Composite Polymer Electrolytes Using Fumed Silica Fillers: Rheology and Ionic Conductivity

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Composite polymer electrolytes prepared from fumed silica fillers, low molecular weight poly(ethylene glycols) and lithium perchlorate exhibit high room-temperature conductivities ($>10^{-4}$ S/cm), processability and mechanical stability. Samples made using polyethylene glycols with and without methyl end-groups had the same level of conductivity ($\sim 2 \times 10^{-4}$ S/cm). Dynamic rheological techniques, useful for probing material microstructure, showed that all samples behave as elastic networks with similar elastic moduli (G'); however, those with methyl end-groups were more sensitive to shear-induced microstructural breakdown. The decreased mechanical stability of composites prepared from glycols with methyl end-groups was interpreted in terms of polymer/particle/lithium salt interactions. Steady shear measurements showed all samples to be processable. The unique combination of elastic-like behavior and processability stems from the use of branched, three-dimensional fumed silica fillers that are capable of forming strong networks that can undergo shear but reforms after processing.

Introduction

Polymer electrolytes are becoming increasingly important because of their potential use in several electrochemical devices: "smart" windows, displays, sensors, and, more importantly, rechargeable solid-state lithium batteries. Their high energy densities combined with the potential for low-cost manufacturing technologies render solid-state lithium batteries with polymer electrolytes extremely attractive for usage in portable consumer electronics products. These batteries are also likely to be important power sources for pollution-free electric vehicles. Compared to liquid electrolytes, solid polymer electrolytes would eliminate electrolyte leakage, limit electrolyte–electrode reactions and allow tremendous flexibility in design. However, the successful use of these materials requires them to be mechanically strong but processable and have conductivities higher than 10^{-5} S/cm at room temperature.

Studies on polymer electrolytes have primarily focused on poly(ethylene oxides) (PEO) and PEO copolymers since these materials form stable complexes with lithium salts.[1-3] These materials conduct well ($\sigma > 10^{-4}$ S/cm) for temperatures above 60 °C but poorly ($<10^{-5}$ S/cm) at room temperature because of the formation of a poorly-conducting crystalline phase.[4] Numerous synthetic approaches were developed to eliminate the crystallinity of PEO-based systems, and now amorphous polymers are available with room-temperature Li ion conductivities greater than 10^{-5} S/cm.[3,5] Unfortunately, most of these polymers have poor mechanical properties and exhibit creeping behavior. Consequently, new approaches[6] such as cross-linking of PEO with PEO-based copolymers have been undertaken to improve the mechanical properties.

The addition of inert fillers to the polymer to improve its mechanical characteristics was first suggested by Weston and Steele[7] and has since been examined more recently by others.[8-10] The idea behind a composite polymer electrolyte is that the filler provides a solid-like support matrix, allowing the amorphous polymer to maintain its liquid-like characteristics in terms of fast ionic mobility at the microscopic level. Studies on composites containing γ-$LiAlO_2$ particles[8-10] or NASICON[11] in a poly(ethylene oxide)–lithium perchlorate complex, have revealed promising results: the mechanical stability and, in many cases, the conductivities have improved.

Our work focuses on an alternative scheme to produce a composite electrolyte using low molecular weight poly-

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Table 1. Descriptions of the Uncapped (PEG), One-End-Capped (PEG–MME), and Both-End-Capped (PEG–DME) Polymers Used To Prepare Composite Electrolytes

polymers		mol wt (M_w)
poly(ethylene glycol) (PEG-300)	$HO-(CH_2-CH-O)_n-H$	300
poly(ethylene glycol) (PEG-400)	$HO-(CH_2-CH-O)_n-H$	400
poly(ethylene glycol) monomethyl ether (PEG–MME)	$CH_3O-(CH_2-CH-O)_n-H$	350
poly(ethylene glycol) dimethyl ether (PEG–DME)	$CH_3O-(CH_2-CH-O)_n-CH_3$	400

(ethylene glycols) and fumed silica as a filler material. The interest in using fumed silica stems from its unique ability to form network structures in a liquid.[12,13] Typically, flame hydrolysis of silicon tetrachloride ($SiCl_4$) in H_2 and O_2 produces spherical silicon dioxide particles (~7–40 nm diameter) that fuse to form a branched, three-dimensional, chainlike aggregate of fumed silica. Because of the enormous surface area (50–400 m^2/g) of these particles, the surface functional groups (silanol, siloxane) play a major role in the behavior of fumed silica. In its pristine or unmodified state, the silanol group imparts a hydrophilic character to the material. In many cases, however, some or all of the hydrophilic silanol groups are chemically replaced by hydrophobic ligands. The degree of network formation by fumed silica in a liquid, therefore, depends on its weight fraction, the surface group as well as the nature of the suspending medium. Thus, fumed silica offers some distinct advantages for composite polymer electrolytes: (i) its inherent three-dimensional, branched chain enables it form network structures easily and at a low solids fraction, (ii) the large surface area leads to an open network structure that is conducive to a high ionic mobility of the polymer, and (iii) the surface group can be modified to tailor the mechanical properties to a specific need.

