# Solid Polymer Electrolytes Based on Nanocomposites of Ethylene Oxide–Epichlorohydrin Copolymers and Cellulose Whiskers

**Michael Schroers, Akshay Kokil, Christoph Weder**

*Department of Macromolecular Science and Engineering, Case Western Reserve University, 2100 Adelbert Road, Cleveland, Ohio 44106-7202, USA*

**ABSTRACT:** With the aim of developing ion-conducting solid polymer electrolytes that combine high ionic conductivity with good mechanical properties, we prepared and investigated nanocomposites of $LiClO_4$-doped ethylene oxide-epichlorohydrin (EO-EPI) copolymers and nanoscale cellulose whiskers derived from tunicates. We show that homogeneous nanocomposite films based on EO-EPI copolymers, $LiClO_4$, and tunicate whiskers can be produced by solution-casting THF/water mixtures comprising these components and subsequent compression-molding. The Young's moduli of the nanocomposites thus produced are increased by a factor of up to >50, when compared to the copolymers, whereas the electrical conductivities experience only comparably small reductions upon introduction of the whiskers. The nanocomposite with the best combination of conductivity ($1.6 \times 10^{-4}$ S/cm at room temperature and a relative humidity of 75%) and Young's modulus (7 MPa) was obtained with a copolymer having an EO-EPI ratio of 84 : 16, a whisker content of 10% w/w, and a $LiClO_4$ concentration of 5.8% w/w. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2883–2888, 2004

**Key words:** polyelectrolytes; ionic conductivity; nanocomposites; cellulose whiskers; Tunicate whiskers; EO-EPI; ethylene oxide–epichlorohydrin copolymer; reinforcements

## INTRODUCTION

During the last three decades, ion-conducting solid polymer electrolytes have attracted considerable interest, because of their potential application in rechargeable batteries, fuel cells, light-emitting electrochemical cells, electrochromics, and many other electrochemical devices.[1–3] Triggered by the exciting early work by Wright et al.[4,5] and Armand et al.,[6,7] polymer systems based on poly(ethylene oxide) (PEO) and alkali salts have become the most comprehensively studied materials platform in this context.[8,9] To achieve high ionic conductivity at ambient temperature, PEO-based electrolytes are usually designed to display a low degree of crystallinity and a low glass transition temperature. Several strategies were employed to achieve this objective, including the use of plasticizers and the copolymerization of ethylene oxide (EO) with comonomers such as epichlorohydrin (EPI).[10–17] Recently, De Paoli et al. reported ion conductivities of up to $2.6 \times 10^{-4}$ S/cm at 24°C and a relative humidity (RH) of 84% for complexes of EO/EPI copolymers [P(EO-EPI), Fig. 1] with lithium perchlorate ($LiClO_4$).[17] Although the ion transport characteristics of these materials are quite remarkable, limited mechanical properties (low Young's modulus and low mechanical strength, which translate into lack of dimensional stability and failure at low stresses) represent a major drawback that is common to many PEO-based electrolytes. To address this and other problems, a number of research groups have focused their attention to organic–inorganic polymer electrolyte nanocomposites in which inorganic nanoparticles are introduced as reinforcing elements into a polymer electrolyte.[18–34] Interestingly, virtually all work in this arena has been focused on the use of inorganic nanoparticles. We show here that a significant mechanical reinforcement can be achieved by the incorporation of a small fraction of high-strength rodlike organic reinforcing elements. Our work follows recent studies by Chanzy and Cavaillé et al., who have investigated nanocomposites based on low-modulus latices and cellulose whiskers derived from tunicates.[35–37] At the example of nanocomposites consisting of EO-EPI copolymers, cellulose whiskers, and $LiClO_4$, we demonstrate that this concept can be applied to create polymer electrolytes with high ionic conductivities and significantly improved mechanical characteristics.
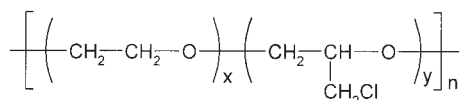
**Figure 1** Chemical structure of the EO-EPI copolymers employed; the ratio of $x$ and $y$ was chosen to be 0.84 : 0.16 [P(EO-EPI)84-16]; 0.60 : 0.40 [P(EO-EPI)60 : 40], and 0.50 : 0.50 [P(EO-EPI)50-50].

