Nanocomposite Polymer Electrolytes based on Poly(oxyethylene) and Cellulose Whiskers

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Abstract: Solid lithium-conducting nanocomposite polymer electrolytes based on poly(oxyethylene) (POE) were prepared from high aspect ratio cellulosic whiskers and lithium imide salt, LiTFSI. The cellulosic whiskers were extracted from tunicate -a sea animal- and consisted of slender parallelepiped rods that have an average length around 1 µm and a width close to 15 nm. High performance nanocomposite electrolytes were obtained. The filler provided a high reinforcing effect while a high level of ionic conductivity was retained with respect to unfilled polymer electrolytes. Cross-linking and plasticizing of the matrix as well as preparation of the composites from an organic medium were also investigated.

Keywords: *Nanocomposite, polymer electrolyte, cellulose, poly(oxyethylene).*

Introduction

Rapid growth in technologies requires the development of a new generation of high performance energy sources. Polymer-based ion conducting materials have generated remarkable interest in the field of lithium batteries due to their application as electrolyte. In this application, the polymer electrolyte provides both the mechanical function of a separator between the two electrodes and the ionic conduction medium of an organic solvent for the lithium salt. In 1979, Armand et al.[1] have foreseen the potential applications of solid polymer electrolytes as ionic conducting materials in electrochemical devices. Solid polymer electrolytes are used as thin films and occur as either dry (organic solvent-free) or plasticized electrolytes. A high specific energy density can be reached at medium temperature using a dry polymer electrolyte and lithium metal as negative electrode.

Many studies have focused on the enhancement of ionic conductivities of polymer electrolytes, most of them performed on poly(oxyethylene) (POE) and its copolymers, due to their strong solvating ability. However, the high degree of crystallinity of POE strongly restricts the ionic conductivity at room temperature (its melting temperature, (T_m) is around 60 °C). Indeed, it was early assumed that ionic conductivity requires an amorphous character of polymer electrolytes[1,2] and it was latter confirmed by NMR investigations[3] that conductivity predominates in the amorphous phases where ion mobility is chain-assisted. Therefore, POE based electrolytes should be used above T_m to display appropriate conductivity. Unfortunately, the mechanical properties are very poor in this temperature range. Several strategies can be considered to reduce or eliminate the crystallinity of POE-based electrolytes or to improve their mechanical properties above T_m :

(i) modification of the host polymer structure. The amorphous state and improved mechanical behavior can be usually easily achieved using cross-linked copolymers. However, suitable mechanical properties require a high cross-linking density that results in a strong reduction of the assisted mobility of the ionic species, and thus of the conductivity.

(ii) use of new lithium salts. The conductivity can be adjusted by varying the salt dissociation, its mobility or attaching the anion to the polymeric chain.

(iii) introduction of liquid additives. The incorporation of liquid compounds like plasticizers into the polymer electrolytes improves the ionic conduction. It generally results from the decrease of the glass transition temperature of the complex, the reduction of crystallinity, the increase of salt dissociation capability and the rise of charge carrier diffusions. However, a decrease in mechanical strength of the resulting polymer electrolytes is predictable.

(iv) introduction of solid additives. Since the work of Weston and Steele[4] the incorporation of solid nanometric fillers seems to be an alternative allowing increase of the

ionic conductivity[5-7]. However, the reinforcing phase should increase the mechanical behavior without decreasing significantly the ionic mobility. Some fillers like TiO$_2$ show strong capability to provide higher conductivity, cationic transference number and mechanical strength[8,9]. The mechanisms responsible of the conduction improvement in these nanocomposite polymer electrolytes are not yet elucidate. However, crystallization delay and fast carriers charge diffusion in the filler/polymer interphase were suggested to play important roles.

In the present study, nanocomposite polymer electrolytes based on POE were processed using lithium trifluorom-ethanesulfonylimide (LiTFSI) salt and cellulosic rigid rods (whiskers) as the reinforcing phase[10].

