embedded in the self-healing agents as opposed to surrounding them as in previous cases. Details of preparing sample; dubbed “sandwich A”, “sandwich B” and “epoxy roll” are provided in Section 4.3.11. Shown in Figure 4-36 are photographs of epoxy sandwich showing that Ancamine and DGEBA were first pipetted on two separate rectangular pieces of PAN fiber mat to wet the fibers. Any excessive liquid was carefully removed from the fibers with a spatula. The embedded PAN fiber mats were then placed on the top of each other which we refer to as Sandwich A. The interface of the two layers in sandwich A was evident after cure indicative of incomplete cure as illustrated in Figures 4-37 and 4-38. Thermal characterization of this sample did not show a distinguishable Tg indicating DGEBA and Ancamine phases remained separated from each other thus the cure was incomplete cure/ cure only occurred at the interface (Figure 4-39). Note that
DGEBA has a $T_g$ at around -20 °C as shown in Figure 2-3. In sandwich B in which the two PAN fiber layers were imbedded in excess amount of DGEBA and Ancamine, no interface was distinguished as shown in Figure 4-40. There results indicate that for the DGEBA and Heloxy phases to diffuse and cure, minimum volume fraction of both phases are to be present at the site. However, if the volume fraction of any of these phases is low, they have a tendency to stay on the surface of PAN fibers probably due to favorable wetting (low contact angle) of self-healing agents on PAN. Note that both DGEBA and Ancamine had contact angles lower than 50º on a PAN film and diffused to a PAN fiber mat in less than a min at RT as discussed earlier.

To stack multiple wetted PAN fibers on the top of each other, two embedded PAN fibers (one embedded with Ancamine and the other with DGEBA/Heloxy) were rolled on the top of each other. Photographs of “Epoxy Roll” preparation process are also provided in Figure 4-41. Ancamine and DGEBA were first pipetted on two separate rectangular pieces of PAN fiber mat. The embedded PAN fiber mats were then placed and rolled on the top of each other. The cross section of the cryofractured epoxy rolled showed presence of a lot of voids arising from the space between different layers of the roll. When cut with a fresh razor blade, such voids disappeared and the cross section of the roll was deformed (Figure 4-42). These results indicate that if the volume fraction of the two self-healing agent phases (DGEBA and Ancamine) are high enough and if they are located in the vicinity of each other, they will interdiffuse and polymerize at the site of damage.

4.5 Conclusions

We were able to successfully fabricate new core-sheath fibers with a thin layer of stiff PAN surrounding self-healing solution. A tri-component epoxy chemistry containing DGEBA as liquid epoxide, Ancamine as hardener and Heloxy as viscosity reducing agent was chosen as our
candidate self-healing formulation. Curing kinetics of the epoxy blend at RT was studied utilizing DSC anticipating pertinence to self-healing agent. We then introduced a new concept labeled fibers with “beads-on-string” structure with which the self-healing weight fraction was significantly increased (up to 35 %). Although these results are very promising, several future steps required to determine the self-healing capability of such novel fiber mats some of which are discussed next.

4.6 Future Work

4.6.1 Mechanical Testing of Impregnated Fibers

We were able to fabricate fiber mats that contained up to ~35 % of encapsulated core material. In order to assess self-healing ability of such fibers, mechanical testing of damaged and healed samples should be conducted on:

A. Multilayer PAN/Ancamine PAN/DGEBA/Heloxy fiber mats. The effect of number of alternating layers on self-healing is to be assessed. We envision self-healing to be improved as the total number of the alternating layers increase.

B. Multilayer FRCs with core-sheath fibers mats at the interface of layers prepare composites. We hypothesize that core-sheath fibers will significantly enhance mechanical and thermal properties of FRCs. In addition, the self-healing feature will enable a damaged FRC component to be healed to near virgin condition

4.6.2 Microcapsules containing Self-Healing Approach

Microcapsules with the ability to automatically heal cracks was first introduced by White et al. in 2001\textsuperscript{36-38}. Such crosslinked microcapsules contained microencapsulated healing agent that is released upon rupture by a mechanical stimuli. Then, polymerization of the healing agent at the
damage site provides the recovery of initial mechanical properties. Also this concept is well-
studied, there is no report of electrospinning such microcapsule. Combining the same approach
with PAN electrospinning provides formation of the desired beads-on-string structure discussed in
this chapter. Specifically, beads containing self-healing agent are formed prior to the
electrospinning process and are mixed with PAN in the electrospinning solution. Thus, we plan to
develop epoxy-containing microcapsules that were then electrospun along with PAN in a DMF
solution resulting in “beads on string” structure. Briefly, crosslinked urea-formaldehyde
microcapsules containing epoxy monomer will be prepared by in situ polymerization in an oil-in-
water emulsion. Shown in Scheme 4-7 are schematic illustration of a PAN fiber mat with
microcapsules containing self-healing agent (epoxy).

4.7 References


Scheme 4-1. Schematic illustration of core-sheath fibers showing (A) cross section view and (B) top view of them. The self-healing agents (liquid epoxide and diamine hardener) are encapsulated in a PAN/CNT (or PAN) polymer sheath.
Mix the reactants and stir for 2-3 min → Store the blend at RT → Run Dynamic DSC → Exothermic Peak in 1st Heating Cycle? → Yes → Cure is complete! → No → Store the blend at RT → Run Dynamic DSC → Exothermic Peak in 1st Heating Cycle? → Yes → Cure is complete! → No

Scheme 4-2. Schematic illustration of the curing protocol.
Figure 4-1. (A) Photographs of the coaxial electrospinning spinneret along with its front and rear end cross section views. (B) The optimized setup for co-axial electrospinning. All the plastic tubing are replaced by tubing are stainless steel to prevent any dissolution or swelling of in the presence of DMF.
Scheme 4-3. Schematic illustration of the tracking core liquid flow mechanisms. The fluorescent dye in the core liquid detects core flow after fiber breakage (due to damage).
Scheme 4-4. Schematic illustration of “epoxy sandwich” preparation process. (A,B) Ancamine and DGEBA were first pipetted on two separate rectangular pieces of PAN fiber mat. (C) The embedded PAN fiber mats were then placed on the top of each other.
Figure 4-2. Thermograms of epoxy for (i) as mixed (t=0), (ii) after 1 day (t=24 h) and (iii) after 2 days (48 h).
Figure 4.3. (A) DSC 1\textsuperscript{st} and (B) 2\textsuperscript{nd} heating cycle (exo up) thermograms of epoxy blend (DGEBA/Heloxy and Ancamine) (i) as mixed (t=0) and after (ii) 2, (iii) 4, (iv) 6, (v) 12, (vi) 24, (vii) 48, (viii) 72 and (ix) 96 h. The curing process takes about 4 days to complete indicating that a curing accelerator is required to shorten this time to less than 12 h.
Figure 4-4. Chemical structures of (A) $N,N$-benzyldimethylamine (BMDA), (B) Aminoethylpiperazine (AEP) and (C) Al POMS.
Figure 4-5. (A) 1\textsuperscript{st} and (B) 2\textsuperscript{nd} heating cycle DSC traces of the epoxy blend (DGEBA/Helox and Ancamine) in the presence of AEP (i) as mixed (t=0) and after (ii) 2, (iii) 4, (iv) 6 h, (v) 8 h, (vi) 24 h and (vii) 48 h. The curing accelerator reduced the curing time to about 12 h.
Figure 4-6. (A) 1st and (B) 2nd heating cycle DSC traces of the epoxy blend (DGEBA/Heloxy and Ancamine) in the presence of BMDA (i) as mixed (t=0) and after (ii) 2, (iii) 6, (iv) 12 h, (v) 24 h and (vi) 48 h. The curing accelerator reduced the curing time to about 12 h.
Figure 4-7. (A) 1\textsuperscript{st} and (B) 2\textsuperscript{nd} heating cycle DSC traces of the epoxy blend (DGEBA/Heloxy and Ancamine) in the presence of Al POMS (i) as mixed (t=0) and after (ii) 2, (iii) 4, (iv) 6 h, (v) 12 h and (vi) 48 h. The curing accelerator reduced the curing time to about 12 h.
Figure 4-8. Curing profiles of the epoxy blend (DGEBA/Heloxy and Ancamine) and epoxy blend in the presence of Al POMS, BMDA and AEP. All curing accelerators reduced the curing time to about the same extent (<12 h).
Figure 4-9. Tensile Storage Modulus (E’) and loss tangent (tan δ) traces of a fully cured DGEBA-Ancamine-Heloxy epoxy as a function of temperature.
Figure 4-10. SEM micrographs of (A) PAN fibers as a control, (B) coaxially electrospun PAN fibers with DGEBA/Helox solution as core and (C) coaxially electrospun fibers with Ancamine solution as core.
Figure 4-11. Fiber diameter histograms and average fiber diameter of (A) PAN and (B) coaxially electrospun fibers with PAN as the sheath and DGEBA/Heloxy in core. PAN fiber histograms follows a normal distribution with one peak as an average whereas the coaxial fibers showed a double peak distribution corresponding to fibers with and without core material.
Figure 4-12. (A) Chemical structure of Rhodamine B. Photographs of Rhodamine B (B) as received and (C) mixed in a PAN/DMF solution.
Figure 4-13. Fluorescent microscopy micrographs of coaxially electrospun fiber mat showing (A) bright field image of the fibers, (B) fluorescent image and (C) overlay of (A) and (B) demonstrating the fibers that contain core material. Note: The core solution was dyed with Rhodamine B. Scale bar represents 100 μm.
Figure 4-14. Step by step demonstration of image analysis showing: (A) bright field (BF) image, (B) inverted brightfield image, (C) image after adjusting brightness and contrast, (D) image after applying threshold and (E) grey level histogram of the image.
Figure 4-15. (A) Overlaid images of coaxially electrospun fabricated fiber mat. Table shows a rough approximation for degree of encapsulation of core material in the sheath. Scale bar represents 100 μm.
Figure 4-16. Representative contact angle micrographs of (A) Ancamine and (B) DGEBA on PAN film prepared by solvent casting technique. Both Ancamine and DGEBA permeated into a PAN fiber mat in less than 1 minute. Note: PAN film was very brittle and curled during the solvent casting process.
Figure 4-17. Bright field (left) and Fluorescent (right) images of (A) as spun fiber mat and heated at 80 °C for (B) 1h, (C) 3 h and (D) 12 h. There was no evidence of core liquid flowing out of PAN fibers after 12 h even at an elevated temperature (80 °C). We attribute this to high mechanical strength of PAN fibers which withstand the inner pressure induced by the core material preventing it from diffusing out of the fiber. Scale bar represents 100 μm.
Figure 4-18. (A) Bright field and (B) fluorescent images of a co-axially electrospun fiber mat chopped several times with a fresh razor baled and kept isothermal at 80 °C for 12 h. Scale bar represents 100 μm.
**Scheme 4-5.** Schematic illustration of a fiber mat with beads on string structures. The beads containing a thin layer of shell outside and self-healing agent inside are at least one order of magnitude bigger than fiber mat diameter allowing to increase the self-healing agent weight fraction.
Figure 4-19. Fluorescent microscopy micrographs of coaxially electrospun fiber mat with PAN and DGEBA/Helox as the shell and core, respectively at (A) 13.5 and (B) 16.0 kV. Left and right images represent bright field and fluorescent images, respectively. Red Circles indicate the presence of sparse beads on the fibers.
**Figure 4-20.** SEM micrograph of coaxially electrospun fiber mat with PAN and Ancamine as the shell and core, respectively. Regular oval beads with up to 8 μm in diameter were observed in the resulting fiber mats.
Figure 4-21. Photographs of (A) 5 ml of 10 % PAN/DMF solution in 0.5 g of Ancamine and (B) 5 ml of 10 % PAN/DMF solution in 0.5 g of DGEBA. Both solutions became homogenous after stirring overnight at RT.
Table 4-1. Compatibility of PAN and epoxy monomers (DGEBA, Ancamine) in a DMF solution.

0.5 g of materials containing PAN and epoxy with different ratios were poured into 5 ml of DMF. Solutions were stirred overnight at RT.

<table>
<thead>
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<th>PAN:Epoxy Ratio (wt.)</th>
<th>2:1</th>
<th>1:1</th>
<th>1:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>✓</td>
<td>✓</td>
<td>X</td>
</tr>
<tr>
<td>Ancamine</td>
<td>✓</td>
<td>✓</td>
<td>X</td>
</tr>
</tbody>
</table>

The table indicates the compatibility of PAN and epoxy monomers (DGEBA, Ancamine) in a DMF solution with different ratios. "✓" represents compatibility, and "X" represents incompatibility.
Figure 4.22. Optical micrographs of co-electrospun (A) 2:1, (B) 1:1 PAN/epoxy solutions and (C) PAN fibers (control). Top and bottom rows represent the results for PAN/Ancamine and PAN/DGEBa solutions in DMF, respectively. Results showed that co-electrospinning can indeed lead to the formation of beads on string structure fiber mat. Scale bar represents 100 μm. Red arrow and dashed circles indicate beads-on-string structure and droplets, respectively. The presence of droplets in the resulting fiber mat indicate partial encapsulation of core material by PAN fibers.
Figure 4-23. Optical micrographs of 2:1 PAN/Ancamine solution in DMF (A) as electrospun and (B) post heating at 200 °C. Given that the morphology and the density of fibers remain intact after heating, we postulate that Ancamine was protected by an outer shell of PAN. Such postulation requires further investigation to confirm which remains subject of future work. Note: At 200 °C, PAN doesn’t degrade but any solvent/Ancamine with boil or degrade completely. Scale bar represents 100 μm.
Figure 4-24. Thermogram traces of (i) Heloxy, (ii) Ancamine, (iii) DGEBA and (iv) PAN as a function of temperature. Thermal stability of PAN is higher than other components specially Ancamine.
Figure 4-25. Thermogram traces of (A) Ancamine/DMF solution, (B) PAN and (C) co-electrospun PAN/Ancamine/DMF Solution. (D) shows the temperature profile during isothermal TGA program indicating that temperature quickly ramps up to 200 °C and stays isothermal for 1 h. While PAN doesn’t degrade or sublime at 200 °C for 1 h, most of DMF and Ancamine was evaporated in less than 10 minutes. The weight loss of PAN/Ancamine/DMF was about 35 % corresponding to Ancamine assuming that all of DMF evaporates during the electrospinning step.
Figure 4-26. (A) Photographs, (B) SEM micrographs and (C) optical micrographs of electrospun PAN/Ancamine co-solution before (left) and after heating isothermally at 50 °C for ~15 min. Note that for optical micrographs (taken with Hirox microscope), brightness and contrast were carefully adjusted without losing any information. Results showed no evidence of core material flowing out of the fibers even after 12 h, although a strong Ancamine odor was evident specially after heating the fiber mat. We postulate that PAN fibers were able to withstand the inner pressure induced by the core material preventing it from diffusing out of the fiber.
Scheme 4-6. Schematic illustration of a coaxial electrospinning setup with co-solution (a solution consisting of PAN, DGEBA and DMF) and pure DMF in the core and sheath, respectively. DMF sheath stabilizes the electrospinning conditions and prevents the droplets to form.
Figure 4-27. Optical micrographs of electrospun PAN/DGEBA/DMF co-solution as core and pure DMF as sheath with flow rates of: (A) 2.0, (B) 1.5, (C) 1.0 and (D) 0.5 ml/h. The core solution flow rate (PAN/DGEBA/DMF) was kept consistent at 1.0 ml/h. Presence of DMF as the sheath even at its lowest flow rate (0.5 ml/h) evidently prevented beads to form indicating that all the core solution was successfully encapsulated in the sheath. As core flow rate increases, the electrospinning conditions became more stable and more beads-on-string structure was observed. The best result was accomplished when sheath flow rate was at 1.5 ml/h given that the beads on string density was maximized. Scale bar represents 50 μm.
**Figure 4-28.** Optical micrographs of electrospun PAN/DGEBA/DMF co-solution as core and pure DMF as sheath at (A) 7.0, (B) 10.0, (C) 13.0 and (D) 16.0 kV. The core and sheath solutions flow rate (PAN/DGEBA/DMF) were kept consistent at 1.0 and 1.5 ml h⁻¹, respectively. Scale bar represents 50 μm.
Photographs of (i) 0.5, (ii) 1.0, (iii) 1.5, (iv) 2.0 and (v) 3.0 g of PAN mixed with 10 ml of DMA (corresponding to concentrations of 0.05, 0.1, 0.15, 2.0 and 3.0 g ml\(^{-1}\), respectively) and stirred at RT overnight for electrospinning. For the highest concentration (0.3 g ml\(^{-1}\)), the polymer did not dissolve completely in DMF. In other words, the solubility limit of PAN in DMF is less than 0.3 g ml\(^{-1}\). 2.0 g of PAN dissolved in 10 ml DMF but it was not electrospinnable due to its extremely high viscosity. All other solutions were used for electrospinning.
Figure 4-30. SEM micrographs of PAN fiber mats electrospun from solutions prepared by dissolving (A) 0.5, (B) 1.0 g and (C) 1.5 g in 10 ml of DMF. Each row represents same PAN concentration and magnifications at 500x, 1000x and, 2000x.
Figure 4-31. Fiber diameter histograms and average fiber diameter of PAN fiber mats electrospun solutions prepared by dissolving (A) 0.5, (B) 1.0 g and (C) 1.5 g in 10 ml of DMF.
Figure 4-32. Fiber diameter as a function of PAN solution concentrations. Results show that fiber diameter linearly increases as polymer solution increases in the electrospinning process. Red line represents the linear regression curve. Note: All electrospinning conditions kept the same except for the variable (flow rate) in all experiments. Number of Measurements: 50.
Figure 4-33. SEM micrographs of PAN fiber mats electrospun at different solution flow rates; (A) 0.5, (B) 1.0, (C) 2.0 and 4.0 ml h⁻¹. Concentration for all fiber mats was 0.1 g ml⁻¹.
Figure 4-34. Fiber diameter histograms and average fiber diameter of PAN fiber mats electrospun at (A) 0.5, (B) 1.0, (C) 2.0 and 4.0 ml h⁻¹. Concentration for all fiber mats was 0.1 g ml⁻¹.
Figure 4-35. Fiber diameter as a function of PAN solution flow rate. Results show that fiber diameter linearly increases as flow rate increases in the electrospinning process. Red line represents the linear regression curve. Note: All electrospinning conditions kept the same except for the variable (flow rate) in all experiments. Number of Measurements: 50.
Figure 4-36. Photographs of “epoxy sandwich” preparation process. (A,B) Ancamine and DGEBA were first pipetted on two separate rectangular pieces of PAN fiber mat. (C) The embedded PAN fiber mats were then placed on the top of each other.
**Figure 4-37.** SEM micrographs of sandwich A (2 PAN fiber mats carefully pipetted and sandwich between glass slides) at two different magnification. Dashed lines represent the interface of the two fiber mats indicating incomplete cure. Note that the entire sample was cured at RT for at least 1 week prior to taking the SEM image.
Figure 4-38. SEM micrographs of interface of two petties of sandwich A where cure was not complete. Arrows indicate the two layers of Sandwich A that are in contact at the interface (highlighted by dashed lines).
Figure 4-39. DSC of sandwich A did not show a distinguishable $T_g$ which indicates DGEBA and Ancamine phases remained separated from each other thus the cure was incomplete cure/cure only occurred at the interface.
**Figure 4-40.** SEM micrographs of sandwich B: two layers of electrospun PAN, one embedded with excessive amount of DGEBA/Heloxy and other with excessive amount of Ancamine sandwiched between two glass sheets. Note that the entire sample was cured at RT for at least 1 week prior to the experiment. No interface observed thus the cure was complete.
Figure 4-41. Photographs of “Epoxy Roll” preparation process. Ancamine and DGEBA were first pipetted on two separate rectangular pieces of PAN fiber mat (A,B). (C) The embedded PAN fiber mats were then placed and rolled on the top of each other.
Figure 4-42. SEM micrographs of the epoxy roll cross section at different magnifications. Top and bottom rows represent cut with a fresh razor blade and cryofractured samples at different magnifications, respectively. Note that the entire sample was cured at RT for at least 1 week prior to the experiment.
Scheme 4-7. Schematic illustration of a fiber mat with encapsulated microcapsules showing: (A) overall fiber mat morphology, (B) a fiber strand with microcapsules “beads” on them, (C) a microcapsule and (D) fractured microcapsules containing self-healing agent in it. Microcapsules can be synthesized with any diameter/thickness by in situ polymerization in an oil-in-water emulsion and subsequently electrospun with PAN fibers in a DMF solution to fabricate a beads on a string structure. (E) and (F) represent examples of microcapsules from literature (adopted with permission from [White, S. R.; Sottos, N.; Geubelle, P.; Moore, J.; Kessler, M. R.; Sriram, S.; Brown, E.; Viswanathan, S.; *Nature* **2001**, *409*, 794-797.] showing microcapsules before and after rupture, respectively.
Chapter 5: Interwoven Polymer Composites via Dual-Electrospinning with Shape Memory and Self-healing Properties

5.1 Synopsis

Material research and development is increasingly focusing on achieving specialized functionality in materials. For example, the ability to “self-heal (SH)”, or naturally repair accrued damage, is attractive because it extends the lifetime of the material by increasing resistance to damaging conditions and prolonging preservation of material properties. Additionally, shape memory (SM) materials, including SM polymers, are actively considered for their ability to change shape one or more times upon application of an external stimulus. Here, we present a polymer composite, composed of poly(vinyl acetate) (PVAc) and poly(ε-caprolactone) (PCL), exhibiting both SH and SM functionality. In fact, the SM assists in the SH ability in a process developed by our group termed, shape memory assisted self-healing (SMASH). The advantage of the SH composite presented here is its simple fabrication. Dual-electrospinning is used to simultaneously electrospin PVAc and PCL, achieving an interwoven polymeric composite of otherwise immiscible polymers. The dual-electrospinning method facilitates precise control of the relative weight fractions of the components, and thus allows for tuning of the material properties. Upon thermal activation, damaged PVAc-PCL composites exhibited SH under a variety of testing conditions. Furthermore, the composites exhibited impressive dual and triple SM capabilities in the dry and hydrated states, respectively. Together, the commercial availability of the components and the simplicity of preparation translate to a SMASH system that could be mass produced and used as a SH coating or alone, as a packaging material.
5.2 Introduction

5.2.1 Self-Healing Materials

In practice, polymeric materials are susceptible to mechanical stress and harsh environmental conditions that can lead to the formation of microcracks and, eventually, material failure. The induced damage is challenging to detect, which makes it even more difficult, if not impossible, to repair\textsuperscript{1,2}. Consequently, the mechanical properties of polymeric materials can be unduly compromised over time. Inspired by biological systems, “self-healing (SH)” is a fascinating and relatively young field of research that can address issues such as material failure due to the propagation of cracks, or more specifically, microcracks. SH materials exhibit the ability to repair themselves and recover functionality using the resources inherently available to them upon damage\textsuperscript{2,3}. There are a variety of ways to classify SH materials. One categorization groups SH materials based on the particular stimulus responsible for triggering the healing mechanism, such as mechanical\textsuperscript{4} and thermal\textsuperscript{5}. Self-healing composites were first introduced by White et al. by incorporating a microencapsulated healing agent and a chemical catalyst in a polymeric host\textsuperscript{4,6}. Upon damage the microcapsules rupture and the SH agent flows to the damaged site and polymerizes, restoring the mechanical properties of the composite\textsuperscript{4,6}. An advantage of this approach is that it does not require any external stimulus and damage itself triggers the SH mechanism. However, a disadvantage of this method is the limited amount of available SH agent. Besides, the ruptured microcapsule itself may act as a defect in the material structure, compromising the material performance in long term.
5.2.2 Shape Memory Assisted Self-Healing (SMASH)

Another approach, introduced by our group, utilizes shape memory\(^7,^8\) (SM) phenomenon to prepare novel SH polymers that are capable of simultaneously closing and rebonding cracks with a simple thermal trigger\(^9,^10\). This strategy, termed “shape memory assisted self-healing (SMASH)”, was first demonstrated in a blend system consisting of a cross-linked poly(\(\varepsilon\)-caprolactone) network (n-PCL) with interpenetrating linear poly(\(\varepsilon\)-caprolactone) (l-PCL). Such unique chemistry exhibited the SM response from the network component and a SH capacity from the linear component\(^9\). A drawback of this SMASH system is its low rubber modulus, which necessitates mechanical support for applications that require stiff materials. In an attempt to overcome this limitation, we report here a new polymeric SMASH system that contains a glassy polymer that leads to higher stiffness. Further, a simple electrospinning method was utilized to prepare the uniformly distributed, interwoven composites.

5.2.3 Multi-Component Composites Prepared via Electrospinning

Electrospinning is a technique that is commonly utilized in various fields of research to fabricate fine, multiscale fibers\(^11,^12\). In a typical electrospinning setup, a polymer solution is charged using a high voltage power supply. As the polymer solution within the syringe becomes charged, a “Taylor” cone forms at the tip of the syringe needle due to like-charge electrostatic repulsion. At a critical point, a charged jet of the polymer solution forms and is propelled towards the grounded drum\(^13\). Before reaching the drum, the electrostatic force overcomes the solvent surface tension force resulting in fiber draw and accelerated solvent evaporation. Dry polymer fibers are then collected on a plate, drum or disk. Fiber properties, such as diameter and orientation, can be
controlled by adjustment of the electrospinning parameters, such as voltage, flow rate, or drum rotation speed.

