

EFFECT OF GRAPHENE OXIDE CONTENT AND LITHIUM
SALT ON THE PHASE SEPARATION BETWEEN POLY
(ETHYLENE GLYCOL) AND EPOXY IN A BINARY MIXTURE
FOR OPTIMIZING MULTIFUNCTIONAL PERFORMANCE
IN A POLYMER ELECTROLYTE

By

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Abstract: Structural supercapacitors represent a promising technology that will help in mitigating range anxiety while providing structural integrity to electric vehicles. Poly (ethylene glycol) (PEG), the ionic component of structural supercapacitor, is responsible for providing percolating channels for ion transfer. The formation of a percolating network of PEG inside epoxy resin is the result of cure-reaction induced phase separation (CRIPS) that occurs at curing temperature due to spinodal decomposition. Various nanofillers have been explored (organoclay, TiO_2 nanoparticles, and LLZO) that enhance the ionic conductivity while improving the mechanical properties. Graphene oxide is a promising nanofiller that has the ability to improve the ionic conductivity due to the presence of its oxygen-rich functional groups on its basal plane, and also provides excellent mechanical properties. It is imperative to understand the effect of graphene oxide on the formation of percolating channels, since the percolating ionic channels will directly impact the ionic conductivity of the structural supercapacitor. This study explores the effect of change in weight percentage of graphene oxide and how it affects phase separation. Graphene oxide content is varied from (0 to 0.7 weight percentage with respect to PEG) to study how phase separation between PEG and epoxy is affected. Scanning electron microscopy (SEM) images show promising results suggesting a decrease in pore diameter as amount of graphene oxide is increased, that will enhance the mechanical and electrical properties. By varying the amounts of graphene oxide, we are able to achieve an electrolyte that provides optimal multi-functional performance. Detailed study on the effect of graphene oxide in percolating PEG network in tailoring of mechanical and ionic conductivity properties will be presented and discussed.

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CHAPTER I

INTRODUCTION

Carbon fiber reinforced epoxy-based composites have many advantageous aspects in regards to multi-functional materials, as they can be lightweight and provide high structural performance[1]. Carbon fibers are also electrically conductive and readily intercalate lithium ions, or serve as electrodes for composite energy storage devices[2, 3]. In this application the carbon fibers bear the responsibility to serve as electrodes and provide rigidity for load-bearing applications. Much research has been dedicated to developing a structural energy storage system that is light weight, mechanically robust, and provides sufficient ionic conductivity for large scale operations[4]. To achieve this multifunctionality, the carbon fibers are embedded in the electrolyte and the fibers serve as the electrodes and structural reinforcement [5].

A structural supercapacitor should have sufficient mechanical performance to be a part of the structure and not only contribute to energy storage[2, 3, 6]. The electrolyte must serve as the matrix, and must be able to adhere to the carbon fiber and be ionically conductive. Such composite energy storage devices include composite batteries and structural supercapacitors, and are a more environmentally-friendly and efficient way for storing energy[7]. Figure 1 is a schematic representation of a structural supercapacitor. The main issue in regards for developing an effective solid-state polymer electrolyte is that mechanical robustness and ionic conductivity remains to have an inverse relationship[8].

To address these issues, numerous methods have been proposed to achieve high ionic conductivity without sacrificing the mechanical properties of the electrolyte[9, 10, 11]. These include implementing fillers, using an epoxy-based polymer electrolyte, plasticizers and using

a two polymer system in which one polymer is providing ionic conductivity and the other polymer is for structural rigidity.

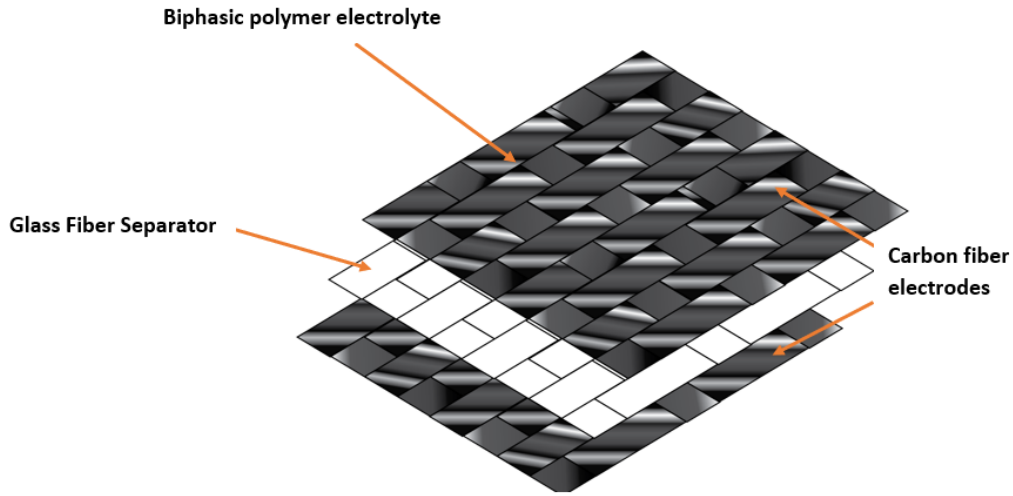


Figure 1: Structural Supercapacitor

1.1 Polymer electrolytes for composite energy storage devices

In early studies, poly (ethylene oxide) (PEO) was found to be able to coordinate lithium ions due to its ether oxygen (EO) repeating unit[12, 13]. Shortly thereafter, the first solid polymer electrolyte (SPE) membrane was formed based on a PEO-Lithium salt for an all solid-state battery film [14]. Since this discovery, much research has been dedicated to finding a suitable polymer regarding ionic conductivity.

Many polymers have been used in developing a suitable electrolyte for electrochemical devices. These include PEO, poly (vinylidene fluoride), poly (methyl methacrylate), poly (vinyl alcohol), poly (vinyl chloride), and poly (acrylonitrile). However, PEO-based solid polymer electrolytes (SPE) have a high dielectric constant, availability, ease of processing, and excellent chemical and thermal stability[15]. SPE also have good mechanical performance, thermal stability, prevent leakage, long shelf life and low flammability[5]. However, PEO has insufficient ionic conductivity for structural supercapacitor (SSC) applications at ambient temperature. This is due to the crystallization of PEO at ambient temperature

which hinders ion transport and results in lower ionic conductivity values[16]. Thus, the incorporation of plasticizers, nanofillers, and polymer blending into a PEO matrix to increase the properties have been widely investigated.

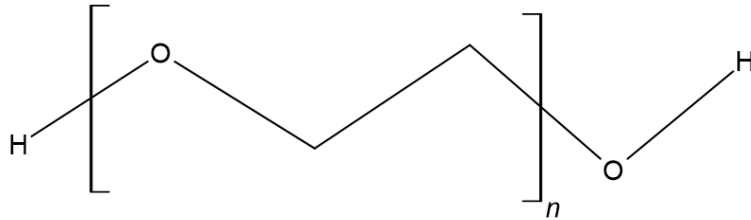


Figure 2: PEG repeating monomer unit

Gel polymer electrolytes (GPE) have many advantages such as the diffusive or ionic properties of liquid electrolytes, but also have the adhesive properties of SPE[17]. They possess high ionic conductivity and address the safety issues such as flammability and leakage that come with liquid electrolytes. The most common way of processing a GPE is heating a polymer matrix like PEO, and a lithium salt with appropriate solvent[16]. However, while it's very easy to process and has several characteristics that make it a potential candidate for SSC applications there is some drawbacks. One of the main issues is relatively poor mechanical strength for larger practical use due to the need to be plasticized by a solvent[18]. Insufficient mechanical strength can not only need to poor load-bearing applications, but also cannot handle the stress between the anode and cathode[19].

To achieve multifunctional performance from a polymer electrolyte, a one polymer system lacks either the mechanical or ionic properties for a structural supercapacitor. A polymer electrolyte consisting of a liquid ionic component and a structural polymer allows for multifunctional performance of high conductivity with structural rigidity. However, to achieve the aforementioned properties listed above, the binary polymer system needs to be in two separate phases in a bi-continuous interconnecting network. This allows for ion transporting pathways that can diffuse through a non conductive network, and the structural polymer to still adhere to the carbon fiber.

One of the first polymer electrolytes for SSC applications that contained an ionic liquid highly conductive phase, and a structural epoxy phase was found to phase separate[20]. They found that a bi-continuous morphology was important due to the conductive ionic liquid pathways that interpenetrated through the mechanically robust cross-linked epoxy network. Many other electrolytes have been formed using this formation of an ionic liquid and epoxy[21, 20, 22, 23, 24]. A system between low molecular weight poly (ethylene glycol) (PEG 200) and a DGEBA epoxy resin was found to be able to phase separate in a continuous network at above 30% volume PEG[10]. However, increasing PEG content was found to be detrimental to the mechanical rigidity of the electrolyte, and only at higher amounts were the ionic channels fully percolated to achieve optimal conductivity. It was also found out that PEG molecular weight of 8000 and an epoxy system were found to be completely compatible up to 30% weight PEG, and after that composition they were in two separate phases[25]. Researchers found that mixing two different molecular weights of PEG with epoxy proved to be promising for SSC applications[26]. They decided on blending PEG 2000 with PEG 600 for increasing the crystalline region for improving mechanical performance.

1.2 Epoxy resin

Epoxy resin is a commonly used thermosetting polymer that has excellent mechanical and thermal properties, and is very common in many structural applications. Most epoxy polymers come with a hardening agent (typically a diamine) that is able to cross-link with the epoxide ring, resulting in a brittle, very tough polymer. Epoxy resin systems can also adhere well to carbon fiber, and is a very common matrix in many composite materials[27]. These properties make it an excellent candidate for solid-state polymer electrolyte for an electrical double layer capacitor (EDLC).

However, even though epoxy has several promising characteristics for SSC applications it has negligible ionic conductivity[21]. It was found that due to the high cross-linking of epoxy enhanced the mechanical properties of the electrolyte, but suppressed the ion transportation

activity[28]. To counteract the negligible ionic conductivity for SSC applications, research has been done to blend a separate polymer or liquid electrolyte high in conductivity in an epoxy matrix[20]. However, the ionic component or polymer needs to be able to phase separate and create ionic channels that are fully percolated throughout the non-conductive epoxy matrix[10].

To create the phase separation that is necessary for optimal ionic conductivity, the binary polymer mixture during cross-linking reaction will phase separate. During cross-linking the molecular weight of the polymer mixture increases resulting in the polymers to become immiscible. This is known as curing reaction induced phase separation (CRIPS)[29]. For better performance of the polymer electrolyte it was found that the polymers need to be miscible before the cross-linking reaction occurs so gross phase separation doesn't take place [5]. Low molecular weight PEG (200) was found to be able to phase separate from an epoxy system during curing reaction by spinodal decomposition [30]. Various factors also influence the way phase separation occurs in binary thermosetting polymer mixtures and include: composition, curing temperature, viscosity and chemical components between the species[31]. These bicontinuous structures provide better overall multifunctional performance of both ionic and mechanical properties.

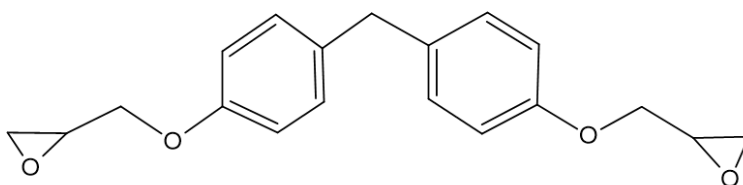


Figure 3: Diglycidyl Ether of Bisphenol F

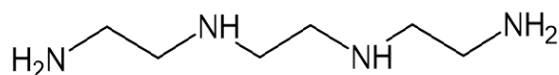


Figure 4: Low aliphatic diamine curing agent

1.3 Various fillers for polymer electrolyte

Adding various fillers into a PEO-based polymer electrolyte has been shown to be an effective way in increasing the properties of the electrolyte[32]. However, most research has been relegated into implementing inorganic (ceramic) fillers into a SPE or GPE membrane. The addition of nanofillers can simultaneously improve the mechanical and conductive properties of the electrolyte.

Various nanofillers have been implemented in regards for improving the properties of epoxy and PEO based SPE. It was found that titania nanoparticles were implemented in an epoxy-ionic liquid SPE and that the properties were improved[11]. However, they reported a single-phase material and not a biphasic one indicating no phase separation took place.

It is well known that the performance and mechanical properties of an immiscible polymer blend is dependant upon their phase morphology[33]. Incorporating nanofillers in an immiscible thermosetting polymer blend have been shown to have an impact on the final phase morphology of this system [34, 35]. Thus, it is imperative to have an understanding of how incorporating a nanofiller has an affect on the final morphology of an immiscible thermosetting polymer blend.

Incorporating nanofillers in an biphasic epoxy-based polymer electrolyte has been shown to be an effective way to control the final morphology, and for tailoring the microstructure for improving both mechanical and ionic properties[22, 23, 26]. Inorganic Al_2O_3 nanowires were found to improve both mechanical and ionic properties when implemented if the particles were will dispersed in the polymer matrix[23]. One study showed that implementing organoclay into an ionic liquid epoxy based electrolyte found that organoclay content had an affect on the final morphology once cured[22]. Based on the final morphology, the electrolyte properties were changed. Nano silica was found to have to create more ion conducting pathways in a PEG epoxy-based electrolyte[26]. However, when more pathways were created a significant drop in mechanical properties was observed.

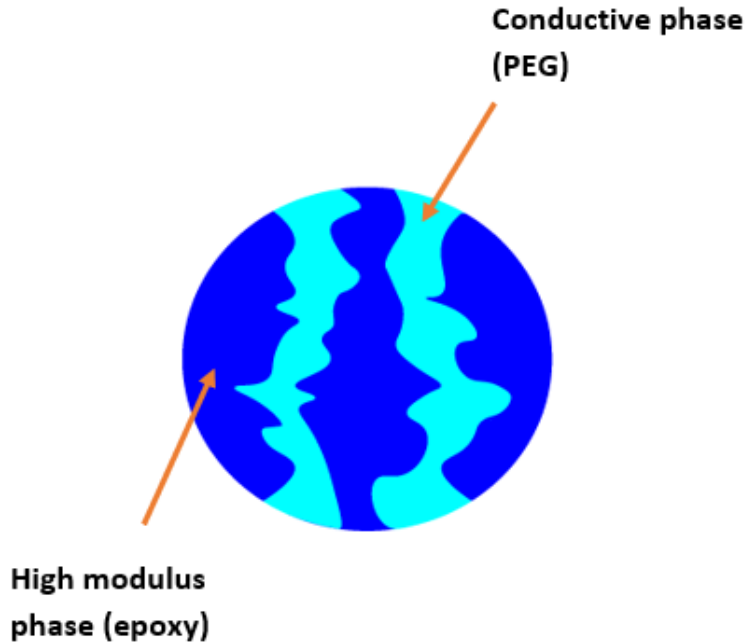


Figure 5: Biphasic structure

1.4 Phase separation

Phase separation in polymer blends is a thermodynamic process in which the gibbs free energy of mixing is positive, and is usually driven by either a change in temperature or molecular weight. Most thermoplastic polymers are initially miscible before curing reaction of the thermosetting polymer, and once cross-linking reaction begins the thermoplastic polymer is phase separated throughout the epoxy matrix[36]. This is known as reaction-induced phase separation, and phase separation occurs until the epoxy reaches its gelation point[37]. Thus, the final morphology of the specimen is highly dependant between the phase separation versus the cross-linking reaction[38]. Figure 4 is a schematic representation of phase separation using a thermoplastic polymer (PEG) and thermosetting polymer (epoxy). Since the final phase structure determines the properties of the final mixture, it is important to understand what impacts the final phase morphology to optimize the electrolytes properties.

1.5 Graphene oxide

Graphene oxide has been the subject of much research especially in polymer composites due to its excellent thermal, electrical, and mechanical properties[39]. Graphene oxide (GO) is a two-dimensional lamellar structure much like its derivative graphene, and contains a large specific surface area that can increase the interfacial interaction effect with the polymer [40].