## EXPERIMENTAL

### Materials

All reagents were used as received. Tetrahydrofuran (THF), sulfuric acid, sodium hypochlorite, and anhydrous $LiClO_4$ were purchased from Aldrich Chemical Co (Milwaukee, WI). Tunicates were harvested off the New England coast by a licensed fisherman. The EO/EPI copolymers Epichlomer® were supplied by Daiso Co. Ltd. (Osaka, Japan) and were characterized by EO : EPI comonomer ratios of 84 : 16, 60 : 40, and 50 : 50; these polymers are herein referred to as P(EO-EPI)84-16, P(EO-EPI)60-40, and P(EO-EPI)50-50. The glass transition temperatures ($T_g$) of these polymers were −50°C [P(EO-EPI)84-16], −44°C [P(EO-EPI)60-40], and −43°C [P(EO-EPI)50-50][17] and, according to the supplier, the $M_w$ of all materials is ∼ $1.3 \times 10^6$ g/mol.

### Preparation of cellulose whisker suspensions

Colloidal suspensions of cellulose whiskers in water were prepared according to published procedures.[35,38] The shells of the tunicates were cut into small fragments and bleached by three successive treatments with sodium hypochlorite in dilute acetic acid according to the procedure of Wise et al.[38] For each cycle, 7.5 g sodium hypochlorite and 2.5 mL glacial acetic acid were added to a mixture of ∼ 6 g of air-dried tunicate mantels in 400 mL water. The mixture was heated to 70–80°C and kept at this temperature for 1 h. After the third cycle, the tunicate mantles were isolated via decanting, washed with ice water, and disintegrated in a Waring blender (four cycles, each 10 min at maximum speed) into an aqueous suspension (tunicate content ∼ 3% w/w). The disintegrated mantles were subsequently hydrolyzed by adding concentrated sulfuric acid so that the sulfuric acid concentration was 55% w/w, heating the mixture to 80°C, and rigorous stirring at this temperature for 20 min to yield a suspension of cellulose whiskers.[35] After washing with water until the pH was neutral, adding water so that the whisker concentration was 1 mg/mL, and ultrasonication, a nonflocculating, highly birefringent suspension of cellulose whiskers was obtained. One drop of $CHCl_3$ was added for preservation purposes

and the exact weight fraction of whiskers was gravimetrically determined.

### Preparation of nanocomposites

THF solutions containing the desired copolymer (4% w/w based on the solvent) and between 0 and 10% w/w of anhydrous $LiClO_4$ (based on the copolymer) were prepared by stirring the components in dry THF. Nanocomposites were produced by combining appropriate amounts of the colloidal whisker suspension and the THF/polymer/$LiClO_4$ solutions and subsequent solution-casting into Petri dishes. The solvent was slowly evaporated under ambient conditions and the resulting films were dried in vacuum at 60°C and 15 mbar. The materials were then compression-molded at 80°C under a pressure of 500 psi in a Carver laboratory press, to yield homogeneous films of a thickness of 200–300 $\mu m$.

### Methods

Mechanical tests were carried out at ambient temperature on an Instron 1123 tensile tester using rectangular film samples with dimensions of 22 mm × 5 mm × 200–300 $\mu m$ and applying a strain rate of 20 mm/min. Mechanical data quoted typically represent averages of two independent measurements. A JEOL JSM-840 scanning electron microscope (SEM) was employed to study the morphology of the nanocomposites; the samples used for SEM studies were fractured in liquid nitrogen and were subsequently coated with Pd by sputtering. Ionic conductivities were measured with in-plane geometry by using a Princeton Applied Research Potentiostat (Model 263A) in connection with an EG&G Instruments Frequency response Analyzer (Model 1025) in a frequency range from 1 Hz to 100 kHz; the RH of the sample compartment was controlled to be 75% by means of an appropriate LiCl solution, and samples were equilibrated for at least 24 h. All conductivity measurements were conducted at room temperature (21 ± 2°C).