Recently, traditional electrospinning has been modified in many ways to improve the functionality and the versatility of the resulting nano-structures. In tissue engineering, for example, the functionalizing agents (biomolecules, such as growth factors or drugs), which are to be maintained in the fluid state, are electrospun through a coaxial capillary. The outside polymer solution encapsulates the fluid, yielding a two-layer, core-sheath fiber structure\textsuperscript{14,15}. Further, composite fiber mats exhibiting a combination of properties of two or more polymers have attracted a lot of attention\textsuperscript{11}. Liu and coworkers reported bicomponent TiO\textsubscript{2}/SnO\textsubscript{2} nanofibers fabricated by a unique electrospinning configuration in which two distinct solutions were jetted simultaneously using a dual-spinneret assembly. The authors postulated that the side-by-side electrospinning approach provided the maximum exposure of both components and increased the surface area, leading to improved efficiency as a photocatalyst for the treatment of organic pollutants in water\textsuperscript{16}.

Seeking to develop a one-step method to fabricate a SH systems, the present work introduces a simple dual-electrospinning method to develop composites consisting of two uniformly distributed immiscible polymers that together, feature SH properties. Interwoven polymer blends with homogenous phase distribution, precise composition, and properties tuned to our specifications were fabricated. Specifically, composites consisting of poly(vinyl acetate) (PVAc) and poly(\(\varepsilon\)-caprolactone) (PCL) that feature both SH and SM functionality were fabricated. In what follows, we discuss the preparation, morphology and thermomechanical characterization of the composites, thus revealing their excellent potential for several industrial applications.
5.3 Experimental Section

5.3.1 Materials

N,N-Dimethylformamide (DMF), chloroform, methanol, Rhodamine-B, and poly(ε-caprolactone) (PCL) (Mn ≈ 70,000-90,000 g mol\(^{-1}\)) were purchased from Sigma Aldrich. Poly(vinyl acetate) (PVAc) (MW = 260,000 g mol\(^{-1}\)) was purchased from Scientific Polymer Products. All chemicals were used as received. For electrospinning, 2 g of PVAc was dissolved in a solution containing 7.0 ml methanol and 3.0 ml DMF by volume to obtain a 20 wt. % polymer solution. About 100 mg of Rhodamine-B (fluorescent dye) was mixed with the PVAc solution, turning the solution from clear and colorless to bright red. A PCL solution was prepared from 2.0 g of PCL, 8.0 ml chloroform, and 2.0 ml DMF to obtain a 20 wt. % polymer solution. Both solutions were stirred at room temperature overnight until a homogenous solution was achieved.

5.3.2 Dual-electrospinning Setup

For this study, an electrospinning setup featuring a two-polymer solution delivery system was designed\(^\text{17}\). The polymer solutions were contained in syringes located on opposite sides of the drum, as illustrated in Scheme 5-1. Having our target application in mind, we selected PVAc and PCL as the SM polymer and SH agent, respectively, for dual-electrospinning. Electrospinning parameters for each polymer solution were set independently:

- PVAc: 13.0 kV applied voltage and 8 cm tip of the needle to collector distance.
- PCL: 12.0 kV applied voltage and 10 cm tip of the needle to collector distance.

The samples are named “PVAc\(x\):PCL\(y\)” where \(x\) and \(y\) stand for the nominal weight fraction of PVAc and PCL, respectively. The nominal weight fractions of the polymers in the composites
were calculated based on the relative flow rates used for PVAc and PCL solutions during the dual-electrospinning process. Two composites, PVAc60:PCL40 and PVAc80:PCL20 were fabricated and compared to neat PVAc and PCL samples as controls.

### 5.3.3 Composite Morphology and Fiber Distribution Investigation

Heating the fiber mat at 80 °C, which is above the characteristic glass transition temperature ($T_g$) and melting transition temperature ($T_m$) of PVAc and PCL, respectively, allows PVAc chains to reconfigure to a relaxed, lower energy state and melts the PCL fibers to a film. The heating step also results in significant shrinkage in size, which aided in filling the voids of the porous fiber mat to form a film (See **Results and Discussion** section). Hereafter, the as-spun and heated samples are called fibers and films, respectively. The morphologies of the composites pre- and post-heating (fibers and films) were studied using a JEOL JSM-5600 scanning electron microscope (SEM). Prior to imaging, samples were sputter coated (Denton Vacuum-Desk II sputter coater) with gold for 45 s.

Interested in investigating fiber-fiber interactions in the dual-electrospinning process, we examined the distribution of the two fiber jets (PVAc and PCL) within the fiber mats. Ideally, both PCL and PVAc fibers should be randomly distributed within the fiber mat to assure SH at any region of the sample. To examine fiber distribution, the bright field (under visible light) and fluorescent (under ultraviolet light with a fluorescent filter) images of the fibers were taken using a Leica DMI 4000B inverted microscope with a Leica DFC 340FX camera using a 40x/1.3 NA objective. Note that only the PVAc solution contained Rhodamine B (a fluorescent dye), so only PVAc fibers appeared under the fluorescent light\(^\text{18}\). Using ImageJ software, histogram stretching was carefully applied to all micrographs to maximize image contrast. The bright field images
were then inverted so that they had a black background, as in fluorescent images. All of these steps were conducted carefully to prevent loss of information in the micrographs. Blue and red lookup tables were then applied to the bright field and fluorescent images, and the images were overlaid to examine the distribution of PVAc and PCL fibers in a single micrograph.

5.3.4 Thermomechanical Properties of the Composites

Thermal properties and phase behaviour of the PVAc:PCL films were studied using differential scanning calorimetry (DSC), with the anticipation of pertinence to mechanical properties and SH behaviour studied later. DSC experiments were conducted using a Q200 (TA Instrument) equipped with a refrigerated cooling system (RCS). Samples with masses of 3-5 mg were encapsulated in Tzero aluminum pans and were heated from -80 °C to 120 °C, cooled back to -80 °C, and finally heated to 120 °C. All heating rates were 10 °C min⁻¹ and all cooling rates were 5 °C min⁻¹. The T_g and T_m of the samples were determined as the middle point of the step transition and the melting endothermic peak transition of the DSC second heating runs, respectively.

Thermomechanical properties of the films were characterized using a Q800 Dynamic Mechanical Analyzer (DMA) (TA Instrument). Dogbone samples (ASTM D63 Type IV, scaled down by a factor of 4) with a typical thickness of 0.3-0.5 mm were loaded under tension and oscillatory deformation with an amplitude of 10 μm, a frequency of 1 Hz, and a “force track” (ratio of static to dynamic force) of 108 %. To determine transition temperatures and rubbery plateaus of the film, the samples were equilibrated and held isothermally at -40 °C for 10 min, then heated to 80 °C at 2 °C min⁻¹.
5.3.5 Microstructure Characterization

To determine the microstructure of the PVAc:PCL composites (as-spun and film), wide-angle X-ray scattering (WAXS) was conducted using a Rigaku S-MAX3000 (Woodlands, TX) instrument in transmission mode. A FujiFilm FLA7000 reader was used to collect the scattered X-ray diffraction patterns. A Rigaku generator (MicroMax-002+) was employed to produce a radiation with a wavelength of 1.5405 Å. An accelerating voltage of 45 kV and a current of 0.88 mA were applied. The distance between sample and image plate was fixed at 122.7 mm for wide-angle X-ray scattering collection. The resulting scattering angular was in range of 0° < 2θ < 40°. The patterns were analyzed using the SAXSgui software without background subtraction, benefiting from the fact that the whole X-ray system was run under high vacuum.

5.3.6 Self-healing Characterization

To evaluate the ability of the film to recover from various types of mechanical damage, 3 different experiments were conducted. First, the SH ability of a PVAc60:PCL40 film (40% PCL previously found to be the optimal loading level for efficient SH in another system) was assessed qualitatively by applying a cross shaped cut on the surface of the sample. The damaged sample was then thermally mended (or “self-healed”) by heating isothermally at 75 °C for 10 min. The SH behaviour was further investigated following a method developed by Yamaguchi and colleagues. First, the top surface of a rectangular sample (23 mm length, 4.2 mm width and 0.8 mm thickness) was notched. The crack was then opened/propagated by pushing the two ends of the sample against a cylindrical object (9.0 mm in diameter). This action almost broke the sample in half, but a thin lesion on the back side held the two halves together. The sample was then heated to 75 °C, held isothermally for 10 min, and then cooled to room temperature to
observe thermal mending qualitatively. Finally, a third, quantitative, SH experiment was conducted using the deeply double-edge notched tensile (DDENT) geometry employed for fracture testing of polymeric films. A dogbone (ASTM D638-03 Type 1, scaled down by a factor of 3) shaped PVAc60:PCL40 sample with a typical thickness of 0.8-1.0 mm and a PVAc (as a control with no PCL, i.e. SH agent) sample were notched using a custom-made dogbone cutting die to create two collinear, gauge-centered edge-cracks that were 0.5 mm long on each side of the dogbone neck. The gauge length for such specimen was 16.67 mm. To controllably propagate the damage, the notched sample was then stretched at a slow rate (10 μm s⁻¹) to 5.00 mm (corresponding to 30 % strain) using a TST350 Linkam Tensile Stress Testing Stage (Linkam Scientific Instruments, Ltd.) with a 200 N load cell. The damaged sample was then heated to 75 °C and held isothermal for 10 min to initiate thermal mending. To evaluate the crack propagation and SH processes, micrographs of notched, stretched, and self-healed samples were taken using a Zeiss Discovery V8 stereo microscope with a QIMAGING (QICAM FAST1394) CCD camera. SH was assessed by comparing the mechanical properties of virgin, damaged, and healed samples. Self-healing efficiency was defined as

\[
\eta(\%) = \frac{F_{\text{Max, Healed}}}{F_{\text{Max, Virgin}}} \times 100
\]  

(5-1)

where the virgin \( F_{\text{Max, Virgin}} \) and healed \( F_{\text{Max, Healed}} \) peak loads were obtained from the force vs. displacement curves recorded for virgin and healed samples stretched in the Linkam tensile stage. For a completely healed sample, the force vs. displacement curve should be identical to that of the virgin sample and thus 100% self-healing efficiency.
5.3.7 Triple Shape Memory Characterization of the Hydrated Composite

One approach to develop triple SM materials is to develop composites featuring two well-separated thermal transitions\textsuperscript{22}. The $T_g$ of PVAc decreases to $\sim 17$ °C upon equilibrium plasticization with water. Therefore, the water-soaked PVAc:PCL film has a $T_g$ around $17$ °C and a $T_m$ (from PCL) around $55$ °C, making it an appropriate candidate for triple SM behavior. To characterize this material, dual SM properties of the dry film were first examined. A rectangular PVAc80:PCL20 film (21.0 mm length, 4.0 mm width and 0.4 mm thickness) was heated to $80$ °C, deformed into a spiral shape by wrapping around a glass rod with a diameter of 5 mm, held isothermal for 5 min, and quenched by placing in a freezer at $-17$ °C for 10 min. For recovery, the sample was heated isothermally in an oven at $80$ °C. In order to qualitatively assess the triple SM behavior of the film, a rectangular piece of PVAc80:PCL20 (20% being established as the optimal PCL loading level for triple SM properties in other systems\textsuperscript{22-25}) film was immersed in water overnight to assure complete hydration. Then, the sample was curled to a “C” shape (temporary shape 1) in an $80$ °C water bath and fixed immediately by quenching in an ice/water bath. For the second temporary shape, the sample was rolled on itself to a compact form in a water bath at room temperature (RT) and quenched in an ice/water bath. For recovery, sample was sequentially immersed in water at RT for 10 min and then heated to $80$ °C. It is noted that triple SM properties are not exhibited in the dry composite, since the transition temperatures of the PVAc and PCL are found in a narrow temperature window.

5.3.8 Mechanical Properties of Hydrated vs. Dry Films

The mechanical properties of PVAc and PVAc80:PCL20 films, in both the dry and wet states, were studied using the same Linkam TST-350 tensile tester at room temperature. Dogbone
shaped samples (ASTM Standard D63 Type IV, scaled down by a factor of 4) with a typical thickness of 0.3-0.5 mm were stretched at 50 μm s⁻¹ at RT to failure. For the dry and hydrated samples, a 200 N (0.1 N resolution) and a 20 N load cell (0.01 N resolution) were used, respectively. Hydrated samples were immersed in water for at least 24 h prior to the experiment, and water was pipetted onto their surfaces during the experiment to maintain hydration.

5.4 Results and Discussion

5.4.1 Dual-Electrospinning Setup

A schematic illustration of the dual-electrospinning setup is provided in Scheme 5-1. Two separate pumps, located on opposite sides of the collecting drum, controlled the flow rates of each solution. The fibers were collected on a rotating drum (diameter of ~5 cm), which rotated at 400 RPM and translated in an oscillatory fashion with a rastering amplitude of ~6 cm. An inherent advantage of this method compared to other methods, such as solvent casting or melt mixing of two immiscible polymers, is that the two different polymeric fibers are uniformly distributed and tightly interwoven with each other throughout the fiber mat. Note that the two polymers can be selected from the vast library of electrospinnable polymers reported in literature¹¹,¹³. Also, precise control over the relative flow rates translates to precise control of each component’s weight fraction as we discuss later.

5.4.2 Composite Morphology and Fiber Distribution

PVAc polymer chains are oriented along the length of the electrospun fibers and the polymer is in a high-energy state given the high electric voltage applied during the electrospinning process²⁶,²⁷. Heating the fiber mat to 80 °C, which is above the characteristic T_g of the PVAc and T_m of PCL, allows PVAc chains to reconfigure to a relaxed, lower energy state and melts the
PCL fibers to yield a film. Figure 5-1 shows the SEM micrographs of a PVAc60:PCL40 fiber mat before and after heating. Upon heating, the composite experiences a significant reduction in size and changes from a porous fiber mat to a stiff, non-porous film consisting of PVAc fibers bound by a PCL matrix (SEM images of neat PVAc and PCL fiber mats before and after heating are provided in Figure 5-2). A quantitative analysis of the heat induced reduction in size is provided in Figure 5-3. Results showed that the dual-electrospun sample (PVAc60:PCL40) has an intermediate shrinkage % value (74%) compared to the two controls (PCL (67%) and PVAc (78%) fiber mats).

Fluorescent microscopy was also utilized to investigate the distribution of the two fiber jets (PVAc and PCL) within the fiber mat. Shown in Figure 5-4 are the bright field and fluorescent images of PVAc60:PCL40 fibers and the overlay of the two micrographs. Results showed that PVAc and PCL fibers were randomly distributed in the fiber mat. This is necessary for SH purposes due to the fact that both SM polymer and SH agent have to be present at any given location in the composite in order to repair damage (For bright field and fluorescent micrographs of PVAc and PCL fibers, see Figure 5-5).

5.4.3 Thermomechanical Properties

DSC experiments were conducted to study the phase transition and composition of the different PVAc:PCL films. Second cycle DSC traces of PVAc:PCL films with different compositions are provided in Figure 5-6. For all PVAc:PCL films, a step-like T_g at 45 °C and a T_m at 56 °C were observed, corresponding to PVAc and PCL phases, respectively. Again, the relative weight fractions of PVAc and PCL fibers in the resulting dual-electrospun fiber mat can be controlled very easily by altering the initial flow rates of PVAc and PCL. Results showed that the actual
weight fraction of PCL (measured gravimetrically: calculated by dividing the PCL enthalpy of melting in the film by that of neat PCL fibers) were very close to the nominal PCL weight fractions in the films, assuring reliability and reproducibility of this method. Upon hydration, the $T_g$ of PVAc plunged to \(~15\, ^\circ C\) providing a wide window between PVAc $T_g$ and PCL $T_m$, a requisite factor for triple SM properties which is discussed in details later (for DSC of hydrated samples, see Figure 5-7). The thermal properties of the films are summarized in Table 1.

Thermomechanical testing was conducted to perceive the effect of composition on the viscoelastic properties of the films. This set of testing is important to provide context for the subsequent SH and SM characterizations. Tensile storage modulus ($E'$) profiles are reported in Figure 5-8 for PVAc60:PCL40, PVAc80:PCL20 and PVAc films. All compositions exhibited glassy stiffness at RT with a modulus above 1 GPa. Given that the transition temperatures of PVAc (45 °C) and PCL (56 °C) are close to each other, all compositions showed a single, combined transition (modulus drop) on-setting at \(~40\, ^\circ C\). The loss tangent (tan($\delta$)) profiles for PVAc60:PCL40 and PVAc80:PCL20 however showed double peaks, indicative of both PVAc $T_g$ and PCL $T_m$ and which was in agreement with DSC results (See Figure 5-9). Therefore, we anticipated that a simple heating step above both transitions (i.e. 75 °C) would simultaneously trigger both SM response of PVAc phase and melting of PCL phase, yielding the two step SMASH mechanism.

5.4.4 Microstructure Characterization

The microphase morphologies of PVAc60:PCL40, PVAc and PCL as-spun fiber mats (bottom row) and post heating films (top row) were characterized using wide angle X-ray scattering (WAXS). Shown in Figure 5-10 are the 2D WAXS patterns (corresponding diffractograms are
shown in Figure 5-11). The PVAc scattering pattern (Figure 5-10(B)) showed two broad halos with no preferred orientation indicative of the amorphous and isotropic structure of the polymer. The PCL pattern, in contrast, showed sharp Debye-Scherrer rings corresponding to diffraction from crystalline planes of the PCL crystallites (Figure 5-10(C)). As expected, the PVAc60:PCL40 composite showed a combination of the aforementioned structures. In the WAXS pattern for this composite (Figure 5-10(A)), a broad halo and two sharp rings were present, corresponding to amorphous PVAc and semi-crystalline PCL phase, respectively. WAXS patterns of neat PVAc and PCL were overlaid, and the compiled pattern predictably matched that of the composite (Figure 5-10(D)). It is noted that the WAXS pattern of fiber mats featured similar but lower intensity values for the same exposure time than those of films due to their reduced thickness relative to their counterpart solid films.

5.4.5 Self-healing Characterization

For successful self-healing, the crack surfaces of a damaged article should close and rebond, restoring mechanical integrity in doing so. In the present system, the healing agent (PCL) transitions to a relatively low viscosity liquid when heated above its T_m and is therefore capable of wetting the damaged area and “gluing” the surfaces together upon recrystallization⁹. Our candidate composition was PVAc60:PCL40 given that a previous report by Rodriguez et al. on SMASH composites revealed that to achieve complete healing, the weight fraction of the healing agent needed to be at least 25 wt. %⁹. To characterize the ability of the composites to recover their initial properties upon damage, we conducted the SH experiments described in the Experimental section.

In the first experiment, the SH ability of a PVAc60:PCL40 film was assessed by scoring the samples with a cross shaped cut on the surface of the sample, as shown in Figure 5-12(A). Upon
thermal mending, the entire scar gratifyingly disappeared (Figure 5-12(B)). In this case, however, the sample surface had been damaged and more experiments were needed to study if the bulk of the sample showed similar features as we now discuss.

The self-repairing behavior was further investigated by inducing relatively more severe damage to the sample. First, the top surface of the sample was notched and the crack was then opened by bending the sample onto a column until it cleaved as illustrated in Figure 5-13(A, B). The healed sample, mended isothermally at 75 °C for 10 min, is shown in Figure 5-13(C). In order to have complete SH, two mechanisms are required: (1) The SM effect should unbend the sample and bring the two cracked surfaces together and (2) the SH agent should diffuse to the damage site, tackify, and consequently rebond the crack surfaces. The healability of the sample was impressive, given that the sample not only returned to its original shape, but also the initial crack was mended.

Lastly, SH efficiency was determined by comparing the peak loads achieved during tensile testing of the virgin and healed states of samples damaged with the DDENT. Each sample in its virgin, damaged, and healed states was stretched above its yield point. Shown in Figure 5-14(I) are the micrographs of a virgin, notched, stretched, and thermally mended sample. Upon heating to 75 °C and holding for 10 min, this sample showed that propagated crack damage was completely mended. By heating above the T_g of the PVAc phase, the SM mechanism was triggered, assisting in crack closure. Meanwhile, heating above the T_m of the PCL phase allowed the crack surfaces to rebond. Force vs. displacement curves for such experiment are shown in Figure 5-14(II), noting that tensile stress is ill-defined for this geometry and, so, not reported. We observed that the peak loads associated with the initial deformations were higher than the peak loads of damaged samples (samples that were notched and stretched prior to the test).
However, thermally mended samples showed peak loads similar to the virgin state with a self-healing efficiency of 99.0%. It is notable that both virgin and healed samples showed similar force-displacement profiles and did not break in the monitored 5.00 mm displacement range. In the absence of PCL (self-healing agent), however, the damaged PVAc film did not recover its original properties after heating. The PVAc films had a relatively lower self-healing efficiency (89%) and failed at significantly lower displacement compared to virgin PVAc. (See Figure 5-15). We attribute this observation to the fact that even though the cracks were closed after heating the PVAc film, the crack surfaces were not rebonded and were not able to withstand the same stress as the virgin sample.

5.4.6 Triple Shape Memory Characterization of the Hydrated Film

The “plasticization” process of PVAc is a well-known process caused by an increase in free volume in the polymer, resulting from the presence of small molecules, such as water or other solvents. Increased free volume allows for more molecular movement, effectively reducing the $T_g$ as evidenced in Figure 5-7$^{28,29}$, where the $T_g$ is seen to reduce from $\sim45$ °C to $\sim17$ °C. Upon hydration, the films (whether pure PVAc or PVAc/PCL composites) becomes elastomeric with a strain to failure above 500% (above the limits of our instrument) and a lower modulus, as shown in Figure 5-16. Such a drastic response to small amount of water uptake makes PVAc an excellent candidate for water triggered SM polymers$^{30}$. Dual SM of a dry composite film was first demonstrated by deforming a rectangular PVAc80:PCL20 sample (Figure 5-17(A)) to a spiral shape (temporary shape) at 80 °C. Upon fixing in a freezer at -17 °C for 10 min, both PVAc and PCL phases were fixed by vitrification and crystallization, respectively (Figure 5-17(B)). The fixed sample immediately recovered after being heated to 80 °C, as illustrated in
**Figure 5-17(C).** This is due to the close vicinity of the PVAc $T_g$ and PCL $T_m$. As such, an almost instantaneous recovery was observed by a simple heating step above them.

Triple shape memory materials can have two temporary shapes (A and B) programmed into them, allowing transition from shape (A) to shape (B) to shape (C)$^{22-24}$, where shape (C) is the permanent shape. Composites featuring two well separated transitions exhibit triple shape memory properties$^{22}$. Considering that the $T_g$ of PVAc decreases to $\sim 17$ °C upon hydration (Figure 5-7), the hydrated PVAc:PCL film had a $T_g$ around $17$ °C and a $T_m$ around $55$ °C, engendering it with triple SM characteristics, as shown in Figure 5-18 for the PVAc80:PCL20 film. There, a flat rectangular sample (13 mm length, 5.2 mm width and 0.9 mm thickness) was first curled to a “C” shape (temporary shape 1: Figure 5-18(B)) in an $80$ °C water bath and fixed immediately by quenching in ice/water bath. The sample was then rolled on itself in a water bath at RT and quenched in an ice/water bath as shown in Figure 5-18(C)). The sample recovered to its “C” shape (Figure 5-18(D)) after immersing in water at RT for 10 min, and it quickly recovered back to its permanent-flat shape after heating the sample at $80$ °C (Figure 5-18(E)).

**5.5 Conclusions**

We have reported on the dual-electrospinning of two immiscible polymers that yields blended films with desirable mechanical functionality. Specifically PVAc and PCL solutions were dual-electrospun, yielding composites with good self-healing and shape memory properties using this novel, one-step method. The process is versatile and any pair of polymers that are each electrospinnable can be utilized to blend properties with fine-scale homogeneity. Given the simplicity of fabrication of composites, we envision mass production of SH and triple shape films for applications that could range from building envelopes to food packaging.
5.6 Future Work

We have successfully designed a setup for co-electrospinning to immiscible polymers. Specifically PVAc and PCL solutions were dual-electrospun to fabricate shape memory assisted self-healing (SMASH) composites using this novel one-step method. In principle any pair of polymers which are electrospinnable can be utilized in this method depending on the desired application and composite properties. Besides, functionally graded composites spatially distributed in a gradient fashion within one single article can be fabricated with this method as we now describe. Functionally graded materials have been widely used in several applications including aerospace\textsuperscript{31,32}. During dual-electrospinning process, if the flow rate of polymer (A) is dialed up whereas the flow rate of polymer (B) is constantly dialed down, the resulting article is a functionally graded polymer with linearly gradient composition throughout its thickness and thus gradient properties as illustrated in Scheme 5-2. Given the simplicity of this method, we envision to exploit it for several industrial applications such as packaging.