GO also has oxygen-containing functional groups that as a result make it have increased interlayer distance between the sheets causing it to be packed more loosely. General consensus regarding the GO structure is that the hydroxyl (-OH) and epoxy groups (-COC) are located within the basal plane, and that the carboxylic acid groups (-COOH) exist on the sheet edges[41]. These oxygen-rich functional groups can help provide dissociation of lithium ions which can promote more lithium ions for coordination [42]. It was also found that GO can promote continuous ion channels which can improve the ionic conductivity[9].

GO was also found to act as a plasticizer, or lower the glass transition temperature (T_g) in a PAN-LiCLO₄ based solid flexible polymer electrolyte[43]. GO was found to decrease crystallinity in PEO-based polymer membranes which resulted in an increase in conductivity due to enhanced polymer chain mobility[44]. Due to its unique characteristics, developing an optimal strategy of dispersing the nano-sheets of GO is crucial in enhancing its properties in a thermo-setting polymer matrix.

Due to its large surface area and strong Van der Waals forces between the sheets, could lead to severe aggregations embedded in the polymer matrix that will limit the performance of nanocomposites[45]. Commonly used as a filler for epoxy, it was also found that the dispersion techniques of bath sonication and shear-mixing lead to an enhancement of both its thermal and mechanical properties for a polystyrene/GO nanocomposite[46]. GO at low filler content was also found to improve the T_g of epoxy nanocomposites[47]. However, longer sonication times can potentially damage the oxygen containing functional groups, and damage the filler itself hindering its performance.

Since much research has been dedicated to the improvement of ionic and mechanical

properties of a PEO based electrolyte with incorporating GO, and the improvements that GO has with the thermal and mechanical properties when well dispersed within an epoxy matrix. It is imperative to understand how GO effects the final morphology of an epoxy-based polymer electrolyte. GO was found to have an impact on the microstructure of a DGEBA/PEI system that followed spinodal decomposition phase separation during curing reaction of the epoxy system[48].

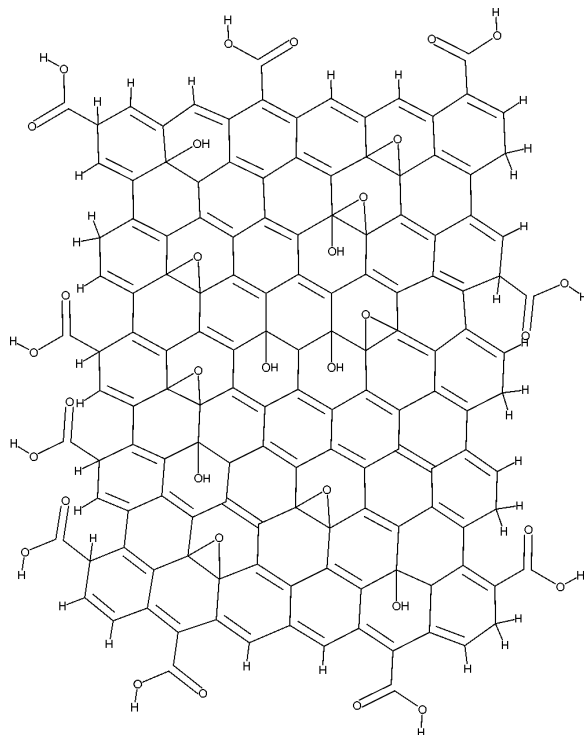


Figure 6: Graphene oxide structure

1.6 Motivation for this study

The goal of this research is to understand how increasing GO content affects phase separation between PEG and epoxy, and how it has an impact on the electrolyte's ionic and mechanical properties. Having a proper understanding of how GO impacts the final microstructure will affect the final ionic and mechanical properties. Since it has been well established that ionic conductivity and mechanical rigidity have an inverse relationship, GO is a promising nanofiller that can provide simultaneous improvement of the electrolyte's properties. The

results so far in using GO for either epoxy-based nanocomposites and PEO based SPE have shown improvements in thermal, mechanical, and ionic properties. However, no research has been done in implementing GO as a nanofiller in a PEO epoxy-based polymer electrolyte for SSC applications.

Here we propose GO not only for its thermal, mechanical, and electrical properties, but also incorporating its use for tailoring the microstructure for optimizing the performance of the electrolyte. The morphology of the specimen will be examined using scanning electron microscopy (SEM), and will show how GO has an affect on phase separation. Visually examining the morphology allows for an idea of how well GO is dispersed at higher contents. Mechanical characterization will be done using Instron 5567 using ASTM D695 as the standard for compressive properties of rigid plastics. By examining the microstructure and relating it to the compressive mechanical characterization tests, a better understanding of how GO content impacts the overall properties of the electrolyte. The results so far have shown us that GO can be used as an effective nanofiller for an epoxy-based polymer electrolyte that exhibits a biphasic structure for SSC applications.

CHAPTER II

EXPERIMENTAL

2.1 Materials and methods

All chemicals were used as received unless otherwise stated. PEG with an average molecular weight (600) which was purchased from Acros Organics™ (Geel, Belgium). Graphene oxide was obtained from Nanoshel® UK LTD (Wilmington, Delaware). The epoxy resin which was used in this study is EPON™ Resin 862 and EPIKURE™ Curing Agent 3724 were supplied by Miller-Stephenson (MillerStephenson, Danbury, Connecticut).

PEG was weighed and added into a clean beaker, and heated to 30°C until it became a liquid. GO was then weighed from 0.1-0.7% with respect to PEG (0.021-0.143g), and added into the liquid PEG. To ensure we achieve a uniform dispersion of GO in PEG the following steps were taken [8]: The PEG and GO mixture were stirred vigorously using magnetic stir for approximately one hour. Shear mixing (ULTRA-TURREX® T 25 basic) is then followed at 11,000 rpm for five minutes. While shear mixing, the PEG/GO mixture was kept in an ice bath to avoid overheating that could potentially damage the functional groups of GO as shown in figure 7. The last step for proper dispersion of GO was bath sonication (VWR® Model 75D) for 30 minutes.

Epoxy was then poured into a separate beaker, and mixed with the hardening agent in a 5:2 ratio. The epoxy mixture was then degassed to remove the bubbles caused by hand mixing. The PEG/GO ionic component was then poured into the epoxy/hardener structural component, and were mixed by magnetic stir for approximately 45 minutes to ensure a homogeneous mixture. The electrolyte was then degassed and poured into a silicone mold

to cure at 60°C in a vacuum oven (Across International) for 24 hours, as shown in figure 8.

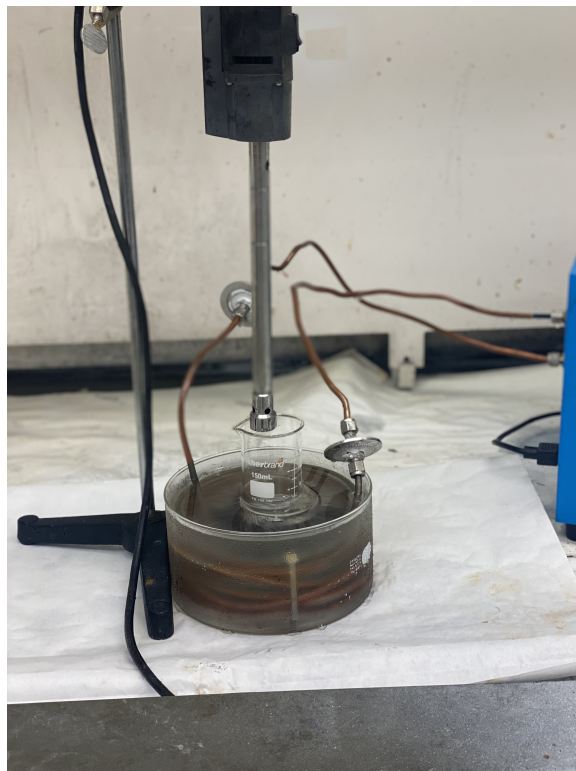


Figure 7: Shear-mixing ice bath setup

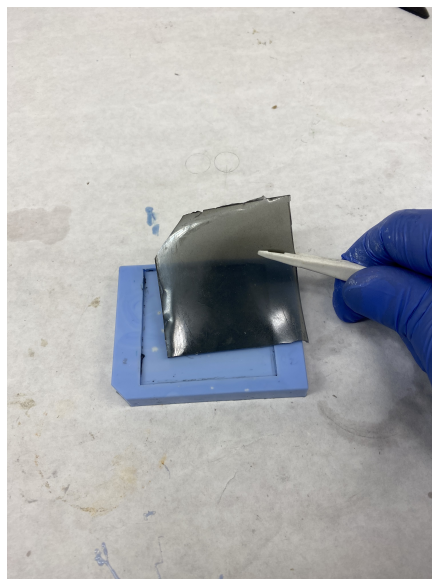


Figure 8: Cured 50:50 sample with graphene oxide

2.2 Physical and mechanical characterization

After the sample is completely cured, a 4.8 mm (3/16") diameter cutting tool was used to cut five circular samples. The initial weight was taken and the samples were placed in a 50:50 water-alcohol solution, and then bath sonication (power level 3) was used for 2 hours. Once bath sonication was complete, the cut samples were then submersed in water for a minimum of 16 hours. The specimens were then placed in a vacuum oven until the mass of the samples were constant and no more weight loss was recorded.

The specimens were then sputtered (Leica EM ACE600) with Iridium Han for 120 seconds. The scanning electron microscope (Hitachi S-4800) was used. The accelerating voltage was set to 15 kV and the emission current was set at 10 μ A.



Figure 9: Hitachi S-4800 FE-SEM

The SPE was made using the same ratios and procedure as previously mentioned, and was prepared for mechanical characterization. ASTM D695 was used for characterizing the compressive strength of the solid polymer electrolyte[49]. For carrying out the ASTM



Figure 10: Samples prepared for SEM

standard, we used Instron 5567 equipped with a 10 kN load cell. Specimens were poured into a silicone mold in the dimensions of 12.7x12.7x25.4 mm (rectangular prism). Five identical specimens were made for each compression test as called for by the standard and the average was taken. Each specimen was then aligned directly in the center of the two platelets and a compressive force was then applied. The standard speed was set at 1.3 mm/min. The compressive stress (σ_c) and compressive strain (ϵ_c) were calculated using the following equations below.

$$\epsilon_c = \frac{\Delta l}{l} \quad (2.2.1)$$

$$\sigma_c = \frac{F_c}{A} \quad (2.2.2)$$

Where (ϵ_c) is equal to the change in length (Δl) divided by the original length (l), and (σ_c) is equal to the compressive force (F_c) divided by the original cross-sectional area (A). The compressive modulus (E_c) was then calculated by taking the slope of the linear portion of the stress-strain curve between 2% and 10% strain, and the values were reported in megapascals



Figure 11: Instron 5567 equipped with a 10kN load cell

(MPa). The ultimate compressive strength denotes the maximum stress prior to failure, regardless of geometry, and was found by taking the maximum (F_c) and dividing it by the original cross-sectional area. The ultimate compressive strength was also reported in MPa.

For further validation of phase separation, differential scanning calorimetry (DSC) was used to analyze the electrolyte's phase transitions. DSC analysis can give us the melting temperature (T_m) by an exothermic peak, and the crystallization temperature with an exothermic peak. The glass transition (T_g) is found by a small step transition. Each specimen was placed in DSC cups and weighed before the test. A heat-cool-heat DSC cycle was performed on each specimen, and the temperature rate was $5^\circ\text{C}/\text{min}$, from -90 to 140C .

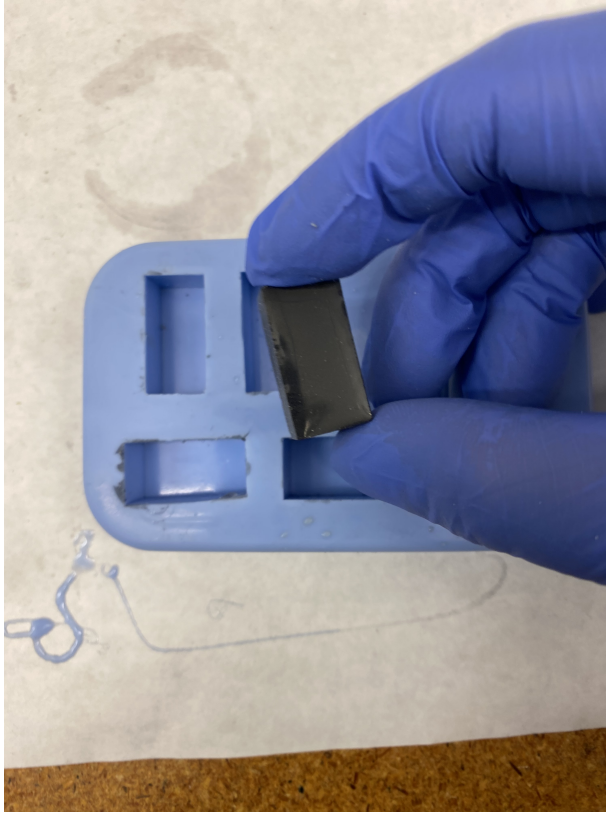


Figure 12: Specimen prepared for compression testing

2.3 Results and discussion

2.3.1 Weight percent loss of ionic component

Table 1 shows the initial weight of SPE before PEG was extracted, and the final weight once PEG was removed. Here, the expected weight loss should be approximately 50% as the samples were made with a 1:1 weight fraction of PEG and epoxy. PEG can be removed from the epoxy matrix using a polar solvent (water and alcohol mixture) since PEG is hydrophilic. Extracting PEG from the epoxy matrix would indicate that two separate phases are present, and that PEG was percolated through the epoxy matrix. Figure 14 is the graph of the amount of percolated PEG by weight was removed from the epoxy matrix. From 0.1-0.3 weight percent GO, the amount of PEG extracted decreases from when no GO was incorporated into the electrolyte. Indicating that when GO is increased, phase separation is potentially suppressed meaning the PEG-rich domains are becoming smaller. At 0.4 and 0.5% GO

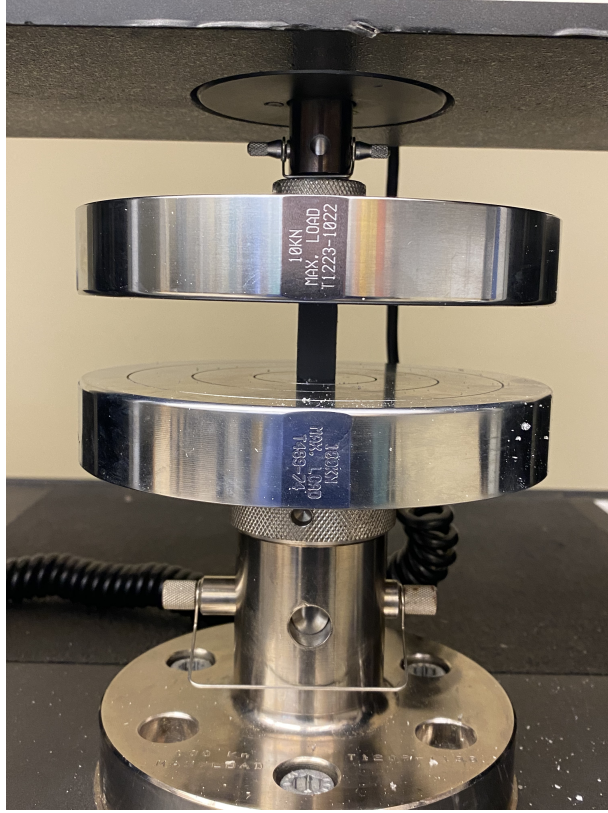


Figure 13: Compression sample under uniaxial load

an increase in PEG being extracted was observed. This could be caused by removing GO since it is hydrophilic due to the oxygen-rich functional groups, or that pores became more percolated in the epoxy matrix. However, at 0.6 and 0.7 weight percent of GO the weight loss of PEG decreases. Using higher amounts of GO created excess aggregations embedded in the polymer matrix indicating that GO was not well dispersed. Increasing amounts of GO that the ionic channels were not fully percolated through the epoxy matrix.

