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Morphological, Rheological and Electrochemical Studies of Poly(Ethylene Oxide)

Electrolytes Containing Fumed Silica Nanoparticles

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Abstract

In this paper, the rheology and crystallization of composite Poly(Ethylene Oxide) (PEO) electrolytes were studied by dynamic mechanical analysis, DSC and polarized light microscopy. The effects of fumed silica nanoparticles on the conductivities of the polymer electrolytes at temperatures above and below their melting point were measured and related to their rheology and crystallization behavior, respectively. The electrolyte/electrode interfacial properties and cycling performances of the composite polymer electrolytes in Li/Li cells are also discussed. The measured electrochemical properties were found to depend heavily on the operational environments and sample processing history.

Keywords

composite polymer electrolytes; Poly(Ethylene Oxide); nanoparticles; rheology

1. Introduction

Since the discovery of ionic conductivity in polymer-salt complexes [1], great efforts have been made to develop solid polymer electrolytes (SPE) for use in rechargeable lithium batteries due to the potential for higher energy densities and improved safety that satisfy the requirements for electric vehicles, for example. Poly(Ethylene Oxide) (PEO) electrolytes are the most extensively studied SPE systems. In order to enhance the ionic conductivity of PEO electrolytes, especially at low temperature, composite polymer electrolytes (CPE) have been

prepared by adding ceramic nanoparticles. It was reported that the conductivity is significantly increased by adding 10% by weight ceramic nanoparticles to PEO electrolytes [2-4]. In this paper, we report our rheological, morphological and electrochemical observations of the most commonly studied PEO electrolytes with ceramic added nanoparticles. Due to the page limitations, more detailed descriptions of experimental details and results will be reported elsewhere [5].

2. Experimental

PEO (Polyox Mw 2×10^5 , 4×10^6) was recrystallized from acetone to remove butylated hydroxytoluene (BHT) stabilizer, and was defined as “lab-pure” PEO. The commercial polymers contain up to 4 wt.% fumed silica and calcium salt residues. A special procedure was followed to remove all additives to obtain “ultra-pure” PEO. PAREL, a commercial available poly(Propylene Oxide) (PPO), was obtained from Zeon Chemicals and has a number average molecular weight of 2.5×10^5 (PDI=2). Fumed silica with a hydrophilic surface (Aerosil 200, 12nm id particle size) and a hydrophobic surface (Aerosil R805, 12nm id particle size) were gifts from Degussa. All polymers, salts and nanoparticles were carefully dried and stored in a “dry” glove box before use. Acetonitrile (Burdick & Jackson HPLC grade (>99.9%) and lowest water content (<0.001%)) was further dried in the “solvent” glove box by percolation through a column of Super-activated Alumina (ICN). Two glove boxes were used. One is defined as “solvent” glove box which is used for solvent-involved operations such as salt and polymer dissolution, film casting, etc. The other is designated as the “dry” glove box which was scrupulously free of organic solvent vapors. It is used for the storage of lithium electrodes, dry chemicals and samples and for cell assembly. Both glove boxes were filled with helium with H₂O and O₂ concentrations <1ppm. Polymer electrolyte films were cast from acetonitrile solution on Teflon plates and

thoroughly dried under vacuum before use. The films were assembled between electrodes in Swagelok cells designed to exert controlled pressure on the cell sandwich and completely sealed. A polypropylene or PVDF spacer ring with known thickness and central area was used to control the dimensions of polymer electrolytes. A Solartron SI 1254 four-channel frequency response (65 kHz to 0.01Hz) analyzer was used to measure the AC impedance from high to low frequency. The polymer electrolytes were annealed at 100°C for 12 hours in cells before conductivity measurements using stainless steel or lithium electrodes. Rheology measurements were conducted on a Rheometric RSAII with parallel plate fittings. Thermal measurements were performed on a Perkin-Elmer DSC-7 apparatus. Polarized light microscopy was carried on Nikon Epiphot invert microscope.

3. Results and Discussion

3.1 Rheology. Figure 1 shows compression moduli of $\text{P(EO)}_{20}\text{LiTFSI}$ containing various amounts and types of fumed silica nanoparticles. Commercially available PEO, no matter from Dow Polyox or Aldrich, contains up to 4% fumed silica. After removing the fumed silica, the moduli of the ultra-pure PEO electrolyte have obviously decreased compared with the lab-pure material that contains 3-4% silica. With 10% additional fumed silica added, the moduli increased significantly. The fact that hydrophilic fumed silica enhances the mechanical property a little more than the hydrophobic fumed silica does is attributed to the stronger interaction of the former to PEO by hydrogen bonding. It is also observed the E'/E'' crossover point moved to lower frequency with higher mechanical properties, which indicates longer relaxation times of the polymers and slower segmental motion in the presence of the nano-particles.