## RESULTS AND DISCUSSION

### Processing and morphology

The materials investigated in this study were based on the $LiClO_4$-doped EO-EPI copolymers displayed in Figure 1 and cellulose whiskers that were isolated from tunicates harvested at the New England Atlantic coast. Colloidal suspensions of cellulose whiskers in water were prepared from these invertebrates according to published procedures.[35,38] Tunicate whiskers exhibit an average length in the micrometer range and an aspect ratio of >100. Due to their high aspect ratio
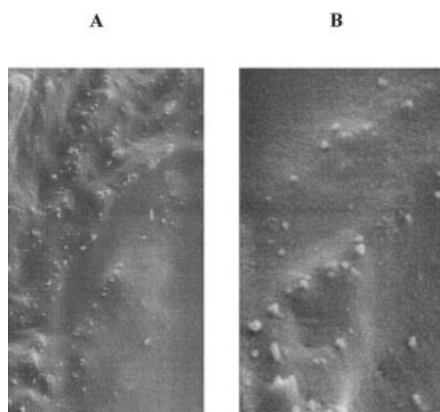
**Figure 2** Scanning electron micrographs of a freshly fractured nanocomposite film based on P(EO-EPI) 50-50 and 10% w/w tunicate whiskers. A: magnification, ×10,000. B: magnification, ×30,000.



**Figure 3** Stress–strain curves of P(EO-EPI)50-50 nanocomposites (solid line: neat Epimer 50-50; dashed-dotted line: 2% w/w cellulose whiskers; dashed line: 5% w/w cellulose whiskers; dotted line: 10% w/w cellulose whiskers).

and an extremely high Young's modulus along their length axis (130–150 GPa[39,40]), these fibrils can display a superb reinforcing effect.[35–37] With the objective to prepare homogeneous nanocomposites of these cellulose whiskers and (LiClO$_4$-doped) EO-EPI copolymers, we have developed and applied a general scheme for the processing of these materials. The protocol is based on mixing a THF solution of the polymer and optionally LiClO$_4$ with an aqueous whisker suspension, solution-casting of the resulting mixtures into films, and subsequent compression-molding at 80°C. We have employed EO-EPI copolymers with EO : EPI comonomer ratios of 84 : 16 [referred to as P(EO-EPI)84-16], 60 : 40 [P(EO-EPI)60-40], and 50 : 50 [P(EO-EPI)50-50] and have systematically varied the contents of LiClO$_4$ and cellulose whiskers. SEM was used to characterize the morphology of the nanocomposites prepared. Figure 2 shows the surface of a freshly fractured nanocomposite film based on P(EO-EPI)50-50 and 10% w/w tunicate whiskers. In analogy to previous studies, we assign the light-colored portions of these micrographs to the cellulose whiskers and con-
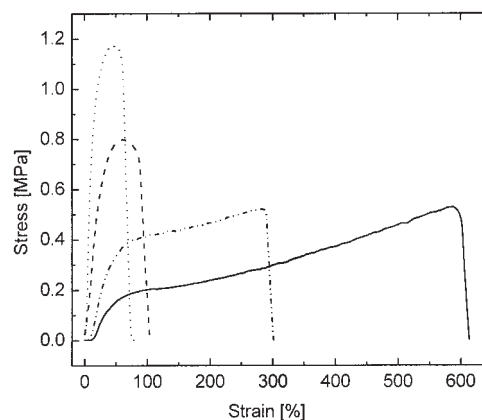
clude that our processing scheme indeed leads to nanocomposites, in which the reinforcing elements are rather well dispersed in the polymer matrix, at least in the compositional range investigated here. Mechanical data (*vide infra*) seem to suggest that the addition of LiClO$_4$ improved the dispersion of the whiskers in the polymer matrices, but, unfortunately, we were unable to support this conclusion by SEM studies.