Table 1: PEG extracted from epoxy matrix

Graphene oxide wt.%	Avg. initial weight (mg)	Avg. final weight (mg)	Weight loss %
0.0	44.7	23.9	49.4±0.2
0.1	44.6	23.5	47.3±0.2
0.2	47.6	25.1	47.3±0.2
0.3	46.3	24.3	47.5±0.2
0.4	48.5	25.1	48.2±0.2
0.5	49.4	25.4	48.6±0.1
0.6	48.8	27.1	44.5±0.3
0.7	52.5	29.3	44.2±0.3

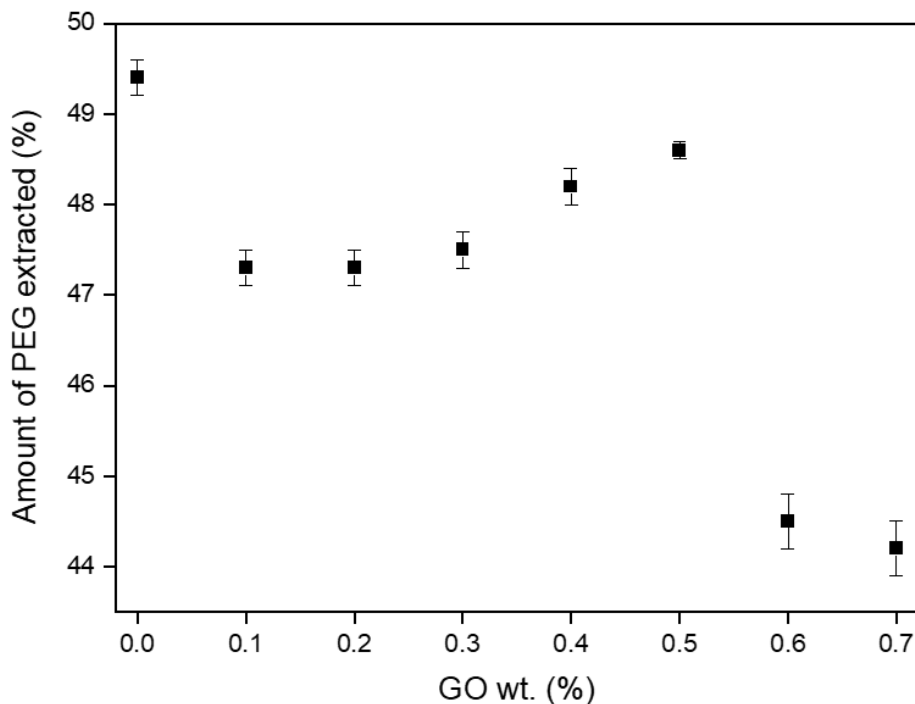


Figure 14: PEG extracted from epoxy matrix

2.3.2 Microstructure variations with increasing graphene oxide

Figure 15a and b shows the micrographs of GO incorporated into the PEG-epoxy electrolyte, and its effects on the final microstructure. The SEM images when there is no GO present in the 50:50 PEG-epoxy binary mixture depicts a porous microstructure where the PEG has been removed from the epoxy matrix. The darker region denotes where the PEG was previously before it was extracted. Figure 16 red lines are drawn revealing cavities that PEG was in a separate phase then epoxy, and thus leaving a concave microstructure. This indicates that PEG was interpenetrated through the cross-linked epoxy network. Leaving a co-continuous morphology where the epoxy-rich domain show up as the bright white region. This results in a morphology that is favorable for ionic properties due to the two separate phases present leaving a disordered porous microstructure[10]. However, while favorable for ionic conductivity it should result in poor mechanical properties due to the large PEG-rich phase in the microstructure.

When 0.1% GO content with respect to PEG is added into the binary polymer electrolyte

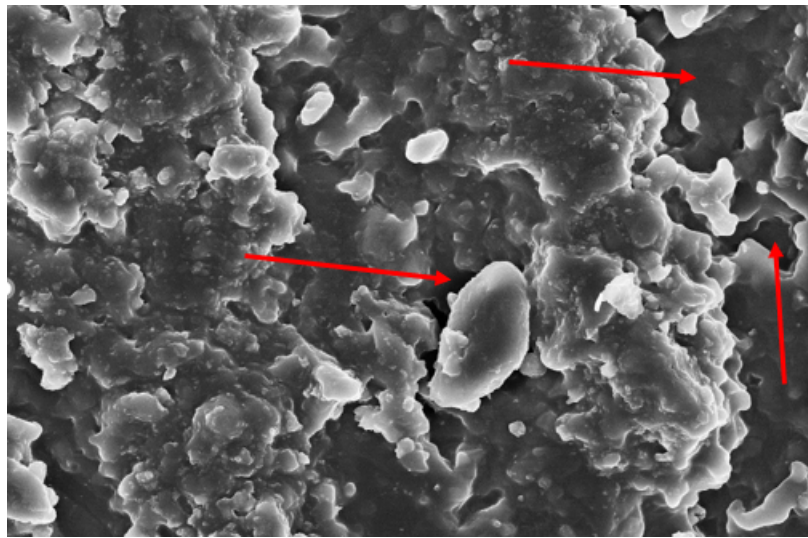
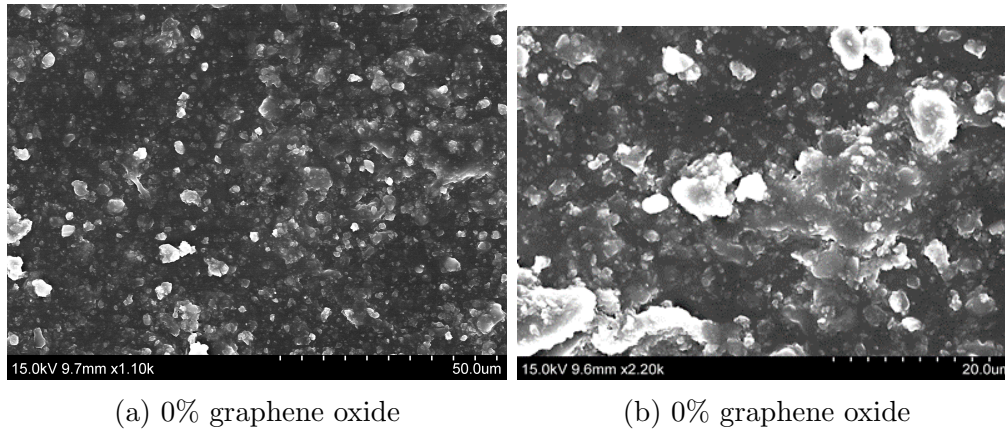
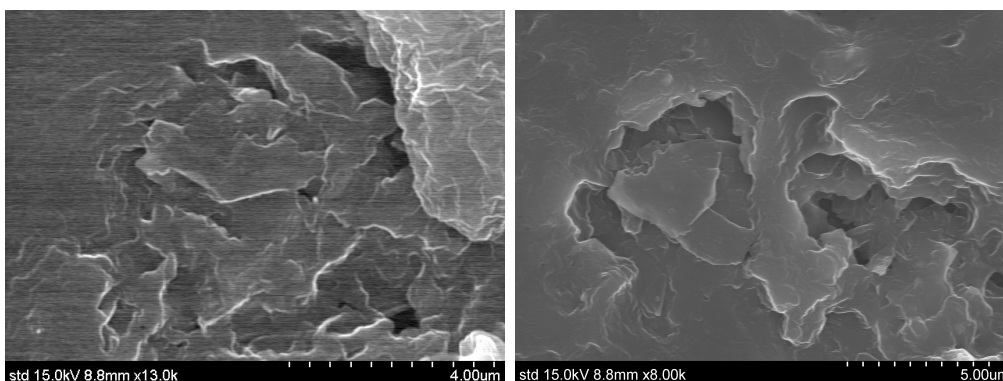


Figure 16: 50:50 PEG/epoxy no graphene oxide

the microstructure reveals a co-continuous morphology. However, the SEM images depicts a more smooth, plasticized structure morphology. The voids from the PEG-rich domain are on a much smaller scale than when no GO was present in the binary polymer blend. As a result the disordered porous microstructure that was generated from when no GO was present was lost. This results in PEG-rich domains more randomly dispersed in the bulk epoxy-rich phase. From figure 14 we see a decrease in PEG being extracted from the epoxy matrix was reported. The smaller PEG-rich domains from the SEM images indicate that GO more PEG was being entrapped in the epoxy matrix. Good dispersion of GO was achieved as no aggregations were visibly seen embedded in the polymer matrix, and thus proper exfoliation of the GO nanosheets was achieved. However, SEM images depict that the addition of just

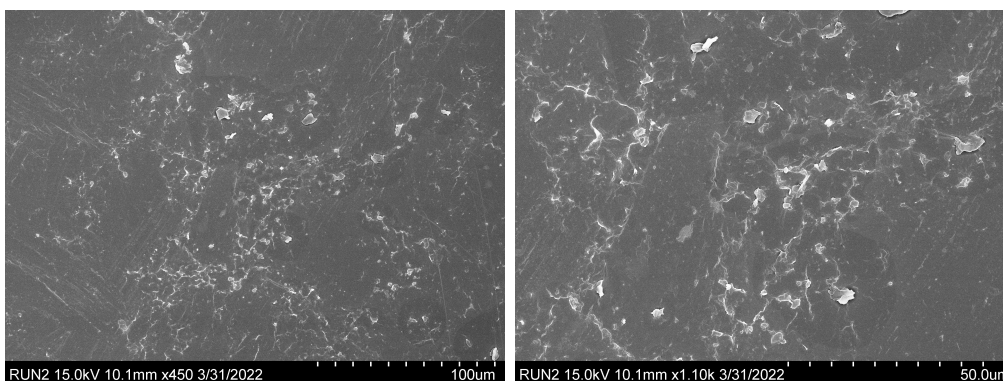
0.1% GO with respect to PEG has an impact on the final microstructure of the binary polymer electrolyte.



(a) 0.1% graphene oxide

(b) 0.1% graphene oxide

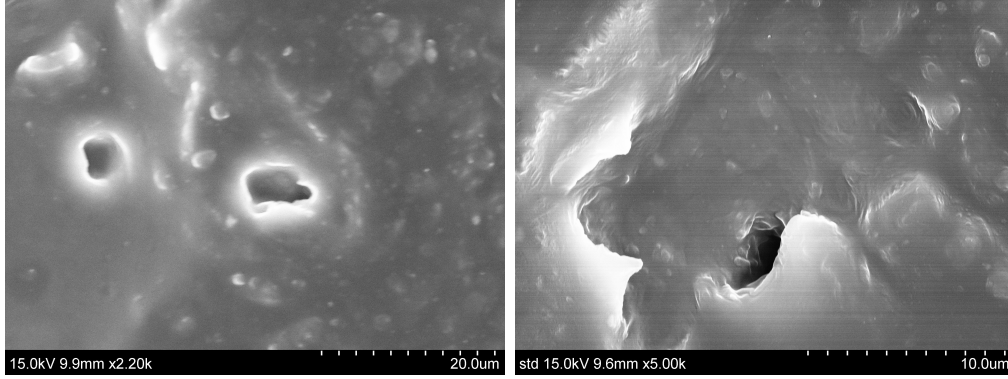
At 0.2% GO incorporated into the binary polymer electrolyte the microstructure changes significantly. The SEM images depict small pores randomly dispersed in the polymer matrix. The pore size or the PEG-rich domain became smaller when increasing from 0.1% to 0.2% GO content. This suggests that increasing GO loading suppresses phase separation between PEG and epoxy. At this amount of GO loading into the binary polymer electrolyte excellent dispersion conditions of GO was achieved as no obvious aggregations are embedded in the polymer matrix. This indicates that the techniques of bath sonication and shear-mixing are providing proper exfoliation between the GO nanosheets.



(a) 0.2% graphene oxide

(b) 0.2% graphene oxide

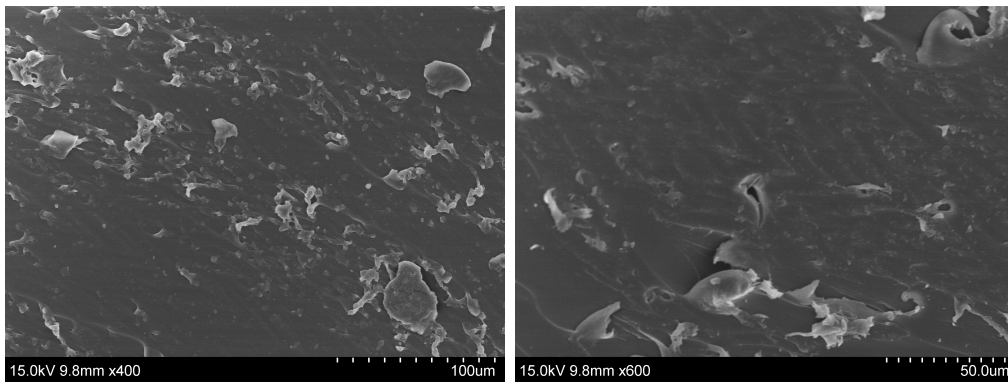
When 0.3% GO with respect to PEG is incorporated into the binary polymer electrolyte, the resulting microstructure reveals a smoother, homogeneous single-phase where small pores



(a) 0.2% graphene oxide

(b) 0.2% graphene oxide

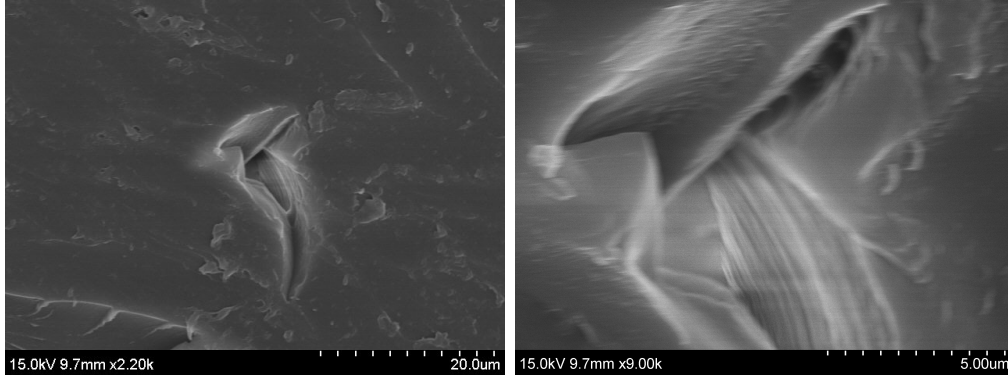
are randomly dispersed in the morphology. GO loading from 0.1-0.3% with respect to PEG we lose the a phase inverted morphology from when no GO is incorporated. With increasing GO loading the microstructure reveals pores that are become increasingly smaller, and are more randomly dispersed in the epoxy matrix. GO loading at 0.3% is well dispersed in the polymer matrix, and minimal aggregations are seen from the SEM images. Since aggregations are kept at a minimum it shouldn't potentially interfere with potential lithium ion transport. It was found that phase separation can be suppressed by the addition of GO into an epoxy/PEI binary blend due to the increased viscosity[50]. Based on the SEM images at this amount of GO content phase separation is suppressed and that increasing GO content has an affect on the pore size caused by the extraction of PEG.