Experimental

Tunicin whiskers

Colloidal suspensions of whiskers in water were prepared as largely described elsewhere[11,12]. The cellulosic whiskers used in this work were obtained by acid hydrolysis of tunicin, the cellulose extracted from tunicate - a sea animal. They consisted of slender parallelepiped rods that have an average length around 1 μm and a width close to 15 nm (Figure 1).
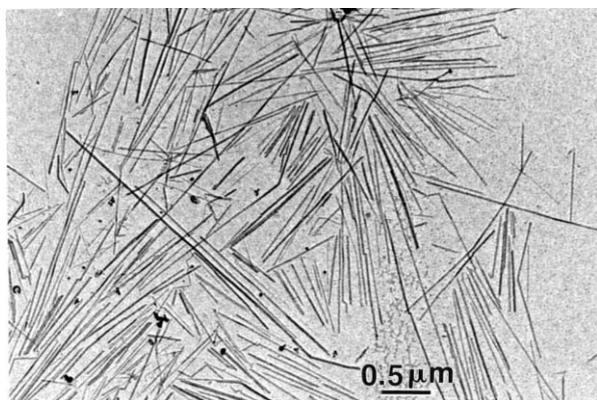

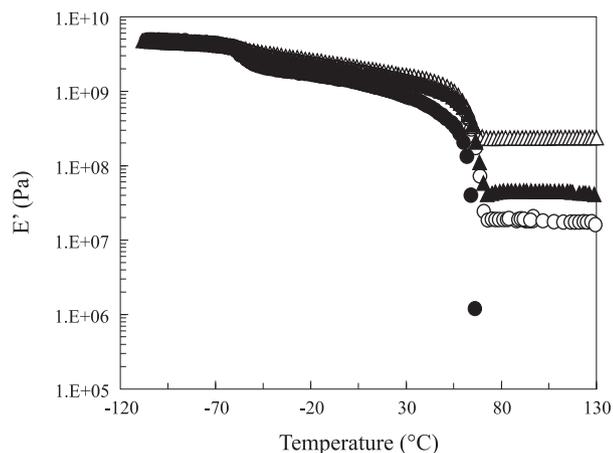**Figure 1.** TEM from a dilute suspension of tunicin whiskers

Figure 2. Storage tensile modulus E' vs. temperature at 1 Hz for POE based composites filled with (●) 0, (○) 3, (▲) 6 and (△) 10 wt% of tunicin whiskers.

The average aspect ratio (L/d, L being the length and d the diameter) and the specific area of these whiskers were estimated to be close to 70 and 170 m^2.g^{-1}, respectively.

Polymeric matrix

Poly(oxyethylene) (POE) with a high molecular weight (M$_w$ = 5×10^6 g.mol^{-1}) and tetraethylene glycol dimethyl ether (TEGDME) (M$_w$ = 222 g.mol^{-1}), used as plasticizer, were purchased from Aldrich. The lithium trifluoromethanesulf-onylimide (LiTFSI) salt from Fluka was dried in vacuum for 24h at 130 °C prior to use and then stored in glove box. An unsaturated linear polycondensate (LPC400) was synthesized by reaction of a α,ω-dihydroxy oligopoly (oxyethylene) (M$_n$ = 400 g.mol^{-1}) with a dihalide isobutenyl compound, 3-chloro-2-chloromethyl-propene. The resulting polymer was purified by ultrafiltration in order to remove any material with a molecular weight lower than 3,000 g.mol^{-1}. The number average molecular weight was M$_n$ = 2.6×10^4 g.mol^{-1} determined in equivalent polystyrene. A photo-initiator, 4-(2-hydroxyethoxy) phenyl-(2-hydroxy-2-propyl)ketone (HPPK) purchased from Ciba Specialty Chemicals was used as cross-linking agent.

