# Cross-Linked Nanocomposite Polymer Electrolytes Reinforced with Cellulose Whiskers

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ABSTRACT: In a previous work [*Macromolecules* **2004**, *37*,1386], a new way of processing cellulose whisker reinforced nanocomposites from an organic solvent (*N*,*N*-dimethylformamide) without a surfactant addition or a chemical surface modification was investigated. This technique is used to prepare nanocomposite polymer electrolytes based on a cross-linked polyether and lithium imide (LiTFSI) reinforced with tunicin whiskers. Both the mechanical and ionic conductive properties of the resulting electrolytes are presented. These performances are compared to those obtained for unfilled cross-linked polyether matrices exhibiting several cross-linking densities. It is observed that the ionic conduction of cellulose whisker filled electrolytes is higher than the one of highly cross-linked polyether networks. In addition, the mechanical stiffness of the former is much higher than that of the latter, allowing the processing of high-performance nanocomposite polymer electrolytes.

## Introduction

Polymer-based ion conducting materials have generated remarkable interest in the field of lithium batteries due to their application as electrolyte. A high specific energy density can be reached at medium temperature using a dry polymer electrolyte and lithium metal as negative electrode. Moreover, the high flexibility of polymers allows to process batteries with various sizes and geometry. In this application the polymer electrolyte provides both the mechanical function of a separator and the ionic conduction medium. It must therefore display a high ionic conductivity as well as electrochemical, thermal, and mechanical stability.

Dry polymer electrolytes employing high molecular weight linear polyoxyethylene (POE) associated with lithium salt form the most studied systems. Ethylene oxide units (EO) of the POE provide a favorable environment for the lithium salt dissociation.[1−3] However, because of the semicrystalline structure of POE/salt complexes, a low ionic mobility is obtained below the complex melting temperature. At high temperature, above 60 °C, the electrolyte provides an appreciable conductivity, whereas its mechanical properties are very poor due to the melting of crystalline domains. The material loses its dimensional stability and behaves like an extremely viscous low-modulus liquid.

The reduction of the host polymer crystallinity may be performed by grafting (EO) solvating units into various polymer chains.[4,7] Cross-linking is one of the most common method used in order to disrupt polymer chains crystallization and to ensure mechanical properties. Numerous electrolytes based on polyether networks were therefore proposed as an alternative to the use of linear POE.[8−15] Good performances were obtained with such polymer electrolytes, but they are strongly dependent on the cross-linking density. Increasing the cross-linking density results in an increase of the mechanical strength but reduces at the same time the conductivity because of the reduction of the polymer chains' mobility.

Improving conductivity was reported for composite polymer electrolytes filled with inorganic nonconducting fillers.[16−18] The increase in conductivity was found to be more significant below the melting point of POE/complexes due to the decrease of crystallization kinetics induced by the filler. In addition, an increase in the lithium transference number has been reported.[19] Despite the large interest in this field, there is still a limited knowledge of the mechanism behind the conductivity enhancement in nanocomposite polymer electrolytes.[20−22] Moreover, only few studies have been performed to evaluate the mechanical properties of nanocomposite polymer electrolytes.

The incorporation of tunicin whiskers in POE polymer electrolytes leads to high-performance nanocomposites[23] with a large increase in the mechanical strength, the gain in storage modulus exceeding by far a factor of 100 with respect to unfilled polymer electrolytes for only a few percent of cellulosic filler. A small decrease in conductivity values was reported for these filled polymer electrolytes compared with unfilled ones. The degree of crystallinity was found to be independent of the filler loading; thus, poor conductivity was obtained below the POE melting point.

To improve the conductivity at low temperatures of the cellulosic whisker based nanocomposite electrolytes, low crystallinity content cross-linked polyethers obtained by polycondensation[24] were synthesized. Conductivities of the three-dimensional polymer electrolytes are clearly higher at ambient temperature than that of electrolytes based on linear POE, but also often at 70 °C.[24]

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In a previous study,[25] we investigated the mechanical properties obtained with such cross-linked salt-free polyether as polymer matrix and cellulose whiskers as the reinforcing phase. Because of the high aspect ratio of these whiskers, mechanical stabilization around 25 and 60 MPa were obtained for the composites filled with 3 and 6 wt % of tunicin whiskers, respectively.

