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by P-A. T. Nguyen and J. F. Snyder

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Multifunctional Properties of Structural Gel Electrolytes

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Multifunctional structural gel electrolytes were prepared by the integration of conductive pathways using non-aqueous solvents into structural resin networks. Poly(ethylene) glycol (200 MW) and propylene carbonate were used as non-aqueous solvents while vinyl ester and epoxy resin were used as structural resins. The monomer and solvents were incorporated together and polymerized to create conductive pathways in crosslinked networks. The impact of chemistry and weight fraction of both liquid and resin were investigated on the electrochemical-mechanical response of the resulting system. The addition of liquid solvent generally improves the performance of electrochemical properties relative to solid state polymer electrolytes, although at the expense of mechanical robustness. Crosslinking the polymer matrix is employed to improve mechanical performance. The ionic conductivity and compressive modulus were measured by AC impedance and compression respectively. Dynamic Mechanical Analysis was utilized to validate the processing conditions and material characterization.

Introduction

Due to the demand for more advanced and lightweight systems, multifunctional composite structures that can function as an electrochemical energy converter while bearing mechanical load are in development. This research has involved a materials-based approach in which each component of the system serves to bear and/or efficiently transfer load, and in which the materials are integrated using standard composites technology. Development of a structural electrolyte that meets all specifications is an especially difficult challenge. Polymer-based electrolytes are desirable owing to their broad and tailorable mechanical properties and the ease with which resin monomers may be used in composites processing. A variety of additives have been previously shown to result in a breadth of electrochemical ionic activity and mechanical durability (1, 2). Previous research has focused on investigating new polymer formulations (3) and the addition of inorganic fillers to polymer electrolytes for ionic conductivity and mechanical properties enhancement (4). The current focus is on plasticizing or swelling resin-based systems with liquid electrolytes, collectively referred to as polymer gel electrolytes, by investigating the impact of chemistry and weight fraction of both liquid and resin on the electrochemical-mechanical response of the resulting system. The present target for conductivity and compressive modulus is 10^{-3} S cm⁻¹ and 100 MPa respectively. The addition of liquid solvent generally improves the performance of electrochemical properties relative to solid state polymer electrolytes, although at the expense of mechanical robustness. Crosslinking the polymer matrix is employed to improve mechanical performance. There is experimental

evidence that polymer gel electrolytes swollen with low molecular weight polar solvent can provide relatively high conductivity in the range of $10^{-3} \text{ S cm}^{-1}$ at room temperature (5, 6).

For this study, two component systems have been developed using structural resins and liquid electrolytes. The structural resins employed include both vinyl ester and epoxy-amine chemistries and involve a broad range of crosslinking and polarity. A third component was copolymerized into some samples to introduce sidechains that provide additional ionic pathways.

Experimental

All materials were handled under dry atmosphere during preparation, processing, and testing. Anhydrous lithium trifluoromethanesulfonate (lithium triflate) (Aldrich) was dried for 2 days at 210°C under high vacuum. Polyethylene glycol (PEG, MW 200) (Aldrich) was dried by azeotropic distillation with toluene and stored over $4\text{\AA}$ molecular sieves for at least 2 days. Anhydrous propylene carbonate (PC) (Aldrich) was used as received. Vinyl ester resins were received from Sartomer Company with the product codes CD553 (methoxy PEG550 monoacrylate), SR209 (tetraethylene glycol dimethacrylate) and SR494 (ethoxylated (4) pentaerythritol tetraacrylate) and dried over $4\text{\AA}$ molecular sieves for at least 2 days. EPON 828 epoxy resin and PACM were received from Miller-Stephenson and Air Products respectively and they were used without further modification.

Lithium triflate was dissolved into PEG and PC in a 1.0M concentration. Lithium triflate was also added to the vinyl ester resins in the following quantities: 9 wt% in CD553; 4 wt% in SR209; and 3 wt% in SR494. The resins are PEG-based and have been shown through previous studies to provide limited ion conductivity, optimized at the concentrations of salt used here. No salt was added to the EPON 828 as it is an undiluted clear difunctional bisphenol A-epichlorohydrin derived liquid epoxy resin that is too non-polar to dissolve salt or provide ion transport. The prepared electrolytes were analyzed by Karl Fischer titration to confirm the absence of moisture. The most hygroscopic materials, the PEG and PC solutions, were found on average to have less than 0.075% residual water, or 0.005 moles of water per mole of salt.