We found the conductivities at high temperature (above melting point) of PEO electrolytes, including $\text{P(EO)}_{20}\text{LiTFSI}$, $\text{P(EO)}_{20}\text{LiTf}$, and $\text{P(EO)}_8\text{LiClO}_4$, were decreased with

added nanoparticles [5]. The nanoparticle fillers are believed to play a role in inhibiting polymer segmental motion. According to Eisenberg's model [6], the interaction of polymer chains with nano-sized silica particles reduces the mobility of polymer chains and leads to the formation of immobilized and restricted mobility regions around the filler particles. The frequency sweep spectra (Figure 1) clearly reveal the polymer-filler interactions which lead to enhanced mechanical properties. More direct evidence of restricted segmental motion should come from measurement of the glass transition. To avoid the effect of the crystalline phase on the glass transition of PEO, completely amorphous PPO (PAREL, Zeon Chemicals) with a similar molecular weight as the PEO ($M_w = 5 \times 10^5$ vs. 2×10^5) was used as a model polymer. Figure 2 shows the glass transition of PPO with different amounts of fumed silica added measured by dynamic mechanical thermal analysis (DMTA). It is observed that the T_g (peak maximum position) shifts to higher temperature, and the peak heights and areas decrease with more added filler. These observations are clear evidence that polymer segmental motion is restricted by the presence of nano-particle filler, and can explain why lowered conductivity of high temperature PEO electrolytes is observed in the presence of filler.

3.2 Crystallization. We observed by DSC measurements that the presence of nanoparticle filler in a PEO polymer electrolyte could effectively inhibit polymer recrystallization. We also observed the conductivity of polymer electrolytes below the melting point is usually increased by adding ~10% nanoparticles, consistent with literature reports. The reduced recrystallization caused by adding filler is further evidence of restricted segmental motion in the presence of nanoparticles because only through segmental motion can the polymer chains be arranged to ordered structures to form crystals. The presence of the particles surfaces slows down the polymer motion and hence the rate of polymer crystallization is reduced.

However, the PEO/salt systems cannot be simply described as binary systems because both the polymer and the polymer/salt complex each contains crystalline and amorphous phases. Moreover, these phases are not in an equilibrium state but present in variable amounts depending on salt type and concentration, processing history, temperature, equilibration time and impurities. We have found the development of crystallinity and crystal morphology depends heavily on these factors. DSC measurements indicate that $\text{P(EO)}_8\text{LiClO}_4$, either with or without fillers, is almost completely amorphous, in contrast to the large melting peak observed for $\text{P(EO)}_{20}\text{LiTf}$ and $\text{P(EO)}_{20}\text{LiTFSI}$. LiClO_4 -PEO samples stored in the “dry” glove box for 5 weeks were still amorphous. Doublet melting peaks begin to appear after 7 weeks storage in dry box. If the sample without filler was exposed to air for a few hours and then stored in dry box for 2 weeks, a broad melting peak appears. However, $\text{P(EO)}_8\text{LiClO}_4$ with fumed silica SiO_2 added which goes through the same process remains amorphous. These results indicate that $\text{P(EO)}_8\text{LiClO}_4$ prepared under strictly dry conditions is originally amorphous and remains so for extended periods provided there is no exposure to moisture. Trace water can induce its crystallization, although only at a slow rate. The addition of filler effectively inhibits crystallization. The effect of water on $\text{P(EO)}_8\text{LiClO}_4$ properties has also been reported by Weston and Steele who found the source of acetonitrile solvent with different water content is critical in controlling the crystallization development of the polymer electrolytes [7].