In this paper, we report our initial results on composite polymer electrolytes prepared from fumed silica, lithium perchlorate, and poly(ethylene glycols) and its derivatives. We believe composite polymer electrolytes will provide (i) the needed mechanical properties through the inherent network structure of fumed silica, and (ii) high conductivity through the use of a low molecular weight polymer with its intrinsic fast ionic mobility.

Experimental Section

Materials. A hydrophobic fumed silica, AEROSIL R805 (Degussa Corp., NJ), was used in all our experiments. This fumed silica has a BET surface area of 130–150 m^2/g, and 50% of its surface OH groups are replaced by octyl chains[14] to render it hydrophobic. Three different polymers were used: poly(ethylene glycol) (PEG), poly(ethylene glycol) monomethyl ether (PEG–MME) and poly(ethylene glycol) dimethyl ether (PEG–DME). The structure and molecular weight of all three samples (obtained from Aldrich) are given in Table 1. Composite polymer electrolytes were prepared by dissolving $LiClO_4$ in the polymer by constant stirring for 10 h. This solution (1 M $LiClO_4$) was added to the fumed silica in a blender and mixed for approximately 1 min. This blending time was required to ensure reproducibility between batches. Samples were made in 60 mL batches and placed in a vacuum oven at 50 °C for 12–15 h to remove air bubbles and any unbound water molecules. To compare the effect of Li^+ addition on both rheology and conductivity, samples were also prepared with fumed silica only. The amount of fumed silica was kept constant at a weight fraction of 0.10 for all samples studied here. The entire process was carried out in an inert nitrogen atmosphere.

Conductivity Measurements. The electrical properties of the samples were measured by ac impedance spectroscopy over the frequency range 5 Hz–13 MHz using a HP4192 impedance analyzer. An ac signal with an amplitude of 10 mV was used to obtain a good signal-to-noise ratio. The real and imaginary part of the dielectric response of a sample was measured in a specially designed cell and extrapolated to obtain the zero-frequency impedance value ($1/R$). The gellike nature of the samples prevented the use of conductivity measuring cells typically employed for solids or liquids.

The specially designed cell consisted of a circular stainless steel disk fitted snugly onto a Teflon collar. The inside diameter of this collar was stepped up at the other open end so that another steel disk could be pressed down to leave a gap of 5 mm between the two disks. The cell can thus be viewed as a very short cylinder (1 cm inside diameter) with Teflon sides and the two ends capped by two stainless steel electrodes, one of which is removable. Samples were placed inside this cylinder and the removable electrode pressed down slowly allowing excess material to come out through a small hole bored in the Teflon. Measurements made in this modified sandwich geometry under constant mechanical pressure provided excellent contact at the sample/electrode interface and precise control over the dimensions of the cell.

Rheology. The rheological properties were measured using dynamic oscillatory shear experiments. A Rheometrics mechanical spectrometer (RMS 800) with a cone-and-plate geometry was used to perform the experiment. In this measurement, a sinusoidal deformation $\gamma = \gamma_0 \sin \omega t$ was imposed on the sample at a fixed frequency, ω, and maximum strain amplitude γ_0. The resulting stress, τ_{yx}, has components given by[15]

$$\tau_{yx} = G'\gamma_0 \sin \omega t + G''\gamma_0 \cos \omega t$$

In this equation, the stress component in-phase with the deformation defines the storage or elastic modulus, G', whereas the stress component out-of-phase with the strain defines the loss or viscous modulus, G''. The shape and magnitude of the elastic modulus is sensitive to the microstructure of the system.[14–18] All samples were initially exposed to an oscillatory shear strain $\gamma_0 = 0.04$ at a frequency $\omega = 1$ rad/s for 40 min to erase any sample loading history. The dynamic moduli of all samples decreased to a plateau value in this time period, indicating the presence of an equilibrium structure. Strain and/or frequency dependent measurements were then conducted on the samples to obtain information on material microstructure and its response to processing.