In the present paper, we evaluate the performance of this nanocomposite material (cross-linked polyether/cellulose whiskers) as polymer electrolyte. The performances of the resulting system were analyzed in terms of both conductivity and mechanical behavior. These performances were compared to those obtained for unfilled cross-linked polyether matrices exhibiting several cross-linking densities.

## Experimental Section

**Tunicin Whiskers.** Cellulose whiskers used in this work were extracted from tunicate (a sea animal). It consists of highly crystalline rodlike particles with an aspect ratio around 100. Suspensions of cellulose whiskers in *N,N*-dimethylformamide (DMF) were prepared as described in a previous work.[25]

**Polymeric Matrix.** The linear unsaturated polycondensates were prepared by a Williamson-type polycondensation.[24] This polycondensation was performed on $\alpha,\omega$-dihydroxyoligo(oxyethylene) ($\bar{M}_n = 400$ g mol$^{-1}$). The resulting polymer was purified by ultrafiltration in order to remove any material with a molecular weight lower than 3000 g mol$^{-1}$. The number-average molecular weight was $M_n = 2.6 \times 10^4$ g mol$^{-1}$ determined in equivalent polystyrene.

**Salt.** Lithium trifluoromethanesulfonylimide, LiTFSI (Fluka), was dried 72 h at 100 °C under vacuum and stored in glovebox The amount of salt was determined by the ratio $n =$ O/Li, corresponding to the ratio of the number of oxygen atoms of the polyether matrix and lithium atoms of LiTFSI.

**Film Processing.** For the preparation of the unfilled network electrolyte films, a solution of the linear polycondensate and LiTFSI in acetonitrile was prepared in a glovebox. A photoinitiator, 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl) ketone (HPPK) purchased from Ciba Specialty Chemicals, was used as cross-linking agent. The amount of HPPK used was calculated with respect to the number of reactive double bonds of the linear polycondensate. After addition of HPPK, the solution was cast into aluminum plates, and the solvent was allowed to slowly evaporate at 55 °C for 30 h in glovebox under argon flow. After solvent evaporation, all the films were cured by UV radiation in an argon atmosphere at room temperature. The distance between the UV lamp and films was fixed to 15 cm, and exposition duration was 10 min. The film was then dried several days at 80 °C under vacuum and stored in a glovebox.

For tunicin whisker reinforced network electrolytes, the previous sample preparation procedure was modified. The sulfate groups, created during hydrolysis at the surface of whiskers, are responsible of the good dispersion and stability of the suspension. The addition of LiTFSI salt induces the sedimentation of the suspension, resulting in a poor dispersion of the filler within the polymeric matrix. To avoid this sedimentation phenomenon, salt-free nanocomposite films were prepared by first mixing the solution of the linear polycondensate with the whiskers suspension in DMF. Homogeneous suspensions were obtained by stirring.

After addition of HPPK, the solution was cast into aluminum plates, and the solvent was allowed to slowly evaporate at 65 °C for 48 h in a glovebox. The UV cross-linking was performed as described for unfilled electrolytes. LiTFSI was added by swelling the cross-linked films with concentrated acetonitrile salt solution. The solvent was evaporated, and the film dried several days at 80 °C under vacuum and stored in a glovebox.

It is worth noting that the tunicin whiskers content in each sample was expressed as a percentage of the total dry weight of cellulose and polycondensate. LPC400 and NPC400 are abbreviations for linear polycondensate and network from polycondensate, respectively, 400 being the number-average molar weight of the solvating oligo(oxyethylene) block between two double bonds in LPC.

**Dynamic Mechanical Analysis (DMA).** Dynamic mechanical tests were performed with a spectrometer DMA Q800 from TA Instruments working in the tensile mode. The setup measured the complex tensile modulus $E^*$, i.e., the storage component $E'$ and the loss component $E''$, as well as the ratio of the two components, i.e., tan $\delta$ ($= E''/E'$). Measurements were performed in isochronal conditions at 1 Hz in a nitrogen atmosphere, and the temperature was varied between $-100$ and 175 °C at a heating rate of 3 °C min$^{-1}$. The strain $\epsilon$ was $5 \times 10^{-4}$ so as to be in the domain of the linear viscoelasticity of the material.