The crystalline morphology (texture) also depends on these factors. Under a polarized light microscope, a completely different crystalline texture was observed for solution cast and annealed $\text{P(EO)}_{20}\text{LiTFSI}$ electrolyte films. The solution cast samples (Figure 3a) show island-like crystals with wide boundaries between the crystals, while annealed samples show typical spherulites that are closely packed and exhibit Maltese Cross shapes under polarized light

microscope (Figure 3b). There are also differences in crystalline texture between nanoparticle-filled and non-filled films, and between different polymer electrolytes. Figure 3c show the microscopic pictures of $\text{P(EO)}_8\text{LiClO}_4$ films from solution casting and stored in dry box for 1 day. The crystal domains in $\text{P(EO)}_8\text{LiClO}_4$ are much smaller and less in number compared with those in $\text{P(EO)}_{20}\text{LiTFSI}$ and $\text{P(EO)}_{20}\text{LiTf}$, but they appear to grow with storage time. This is consistent with DSC measurements which show the as-prepared $\text{P(EO)}_8\text{LiClO}_4$ exhibit negligible melting peaks compared with the other two electrolytes. Kumar has reported LiClO_4 was the most effective salt in producing and stabilizing amorphous structure compared with LiBF_4 and LiPF_6 (reference). However, the difference observed among our polymer electrolytes should be mainly attributed to salt concentration, not the salt type. The relatively higher concentration of salt in $\text{P(EO)}_8\text{LiClO}_4$ gives more ionic crosslinking and physical immobilization of polymer chains, and therefore reduces the crystallization kinetics. LiTFSI is found to be more likely to act as a crystallization inhibitor, if used in same concentration as other salts. The as-prepared $\text{P(EO)}_8\text{LiTFSI}$ shows no crystal domain under polarized light microscope (Figure 3d) and no melting peak in DSC. A “crystallinity gap” has been reported for this composition, but a later paper revealed the absence of the distinct melting transitions was actually attributed to the extremely slow kinetics of recrystallization of this system [8].

Due to the complicated phase diagrams and crystalline structures of polymer electrolytes, the interpretation of their conductivity below melting point could be controversial. Although it has been long recognized that ionic transportation is mainly through amorphous phases, there is new opinion that conductivity in crystalline phase could be even higher than that in the amorphous phase [9]. Golodnitsky et.al. [10, 11] proposed the interfacial conduction mechanism, or “grain boundary” effects, in which the crystalline phase does not inhibit

conductivity, but rather is the major contribution to overall conductivity in concentrated composite polymer electrolytes. If crystalline structure and morphology can affect ionic transportation by any mechanism, the conductivity is expected to rely on processing history of samples and measurement procedures. The effects of history and salt concentrations on crystallinity described here may explain some of the discrepancies of conductivity between heating scan measurement (on solution-cast samples) and cooling scan measurement in many literature reports.

3.3 Interfacial properties and cycling. We observed that the interfacial impedance between PEO electrolytes and Li electrodes in open-circuit state was not changed very much by adding fillers. But when PEO (oxymethylene-linked poly(ethylene glycol)), a viscous liquid (M.Wt. ~10k) was used, the addition of filler lower the electrolyte/Li interfacial impedance by 70% . Appetecchi et. al. [12] reported a moderate influence of the presence of fillers on the lithium-polymer interfacial properties, while the preparation conditions (drying, vacuum, hot laminating, etc.) play major roles with respect to the addition of the fillers in affecting interfacial properties. We believe the effects of fillers on interfacial properties mainly come from scavenging of impurities such as water. For pure and well-dried electrolytes and well-controlled cell assembly environments, the effect of fillers is not obvious on the interfacial impedance .

Addition of 10% by weight of fumed silica nano-particle significantly changes the cycling behavior of PEO electrolyte in Li/Li cells. The cycling duration before cell failure (characterized by short circuit behavior) is much extended. The fillers do not seem to prevent the voltage perturbation associated with dendrite development but the increased mechanical strength of the electrolyte inhibits the growth of dendrites completely across the cell. We will report the effects of nanoparticles on the interfacial stability and galvanostatic cycling

performance of Li/Li cells in another paper.

4. Conclusions

The addition of nanoparticles significantly increased the mechanical properties, restricted polymer segmental motion, and inhibited polymer recrystallization ability. Correspondingly, the conductivity of polymer electrolytes was decreased at temperatures above the melting point, but increased below it. The fillers were also found to improve cycling behavior of polymer electrolytes in Li/Li cells. The filler's effect on electrolyte/electrode interfacial properties varies among different polymer electrolytes.