(a) 0.3% graphene oxide

(b) 0.3% graphene oxide

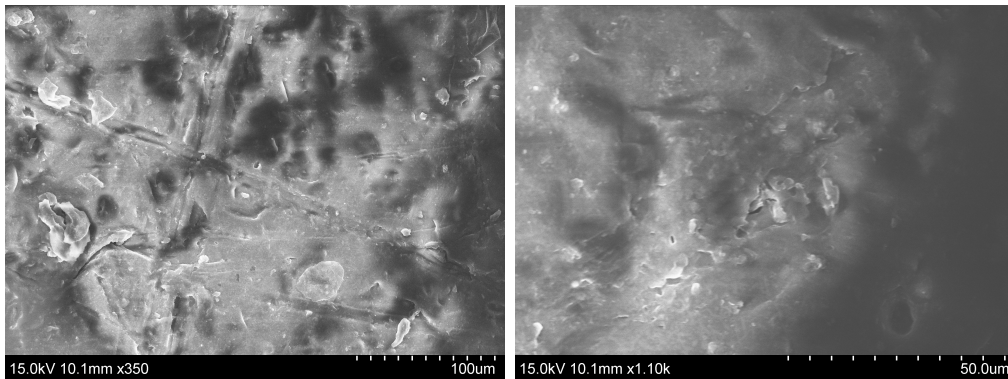
The SEM images of 0.4% GO with respect to PEG are shown below. The final microstructure depict a slightly "rougher" morphology than when GO loading is from 0.1-0.3%



(a) 0.3% graphene oxide

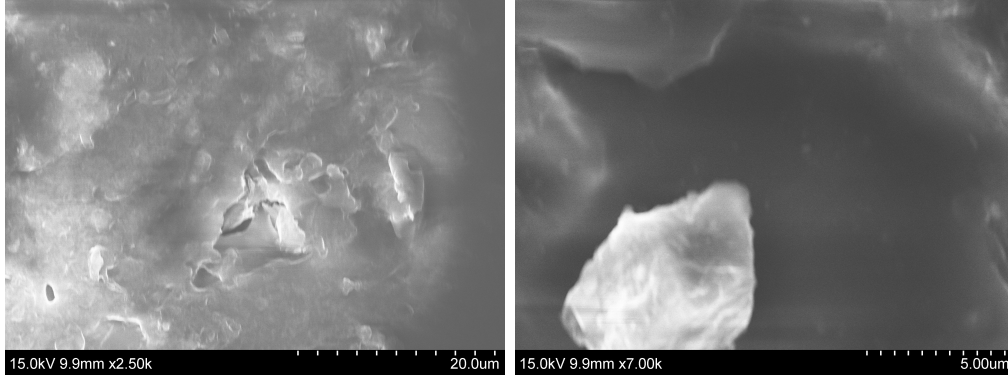
(b) 0.3% graphene oxide

GO. This is expected because increasing nanofiller content makes optimal dispersion and exfoliation conditions more difficult to achieve. Good dispersion of GO is still achieved as there is minimal aggregations visually seen from the SEM images. This indicates that shear-mixing and bath sonication helps in preventing GO from agglomeration. The importance of dispersion condition is that GO agglomerations show up as aggregations in the matrix. These aggregations could serve as potential defects in mechanical properties and could potentially hinder ion transport. A slight uptick in PEG extraction occurs at 0.4% GO content compared to GO content from 0.1-0.3%. This could be due to GO being extracted as it is also hydrophilic thanks to its oxygen-rich functional groups. Increasing GO loading in the binary polymer electrolyte acts as a compatibilizer in the polymer blends, and the reason for the increased miscibility is due to the accumulation of GO at the blend interface[51]. This can be seen as the PEG-rich domain is seen as the cavity left in the matrix once extracted.



(a) 0.4% graphene oxide

(b) 0.4% graphene oxide



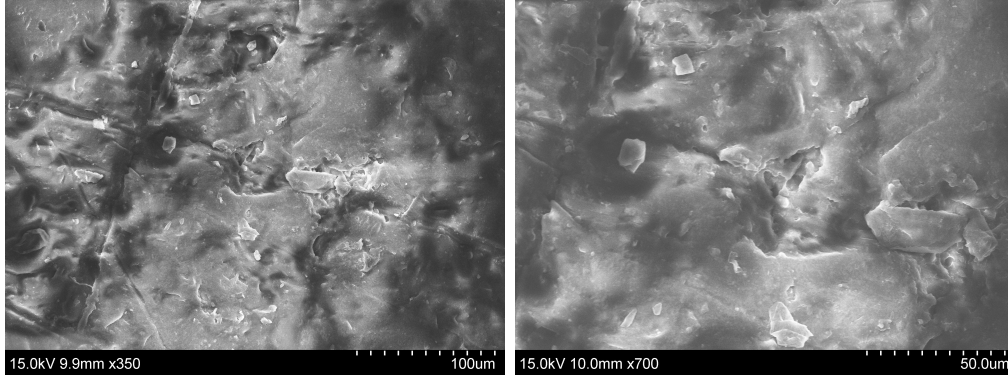
(a) 0.4% graphene oxide

(b) 0.4% graphene oxide

The SEM images of 0.5% GO with respect to PEG depict a microstructure that is similar to that of 0.4% GO.

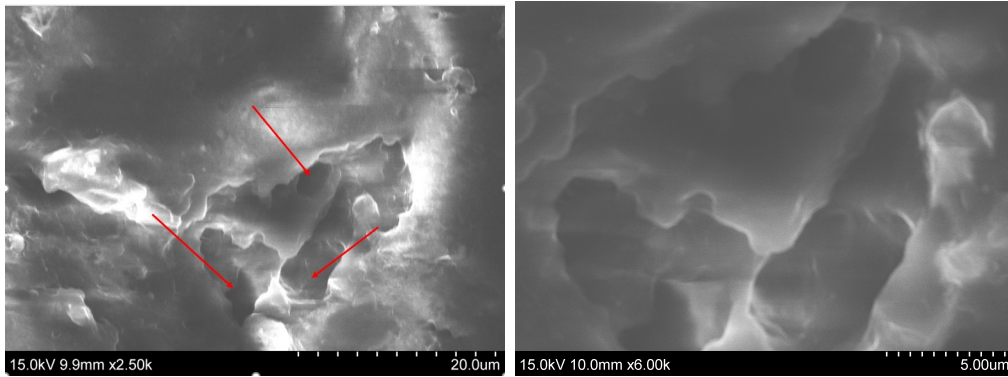
Good dispersion condition of GO is achieved as minimal aggregations are visually seen embedded in the matrix by the SEM images. The importance of dispersion condition is that agglomerations of GO show up as aggregations in the matrix. These aggregations could serve as potential defects in mechanical properties. This is expected because increasing nanofiller content makes optimal dispersion and exfoliation conditions more difficult to obtain. However, the bath sonication and shear-mixing times seem to achieve a morphology that should have a good balance between mechanical and conductive performance. This amount of GO loading recorded the highest amount of PEG extracted from epoxy matrix when GO is incorporated in the electrolyte. Indicating that ionic channels were further percolated, or GO was also extracted due to its hydrophilic nature. The SEM images show three pores approximately $4\mu\text{m}$ in close proximity to one another as indicated by the red arrows. Increasing nanofiller loading the pores where PEG is extracted are becoming increasingly smaller, and closer in proximity to one another. GO when incorporated into the binary mixture PEG and epoxy acts as a compatibilizer in the polymer blends, and the reason for the increased miscibility is due to the accumulation of GO at the blend interface[51]. This can be seen as the PEG-rich domain are becoming increasing smaller as GO loading increases in the epoxy matrix.

The SEM images of when 0.6% GO with respect to PEG is added, noticeable aggregations



(a) 0.5% graphene oxide

(b) 0.5% graphene oxide

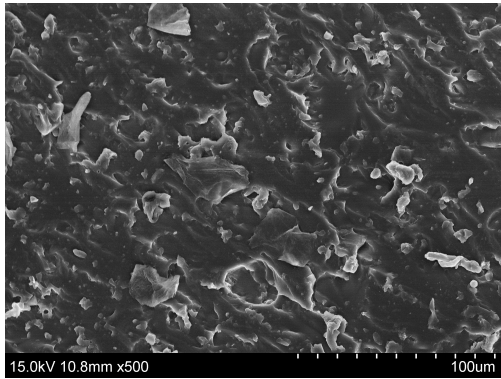


(a) 0.5% graphene oxide

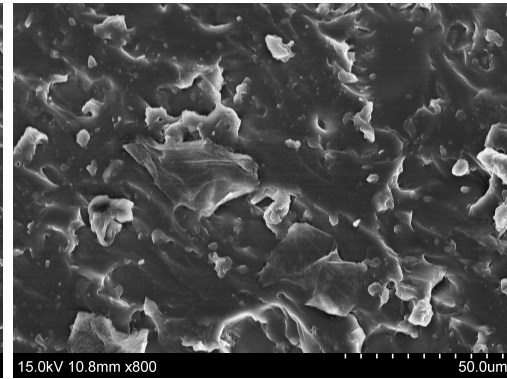
(b) 0.5% graphene oxide

are seen embedded in the polymer matrix. These aggregations embedded in the matrix indicate at this amount of GO loading that optimal dispersion conditions are harder to obtain due to agglomerations of GO. These aggregations could possibly hinder ion transport, and thus hurting the potential of ionic conductivity[46]. The mechanical properties could be compromised as well since aggregations could serve as sites of mechanical defects. Ionic channels or pores from PEG being extracted are still visible and range from approximately 3-5 μm and are not as randomly dispersed throughout the matrix as GO content 0.1-0.5%. The red arrow indicates a small pore at 20 μm and is not visually seen, but at 5 μm you can see the pore. Indicating that phase separation is becoming less apparent as GO loading increases the electrolyte channel is becoming increasingly smaller. This amount of GO content also showed less PEG being extracted than in all previous samples, and could be caused by the restacking of GO sheets due to agglomeration. Since GO is hydrophilic, the aggregations

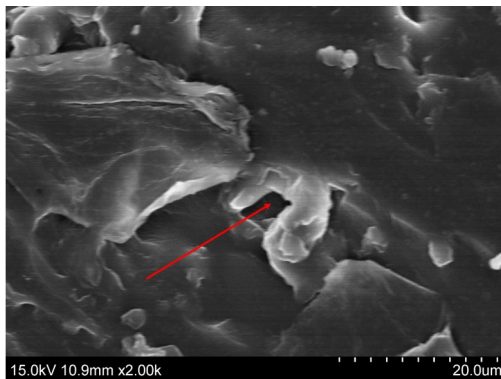
could be mean less GO is possibly being extracted as well as more PEG being entrapped in the epoxy network.



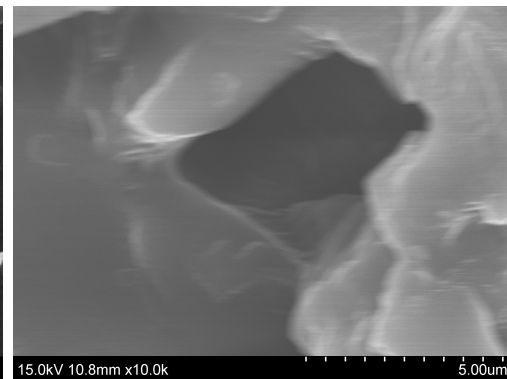
(a) 0.6% graphene oxide



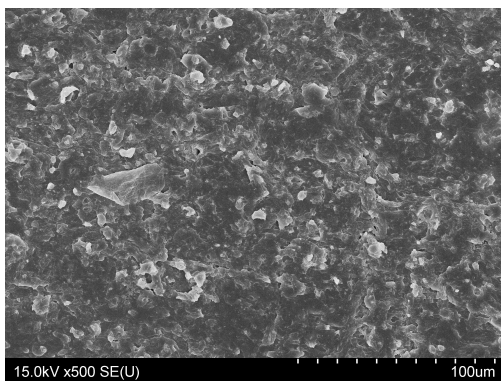
(b) 0.6% graphene oxide



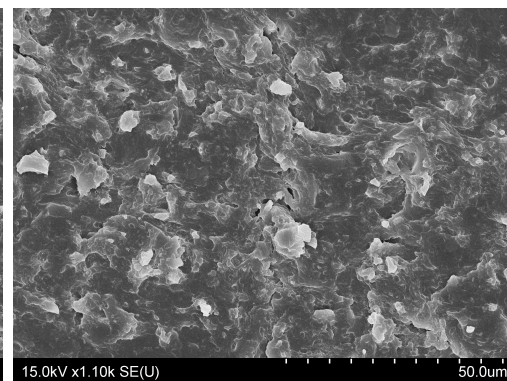
(a) 0.6% graphene oxide



(b) 0.6% graphene oxide

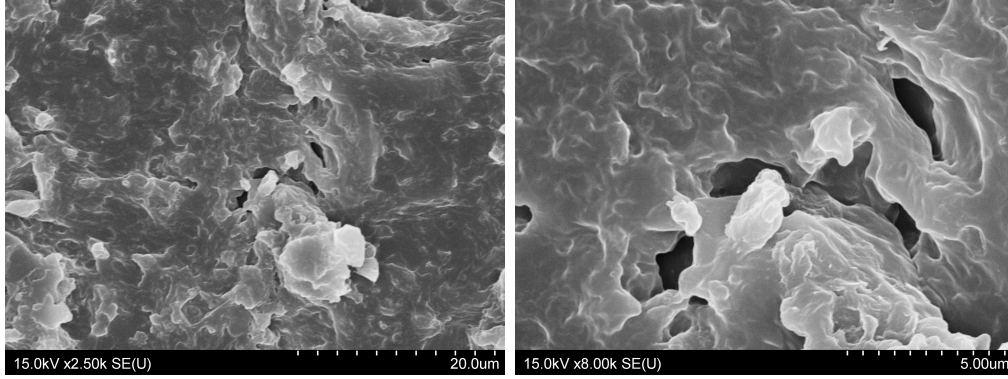


(a) 0.7% graphene oxide



(b) 0.7% graphene oxide

At 0.7% GO with respect to PEG, a very rough microstructure is observed indicating obvious aggregations are caused by GO agglomerations. This is less than optimal dispersion



(a) 0.7% graphene oxide

(b) 0.7% graphene oxide

and exfoliation conditions of GO. The aggregations are caused by the agglomeration of GO, meaning as increasing nanofiller loading the GO nanosheets have a tendency to restack due to the van der Waals forces and high specific surface area. These aggregations serve as potential sites for cracks and defects which could lead to possible detrimental affects on the mechanical properties of the electrolyte[52]. Also, these aggregations could potentially hinder lithium ion transport. Based on the SEM images, pores are approximately 1-1.5 μm and are more in closer than proximity to one another. This can be explained because at the site of the aggregations the PEG seems to be more concentrated and not evenly dispersed throughout the matrix. Even though the pores are still visible throughout the epoxy matrix, weight loss of PEG extraction was the lowest than all previous samples with GO loading. Indicating that more PEG was entrapped in the cross-linked epoxy network, or due to agglomerations that less GO was being potentially being extracted. At 0.7% GO content PEG and epoxy were in separate phases, but that PEG-rich domains are on a much smaller scale. Based on increasing GO loading into the electrolyte the viscosity increases as well. The viscosity increase with further addition of GO suppresses phase separation. As mentioned previously, viscosity increase slows the phase separation rate down during curing reaction.

When no GO was implemented large voids are left in the microstructure indicating large PEG-rich domains where phase separated from the epoxy domain. However, when GO loading was from 0.1-0.5% GO with respect to PEG a smooth, plasticized microstructure where small PEG-rich domains were observed. Indicating that phase separation was suppressed,

and smaller percolating channels are created. GO content at 0.6 and 0.7% with respect to PEG shows even smaller PEG-rich domains. Here aggregations are visibly present and could potentially interfere with future lithium ion mitigation, and create defects that could harm the mechanical properties of the electrolyte.

2.3.3 Mechanical characterization results

To achieve a better understanding of how PEG would affect the mechanical properties of pure epoxy, compression testing was done on 100% pure epoxy until the 50:50 weight fraction of PEG and epoxy that was settled to study the phase morphology. The decision to stop at the 50:50 weight fraction of PEG and epoxy was because phase separation was observed by SEM images, and weight loss of extracted PEG was almost 100%. Indicating the ionic channel caused by PEG phase separating from epoxy was percolated through the epoxy matrix. From pure epoxy, PEG content was increased by approximately 10% weight until 50% PEG was incorporated. Table 2 shows the weight fractions of PEG and epoxy and the corresponding compression modulus for each sample.

Table 2: Compression testing values of PEG and epoxy

PEG wt.%	Epoxy wt. %	Compressive Modulus (MPa)
0	100	1942.2±120.2
10	90	13.83±0.44
20	80	3.47±0.14
30	70	1.61±0.01
40	60	1.18±0.21
50	50	0.78±0.03

Pure epoxy showed typical stress-strain behavior of a hard and tough plastic under compression, and the compression modulus recorded was approximately 2 gigapascals (GPa). However, at just 10% weight of PEG into pure epoxy, the compression modulus dropped drastically. Under uniaxial compression just 10% PEG weight caused sample to behave like an elastomer. Past 10% PEG weight there was a steady decline in the compression modulus. This indicates that the addition of low molecular weight PEG into epoxy plasticizes the

cross-linked network. Plasticizing the epoxy increases the molecular mobility, and further decreasing the stiffness of pure epoxy. To get a more comprehensive understanding at why such a drastic drop in the compression modulus; one percent addition of PEG by weight was added to pure epoxy from 100-90%. Table 3 shows the weight fractions of PEG and epoxy with their compression modulus values.