Film processing

Nanocomposite polymer electrolytes were prepared in two steps, the first one consisting in the preparation of POE/ whiskers films and the second one in the introduction of the lithium salt within the resulting tunicin whiskers reinforced POE films. The desired amount of tunicin whiskers (water suspension) was added to the aqueous POE solution. The resulting suspension was stirred for 24h and cast into Teflon plates. Water evaporation was carried out at 40 °C for one week. Films were dried under vacuum for 72h at 100 °C to eliminate the remaining water. 2,2 dimethoxypropane was used as dehydration agent. Finally, the lithium salt was introduced by swelling the nanocomposite films with a concentrate acetonitrile salt solution. The amount of salt was determined by the molar ratio n = O/Li. POE based electrolytes will be labeled as POE$_n$-LiTFSI. This procedure was chosen because the direct incorporation of the salt to the tunicin whiskers aqueous suspension caused its sedimentation. The preparation of cellulose whiskers suspensions in N,N-dimethylformamide (DMF) was detailed in a recent publication[13]. Plasticized nanocomposite polymer electrolytes were prepared in the DMF medium. High molecular weight POE, TEGDME and salt were added to the DMF suspension of whiskers. The dissolution of POE was achieved by heating the mixture at 60 °C for two hours under stirring. The suspension was then degassed, cast into Teflon mold and DMF was allowed to evaporate at 50 °C. Resulting films were dried under vacuum at 80 °C overnight and then stored in glove box. Cross-linked nanocomposite polymer electrolytes were also prepared. Salt-free films were prepared by first mixing the solution of LPC400 with the whiskers suspension in DMF. After addition of HPPK, the solution was cast into aluminum plates and the solvent was allowed to slowly evaporate at 65 °C for 48 hours in a glove box. After solvent evaporation, all the films were cured by UV

radiation in argon atmosphere at room temperature. The film was then dried several days at 80 °C under vacuum and stored in glove box. LiTFSI was added by swelling the cross-linked films with concentrated acetonitrile salt solution. The solvent was evaporated, and the film was dried several days at 80 °C under vacuum and stored in glove box.

It is worth noting that scanning electron microscope (SEM) observations revealed an evenly dispersed cellulosic phase within the polymeric matrix regardless of its nature and the processing technique.

Results and Discussion

Salt-free POE based nanocomposites

Differential scanning calorimetry (DSC) measurements performed on salt-free nanocomposites show that the glass-rubber transition temperature (T_g) of POE was not influenced by the cellulosic filler, contrarily to the melting temperature (T_m) and degree of crystallinity (χc) which were found to both decrease for highly filled (10 wt% and above) materials. This restricted crystallinity was confirmed by dynamic cooling crystallization experiments[14]. Both the crystallization and the onset temperatures were found to decrease as the cellulose whiskers content increases. This anti nucleation effect of the filler was ascribed to both strong interactions between the POE chains and cellulosic surface and increased viscosity of the melt composite. Polarized optical microscopic observations showed that the size of the POE spherulites was lower for composites but their growth rate was similar to the one observed for the unfilled matrix. Cellulose/POE interactions were quantified using heat flow microcalorimetry measurements[14].

The mechanical behavior of tunicin whiskers/POE nanocomposites was evaluated in the linear range over a broad temperature range from dynamic mechanical analysis. Figure 2 shows the temperature dependence of the storage tensile modulus E' of the unfilled POE matrix and related composites. A weak modulus drop associated to T_g of the POE matrix is observed around -60 °C. Compared to the unfilled POE matrix, the magnitude of this modulus drop is lower for composites. The temperature position of this relaxation process does not vary with the cellulose content in agreement with DSC measurements. The highest rubbery modulus for composites could result from a highest degree of crystallinity of POE in composite formulations. However, DSC measurements shown that and the degree of crystallinity of POE was composition-independent up to about 10 wt% tunicin whiskers and then decreases for higher whiskers content. Therefore, the increase of the relaxed modulus should be ascribed to a reinforcing effect of cellulose whiskers.

The main effect of the filler is a thermal stabilization of E' for the composites above T_m (around 60 °C for the POE matrix). Whereas E' of the unfilled matrix drops irremediably with the melting of the crystalline POE domains, whiskers bring a thermal stabilization effect. The modulus of composites remains constant up to temperatures higher than 130 °C. In the first study performed on tunicin whiskers filled

nanocomposites[12] a thermal stabilization of the modulus was observed at high temperature. It was ascribed to the formation of a rigid percolating cellulose whiskers network. This network, assumed to be formed through strong whisker/whisker hydrogen bonds interactions, was observed for whiskers content higher than the percolation threshold, around 1 vol%, i.e. 1.25 wt%, for tunicin whiskers/POE composites. This phenomenon was well predicted from a model based on the percolation concept. The high temperature E' value increases with increasing the filler content in agreement with increasing whisker/whisker interaction probability and density of the cellulosic network. For instance, the experimental and predicted moduli are around 235 and 255 MPa, respectively, for the composite filled with 10 wt% whiskers. Therefore, the formation of the cellulosic network through inter-whiskers hydrogen bonds, assumed to be responsible for the high mechanical properties of the composites, is not affected by the matrix crystallization process and filler/POE interactions.