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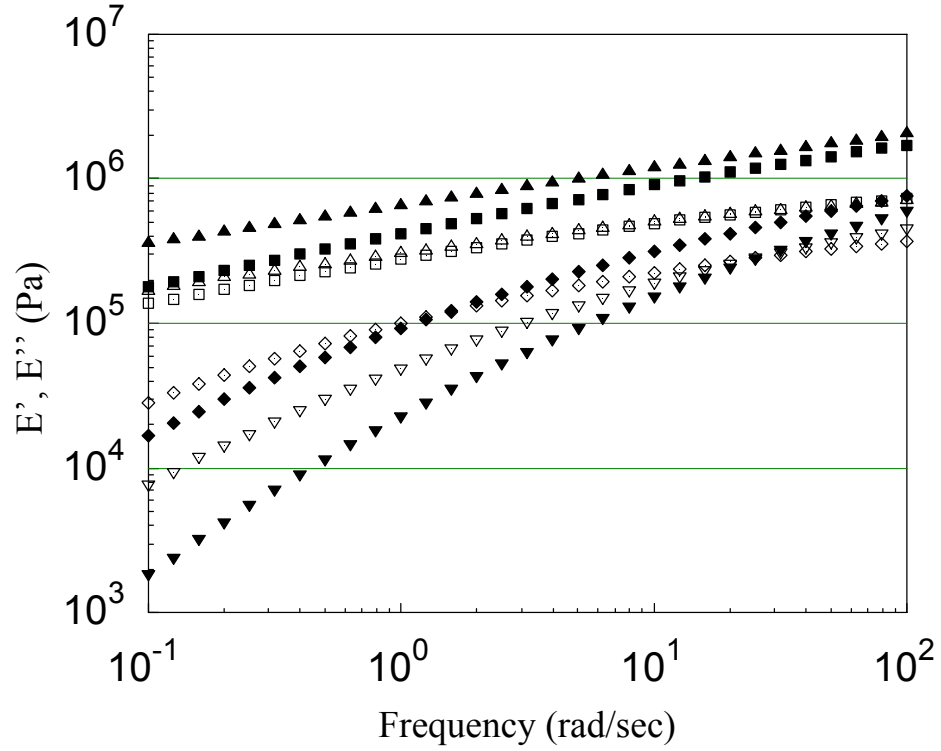


Figure 1. Compression moduli of P(EO)₂₀LiTFSI (Mw 2x 10⁵) at 85°C with different amount of fumed silica. The filled symbol is elastic moduli (E') and unfilled symbol is viscous mudili (E''). ▼ ▽ ultra-pure (0% SiO₂); ♦ ◇ lab-pure (~3% SiO₂) ■ □ 10% hydrophobic fumed silica added (~ 13% SiO₂) ▲ △ 10% hydrophilic fumed silica added (~ 13% SiO₂)