Table 3: Compression testing values of 0-10% PEG in epoxy

PEG wt. %	Epoxy wt. %	Compressive Modulus (MPa)
0	100	1942.2±120.2
1	99	1620.0±68.7
2	98	876.8±118.3
3	97	806.8±55.8
4	96	803.3±49.6
5	95	679.1±49.8
6	94	65.5±4.2
7	93	47.1±9.6
8	92	25.3±2.7
9	91	11.7±0.88
10	90	13.83±0.44

Table 3 shows from when 0-5% PEG weight was added, there was a linear decrease of the compression modulus. Thus, small amounts of PEG plasticizing the epoxy network. However, the stress-strain behavior under compression is typical of a hard and tough plastic. Figure 29 is a schematic representation the compression modulus when PEG addition was from 0-5%.

However, from 6-10% PEG addition by weight into epoxy there is a drastic drop in the compression modulus. The stress-strain behavior of these specimens started to show elastomeric behavior under uniaxial compression. Thus, the sharp decrease in the stiffness of the material. Also, when the specimens deform under compression it returns back to its original dimensions. Indicating that this deformation is still in the elastic region of the stress-strain curve. Figure 30 shows a linear decrease of the compressive modulus from 6-10% addition of PEG into epoxy. Past 5% PEG addition the binary polymer blend behaved like an elastomer. Further addition showed a steady decrease in the compressive modulus.

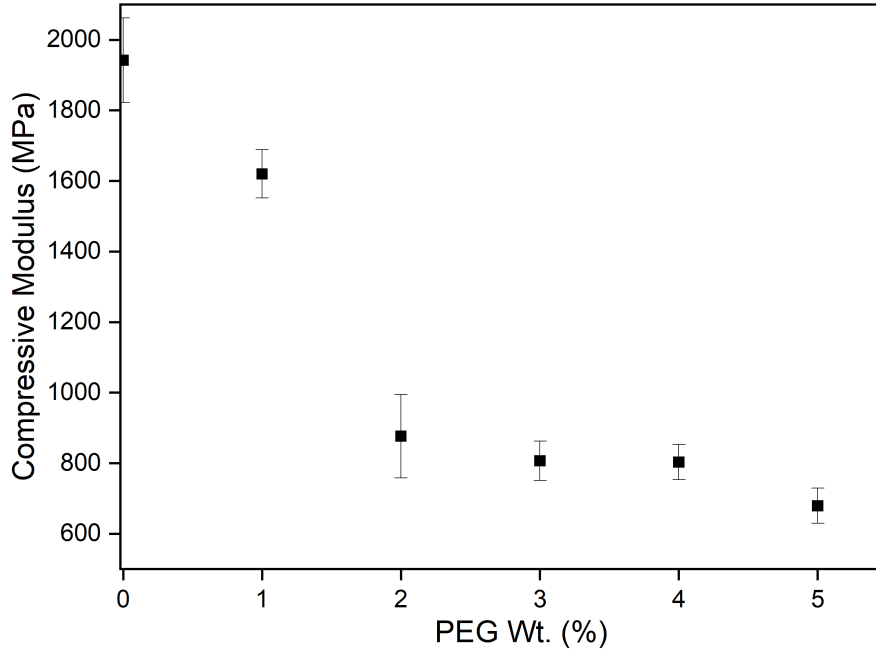


Figure 30: 0-5% weight PEG in epoxy

These results give us a clear indication that PEG is not only plasticizing the epoxy, but after approximately 5% percent PEG incorporation it's lowering the cross-linking density of pure epoxy to the point of behaving as an elastomer.

The results of the mechanical characterization with increasing GO loading (0-0.7 weight % with respect to PEG) in 50:50 weight fraction of the binary PEG-epoxy mixture is shown in Table 2. When GO is not incorporated in the electrolyte, the resulting morphology is typical of a liquid-rich phase separated system[10] as shown in the SEM images. The compression tests when no GO is incorporated resulted in the weakest compressive modulus and strength of the samples. When GO (0.1-0.5% GO) is added with respect to PEG, the morphology changes from a bicontinuous network to a single-phase material where smaller sized pores are randomly distributed throughout the non-conductive epoxy matrix[48]. This morphology resulted in improvement of the compressive modulus. This is a result of the PEG-rich domains becoming increasingly smaller, and as filler content increases the stiffness

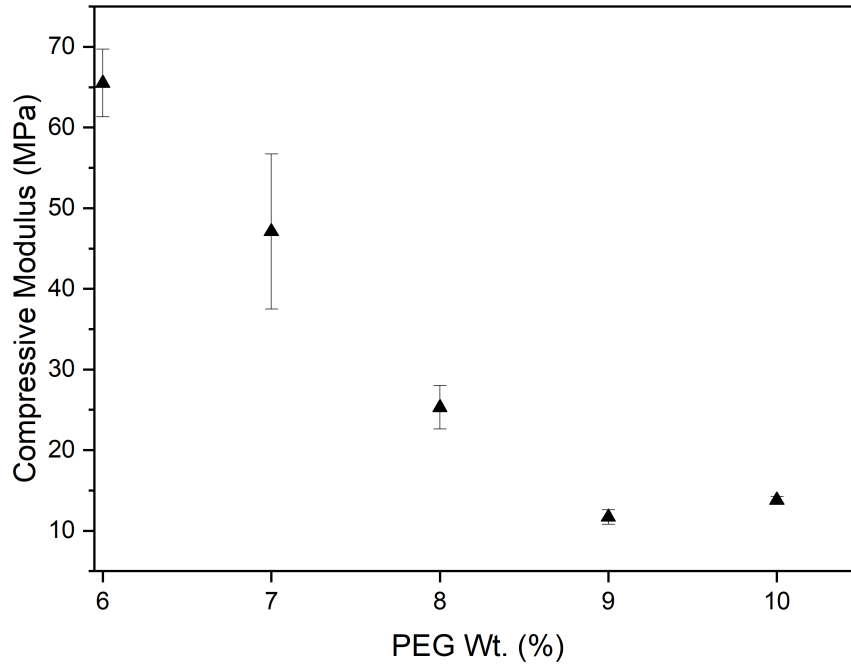


Figure 31: 6-10% weight PEG in epoxy

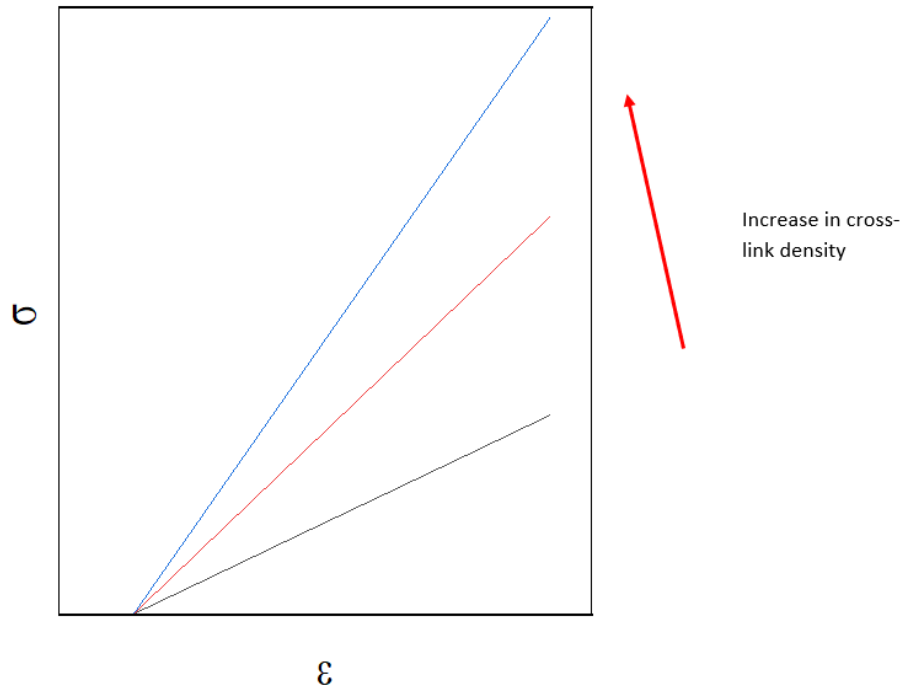


Figure 32: Cross-linking density

of the material. However, after 0.2% GO with respect to PEG as shown in table 2 the ultimate compressive strength decreased. While, increasing filler should result in a stiffer material (higher modulus), it doesn't necessarily increase the toughness of the material[53]. Restacking of the GO nanosheets could have resulted in the decrease of the compressive strength. Further research is being done to fully understand this behavior. The compressive modulus shows a linear progression of increasing, and the highest compressive modulus was recorded at 0.6% GO. This is a 42.3% increase in compressive modulus when there is no GO present in the 50:50 binary mixture.

When GO is at 0.7% with respect to PEG, the compressive modulus declines due to agglomeration of GO embedded in the polymer matrix. At the aggregation sites more pores are observed at 0.7% GO, but the aggregations can serve as sites of defects. To see if such a drop off in mechanical properties was consistent, compression tests were done at 0.8% GO. The resulting modulus was approximately 0.83 MPa, and can conclude that at higher concentrations of GO aggregations are only going to intensify. Increasing filler (GO) does increase the stiffness, but how well the GO is dispersed in the matrix allows for better overall properties[48]. It has been reported that at higher filler content the functional groups on the surface of GO may hinder the epoxy cross-linking reaction [41]. Further research is being conducted to understand why the compressive modulus declines at 0.7% GO. The compressive strength peaked at 0.2% GO and is a 50% increase in maximum compressive strength, and then the compressive strength drops and stays consistent from GO content 0.3-0.7%.

2.3.4 Thermal analysis

Figure 35 is the DSC curve of pure epoxy. The DSC curve shows no exothermic and endothermic peak indicating no melting temperature (T_m) or crystallization. This is typical of thermosetting polymers. However, a distinct phase transition occurs at approximately 40.42°C which is the T_g . To get a baseline understanding of PEG thermal behavior, DSC

Table 4: Compression values of 0-0.7% graphene oxide

GO wt. %	E_c (MPa)	E_c (%) Increase	Max. Compressive Strength (MPa)	σ_c (%) Increase
0.0	0.78 ± 0.03	-	0.42 ± 0.06	-
0.1	0.91 ± 0.03	16.7	0.62 ± 0.06	47.6
0.2	0.95 ± 0.03	21.8	0.63 ± 0.08	50.0
0.3	0.97 ± 0.01	24.4	0.54 ± 0.03	28.6
0.4	1.01 ± 0.04	29.5	0.55 ± 0.05	30.9
0.5	1.04 ± 0.04	33.3	0.54 ± 0.05	28.6
0.6	1.11 ± 0.05	42.3	0.53 ± 0.07	26.2
0.7	0.89 ± 0.03	14.1	0.54 ± 0.04	28.6

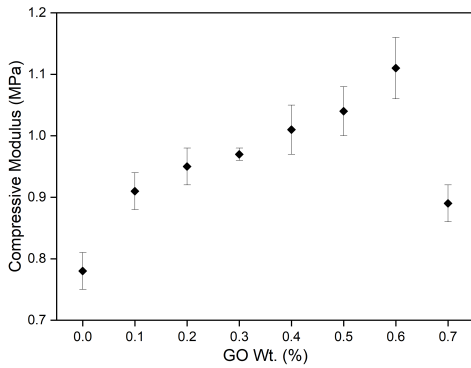


Figure 33: E_c GO content 0-0.7%

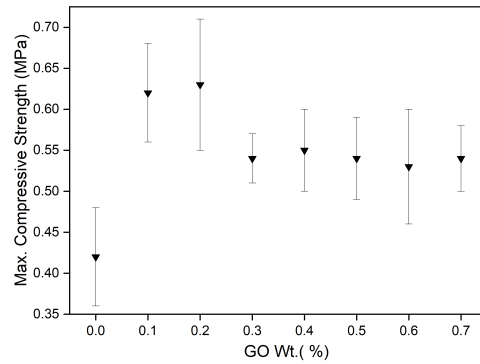


Figure 34: Ultimate σ_c GO content 0-0.7%

analysis was performed on pure PEG. There is an endothermic and exothermic indicating low temperature crystallization and melting temperature. This is much different behavior than what was observed from the DSC curve of pure epoxy. Figure 38 a red arrow is drawn to a small transition at approximately -34°C . This small transition is indicative of the T_g , and falls within the range found in literature[26].

For further understanding of how increasing PEG content impacts the thermal properties of epoxy, 10 and 30% PEG by weight are implemented into epoxy. Figure 39 and 40 show the endothermic and exothermic peaks of the epoxy and PEG mixture. The addition of just 10% PEG showed us a slight endothermic peak at approximately 22°C which is typical of PEG. A small exothermic peak was also observed, and a phase shift was also observed approximately at 40°C which is indicative of the T_g of pure epoxy. From the DSC curves, PEG at 10% weight is highly entrapped within the cross-linked epoxy matrix, and as a

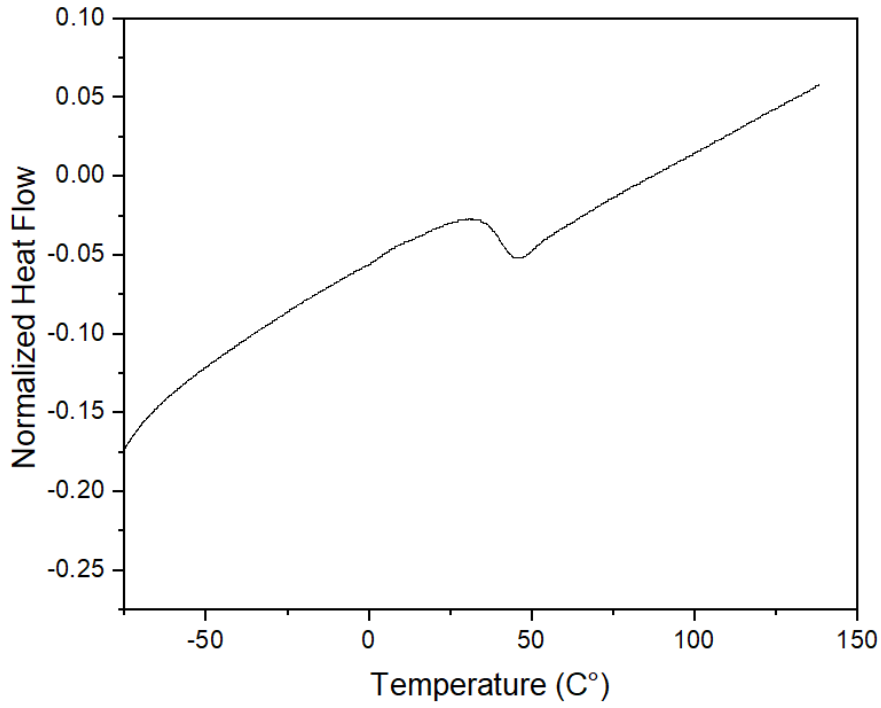


Figure 35: DSC pure epoxy

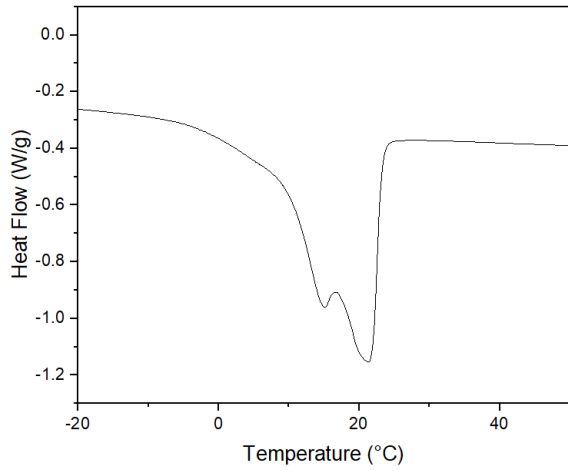


Figure 36: PEG endothermic peak

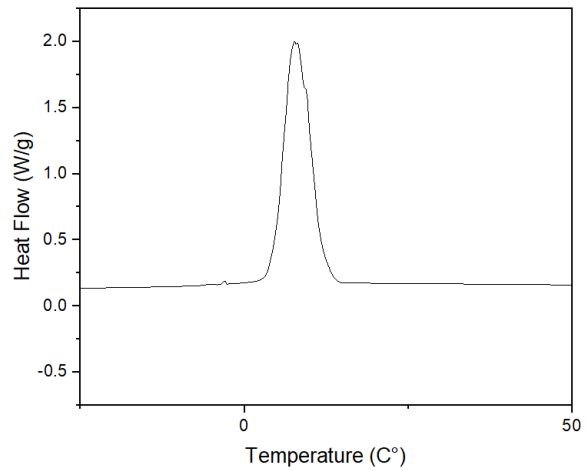


Figure 37: PEG exothermic peak

result the phase transition peaks are minimal[25]. At 30% weight PEG content an increase in intensity of an endothermic peak at 22°C, which is the T_m of PEG. The increase in intensity of the peaks is due to higher amounts of PEG decreasing the cross-linking density of pure epoxy. However, the small step transition that was noticeable in the 10:90 PEG epoxy