Results and Discussion

The feasibility of using these materials as polymer electrolytes was initially examined by measuring their ionic conductivities. Table 2 compares the conductivities (σ) of composites with and without lithium perchlo-

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Table 2. Conductivities of Various Fumed Silica/Polymer Composites at 25 °C[a]

sample	ionic conductivity (S/cm) with Li^+	ionic conductivity (S/cm) no Li^+
PEG-300	1.4×10^{-4}	2.2×10^{-7}
PEG-400	1.1×10^{-4}	9.8×10^{-8}
PEG–MME	2.7×10^{-4}	1.6×10^{-7}
PEG–DME	4.3×10^{-4}	1.0×10^{-7}

[a] A 10% by weight commercially available fumed silica, Aerosil R805 (Degussa Corp.), was used.

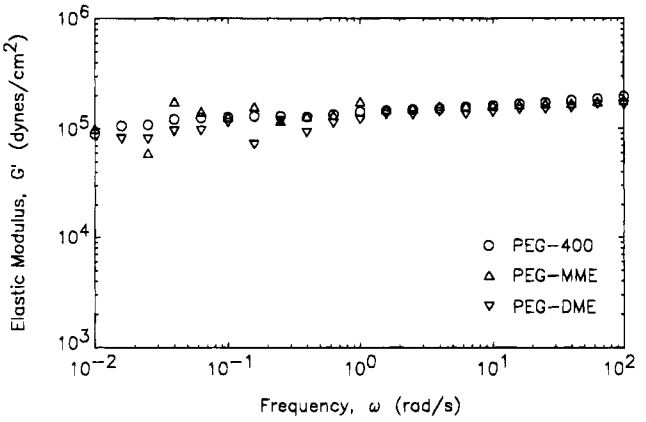

Figure 1. Dynamic elastic modulus of an uncapped (PEG-400), one-end capped (PEG–MME) and both-end capped (PEG–DME) glycol are shown as a function of frequency (ω). The $G'-\omega$ responses fall within a small range and are flat, indicative of an elastic network. All samples contained 10 wt % fumed silica and 1 mol of $LiClO_4$ salt. Experiments were conducted at 25 °C.

rate. We find that pure fumed silica suspensions have a low conductivity ($\sim 10^{-7}$ S/cm^2) at room temperature, indicating protonic conductivity to be negligible. One concern in using glycols instead of end-capped glycols as a polymer electrolyte is that the former may exhibit protonic conduction through hydroxyl groups of the glycols or from absorbed water because of their inherent hygroscopicity. The similar conductivities of all four samples (capped and uncapped), however, rule out conduction as a major effect in these materials. The addition of lithium salts results in a significant increase in the electrical conductivity of all samples. We also find the conductivity to increase with end-capping of the glycols; PEG–MME and PEG–DME show respectively 2- and 4-fold increases in σ. However, all samples have conductivity values $\geq 10^{-4}$ S/cm^2 making them viable materials for use as an electrolyte.

The dynamic elastic moduli (G') of composite electrolytes prepared using uncapped (PEG-400), one-end capped (PEG–MME) and both-end capped (PEG–DME) glycols are plotted in Figure 1 as a function of frequency (ω). We find the modulus values of all samples to be within a small range, with the G' of PEG–DME slightly lower than the rest. However, the $G'-\omega$ responses are essentially flat in all cases, suggesting the presence of a gellike network in all three types of materials.[14] Note that a gellike network is important for many applications since it reinforces the composite.

An important design consideration, besides modulus, is the sensitivity of the samples to shear. In Figure 2, we have plotted the G' of the same three materials as a function of increasing strain, γ. In this experiment, the frequency of oscillation was kept constant at 1 rad/s.

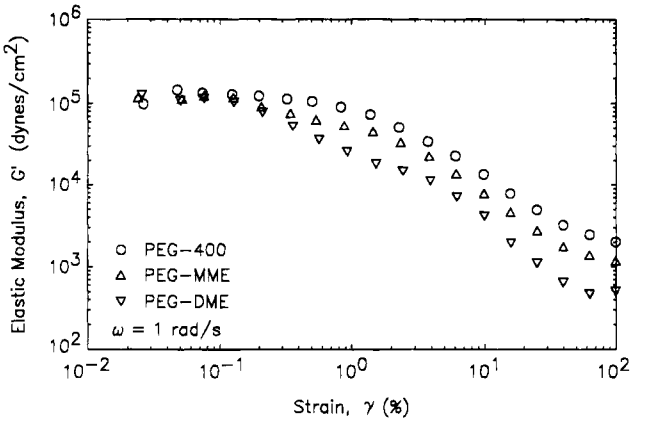

Figure 2. Elastic modulus (G') of three fumed silica/polymer/Li^+ composite shown as a function of increasing shear strain. The modulus decreases significantly as the microstructure breaks down. The breakdown is reversible. Here, each sample has 10 wt % fumed silica and 1 mol of $LiClO_4$; temperature of experiment 25 °C.