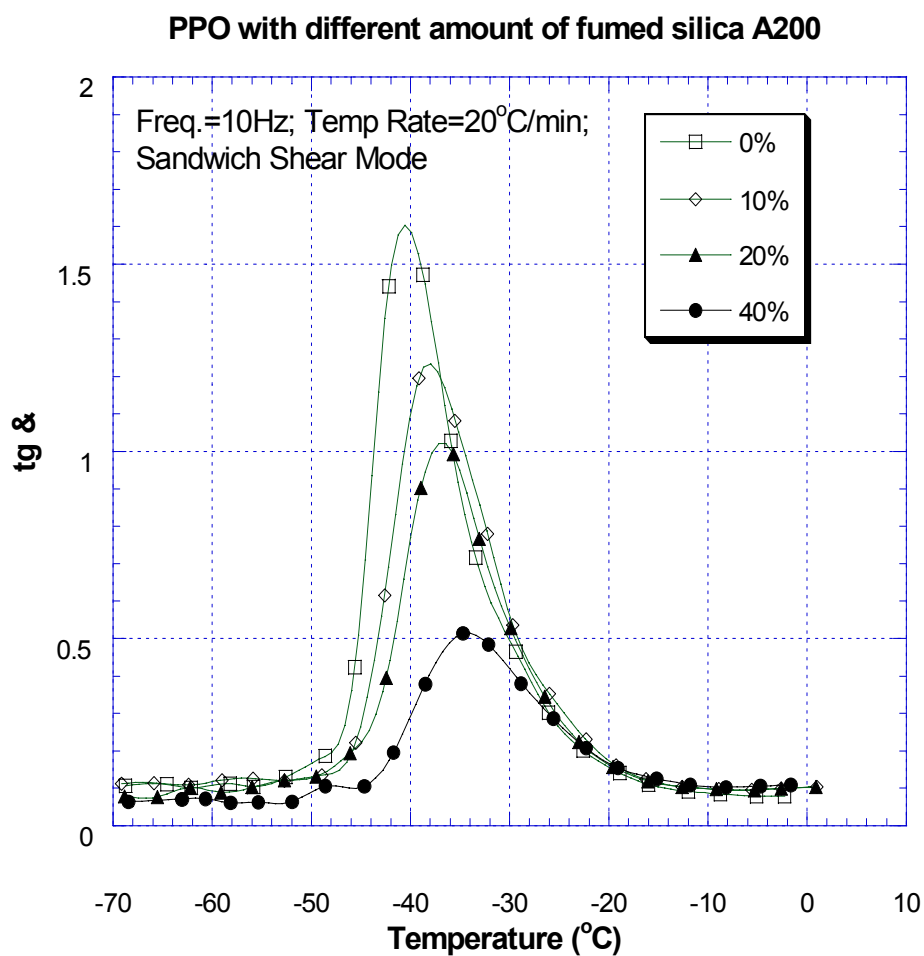


Figure 2. Glass transition of PPO ($M_n = 2.5 \times 10^5$) with different amounts of fumed silica by dynamic mechanical thermal analysis (Tan δ vs. temperature)

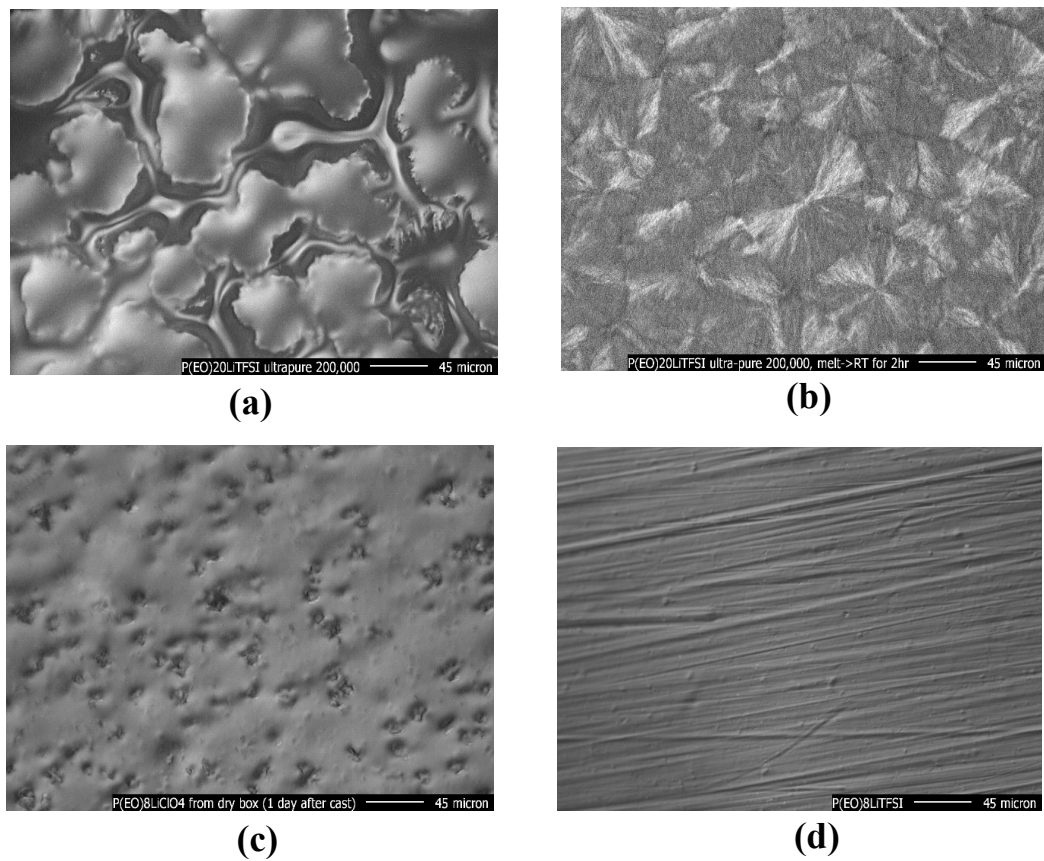


Figure 3. polarized light microscope of P(EO)₂₀LiTFSI: (a) solution cast (b) annealed; and (c) P(EO)₈LiClO₄ (d) P(EO)₈LiTFSI (both from solution cast, after 1 day storage).