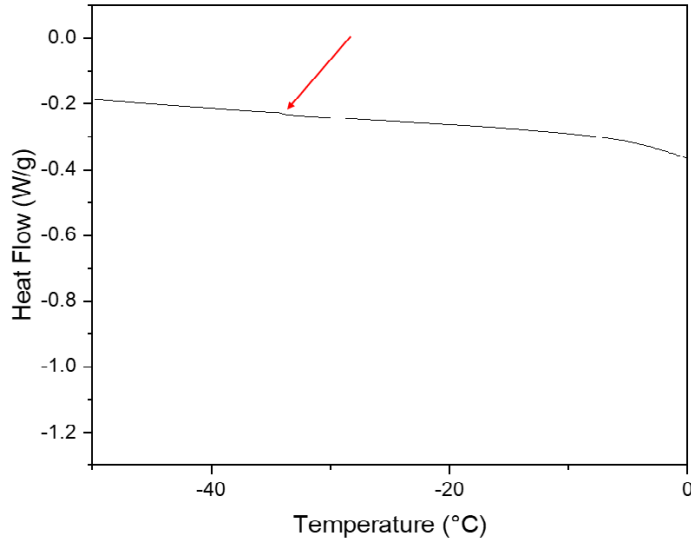


Figure 38: T_g of PEG

sample wasn't present. Figure 41 are the DSC curves of the 50:50 electrolyte with increasing

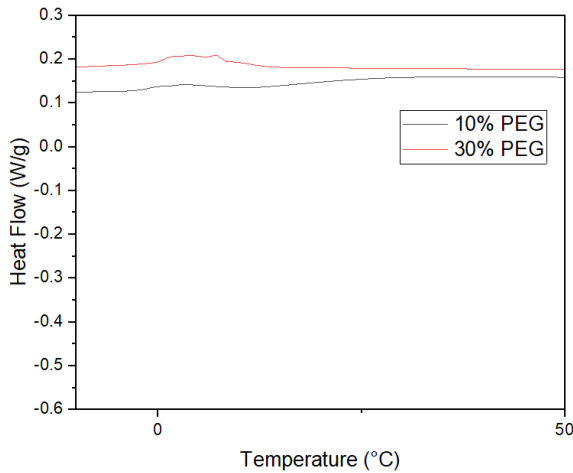


Figure 39: Exothermic peak of 10 and 30% PEG

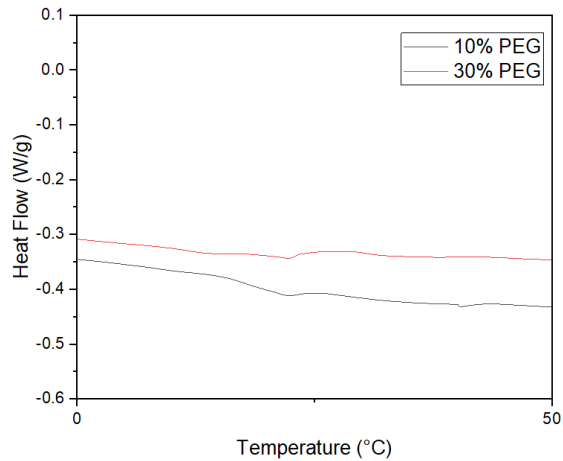


Figure 40: Endothermic peak of 10 and 30% PEG

GO content 0-0.7%. When the PEG content increases to 50% of the electrolyte there is an exothermic and endothermic peak indicating the low temperature crystallization and T_m of PEG. Indicating that PEG while encapsulated by epoxy is in a separate phase. Here, at a 50:50 weight fraction of PEG and epoxy, the T_m and crystallization temperature is actually lower than pure PEG. This is due to the dissociation, interaction, and confinement of PEG in epoxy[54]. Increasing GO content has very minimal impact on the melting and crystallization

temperature of the PEG epoxy binary mixture. When no GO oxide is implemented the T_m is 17.8, and the lowest T_m recorded was at 0.6% GO content. Indicating that GO reduces crystallinity but has a very minimal impact overall. The endothermic and exothermic peaks are much more significant indicating that PEG domains are much less constricted by the cross-linked epoxy matrix. Two red arrows are drawn to small step transitions indicating T_g . Two T_g is indicative of phase separation of a binary polymer system and is found in a similar system[23]. However, the second small step transition occurs at approximately 0° C. This is due to partial miscibility that PEG has in epoxy matrix.

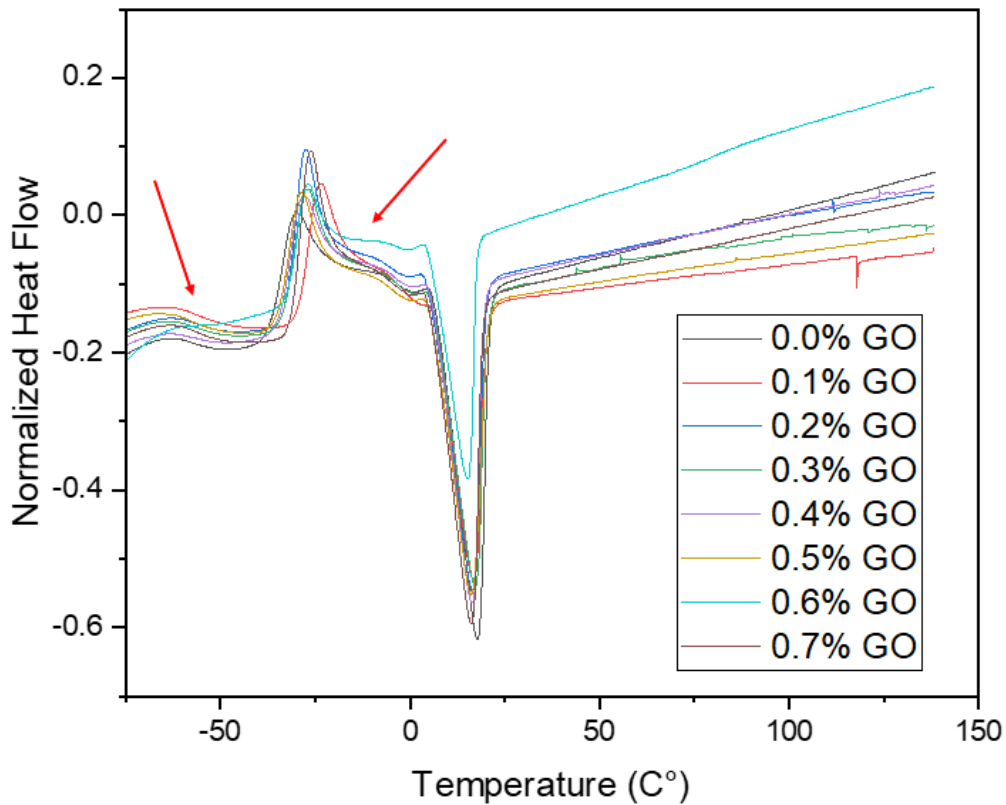


Figure 41: DSC curves 50:50 Epoxy/PEG with GO content 0-0.7%

2.4 Conclusion

This research takes a look into how increasing GO addition into a binary polymer electrolyte with a 50:50 weight fraction of structural and conductive polymers, and its effects on phase

separation and relate to its compressive properties. The final microstructure has a significant impact on the performance of a polymer electrolyte[34], and GO allows for tailoring of the microstructure to achieve multifunctional performance. Increasing GO loading into the binary polymer electrolyte changed the microstructure from a bicontinuous two-phase morphology to a more homogeneous single phase where small pores are distributed throughout the matrix. The addition of GO made the pores become increasingly smaller. Thus, the addition of GO made PEG more miscible in epoxy when cross-linking reactions occurs.

The electrolyte shows improvement in structural properties when GO is incorporated. An increase in maximum compressive strength up to 50% was achieved at 0.2% GO content compared to when no GO was added in the 50:50 PEG epoxy mixture, and the compressive modulus was increased up to 42.3% at 0.6% GO compared to no GO in the 50:50 PEG epoxy mixture. However, increasing GO loading past 0.6% poor dispersion conditions were achieved leaving large aggregations embedded in the matrix, and were found to be detrimental to the mechanical properties of the electrolyte.

DSC analysis shows how that increasing PEG content affects the thermal properties of epoxy. When the 50:50 PEG epoxy mixture was reached varying GO content was studied by DSC. Increasing GO loading had minimal impact on the thermal properties, but phase separation was validated from the DSC curves. The addition of GO content from 0.4-0.5% with respect to PEG, allows for good dispersion in the polymer matrix, and shows improvement in structural properties. At this amount of GO loading, PEG was extracted from the epoxy matrix at a higher percentage than the rest of the samples with GO added. This could indicate that ionic channels were further percolated through the epoxy matrix. Based on this data, the addition of GO between 0.4-0.5% with respect to PEG is promising for an epoxy-based polymer electrolyte for future SSC applications.

CHAPTER III

INCORPORATION OF LITHIUM SALT INTO EPOXY-BASED ELECTROLYTE

3.1 Introduction

It is understood that graphene oxide increases the mechanical properties of epoxy nanocomposites, and can provide increased ionic conductivity in PEO-based solid polymer electrolytes[55]. This is due to its rich oxygen containing functional groups that help dissociate lithium ions which free up more lithium ions to coordinate with the ether oxygen unit. However, even with an epoxy-based polymer system there is still an inverse relationship between the mechanical and ionic properties. The role of PEG content and LiTFSI on phase separation will be explored. The goal of implementing GO in the PEG-epoxy binary electrolyte is to simultaneously improve both the ionic and mechanical properties. Proper dispersion and exfoliation of GO nanosheets is crucial for achieving optimal functionalization of its properties. Here, GO content from 0.3-0.7% with respect to PEG was used, and half the samples underwent centrifugation. The other half of the samples didn't undergo centrifugation. Centrifugation is a process that allows for removal of any impurities of GO[56].

3.2 Materials and methods

The ionic polymer incorporated was PEG with an average molecular weight (600) which was purchased from Acros Organics™ (Geel, Belgium). Graphene oxide was obtained from Nanoshel® UK LTD (Wilmington, Delaware). Lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) from Acros Organics™ (Geel, Belgium). The epoxy resin which was used in this

study is EPON™ Resin 862 and EPIKURE™ Curing Agent 3724 was supplied by Miller-Stephenson (MillerStephenson, Danbury, Connecticut).

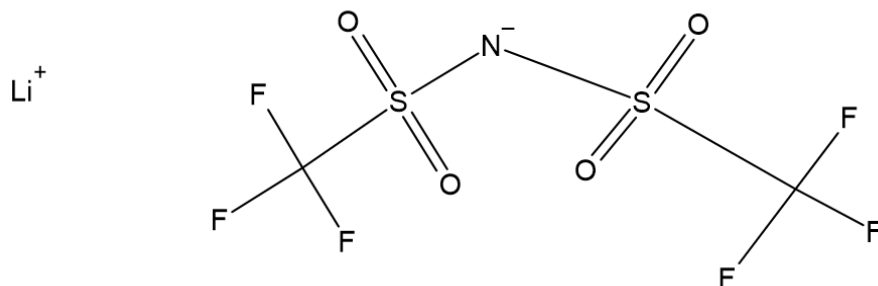


Figure 42: LiTFSI

3.2.1 Synthesis of PEG-GO-LiTFSI epoxy network

PEG was weighed and added into a clean beaker, and heated to 30°C until it becomes a liquid. GO was then weighed from 0.3-0.7% with respect to PEG, and added into the liquid PEG. To ensure a uniform dispersion of GO the same steps were taken as above. After shear mixing and bath sonication, half the samples underwent centrifuging at 3500rpm for 15 minutes. The supernatant was then collected and LiTFSI was added into PEG/GO ionic component at 10% with respect to PEG, and stirred in an inert atmosphere due to its hydrophilic nature. Epoxy is then poured into a separate beaker, and is mixed with the hardening agent in a 5:2 ratio. It was then degassed to remove the bubbles caused by hand mixing. The PEG-GO-LiTFSI solution was then added with the epoxy, and mixed vigorously by magnetic stir to ensure a homogeneous mixture. The electrolyte was then degassed and poured into a silicone mold to cure at 60°C in a vacuum oven (Across International) for 24 hours.

3.2.2 Characterization

After the SPE is completely cured, a 4.8 mm (3/16") diameter cutting tool was used to cut five circular samples. The initial weight was taken and the samples were placed in a 50:50



Figure 43: Centrifuge

water-alcohol solution, and then bath sonication (power level 3) was used for 2 hours. Once bath sonication is complete, the cut samples were then submersed in water for a minimum of 16 hours. The specimens were then placed in a vacuum oven until the mass of the samples were constant and no more weight was being lost. The final weight was taken and averaged for the five specimens. The specimens were then sputtered (Leica EM ACE600) with Iridium Han for 80 seconds. The scanning electron microscope (Hitachi S-4800) was used. The accelerating voltage was set to 15 kV and the emission current was set at 10 μ A.

Ionic conductivity at room temperature was measured using a potentiostat (Make-Princeton Applied Research, Versastat 3F, Ametek Scientific Instruments, Oak Ridge, TN). The SPE was cut into circular discs of 4 mm radius, and conductivities were measured using two outer working electrodes by sandwiching the disc between two stainless steel electrodes. The AC impedance spectroscopy was collected from 1 Hz to 1MHz. The resistance of the SPE (R) was calculated from the intersection of the real impedance in the Nyquist plot with the semicircle fit. The through-plane conductivity (σ) was determined using the following equation

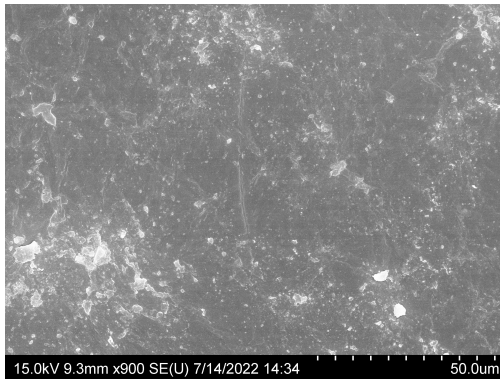
$$\sigma = \frac{d}{R \times A'} \quad (3.2.1)$$

Where d and A are the thickness of the specimen.