5.7 References


**Scheme 5-1.** Schematic illustration of the dual-electrospinning setup showing that the two needles are located on opposite sides of the collecting drum.
Figure 5-1. SEM micrographs of (A) an as spun and (B) a heated PVAc60:PCL40 fiber mat. During heating, the PVAc polymers chains reconfigure to a relaxed state and the semicrystalline self-healing fibers melt and form a film resulting in significant fiber mat shrinkage.
Figure 5-2. SEM micrographs of (A) as spun PCL (B) heated PCL, (C) as spun PVAc and (D) heated PVAc fiber mats. During heating, PVAc polymers chains reconfigure to a relaxed state and the semicrystalline self-healing fibers melt and form a film resulting in significant fiber mat shrinkage. Scale bar represents 50 µm.
Figure 5-3. (I) Photographs of (A) PVAc60:PCL40, (B) PVAc and (C) PCL fiber mat. Left and right columns represent as spun samples and corresponding heated samples, respectively. All scale bars represent 1 mm. During heating, PVAc polymers chains reconfigure to a relaxed state and the semicrystalline self-healing fibers melt and form a film resulting in significant fiber mat shrinkage. Such reduction in size was quantified by heating 1 cm$^2$ square pieces of the PVAc60:PCL40 fiber mats at 80 ºC for 20 min. The shrinkage was calculated using the following equation:

\[
Shrinkage\% = \left(1 - \frac{A_{\text{Film}}}{A_{\text{Fiber}}}\right) \times 100
\]

where $A_{\text{Film}}$ and $A_{\text{Fiber}}$ correspond to surface area values of the fiber mat after heating (film) and as spun, respectively. (II) Quantitative characterization of fiber mat shrinkage showing average fiber mat sizes and shrinkage percentages for PVAc60:PCL40, PVAc and PCL (n=5). Results showed that the dual-electrospun sample (PVAc60:PCL40) has an intermediate shrinkage % value compared to the two controls (PCL and PVAc fiber mats).
Figure 5-4. Representative optical micrographs showing (A) bright field, (B) fluorescent and (C) overlaid (combined (A) and (B)) images of the dual-electrospun PVAc60:PCL40 fibers. Blue and pink colors correspond to PCL and PVAc, respectively. To take the images, the fibers were electrospun on a thin glass slide for ~10 s. Note that the PVAc solution contained ~0.5 wt. % of Rhodamine B. Scale bar represents 100 µm.
Figure 5-5. Micrographs of (A) PCL and (B) PVAc fibers. The top and bottom rows represent the bright field and fluorescent micrographs of such fibers, respectively. To take the images, the fibers were electrospun on a thin glass slide for ~10 s. Note that PVAc solution contained ~0.5 wt. % of Rhodamine B. PCL solution however, did not contain any Rhodamine B (fluorescent dye) and did not appear under fluorescent light. Scale bar represents 100 µm.
Figure 5-6. DSC thermograms (2nd heating cycle) of (i) PVAc, (ii) PVAc80:PCL20, (iii) PVAc60:PCL40 and (iv) PCL composites. The temperature was ramped at 10 °C min⁻¹ and 5 °C min⁻¹ for heating and cooling, respectively.
**Figure 5-7.** DSC thermograms (2nd heating cycle) of (i) hydrated PVAc and (ii) hydrated PVAc80:PCL20 composite. Heating rates were 10 °C min⁻¹ and 5 °C min⁻¹ for heating and cooling, respectively.
Table 5-1. Summary of the thermomechanical properties of PVAc:PCL composites in dry and hydrated states.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>ΔH_{m,PCL} (J/g)</th>
<th>PCL Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc</td>
<td>45.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PVAc-Hydrated</td>
<td>16.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PVAc60:PCL40</td>
<td>42.4</td>
<td>56.4</td>
<td>16.4</td>
<td>41.0</td>
</tr>
<tr>
<td>PVAc80:PCL20</td>
<td>43.0</td>
<td>56.4</td>
<td>10.1</td>
<td>25.0</td>
</tr>
<tr>
<td>PVAc80:PCL20-Hydrated</td>
<td>15.5</td>
<td>51.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PCL</td>
<td>-</td>
<td>58.8</td>
<td>40.0</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5-8. Storage modulus ($E'$) traces of (-) PVAc60:PCL40 film, (-) PVAc80:PCL20 film, and (-) PVAc film.
The loss tangent (tan(δ)) profiles for PVAc60:PCL40 and PVAc80:PCL20 showed double peaks indicative of both PVAc T_g and PCL T_m transitions.

**Figure 5-9.** Tan (δ) traces (-) PVAc60:PCL40 film, (-) PVAc80:PCL20 film and (-) PVAc film.
**Figure 5-10.** Wide angle Xray scattering (WAXS) patterns of (A) PVAc60:PCL40, (B) PVAc, (C) PCL. The Top and bottom rows represent films and fiber mats, respectively. Shown in (D) are the overlaid patterns of PVAc (B) and PCL (C), which is in good agreement with PVAc60:PCL40 results. The Xray wavelength ($\lambda$) is 1.5405 Å.
Figure 5-11. Intensity vs. 2θ profiles of (i) PVAc60:PCL40 film, (ii) PVAc60:PCL40 fibers, (iii) PVAc film, (iv) PVAc fibers, (v) PCL film and (vi) PCL fibers. The X-ray wavelength (λ) is 1.5405 Å.
Figure 5-12. Photographs of PVAc60:PCL40 composite showing (A) scratched and (B) thermally mended (75 °C for 10 min) sample. Scale bars denote 1 mm.
Figure 5-13. Schematic illustration of the crack opening method. The surface of the sample was first cleaved by a fresh razor blade. The sample was then bent on a cylindrical rod to propagate the crack. Shown in (B) and (C) are the photographs of the damaged and self-healed sample, respectively. Insets present the zoomed in stereo micrographs of the damaged and self-healed sample, respectively. All scale bars denote 1 mm.
Figure 5-14. (I) Optical microscope images of PVAc60:PCL40 composite showing: (A) notched sample, (B) crack propagated sample and (C) thermally mended sample (75 °C for 10 min). Sample was first notched using a custom-made dogbone cutting die (A). The damage was then controllably propagated by stretching the notched sample (B). The damaged sample was then “self-healed” by heating isothermally at 75 °C for 10 min. Scale bar denotes 1 mm. (II) Force vs displacement curves for the virgin, notched damaged and healed state of a PVAc60:PCL40 film. The healed sample shows a profile almost identical to the virgin sample indicating complete recovery of mechanical properties.
Figure 5-15. Force vs displacement curves for the virgin, damaged and healed state of a PVAc film.
Figure 5-16. (A) Stress vs. strain profiles for PVAc and PVAc80:PCL20 in both dry and hydrated state. Samples were stretched at 50 μm s⁻¹ at RT. Both composites showed stiff characteristics with low strain to failure and high modulus at RT. Upon hydration though, they become elastomeric with low modulus and high strain to failure as PVAc plasticizes. (B) Photograph of a hydrated PVAc80:PCL20 dogbone sample pre and post stretching to 500 % on Linkam. Hydrated samples were immersed in water for at least 24 prior to the experiment. Sample was kept hydrated during the experiment by constantly pipetting water onto it.
Figure 5-17. Dual shape memory demonstration of PVAc80:PCL20 composite showing (A) permanent shape at RT, (B) a temporary spiral shape, which was deformed at 80 °C and fixed by quenching at -17 °C and (D) the recovered shape. Scale bar represents 1 cm.
Figure 5-18. Triple Shape memory demonstration of hydrated PVAc80:PCL20 composite showing (A) the permanent shape at RT, (B) temporary shape 1, a curled “C” shape, which was deformed in an 80 °C water bath and fixed by immersing in ice/water bath, (C) temporary shape 2, a rolled shape which was deformed in a water bath at RT and fixed by immersing in ice/water bath, (D) recovered temporary shape 1, obtained by submerging in a water bath at RT for 10 min and (E) recovered permanent shape obtained by heating at 80 °C in water. All scale bars represent 1 cm.
Scheme 5-2. Schematic illustration of gradient component distribution of a binary composite prepared by dual electrospinning. During dual-electrospinning process, the flow rate of polymer (A) is dialed up whereas the flow rate of polymer (B) is constantly dialed down. The resulting article is a functionally graded polymer with linearly gradient composition throughout its thickness and thus gradient properties.
Chapter 6: Development of Novel Nano-Rubber Composites Based with Organically Functionalized Layered Double Hydroxides (LDHs)

6.1 Synopsis

Pneumatic tires are composite structures inflated with pressurized gas to provide weight support, shock absorbance and traction transmission for an automotive. One of the key factors in tires performance is to hold inflation pressure for an extensive period of time which leads to lower gas consumption and enhanced safety standards. Therefore, there has been extensive research in the tire industry to provide materials with enhanced barrier properties.

Layered double hydroxides are layered crystalline materials with ionic interlayer species that have tremendous potential as fillers in polymers to improve the mechanical properties\(^1\) and lower gas permeability\(^2\). The novelty of LDHs with respect to other materials includes a great flexibility in choosing organic modifiers such as carboxylates, sulfonates, phosphates, among others. The resulting polymer/LDH composites have unique properties such as enhanced barrier properties. However, currently available organically functionalized LDHs are both expensive and poorly designed for tires innerliners. To approach this problem, an enzyme mediated process using renewable plant oil, developed by our collaborator, Flow Polymers, is employed anticipating to have several advantages over current methods including lower cost and higher performance. The objective of this chapter is to characterize microstructure of the LDHs followed by fabrication of nano-composites containing polymers (including polycyclooctane (PCO) and Bromobutyl)/LDHs to reveal the effect of LDHs on mechanical and barrier properties of the polymers.
6.2 Introduction of Layered Double Hydroxides (LDHs)

Layered double hydroxides (LDHs) are inorganic materials that are composed of stacked, positively charged layers with charge-balancing interlayer anions (Scheme 6-1). This structure resembles that of the more usual, layered silicate-based cationic clays such as Brucite (Mg(OH)$_2$) in which some of the divalent cations have been replaced with positively charged sheets. Regular cationic clays contain negatively charged layers whereas LDHs contain positively charged layers. As such, LDHs are commonly referred to as anionic clays.

LDHs can be represented by the general formula [M$^{2+}$,M$^{3+}$(OH)$_2$]$A^{n-} \cdot m$H$_2$O where M$^{2+}$ and M$^{3+}$ are divalent and trivalent cations, respectively, and most commonly M$^{2+}$ = Mg$^{2+}$, Zn$^{2+}$, Fe$^{2+}$ and M$^{3+}$ = Al$^{3+}$, Fe$^{3+}$, Cr$^{3+}$; x is equal to the ratio M$^{3+}$/(M$^{2+}$ + M$^{3+}$) and $A^{n-}$ stands for an interlayer anion of valence $n$. Each LDH layer exhibits a crystal structure similar to brucite [Mg(OH)$_2$], in which the cation is coordinated octahedrally to 6 hydroxyl groups. Isomorphous replacement of some divalent cations (M$^{2+}$) with trivalent cations (M$^{3+}$) leads to an overall positive charge, and necessitates the presence of interlayer anions ($A^{n-}$) for charge-balancing. LDHs can be either naturally occurring or synthetic. In naturally occurred LDHs, anion is found to be primarily CO$_3^{2-}$ while synthetic LDHs can have a variety of different anions such as OH$^-$, Cl$^-$, NO$_3^{-}$, and SO$_4^{2-}$. Synthetic LDHs were first reported by Feitknecht but the first in-depth structural analysis of them were not conducted until the late 1960s. Flexibility in composition and structure allows LDHs to feature a wide range of properties making them attractive for several applications some of which are briefly discussed next. In addition to this compositional versatility, synthetic LDHs also offer better control over purity and particle size.
6.2.1 Applications of LDHs

6.2.1.1 LDHs as Heat Retention Additives

Expensive glass greenhouses can be substituted by plastic house commonly made with low cost low density polyethylene (LDPEs). However, such materials exhibit poor heat retention and low light transparency. Thermal retention of LDPEs can be improved by incorporating LDHs as nano-additives to them\textsuperscript{16}.

6.2.1.2 Catalytic Applications

Reichle et al. studied thermal decomposition products of several LDHs. Results showed that these products are typically very stable and can be applied for vapor-phase aldol condensation of acetone\textsuperscript{14}.

6.2.1.3 LDHs as Flame Retardants

There has been growing concern about safety hazards of flame retardants that contain halogen. Halogen produce highly toxic products during a fire or recycling\textsuperscript{17,18}. Several commercially available halogen-free flame retardants exist including aluminum hydroxide\textsuperscript{19} and magnesium hydroxide\textsuperscript{20}. Recent studies however show that due to their layered structures, LDHs can also be incorporated in polymers as effective flame retardants\textsuperscript{12,21}. Camino and colleagues have shown that inorganic hydroxides, like aluminum hydroxide and magnesium hydroxide in ethylene vinyl acetate copolymer, exhibited enhanced flame retardant and mass loss properties than either of aluminum hydroxide or magnesium hydroxide\textsuperscript{21}. The mass calorimetry results showed that ethylene-vinyl acetate (EVA) polymer filled with 50 wt. % of hydrotalcite has the slowest heat release rate and the lowest evolved gas temperature reported so far. Using x-ray results combined
with thermal analysis results, they speculated that the layered structure of hydrotalcite may play a role in the heat retardant and degradation mechanism\textsuperscript{21}. Zammarano et al. fabricated hydroxides/epoxy (LDHs/EP) nanocomposites from organo-modified LDHs, a diglycidyl ether of bisphenol A monomer (DGEBA) and amine curing agents. They obtained organo-modified LDHs by ionic exchange of a magnesium– aluminum carbonate LDH in an acid medium. They showed that use of precursors of strong mineral acids (i.e. sulfonate anions) as modifiers, catalyze charring reactions in LDH based nanocomposites during thermal degradation, enhancing the formation of a carbonaceous char and decreasing the release rate of combustible volatiles\textsuperscript{22}.

### 6.2.1.4 LDHs as Stabilizing Agents

Chlorine-containing materials such as poly(vinyl chloride) (PVC) can undergo autocatalytic dehydrochlorination at elevated temperatures or when exposed to UV radiation. Symptoms of such reaction include but are not limited to change in color or mechanical properties\textsuperscript{23,24}. This reaction is considered autocatalytic given that HCl, a by-product of it, is believed to sustain or even accelerate the degradation process. Chemical stabilizers that can irreversibly bond to HCl can slow down or stop this process. Heavy metals have been traditionally used for this purpose though alternatives are obligatory in view of the environmental concerns and toxicity of heavy metals.

Van der Ven and coworkers prepared Zn–Mg–Al-hydrotalcites as stabilizing agents for PVC\textsuperscript{25}. They showed that a linear relationship exists between HCl-capacity of LDHs with different counter-ions and their action as heat stabilizer in PVC. Supported by X-ray diffraction results, they concluded that this reaction takes place in a two-step fashion: First, the counterions between the LDH layers tend to react with the HCl gas, and secondly, the LDHs themselves react with the HCl with complete destruction of the LDH structure and formation of metal chlorides\textsuperscript{25}. 
6.2.1.5 LDHs in Medicine

Recently, application of LDHs as carriers for biomolecules has attracted tremendous attention\(^3\). Due to their stacked, layered structure, LDHs can be used as hosts for drugs\(^{26,27}\), genes, nucleosides including DNA\(^{28,29}\), peptides\(^{30}\) and ATP\(^{31,32}\). Choy showed that biomolecules could be intercalated into LDH via ion-exchange reaction to construct bioinorganic nanohybrids, which can be used as drug delivery careers. They showed that LDH-As-myc antisense compound can suppress the cancer cell more than As-myc antisense alone and consequently, LDH can protect and deliver the intercalated oligonucleotide, and that interlayer As-myc can be effectively released from the hydroxide layer of LDH into cell fluids under physiological conditions. Authors then claimed that LDHs can act as a new inorganic carrier in gene therapy division\(^{28}\). LDHs can also be applied for cancer imaging and therapy\(^{33}\). Flesken-Nikitin and colleagues incorporated potassium salt of Lucifer Yellow fluorescence dye into positively charged magnesium-aluminum (Mg/Al) LDHs. Upon ion exchange, the fluorescent dye was successfully incorporated in between the layers as nano-sized galleries. The toxicity of the LDHs were first evaluated by subjecting mice to subcutaneous, intraperitoneal, and intravenous injections of these nanoparticles at three doses. There was no fatality in all cases except for the highest does in which only one out of 12 lethality was reported. Besides, LDH-Lucifer Yellow were injected into the ovarian bursa and successfully visualized by multiphoton microscopy within the ovarian surface of epithelial cells demonstrating the potential of such materials for intravital imaging\(^{34}\).
6.2.1.6 LDHs as Barrier Enhancement Agents in Tire Innerliners

Several plastic and rubber articles including tires, balloons and packaging materials are required to exhibit good barrier properties. This is specifically essential for the case of tires because of 3 primary reasons:

1. Fuel economy: A recent study by Department of Transpiration (DoT) showed that “Out of the 11,000 vehicles inspected at randomly selected gas stations throughout the US, only 30% of surveyed drivers check the pressure in their tires at least once a month and 7% do not check the pressure at all”\(^{35}\). This is particularly important considering that underinflated tires are shown to have direct effect in increasing fuel consumption. Studies have shown that fuel consumption increases when tires are not appropriately inflated.\(^{36,37}\) Therefore, there is high demand for tires that can hold the pressure for a prolonged period of time.

2. Safety: Underinflated tires have shorter tread life, less lateral traction and consequently longer stopping distances\(^{38}\). It is stated by National Highway Traffic Safety Administration (NHTSA) that “Operating a vehicle with substantially under-inflated tires can result in a premature tire failure, such as instances of tread separation and blowouts, with the potential for a loss of control of the vehicle.”\(^{39}\).

3. Lower Manufacturing costs: Tire and automotive manufacturers, like any other for-profit business entities, are always motivated to lower the manufacturing cost for more competitive products and higher profit margins. Using materials with enhanced barrier properties lead to using less materials and inevitably lower cost. Such lower material consumption provides more profit for tire manufacturers, lower amount of waste and certainly a competitive advantage.
Given the above factors, there is a significant interest for technologies that enhance the barrier properties of tires. In this chapter, we explore characterization of organic based LDHs as high performance additives that are formulated into tire innerliner compounds to enhance their mechanical and barrier properties. It is important to note that the LDHs were synthesized in Flow Polymers Inc. and provided to us. Therefore, the synthesis of LDHs remains Flow Polymers proprietary and details of such reaction process is not discussed in this dissertation.

6.3 Experimental Section

6.3.1 Materials

The following LDHs were supplied to us from Flow Polymers Inc.:

1. **Perkalite LD** is an inorganic Mg/Al LDH with inter-layer anions being predominantly OH\(^-\). This is a commercial product of AkzoNobel.

2. **Perkalite F100** is an Mg/Al LDH functionalized with hydrogenated fatty acid, also a commercial product from AkzoNobel.

3. **Perkalite A100** is an Mg/Al LDH functionalized with rosin, also a commercial product from AkzoNobel.

4. **LDHAcetate** is an acetate functionalized LDH prepared by adding acetic acid to Perkalite LD (LDHOH dispersed in water) until pH reaches 8.

5. **LDHRicinoleate** is Ricinoleate functionalized LDH prepared by anion exchanging LDHacetate with potassium Ricinoleate at 60 °C for 4 h.

6. **LDHSB** is LDHOH functionalized with soybean (SB) (mixed fatty acids from soybean oil, primarily oleic (20-30%) and linoleic (50-60%) acids). This was prepared from directly reacting LDHOH with SB.
7. **Pural MG70** is a LDHCO$_3$ from Sasol.

Note that only LDHRicinoleate and LDHSB are organically functionalized and are formulated into a polymeric guest to enhance its mechanical/barrier properties. All other LDHs were only characterized thermally and morphologically for the sake of comparison with organically functionalized LDHs.

### 6.3.2 Preparation of LDHs

The preparation of LDHs developed in Flow Polymers is provided in the US patent (US20130005871 A1):

“The process for preparing organically functionalized layered double hydroxide in accordance with this invention utilizes an inorganic layered double hydroxide, a natural triglyceride oil, and a lipase enzyme which are normally dispersed in an aqueous medium. The inorganic layered double hydroxide utilized as a starting material in the process of this invention will normally be substantially free of organic constituents and is typically void of organic constituents. In this process the natural triglyceride oil is hydrolyzed enzymatically by the lipase to yield long-chain fatty acids and glycerol. Both of these hydrolysis products then participate in the anion exchange process with the inorganic layered double hydroxide. In this process glycerol serves to swell the layered double hydroxide and increase its interlayer spacing. The long-chain fatty acids then undergo an anion exchange with the layered double hydroxide to yield organically functionalized layered double hydroxide bearing alkyl chains which may contain unsaturated carbon-carbon double bonds. The swelling caused by the glycerol allows for the anion exchange to occur under mild conditions and is accomplish in a relatively short reaction time. The glycerol can then be easily washed away when the anion exchange is completed.”
6.3.3 Preparation of PCO-LDH composites by Extrusion

Polycyclooctene (PCO) was chosen as a cheaper readily available substitute to tire rubber due to its similar elastomeric properties and our prior experience with the polymer. PCO and LDH (either LDHRicinoleate or LDHSB50) were dried in vacuum oven at RT several days prior to processing. Binary blends of PCO and LDH (or LDH-Promix) were prepared by feeding the appropriate amount (LDH weight % in the composite was either 10 or 50 %) to a recycling, co-rotating twin-screw mini-extruder (DACA Instruments), and subsequently extruded at 160 °F (zone 1), 175 °F (zone 2), 185 °F (zone 3) and 185 °F (zone 4) as shown in Figure 6-1. The extruded composites were molded into discs or strands and then hot pressed at 1.5 mTons and 100 °C to from films (Figure 6-1(C)). The films were then used for microstructure characterization by Xray or cut to a dogbone shape (ASTM D63 Type IV, 1/4 scale) for mechanical testing.

6.3.4 Addition of Promix® to the Composite

To improve dispersion of LDH in the polymer during the extrusion process, LDH was premixed with Promix® (dubbed Promix hereafter). Promix exists as a brittle solid (in an easily handled pellet form) at room temperature (RT) and softens to become a viscous liquid as the temperature increases. Experimentally, 200 g of Promix was first heated to 232 °C (450 °F) and 100 g of pre-grounded LDH was quickly added. For extrusion, 45 g of dried PCO (in vacuum oven) and 5 g LDH-Promix mixture (weight ratio: 2:1) were premixed with each other and then extruded. Temperature of 4 different zones of extruder were 160, 170, 175, and 180 °F, respectively. As the fibers were coming out of extruder and before cooling down, they were rolled up to form a disk-shape film and then hot pressed at 140 °C and 1.5 metric Tons for about 5 min. The film was then quenched to RT.
6.3.5 Preparation of PCO-LDH Composites by Solvent Mixing

PCO and LDHRicinoleate were first separately dissolved in excessive amount of THF and stirred for 72 h at RT until completely dissolved following a method developed by Kumar and colleagues\textsuperscript{43,44}. Two solutions were then combined and stirred for another 24 h. The solution was then solvent casted and dried at RT for 24 h followed by vacuum oven at RT for 24 h and finally 50 °C for 8 h. Schematic illustration of the solvent mixing process is provided in Scheme 6-2.

6.3.6 Blending Tire rubber (Bromobutyl) with LDHs

Modern pneumatic tires feature a tubeless design in which the tire is tightly fixed to the metal rim. The innerliner is the innermost layer of the tire and is typically made from halobutyl (primarily Bromobutyl) rubber mixed with conventional fillers such as carbon black as illustrated by Scheme 6-3. Bromobutyl in innerliner is the primary component responsible for the retention of internal air pressure, characterized as the tire inflation pressure retention (IPR) loss rate\textsuperscript{45,46}. Synthesized organic based LDHs (LDHSB) were incorporated into Bromobutyl to improve barrier properties of Bromobutyl. Note that such composites containing Bromobutyl, Promix and LDHs were prepared and provided to us by Flow Polymers following this recipe: Bromobutyl, LDHSB and Promix were mixed in a Brabender Plasti-Corder\textsuperscript{®} internal mixer at 80 °C and 60 rpm for 5 min to fabricate Bromobutyl-LDH (10 Phr, with no Promix) and Bromobutyl-LDH-Promix (10 Phr, LDHSB:Promix weight ratio: 2:1) Composites. Note that 2 different functionalized LDHs, LDHSB50 and LDHSB250 were used in the composites to investigate the effect of functionalization on compatibility and exfoliation of LDH when mixed with Bromobutyl. Details of LDH functionalization is reported in the next section 6.3.7. Phr stands for “parts per hundred rubber”.

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6.3.7 Functionalization of LDHs

TGA results showed that the mass remaining for LDHSB synthesized by 250 g of plant oil was about 20 % meaning that 80 % of the material is organic (For details, see Results and Discussion). Such functionalization can be detrimental to the material properties, in particular barrier properties since the benefit from the LDH is negatively compensated by the highly permeable fatty acid molecules. In other words, initial LDH was over functionalized in the preparation process of organic based LDHs. To overcome this issue, different levels of functionalization were achieved by varying the amount of plant oil (50, 100 and 250 g) to synthesize LDHDBs with different functionalities. The LDHSB levels were 50 wt. %, 100 wt. % and 250 wt. % of the LDH-OH which are referred to as LDHSB50, LDHSB100 and LDHSB250, hereafter.