**Conductivity Measurements.** The ionic conductivity of nanocomposite polymer electrolytes was measured by impedance spectroscopy using a HP4192A impedance analyzer over the frequency range 5 Hz−13 MHz. The samples were placed between two stainless steel blocking electrodes under vacuum. The temperature sweep test was conducted from 10 to 100 °C. The temperature was equilibrated for 1 h every 10 °C.

## Results and Discussion

The performance of the composite electrolyte was evaluated for a salt concentration O/Li = 12. An optimum of conductivity was obtained near this concentration. This maximum of conductivity is attributed to two opposite effects. An increase in the charge carriers is obtained with increasing the salt concentration, but an increase of $T_g$ is also observed, related to a reduction of the polymer chain flexibility.

**Mechanical Behavior.** Figure 1a shows the variation of the storage tensile modulus at 1 Hz as a function of temperature for composite NPC400/LiTFSI electrolytes. A low amount of photoinitiator (2% of the number of reactive double bonds) was chosen to avoid high cross-linking density. Actually, the mechanical properties were expected to be ensured by the in-situ formation of a whiskers network.[25]

The films were soft at room temperature, and it was very difficult to obtain a constant and precise thickness along these samples. Moreover, samples were positioned rapidly in the apparatus to limit the water uptake. To minimize the error induced by the sample dimensions on modulus, the elastic tensile modulus, $E'$, at $-100$ °C was normalized at 3.5 GPa for all the samples. This can be justified by the fact that the difference between the elastic modulus of the glassy polymer and whiskers was not high enough to easily appreciate any reinforcing effect for the low filler loading used.

The mechanical behavior of the unfilled polymer electrolyte is typical of amorphous polymer ones. At very low temperatures, the electrolyte is in the glassy state, and the modulus remains constant until a critical temperature corresponding to the start of energy dissipation and cooperative chains motions. Around $-50$ °C, a sharp drop in modulus value is observed. It corresponds to the main relaxation process associated with the glass−rubber transition. In this temperature range, the loss angle tan $\delta$ reaches its maximum (Figure 1b) and the relaxation temperature can be deduced (Table 1). $T_\alpha$ is the relaxation process temperature associated with the anelastic manifestation of the glass−rubber transition of the amorphous domains of the polymeric matrix. $T_\alpha$ is directly linked to $T_g$ of the matrix and to the magnitude of the drop of the storage

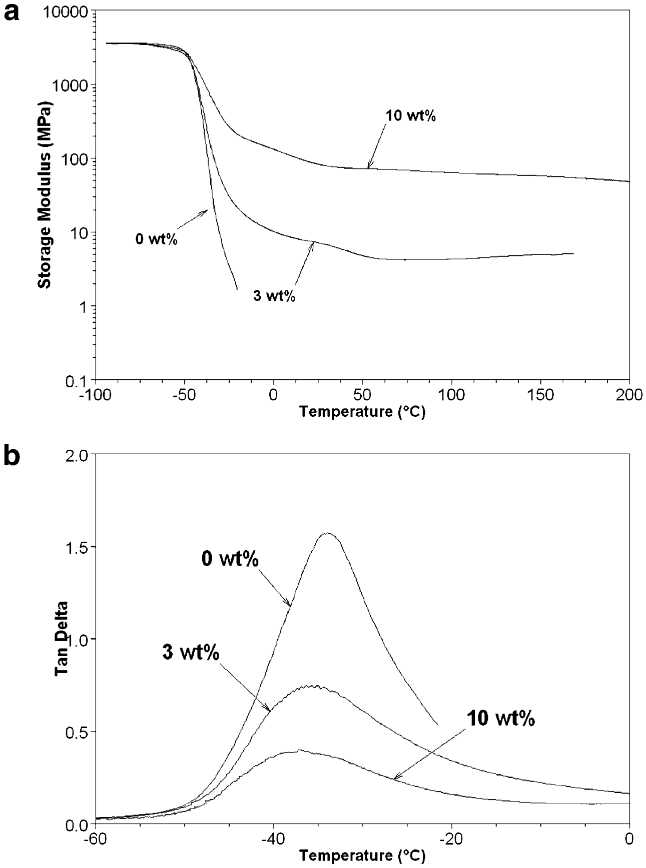

**Figure 1.** (a) Storage tensile modulus $E'$ and (b) loss angle tangent tan $\delta$ vs temperature at 1 Hz for nanocomposite NPC400−LiTFSI (O/Li = 12) based electrolytes filled with tunicin whiskers. The whiskers content is indicated in the figure.