Nanocomposite polymer electrolytes

The gain in storage modulus was similar to the one reported for salt-free composites and exceeded by far a factor 100 with respect to the unfilled polymer electrolyte[15]. The mechanical reinforcing effect of tunicin whiskers was compared to that of the more classical TiO_2 inorganic filler. Figure 3 shows the evolution of the storage tensile modulus as a function of temperature for unfilled POE_{30}-LiTFSI polymer electrolyte and related composites filled with 10 wt% of tunicin whiskers or TiO_2. It was observed that the modulus drop at the glass-rubber transition is shifted toward higher temperature for the TiO_2 based composite. Both fillers induce a significant increase of the relaxed modulus. However, the reinforcing effect is markedly higher for the composite polymer electrolyte obtained from the organic one, especially above the melting point, that is to say in the temperature operating range of lithium polymer battery. The high temperature modulus, estimated around 100°C, is about 4 MPa for the POE_{30}-LiTFSI polymer electrolyte reinforced
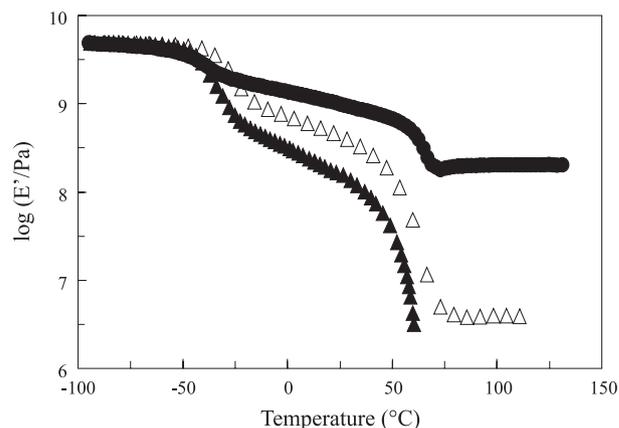
Figure 3. Logarithm of the storage tensile modulus E' vs. temperature at 1 Hz for the unfilled POE_{30}-LiTFSI polymer electrolyte (▲) and related composites filled with 10 wt% of TiO_2 (△) and tunicin whiskers (●).
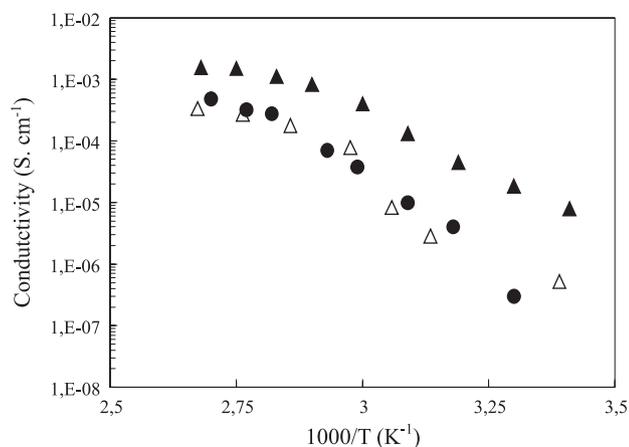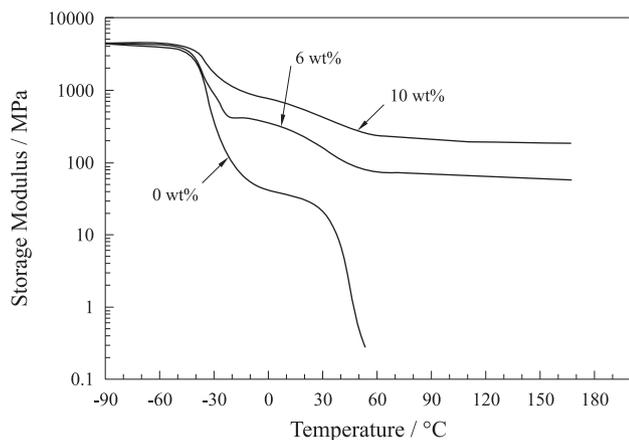
Figure 4. Arrhenius plot of ionic conductivity for composite polymer electrolytes (O/Li = 30) filled with 0 (▲), 6 (△) and 10 wt%(●) of tunicin whiskers