Table 3. Crossover Strain γ_{co} at Which the Elastic Modulus (G') Equals the Loss Modulus (G'') Shown for Composites Prepared from Different Polymers[a]

composite with:	crossover strain (%)	composite with:	crossover strain (%)
PEG-300	7.5	PEG–MME	2.5
PEG-400	6	PEG–DME	0.6

[a] Details on the polymers are given in Table 1.

The $G'-\gamma$ behavior is characterized by a high, short plateau at low strains corresponding to the linear viscoelastic (LVE) regime. In this regime, the loss modulus G'' (not shown) is significantly lower than G'. With increasing strain, the material network structure is disrupted; G' decreases and eventually becomes smaller than G''. We denote the crossover strain ($G' = G''$) as γ_{co}. We find G' to be essentially the same for all samples in the LVE regime, corroborating with the frequency-dependent results of Figure 1. As the strain is increased, the two-end-capped PEG–DME exhibits the most susceptibility to shear; it has the smallest LVE regime and its elastic modulus decreases most rapidly with strain. The glycol (PEG-400), on the other hand, is least sensitive to shear with the onset of network disruption occurring at a large strain and G' decreasing slowly. Thus, the three types of composites exhibit different shear sensitivity although their elastic moduli are similar.

Studies often use the strain where the LVE regime ends[16] as a measure of the shear sensitivity; however, this value can be obtained only through extrapolation resulting in some uncertainty. We, instead, used the crossover strain, γ_{co}, which can be interpreted as the deformation necessary to disrupt a network sufficiently so that its elastic and viscous contributions are same, to quantify the effects of shear. We find from Table 3 the γ_{co} of the samples to follow the sequence PEG-300 $\geq$ PEG-400 > PEG–MME > PEG–DME, indicating that end-capping creates a weaker gel structure that is more susceptible to shear. To understand how the internal structure is affected at these strain levels, we measured the elastic modulus at γ_{co} of PEG–DME as a function of frequency (Figure 3). We find the elastic modulus to be flat at low frequencies indicating that even at this high strain the material possesses considerable solidlike characteristics. Note, however, that the

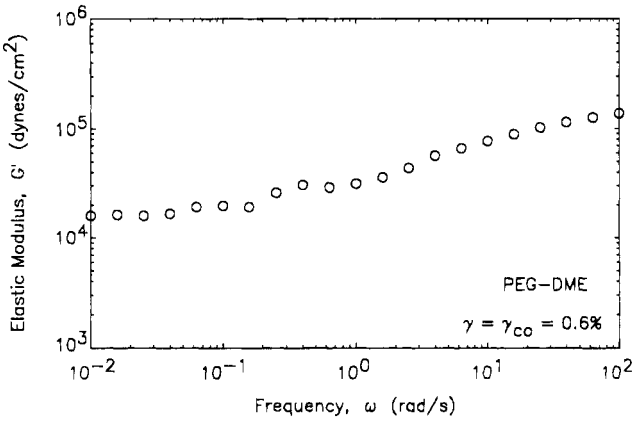

Figure 3. Frequency-dependent elastic modulus (G') of a composite polymer electrolyte prepared from a methyl-terminated (both ends) glycol is shown. The experiment was conducted at the cross-over strain γ_{co} where the both the elastic (G') and loss (G'') moduli were equal. The elastic characteristics, even at this strain level, is evident from the flat G'.

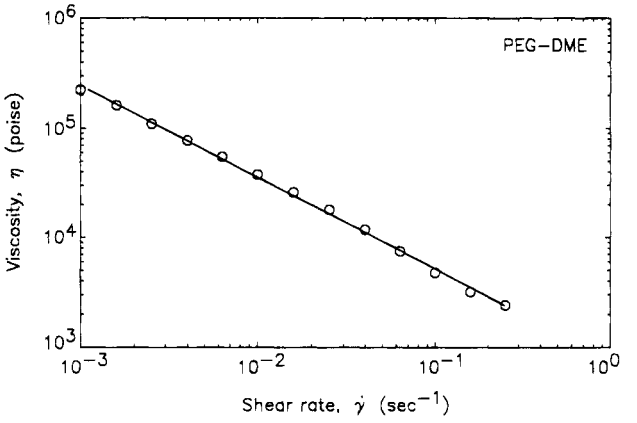

Figure 4. Steady shear viscosity of a two-end capped gycol/fumed silica/Li^+ composite shown as a function of shear rate. The experiment was conducted at 25 °C.