**Table 1. Main Relaxation Temperatures Associated with the Maximum of the Loss Factor ($T_\alpha$) and Onset Point of $E'$ ($T_{\alpha_{E'}}$) for NPC400−LiTFSI Based Electrolytes Using Data Obtained from DMA**

| whiskers content (wt %) | $T_\alpha$ (°C) | $T_{\alpha_{E'}}$ (°C) |
|---|---|---|
| 0 | −34 | −48 |
| 3 | −36 | −47 |
| 10 | −37 | −47 |

tensile modulus (mechanical coupling effect). For the salt-free NPC400 material a rubbery modulus was reported around 200 MPa.[25] In the present system, the presence of the lithium salt prevents the crystallization of the polymer since the relaxed modulus decreases down to values lower than 1 MPa. The experimental setup fails to measure the tensile modulus because of the tearing of the sample despite the chemical cross-linking of the material.

No effect of whiskers incorporation was observed on $T_\alpha$ (Table 1) as reported for salt-free composites.[25] Two competitive effects, namely (i) a restricted mobility of the polymer in the presence of the cellulosic filler[26] and (ii) a decrease of the cross-linking density of the polymeric matrix in the presence of whiskers,[25] could explain the weak variation of the values of $T_g$.

The poor mechanical properties of the NPC400/LiTFSI electrolyte in the rubbery state are significantly improved in the presence of tunicin whiskers. The relaxed storage tensile modulus of the electrolyte increases when the whiskers content increases. $E'$ values at high temperatures are around 3 and 60 MPa for the electrolyte filled with 3 and 10 wt % of whiskers, respectively. This performance was conserved until 200 °C, the temperature at which cellulose starts to degrade. Both this high reinforcing effect and high thermal stability are provided by a mechanical percolation mechanism of the cellulosic rodlike particles being linked through hydrogen bonds.[25]

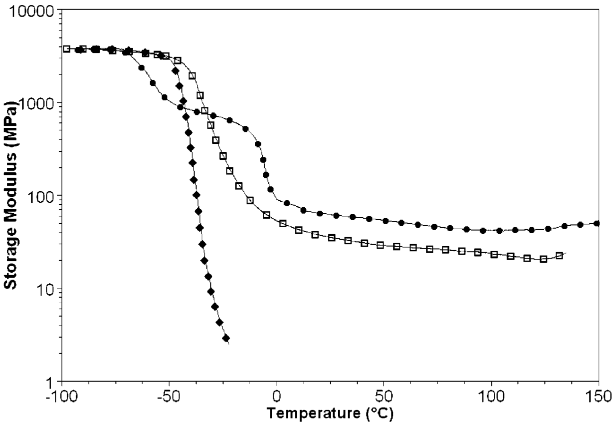

**Figure 2.** Storage tensile modulus $E'$ vs temperature at 1 Hz for POE based materials: unfilled NPC400−LiTFSI (O/Li = 12) electrolyte (◆), salt-free NPC400 filled with 6 wt % tunicin whiskers (●), and NPC400−LiTFSI (O/Li = 12) electrolyte filled with 6 wt % tunicin whiskers (□).

The influence of the salt incorporation on the mechanical properties was evaluated for the composite filled with 6 wt % tunicin whiskers (Figure 2). The behavior of the unfilled NPC400/LiTFSI electrolyte is added as reference. By comparing the behavior of the salt-free NPC400 film and NPC400/LiTFSI electrolyte film, both reinforced with 6 wt % tunicin whiskers, an increase of the main relaxation temperature is observed with the salt incorporation. It is ascribed to the classical increase of $T_g$ reported for polyether electrolytes and induced by polyether/cation interaction. In addition, for the salt-free composite the matrix displays a semicrystalline behavior easily identified through the two-step modulus drop. For temperatures ranging between −60 and −5 °C, the crystalline POE domains act as physical cross-links, providing a rubbery modulus around 650 MPa. Above the melting point of the salt-free NPC400 (∼−5 °C), the elastic tensile modulus drops again. For the composite electrolyte, a single drop in the modulus is observed due to the glass−rubber transition of the NPC400−salt mixture, displaying the amorphous nature of the polymeric matrix.