## Mechanical properties

The mechanical properties of the nanocomposite films were investigated by standard tensile tests at ambient temperature, which is well above the $T_g$ of the matrix copolymers (−43 to −50°C), even if they are doped with high weight fractions of LiClO$_4$ ($T_g < −30°C$).[17] We first investigated samples containing 0 to 20% w/w cellulose whiskers but no LiClO$_4$ at a strain rate of 20 mm/min. The results are compiled in Table I and Figure 3. The stress–strain curves recorded for the neat matrix copolymers demonstrate nonlinear elastic be-

**TABLE I**
**Influence of the Whisker Content on the Mechanical Properties of LiClO$_4$-Free P(EO-EPI)-Cellulose Whisker Nanocomposites**

| Whisker content[a] [% w/w] | P(EO-EPI)84-16 | | P(EO-EPI)60-40 | | P(EO-EPI)50-50 | |
|---|---|---|---|---|---|---|
| | $E^b$ [MPa] | Strain/stress at break [%]/[MPa] | $E^b$ [MPa] | Strain/stress at break [%]/[MPa] | $E^b$ [MPa] | Strain/stress at break [%]/[MPa] |
| 0 | 0.2 | 91/0.1 | 0.1 | 139/<0.1 | 0.5 | 593/0.5 |
| 1 | 0.5 | 91/0.2 | 0.7 | 105/0.2 | 1.1 | 285/0.5 |
| 2 | 0.5 | 100/0.5 | 1.1 | 111/0.4 | 2.0 | 190/0.6 |
| 5 | 1.1 | 111/0.6 | 1.7 | 93/0.4 | 3.6 | 93/0.8 |
| 10 | 2.8 | 66/0.6 | 4.5 | 40/0.7 | 7.1 | 81/1.2 |
| 20 | 7.5 | 22/0.7 | 14 | 28/1.5 | 12 | 71/1.0 |

[a] Based on the amount of P(EO-EPI).
[b] Young's modulus.

**TABLE II**
**Influence of the Whisker Content on the Mechanical Properties of LiClO$_4$-Doped**
**P(EO-EPI)-Cellulose Whisker Nanocomposites**

| Whisker content[a] [% w/w] | P(EO-EPI)84-16 + 5.8% w/w[a] LiClO$_4$ | | P(EO-EPI)60-40 + 3.6% w/w[a] LiClO$_4$ | | P(EO-EPI)50-50 + 2.6% w/w[a] LiClO$_4$ | |
|---|---|---|---|---|---|---|
| | $E^b$ [MPa] | Strain/stress at break [%]/[MPa] | $E^b$ [MPa] | Strain/stress at break [%]/[MPa] | $E^b$ [MPa] | Strain/stress at break [%]/[MPa] |
| 0 | n.a.[c] | n.a.[c] | n.a.[c] | n.a.[c] | 0.6 | >700/0.9 |
| 5 | 2.3 | 75/0.4 | 5.7 | 75/0.8 | 7.2 | 65/1.0 |
| 10 | 6.9 | 43/0.6 | 13 | 30/1.1 | 24 | 40/1.8 |
| 15 | 6.7 | 20/0.6 | 21 | 22/1.4 | 32 | 23/2.1 |

[a] Based on the amount of P(EO-EPI).
[b] Young's modulus.
[c] Sample was too fragile for tensile tests.