The SR209, SR494, and EPON 828 resin-salt complexes were each mixed with the PEG- and PC- based liquid electrolytes to form homogenous solutions with the desired compositions. Samples were also made with the resin mixtures SR209-CD553 and SR494-CD553 each mixed with the PEG-based liquid electrolytes. The vinyl ester monomer-solvent-salt complexes were cured at 80°C for approximately 14 hours using an organic peroxide initiator, while the epoxy-based samples were cured at room temperature for at least 48 hours. Samples were post-cured at elevated temperature above the glass transition temperature (T_g). While T_g varied with composition, the post-cure temperature was typically between $40^{\circ}\text{C} - 80^{\circ}\text{C}$.

To characterize the gel electrolytes, they were cured in the form of pellets and prismatic bars using silicone molds. Sample dimensions were measured precisely using digital calipers. The pellets were 10 mm in diameter and 3 - 4 mm thick, while the bars were ca. 60mm long, 12 mm wide, and 4 mm thick. AC impedance measurements to measure ionic resistivity were performed using a Solartron 1260 Impedance / Gain – Phase Analyzer and Solartron 1287 Electrochemical Interface over the frequency range of $10 - 10^6 \text{ Hz}$ at room temperature (18 –

20°C). Mechanical characterization was accomplished by compressing the pellets in an MTS load frame employing a 5 kN load cell and a cross-head speed of 1 mm/min. The reported compressive modulus values are calculated from the initial, relatively elastic portion of material loading curves. Viscoelastic properties were measured using dynamic mechanical analysis on a DMA Q800 at 1 Hz and 7.5 amplitude over the range of -150 – 250°C . Each specimen was clamped using a dual cantilever configuration.

Results and Discussion

Figure 1 compares the multifunctional behavior for solvent-plasticized gel electrolytes with that of solvent-free neat polymer electrolytes. In this plot, ion conductivity represents desired electrochemical behavior and compressive modulus represents desired mechanical behavior. Commercial electrolytes and structural materials are monofunctional and would lie upon either axis. The homopolymer and random copolymer samples (open circle, filled circle, respectively) include a wide variety of chemistries and architectures as described elsewhere. The copolymer system shown on the plot involves the monomers CD553 and SR494 at several compositions. The evident behavior is for the copolymer to exhibit equal to or greater multifunctional behavior than may be achieved through a homopolymer and the endpoints generally define the limits for performance in these systems. Similar behavior has been observed for other copolymers, including CD553-SR209 (not shown). The gel samples in Figure 1 utilize either of two structural resins, SR494 or SR209, and employ a liquid electrolyte instead of the conductive resin CD553. The conductivity limit is accordingly raised by almost two orders of magnitude, thereby allowing for greater multifunctional performance. There is not a significant difference in multifunctionality when either PEG 200 or PC are used as solvent, nor when either SR209 or SR494 are used as the structural phase. For all three gel series the endpoints are approximately the same and so are the trends between them. However, the gel data does not follow the smooth trend that is evident for copolymers. This may originate from a disparity in which the conductive phase is dispersed. In the copolymers, the PEG oligomers are covalently affixed as sidechains to CD553, whereas in the gels the PEG oligomers are free to move independent of the polymer matrix. Although it is anticipated that the PEG is at least in part mechanically locked into the heavily crosslinked matrix, during polymerization the PEG may phase segregate in the gel to form percolated networks of high conductivity regions, particularly at compositions with high liquid content. Further studies are underway to examine the microstructure in these systems. The significant decline in gel conductivity at ca. 100 MPa may signify the loss of percolated networks of high conductivity regions, although the dispersed liquid does continue to plasticize the system. This plasticizing effect was evident in the DMA data and will be described below with regard to the epoxy samples. In these lower liquid regions the gel materials perform the same as copolymers. Figure 1 demonstrates the beneficial impact of a multicomponent system. However, the sample sets described include only two components – a structural matrix, and a conductive material that may be liquid or resin. Both copolymers and gels perform similarly when the structural matrix is a major component of at least 50 wt%.