The high-temperature modulus of the composite is higher for the salt-free composite compared to its electrolyte counterpart. It is around 22 MPa for the composite electrolyte filled with 6 wt % tunicin whiskers and 60 MPa for the salt-free material. The experimental processing procedure, involving the introduction of the salt by swollen the composite membrane from a saline solution, i.e., after formation of the whiskers network, prevents any modification of the later. Actually, the modulus decrease is only due to a dilution effect. After salt incorporation, the whiskers content in the composite is no more than 6 wt %. The effective concentration of whiskers is 4 wt % when we take into account the weight of added salt.

To appraise the effectiveness of the tunicin whiskers for improving the mechanical properties of the network electrolytes, we studied the effect of a cross-linking density increase on the mechanical behavior of unfilled

**Table 2. Storage Tensile Modulus Appraised at 298 K ($E'_{298}$) and Calculated Molecular Weight ($M_c$) and Average Number of Monomer Units between Cross-Links ($DP_n$) for Unfilled Salt-Free NPC400 at Different Cross-Linking Agent Amount**

| HPPK content (wt %) | $E'_{298}$ (MPa) | $M_c$ (g mol$^{-1}$) | $DP_n$ |
|---|---|---|---|
| 2 | 1.8 | 5000 | 11 |
| 5 | 6.0 | 1500 | 3 |
| 10 | 8.4 | 1000 | 2 |

network electrolytes. First we evaluated the influence of the amount of UV initiator on the cross-linking density of the salt-free network. For cross-linked polymers, the modulus is assumed to be proportional to the cross-linking density. So the molecular weight between cross-links ($M_c$) can be derived using from the following equation:

$$M_c = \frac{3\rho RT}{E} \quad (1)$$

where $\rho$ is the density of LPC400 ($\rho = 1.2$ g cm$^{-3}$), $R$ is the gas constant (8.32 J mol$^{-1}$ K$^{-1}$), and $T$ is the temperature fixed at 298 K. From the rubbery modulus values of the unfilled salt-free membranes, the evolution of $M_c$ with the amount of HPPK was evaluated (Table 2).

Using 454 g mol$^{-1}$ for the monomeric molecular weight of LPC400, the average number of monomer units between cross-links was calculated (Table 2). The decrease of $M_c$ is significant between 2% and 5% of added HPPK. With 10% of HPPK, the improvement of cross-linking density is very poor. Therefore, even with 5% HPPK the amount of HPPK is large enough to have an almost complete reaction of the double bonds. The presence of residual double bonds could be due to steric entanglements, which favor termination reactions. The soluble fraction was calculated from the difference in weight before and after the immersion of nanocomposite films in acetonitrile. The insoluble fractions are higher than 95 wt %.[25] The insoluble fractions seem to be independent of the amount of HPPK in the studied range. This is probably due to the high reactivity of the isobutenyl double bonds and to their random distribution along the polymeric chain, in addition to the steric entanglement effect.

The variation of the storage tensile modulus vs temperature is displayed in Figure 3a for unfilled network electrolytes (O/Li = 12) cross-linked with 2%, 5%, and 10% of HPPK. The evolution of the tangent of the loss angle vs temperature is reported in Figure 3b. The magnitude of the relaxation peak associated with the glass−rubber transition decreases as the cross-linking density increases. In addition, its temperature position, whose values are collected in Table 3, increases with increasing the HPPK content. These two classical phenomena are related to the increase in the modulus above the glass transition temperature and to the restriction of chain mobility when the cross-linking density increases. Table 3 also reports the values of the onset of the storage modulus associated with the relaxation.