6.3.8 Microstructure Characterization of the LDHs and Their Nano-Structure in Polymeric Composites

X-ray diffraction (XRD) was conducted to study structural changes of LDHs when mixed with polymeric hosts\cite{5,12,27}. Schematic illustration of polymer-LDH composites morphologies showing (A) separated (microstructure), (B) intercalated (nanostructure) and (C) exfoliated nanostructure is provided in Scheme 6-4. When phase separated, LDH has low affinity to the polymer and LDH layers remains tightly bound to each other in the composite. As a result, the intensity and 2θ (basal spacing) values of LDH in the composite remain almost identical to that of pure LDH. When intercalated, LDH retains its layered structure but basal spacing increases and as a result, 2θ values shift to the left in XRD patterns. If the LDH is highly compatible with the polymer, the layers would fully exfoliate and completely lose their stacking order. In that case, the basal diffraction peaks would disappear in the XRD profile. For our application, an exfoliated or at least intercalated
morphology is desired given that the interfacial area and consequently load transfer and barrier properties are maximized in both cases\textsuperscript{13}.

To study exfoliation of LDHs in the polymeric hosts, wide-angle X-ray scattering (WAXS) was conducted using a Rigaku S-MAX3000 (Woodlands, TX) instrument in transmission mode. A FujiFilm FLA7000 reader were used to collect the scattered X-ray patterns. A Rigaku generator (MicroMax-002+) was employed to produce a Cu K\(\alpha\) radiation with a wavelength of 1.5405 Å. An accelerating voltage of 45 kV and a current of 0.88 mA were applied. The distance between sample and image plate was fixed at 122.7 mm for wide-angle X-ray scattering collection and exposure time was 30 min unless otherwise stated. The resulting scattering angular was \(2\theta < 40^\circ\). The patterns were analyzed using the SAXSgui software without background subtraction, benefiting from the fact that the whole X-ray system was run under high vacuum.

6.3.9 Thermomechanical Characterization

Thermal stability of LDHs, dependent of their inorganic components and charge balance, is a key factor for our prospective application\textsuperscript{47}. Thermal stability of the LDH samples with different functionalities and organic content was studied by thermogravimetric analysis (TGA) using a TA Q500 TGA instrument under a constant nitrogen purge. For all samples, a small amount of material ranging from 10–20 mg was loaded on the TGA pan and heated at a fixed rate of 10 \(\degree\)C min\(^{-1}\) to 600 \(\degree\)C while recording the sample mass as a function of temperature.

Thermal properties of the polymer-LDH composites, particularly the effect of LDHs on crystallinity and transition temperature, were characterized using Differential Scanning Calorimetry (DSC). DSC experiments were conducted using a Q200 (TA Instrument) equipped with a refrigerated cooling system (RCS). Samples of mass 3–5 mg were encapsulated in a Tzero
aluminum pan. Each sample was then equilibrated at 80 °C, ramped to 120 °C, cooled back to 80 °C, and heated to 120 °C. All heating and cooling rates were 10 and 5 °C min⁻¹, respectively. Glass transition temperature (T_g) was determined as the middle point of the step transition of the DSC second heating runs.

Thermomechanical properties of the Bromobutyl-LDH-Promix composites were characterized using a Q800 Dynamic Mechanical Analyzer (DMA) (TA Instrument). Dogbone samples (ASTM D63 Type IV, scaled down by a factor of 4) with a typical thickness of 0.3-0.5 mm were loaded under tension and oscillatory deformation with an amplitude of 10 μm, a frequency of 1 Hz and a “force track” (ratio of static to dynamic force) of 108 %. To determine transition temperatures and rubbery plateaus of the film, the samples were equilibrated and held isothermally at -40 °C for 10 min, then heated to 80 °C at 2 °C min⁻¹. Glass transition temperature, glassy modulus and rubbery modulus were determined from onset of the Storage Modulus drop, storage modulus at -90 °C and storage modulus at 50 °C in DMA, respectively.

6.3.10 Mechanical Characterization

Mechanical properties of the polymer-LDH composites were further investigated by tensile testing to explore the effect of LDH exfoliation on mechanical properties of the polymers. Average Young Modulus and Ultimate Stress values were estimated from the slope of linear portion of stress-strain curve and stress before sample failure, respectively in Linkam (n=3). Photographs of the Linkam instrument and a typical dogbone sample are provided in Figure 6-2.
6.4 Results and Discussions

6.4.1 Thermal Stability of LDHs

Thermal stability of LDHs are commonly indicative of their inorganic components. LDHs featuring higher weight fraction of LDHs have larger remaining weight fraction at elevated temperature given that metals (Al, Mg, …) do not degrade at or below 800 °C\textsuperscript{47-49}. Commercially available LDHs such as Perkalite-LD (from AkzoNobel) or Pural MG70 (from Sasol) normally are substantially free of organic constituents. Therefore, these materials exhibit higher weight % remaining at 800 °C as shown in Figure 6-3. The LDHs prepared by the enzymatic process such as LDHSB however show much lower weight fraction compared to their inorganic counterparts. Both long-chain fatty acids and glycerol (products of triglyceride enzymatically hydrolyzed by the lipase) participate in the anion exchange process with the inorganic layered double hydroxide increasing the organic content of such materials.

6.4.2 Morphology of LDHs

Synthetics LDHs significantly vary in terms of their macroscopic and mechanical appearance depending on the preparation method and their organic/inorganic constitutes. Shown in Figure 6-4 are the SEM micrographs of LDHs listed in Section 6.3.1. Typically, commercially available LDHs that are free of organic constitutes such as Perkalite FD or Perkalite F100 and appear as fine white powders (Figure 6-4(A,B)). Morphology of organically functionalized LDHs though depends on their functionalization level. LDHSB250 for example is macroscopically yellow and comes in big chunks as synthesized (Figure 6-4(F)). Less functionalized LDHSB50 though appears as light yellow fine powders. Such mechanical appearance was taken into consideration and LDHs were grinded if necessary prior to extrusion.
6.4.3 PCO-LDH Composites Prepared by Extrusion

Extrusion is commonly used to incorporate additives into polymers. PCO-LDH composites containing 10 and 50 % LDHRicinoleate as additives were prepared by extrusion. Note that LDHRicinoleate was recommended by our collaborators in Flow Polymers Inc. as the candidate to be incorporated in PCO. Thermograms of these composites are provided in Figure 6-5. The actual weight fraction of the LDHRicinoleate in the final extruded film was calculated from the following equation based on TGA results:

\[
wt_{\text{actual},\%} = \frac{wt_{\text{TGA},\%}}{wt_{\text{TGA-LDHRicinoleate},\%}}
\]  

(6-1)

where \( wt_{\text{actual},\%} \), \( wt_{\text{TGA},\%} \) and \( wt_{\text{TGA-LDHRicinoleate},\%} \) stand for the actual weight fraction of LDHRicinoleate in the composite, the final weight fraction of the composite in TGA at 800 °C and the final weight fraction of neat LDHRicinoleate (10 or 50 %), respectively. Results showed that actual weight fractions of LDH in the PCO film were slightly lower but close to their initial weight fraction (41.1 and 5.3 % for the samples with initial weight fraction of 10 and 50 %).

The microstructure properties of such composites were also studied by WAXS technique. Ideally, the LDH and polymer have high affinity to each other resulting complete exfoliation or at least intercalation of the LDH in the polymer. 2D WAXS patterns and normalized WAXS profiles of PCO, PCO-LDH (10 %) and PCO-LDH (50 %) composites are provided in Figure 6-6 and Figure 6-7, respectively. LDHRicinoleate retained its sharp rings corresponding to its layered structure in both composites indicating that LDHRicinoleate was not exfoliated. Not only did LDHRicinoleate retained its layered structure, but also the associated basal spacing and as result, \( 2\theta \) values were also identical in XRD patterns (Figure 6-7(B)). These results suggest that LDH has low affinity
to the polymer and its crystalline layers remains tightly bound to each other and phase separated from the polymer in the composite.

The phase separation of LDH and PCO was even macroscopically evident for the PCO-LDH (50 %) case. Shown in Figure 6-8 are the stereo microscope micrographs of a PCO-LDH-Ricinoleate (50 %) sample during tensile testing by Linkam. As highlighted by dashed circles, when phase separated, LDH-Ricinoleate is very brittle, cannot hold any stress and acted as defects in the film within which the crack was initiated and propagated. These results indicate, that not mixed with the host polymer, the LDH can indeed compromise the overall mechanical properties.

6.4.4 Premixing LDH and Promix

Previous results ascertained that dispersion of LDH in polymer using extrusion method was not perfectly homogeneous and intercalation of LDH is also partial. To overcome this issue, Promix, a main product of Flow Polymers Inc. can be premixed with LDH to disrupt its layered structure. Promix, a proprietary blend of different hydrocarbon resins that functions as a homogenizing agent, improves the compatibility between Bromobutyl and natural rubber and is commonly used for dispersion aid for most synthetic and natural elastomers\textsuperscript{42,50}. X-ray diffraction patterns expectedly showed much improved exfoliation of LDH-Ricinoleate in PCO, attributed to the presence of Promix (Figure 6-9). Besides, macroscopically the extruded PCO-LDH-Ricinoleate-Promix (10 %) film appeared uniformly dispersed unlike PCO-LDH-Ricinoleate (50 %) (See Figure 6-8). To make sure that LDH-Ricinoleate was homogenously mixed with PCO and Promix, TGA was conducted on 5 randomly selected regions of an extruded PCO-LDH-Ricinoleate-Promix (10 %) composites. Results showed that all samples picked from all regions displayed almost
identical degradation profile with about the same residual weight remaining at 800 °C as provided in Figure 6-10 signifying a homogenous blend.

Furthermore, to study mechanical properties of sample polymer (PCO) and PCO-Promix-LDH Ricinoleate composite, tensile test was performed using Linkam. All samples were stretched to failure at a displacement rate of 200 μm s⁻¹ at 25 °C. As shown in Figure 6-11, mechanical properties of PCO and composite are not significantly different from each other. PCO showed behaviour typical of polyolefin (semicrystalline, Tg < RT) with an average Modulus of 96.9 MPa and strain to failure of >300 %. Both Young Modulus (62.2 MPa) and strain to failure (<250 %) of the PCO-LDH Ricinoleate (10 %) was lower than neat PCO due to heterogeneous dispersion of LDH within PCO in the extrusion process indicating low affinity of the LDH to polymer as discussed earlier. This is in agreement with WAXS results where LDH Ricinoleate layers remained tightly bound to each other in the composite and consequently, intensity and 2θ (basal spacing) values of LDH Ricinoleate in the composite remained almost identical to that of pure LDH Ricinoleate. Better dispersion of LDH Ricinoleate was achieved in the presence of Promix resulting in improvement in both average Young Modulus and strain to failure results in the PCO-LDH Ricinoleate-Promix (10 %) compared to PCO-LDH Ricinoleate composite as evidenced in Figure 6-11(C). Though, no significant difference was observed between PCO-LDH Ricinoleate-Promix (10 %) and neat PCO. Such results suggest that only in the presence of Promix, LDH is exfoliated in the polymer contributing to improved mechanical properties.

6.4.5 PCO-LDH Composites Prepared by Solvent Mixing

Seeking to develop a relatively simple method to develop the PCO-LDH Ricinoleate composites, a solvent mixing method was employed where both polymer and LDH were dissolved in a co-
solvent and then solvent cast. 2D WAXS patterns and normalized WAXS profiles of PCO, LDHRicinoleate and PCO-LDHRicinoleate (10 %) composite prepared by solvent mixing method are provided in Figure 6-12 and Figure 6-13, respectively. Corresponding X-ray diffraction (XRD) profile of LDHRicinoleate in PCO-LDHRicinoleate (10 %) stayed almost identical to the LDH before blending indicating low affinity of the LDH to mixing with the polymer. In other words, d-spacing and 2θ values of WAXS profile peaks remain almost intact in PCO-LDHRicinoleate composite compared to neat LDHRicinoleate.

6.4.6 Blending Tire rubber (Bromobutyl) with LDHs

6.4.6.1 Bromobutyl-LDHSB250 Composite

Bromobutyl in innerliner is the primary component responsible for the retention of internal air pressure, characterized as the tire inflation pressure retention (IPR) loss rate\textsuperscript{45,46}. Seeking to investigate on how LDHs affect the mechanical and microstructural properties of Bromobutyl, we opted to incorporate LDHs in Bromobutyl following a method reported in Section 6.3.6. Note that LDHSB was chosen as the candidate given its anticipated compatibility with Bromobutyl and low synthesis cost.

The synthesized LDHs were incorporated in tire rubber (primarily consisting of Bromobutyl rubber) to improve their mechanical and barrier properties. Therefore, it is of utmost significance that Bromobutyl and LDH exhibit strong affinity resulting in complete exfoliation of the LDH. 2D WAXS patterns and normalized WAXS profiles of neat Bromobutyl and Bromobutyl with 3 different Phrs (5, 10 and 15) of LDHSB250 composites are provided in Figure 6-14 and Figure 6-15, respectively. LDSB250 basal spacing and as result, 2θ values were identical in XRD patterns suggesting that LDH has low affinity to the polymer, LDH layers remains tightly bound to each
other and phase separated from the polymer in the composite. Therefore, LDHSB250 should be premixed with Promix to assure uniform distribution of LDH in polymer.

### 6.4.6.2 Bromobutyl-LDHSB50-Promix Composite

Lower functionalized LDH (LDHSB50, synthesized from 50 g of soybean oil) with lower fatty acid molecules was used given that such molecules are highly permeable and can lower the barrier properties of LDH in the composite. Besides, LDHSB50 was premixed with Promix to assure complete exfoliation. TGA thermograms of neat Bromobutyl, LDHSB50, Bromobutyl-Promix (10 Phr), Bromobutyl-LDHSB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1), LDHSB50-Promix (15 Phr, LDHSB50:Promix weight ratio: 2:1) neat Promix and neat Bromobutyl is provided in Figure 6-16. As anticipated, only the samples containing LDHSB50 or Promix had residual weight remaining after heating to 800 °C given their inorganic constituents. Specifically, LDHSB50, Promix, Bromobutyl- LDSHB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1) and Bromobutyl-LDHSB50-Promix (15 Phr, LDHSB50:Promix weight ratio: 2:1) had about 40, 21, 25 and % residual mass at 800 °C. In what follows, the microstructure and thermomechanical characterization of the composites is discussed. In the presence of Promix, WAXS results indicate that LDHSB50 has lost its layered structure in the rubber as shown in Figure 6-17 and Figure 6-18, respectively. Note that this is after the premixing step and LDHSB50 was exfoliated before incorporating into Bromobutyl. The same trend was observed for the Bromobutyl-LDHSB50-Promix composites as shown in Figure 6-19 and Figure 6-20. These results clearly emphasize the importance of premixing LDHs with Promix to guarantee exfoliation. It is essential to consider that mixing Promix and LDH potentially can have several advantages including simplifying the processing challenges. Given that Promix is already a key component of
commercial tires innerliners, the Promix-LDH blend in this context is contemplated as a potential improvement compared to neat Promix.

DSC experiments were also conducted to determine the transition temperature of the composites as they are related to the mechanical properties, as we now describe. All samples (neat Bromobutyl, Promix, Bromobutyl-Promix (10 Phr) and Bromobutyl-LDHSB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1)) showed one glass transition temperature at -63 °C corresponding to Bromobutyl transition temperature (Figure 6-21). From these results, we concluded that DSC was not sensitive enough to determine any subtle changes in thermomechanical properties of the composites caused by incorporation of LDHs whereas dynamic mechanical analysis has the capability to detect any changes which is reported below.

Thermomechanical properties of the composites were also investigated to understand the effect of LDHSB50 and Promix on the viscoelastic behaviour of Bromobutyl rubber. It is established that a nanocomposite features a combination of properties that are unattainable in any of the single particles in the composite. Tensile Storage Modulus ($E'$) as a function of temperature is provided for the Bromobutyl-Promix (10 Phr) compositions is provided in Figure 6-22. The remaining composites (neat Bromobutyl and Bromobutyl-Promix-LDHSB50-(10 Phr) showed similar behaviour with a single glass transition temperature at ~ 63 °C, glassy modulus > 2 GPa and rubbery modulus < 1.0 MPa at -90 and 50 °C indicating elastomeric properties of the composites at ambient temperatures (Table 6-1). Glass transition temperature determined from onset of the Storage Modulus drop in DMA was in accordance with DSC results. The presence of Promix and LDHSB50 increased both glassy Modulus and rubbery Modulus of the composites compared to neat Bromobutyl, indicating improvement in mechanical properties. Note that the composition
containing LDHSB50 showed slightly higher standard deviation which may be due to the presence of LDH in the rubber.

As mentioned in the Introduction Section, LDH is known to be utilized for several application including mechanical enhancement\textsuperscript{1,51}. Tensile testing of the composites showed that Promix and LDHSB50 reinforced Bromobutyl resulted in improvement of both Ultimate Stress (sample stress before failure) and strain to failure (Figure 6-23). Based upon WAXS and mechanical characterization results, we conclude that not only premixed LDHSB50-Promix blend was uniformly dispersed and exfoliated in Bromobutyl, but also it enhanced the mechanical properties of Bromobutyl. Again, it is absolutely essential to premix LDHSB50 with Promix to assure disruption of LDHSB50 crystalline structure before incorporation in a polymeric host. As for barrier properties, we envision that the combination of LDH and Promix will significantly decrease the permeability of Bromobutyl against air, though this was beyond the scope of this dissertation.

6.4.7 Functionality of LDHs

The objective of the enzymatic process was to synthesize organic based LDHs. The process of anion exchange in which inorganic materials are replaced by organic moieties is called “Functionalization”. Over-functionalization of LDHs in the preparation process of organic based LDHs can be detrimental to the material properties, in particular barrier properties, since the benefit from the LDH is negatively compensated by the highly permeable fatty acid molecules. Different levels of functionalization can be achieved by varying the amount of plant oil (50, 100 and 250 g) used to synthesize LDHSBs with different functionalities. The LDHs prepared by 50, 100 and 250 g of plant oil is referred to as LDHSB50, LDHSB100 and LDHSB250, respectively. As functionality was increased, the layered structure became more pronounced in as evidenced by
appearance of more intense rings in WAXS patterns as provided in Figure 6-24 and Figure 6-25). As evident in Figure 6-26, the organic content (estimated based on TGA results) can be controlled almost continuously by varying the usage levels of soybean oil, while the morphology, as characterized by the basal spacing, is less affected in the experimental range. In fact, there seems to be an inverse correlation between concentration of soybean oil used and final weight remaining of functionalized LDH (thus, degree of functionalization). LDHSB samples with various functionalization levels appear physically different too. LDHSB50 and LDHSB100, which have low levels of functionalization appear as brittle solids (similar to the inorganic LDHs), whereas the higher functionalization in LDHSB250, yielded much softer and more ductile, and cannot be ground into a powder without cryogenic conditions.

6.5 Conclusions

The polymer-LDH composites are known to feature unique properties such as enhanced barrier properties. Though currently available organically functionalized LDHs are poorly designed for tires/innerliners. To approach this issue, LDHs prepared by an enzymatic mediated method were characterized and incorporated in rubber tire innerliner (Bromobutyl). Results revealed that LDHs stacked structure was disrupted when premixed with Promix (a commercially available additive from Flow Polymers Inc.) leading to enhanced mechanical and potentially barrier properties of the host-polymers. Quantitative investigation as to whether LDH enhances the barriers properties of the host polymer remains subject of future work as explained below.

6.6 Future Work

The ultimate objective of this work was to reduce air permeability of the tire by incorporation of organic based LDHs in the tire innerliner (Bromobutyl). Therefore, air permeability of Bromobutyl
(main component of tire innerliner) in the presence of LDH-Promix mixture as high performance additives should be studied. Given that exfoliation of nano-clays (LDHs) in Bromobutyl is known to increase their barrier properties, we expect to observe higher barrier properties in the composites in which premixed LDH-Promix blend is incorporated\textsuperscript{2,52-54}.

6.7 References


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**Scheme 6-1.** Schematic illustration of multi-stack nano structure of LDHs. Adopted with permission from [David G. Evans, *Journal Chemical Communications*, 2006, 45, 485-496]. LDHs are composed of positively charged layers with interlayer anions. (Anion Clays) resembling brucite structure.
Figure 6-1. Photograph of a co-rotating twin-screw mini-extruder (DACA Instruments). Binary blends of PCO and LDH were prepared by feeding the pre mixed appropriate amount of PCO and LDH into extruder funnel and subsequently extruded at 160 °F (zone 1), 175 °F (zone 2), 185 °F (zone 3) and 185 °F (zone 4). The extruded composites were molded into discs or strands and then hot pressed at 1.5 mTons and 100 °C to form films. Shown in (B) and (C) are photograph of an extruded and hot pressed film, respectively. Scale bars represent 1 cm.
**Scheme 6-2.** Schematic illustration of preparing PCO-LDH Ricinoleate composite using solvent mixing method. First, (A) PCO and (B) LDH Ricinoleate were separately dissolved in excessive amount of THF and stirred for 72 h at RT until completely dissolved. (C) Two solutions were then combined and stirred for another 24 h. (D) The solution was then solvent casted and dried at RT for 24 h followed by vacuum oven at RT for 24 h and finally 50 °C for 8 h.
Scheme 6-3. Schematic structure of a modern tubeless tire innerliner whose main responsibility is to withstand air pressure is the innermost layer of the tire. It is a thin layer of rubber laminated to the inside of a pneumatic tire that serves as a barrier layer to the pressurized internal gas. Scheme was taken from http://www.changemytyre.com/.
Scheme 6-4. Schematic illustration of polymer-LDH composites morphologies showing (A) separated (microstructure), (B) intercalated (nanostructure) and (C) exfoliated nanostructure. When phase separated, LDH has low affinity to the polymer and LDH layers remains tightly bound to each other in the composite. As a result, the intensity and $2\theta$ (basal spacing) values of LDH in the composite remain almost identical to that of pure LDH. When intercalated, LDH retains its layered structure but basal spacing increases and as result, $2\theta$ values shift to the left in XRD patterns. If the LDH is highly compatible with the polymer, the layers would fully exfoliate and completely lose their stacking order. The basal diffraction peaks would disappear in the XRD profile. For our application, an exfoliated or at least intercalated morphology is desired given that the interfacial area and consequently load transfer and barrier properties are maximized in both cases.
Figure 6-2. Photographs of (A) a TST350 Linkam Tensile Stress Testing Stage (Linkam Scientific Instruments, Ltd.) with a 20 N load cell and (B) a dogbone sample (ASTM D63-Type IV, scaled down by a factor of 4). Scale bar represents 5 mm.
The remaining weight in all LDHs correspond to the inorganic portion of the material. Commercially available LDHs such as Perkalite-LD (from AkzoNobel) or normally are substantially free of organic constituents. Therefore, these materials exhibit higher weight % remaining at 800 °C. The LDHs prepared by the enzymatic process such as LDHSFBA however show much lower weight fraction compared to their inorganic counterparts.

Figure 6-3. Thermogram traces of (i) Perkalite LD, (ii) Pural MG70 (from Sasol), (iii) LDHRicinoleate, (iv) LDHAcetate, (v) Perkalite A100, (vi) Perkalite F100 and (vii) LDHSB250.
Figure 6-4. SEM micrographs of (A) Perkalite LD, an inorganic Mg/Al LDH with inter-layer anions being predominantly OH⁻ (a commercial product of AkzoNobel), (B) Perkalite F100, an Mg/Al LDH functionalized with *hydrogenated* fatty acid (a commercial product from AkzoNobel), (C) Perkalite A100, an Mg/Al LDH functionalized with rosin (a commercial product from AkzoNobel), (D) LDHAcetate, acetate functionalized LDH prepared by adding acetic acid to Perkalite LD (LDH-OH; dispersed in water) until pH reaches 8, (E) LDHRicinoleate, Ricinoleate functionalized LDH prepared by anion exchanging LDHAcetate with potassium Ricinoleate at 60 °C for 4 h, (F) LDHSB: LDH functionalized with soybean (SB) (mixed fatty acids from soybean oil, primarily oleic (20-30%) and linoleic (50-60%) acid) and (G) Pural MG70: a LDHCO₃ from Sasol with nominal Mg/Al of 70/30.
Figure 6-5. TGA profiles of (i) PCO, (ii) PCO-LDH Ricinoleate (10 %) and (iii) PCO-LDH Ricinoleate (50 %). The nominal and actual weight fractions of the LDH in the composite calculated from eqn. (6-1) are provided in the table. Results indicate that the actual weight fraction of the LDH is close but slightly lower than the nominal value.
Figure 6-6. 2D WAXS patterns of (A) PCO, (B), (C) extruded PCO-LDHRicinoleate (10 %) and (D) extruded PCO-LDHRicinoleate (50 LDHRicinoleate%). Sample to IP collector distance was 142.7 mm and exposure time was 30 min.
Figure 6-7. (A) Normalized WAXS profiles of (i) PCO, (ii) PCO-LDHricinoleate (10 %), (iii) PCO-LDHricinoleate (50 %) and (iv) LDHRicinoleate. Sample to IP collector distance was 142.7 mm and exposure time was 30 min. Corresponding X-ray diffraction (XRD) profiles of LDHRicinoleate in both PCO-LDHricinoleate (10 %) and PCO-LDHricinoleate (50 %) stayed almost identical to the LDH before blending indicating low affinity of the LDH to mixing with the polymer. Interestingly, the crystalline peaks corresponding to PCO phase substantially attenuated after mixing with LDH Ricinoleate. We postulate this is due to interrupted crystalline structure of PCO in the presence of LDH.