Figure 2 explores this relationship further by expanding the multicomponent system to include gels that have been fabricated from a copolymer such that there is a structural resin, a conductive resin, and a conductive liquid all within the same sample. Each copolymer series takes as one endpoint a point on the homopolymer gel curve that was also displayed in Figure 1. It is clear from the figure that substituting part of the structural resin for a more conductive resin impairs

the multifunctional properties. The conductive resin does not possess the high conductivity of liquid electrolyte or the stiffness of crosslinked resins, and while it does provide some of both properties the overall compromise hurts performance. There may be benefit to these types of multi-component systems, perhaps when there are limitations on the amount of liquid that may be included, but in general it is evident that the most desirable solution is a two-part system in which one part provides as high ionic conductivity as possible and the other part provides as high mechanical strength as possible. However, other configurations, such as may be achieved through block copolymers, may yield more controllable architectures that allow for more than two components to be desirable. Figure 1 and figure 2 focus on radically cured PEG-based vinyl ester resins and PEG-based liquids to achieve a broad understanding of behavior in these systems.

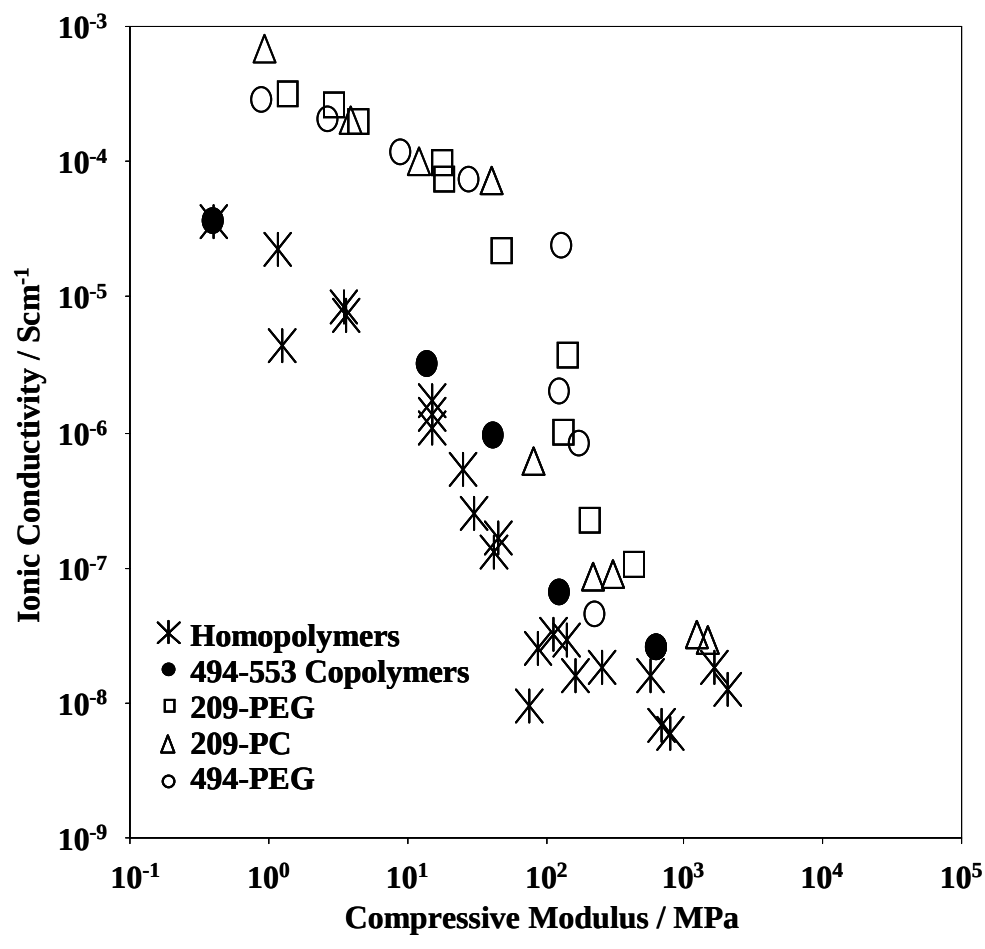


Figure 1: Room temperature ionic conductivity versus compressive modulus for vinyl ester electrolytes that are solvent-free homopolymers with varying chemistry and architecture, solvent free copolymers of CD553 and SR494, gels of SR209 with PEG 200, gels of SR209 with PC, and gels of SR494 with PEG 200. The multiple points for each copolymer and gel series refers to different compositions in increments of 25% (copolymer) or 10% (gels) weight fraction structural resin.