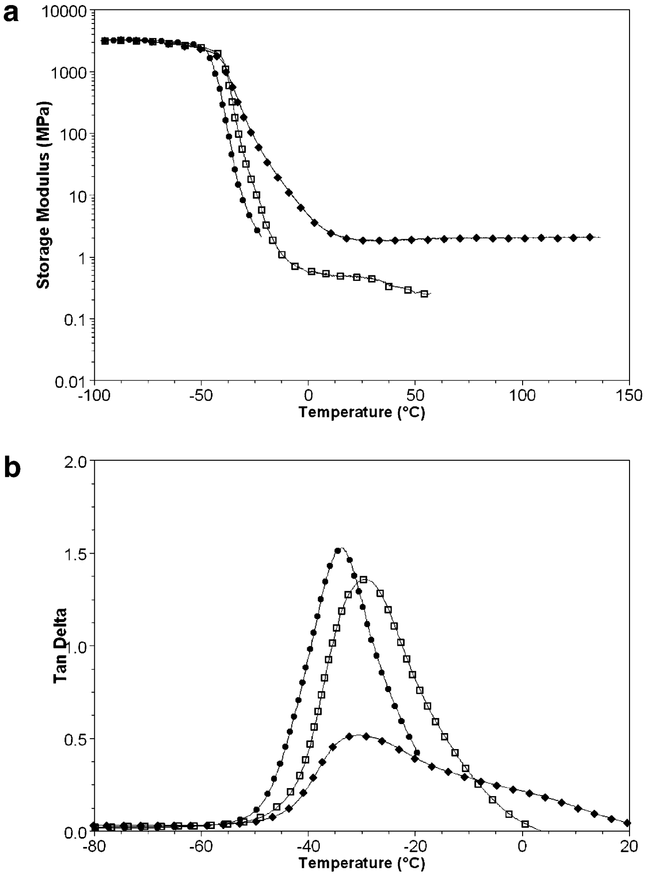

**Figure 3.** (a) Storage tensile modulus $E'$ and (b) loss angle tangent tan $\delta$ vs temperature at 1 Hz for unfilled NPC400−LiTFSI (O/Li = 12) based electrolytes cross-linked with 2% (●), 5% (□), and 10% HPPK (◆).

**Table 3. Main Relaxation Temperatures Associated with the Maximum of the Loss Factor ($T_\alpha$) and Onset Point of $E'$ ($T_{\alpha_{E'}}$) for Unfilled Cross-Linked NPC400−LiTFSI Based Electrolytes Using Data Obtained from DMA**

| HPPK content (wt %) | $T_\alpha$ (°C) | $T_{\alpha_{E'}}$ (°C) |
|---|---|---|
| 2 | −34 | −48 |
| 5 | −29 | −41 |
| 10 | −30 | −42 |

The rubbery modulus increases with increasing the HPPK content. It increases from a value lower than 1 MPa up to about 2 MPa for the electrolyte cross-linked with 5% and 10% HPPK, respectively. This is ascribed to the classical stiffening effect induced by the cross-linking process. However, by comparing values reported in Table 2 and Figure 3, it is observed that for a given HPPK content the storage tensile modulus is systematically lower for the electrolyte than for the salt-free material. It is most probably due to the decreasing efficiency of HPPK in the presence of the lithium salt.

We can compare the mechanical reinforcing effect provides by either the cross-linking of the polymer or the loading with tunicin whiskers. This can be carried out by comparing values reported in Figures 1 and 3. It is observed that the high-temperature storage tensile modulus of the NPC400/LiTFSI electrolyte cross-linked with 2% HPPK and filled with 6 wt % tunicin whiskers is more than 1 order of magnitude higher (22 MPa vs 2 MPa) than the one obtained for the highly cross-linked (10% HPPK vs double bonds) unfilled electrolyte.The stiffening effect provided by covalent links between polymeric chains leading to a flexible network is much lower than the one provided the establishment of a rigid percolating cellulosic network. It is now of interest to compare the ionic conductivity performances of both systems, i.e., cross-linked and tunicin whiskers reinforced electrolytes.