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<td>PCO-LDH(10%)</td>
<td>7.67</td>
<td>11.53</td>
</tr>
<tr>
<td>PCO-LDH (50%)</td>
<td>8.70</td>
<td>10.61</td>
</tr>
</tbody>
</table>
Figure 6-8. Stereo microscope micrographs of a PCO-LDHRicinoleate (50 %) during tensile testing by Linkam showing a dogbone sample (A) before stretching, (B) right before failure and (C) after failure. During extrusion, LDH was not uniformly dispersed in PCO and LDH regions were macroscopically visible in the film (highlighted by red circles). As a results, these regions did not hold stress, acted as defects within which the crack was initiated and propagated (shown by arrow). Scale bar denotes 1 mm.
Figure 6-9. 2D WAXS pattern and (B) WAXS profiles of extruded PCO-LDHRicinoleate-Promix (10 %, LDHRicinoleate: Promix weight ratio: 2:1) which shows complete exfoliation of LDH. The very sharp peak at low 2θ is due to Xray beam.
Figure 6-10. TGA results for five different regions of PCO- LDHRicinoleate-Promix (10 %, LDHRicinoleate: Promix weight ratio: 2:1) film. All 5 samples show almost identical degradation profile indicative of homogenous dispersion.
**Figure 6-11.** (I) Stress vs. strain profiles of Tensile tests of extruded (A) PCO, (B) PCO-LDH Ricinoleate and (C) PCO-LDH Ricinoleate-Promix (10 %, LDHRicinoleate: Promix weight ratio: 2:1) and (II) Average Young Modulus values estimated from the slope of linear portion of stress-strain curve for each sample (n=3). All samples were hot pressed and then cut to a dogbone shape prior to tensile testing. All the experiments were conducted at 25 °C. The samples were stretched at 200 µm s⁻¹. PCO showed elastomeric behaviour with an average Modulus of 96.9 MPa and strain to failure of >300 %. Both Young Modulus (62.2) and strain to failure (<250 %) of the PCO-LDH Ricinoleate was lower than neat PCO due to heterogeneous dispersion of LDH within PCO in the extrusion process indicating low affinity of the LDH to polymer. This is in agreement with WAXS results where LDH layers remained tightly bound to each other in the composite and consequently, intensity and 2θ (basal spacing) values of LDH in the composite remained almost identical to that of pure LDH. Better dispersion of LDH was achieved in the presence of Promix resulting improvement in both average Young Modulus and strain to failure results in the PCO-LDH Ricinoleate-Promix (10 %) composite given that Promix exfoliates and entirely disrupts the layered structure of LDH as evidenced in **Figure 6-9**.
Figure 6-12. WAXS patterns for (A) PCO, (B) LDHRicinoleate and (C) PCO-LDH composite prepared by solvent mixing method.
Figure 6-13. (A) Normalized WAXS profiles of (i) PCO, (ii) PCO-LDHricinoleate (10 %) prepared by solvent mixing method, (iii) LDHRicinoleate, (iv) zoomed in LDHRicinoleate and (B) d-spacing/2θ values of the WAXS profiles peaks of both LDHRicinoleate and PCO-LDHricinoleate (10 %) prepared by solvent mixing method. Sample to IP collector distance was 142.7 mm and exposure time was 30 min. Corresponding X-ray diffraction (XRD) profile of LDHRicinoleate in PCO-LDHricinoleate (10 %) stayed almost identical to the LDH before blending indicating low affinity of the LDH to mixing with the polymer. In other words, d-spacing and 2θ values of WAXS profile peaks remain almost intact in PCO-LDHricinoleate composite compared to neat LDHRicinoleate.
Figure 6-14. WAXS results for (A) neat Bromobutyl, (B) LDHSB250, (C) Bromobutyl-LDHSB250 (2.5 Phr), (D) Bromobutyl –LDHSB250 (5.0 Phr) and (E) Bromobutyl-LDHSB250 (10 Phr).
Figure 6-15. WAXS results for (i) Neat Bromobutyl, (ii) Bromobutyl-LDHSB250 (2.5 Phr), (iii) Bromobutyl-LDHSB250 (5.0 Phr), (iv) Bromobutyl-LDHSB250 (10 Phr) and (v) neat LDHSB250.
Figure 6-16. (A) TGA thermograms and (B) final residual weight remaining of (i) neat cured Bromobutyl, (ii) Bromobutyl-LDHSB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1), (iii) Bromobutyl-LDHSB50-Promix (15 Phr, LDHSB50:Promix weight ratio: 2:1), (iv) Promix, (v) LDHSB50 and (vi) Bromobutyl-Promix (10 Phr) (overlaps with (ii) and (iii)).
Figure 6-17. 2D WAXS patterns of (A) Neat Promix, (B) premixed LDHSB50-Promix (weight ratio: 2:1) and (C) LDHSB50. Sample to IP collector distance was 142.7 mm and exposure time was 30 min.
Figure 6-18. (A) Normalized WAXS profiles of (A) Neat Promix, (B) LDHSB50 and (C) premixed LDHSB50-Promix (weight ratio: 2:1). Sample to IP collector distance was 142.7 mm and exposure time was 30 min. Intensity (A.U.) axis is in log-scale to reduce data noise and amplify peaks. Clearly, LDHSB50 lost its layered structure when mixed with Promix indicating exfoliation of LDH by Promix.
Figure 6-19. 2D WAXS patterns of (A) neat Bromobutyl, (B) Bromobutyl-LDHSB50 (10 Phr, with no Promix) and (C) Bromobutyl-LDHSB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1). Sample to IP collector distance was 142.7 mm and exposure time was 30 min.
(II) Normalized WAXS profiles and (II) corresponding 2θ and d-spacing values of (A) neat Bromobutyl, (B) Bromobutyl-LDHSB50 (10 Phr) and (C) Bromobutyl-LDHSB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1). Sample to IP collector distance was 142.7 mm and exposure time was 30 min. When Bromobutyl was mixed with LDHSB50 the 2θ values shifted to lower values indicating partial intercalation. After adding Promix to the composite however, the basal spacing peaks disappeared indicating successful exfoliation (II).
Figure 6-21. (A) 1st and (B) 2nd DSC cycles of neat Bromobutyl, Promix, Bromobutyl-Promix (10 Phr) and Bromobutyl-LDH SB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1). All samples except for neat Promix showed single glass transition temperature at $\sim 63$ °C as highlighted by black vertical lines.
Figure 6-22. Tensile storage modulus (E’) traces of Bromobutyl-Promix (10 Phr) replicated 3 times to assure reproducibility. All composites (neat Bromobutyl, Bromobutyl-Promix (10 Phr) and Bromobutyl-LDHSB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1) showed a single glass transition temperature at ~ 63 °C, glassy modulus > 2 GPa and rubbery modulus < 1.0 MPa at -90 and 50 °C, respectively. Summary of thermomechanical properties of all the composites are provided in Table 6-1.
Table 6-1. Summarized thermomechanical properties of Neat Bromobutyl, Bromobutyl-Promix (10 Phr) and Bromobutyl-LDHSB50-Promix (10 Phr, LDHSB50:Promix weight ratio: 2:1). Glass transition temperature was determined from onset of the Storage Modulus drop in DMA. The presence of Promix and LDHSB50 increased both glassy Modulus and rubbery Modulus of the composites compared to Neat Bromobutyl.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
<th>$E_{\text{glassy state @ } 90^\circ\text{C}}$ (MPa)</th>
<th>$E_{\text{rubbery plateau at } 50^\circ\text{C}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Bromobutyl</td>
<td>-64.0±2.9</td>
<td>2380±72.1</td>
<td>0.41±0.04</td>
</tr>
<tr>
<td>Bromobutyl-Promix-(10 Phr)</td>
<td>-63.0±1.1</td>
<td>2750±98.8</td>
<td>0.64±0.1</td>
</tr>
<tr>
<td>Bromobutyl-Promix-LDHSB50-(10 Phr)</td>
<td>-63.1±3.1</td>
<td>3026±326.0</td>
<td>0.67±0.2</td>
</tr>
</tbody>
</table>
Figure 6.23. (I) Stress vs. strain profiles of Tensile tests of (A) Bromobutyl, (B) Bromobutyl-Promix (10 Phr) and (C) Bromobuytl-Promix-LDHSB50 (10 Phr, LDHSB50:Promix weight ratio: 2:1) and (II) average Ultimate Stress values estimated from for each sample (n=3). All samples were cut to a dogbone shape prior to tensile testing. All the experiments were conducted at 25 °C. The samples were stretched at 200 μm s⁻¹.

Incorporation of Promix and LDH yielded Better dispersion of LDH was achieved improvement in both average ultimate stress and strain to failure results. Average Young Modulus values are not reported given that all the samples showed highly elastomeric behaviour and stress-strain profiles did not exhibit any meaningful linear region.
Figure 6-24. 2D WAXS patterns for enzymatic LDHSB synthesized from (A) 50, (B) 100 and (C) 250 g of soybean oil.
Figure 6-25. Normalized WAXS results for enzymatic LDHSB synthesized from (A) 250 g, (B) (100) g, and (C) 50 g of soybean oil.
Figure 6-26. (A) TGA results for enzymatic LDHSB produced from (i) 50 g, (ii) 100 g and (iii) 250 g of soybean oil mixed with LDH-OH. (B) Results show that with increase in initial soybean oil used, more functionalization occurs and consequently less weight remaining at high temperatures due to degradation of functionalized moieties.
7.1 Synopsis

Research in the field of shape memory polymers has recently witnessed the introduction of increasing complexity of material response, including such phenomena as triple/multishape behaviour, temperature memory, and reversible actuation. Ordinarily, such complexity in physical behaviour is achieved through comparable complexity in material composition and synthesis. Seeking to achieve triple shape behaviour with a simple route to materials synthesis, we introduce here a method that utilizes polymerization induced phase separation (PIPS) to yield the requisite combination of microstructure and composition. Thus, two blends incorporating epoxy and poly(ε-caprolactone) were developed using commercially available reactants, one featuring a semicrystalline epoxy and the other featuring an amorphous epoxy. We show that both blends undergo PIPS during epoxy polymerization and crosslinking and that both blends exhibited distinct transition temperatures and three modulus-temperature plateaus needed for triple shape behaviour. Despite these similarities, their physical character at room temperature is vastly different: the semicrystalline epoxy material is elastomeric and the amorphous epoxy material is highly stiff. Characterization of the triple shape behaviour revealed an ability of both systems to fix two separate deformations independently, one by PCL crystallization and a second one by epoxy crystallization or vitrification, and recover both programmed shapes separately upon heating. Given the simplicity of fabrication, we envision application as multi-shape coatings, adhesives, and films.

7.2 Introduction

Shape memory polymers (SMPs) are a class of materials that feature dramatic shape changes in response to an external trigger.\textsuperscript{1-6} While one or more macroscopic “permanent shapes” can be memorized by the material through crosslinking, additional, temporary, shapes can be programmed by immobilization of the constituent network chains using crystallization, vitrification, or other means. Transformation between temporary and permanent shapes is triggered by application of an external stimulus, leading to mobilization of constituent network chains and recovery by entropic elasticity.\textsuperscript{3,4} SMPs have several advantages relative to other shape memory materials such as shape memory alloys (SMAs) including large deformation strain that can exceed 100\%, lower stiffness, cost, simple processing and potential biocompatibility and biodegradability.\textsuperscript{3} Typically, a shape memory (SM) cycle consists of three sequential steps: elastic deformation at elevated temperature, shape fixing by cooling, and recovery by heating.\textsuperscript{7} In the first stage, the material is deformed to a certain strain at a temperature higher than the SMP transition temperature. Subsequent cooling under constant stress microscopically freezes constituent polymer chains. Thus, an SMP maintains its deformed shape even after releasing the stress. To achieve shape recovery, the material is heated under stress-free or loaded condition which leads to polymer chain segments relaxation to their entropically favoured conformational state.\textsuperscript{4} To our knowledge, the first observation of SM effects in polymers was reported by L. B. Vernon in 1941.\textsuperscript{3} However, extensive research in the field of SMPs embarked on from the 1960s when covalently bonded SMPs were used as heat shrinkable tubing and films. Since then, due to their great potential of applications in several
fields such as actuators, temperature sensors, thermally reversible recording, SMPs have attracted a lot of attention.

Recently, activity in the SMP field has shifted focus to biomedical applications such as biodegradable sutures, actuators and smart stents.\textsuperscript{7,8} Direct heat remains the most extensively investigated stimuli for SM behaviour, though alternative triggering mechanisms including light,\textsuperscript{9,10} moisture,\textsuperscript{11,12} magnetic field,\textsuperscript{13,14} solvents,\textsuperscript{15} electrical current\textsuperscript{16,17} and pH\textsuperscript{18} have been reported. Two-way (reversible) SMPs have also been reported. For example, our group developed a two-way SMP by crosslinking a semi-crystalline polycyclooctene\textsuperscript{19} and this has been found to be quite general among other semicrystalline networks.\textsuperscript{20-22} Such systems exhibit crystallization-induced elongation on cooling and melting-induced contraction on heating, phenomena that enable construction of reversible actuators when biased with an applied mechanical load.\textsuperscript{23}

A limitation to conventional SMPs has been their restriction to two shapes: one temporary shape and one permanent shape. Addressing this limitation, “triple shape” SMPs – the subject of this study – were introduced.\textsuperscript{24} Unlike conventional dual-shape SMPs with one temporary and one permanent shape, triple-shape SMPs can have two temporary shapes and one permanent shape.\textsuperscript{25,26} Therefore, they can successively switch from temporary shape (A) to temporary shape (B) and eventually to permanent shape (C), all upon external stimulation. To achieve such properties, two distinct thermal transitions (e.g., glass transition and melting transition) should be built into the material to occur within the temperature range appropriate for an intended application.\textsuperscript{26} In light of this design consideration, SMPs are normally crosslinked networks with network chains featuring a desirable switching temperature near but above room temperature.
In contrast to dual shape SMPs that feature one switching temperature, triple shape memory polymers (TSMPs) feature two separate transitions that can be exploited to fix two temporary shapes somewhat independently. When such a material is deformed from its equilibrium shape, (C), and cooled below the higher transition temperature for one switching phase (but above the transition temperature of the other), the higher temperature phase is immobilized and one temporary shape is programmed: (B). Further deformation at this point, followed by cooling below the lower transition temperature of the second switching phase causes immobilization of that phase and programming of the second temporary shape: (A). Subsequent continuous heating leads to the shape changes: (A) \(\rightarrow\) (B) \(\rightarrow\) (C). It is interesting to note that in dynamic mechanical analysis (DMA), TSMPs exhibit three elastic modulus plateaus that decrease in a stepwise manner as temperature is increased. Each of these plateaus correspond to one specific shape in the SM cycle.\(^{26}\)

A number of different approaches yielding triple shape memory polymers have been reported. Bellin et. al. developed two polymer network structures.\(^{27}\) The first network contained poly(\(\varepsilon\)-caprolactone) (PCL) and poly(cyclohexyl methacrylate) (PCHMA) in which first transition is a melting (crystallizable PCL \(T_m=50\text{-}60 \, ^\circ C\)) and second transition is a glass transition (amorphous PCHMA \(T_g=140 \, ^\circ C\)). In the second system, PCL segments were grafted with poly(ethylene glycol) (PEG) as side chains having one dangling end and PCL segments connect two net points. In this network, both transitions are melting points (crystallizable PCL, \(T_m=50\text{-}60 \, ^\circ C\)) and (crystallizable PEG \(T_m=17\text{-}39 \, ^\circ C\)). They also found that for an AB polymer (PCL-poly(cyclohexyl methacrylate)(PCHMA)) triple-shape capability can be obtained by utilizing one-step dual shape programming, as long as the two populations of polymer chains were
covalently bonded to polymer network through chain ends.\textsuperscript{28} Deforming the sample above higher transition temperature ($T_H$) led to an associated deformation of the constituent network chains, while cooling it below the lower transition temperature ($T_L$) led to triple-shape behaviour. The same group has also reported triggering the triple-shape effect (TSE) using an alternating current (AC) magnetic field by incorporating silica coated iron(III)oxide nanoparticles into multiphase polymer network composites containing PCL and (PCHMA) segments.\textsuperscript{29} Following a copolymer strategy, Pretsch et al. also reported triple shape memory behaviour of multiblock polyurethanes.\textsuperscript{30} The triple shape effect was achieved by a two-step programming procedure where shape (B) was programmed using crystallization of soft segments and shape (B) was programmed by vitrification below $T_g$ of the same blocks.

Researchers have also attempted to develop multishape (greater than three shape) systems. Kolesov et al. developed a branched copolymer containing ethylene 1-octane and linear high density polyethylene (HDPE) with different 1-octane content and consequently different degrees of branching.\textsuperscript{31} As a result, the material featured a very broad melting transition. However, triple and quadruple SM effects were not successfully achieved due to the lack of distinct transitions. More success with such a concept was achieved by Xie et al., who showed that a broad phase transition temperature can be considered as having near-infinite number of sharp transition and each featuring incremental shape fixing capability. In their work, a perfluorosulphonic acid ionomer (PFSA) with a broad transition from $\sim$55 °C to 130 °C showed quadruple SM behaviour.\textsuperscript{32} In terms of material processing, this method is simpler than the other approaches described due to the fact that introducing additional transitions to reversible transitions of the polymer can be challenging.
Quite recently, a mixing approach to achieve triple shape materials was reported, while Xie et al. also adopted a macroscopic “blending” approach by bonding two dual SM epoxy layers together into a bimorph. Triple shape behaviour in bending was afforded by the two well-separated glass transitions temperatures and the authors concluded that optimal response demanded a strong interface between the layers, appropriate balance of moduli, and relative thicknesses. Recently, Zhao et al. took a melt-mixing approach to fabricate a co-continuous blend of immiscible cross-linked polyethylene (PE) and polypropylene (PP) to achieve triple shape memory property.

Our group introduced a composite materials approach to TSMPs by electrospinning a microfiber mat of poly(ε-caprolactone) (PCL) and infiltrating with a dual shape memory epoxy. The advantage of this method to our previously structured shape memory elastomeric composites was the introduction of one more transition (epoxy glass transition \(T_g\) in addition to PCL melting transition \(T_m\)) which allowed the ability to fix a second temporary shape. Another advantage of this approach is flexibility in design through independent control of fiber and matrix properties. Nevertheless, electrospinning is a complex process and the weight fraction of PCL relative to epoxy matrix could not be altered easily.

In this work, we report on the preparation of triple shape memory composites (TSMCs) with well controlled properties and simple, scalable preparation procedures. We use phase separation (PIPS) to yield multiphase crosslinked composites with one permanent shape and two distinct transition temperatures that are able to fix two temporary shapes. In what follows, we explain the preparation, thermo-mechanical, and bulk triple shape behaviour of the TSMCs, revealing high performance and excellent potential for large-scale manufacturing.
7.3 Experimental Section

7.3.1 Materials

Diglycidyl ether of bisphenol-A (DGEBA) (Mw=340 g/mol), an aromatic diepoxide monomer, neopentyl glycol diglycidyl ether (NGDE) (Mw=216 g/mol), an aliphatic diepoxide monomer, o,o′-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeffamine® ED2000) (Mw=2000 g/mol), a polyether diamine, poly(propylene glycol) bis(2-aminopropyl ether) (Jeffamine® D230) (Mw=230 g/mol), a polyether diamine, and poly(ε-caprolactone) (PCL) (Mw=10,000 g/mol) were purchased from Sigma-Aldrich. All chemical structures are shown in Scheme 7-1.

7.3.2 Fabrication of TSMPCs

Two types of TSMPCs were prepared, differing in the nature of the fixing mechanism (crystallization vs. vitrification) for shape (A), the low temperature fixing. Both composites were prepared following the same polymerization induced phased separation method reported in Chapter 2. In Schematic 7-1, we show the chemical structures of the reactants (A-E) and final networks of PPG-EP/PCL and PEO-EP/PCL composites (I-II). The first TSMC of polypropylene glycol-epoxy/poly(ε-caprolactone) (dubbed PPG-EP/PCL hereafter) was prepared by reacting DGEBA and NGDE with Jeffamine D230 cross-linker with the molar ratios of 1:1:1 in the presence of dissolved PCL (10 wt-%). To prepare the PPG-EP/PCL samples, DGEBA, NGDE, and PCL were melted at 80 °C in a Teflon® dish, following which the mixture was cooled to room temperature and the prescribed amount of Jeffamine D230 added and mechanically stirred until dissolution evidenced by transparency. Next, the mixture was
transferred to a Teflon® mold and thermally cured using the following cure profile: room temperature for 24 h, 40 °C for 48 h, and 60 °C for 24 h, after which samples were removed from the mold. The molds were custom fabricated into ¼-scale ASTM Type IV dogbones (ASTM D63) and with sample thicknesses ranging from 0.5 to 0.7 mm. During cure of the epoxy/PCL blend the initially miscible system phase separates into two phases, one that is epoxy rich and one that is PCL-rich. This process, called Polymerization Induced Phase Separation (PIPS), is largely reviewed in literature and our group.\textsuperscript{24,36-41} The PPG-EP/PCL material was picked after a systematic study on a triple shape memory composite by Luo et al.\textsuperscript{24} from our group. In the aforementioned study, a composite was fabricated using a PCL fibrous web infiltrated with an epoxy mixture. That study led to the present research that focuses on a blend approach to triple-shape polymers using similar components to fabricate triple shape memory polymers with different morphology. Our strategy to design a second TSMC, that exhibits rubbery behaviour at room temperature, utilizes a semicrystalline epoxy with a melting transition as opposed to the amorphous epoxy used in the PPG-EP/PCL sample. The second epoxy-based TSMC of polyethylene oxide-epoxy/poly(ε-caprolactone) (dubbed PEO-EP/PCL hereafter) was prepared by reacting DGEBA and Jeffamine ED2000 cross-linker (containing crystallizable poly(ethylene oxide) PEO) in the presence of PCL (10 wt.%). The molar ratio of Jeffamine ED2000 and DGEBA was 2:3 to provide excess amount of cross-linker and achieve non-stoichiometric mixture. This non-stoichiometric ratio was necessary to achieve a melting temperature above room temperature. We note that early formulation trials revealed that stoichiometric mixtures of the epoxy or epoxy/PCL blend led to a melting transition for epoxy lower than room temperature. Excess ED2000 (2:3 instead of 1:2) crosslinked well but had the added benefit of increasing the melting point of the epoxy. To prepare the PEO-EP/PCL samples, a process very
similar to that for **PPG-EP/PCL**, described above, was adopted. DGEBA and Jeffamine ED2000 were melted and mixed at 65 °C in a Teflon® dish, following which a required amount of PCL was dissolved in the melt and mechanically stirred until the mixture turned visually homogeneous. Next, the mixture was transferred to a Teflon® mold. This formulation was then thermally cured using the following cure profile: 90 °C for 24 h, followed by 110 °C for 6 h. As with the **PPG-EP/PCL** system, **PEO-EP/PCL** also exhibits PIPS, and this occurs during the second stage of the cure profile. In **Scheme 7-1**, we show the chemical structures of the reactants (A-E) and final networks of **PPG-EP/PCL** and **PEO-EP/PCL** composites (I-II). It is important to note that distinct curing protocols were used for each composite due to differences observed for their curing kinetics. A detailed study of cure kinetics is provided in **Chapter 2** while here we focus on the shape memory properties of the final, cured states.

In addition to the TSMCs explained above, neat epoxy samples of PPG-EP and PEO-EP were made by omitting the PCL from the reaction for comparison purposes and study of PIPS. The PPG-EP was prepared by reacting DGEBA and NGDE with Jeffamine D230 cross-linker with the molar ratios of 1:1:1 using the same curing procedure that was explained above for PPG-EP/PCL. The PEO-EP was prepared by reacting DGEBA and Jeffamine ED2000 cross-linker with the molar ratios of 3:2 using the same curing procedure that was explained above for PEO-EP/PCL.

**7.3.3 Thermal Characterization**

Thermal properties and phase behaviour of PCL/epoxy composites and neat epoxy were characterized using Differential Scanning Calorimetry (DSC) anticipating pertinence to SM behaviour studied later. DSC experiments were conducted using a Q200 (TA Instruments, Inc.)
equipped with a refrigerated cooling system (RCS). 3-5 mg samples were encapsulated in Tzero aluminum pans and were heated from -80 °C to 120 °C, cooled back to -80 °C, and finally heated to 120 °C. All heating and cooling rates were 10 °C min⁻¹. Glass transition (T_g) and melting temperatures (T_m) were determined from the midpoint of step transition and melting peak, respectively. The melting enthalpy was calculated by integrating the melting peak. PCL and PEG degrees of crystallinity in the composites were then calculated using the equation below:

\[ X(\%) = \frac{\Delta H_a}{w_a \Delta H^o_a} \]  

Where \( \Delta H_a \), \( \Delta H^o_a \) and \( w_a \) are the observed melting endotherms for the sample (whether due to PEO or PCL), the heat of fusion of 100% crystalline polymer, and the weight fraction of polymer relative to the entire blend, respectively. A literature value of 202.41 J/g was used for \( \Delta H^o_{PEG} \) and literature value of 139.5 J/g was used for \( \Delta H^o_{PCL} \).