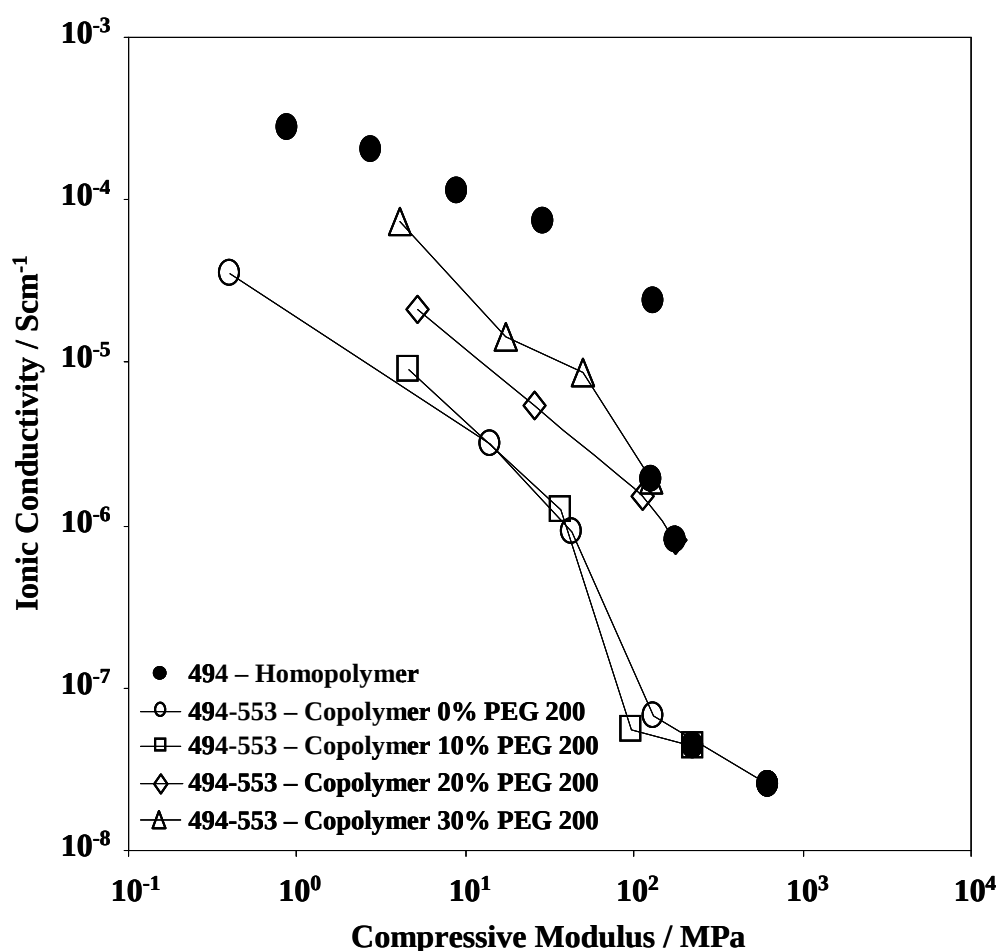


Figure 2: Room temperature ionic conductivity versus compressive modulus of SR494 with PEG, copolymer having acrylated reactive groups and monoacrylate swollen with 0, 10, 20 and 40 wt% PEG gel electrolytes.

For many applications there is a benefit to using epoxy-amine resins that cure using step growth polymerizations. Epoxy materials can achieve very desirable mechanical properties and enable the creation of partially cured prepreg laminates that can facilitate processing. Figure 3 presents data corresponding to gel-type electrolytes that are similar to those in Figure 1 but use an epoxy-amine resin system as the hard phase. The vinyl ester gel data are included in the plot for comparison. As with the vinyl ester samples, the liquid was blended with the uncured epoxy resin and the mixture was polymerized, allowing for a more homogenous dispersion of liquid in the samples. Figure 4 shows little change in performance between resin chemistries, with the exception of the epoxy-PC systems at high liquid content, which demonstrate encouraging properties. Epoxy samples with less than 50 wt% liquid there was no discernable conductivity, reinforcing the hypothesis that the higher conductivity regions are related to percolated networks of liquid. The vinyl ester structural resins contain some PEG units in the backbone that can sustain limited ion transport, and a more polar nature that may facilitate liquid-polymer interaction. The epoxy resins are not inherently conductive and tend to be very nonpolar, possibly resulting in more aggravated phase segregation with the highly polar liquid electrolytes.