low-frequency elastic modulus (G') values are smaller than the G' in the LVE regime. From a processing standpoint, it is also important to know how steady shearing affects a sample. Viscosity measurements were conducted on PEG–DME again because this sample is most prone to shear-induced breakdown. In Figure 4, which shows a plot of viscosity (η) versus shear rate ($\dot{\gamma}$), we find the material to have a power-law behavior with a slope of ~0.83 at all low shear rates, indicating that sufficient structure is preserved during processing. It should be mentioned that this sample was subjected to two shear rate sweeps from 0.001 to 0.1 s^{-1} prior to obtaining this data. Experiments conducted on all samples revealed that they attain an equilibrium structure by the end of the second shear rate sweep, and no change was observed in their $\eta-\dot{\gamma}$ behavior in subsequent measurements.

The dynamic and steady rheology results indicate all composite electrolytes to be elasticlike yet processable. This unique combination, which is desirable for many applications, stems from the use of fumed silica fillers which are capable of forming reformable, three-dimensional network structures. Our study also shows that glycols (without methyl end groups) form composites with better mechanical properties, whereas end-capped glycols give higher conductivities. To improve the properties of these systems further, one needs a better understanding of the particle/solvent/ion interactions. In Table 4, we have compared the elastic modulus of materials with and without $LiClO_4$. The incorporation of salts results in a 5-fold increase in G' for PEG–DME, a 50% increase for PEG–MME and approximately 20% increase for the glycols. This trend in G' increase can be attributed to two possible mechanisms. First, the Li^+ cation may either directly or indirectly form effective cross-links between polymer chains making the poly(ethylene oxide)-based materials become more rigid; Li^+ cations may form direct links between two oxygen atoms of separate polymer chains[19] or they may attach themselves to the oxygen atoms of individual chains and the anions from the "cross-links" between them.[20] Second, Li^+ may bridge the surface silanol groups of the fumed silica and the terminal OH groups or ether linkages of the polymers. A result of these interactions is the development of network structure as is corroborated by the rheology results. We believe that the main mode of interaction between the fumed silica and poly(ethylene glycol) is through hydrogen bonds between the silica silanol groups and one of the terminal OH groups of the glycol.[14] With end-capped polymers, weaker interactions occur between the ether group of the polymer and the silica OH resulting in a lower elastic modulus. This trend is observed (Table 4) very clearly in the case of PEG–DME. The addition of ions apparently strengthens the linkages between two ethers or between an ether and OH group, giving rise to a higher G'. This effect, as expected, is most pronounced in two-end capped PEG–DME.

Table 4. Effect of Adding Lithium Perchlorate on the Elastic Modulus of Various Fumed Silica/Polymer Composites

	elastic modulus, G' (dyn/cm²)	
sample	with Li^+	no Li^+
PEG-300	1.1×10^5	9.1×10^4
PEG-400	1.2×10^5	1×10^5
PEG–MME	1.2×10^5	8×10^4
PEG–DME	1×10^5	2×10^4

Conclusion

We have found that composite polymer electrolytes with good mechanical and conductive properties can be prepared by combining fumed silicas and lithium perchlorate with low molecular weight PEGs. These materials display many of the characteristics (low cost, processability, mechanical stability, and high ionic conductivity) needed in a practical solid-state electrolyte. Because the formation of a reinforcing fumed silica network is primarily responsible for the good mechanical properties of the composites, composites based on alternative oligomeric polyethers and electrolytes should display similar improvements in mechanical properties without significant degradation in conductivity. Clearly, additional work needs to be done to match the properties of the composite to that required in specific applications. For example the use of composite electrolytes in lithium batteries will require extensive characterization of the electrochemical stability of the electrolyte toward cath-

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odes (metal oxide insertion compounds) and anodes (lithium metal or lithium intercalated carbon). Mechanical and electrochemical stability must also be defined. Although conductivity increases with temperature, the mechanical properties of most polymers deteriorate at elevated temperatures. Fortunately, the inherent, 3-D aggregate structure of fumed silica are known to provide good temperature stability.[12,13,21] While further studies are being undertaken to resolve these issues, the initial prognosis on these materials are promising: they exhibit respectable conductivities at low lithium/oxygen ratios and have solidlike, yet processable, characteristics at low volume fraction of fillers.

(21) Unpublished results on fumed silica in poly(propylene glycol); temperature-dependent measurements conducted up to 80 °C show that the elastic structure is retained in this temperature range.

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