with TiO_2, i.e. roughly 50 times lower than its tunicin whiskers counterpart. This strong difference illustrates the original mechanical reinforcing effect of tunicin whiskers thanks to the whiskers/whiskers interactions.

Results of conductivity measurements for composite polymer electrolytes with O/Li = 30 are reported in Figure 4. For a given temperature the presence of tunicin whiskers induces a decrease of the polymer electrolyte conductivity. However, the values of ionic conductivity in the composites remain higher than 10^{-4} S.cm^{-1} above 60 °C. The decrease in conductivity cannot be related to thermal property modifications, because it was shown from DSC measurements that tunicin whiskers did not affect the glass-rubber transition temperature nor the degree of crystallinity of the polymer electrolyte. Possible explanations could be (i) the low dielectric constant of cellulosic fillers, (ii) the existence of interactions between cellulose and POE, as reported for tunicin whiskers reinforced salt-free POE and iii) the effect of whiskers on salt dissociation and the mobility of ions.

Pulsed magnetic field gradient nuclear magnetic resonance (PMFG NMR) investigation allowed the calculation of the cation, anion and chain diffusion coefficients vs temperature.

Figure 5. Storage modulus E' vs. temperature at 1 Hz for 30 wt% TEGDME plasticized POE$_{12}$-LiTFSI nanocomposite electrolytes filled with tunicin whiskers. The whiskers content is indicated in the figure.
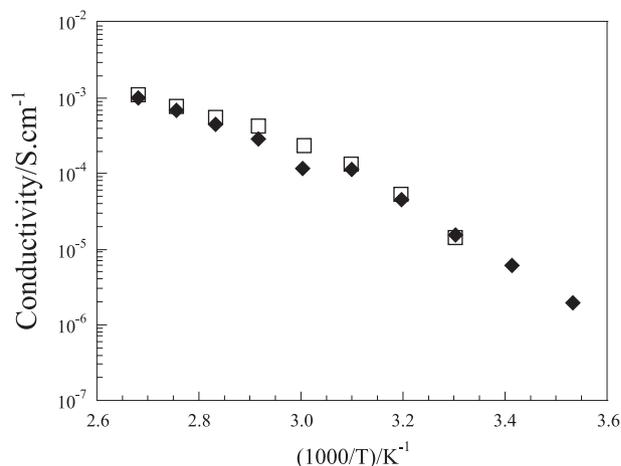
Figure 6. Arrhenius plot of ionic conductivity for unplasticized POE$_{12}$-LiTFSI electrolyte (□) and 30 wt% TEGDME plasticized POE$_{12}$-LiTFSI nanocomposite electrolytes filled with 6 wt% tunicin whiskers (◆).

From a comparison between filled and unfilled polymer electrolytes, POE chains, anion and lithium cation mobility were found to decrease in filled electrolytes. However the cationic transference number was roughly the same in filled and unfilled polymer electrolytes. The electrochemical stability of the composite electrolytes was investigated via cyclic voltammetry. The incorporation of tunicin whiskers weakly modified the stability in reduction. However the substitution of water by DMF[13], as film casting solvent, should probably improve the electrochemical stability.

Plasticized nanocomposite polymer electrolytes

Since the mechanical performances of the tunicin whiskers reinforced POE-LiTFSI polymer electrolyte are only ascribed to the percolating filler network and are totally independent on the mechanical properties of the host matrix, it was of interest to use a plasticized polymer as matrix[16]. POE-LiTFSI-based polymer electrolyte with TEGDME as plasticizer and tunicin whiskers as nanometric reinforcing phase were processed. A high reinforcing effect above T_g of the matrix and a thermal stabilization effect of the material above T_m were observed (Figure 5). This is an indication that the plasticization of the matrix did not interfere with the formation of the cellulosic network within the matrix.