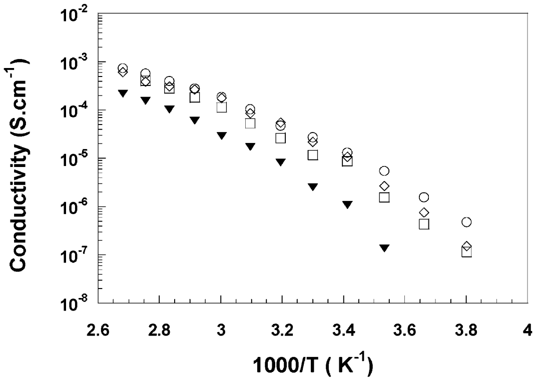

**Figure 4.** Arrhenius plot of the ionic conductivity for composite NPC400−LiTFSI (O/Li = 12) electrolytes cross-linked with 2% HPPK and filled with 0 (◇), 6 (○), and 10 wt % (□) of tunicin whiskers and unfilled NPC400−LiTFSI (O/Li = 12) electrolyte cross-linked with 10% HPPK (▼).

**Ionic Conductivities.** Conductivity measurements for nanocomposite NPC400−LiTFSI electrolytes are shown in Figure 4. The conductivities are higher than $10^{-5}$ S cm$^{-1}$ at 30 °C ($1000/T = 3.3$ K$^{-1}$) and reach $5 \times 10^{-4}$ S cm$^{-1}$ at 90 °C ($1000/T = 2.75$ K$^{-1}$). At high temperature, the conductivity of composite electrolytes is almost composition-independent, and similar values are reported for unfilled NPC400−LiTFSI cross-linked with 2% HPPK.

At lower temperatures, the ionic conductivity of the composite network electrolyte reinforced with 10 wt % cellulosic whiskers is globally slightly lower than the one of other compositions.

NMR investigations were performed for un-cross-linked POE/tunicin whisker based nanocomposite electrolytes.[26] It was shown in this study that the tunicin whiskers induce (i) the reduction of the relaxation time of protons and (ii) the reduction of the diffusion coefficient of both anion and cation. These two effects could explain the decrease of conductivity observed for highly whisker filled (10 wt %) NPC400−LiTFSI nanocomposite electrolytes. For lower whiskers content these mobility reductions might be offset by the decrease of the network cross-linking density when the whiskers content increases.[25] The reduction of the cross-linking density has two effects, viz., (i) an increase of the soluble polymer chain ratio and (ii) an increase of the global network flexibility. Because of the high molecular weight of LPC400, the occurrence of free chains increases only weakly the ionic conductivity of the electrolyte and has no dramatic effect on its electrochemical stability.[27]

In Figure 4, the conductivity of the unfilled NPC400/LiTFSI electrolyte (O/Li = 12) with a high cross-linking density (10% HPPK) is reported for comparison. Compared to the weakly cross-linked electrolytes filled with tunicin whiskers, the ionic conductivity is significantly lower. The conductivity level of the composites at 20 °C ($1000/T = 3.4$ K$^{-1}$) is around $10^{-5}$ S cm$^{-1}$; it is similar to that of the highly cross-linked electrolyte at 40 °C ($1000/T = 3.2$ K$^{-1}$). This difference could be due to (i) a reduction of the matrix mobility by covalent links and/or (ii) a decrease of the soluble chain ratio related to high cross-linking efficiency. However, the presence of a weak amount of soluble polymer chains (around 5%) cannot explain the observed modifications of conductivity. Moreover, the insoluble chain fraction was found to be almost constant regardless of the degree of cross-linking.

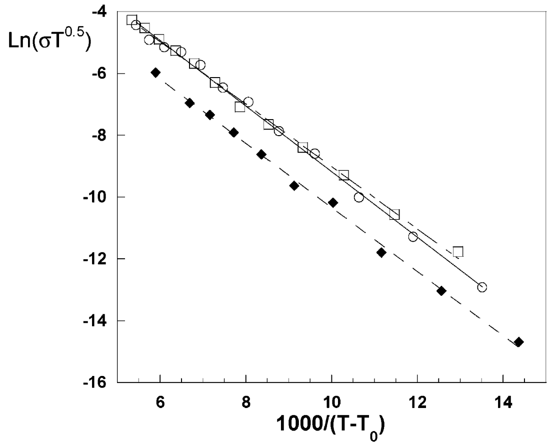

**Figure 5.** VTF fitting curves for unfilled networks electrolytes cross-linked with 2% (○) and 5% HPPK (□) and for the composite filled with 6 wt % tunicin whiskers (◆).