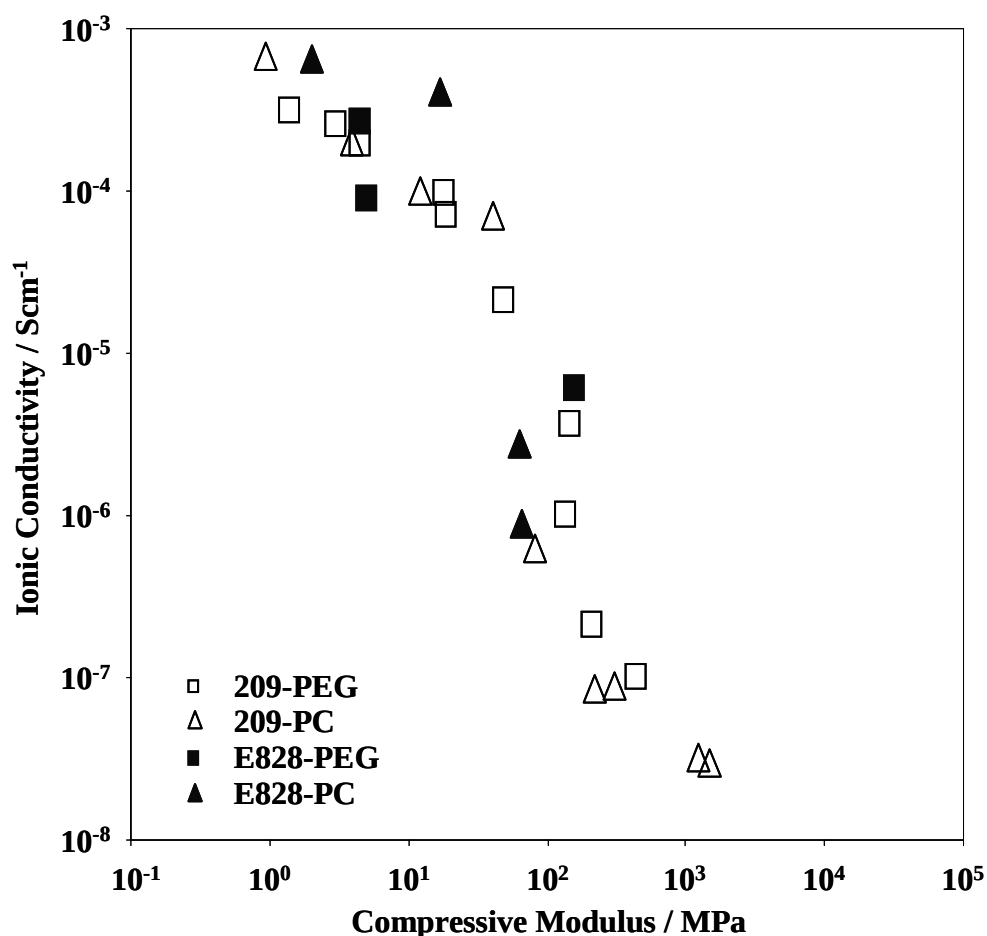


Figure 3: Room temperature ionic conductivity and compressive modulus of SR209 - PEG, SR209 - PC, EPON 828 - PEG, and EPON 828 - PC gel electrolytes

This polymer-solvent may be even more relevant for gels containing PC, as the dielectric constant of PC (65) approaches that of water and is a factor of five higher than that of PEG (12). Although conductivity data is unavailable for the lower liquid content epoxy samples, mechanical data for the full range of liquid content is compared in Figure 4. Below 50% liquid, the epoxy-PC samples significantly outperform the other series, which are all otherwise similar. One explanation may be inhibited plasticization resulting from greater resin-liquid repulsion in the epoxy-PC samples, which have the greatest polarity mismatch.