In Figure 6 the conductivity of two different POE-based electrolytes is compared. It is observed that POE$_{12}$-LiTFSI plasticized with 30 wt% TEGDME and filled with 6 wt% tunicin whiskers displays a similar conductivity level than the unplasticized and unfilled POE$_{12}$-LiTFSI polymer electrolyte. However, the composite polymer electrolyte possesses much higher mechanical properties especially at high temperatures. This illustrates the successful addition of cellulosic fillers and TEGDME to prepare new nanocomposite polymer electrolytes with both good ionic conductivities and high mechanical performances.

Cross-linked nanocomposite polymer electrolytes

A classical way used to improve both the mechanical
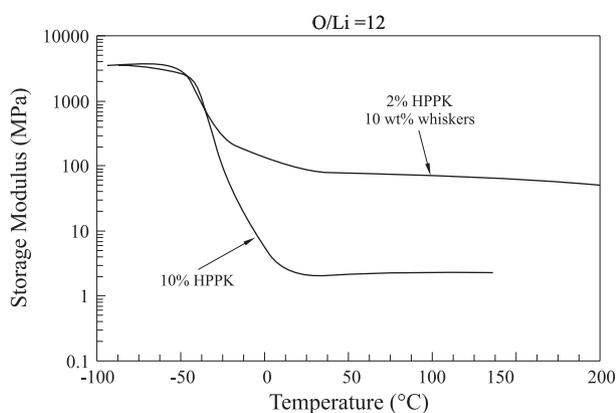
Figure 7. Storage modulus E' vs. temperature at 1 Hz for composite electrolytes (O/Li = 12) cross-linked with 2% HPPK and filled with 10 wt% tunicin whiskers and unfilled electrolyte (O/Li = 12) cross-linked with 10% HPPK.
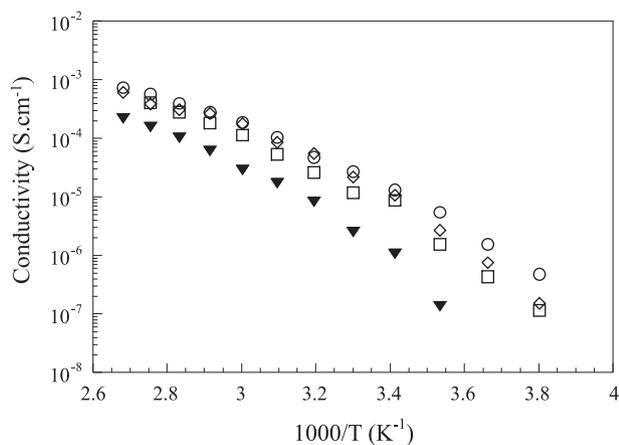
Figure 8. Arrhenius plot of ionic conductivity for composite electrolytes (O/Li = 12) cross-linked with 2% HPPK and filled with 0 (◇), 6 (○) and 10 wt% (□) tunicin whiskers and unfilled electrolyte (O/Li = 12) cross-linked with 10% HPPK (▼).

properties and the low temperature conductivities of POE based electrolytes is the cross-linking of the polymeric chains. We have compared the behavior of weakly cross-linked polyether filled with tunicin whiskers and the one of unfilled materials exhibiting different cross-linking density[17]. Both mechanical and ionic conductive properties were investigated. The cellulosic nanofiller provided a much higher reinforcing effect at high temperature than the cross-linking process (Figure 7). In addition, nanocomposite electrolytes display a higher ionic conductivity on the whole temperature range due to the high cross-linking density that should be used for unfilled electrolytes in order to ensure satisfactory mechanical properties (Figure 8). It was also shown that tunicin whiskers seem to have no effect on the conduction mechanism of the polymer electrolyte[17]. Therefore, the used cross-linked nanocomposite polymer electrolytes allow conciliating both higher ionic conductivities and higher mechanical performances.

Conclusion

From these results, we must emphasize that those promising reinforced polymer electrolytes could be used in various electrochemical energy sources. Cellulose can also be used as microfibrils, which are more accessible in terms of both available amounts and preparation.

Acknowledgments

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