havior, characterized by low Young's moduli $E$ ($\sim$ 0.1–0.5 MPa) and high elongations at break [up to 600% for P(EO-EPI)50-50]. As expected, the elongation at break significantly increases with the fraction of the epichlorohydrin comonomer, but there is no apparent trend as far as the modulus is concerned. This may reflect a limited experimental accuracy of the tensile tests in the sub-MPa regime. Reinforcement of the matrix copolymers with cellulose whiskers results in a significant increase of the Young's modulus, a reduced elongation at break, and an increased tensile strength (Table I, Fig. 3). Even small weight fractions of cellulose whiskers influence the mechanical properties significantly. At a whisker content of 20% w/w, the Young's moduli of all nanocomposites investigated here are increased by more than an order of magnitude. At the same time, the tensile strength is also significantly increased, while the elongation at break is reduced; the data for strain/stress at break show some scattering, which is consistent with sample defects that arise, for example, from imperfections in the mold. We subsequently investigated the mechanical properties of LiClO$_4$-doped nanocomposites of P(EO-EPI) and cellulose whiskers. On the basis of the data reported by De Paoli et al., who have shown that the three copolymers used here display maximum ionic conductivities at different LiClO$_4$ concentrations,[17] we doped nanocomposites of these copolymers and various weight fractions of cellulose whiskers with 5.8% w/w [P(EO-EPI)86-14], 3.6% w/w [P(EO-EPI)60-40], and 2.6% w/w [P(EO-EPI)50-50] of LiClO$_4$ (based on the total weight of the polymer). The data compiled in Table II show that the addition of LiClO$_4$ further enhanced the reinforcing effect of the cellulose. As a matter of fact, a comparison of the data shown in Tables I and II shows that the average Young's modulus is increased by a factor of $\sim$ 2–3 when comparing whisker-reinforced polymers with and without LiClO$_4$. Interestingly, the Young's moduli of samples containing no cellulose whiskers remained essentially unchanged upon addition of small amounts of LiClO$_4$.

Thus, we speculate that this significant increase of $E$ may be caused by a stabilizing influence of the salt during processing, possibly through Li-complexation of sulfate groups on the whisker surfaces, which might lead to a better dispersion of the whiskers in the polymer matrix. It is also possible that the whisker–whisker interactions in the LiClO$_4$-doped systems are more pronounced. The highest stiffness (32 MPa) was observed for a nanocomposite comprising P(EO-EPI)50-50, 15% w/w of cellulose whiskers, and 2.6% w/w of LiClO$_4$; in this case, the Young's modulus was increased by a factor of well above 50 compared to the sample comprising no cellulose whiskers (0.6 MPa). The data in Table II show that, at all whisker fractions investigated in this study, the stiffness of the LiClO$_4$-doped nanocomposites increases as the fraction of ethylene oxide comonomer is reduced, whereas the neat EO-EPI copolymers display similar moduli (Table I); the cause of this trend is, however, uncertain. Studying a series of nanocomposite comprising P(EO-EPI)50-50 and 10% w/w of cellulose whiskers, we have also studied the influence of the LiClO$_4$ concentration (Table III). The data show that already at a LiClO$_4$ content of 1% w/w the Young's

**TABLE III**
**Influence of the LiClO$_4$ Content on the Mechanical**
**Properties of LiClO$_4$-Doped P(EO-EPI)50-50-Cellulose**
**Whisker Nanocomposites**

| LiClO$_4$ content[a] [% w/w] | P(EO-EPI)50-50 + 10% w/w whiskers | |
|---|---|---|
| | $E^b$ [MPa] | Strain/stress at break [%]/[MPa] |
| 0 | 7.1 | 81/1.6 |
| 1.1 | 20 | 35/1.5 |
| 2.6 | 24 | 40/1.8 |
| 5 | 20 | 30/1.3 |
| 10 | 14 | 39/1.0 |

[a] Based on the amount of P(EO-EPI); the weight fraction of cellulose whiskers was 10% w/w for all samples.
[b] Young's modulus.

## TABLE IV
### Influence of the Whisker Content on the Ion-Conducting Properties of LiClO$_4$-Doped P(EO-EPI)-Cellulose Whisker Nanocomposites[a]

| Whisker content[b] [% w/w] | P(EO-EPI)84-16 5.8% w/w[b] LiClO$_4$ $\sigma$ [S/cm] | P(EO-EPI)60-40 3.6% w/w[b] LiClO$_4$ $\sigma$ [S/cm] | P(EO-EPI)50-50 2.6% w/w[b] LiClO$_4$ $\sigma$ [S/cm] |
|---|---|---|---|
| 0 | $2.2 \times 10^{-4}$ | n.a. | $7.3 \times 10^{-5}$ |
| 5 | $1.7 \times 10^{-4}$ | $3.8 \times 10^{-5}$ | $1.2 \times 10^{-5}$ |
| 10 | $1.6 \times 10^{-4}$ | $3.8 \times 10^{-5}$ | $9.3 \times 10^{-6}$ |
| 15 | $1.3 \times 10^{-4}$ | $2.9 \times 10^{-5}$ | $7.3 \times 10^{-6}$ |