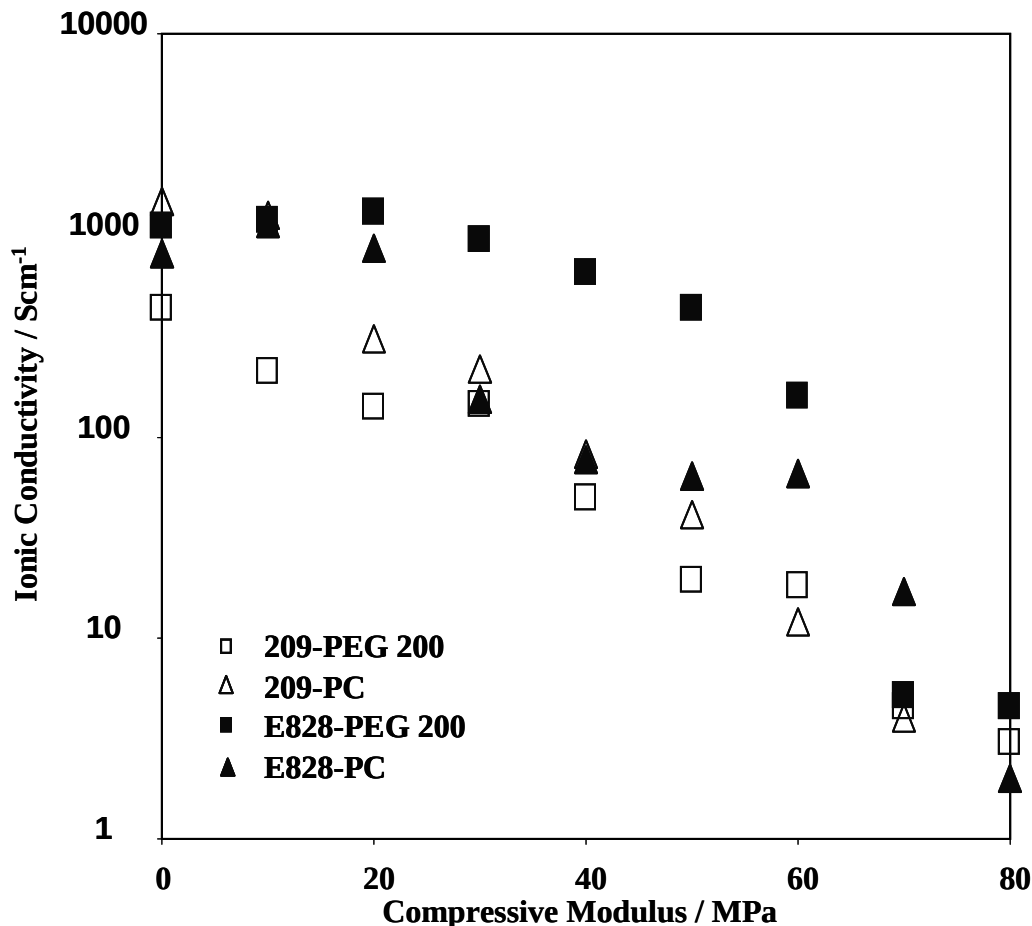


Figure 4: Room temperature compressive modulus of SR209 – PEG, SR209 - PC, EPON 828 – PEG, and EPON 828 - PC gel electrolytes.

DMA studies in these samples are underway to study the impact of liquid on viscoelastic properties and the potential for plasticization. Figure 5 displays the T_g and storage modulus data for the epoxy-PEG samples. This study was conducted for epoxy resin gel electrolyte with 10 – 60 wt% PEG as solvents. Figure 6 shows the impact of a series of solvent weight fraction on the T_g and storage modulus of the specimens. As solvent concentration increases, the primary glass transition initially decreases and quickly plateaus while the storage modulus continues to decline. A second transition, visible in the storage modulus data in Figure 6 and the tan delta data in Figure 7, begins to appear at 30 wt% liquid, which is about when the primary transition temperature plateaus. This suggests that the polymer interacts with only a very limited amount of liquid before a second liquid-dominant phase begins to develop. Similar studies for the other series are underway. The T_g data from these DMA tests were also used to develop the post-cure schedules, as plasticized matrices allow for a lower temperature post-cure. Secondary transitions were noticed at 30 wt% and the peak broadens up to 50 wt% at around -50°C . At 60 wt%, a weak transition started to appear at -25°C .