### 7.3.4 Polarized Optical Microscopy (POM)

The final morphologies of fully cured epoxy/PCL samples, pure epoxy networks with and without PCL were determined by polarized optical microscopy (POM). An Olympus BX51 microscope with crossed polarizer analyzer was used. For this experiment, one drop of blend as mixed was sandwiched between two glass slides and cured according to the curing protocol explained above using an Instec HCS402-STC2-A heating/cooling hot stage. All micrographs were taken at room temperature.
7.3.5 Determining Onset of PIPS via Turbidity Experiment

In order to quantitatively measure the phase separation onset time, or the cloud point, a turbidity experiment was conducted to measure the transmittance of the light as the sample undergoes PIPS. The light from a visible light source (in our case the halogen lamp of the microscope) was allowed to pass through the sample, and finally detected by a UV/Vis spectrometer (Ocean Optics S2000 miniature fiber optic spectrometer). The intensity vs. wavelength profile generally exhibits Gaussian distribution with a maximum at 550 nm. Therefore, this profile was used to determine the onset of PIPS as where the maximum density drops. One drop of the as mixed epoxy/PCL blend was first sandwiched between two glass slides and then placed on a hot-stage (Instec HCS402). Three experiments were conducted where (A) sample was kept isothermally at 80 °C, (B) isothermally at 100 °C and (C) ramped up from 80 to 120 °C at 0.2 °C min⁻¹.

7.3.6 Dynamic Mechanical Analysis

Thermomechanical properties of the composites were characterized using a Q800 Dynamic Mechanical Analysis (DMA) (TA Instruments, Inc). Dogbone-shaped samples were loaded under tension and oscillatory deformation with an amplitude of 10 µm, a frequency of 1 Hz and with a “force track” (ratio of static to dynamic force) of 108% being applied. To determine transition temperatures and rubbery plateaus of the composite, the samples were equilibrated and held isothermally at -100 °C for 20 min, then heated to 80 °C at 2 °C min⁻¹.

7.3.7 Bulk Shape Memory Characterization

In order to perform quantitative characterization of both dual and triple shape properties of the composites, the same Q800 DMA instrument was used, but in “Force Control” mode. Dogbone
samples were used as described above. Two different fixing protocols with distinct thermomechanical histories were conducted. First, triple shape behaviour was explored using a single fixing method. Each sample was deformed at 75 °C (above both composite transitions) by ramping the force at 0.05 N.min\(^{-1}\) from a small preload force to 10% strain. The sample was then cooled to -10 °C at 2 °C.min\(^{-1}\) while holding the applied force constant. The sample temperature was then kept isothermal for 5 min followed by unloading the force to 0.01 N (small preload) at 0.1 N.min\(^{-1}\). In the final step, the sample was heated to 75 °C, completing the SM cycle. For comparison, another shape memory cycle was utilized, the second method utilizing two fixing steps. Similar to the first method samples were first deformed to 10 % strain under the same force rate. The temperature was then reduced to -10 °C followed by an isothermal hold for 20 min. Then, the temperature was ramped to 40 °C (intermediate between the two transitions) and held isothermally for 3 min, completing the first fixing step. Samples were next stretched an additional 20 % strain at 0.05 N.min\(^{-1}\) while the temperature was maintained at 40 °C and following which the temperature was decreased to -10 °C. Next, the sample was held isothermally for 20 min, following which the external force was released by unloading the force to 0.01 N at a rate of 0.1 N.min\(^{-1}\), completing the second fixing method. Finally, the sample was heated to 75 °C at 2 °C.min\(^{-1}\), revealing the transition from shape (A) to (B) to (C).

To quantify triple shape properties of the composites, the fixing ratios and the recovery ratios for all SM cycles were calculated using the following equations:

\[
R_f(x) = \frac{\varepsilon_x}{\varepsilon_{x,load}}
\]  

(7.2)
Here $\varepsilon_x$, $\varepsilon_{x,\text{load}}$ and $\varepsilon_{y,\text{rec}}$ represent the strain before and after unloading and the strain after recovery for shape x, respectively ($x$ can be strain at 75 °C, 40 °C or -10 °C, the same holds for y). For strain at 75 °C, $\varepsilon_c$ is simply the starting strain. For intermediate recovery, strains at two temperatures were calculated: one at 40 °C and the other at the temperature where strain differentiation with respect to temperature was the lowest; i.e. the intermediate plateau.

The bulk triple shape properties of the composites were also characterized using a visual demonstration. To do so, each sample was cut from a film to yield a relatively long strip with typical dimensions of 41 mm (length), 4.7 mm (width), and 0.4 mm (thickness). A protocol similar to the second fixing method was utilized for SM fixing, as we now describe. Samples were first equilibrated at 80 °C in an isothermal oven for 20 min and then one side of strip quickly folded on one end. Next, the samples were tightly constrained with aluminum foil (to keep the temporary shape) and maintained at 80 °C for another 5 minutes. Following this step, samples were quickly moved to a freezer at -17 °C, aluminum foil was removed (to release the constraint) and kept isothermal for another 20 minutes. To program the second temporary shape, the other end of each strip was deformed at 40 °C to a curved shape by wrapping around a cylindrical rod with diameter of 5.3 mm and again moved to the freezer for 20 minutes. Triple shape recovery was observed for each sample by placement on a hot plate held at 40 °C and holding for 10 min, allowing observation of the first shape recovery, followed by placement on a second hot plate held at 80 °C and holding for 10 min, allowing observation of the second shape
recovery.

7.3.8 Surface Triple Shape Memory Characterization

In order to characterize and compare triple shape properties of the fabricated composite at bulk and surface, two experiments were conducted following similar protocol for the triple shape memory demonstration experiment reported earlier: First one temporary shape was fixed at the surface and the second was fixed at the bulk of the sample. In second experiment both temporary shapes were fixed only at the surface of the sample. In what follows, details of each experiment are provided:

(A) Bulk-Surface: In this experiment, sample was first embossed with circular pattern at 80 °C at the surface and fixed at -17 °C (by placing in the freezer). For the second temporary shape, the bulk of the sample was strained with a custom made stretcher to 10 % of strain at 40 °C and fixed at -17 °C. When strained circular pattern become oval. The sample was then heated back up to 40 and then 80 °C for recovery.

(B) Surface-Surface: In this experiment, sample was first embossed with circular pattern at 80 °C, fixed at -17 °C and then embossed with parallel strips at 40 °C and again fixed at -17 °C. Note that both temporary shapes were embossed and then fixed only at the surface of the sample with the bulk of the sample staying in its equilibrated permanent shape. The sample was then heated back up to 40 and then 80 °C for recovery.

7.3.9 Reversibility of Adhesion

In order to demonstrate the reversibility of the adhesion of our composite, a rectangular bar was placed on a stainless steel sheet (weight ~ 200 g) and heated to 80 °C in hot press and kept
isothermal for 10 min to melt the PCL phase at the surface of the specimen. The specimen and stainless steel substrate were then pressed against each other at a relatively low pressure (less than 0.2 mTons, the limit of the of the hot press), cooled down to 15 °C while holding the pressure to crystallize the molten PCL and then the pressure was removed. The interface of the specimen and stainless steel substrate were then heated up to 80 °C to debond the adhesion.

7.4 Results and Discussion

7.4.1 Thermal Characterization

DSC experiments were conducted to understand the phase transition behaviour of the composites as described below. First, cooling and second heating DSC traces are shown Figure 7-1. We found that that both TSMCs showed well separated thermal transitions, though with one showing glass transition of one phase followed by melting of another phase upon heating (PPG-EP/PCL) and the other showing a melting transition of one phase followed by a separate melting transition of another phase upon heating (PEO-EP/PCL). For the PPG-EP/PCL composite, a step transition at 40 °C (with modest physical aging peak) and an endothermic transition at 59.7 °C were observed in the heating trace. These two transitions correspond to glass transition of the epoxy network and the melting of PCL, respectively. The cooling cycle showed a crystallization exotherm for PCL (the epoxy phase vitrification is hard to distinguish). For the PEO-EP/PCL composite, endothermic transitions at 24.4 °C and then at 53.7 °C were observed during heating. The transitions correspond to PEG and PCL melting transition respectively. A separate PCL melting transition observed in both samples is an indication of PIPS explained earlier in the method section. Moreover, the clear separation between transitions needed for triple shape behaviour was exhibited by both composites. It is interesting to note that the crystallinity in the
PPG-EP/PCL composite was significantly higher (47%) than that of PEO-EP/PCL (25.3%) despite near-identical incorporation levels. The higher degree of crystallinity in PPG-EP/PCL sample compared to PEO-EP/PCL may also explain the higher PCL T$_m$ observed in this system. *Table 7-1* summarizes the thermal properties of the composites determined by DSC (2$^{nd}$ heating and 1$^{st}$ cooling cycles).

**7.4.2 Composite Morphology**

Following the observation of multiple transitions in DSC for each composite, we sought to observe their multiphase morphologies using POM, applied to the fully cured, thin-film specimens. *Figure 7-2* shows macro-photographs of each composite, viewed above a checkerboard pattern before and after curing. This reveals the turbidity that accompanies PIPS. POM observations were able to distinguish semi-crystalline PCL from amorphous epoxy, since the former is birefringent and the latter is not. POM micrographs of the cured composites are shown in *Figure 7-2 I(C) and II(C)*. For the PPG-EP/PCL composite, we observed a feather-like birefringent phase that is attributed to semicrystalline PCL phase and a dark amorphous matrix phase that corresponds to the epoxy network. For the PEO-EP/PCL composite, birefringent spheres corresponding to PCL phase were evident, along with a lightly birefringent background attributed to PEO crystallinity in the epoxy matrix. POM micrographs of cured epoxy networks (PPG-EP and PEO-EP) without the PCL and POM micrograph of PCL at room temperature are shown in Supplementary *Figure 7-3*.

In both cases, POM micrographs showed two distinct phases. Together with our observation of optical transparency for both systems prior to cure (*Figure 7-2(a)*), these observations support the notion that PIPS occurred (We will address the completeness of phase separation below,
following presentation of thermomechanical and shape memory properties.). The difference in two morphologies arose from different compositions and curing protocols as explained here. For PPG-EP/PCL, the curing temperature is lower than the PCL T_m. Consequently, as phase separation occurs, PCL crystallization also occurs and apparently at a low interfacial tension that yields feather-like PCL crystals. For PEO-EP/PCL, however, cure is conducted above the PCL T_m. As such, PIPS yields spherical, isotropic droplets of PCL that crystallize after cure and during cooling, preserving the spherical shape.

7.4.3 Determining Onset of PIPS via Turbidity Experiment

As discussed in section 7.4.2, the as mixed epoxy/PCL blend is transparent but became opaque as PIPS occurred. Therefore, we defined the onset of PIPS as the time point at which visible light transmittance of the blend drops. Intensity vs. time profiles of the PPG-EP/PCL composite is shown in Figure 7-4. Quite interestingly, at 80 °C, the turbidity drops and material turns cloudy indicating PIPS occurrence. However, when cured at 100 °C, the intensity does not drop and the material remains transparent indicating upper critical solution temperature (UCST) behavior (See section 2.2.2 for phase diagram of polymeric binary blends.). Note that Generally, the miscibility of a two polymer or a polymer/solvent system that are immiscible at ambient conditions are higher as temperature increases and above a critical temperature (known as Upper-Critical-Solution-Temperature (UCST)), a one phase solution forms. Furthermore, when the temperature was ramped up from 80 to 120 °C, PIPS occurred even at a faster rate. Therefore, once the PIPS initiated, temperatures higher than UCST not only won’t freeze the process but also accelerate the PIPS.
7.4.4 Dynamic Mechanical Analysis

To understand viscoelastic properties of the TSMCs and to provide context for the subsequent “Dual Shape” and “Triple Shape” SM cycles, dynamical mechanical analysis of each composite was conducted. Tensile storage modulus (E’) and tan(δ) as a function of temperature are reported in Figure 7-5. Both composites showed multiple transitions, which is in agreement with DSC results. The PPG-EP/PCL composite (trace I) shows a high modulus plateau at low temperature, followed by an intermediate plateau above the epoxy T_g but below the PCL T_m and finally a rubbery plateau above the PCL T_m, where the material exists as an epoxy rubber with liquid PCL inclusions. By comparison, the PEO-EP/PCL composite is quite distinct, with multiple modulus plateaus and transitions evident. At the lowest temperatures, a glassy modulus is observed, and this steps down twice with broad T_g transition until a leathery modulus is achieved at about 10 °C, below the epoxy-based PEO T_m. Upon further heating, the PEO segments melt and a rubber plateau is achieved at room temperature, below the PCL T_m. Continued heating yield a second rubber plateau similar to that of PPG-EP/PCL where the material also exists as an epoxy rubber with liquid PCL inclusions. Quantitatively, we note that the storage modulus of PPG-EP/PCL is 1677 MPa at 25 °C while the storage modulus of PEO-EP/PCL is 4.5 MPa at the same temperature. DMA loss tangent (tan δ) trace of (I) PPG-EP/PCL and (II) PEO-EP/PCL in log scale demonstrating all three transition temperatures is provided in Figure 7-6. This storage modulus is 46.3 and 3.20 MPa at 40 °C for PPG-EP/PCL and PEO-EP/PCL, respectively. The storage modulus further decreases to 3.82 and 2.14 MPa for PPG-EP/PCL and PEO-EP/PCL, respectively, at 75 °C, which is above the PCL melting transition. Therefore, while the samples are similar in composition, processing and morphology, they are drastically different in their physical properties at room temperature, yielding good design flexibility for applications that
may feature different stiffness requirements.

### 7.4.5 Bulk Triple Shape Memory Characterization of TSMCs

The same dynamic mechanical analyser was used to investigate the SM properties of PPG-EP/PCL and PEO-EP/PCL samples. For this purpose, one-step and two-step methods explained in the Materials and Methods section were used. The results of one-step triple SM cycle (SMC) testing are shown in Figure 7-7. In this method, starting from the asterisk (*), samples were loaded to a tensile strain of 14% for PPG-EP/PCL sample and 20% for PEO-EP/PCL sample, cooled to -10 °C and unloaded to reveal fixing, followed by continuous heating to 75 °C, revealing multistep recovery. For the PPG-EP/PCL sample, a first recovery event occurred on passing through T_g, while a second recovery occurred as the PCL melting transition (60 °C) was surpassed. For the PEO-EP/PCL sample, the first strain recovery event occurred on passing through the network’s PEG melting transition around 28 °C and the second recovery occurred above the PCL melting transition.

Such two-step recovery behaviour during continuous heating is an indication of triple shape memory behaviour of both networks. To further validate the triple shape memory behaviour, a two-step method was also performed on samples, as described previously. The results of such testing are shown in Figure 7-8. In this method, starting from the asterisk (*), samples were first loaded at 75 °C to a tensile strain of 5% for the PPG-EP/PCL and 10% for PEO-EP/PCL, cooled to 10 °C and unloaded, yielding for fixing a temporary shape (B). Then samples were heated to an intermediate temperature to observe and calculate the fixing ratio of shape (B). We found that the PPG-EP/PCL sample showed better fixing of this temporary shape than the PEO-EP/PCL specially upon heating to an intermediate temperature (step 3). In order to fix
temporary shape (A), samples were loaded further to a total tensile strain of 16% for **PPG-EP/PCL** and 20% for **PEO-EP/PCL** (step 4) at an intermediate temperature and cooled to -10 °C followed by unloading. Both samples showed good fixing of the temporary shape, as witnessed upon unloading. It is interesting to observe that the **PEO-EP/PCL** sample elongated during the second fixing. This is caused by stress-induced crystallization that causes an increase in strain during cooling below the melting point.\(^{45,46}\)

After fixing two temporary shapes, samples were continuously heated to 75 °C. During heating, sequential recovery from shape (A) to shape (B) and from shape (B) to the permanent shape, shape (C), were observed. The first recovery of the samples happened at an intermediate temperature. As the samples were heated from the intermediate temperature to 75 °C, the second recovery occurred. Table 7-2 shows the fixing and recovery ratios calculated using one-step and two-step SM cycles using the corresponding equations explained earlier in the method section. Both samples showed a good fixing of temporary shape (A). However, the fixing of temporary shape (B) was better for the **PPG-EP/PCL** sample. We attribute this to the higher degree crystallinity of PCL in **PPG-EP/PCL** composite (Table 7-1), and to the higher storage modulus of the **PPG-EP/PCL** sample compared to the **PEO-EP/PCL** sample at an intermediate temperature (Figure 7-5). Had these steps in modulus been larger, for example by percolation of PCL phases, then we would have expected higher shape fixing. The higher PCL degree of crystallinity and higher storage modulus of the **PPG-EP/PCL**, above the first transition temperature, provides better fixing of shape (B) \((R_f(b))\); and consequently, the poor fixing of shape (B) \((R_f(b) = 38.8\%)\) in the **PEO-EP/PCL** is mainly due to its lower storage modulus above the first transition temperature and lower PCL degree of crystallinity. Again, had these steps in modulus been larger, for example by percolation of PCL phases, we would have expected higher shape fixing. By controlling the individual
components (semicrystalline PCL and amorphous epoxy), the overall shape memory properties of the composites can be controlled.\textsuperscript{47} A model is needed to explain the mechanism behind fixing of these particular morphologies which is saved for future work.

The subsequent recoveries from shape (A) to shape (B) and finally to permanent shape (C) were all above 93\% as quantified using the equations explained earlier. For the PPG-EP/PCL composite, recovery from shape (A) to shape (B) was only 14.1 \% at 40 °C due to the higher and broader transition of the epoxy relative to PEG melting transition. However, recovery at intermediate plateau, 54.2 °C, (where \(\frac{dE}{dT}\) was minimum) was 98.2 \%.

\textbf{7.4.6 Demonstration of Sequential Shape Recovery of TSMCs}

In order to qualitatively demonstrate the triple shape memory capabilities of the new composites, slender strips of each sample were heated to 80 °C in an isothermal oven, following which one end was folded and fixed by cooling in a freezer (For details see Methods section). This process fixed a temporary shape (B) using the PCL melting temperature for both networks. In order to fix a temporary shape (A), the other end of each sample was curled, immobilized and cooled in a freezer. This process fixed temporary shape (A) using network vitrification for the PPG-EP/PCL sample and PEG crystallization for the PEO-EP/PCL. A schematic illustration of this procedure is shown in \textbf{Figure 7-9 (I)}: the right side of the sample is fixed using the lower transition temperature and the left side of the sample is fixed using the higher transition temperature. As the sample is heated above the lower transition temperature, the right side recovers; and as the sample is heated further, above the higher transition temperature, the left side recovers. Photographs of fixed PPG-EP/PCL and PEO-EP/PCL samples at room temperature are shown in \textbf{Figure 7-9 (II-A)} and \textbf{Figure 7-9 (III-A)} respectively. As both
samples are heated to an intermediate temperature, first the curved shape recovers and the sample goes from shape (A) to shape (B). When samples are heated to 75 °C, the left side of the sample (which was programmed first) starts to recover and the sample goes from shape (B) to its permanent, flat shape, or shape (C).

7.4.7 Completeness of Phase Separation and its Impact on Shape Memory Response

We have reported thermal, thermomechanical, and triple shape memory properties of two epoxy/PCL blends prepared using PIPS, phase separation led to two distinct phases capable of fixing two distinct shapes. Here we discuss the apparent level of phase separation completeness in the blends and the role of this completeness in determining the final physical properties.

In the case of the PPG-EP/PCL blend, the final material is a glassy epoxy blended with semicrystalline PCL. In such a blend, incomplete phase separation would yield a percentage of PCL dissolved in the epoxy-rich polymer, lowering the $T_g$ of that phase but not the degree of fixing of that low temperature shapes (shape A), owing to the nature of the glass transition for shape fixing. Further, incomplete phase separation of PPG-EP/PCL would yield a percentage of epoxy oligomers in the PCL-rich phase, likely lowering the degree of crystallinity of that phase while also impacting the stoichiometry of the epoxy formulation and thus lowering the high temperature rubber modulus. Inspection of Table 7-1 (and DSC traces; Figure 7-10) reveals that the $T_g$ of the blend is 4 °C lower than pure PPG-EP cured under the same conditions while the degree of crystallinity for PCL is approximately the same in both the blend and pure PCL (~47%). In light of these findings, along with triple shape characterization results with $R_a = 99.2\%$ and $R_b = 91.6\%$, we conclude that the epoxy phase is slightly plasticized by dissolved PCL chains, impacting glass transition but not fixing by that phase, while the PCL phase is
apparently quite pure compositionally.

In the case of the **PEO-EP/PCL** blend, the final material is a soft, semicrystalline epoxy blended with semicrystalline PCL. In such a blend, incomplete phase separation would yield a percentage of PCL dissolved in the epoxy-rich polymer, likely lowering the crystallinity of the PEO crystals of that phase and thus fixing of the lower temperature shapes (shape A). Similar to the **PPG-EP/PCL** blend, incomplete phase separation could yield a small percentage of epoxy oligomers in the PCL-rich phase, lowering crystallinity and shape fixing of the higher temperature fixed shape (shape B). In addition, disruption of epoxy stoichiometry would significantly impact the rubber modulus observed at high temperature. Thermal analysis data (Table 7-1; Figure 7-10) shows that the degree of crystallinity is lower in the blend (29% vs. 39%), suggesting that some PCL remains dissolved in that phase. However, the fixing of shape A is very high (98 – 99%), showing relative insensitivity to crystallinity degree. The Storage Modulus profile and triple shape-memory cycles of **PEO-EP** with one step recovery and **PEO-EP/PCL** with two step recovery are shown in Figure 11 and Figure 7-12. The PCL crystallinity in **PEO-EP/PCL** is much lower than pure PCL (25.3% vs. 47%), indicating that some epoxy oligomers (or pure Jeffamine® ED2000) remain dissolved in the PCL-rich phase. A consequence of this is the relatively poor fixing of the intermediate shape (shape B). Nevertheless, DMA analysis showed a flat and substantial rubber modulus above the PCL T_m, indicating that the stoichiometry of the epoxy formulation was not substantially altered (Figure 7-11).

While not quantified in this study, the degrees of phase separation for the two blend systems were distinct from each other, with little impact on triple shape behaviour of the **PPG-EP/PCL** system and significant impact on the **PEO-EP/PCL** system through diminished crystallinity of PCL and associated lowering of fixing for intermediate shape (B).
7.4.8 Surface Triple Shape Memory Characterization

We also, further characterized triple shape properties of the composite in bulk-surface and surface-surface level as shown in Figure 7-13 and 7-14, respectively. Results showed almost prefect fixing and recovery in both cases indicating that not only the bulk of the sample, but also the surface of the sample have the ability to sequentially recover upon heating even if the bulk of the sample remains at its equilibrated permanent shape.

7.4.9 Reversibility of Adhesion

The fabricated triple shape composites exhibited a surprisingly well reversible adhesion properties. We believe this is due to a phenomenon called “differential expanding bleeding (DEB)” which was previously developed for a poly(ε-caprolactone)/Diglycidyl ether of bisphenol-A/4,4’-diaminodiphenylsulfone (PCL/DGEBA/DDS) system in our group\(^41\). Physically, the DEB originates from the phase transition (melting) of the PCL matrix and the resulting difference in volumetric expansion of the two phases. The main difference between PCL/DGEBA/DDS and our particular composite system is the T\(_g\) of epoxy matrix. In the former the T\(_g\) was about 203 °C whereas in the latter the T\(_g\) was just above RT. When the heated at 150 °C, all the surfaces of the PCL/DGEBA/DDS composite were covered by a thin layer of PCL as a result of DEB, while the bulk of the material is still a rigid solid below its glass transition temperature. In our system however, when the sample is heated at 90 °C, the bulk of the material becomes a soft rubber-like above its T\(_g\) (32 °C). Figure 7-15 shows (A) a stainless steel substrate bonded to a PPG-EP/PCL20 sample(Weight fraction of PCL was 20 % in this case to increase adhesion strength) , (B) bonded specimen withstanding the stainless steel substrate weight, (C) debonded specimen after heating up to 80 °C and (D) metal substrate surface indicating some
PCL residue (highlighted). Results showed strong bonding between the specimen and the stainless steel substrate which easily debonds by heating above PCL melting temperature.

7.5 Conclusions

Two TSMCs with distinct properties were prepared using a PIPS approach. Differences and similarities of PEO-EP/PCL system with two well separated melting temperatures and PPG-EP/PCL system with one glass transition temperature and one melting temperature, each capable of fixing a temporary strain were highlighted. The effects of epoxy crystallization in PEO-EP/PCL system, epoxy vitrification in PPG-EP/PCL, and PCL crystallization in both systems on shape fixing and recovery were investigated. Ease of synthesis, good shape fixing, and good recovery of two distinct programmed shapes independently in response to heat stimulus make these materials good candidates for triple-shape applications demanding scalability. As an example, triple shape materials could allow for geometrically complex actuation events, such as bending followed by a twist or contraction event useful for mechanical device development. Further study is required to investigate the capability of composites to deform to more complex patterns on the surface and in the bulk of the TSMCs.