The decrease of conductivity is most probably related to a decrease of the chain mobility. A weak but significant increase of the glass−rubber transition temperature through the occurrence of the main relaxation process was observed with increasing HPPK content, mainly between 2 and 5% (Table 3).

As already reported[24] for such a polymeric network, the cross-linking density has only a small effect on $T_g$. It could be ascribed to the presence of flexible links on side chains. We evaluated[24] the conductivity of networks, obtained by polycondensation, with several solvating ability lengths. For such electrolytes, the cross-linking density has an influence on conductivity especially at high temperature. The effect of cross-linking density on conductivity has also been noted by Kim et al.[28]

The conductivity curves of the nanocomposites cross-linked polymer electrolytes are not linear, suggesting a VTF (Vogel−Tamman−Fulcher) behavior as is generally the case for salt−polymer complexes studied above their glass transition temperature.[11,29] In such a case, the dependence of conductivity with temperature obeys the relationship

$$\sigma(T) = AT^{-1/2}\exp\left(\frac{-B}{R(T - T_0)}\right) \qquad (2)$$

where $A$ is the preexponential factor, which is related to the charge carrier concentration in the polymer electrolyte. $B$ is the pseudo-activation energy of the ion transport related to the configurational entropy of the polymer chains. $T_0$ is the ideal transition temperature at which relaxation times become infinite and the free volume disappears, and $R$ is the perfect gas constant, 8.314 J K$^{-1}$ mol$^{-1}$.

Conductivity data expressed as $\ln(\sigma T^{0.5})$ vs reverse reduced temperature ($T - T_0$) are represented in Figure 5 for both unfilled and filled electrolyte networks. Table 4 reports the results of the VTF fits. The simultaneous determination of the three parameters, namely $A$, $B$, and $T_0$, is rather inaccurate when the conductivity is measured far above $T_g$. For this reason, the value of the parameter $T_0$ used in the fit was fixed at 50 K below the glass transition temperature, in accordance with the empirical relationship.[30]

The calculated values for $B$ are quasi-independent of the whiskers content. The pseudo-activation energy is near 0.1 eV, in good agreement with those reported for

**Table 4. VTF Parameters for the Unfilled Electrolytes at Different Cross-Linking Density and for Tunicin Whisker Based Composites Electrolytes**

| polymer electrolyte | $T_0$ (K) | $A$ (S cm$^{-1}$ K$^{1/2}$) | $B$ (eV) |
|---|---|---|---|
| 2% HPPK−0% whiskers | 188 | 4 | 0.09 |
| 5% HPPK−0% whiskers | 193 | 1 | 0.09 |
| 10% HPPK−0% whiskers | 193 | 7 | 0.11 |
| 2% HPPK−6% whiskers | 186 | 3 | 0.08 |
| 2% HPPK−10% whiskers | 197 | 2 | 0.08 |

NPC1000/LiTFSI networks[24] (1000 being the number-average molar weight of the solvating oligo(oxyethylene) block between two double bonds in LPC) or other polymer electrolytes.[31] Thus, the incorporation of whiskers seems to have no effect on the conduction mechanism.

## Conclusions

In this work, we used a recently published processing way to prepare nanocomposite polymer electrolytes using a cross-linked polyether, lithium trifluoromethyl sulfonyl imide (LiTFSI), and cellulosic rodlike nanoparticles extracted from tunicate. It consisted in using an organic solvent (*N*,*N*-dimethylformamide) medium without a surfactant addition or a chemical surface modification of the tunicin whiskers. Cross-linking is one of the most common methods used to disrupt polymer crystallinity and to ensure mechanical properties. It is classically performed to provide both low-temperature conductivity and high-temperature mechanical stability. 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. 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. 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. It was also shown that tunicin whiskers seem to have no effect on the conduction mechanism of the polymer electrolyte. Therefore, the used cross-linked nanocomposite polymer electrolytes allow conciliating both higher ionic conductivities and higher mechanical performances.

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