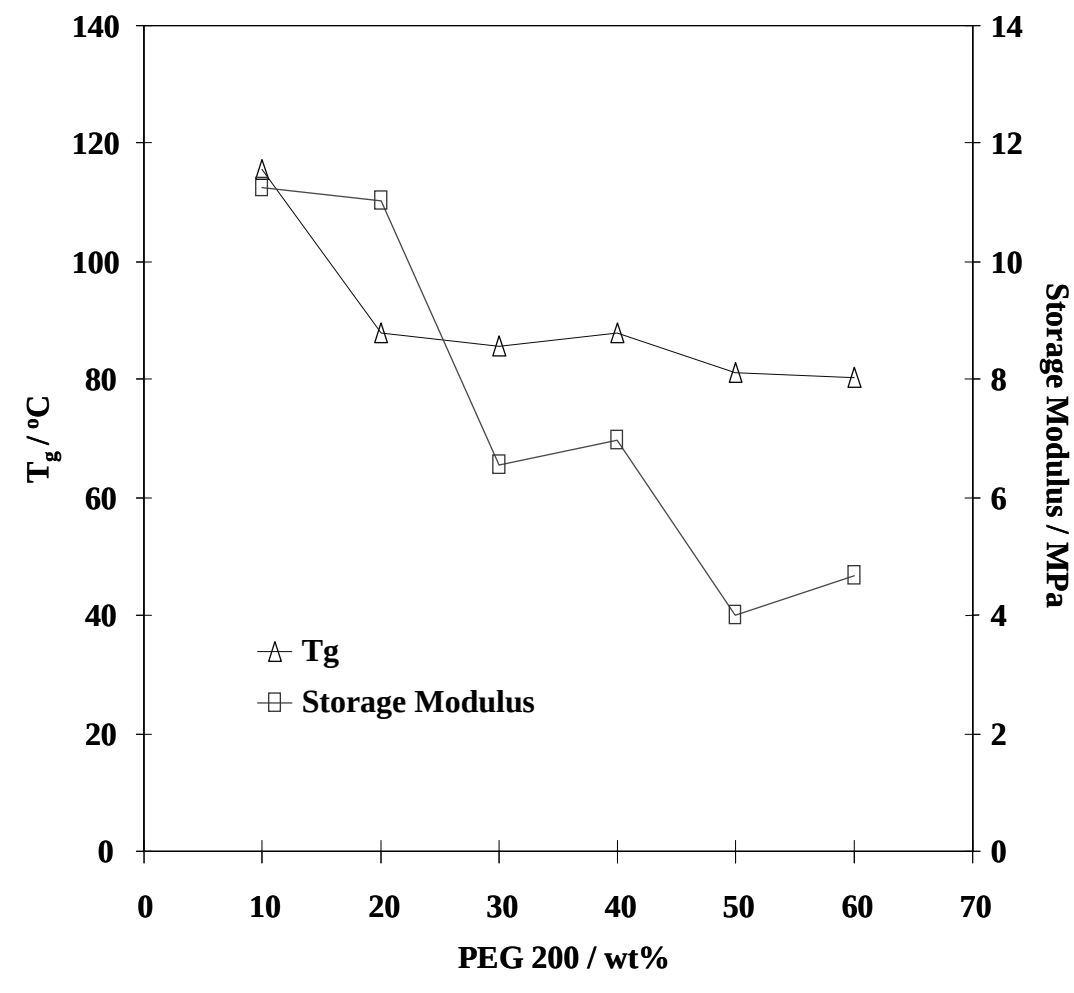


Figure 5: DMA of T_g and storage modulus of epoxy resin gel electrolyte temperature sweep from -150 – 250°C