7.6 References


**Scheme 7-1.** The chemical structures of (A) diglycidyl ether of bisphenol-A (DGEBA), (B) neopentyl glycol diglycidyl ether (NGDE), (C) Jeffamine D230, (D) Jeffamine ED2000, and (E) poly(ε-caprolactone) for preparation of (I) PPG-EP/PCL and (II) PEO-EP/PCL.
Figure 7-1. DSC thermograms of 1st cooling and 2nd heating for: (I) PPG-EP/PCL and (II) PEO-EP/PCL. Heating rate of 10 °C min⁻¹ was used for cooling and heating of both samples.
Table 7-1. Summary of thermal properties determined from DSC experiments. Melting transitions were determined as the middle point of the transitions of the second heating runs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ Epoxy (°C)</th>
<th>$T_m$ PEG (°C)</th>
<th>$\Delta H_m$ PEG (J/g)</th>
<th>Weight ratio of PEG</th>
<th>PEG % Crystallinity</th>
<th>$T_m2$ PCL (°C)</th>
<th>$\Delta H_m$ PCL (J/g)</th>
<th>Weight ratio of PCL</th>
<th>PCL % Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG-EP/PCL</td>
<td>40.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>59.7</td>
<td>6.55</td>
<td>0.10</td>
<td>47.0</td>
</tr>
<tr>
<td>PEO-EP/PCL</td>
<td>-50.9 $^c$</td>
<td>24.4</td>
<td>40.6</td>
<td>0.899</td>
<td>28.7</td>
<td>53.2</td>
<td>3.78</td>
<td>0.107</td>
<td>25.3</td>
</tr>
</tbody>
</table>

$^a$ Heat of fusion value for 100% crystalline PEG is 202.4 J/g $^{21}$

$^b$ Heat of fusion value for 100% crystalline PCL is 139.5 J/g $^{22}$

$^c$ Determined from DMA
Figure 7-2. (I) PPG-EP/PCL and (II) PEO-EP/PCL exhibit: (A) Photographs of samples before curing, (B) photographs of samples after curing, and (C) POM images of cured samples under crossed polarizers. The scale bars for (A) and (B) represents 2 mm. The scale bars for (C) represents 100 μm.
Figure 7-3. POM images under crossed polarizers at room temperature exhibited by: (A) PPG-EP, (B) PEO-EP, and (C) PCL. The scale bar represents 200 μm.
Figure 7-4. Intensity value at $\lambda = 550$ nm plots for epoxyPCL(10) blend for isothermal at 80 °C (▼), isothermal at 100 °C (■) and ramped up from 80 °C to 120 °C at 0.2 °C min$^{-1}$ (●). Temperature profile for (C) is shown in red.
Figure 7-5. Tensile storage modulus (E’) and loss tangent (tan δ) trace of (I) PPG-EP/PCL and (II) PEO-EP/PCL. Dashed lines separate different thermomechanical regions for each composite.
Figure 7-6. DMA loss tangent (tan δ) trace of (I) PPG-EP/PCL and (II) PEO-EP/PCL in log scale demonstrating all three transition temperatures. Red lines show the transition temperatures of each composite.
Figure 7-7. The triple-shape memory cycle of (A) PPG-EP/PCL and (B) PEO-EP/PCL using one-step fixing. The beginning of the cycles are marked by the asterisk. Samples were loaded, cooled to -10 °C and unloaded (fixing), followed by continuous heating to 75 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) fixing, (3) unloading, and (4) recovery.
**Figure 7-8.** The triple-shape memory cycle of (A) PPG-EP/PCL and (B) PEO-EP/PCL (b) using two-step fixing. The beginning of the cycles are marked by the asterisk. Samples were loaded at 75 °C, cooled to 10 °C and unloaded (1st fixing), heated to an intermediate temperature and loaded again, cooled to -10 °C (2nd fixing), followed by continuous heating to 75 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) 1st fixing, (3) 1st unloading, (4) 2nd fixing, (5) 2nd unloading, and (6 and 7) recovery.
Table 7-2. Fixing and recovery ratios calculated using one-step and two-step shape memory cycles to demonstrate the triple-shape memory.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fixing Method</th>
<th>( R_t(a))%</th>
<th>( R_t(b))%</th>
<th>( R_t(a \rightarrow b))%</th>
<th>( R_t(b \rightarrow c))%</th>
<th>( R_t(a \rightarrow c))%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG-EP/PCL</td>
<td>One-Step</td>
<td>98.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Two-Step</td>
<td>99.2</td>
<td>91.6</td>
<td>14.1 (40 °C)</td>
<td>98.2 (54.2 °C)</td>
<td>99.2</td>
</tr>
<tr>
<td>PEO-EP/PCL</td>
<td>One-Step</td>
<td>99.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Two-Step</td>
<td>98.4</td>
<td>38.8</td>
<td>97.2</td>
<td>93.2</td>
<td>99.2</td>
</tr>
</tbody>
</table>
**Figure 7-9.** (I) Schematic Illustration of Triple Shape memory demonstration experiment showing sample shapes: (A) at RT, below the 1st transition temperature with two ends fixed, (B) at intermediate temperature of 40 °C with left end fixed and right end recovered, and (C) at 75 °C, above the 2nd transition temperature (completely recovered); Photographs showing dual shape recovery of fixed (II) PPG-EP/PCL, and (III) PEO-EP/PCL samples from R.T. (A) to two different temperatures of 40 °C (B) and 75 °C (C). All scale bars represent 1 cm.
Figure 7-10. DSC thermograms of 1\textsuperscript{st} cooling (dashed line) and 2\textsuperscript{nd} heating (solid line) for: (I) PPG-EP, (II) PPG-EP/10\% PCL, (III) PEO/EP, (IV) PEO-EP/10\% PCL, and (V) PCL. Heating rate of 10 °C/min was used for cooling and heating of both samples. It is noted that the heat flow magnitude of the DSC thermogram for PCL was reduced by half for scaling purposes.
Figure 7-11. (a) Tensile storage modulus (E’) and (b) loss tangent (tan δ) trace of PEO-EP/PCL with different PCL content in comparison with neat epoxy PEO-EP, measured by DMA. (i) PEO-EP and (ii) PEO-EP/10%PCL.
**Figure 7-12.** The triple-shape memory cycle of PEO-EP/PCL with (a) 0% and (b) 10% PCL content using one-step fixing. The beginning of the cycles are marked by the asterisk. Samples were loaded to a tensile strain of 20%, cooled to -10 °C and unloaded (fixing), followed by continuous heating to 75 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) fixing, (3) unloading, and (4) recovery.
**Figure 7-13.** (I) Schematic of a thermomechanical triple shape memory cycle. At $T_H$ the material is initially embossed with circular pattern. The temperature is then decreased to $T_0$ to fix one temporary shape (1). The sample is then stretched at $T_L$ and cooled down to $T_0$ to fix the second temporary shape (2). The sample then material recovers into its first temporary shape by heating to $T_L$ and the permanent shape is reached by heating to $T_H$. (II) Micrographs of sample showing (A) fixed temporary shape 1, (B) temporary shape (2) and (C) permanent flat shape. Blue mark indicates exactly the same spot on the sample. Scale bar represents 1 mm.
Figure 7-14. (I) Schematic of a thermomechanical triple shape memory cycle. At $T_H$ the material is initially embossed with circular pattern. The temperature is then decreased to $T_0$ to fix one temporary shape (1). The sample is then embossed with parallel stripes at $T_L$ and cooled down to $T_0$ to fix the second temporary shape (2). The sample then material recovers into its first temporary shape by heating to $T_L$ and the permanent shape is reached by heating to $T_H$. (II) Micrographs of sample showing (A) fixed temporary shape (1), (B) temporary shape (2) and (C) permanent flat shape. Blue mark indicates exactly the same spot on the sample. Scale bar represents 1 mm.
Figure 7-15. Demonstration of reversibility of adhesion showing (A) stainless steel bonded specimen, (B) bonded specimen withstanding the stainless steel substrate weight, (C) debonded specimen after heating up to 80 °C and (D) metal substrate surface indicating some PCL residue (highlighted).
Chapter 8: Preparation and Characterization of Triple Shape Memory Composite Foams*

8.1 Synopsis

Foams prepared from shape memory polymers (SMPs) offer the potential for low density materials that can be triggered to deploy with a large volume change, unlike their solid counterparts that do so at near-constant volume. While examples of shape memory foams have been reported in the past, they have been limited to dual SMPs: those polymers featuring one switching transition between an arbitrarily programmed shape and a single permanent shape established by constituent crosslinks. Meanwhile, advances by SMP researchers have led to several approaches toward triple- or multi-shape polymers that feature more than one switching phase and thus a multitude of temporary shapes allowing for a complex sequence of shape deployments. Here, we report the design, preparation, and characterization of a triple shape memory polymeric foam that is open cell in nature and features a two phase, crosslinked SMP with a glass transition temperature of one phase at a temperature lower than a melting transition of the second phase. The soft materials were observed to feature high fidelity, repeatable triple shape behavior, characterized in compression and demonstrated for complex deployment by fixing a combination of foam compression and bending. We further explored the wettability of the foams, revealing composition-dependent behavior favorable for future work in biomedical investigations.

8.2 Introduction

Shape memory polymers (SMPs) are a class of smart materials that can be designed to undergo programmed changes in shape and stiffness in response to an external stimulus, such as heat\textsuperscript{1}, light\textsuperscript{2}, magnetic field\textsuperscript{3}, and pH.\textsuperscript{4, 5, 9} Thermally triggered SMPs are the most extensively employed, and have been used in a wide range of applications including smart textiles and apparel.\textsuperscript{10}

biomedical devices\textsuperscript{11,12} and deployable aircraft structures\textsuperscript{13}. The shape-changing functionality of SMPs is achieved by memorization of a permanent shape through physical or chemical crosslinks, and programming of an arbitrary temporary shape by deformation and subsequent immobilization of the polymer chains. Upon mobilization of the polymer chains through application of a stimulus, such as heat, the SMP object changes shape from the programmed temporary state to the memorized permanent state, driven by entropic elasticity.\textsuperscript{7,8}

Recently, shape memory functionality has been married with the high compressibility and low density of porous materials to develop SMP foams\textsuperscript{14-16}. While some studies have reported on closed-cell SMP foams\textsuperscript{17,18}, most studies to-date have focused on open-cell foams based on polyurethane\textsuperscript{13,19,20} or epoxy\textsuperscript{21} chemistries. These foams are well-suited for applications where large expansion ratios are required from a light-weight, compact packaged state. For instance, Solowski and colleagues developed cold-hibernated elastic memory foams (CHEM) for deployable space aircraft structures\textsuperscript{13,22}. These polyurethane-based SMP foams had high full/stowed volume ratios of up to 40 and were capable of being stored in the cold hibernated condition for over 1 year\textsuperscript{13,16,23}. SMP epoxy-based foams with increased electrical conductivity and large compressibility have also been reported\textsuperscript{24}.

SMP foams have also recently received increased attention for biomedical applications\textsuperscript{15}. Metcalfe et al. reported the use of CHEM polyurethane-based foams as an occlusive material for embolization of aneurysms\textsuperscript{23}. It was found that CHEM foams were able to successfully occlude internal maxillary arteries in a dog model, although some residual necks and recurrences were reported. Maitland and colleagues developed a laser-triggered SMP foam as an aneurysm occlusion device\textsuperscript{25}. There, an SMP comprised of hexamethylene diisocyanate, N,N,N’,N’-tetrakis(2-hydroxypropyl)eythlenediamine, and triethanolamine with a glass transition
temperature ($T_g$) of 45 °C was placed in a PDMS basilar-necked aneurysm model and deployed by laser activation. The SMP foam was able to fully expand within 60 s of activation\textsuperscript{25}. With recent developments in polymer systems with triggering temperatures near body temperature, SMP foams with potential for studies under physiological conditions have also been enabled. For instance, our group recently developed a poly(ε-caprolactone)-co-poly(ethylene glycol) SMP foam capable of expanding once hydrated at 37 °C that can be used for cell mechanobiology studies\textsuperscript{26}.

A limitation of current SMP foams is the inability to prescribe both the programmed and recovered shapes, as the recovered shape is restricted to the permanent, as-fabricated shape of the foam. Triple shape memory polymers (TSMPs) offer a unique way to overcome this limitation, where control over two temporary shapes can be achieved\textsuperscript{27-31}. As opposed to conventional SMPs that feature one transition temperature, TSMPs possessing two separate transition temperatures enable programming of two independent temporary shapes. TSMPs can be programmed to undergo two controlled shape changes, from temporary shape 1 to temporary shape 2, and from temporary shape 2 back to the permanent shape. This approach could be used to control both the programmed shape of an SMP foam (temporary shape 1) and the deployed state upon recovery (temporary shape 2)\textsuperscript{27,29}.

Researchers have developed several approaches to fabricate TSMPs. Bellin et al. reported the first triple shape memory effect in two different polymer network systems where each had two distinct transition temperatures\textsuperscript{27}. TSMPs have also been developed using bilayer systems, where two epoxy dual-shape polymers with $T_g$ of 38 and 75 °C were bonded together\textsuperscript{32} to create a bimorph. Other approaches to TSMP fabrication and triggering have also recently been reported. Han et al. recently developed a TSMP hydrogel that employed dipole-dipole interactions to achieve triple shape behavior\textsuperscript{33}. Chen et. al. developed a supermolecular composite containing a SMP
polyurethane and cholesteryl isonicotinate where the hydrogen bonding between the carboxyl
groups of the polyurethane and the pyridine ring of the cholesteryl isonicotinate enable triple shape
memory\textsuperscript{34}. Recent advances have also resulted in the development of TSMPs triggered through
alternating magnetic fields rather than thermal triggering\textsuperscript{35}, as well as TSMPs with reversible
actuation\textsuperscript{36}. Our group developed a new approach to creating TSMPs by fabricating a composite
system where poly(\(\varepsilon\)-caprolactone) electrospun fibers were embedded in an epoxy matrix\textsuperscript{28}. In that
approach, triple shape memory was achieved through the two distinct transition temperatures: melt
transition of the poly(\(\varepsilon\)-caprolactone) fibers and glass transition of the epoxy matrix. We coined
these composite-based triple shape polymers as triple shape memory composites (TSMCs)\textsuperscript{28}.

Our group recently reported a new approach to easily fabricate TSMCs using polymerization
induced phase separation (PIPS)\textsuperscript{37}. There, two TSMC systems were fabricated differing in the
nature of their fixing mechanisms. The first was a polypropylene glycol-epoxy/poly(\(\varepsilon\)-
caprolactone) where the epoxy and poly(\(\varepsilon\)-caprolactone) began as a miscible blend when mixed
80 °C and phase separated upon curing of the epoxy phase. This system achieved triple shape
memory through a lower \(T_g\) of the epoxy phase and a separate higher melt transition temperature
of the poly(\(\varepsilon\)-caprolactone) phase. The second system incorporated a poly(ethylene oxide)-based
epoxy rather than the polypropylene glycol-epoxy, and triple shape memory behaviour was
achieved through two separate melt transition temperatures of the epoxy and poly(\(\varepsilon\)-caprolactone)
phases. Both materials exhibited good shape memory fixing and recovery of two temporary shapes,
but with vastly different stiffness at room temperature and water sensitivity.

In this work, our goal was to develop SMP foams possessing triple shape memory properties.
Herein we report a simple method for fabricating TSMC foams via polymer-induced phase
separation (PIPS). Open-cell foams with two distinct transition temperatures and high
compressibility were fabricated and their thermal and thermomechanical properties investigated. The ability of the TSMC foams to fix and recover two temporary shapes is reported, and results are compared to triple shape behaviour with films of the same composition.

8.3 Experimental Section

8.3.1 Materials

Diglycidyl ether of bisphenol-A (DGEBA) \((M_w = 340 \text{ g mol}^{-1})\), an aromatic diepoxide monomer, neopentyl glycol diglycidyl ether (NGDE) \((M_w = 216 \text{ g mol}^{-1})\), an aliphatic diepoxide monomer, a polyether diamine, poly(propylene glycol) bis(2-aminopropyl ether) (Jeffamine® D230) \((M_w = 230 \text{ g mol}^{-1})\), and poly(ε-caprolactone) (PCL) \((M_w = 10000 \text{ g mol}^{-1})\) were purchased from Sigma-Aldrich. All the materials were used as received. Sodium chloride was also purchased from Sigma-Aldrich and used for the salt template. Prior to salt fusion, salt particles were sequentially sieved, and particles with a 300-500 μm diameter were isolated for further use.

8.3.2 Foams Preparation Protocol

8.3.2.1 Fabrication of Interconnected Salt Template

About 6 g of salt with 150-300 μm diameter was added to a 20 ml high density polyethylene (HDPE) vial. The vial was then placed in a Styrofoam box (9.25 x 6.25 x 8.25 in) with the lid off in which a 2 L water at 40 °C was placed to provide a humidity saturated environment. The salt was kept in Styrofoam for 24 h during which the humidity of this chamber facilitates the fusion of the salt. The salt was then dried under light vacuum at RT for 24 h. Scanning electron microscopy (SEM) micrograph of a salt template is provided in Figure 8-1.
8.3.2.2 Fabrication of the Foams

Scheme 8-1 provides a schematic illustration for preparation of “Triple Shape Memory Composite Foams.” The composite was prepared by copolymerizing DGEBA/NGDE mixtures of varying proportions in the presence of a stoichiometric amount of JD230 as the crosslinker following our previous reports\textsuperscript{1,28,37}. Epoxy monomers (DGEBA and NGDE) and PCL were first vigorously stirred at 75 °C for 20 min until a clear, homogenous blend was achieved. Then the blend was cooled to room temperature, where it remained a single phase liquid, after which the crosslinker (JD230) was added. The blend was then stirred for another 2-3 min\textsuperscript{37}. The product, a low viscosity blend, was then poured into an interconnected salt template and was kept at room temperature (RT) for 10 min, followed by pulling light vacuum for an additional 10 min to allow the blend to completely diffuse into the salt template and replace the air.

The product was then cured at RT for 24 h followed by curing at 40 °C for an additional 3 days, during which time the initially miscible system phase separated into two phases, one that is epoxy-rich and one that is PCL-rich. This well-known process, Polymerization Induced Phase Separation (PIPS), has been previously reported\textsuperscript{37-40}. The fully cured samples were then immersed in water at 40 °C for 48 h to extract the salt, yielding interconnected foams with high porosity. The samples are named as D\textsubscript{x}N\textsubscript{y}J\textsubscript{z}PCL\textsubscript{10} where x, y, z and 10 indicate the molar ratio of DGEBA, NGDE, JD230 and overall weight fraction of PCL in the composite, respectively. The following two compositions were prepared using the aforementioned method: D\textsubscript{1}N\textsubscript{2}J\textsubscript{1.5}PCL\textsubscript{10} and N\textsubscript{2}J\textsubscript{1}PCL\textsubscript{10}. We note that even though both of these samples were prepared using the same method, the latter is very soft and rubbery while the former is stiff at RT. For comparison, films with similar compositions were prepared following a previously reported method\textsuperscript{37}. Briefly, after adding the crosslinker, the blend was poured into a ~1.0 mm deep mold and cured following the same protocol for the foams.
In what follows, characterization of both foams and their corresponding films with the same composition is reported.

### 8.3.3 Thermal Characterization

The thermal stability and salt content of fully cured foams was studied by thermogravimetric analysis (TGA) using a TA Q500 TGA instrument under a constant nitrogen purge. For all samples, a small amount of material ranging from 10-20 mg was loaded on the TGA pan and heated at a fixed rate of 10 °C min$^{-1}$ to 600 °C while recording the sample mass as a function of temperature.

Thermal properties of the composites were characterized using Differential Scanning Calorimetry (DSC) anticipating relatedness to the triple shape memory behaviour studied later. DSC experiments were conducted using a Q200 (TA Instrument) equipped with a refrigerated cooling system (RCS). Samples of mass 3-5 mg were encapsulated in a Tzero aluminum pan. Each sample was then equilibrated at -80 °C, ramped to 120 °C, cooled back to -80 °C, and finally heated to 120 °C. All heating and cooling rates were 10 and 5 °C min$^{-1}$, respectively. Glass transition ($T_g$) and melting transition ($T_m$) of the samples were determined as the middle point of the step transition and the melting peak transition of the DSC second heating runs, respectively.

### 8.3.4 Foams Interconnected Structure

The porous structure of the foams was studied using a JEOL JSM-5600 scanning electron microscope (SEM). To preserve the inner structure of the foam, a rectangular sample was first double notched on the sides, immersed in liquid nitrogen and immediately broken in half. The cryofractured sample was then sputter coated (Denton Vacuum-Desk II sputter coater) with gold for 45 s prior to SEM imaging.
8.3.5 Dynamic Mechanical Analysis

To study thermomechanical properties of the foams a Q800 Dynamic Mechanical Analyzer (DMA) (TA Instruments, Inc.) was used. Rectangular foam samples (typical dimensions of 9.0 mm (length) x 5.0 mm (width) x 3.0 mm (thickness) were loaded under tension and oscillatory deformation with an amplitude of 10 μm, a frequency of 1 Hz and with a “force track” (ratio of static to dynamic force) of 108% applied. Samples were equilibrated and held isothermally at -40 °C for 20 min, then heated to 80 °C at a rate of 2 °C.min⁻¹. For comparison, the same experiments were conducted on 1/4 scale ASTM Type IV dogbone (ASTM D63) with a typical thickness of 1.0 mm. Tₖ and Tₘ were determined as the onset of tensile modulus drop. Shape programming (deformation) temperatures for subsequent shape memory testing were selected to be within the rubbery plateau regions of the storage modulus. Details of this shape memory characterization are explained below.

8.3.6 Wettability Study

Static contact angle measurements of foams and films were studied with a Rame-Hart 250-F1 standard goniometer. A droplet of water was placed on a clean, dry surface of the sample and the contact angle was immediately measured. For each compositional group, the experiment was replicated 3 times on 3 individual samples (total number measurements: 9). To analyze the effect of apparent modulus of the foam on contact angle, the same experiment was conducted for the D₁N₂J₁.₅PCL10 at RT and 40 °C at which the foam had stiff and rubber like characteristics, respectively. All samples were stored at RT for at least 48 h prior to testing.
8.3.7 Shape Memory Characterization

Both dual and triple shape memory properties of the composites were characterized with the same Q800 dynamic mechanical analyzer (DMA) mentioned above, but in “Force Control” mode. Two different fixing protocols with distinct thermomechanical histories were conducted, as we now explain.

8.3.7.1 One-Step Fixing Method

First, triple shape behaviour was explored using a single fixing method. A cylindrical disc sample was compressed to 20% strain at 65 °C (above both thermal transitions) by ramping the force at 0.1 N.min⁻¹. The sample was then cooled to −20 °C at 2 °C.min⁻¹ while holding the applied force constant to induce both PCL crystallization and epoxy vitrification. After an isothermal step of 5 min, the compression force was gradually unloaded at 0.1 N.min⁻¹ to the preload force (0.005 N) to fix the temporary shape. In the final step, the sample was heated to 80 °C, completing the shape memory (SM) cycle. This thermomechanical cycle was replicated 2 more times on the same sample to ensure reproducibility of the results. As a control experiment, shape memory behaviour of films in tension was explored.

8.3.7.2 Two-Step Fixing Method

For comparison, another shape memory cycle was designed utilizing two fixing steps, following a method developed by us previously. A cylindrical disc of the foam was heated to 65 °C and uniaxially compressed to a strain of 20%. While maintaining the compressive deformation, the sample was then cooled to -20 °C to promptly induce crystallization of the PCL-rich phase, immobilizing the chains and fixing the deformation. The PCL phase having been crystallized, the sample was then heated to an intermediate temperature above the T_g of epoxy (35 °C for
D1N2J1.5PCL10 and 10 °C for N2J1PCL10), further uniaxially compressed to a strain of 40% and fixed by cooling to -20 °C, upon which the epoxy-rich phase was vitrified. (As will be described in Results, the Tg and Tm of both composites are provided in Table 8-1.) For recovery of both fixed strains, the sample was heated continuously to 80 °C. This thermomechanical cycle was replicated two additional times on the same sample to ensure reproducibility of the results. The same protocol was applied to the films in tension mode.

The fixing ratios, Rf, and recovery ratios, Rr were quantified following equations:

\[ R_f(x) = \frac{\varepsilon_x}{\varepsilon_{x, \text{load}}} \]  \hspace{1cm} (8-1)

\[ R_r(x) = \frac{\varepsilon_x - \varepsilon_{x, \text{rec}}}{\varepsilon_x - \varepsilon_y} \]  \hspace{1cm} (8-2)

where \( \varepsilon_{x, \text{load}} \), \( \varepsilon_x \) and \( \varepsilon_{y, \text{rec}} \) represent the strain before and after unloading and the strain after recovery for shape x, respectively (x can be strain at 80 °C, 35 °C, 10 °C or -10 °C; the same holds for y). For strain at 80 °C, \( \varepsilon_c \) is simply the starting strain. For intermediate recovery, strains at two temperatures were calculated: one at 35 °C or 10 °C (35 °C for D1N2J1.5PCL10 and 10 °C for N2J1PCL10) and the other at the temperature where strain differentiation with respect to temperature (\( \text{d} \varepsilon / \text{d} T \)) was the lowest; i.e. the intermediate plateau.

To visually demonstrate the shape memory behaviour of the foam, a protocol similar to “Quantitative Shape Memory Characterization- Two Step fixing method” was used, as we now describe. A rectangular D1N2J1.5PCL10 foam was equilibrated at 80 °C in an isothermal oven for 10 min, sandwiched between two glass slides and compressed to ~70% strain. The sample was then immediately placed in a freezer at -17 °C, while holding the compressive force, and kept
isothermal for 10 min to fix the first temporary shape. To program the second temporary shape, the already compressed foam was heated to 40 °C, curled to a “C” shape, and placed in a freezer at -17 °C. For sequential recovery the sample was first heated to 40 °C triggering recovery of the 1st shape, followed by heating to 80 °C triggering recovery of the 2nd shape.