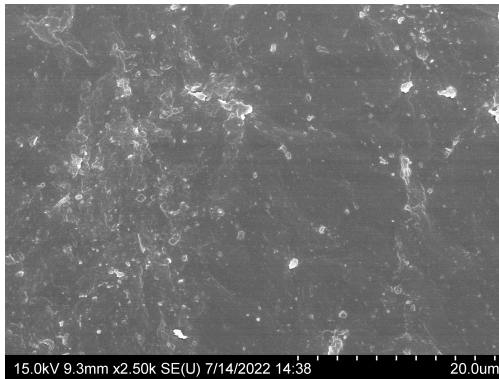
3.3 Results and discussion

3.3.1 PEG content and LiTFSI on phase separation

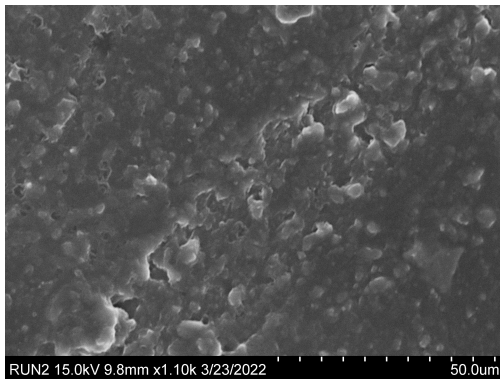
To counteract the negligible mechanical properties of high amounts of PEG in epoxy, samples were made with higher epoxy resin content (60-70%) to see how the affect of PEG content and LiTFSI would affect the phase separation. The SEM images at 70% epoxy content without LiTFSI phase separation appears to be minimal at best. A smooth, plasticized morphology is obtained and no PEG-rich domains are visually seen.



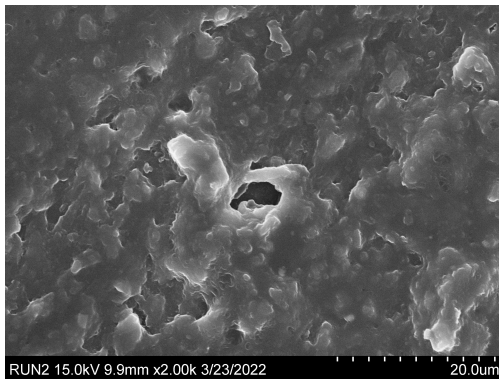
(a) 30:70 PEG/Epoxy no Li



(b) 30:70 PEG/Epoxy no Li



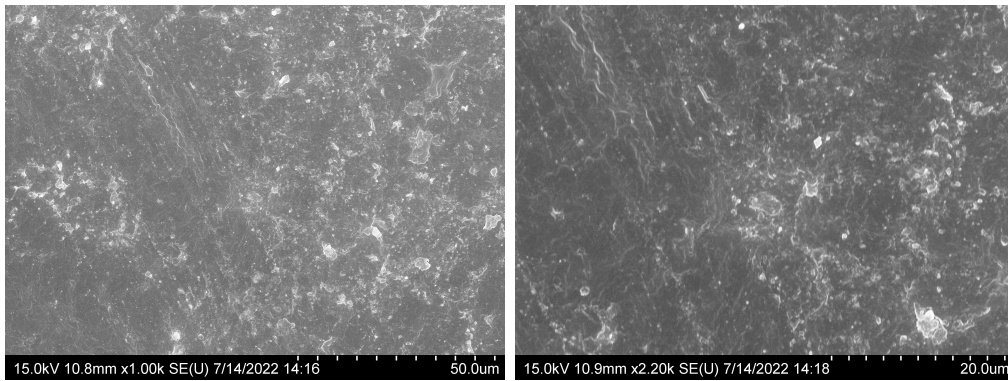
(a) 30:70 PEG/Epoxy with Li



(b) 30:70 PEG/Epoxy with Li

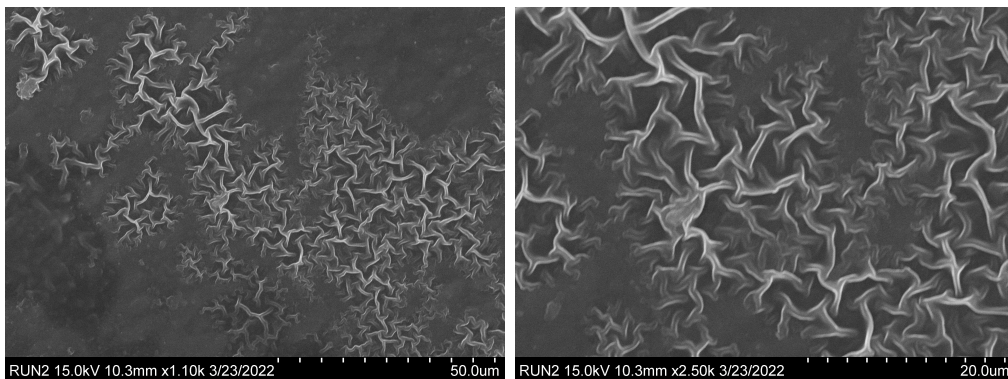
The SEM images of 70% epoxy content with LiTFSI, the microstructure consists of PEG-rich domains dispersed in the bulk epoxy phase[24]. Shear banding is taking place and is a microstructure that is indicative of phase separation. However, the high epoxy content and small pore size resulted in negligible ionic conductivity. Which could mean that the phase separated PEG-rich domains are not fully percolated[10].

The SEM images of epoxy content at 60% with no LiTFSI present reveal a microstructure much like at 70% epoxy content with no LiTFSI. No pores are visually seen at up to $20\mu\text{m}$, indicating phase separation is minimal. Comparitively, the SEM images of 60% epoxy content with LiTFSI show bulk PEG-rich domains dispersed in the epoxy matrix. Increasing pore size as seen in the SEM images. Thus, LiTFSI promotes phase separation between PEG and epoxy. This is due to the nucleophilic attack on the epoxide oxygen, but when cross-linking occurs the lithium ion has a strong repulsion to the hydroxyl unit[57].



(a) 40:60 PEG/Epoxy no Li

(b) 40:60 PEG/Epoxy no Li



(a) 40:60 PEG/Epoxy with Li

(b) 40:60 PEG/Epoxy with Li

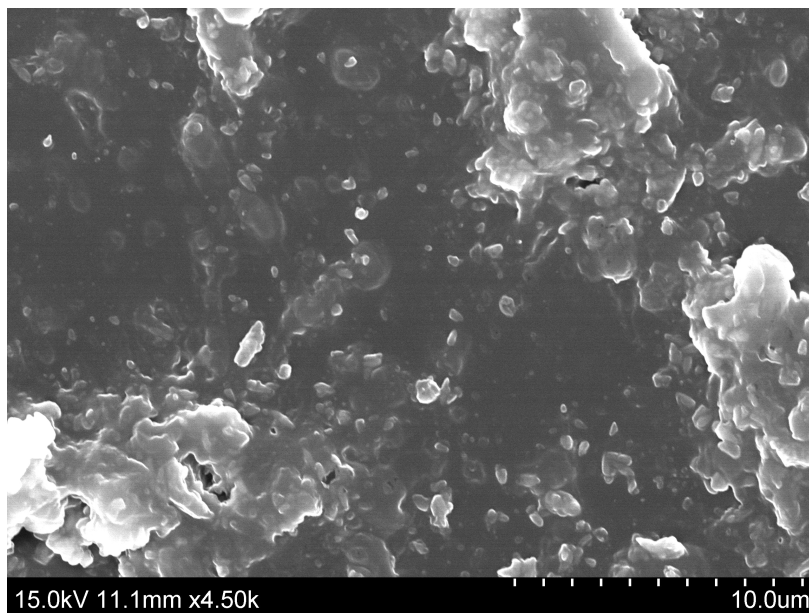


Figure 48: 55:45 PEG/Epoxy with Li

At 55% PEG the morphology changes where the dark region that is present was where the PEG left a void in the bulk epoxy phase. At higher PEG composition the effect of phase separation is increased dramatically. The PEG domain is much larger than that at 30-40% PEG which is as expected. However, previously when large voids were left in the epoxy phase after extraction, the compressive values were at their lowest. However, the ionic conductivity increased due to the higher amounts of PEG. Higher amounts of PEG added lowers the cross-linking density between the epoxy/amine, which in turn lowers the restriction of PEG segmental motion. This in turn increases ion transport and results in increased ionic conductivity values.

Since at higher GO contents into the PEG epoxy dispersion condition of GO was poor, to try and improve dispersion centrifuging was used. Here, we used 0.3-0.7% GO with respect to PEG and centrifuged half the samples, while the other half just used bath sonication with five minutes of shear-mixing. The half that were centrifuged were the odd numbers while the even numbers were not centrifuged. The final distribution of nanoparticles are strongly dependant on the final morphology of the electrolyte[58]. Better dispersion of GO will allow for optimizing of the electrolyte. To get a better understanding of how centrifuging could

change the morphology, SEM was used to compare the morphology between the centrifuged and non-centrifuged samples. The ionic conductivity was tested to see how the morphology could impact the ionic conductivity as well.

Table 5: Centrifuged and non-centrifuged samples

Sample	GO wt. (%)	PEG wt. (%)	Epoxy wt. (%)	LiTFSI wt. (%)
CF	0.3	55	45	10
NCF	0.3	55	45	10
CF	0.5	55	45	10
NCF	0.5	55	45	10
CF	0.7	55	45	10
NCF	0.7	55	45	10

3.3.2 PEG extraction of centrifuged and non-centrifuged samples

Figure 47 plots the GO content vs the amount of PEG extracted for the centrifuged vs non-centrifuged samples. As you can see, there is a big discrepancy between the amount of PEG extracted from the samples that used the supernatant for making the electrolyte, and the electrolyte that didn't undergo centrifugation. This could be due to the removal of any impurities or agglomeration of the GO nanosheets, or could be due to the fact that using the supernatant for processing the electrolyte lessens the GO content. From the previous chapter we saw a decrease in PEG being extracted when GO loading is implemented into the electrolyte. At 0.3% GO content the electrolyte that didn't use the supernatant had the lowest amount of PEG extracted. For the centrifuged sample at 0.7% GO the least amount of PEG was extracted. Indicating that the electrolyte miscibility parameters changed with incorporating LiTFSI and using the supernatant. The highest amount of PEG extracted was at 0.5% GO with respect to PEG for the centrifuged and noncentrifuged sample. This is consistent with the results that were achieved in when no lithium was incorporated into the electrolyte.

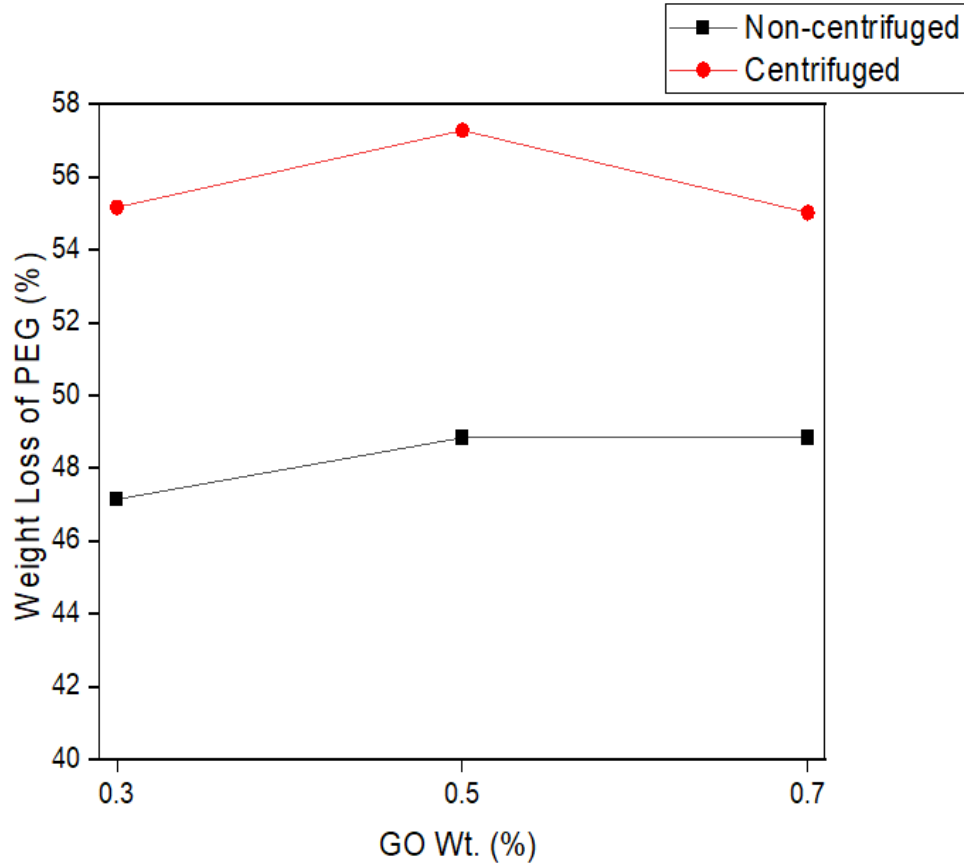
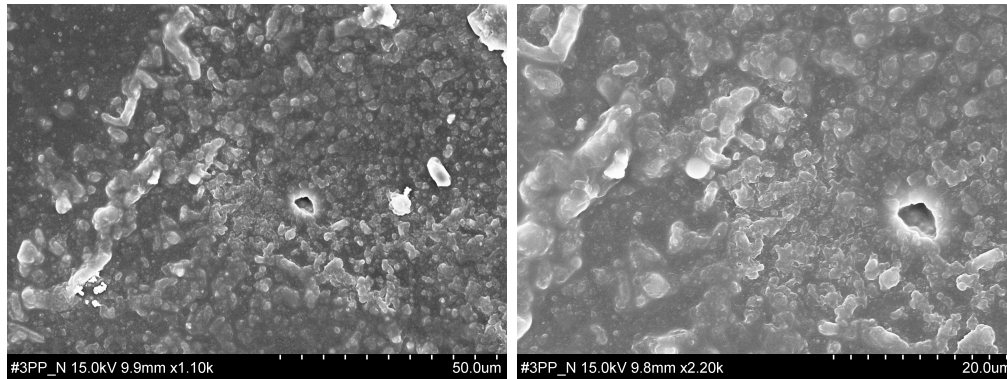


Figure 49: Centrifuged vs. non-centrifuged samples

3.3.3 Morphology variations of centrifuged and non-centrifuged

The SEM images of 0.3% GO centrifuged shows epoxy nodules appear similar to interconnected spheres similar to the image above when no GO is present in the electrolyte. In figure 42 a red arrow shows an epoxy nodule shaped as an interconnected sphere. However, the SEM images depict the electrolyte underwent nodular coarsening, indicating that phase separation took place, but that the phase separation took place on a much shorter scale than when no GO is added[59]. This is indicative from the SEM images when no GO is added we lose the phase inverted structure where large pores are present. The dark region where PEG was present becomes increasing smaller. The SEM images of 0.3% GO non-centrifuged a very different microstructure is obtained even though GO content was approximately the same. Here, phase separation is much less noticeable than the centrifuged sample. This is due to the fact that we lose the disordered microstructure that was observed in the centrifuged sam-

ple. The morphology depicts small pores that are randomly distributed through the matrix, and not as interconnected spheres such as in the centrifuged sample. Centrifuging removes any GO agglomerations since the supernatant was used, or just lessening the amount of GO content slightly has a drastic impact on the final morphology of the electrolyte. The supernatant potentially has less impact on the phase separation between PEG and epoxy than the non-centrifuged sample.