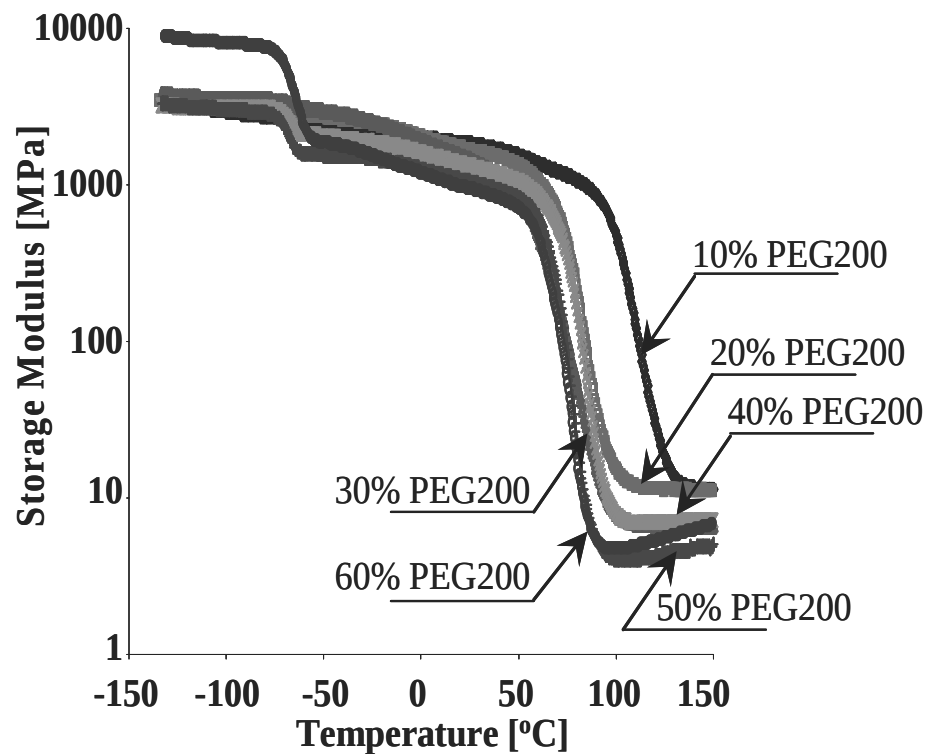


Figure 6: Storage modulus profile of epoxy resin gel electrolyte with 10 – 60 wt% PEG.

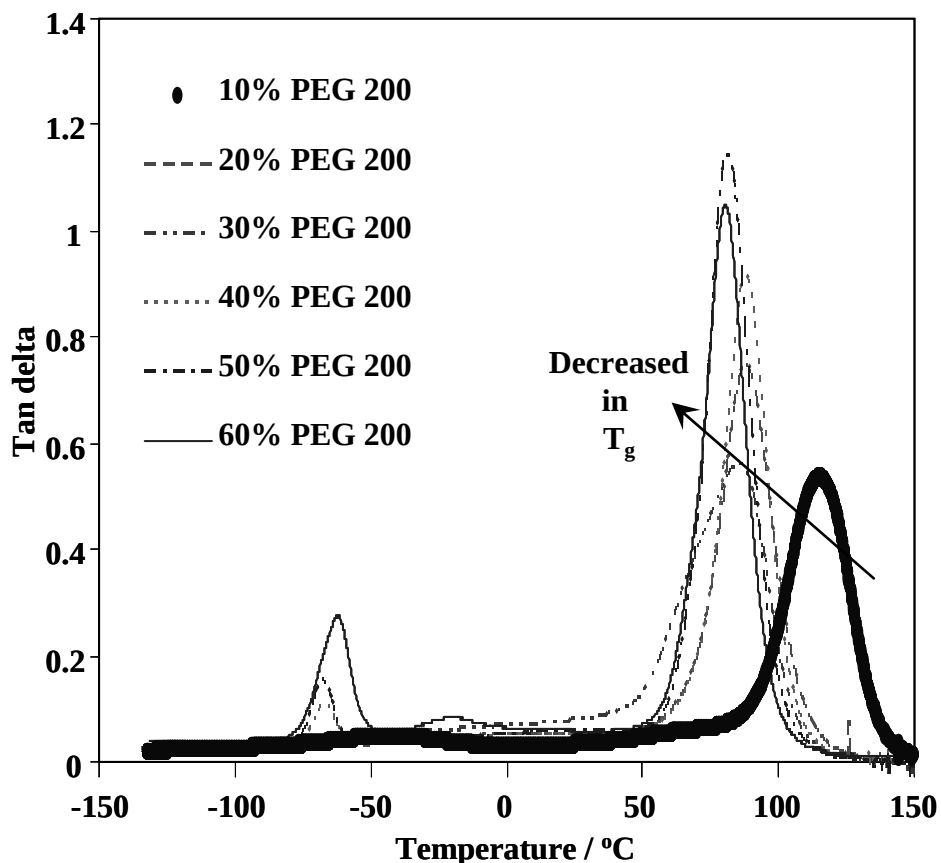


Figure 7: DMA of tan delta profile of epoxy resin gel electrolyte with 10 – 60 wt% PEG from -150 – 250°C.

Conclusion

Electrolytes composed of structural resin and liquid electrolyte were found to be superior to solvent-free electrolytes comprised of homopolymers or copolymers that contain ion-conducting components and structural components. Two-component electrolytes that contain a highly conductive component and a highly structural component were found to be superior to systems in which a third component was added that contains a compromise of both conductive and structural properties. Epoxy systems yielded better solvent retention and improvement in mechanical performance, but otherwise there was no significant difference resulting from the use of structural matrices or liquid electrolytes with differing composition as long as the properties were similar. All systems demonstrated a rapid decline in multifunctional performance at a critical liquid concentration that may indicate a percolation threshold for highly conductive regions.

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