8.4 Results and Discussion

8.4.1 Foam Preparation

Highly porous, interconnected foams were fabricated as shown in the optical micrograph and SEM micrographs in Figure 8-2. SEM analysis of the cryofractured cross-sections of N2J1PCL10 and D1N2J1.5PCL10 foams in Figure 8-2(B) and Figure 8-2(C) reveals both foams have an interconnected porous architecture that is cuboidal in morphology. This cuboidal morphology is dictated by the cuboidal structure of the salt particles (Figure 8-1). The size and shape of the porous architecture can be therefore tuned by using porogens with different sizes and morphologies. The micrographs in Figure 8-2 also show the high porosity of the foams, which was determined to be ~73% by microtomography (Figure 8-3). Such high porosity enables high compressibility and shape change capability of the foams compared as characterized and discussed below.

8.4.2 Thermal Characterization

TGA thermograms of D1N2J1.5PCL10 and N2J1PCL10 are provided in Figure 8-4. The final weight fraction of both the film and the foam are the same in both compositions. Given that salt doesn’t degrade in the prescribed temperature range (as shown in Figure 8-5), this indicates that salt was completely extracted from the foam. DSC experiments were conducted to study the phase transition temperatures of the foams as discussed in what follows. Second heating DSC traces of
D1N2J1.5PCL10 and N2J1PCL10 as both foams and films are shown in Figure 8-6. Both compositions showed two well-separated transitions: a step-like transition at lower temperature followed by a sharp peak at higher temperature which correspond to the Tg of the epoxy-rich phase and the Tm of the semi-crystalline PCL phase, respectively. As a wide window in between two transitions is necessary for triple shape memory behavior, we were encouraged to observe this for both composites. The epoxy Tg increased as DGEBA was used in the formulation while the PCL melting transition remained relatively unaffected. This indicates that the PCL and epoxy phases are well separated from each other as explained previously in the section 8.3.2.2. The D1N2J1.5PCL10 foam exhibited a glass transition at 29.2 °C and a melting transition at 51.9 °C whereas the N2J1PCL10 foams showed a glass transition at 5.3 °C and a melting transition of 54.7 °C. Importantly, all composites featured a latent heat of fusion for PCL phase about 10 times smaller than that of pure PCL, indicating that the actual weight fraction of PCL in the composite is ~10% (DSC traces of neat D1N2J1.5, neat N2J1 and pure PCL are available in Figure 8-7).

Moreover, both the Tg of epoxy and the Tm of the PCL were observed to be slightly higher in the foam form when compared to films. We speculate this is due to slower heat transfer kinetics in the foams.

8.4.3 Dynamic Mechanical Analysis

To understand viscoelastic properties of the TSMCs and to provide perspective for the succeeding “Dual Shape” and “Triple Shape” SM cycles, dynamical mechanical analysis of each composite was conducted. Figure 8-8 shows the temperature dependence of storage modulus of the D1N2J1.5PCL10 and N2J1PCL10 composites for both foam and film forms. The corresponding loss tangent profiles are available in Figure 8-9. Both composites showed two transitions, which is in agreement with DSC results. Both foams (traces ii and iv) and films (traces i and iii) exhibited
high modulus plateaus at low temperature, followed by an intermediate plateau between the epoxy \( T_g \) and the PCL melting transition and finally a third rubbery plateau above the PCL \( T_m \), where the material exists as an epoxy rubber with an encapsulated liquid PCL phase. The two distinct transition temperatures observed by both DSC and DMA, along with three modulus-temperature plateaus observed by DMA were all prerequisites to achieve triple shape behaviour. We note that three modulus plateaus were not observed (only two were) for epoxy samples without PCL indicating dual SM properties as illustrated in Figure 8-10.

In comparing films with foams, we clearly in Figure 8-8 see that the apparent modulus of the foam is more than one order of magnitude lower than the film, a finding expected due to high porosity of the foam. Because of this lower modulus, the foams require significantly less force to be deformed and feature much higher compressibility relative to the film with the same composition. Table 8-1 summarizes the thermal properties of the composites determined by DSC (2\(^{nd}\) heating cycle) and DMA. The moduli of the composites at 20, 45 and 75 °C are reported in this table. In contrast to the \( N_2J_1PCL10 \) foam which is in the intermediate rubbery plateau at 20 °C with a storage modulus of 1.04 MPa, the \( D_1N_2J_{1.5}PCL10 \) foam is very stiff at 20 °C with a modulus of 50.1 MPa. Therefore, the \( D_1N_2J_{1.5}PCL10 \) foam is a better candidate to serve as a triple shape memory foam since it has both transitions above RT and the ability to fix the epoxy matrix phase and not recover at RT.

**8.4.4 Wetting Behavior**

Representative contact angle measurements and micrographs (and average contact angle) of for the SMP foams and films are provided in Figure 8-11. The \( D_1N_2J_{1.5}PCL10 \) film was found to feature a contact angle several degrees larger than the neat \( D_1N_2J_{1.5} \) film as reported in Figure 8-11(A) and Figure 8-11(B). This indicates that the epoxy/PCL composite has a moderate
hydrophobic surface that is more hydrophobic than neat epoxy yet less hydrophobic than PCL. The contact angle of the N1J2PCL10 film was also measured to be slightly higher than that of the neat N2J1 film, though both were significantly lower (more hydrophilic) than the DGEBA-based epoxy compositions (D1N2J1.5PCL10).

Interestingly, the D1N2J1.5PCL10 foam retained the water droplet on its surface while the water droplet permeated into the N2J1PCL10 foam in less than 30 s as shown in Figure 8-11(C) and 8-11(F), respectively. We interpret this finding as a result of the more hydrophobic DGEBA aromatic diepoxide making the composite relatively more hydrophobic. Even when heated above the Tg of the epoxy phase at 45 °C, water did not permeate into the rubbery D1N2J1.5PCL10 foam within our observation time of 20 min, as indicated in Figure 8-12. These results suggest that higher contact angle (hydrophobicity) of the D1N2J1.5PCL10 foam arose from higher hydrophobicity of chemical components rather than different mechanical properties of the foams at RT.

8.4.5 Quantitative Characterization of Triple Shape Memory Behaviour

The same DMA used above for viscoelastic property measurements was used under the “Control Force” mode to analyze the dual and triple shape memory behaviour of the foams. Figure 8-13 shows the results for the one-step fixing method for all films and foams. Starting at the point indicated with the asterisk (*) symbol, the foams were first uniaxially compressed to 20% strain at 65 °C, cooled to -20 °C and unloaded to fix the temporary shape. For recovery, the samples were then continuously heated to 80 °C at 2 °C min⁻¹. Both foams showed a two-step recovery revealing triple shape memory behaviour. The first broad recovery takes place as the foam is heated above the Tg of the epoxy followed by a second sharp recovery by heating above the PCL Tm. The onset points for both recoveries in the foams were located at slightly higher temperatures compared to the films. Moreover, the films showed a sharper 1st recovery compared to foams. Both of these
phenomena are again attributed tentatively to slower heat transfer in the foams associated with the open cell morphology, though we have no direct proof of that. It’s important to note that in absence of a phase (PCL) with a second transition the epoxy samples showed simple one step recovery events, starting at their $T_g$s, consistent with dual shape memory behavior (See Figure 8-14). Shape memory characterization revealed that both films and foams have repeatable shape memory responses as the three consecutive cycles overlap. This suggests that the pore walls in the foams bend yet do not break when subjected to compression, as the loading traces for each cycle are identical. The porous architecture dictates the type of pore wall deformation that occurs, as has been previously investigated for polyurethane-based shape memory foams$^{42,43}$. Given the porous architecture is not compromised during shape fixing or recovery, it can be expected that these foams would perform well cyclically under significantly more loading cycles.

To further characterize the triple shape memory behaviour of the foam, we developed a two-step fixing method, following a method introduced by Luo and Mather$^{28}$. The result of such triple shape memory testing is provided in Figure 8-15 for all foams and films. A circular disc of the foam was heated to 65 °C and uniaxially compressed to 20% while maintaining the compressive deformation, the sample was then cooled to -20 °C to induce crystallization of the PCL-rich phase, immobilizing the chains and fixing the deformation (for different modulus plateaus, refer to Figure 8-8). Each sample was then heated to approximately 35 °C for $D_1N_2J_{1.5}PCL10$ and 10 °C for $N_2J_1PCL10$, further compressed to 40% strain and fixed by cooling to -20 °C during which the epoxy-rich phase was vitrified. For recovery, each sample was heated continuously to 80 °C where the sample completely recovered to its original strain in a two-step fashion as the epoxy and PCL phases recovered sequentially. Such two step recovery of the sample during continuous heating indicates triple shape memory behavior with recovery from shape (A) to shape (B) (prescribed
during fixing) to shape (C). Without a second transition, neat epoxy samples, however, exhibited dual shape memory behaviour and were not capable of holding the second temporary shape as indicated in Figure 8-16. While a compressive strain of 40% was programmed for triple shape memory characterization, these foams are capable of fixing and recovering strains of 70% or greater, which may be necessary for biomedical applications where large expansion ratios are required.

Reported in Table 8-2 are the calculated fixing and recovery ratios of both composites as film and foam using the equation explained in the Section 8.3.7.2. All samples showed a good fixing of temporary shape (A). However, the fixing of temporary shape (B) in both foams were higher than the corresponding films. A simple explanation exists: For these experiments, we selected common unloading temperatures of 10 °C (lower T_g epoxy) and 35 °C (higher T_g epoxy) to examine the fixing of shape B for both films and foams. With the films recovering slightly at this temperature (due to lower recovery temperature) they were observed to feature a lower fixing degree. Had we selected lower unloading temperatures for the films, the observed fixing of shape B would have been higher. However, we opted to keep the conditions constant between the two types of samples. The fixing ratios—how much of the programmed deformation is maintained upon unloading—were above 99% for the foams. Recovering ratios—how much of the programmed deformation was recovered upon heating—were also above 99% for the foams. Such high fixing and recovery ratios indicate outstanding ability of the foam to deform to 2 separate shapes and recover upon heating. To our knowledge, these are the highest fixing and recovery ratios for triple shape memory foams reported in literature.

To visually demonstrate the triple shape memory behaviour of the foam, a rectangular piece of D1N2J1.5PCL10 foam (with dimensions of 22.4 mm (length) x 5.3 mm (width) x 3.8 mm
(thickness)) was equilibrated at 80 °C in an isothermal oven for 10 min, sandwiched between two glass slides and compressed to ~70% strain. The sample was then immediately placed in a freezer at -17 °C to fix the 1st temporary shape. The compressed foam was deformed to a “C” shape at 35 °C and again cooled to -17 °C to fix the 2nd temporary shape. Figure 8-17 shows triple shape recovery of the sample uncurling from the 2nd temporary shape (shape (A)) to the 1st temporary shape (shape (B)) after heating to 40 °C and then expanding to the permanent shape (shape (C)) after heating to 80 °C.

8.5 Conclusions

We have designed, fabricated, and tested a new family of epoxy-based foams featuring triple shape memory behaviour using a simple, inherently scalable method. Two high porosity foams with drastic differences in hydrophobicity and mechanical properties at RT were fabricated and characterized. Both foams exhibited two well-separated transitions which are attributed to the T_g of epoxy-rich phase followed by the T_m of the PCL-rich phase. Wetting characteristics pertinent to medical applications were quite distinct among the compositions, with DGEBA-based epoxies being more hydrophobic. Dual and triple shape memory characterization of the foams revealed excellent capability of fixing two independent temporary shapes and sequentially recovering upon heating. Given the simplicity of fabrication of the composites and low costs/good mechanical properties of the foams, we envision mass production of the foams for applications spanning healthcare, aerospace, and packaging industries where geometrically complex actuation may be required.
8.6 Future Work

8.6.1 Foam porosity

As discussed earlier, the size and shape of the porous architecture and therefore the overall porosity of the foams can be tuned by using porogens with different sizes and morphologies. The effect of foam porosity and cell geometry on thermomechanical and SM properties of the foams remains a subject of future work. Salt particle size range for the template can be varied anywhere between 100 to 1000 µm range changing the porous structure and consequently thermomechanical behaviour of the foam.

8.6.2 Heat Transfer in Foams

We showed that all composites featured a latent heat of fusion for PCL phase about 10 times smaller than that of pure PCL, indicating that the actual weight fraction of PCL in the composite is ~10% in DSC. Moreover, both the $T_g$ of epoxy and the melting transition of the PCL were observed to be slightly higher in the foam form when compared to films. We speculate this is due to slower heat transfer kinetics in the foams which requires further investigation. The effect of DSC heating rate on apparent transition temperatures of the foams compared to films can reveal some insights into heat transfer kinetics of the foams. Also, mathematical modeling can be utilized to compare the heat transfer in between foams and films.

8.7 References

(1) Xie, T.; Rousseau, I. A. Facile tailoring of thermal transition temperatures of epoxy shape memory polymers. Polymer 2009, 50, 1852-1856.


(12) Yakacki, C. M.; Gall, K.: Shape-memory polymers for biomedical applications. In *Shape-Memory Polymers*; Springer, 2010; pp 147-175.


Figure 8-1. SEM micrographs of NaCl templates used to fabricate the foams. To improve pore interconnectivity, salt was fused prior to polymer synthesis, as we now describe. About 6 g of salt with 150-300 μm diameter was added to a 20 ml high density polyethylene (HDPE) vial. The vial was then placed in a Styrofoam box (9.25 x 6.25 x 8.25 in) with the lid off in which a 2 L water at 40 °C was placed to provide a humidity saturated environment. The salt was kept in Styrofoam for 24 h during which the humidity of this chamber facilitates the fusion of the salt. The salt was then dried under light vacuum at RT for 24 h. Dashed lines represent some of the regions where salt crystals were welded together. Scale bar is 500 μm.
Scheme 8-1. Step-by-step illustration for preparing the triple shape memory composites. Epoxy monomers and PCL were first mixed at 75 °C for 20 min until a clear, homogenous blends was achieved (A). Then the blend was cooled down to room temperature (RT) after which the crosslinker (JD230) was added (B). The blend was mixed again for another 2-3 min. The product, a low viscosity blend was then poured into a salt template (C) and was kept at ambient for 10 min followed by pulling light vacuum for an additional 10 min in to allow the blend to completely diffuse into the salt template and replace the air. The product was then cured at RT for 24 h followed by curing at 40 °C for 3 days after which the salt was distracted. After drying, the product was a porous interconnected foam (G).
Figure 8-2. Optical micrograph and SEM micrograph of cryofractured (A, B) N$_2$J$_1$PCL10 and (C) D$_1$N$_2$J$_{1.5}$PCL10 foam cross section. Both foams have an interconnected porous architecture that is cuboidal in morphology. This cuboidal morphology is dictated by the cuboidal structure of the salt particles (See Figure 8-1). Scale bars represent 1.0 mm.
Figure 8-3. Representative MicroCT image of a triple shape memory foam. Such high porosity enables high compressibility and shape change capability of the foams. To obtain the image, a 6.0 mm diameter and 9.0 mm thick disc was scanned using a Scanco Medical μCT40 scanner at voltage of 45 kV and current of 177 μA. Scanning parameters led to a nominal voxel resolution of 12 μm. Porosity of the foam was obtained to be about 73%. Scale bar represents 1.0 mm.
Figure 8-4. Thermogram traces of (-) D\textsubscript{1}N\textsubscript{2}J\textsubscript{1.5}PCL10 film, (--) D\textsubscript{1}N\textsubscript{2}J\textsubscript{1.5}PCL10 foam, (-) N\textsubscript{2}J\textsubscript{1}PCL10 film and (--) N\textsubscript{2}J\textsubscript{1}PCL10 foam. The remaining weight % of each film and foam group are almost identical indicating successful extraction of salt.
Figure 8-5. Thermogram traces of (-) D_{1N2J_{1.5}} film, (-), (-) N_{2J_{1}} film, (-) PCL and (-) NaCl template. The salt thermograms stays at 100 % indicating its stability over the temperature monitoring range.
Figure 8-6. DSC thermograms (2nd heating cycle) of (i) D₁N₂J₁.₅PCL10 film, (ii) D₁N₂J₁.₅PCL10 foam, (iii) N₂J₁PCL10 film and (iv) N₂J₁PCL10 foam. Both compositions showed two well-separated transitions: a step-like transition at lower temperature followed by a sharp peak at higher temperature which correspond to the T_g of the epoxy-rich phase and the melting transition of the semi-crystalline PCL phase, respectively. Heating rates were 10 °C min⁻¹ and 5 °C min⁻¹ for heating and cooling, respectively.
Figure 8-7. DSC thermograms (2\textsuperscript{nd} heating cycle) of (i) D\textsubscript{1}N\textsubscript{2}J\textsubscript{1.5} film, (ii) N\textsubscript{2}J\textsubscript{1} film and (iii) PCL.

It is noted that the heat flow magnitude of the DSC thermogram for PCL was scaled down 5 times. Heating rates were 10 °C\textsuperscript{min}\textsuperscript{-1} and 5 °C\textsuperscript{min}\textsuperscript{-1} for heating and cooling, respectively.
Figure 8-8. Tensile storage modulus (E’) traces of (i) D$_1$N$_2$J$_{1.5}$PCL10 film, (ii) D$_1$N$_2$J$_{1.5}$PCL10 foam, (iii) N$_2$J$_1$PCL10 film and (iv) N$_2$J$_1$PCL10 foam. Both foams (traces ii and iv) and films (traces i and iii) exhibited high modulus plateaus at low temperature, followed by an intermediate plateau between the epoxy T$_g$ and the PCL melting transition and finally a third rubbery plateau above the PCL Tm, where the material exists as an epoxy rubber with an encapsulated liquid PCL phase.
Figure 8-9. Tan Delta traces of (i) D$_1$N$_2$J$_{1.5}$PCL10 film, (ii) D$_1$N$_2$J$_{1.5}$PCL10 foam, (iii) N$_2$J$_1$PCL10 film and (iv) N$_2$J$_1$PCL10 foam.
Figure 8-10. Tensile storage modulus (E’) traces of (-) D$_1$N$_2$J$_{1.5}$ film and (-) N$_2$J$_1$ film. Samples go through only one transition temperature in the absence of PCL.
Table 8-1. Summarized thermomechanical properties determined from DSC and DMA experiments. Glass transition and melting transition were determined as the middle point of the step transition and the melting peak transition of the DSC second heating runs, respectively. In DMA, glass transition and melting transition were determined as the onset of tensile modulus drop.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)$^a$</th>
<th>$T_g$ (°C)$^b$</th>
<th>$T_m$ (°C)$^a$</th>
<th>$T_m$ (°C)$^b$</th>
<th>$\Delta H_{m,PCL}$ (J/g)$^a$</th>
<th>$E_{@20^\circ C}$ (MPa)$^b$</th>
<th>$E_{@45^\circ C}$ (MPa)$^b$</th>
<th>$E_{@75^\circ C}$ (MPa)$^b$</th>
</tr>
</thead>
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<tr>
<td>D$<em>2$N$</em>{2.15}$PCL10 Foam</td>
<td>29.2</td>
<td>29.1</td>
<td>55.1</td>
<td>60.6</td>
<td>5.0</td>
<td>51.0</td>
<td>0.54</td>
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<td>54.9</td>
<td>5.9</td>
<td>847.0</td>
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<td>0.7</td>
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<td>53.7</td>
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<td>14.4</td>
<td>7.94</td>
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<td>--</td>
<td>821.4</td>
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<td>1.86</td>
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<td>--</td>
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<td>0.71</td>
<td>0.75</td>
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<td>PCL</td>
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<td>--</td>
<td>55.1</td>
<td>--</td>
<td>59.1</td>
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$^a$ Determined from DSC

$^b$ Determined from DMA

--: Not applicable
Figure 8-11. Representative contact angle micrographs (and average contact angle) of (A) D$_1$N$_2$J$_{1.5}$PCL10 film, (B) D$_1$N$_2$J$_{1.5}$ film, (C) D$_1$N$_2$J$_{1.5}$PCL10 foam, (D) N$_2$J$_1$PCL10 film, (E) N$_2$J$_1$ film and, (F) (D) N$_2$J$_1$PCL10 foam. Water permeated into N$_1$J$_2$PCL10 foam in less than 30 s.
Figure 8-12. Representative contact angle micrograph of (A) D\textsubscript{1}N\textsubscript{2}J\textsubscript{1.5}PCL10 foam at RT, (B) D\textsubscript{1}N\textsubscript{2}J\textsubscript{1.5}PCL10 foam at 45 °C and (C) D\textsubscript{1}N\textsubscript{2}J\textsubscript{1.5}PCL10 foam after 20 min at 45 °C. Even when heated above the T\textsubscript{g} of the epoxy phase at 45 °C, water did not permeate into the rubbery D\textsubscript{1}N\textsubscript{2}J\textsubscript{1.5}PCL10 foam within our observation time of 20 min indicating hydrophobic characteristics of composites arising from higher hydrophobicity of chemical components rather than different mechanical properties of the foams. Scale bar represents 1.0 mm.
Figure 8-13. Triple shape memory characterization of (A) $D_1N_2J_{1.5}$PCL10 foam, (B) $D_1N_2J_{1.5}$PCL10 film, (C) $N_2J_1$PCL10 foam and (D) $N_2J_1$PCL10 film using one-step fixing method. The beginning of the cycles are marked by the asterisk (*) symbol. Samples were deformed at 65 °C (deformation), cooled to -20 °C and unloaded (fixing), followed by continuous heating to 80 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) fixing, (3) unloading, and (4) recovery.
Figure 8-14. Triple shape memory characterization of (A) D$_1$N$_2$J$_{1.5}$ film and (B) N$_2$J$_1$ film using one-step fixing. The beginning of the cycles are marked by the asterisk. Samples were deformed at 65 °C (deformation), cooled to -20 °C and unloaded (fixing), followed by continuous heating to 80 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) fixing, (3) unloading, and (4) recovery. One step recovery of both samples indicate dual shape memory behavior.
Figure 8-15. Triple shape memory characterization of (A) D$_1$N$_2$J$_{1.5}$PCL10 foam, (B) D$_1$N$_2$J$_{1.5}$PCL10 film, (C) N$_2$J$_1$PCL10 foam and (D) N$_2$J$_1$PCL10 film using a two-step fixing method. Samples were deformed at 65 °C, cooled to -20 °C and unloaded (1st fixing), heated to an intermediate temperature and deformed again, cooled to -10 °C (2nd fixing), followed by continuous heating to 85 °C (recovery). The beginning of the cycles are marked by the asterisk (*) symbol. The arrows denote the various stages of a shape memory cycle; specifically (1) deformation, (2) 1st fixing, (3) 1st unloading, (4) 2nd fixing, (5) 2nd unloading, and (6 and 7) recovery.
Figure 8-16. Triple shape memory characterization of (A) D$_1$N$_2$J$_{1.5}$ film and (B) N$_2$J$_1$ film using a two-step fixing method. Samples were deformed at 65 °C, cooled to -20 °C and unloaded (1$^{st}$ fixing), heated to an intermediate temperature and deformed again, cooled to -10 °C (2$^{nd}$ fixing), followed by continuous heating to 85 °C (recovery). The beginning of the cycles are marked by the asterisk. The arrows denote the various stages of a shape memory cycle; specifically (1) deformation, (2) 1$^{st}$ fixing, (3) 1$^{st}$ unloading, (4) 2$^{nd}$ fixing, (5) 2$^{nd}$ unloading, and (6 and 7) recovery. In both cases, sample completely recovered after heating to an intermediate temperature indicating dual shape memory properties of epoxy films.
Table 8-2. Fixing and recovery ratios calculated using one-step and two-step shape memory cycles to demonstrate the triple-shape memory. --: Not applicable.

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<th>Sample</th>
<th>Fixing Method</th>
<th>$R_f(a)%$</th>
<th>$R_f(b)%$</th>
<th>$R_r(a \rightarrow b)%$</th>
<th>$R_r(b \rightarrow c)%$</th>
<th>$R_r(a \rightarrow c)%$</th>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>99.1</td>
</tr>
<tr>
<td></td>
<td>Two Step</td>
<td>97.0</td>
<td>103.8</td>
<td>1.9 @35 °C</td>
<td>99.4</td>
<td>99.7</td>
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<tr>
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<td>--</td>
<td>--</td>
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<td></td>
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<td>64.3</td>
<td>70.1 @35.0 °C</td>
<td>86.3</td>
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**Figure 8-17.** Triple Shape memory demonstration experiment showing: (A) permanent shape at RT, (B) compressed to 75% at 80 °C strain and fixed (C) curled to a “C” shape at 40 °C and fixed, (D) recovered at 40 °C and, (E) recovered at 80 °C. Top and bottom rows show top and side views, respectively. All scale bars represent 1 cm.
VITA

NAME OF AUTHOR: Hossein Birjandi Nejad

PLACE OF BIRTH: Tehran, Iran

DATE OF BIRTH: September 18th, 1987

EDUCATION

B.S. in Chemical Engineering, Tehran University (2010)

Ph.D. in Bioengineering, Syracuse University (2010 to present)

INVENTION DISCLOSURES


PUBLICATIONS


4. H.B. Nejad and P.T. Mather, “Analysis of Polymerization Induced Phase Separation (PIPS) in a Thermoplastic/Thermoset Blend”, Submitted to *TA instruments*