(a) 0.3% graphene oxide centrifuged

(b) 0.3% graphene oxide centrifuged

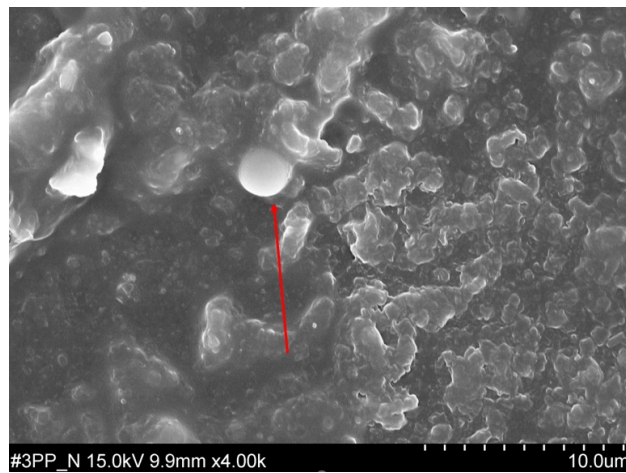
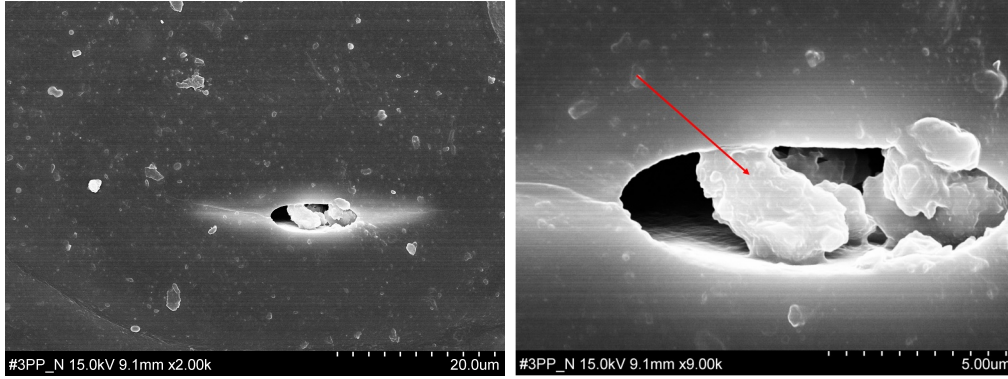


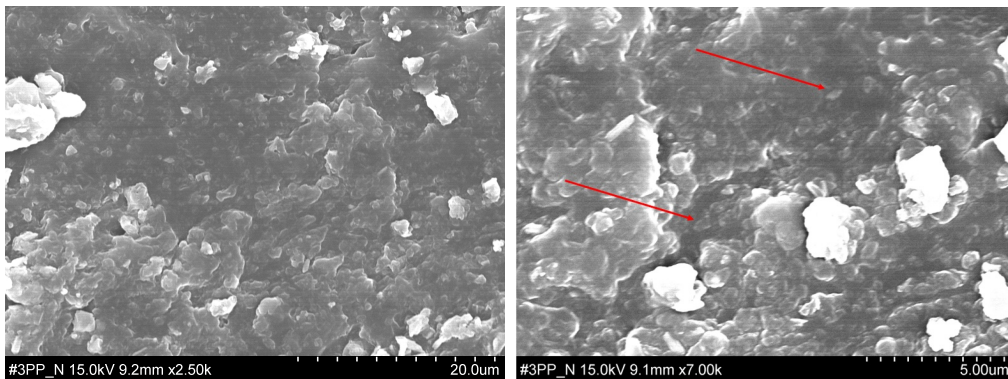
Figure 51: Interconnected sphere

The SEM images of 0.5% GO CF shows a morphology similar to that of 0.3% GO CF. However, the epoxy nodules don't show up as interconnected spheres. With increasing GO content from 0.3 to 0.5% with respect to PEG, the channels lose some concavity indicating more miscibility between PEG and epoxy. However at 0.5% GO content with respect to PEG, phase separation is still observed due to the disordered microstructure that is depicted

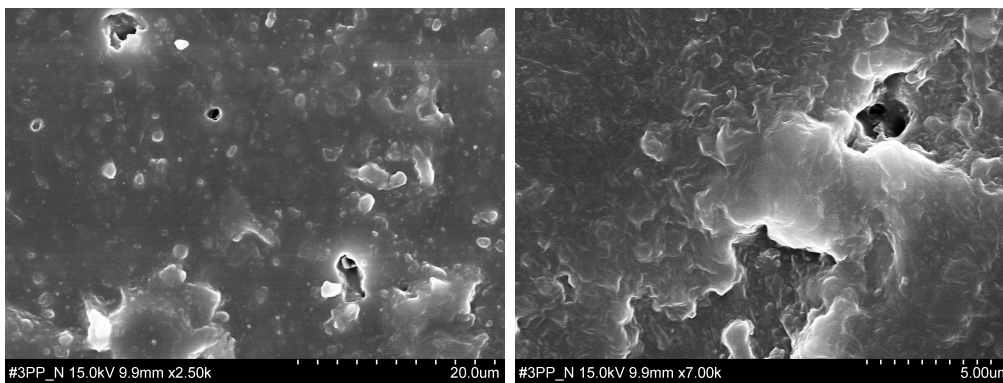


(a) 0.3% graphene oxide noncentrifuged (b) 0.3% graphene oxide noncentrifuged

from the SEM images. The amount of PEG extracted indicates that PEG was fully removed meaning that PEG and epoxy were in two distinct phases, and that there was minimal PEG entrapped in the epoxy network. The SEM images of 0.5% GO that didn't undergo centrifugation reveals a microstructure that is more homogeneous than the morphology of 0.5% GO that used the supernatant. This is indicative of less phase separation taking place between PEG and epoxy. Very discrete pores are visibly seen throughout the matrix, and range roughly from 3-5 μ m in diameter. However, the weight loss of PEG extracted in the non-centrifuged was noticeably less than in the centrifuged sample. This indicates that PEG was much more entrapped in the epoxy network. Centrifuging removes any of the impurities and bigger particles that were not properly exfoliated. Indicating that the dispersion of GO and not just the amount of GO content in the electrolyte has an effect on phase separation between the PEG and epoxy.

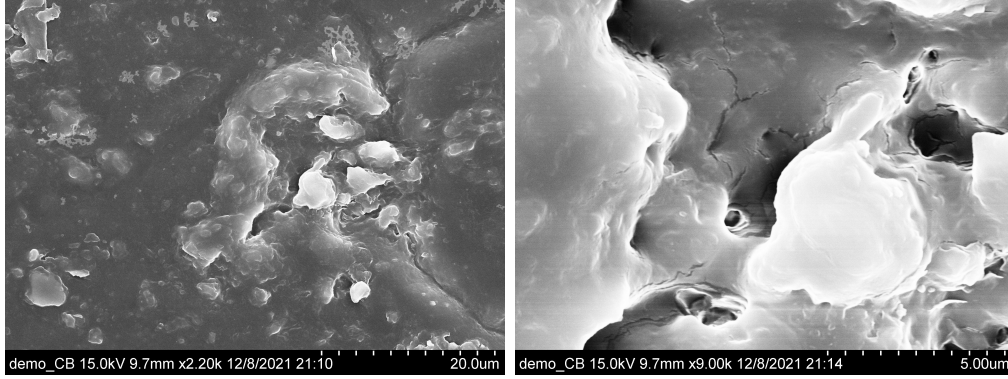


(a) 0.5% graphene oxide centrifuged (b) 0.5% graphene oxide centrifuged



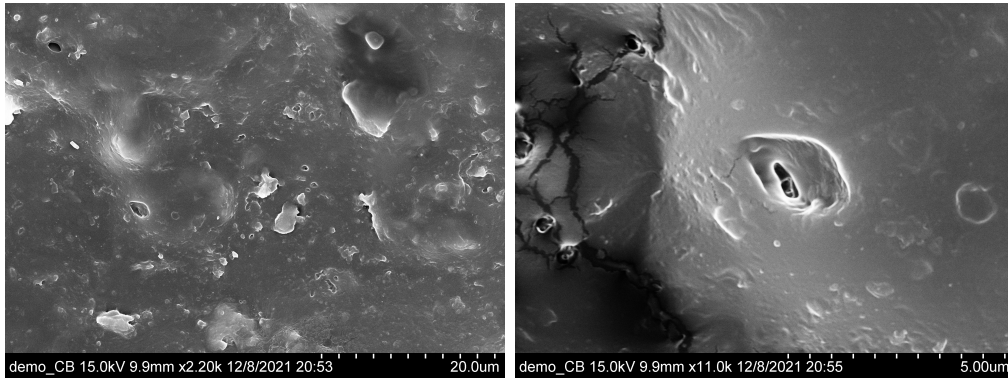
(a) 0.5% graphene oxide noncentrifuged (b) 0.5% graphene oxide noncentrifuged

The SEM images of GO content at 0.7% that underwent centrifugation pores are becoming even more discrete. Figure 48 shows pores in the nanometer range. Indicating that when no GO is incorporated in the electrolyte large cavities are present indicating mass phase separation. The introduction GO into the electrolyte reduces to micro-scale phase separation. Further increasing GO content the PEG-rich domains are becoming increasingly smaller indicating less phase separation is taking place. However, 0.7% GO CF revealed the most amount of PEG being extracted from the epoxy matrix. Indicating that an electrolyte channel was defined, and percolated through the cross-linked network. The SEM images of reveal a microstructure that has minimal aggregations embedded in the matrix. Indicating that a good dispersion of GO was achieved. The SEM images of 0.7% GO that didn't use the supernatant was incorporated into the electrolyte show small pores randomly dispersed in the polymer matrix. However, only one pore was visible while examining the phase morphology, and it was approximately 1-1.5 μ m. Much like at 0.7% GO CF, PEG-rich domains are becoming smaller with increasing GO content. 0.7% GO NCF was also revealed to have the most electrolyte being extracted out the non-centrifuged samples. However, more PEG is entrapped in the network than the centrifuged sample. Good dispersion of GO was achieved as there are no obvious aggregations that could potentially hinder ion transport.



(a) 0.7% graphene oxide centrifuged

(b) 0.7% graphene oxide centrifuged



(a) 0.7% graphene oxide noncentrifuged

(b) 0.7% graphene oxide noncentrifuged

3.3.4 Ionic conductivity values

The ionic conductivity of the electrolyte was measured for the samples that used the supernatant and the electrolyte that didn't. Figure 55 reveals the ionic conductivity values of the electrolyte and confirms that using the supernatant provided higher values compared to the samples that didn't undergo centrifugation. At 0.5% GO with respect to PEG that used the supernatant for synthesis of the electrolyte had the highest ionic conductivity at 9.94×10^{-6} (S/cm). PEG being extracted from the epoxy matrix was the highest during this configuration as well, indicating that PEG was percolated through the epoxy matrix. The SEM images also confirmed that phase separation was apparent between PEG and epoxy. 0.5% GO provided the highest conductivity for the electrolyte that didn't use the supernatant. Indicating that 0.5% GO provides a microstructure that is favorable for ionic conductivity, as well as the appropriate amount of GO loading for maximizing it's properties. At 0.7%

GO loading with respect to PEG, the microstructure reveals discrete pores indicating less electrolyte channels are generated.

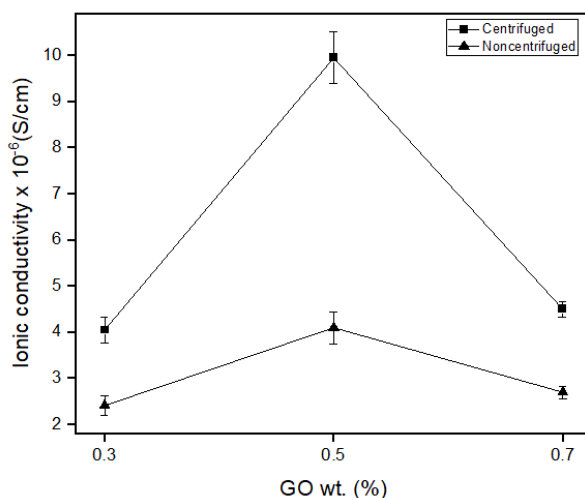


Figure 57: Ionic conductivity of electrolyte

To understand how bath sonication can affect the ionic conductivity, the ionic properties were measured at different intensities and duration. GO content was kept at 0.5% with respect to PEG and the remaining electrolyte was processed using the same configuration.

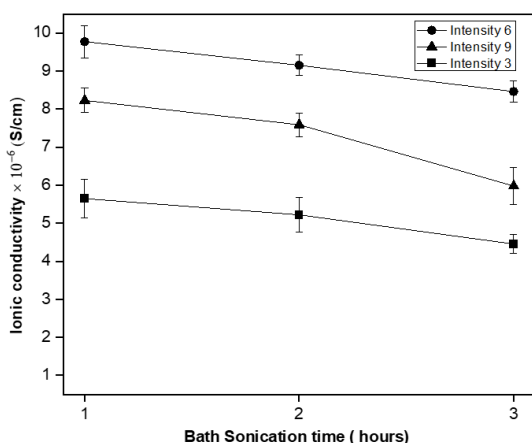


Figure 58: Ionic conductivity with different bath sonication durations and intensities

Figure 56 shows the ionic conductivities of the electrolyte with the duration of bath sonication as well as the different intensities. From the graph you can clearly see that the increase in duration of bath sonication hinders the ionic properties of the electrolyte. This is potentially caused by longer sonication damaging the oxygen-rich functional groups of GO, or potentially damaging the filler itself. The intensity of sonication also

had an impact on the conductivity as well. Intensity level 3 had the lowest conductivity due to the intensity not being strong enough to achieve proper dispersion conditions, and inten-

sity level 9 potentially had low conductivity due to at higher intensities the damaging of the filler. Bath sonication at intensity level 6 was determined to be the best for ionic properties. For further understanding of how duration of bath sonication impacts the conductivity of

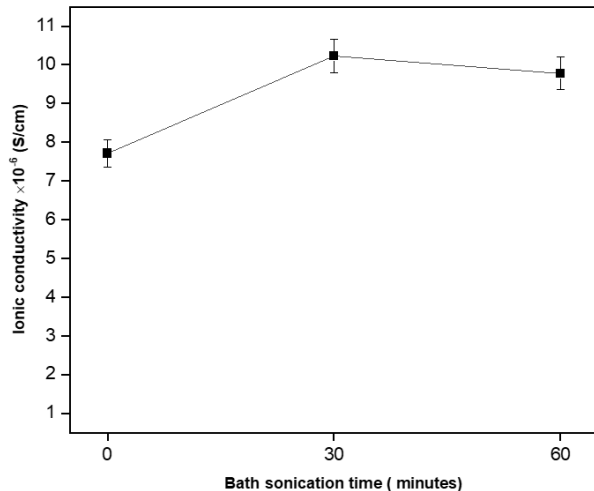


Figure 59: Ionic conductivity of bath sonication 0-60 minutes

the electrolyte. Figure 57 is the ionic conductivity values with the bath sonication times ranging from 0, 30, and 60 minutes at intensity level 6. Here, the electrolyte was processed using the same configuration as figure 25. When no bath sonication was done the lowest conductivity values were achieved. Due to the large surface area and the van der Waals forces, agglomeration of GO is likely to occur. GO agglomeration can hinder ion transport causing lower ionic conductivity values. Whereas, at 30 minutes of bath sonication the ionic conductivity was the highest. Indicating that 30 minutes of bath sonication was the optimal amount of sonication to achieve good dispersion of GO, and less damage to the filler itself. At 60 minutes of bath sonication the ionic conductivity decreased indicating that at this duration the GO particles were damaged or started to saturate.

3.4 Conclusion and future work

This work demonstrates the ability to tailor various microstructures based on different dispersion and exfoliation techniques of GO in an immiscible blend of PEG and epoxy. The

ability to be able to tailor the microstructure with varying amounts of GO and different dispersion processes, allows for optimizing of the electrolytes properties for SSC applications. SEM analysis shows that increasing GO content suppresses phase separation at a greater extent, but that phase separation is still occurring between PEG and epoxy. Incorporating GO into an immiscible blend improves the mechanical properties by having an affect on the microstructure once cured, and not just by the properties of GO. The data shows that the addition of GO at higher amounts has a detrimental affect of the electrolytes mechanical and ionic properties. The mechanical properties are decreased due to the poor exfoliation of GO nano-sheets which cause aggregations embedded on the matrix. These aggregations provide places for defects and cracks to be present, and providing a weak point for mechanical failure. Also, large aggregations that where shown in the SEM images had the lowest ionic conductivity due to the ion transport being hindered.

The future work will revolve around optimizing the dispersion and exfoliation conditions of GO. Dispersion of GO allows for optimizing the fillers properties, but excessive sonication and shear-mixing might damage the functional groups of GO and the filler itself. Epoxy-based polymer electrolytes that use a conductive polymer or component have a large degree of tailoring options for optimizing the properties of the electrolyte. These include various hardening agents, different lithium salt loading, curing temperatures, and different fillers and contents.

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