[a] Measured at room temperature and 75% RH.
[b] Based on the amount of P(EO-EPI).

modulus is significantly increased from 7.1 to 20 MPa. It is equally high (20–24 MPa) in a concentration regime of about 1–5% LiClO$_4$, but drops considerably at higher LiClO$_4$ concentrations.

## Ionic conductivity

Ionic conductivities were measured by using a potentiostat in connection with a frequency response analyzer in a frequency range from 1 Hz to 100 kHz. All experiments were conducted at room temperature and at a RH of 75%. In accordance with the results of De Paoli and coworkers, who established optimum doping levels for the matrix polymers employed,[17] we focused our attention on nanocomposites comprising 5.8% [P(EO-EPI)84-16], 3.6% [P(EO-EPI)60-40], and 2.6% [P(EO-EPI)50-50], of LiClO$_4$ (*vide supra*). As can be seen from Table IV, the conductivity of the reference systems comprising only the polymer and LiClO$_4$ (but no whiskers) decreases with increasing content of the epichlorohydrin monomer; the absolute conductivities determined [$2.2 \times 10^{-4}$ and $7 \times 10^{-3}$ S/cm for P(EO-EPI)84-16 and P(EO-EPI)50-50, respectively] were of the same level as those reported (although measured under slightly different conditions) in prior studies.[17] Interestingly, as is evident from the data presented in Table IV, the introduction of cellulose whiskers only had a modest influence on the ionic conductivity of the nanocomposites based on a P(EO-EPI)84-16 matrix comprising 5.8% LiClO$_4$; the conductivity was reduced from $2.2 \times 10^{-4}$ to $1.3 \times 10^{-4}$ S/cm upon introduction of 15% w/w of cellulose whiskers. This finding is intriguing as it demonstrates that a significant improvement of the material's modulus can be achieved through the introduction of organic reinforcing elements, while keeping the ionic conductivity largely unchanged. A more pronounced reduction in conductivity was, however, observed for the nanocomposites based on copolymers with higher mol-fractions of the epichlorohydrin comonomer; it should be noted that these samples also contained a lower concentration of LiClO$_4$. For example, the conductivity of the nanocomposites based on a P(EO-EPI)50-50 matrix comprising 2.6% LiClO$_4$ was reduced by about one order of magnitude from $7.3 \times 10^{-5}$ to $7.3 \times 10^{-6}$ S/cm upon introduction of 15% w/w of cellulose whiskers (note, however, that as discussed above, the Young's modulus is increased by a factor of >50). This finding is consistent with the above-discussed assumption that some fraction of the Li$^+$ ions indeed formed complexes with the sulfonate groups present on the whisker surfaces. This effect, of course, would lead to a reduced concentration of ether–LiClO$_4$ complexes and result in a reduction of the ionic conductivity. The fact that the highest reduction of the conductivity was observed for the materials system with the lowest LiClO$_4$ content further supports this view. Conclusive evidence is expected from a systematic study that is focused on elucidating the influence of the LiClO$_4$ concentration. We note that the composition determined to be optimal for the not-reinforced P(EO-EPI)50-50–LiClO$_4$ mixtures may be too low for the nanocomposites investigated here.

## CONCLUSION

In summary, we have shown that LiClO$_4$-doped nanocomposites of EO-EPI copolymers and cellulose whiskers can readily be produced by solution casting THF/water mixtures comprising the components and subsequent compression-molding of the resulting nanocomposites. Films of these materials display substantially improved mechanical properties, when compared to the not reinforced LiClO$_4$/EO-EPI, and their electrical conductivities experience comparably small reductions. We surmise that the approach may be broadly applicable for the design of new polymer electrolytes which demonstrate both high ionic conductivities and good mechanical characteristics.

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