

# Influence of LiClO<sub>4</sub> on the Thermal, Mechanical, and Morphological Properties of P(DMS-co-EO)/P(EPI-co-EO) Blends

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**ABSTRACT:** The UV-vis absorption, thermal analysis, ionic conductivity, mechanical properties, and morphology of a blend of poly(dimethylsiloxane-co-ethylene oxide) [P(DMS-co-EO)] and poly(epichlorohydrin-co-ethylene oxide) [P(EPI-co-EO)] (P(DMS-co-EO)/P(EPI-co-EO) ratio of 15/85 wt %) with different concentrations of LiClO<sub>4</sub> were studied. The maximum ionic conductivity ( $\sigma = 1.2 \times 10^{-4}$  S cm<sup>-1</sup>) for the blend was obtained in the presence of 6% wt LiClO<sub>4</sub>. The crystalline phase of the blend disappeared with increasing salt concentration, whereas the glass transition temperature ( $T_g$ ) progressively increased. UV-vis absorption

spectra for the blends with LiClO<sub>4</sub> showed a transparent polymer electrolyte in the visible region.

The addition of lithium salt decreased the tensile strength and elongation at break and increased Young's modulus of the blends. Scanning electron microscopy showed separation of the phases between P(DMS-co-EO) and P(EPI-co-EO), and the presence of LiClO<sub>4</sub> made the blends more susceptible to cracking. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1230–1235, 2004

**Key words:** electrochemistry; mechanical properties; polymer blends; thermal properties; UV-vis spectroscopy

## INTRODUCTION

The science of polymer electrolytes is a specialized, interdisciplinary field which encompasses the disciplines of electrochemistry, polymer science, organic chemistry, and inorganic chemistry. The field has attracted increasing interest in the past 2 decades because of the promising applications of polymer electrolytes, not only in solid-state rechargeable lithium or lithium-ion batteries, but also in other electrochemical devices, such as supercapacitors, electrochromic windows, and sensors.<sup>1–4</sup>

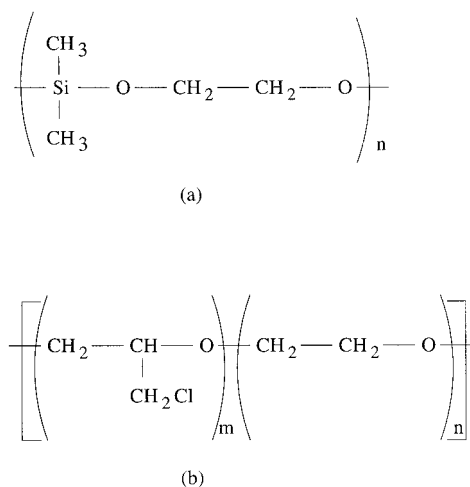
Solid polymer electrolytes, which consist of an ionic conducting polymer matrix and a supporting electrolyte salt, were introduced as a new electrolyte material for lithium batteries by Fenton et al.<sup>5</sup> and Armand et al.<sup>6</sup> At room temperature, the complexes of polyethylene oxide (PEO) and lithium salts show an important crystallinity,<sup>7</sup> and good conductivity can be achieved only at moderately high temperature.<sup>8</sup> In principle, a polymer electrolyte battery is

formed by laminating a lithium metal (or composite carbon) anode, a lithium-ion conducting membrane, and a composite cathode in a sandwich structure.<sup>9</sup> The entire cell assembly can be produced as a continuous tape or can be rolled or folded into its finished shape. The key component of this device is the electrolyte, and its proper choice is governed by a series of requirements which include high ionic conductivity, good mechanical properties, and compatibility with the electrode materials.

P(DMS-co-EO) (Figure 1a)<sup>10</sup> has a high ionic conductivity ( $\approx 1 \times 10^{-4}$  S cm<sup>-1</sup>) and wide electrochemical stability windows, but has no mechanical support since it is a gel polymer electrolyte. In contrast, P(EPI-co-EO) (Figure 1b)<sup>11</sup> has a lower ionic conductivity than P(DMS-co-EO) ( $\approx 1 \times 10^{-6}$  S cm<sup>-1</sup>), an electrochemical stability window of 3.5 V, and good mechanical properties that make it an elastomeric polymer. A maximum ionic conductivity  $\sigma$  of  $1.2 \times 10^{-4}$  S cm<sup>-1</sup> was obtained for the P(DMS-co-EO)/P(EPI-co-EO) blends 20/80 and 15/85 containing 6% wt LiClO<sub>4</sub>. These films had an electrochemical stability >5.0 V at room temperature, indicating that these blends can be used as solid-state polymeric electrolytes.

Manufacturability is by far the most important factor to be considered in battery production. Although

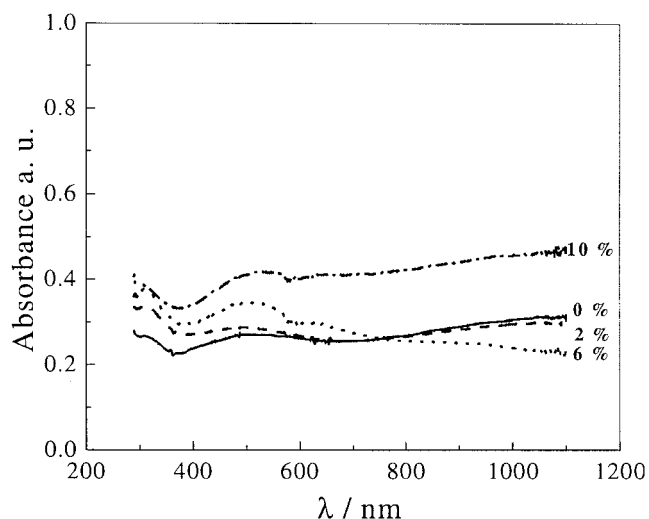
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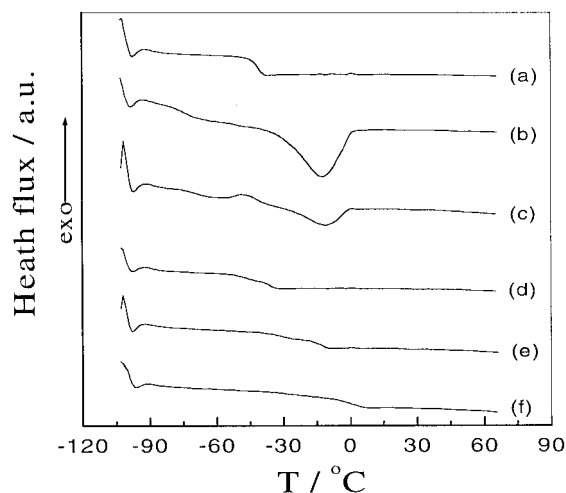
**Figure 1** Chemical structure of (a) P(DMS-co-EO) and (b) P(EPI-co-EO).

many electrolyte systems can be fabricated as free-standing membranes and show favorable electrochemical properties, their mechanical strength still requires further enhancement to allow manufacture by conventional, large-scale coating processes. This problem has led to the development and synthesis of new polymer electrolytes, with physical studies of their structure and charge transport, theoretical modeling of the charge-transport processes, and determination of the physical and chemical properties at the electrolyte/electrode interface.

The aim of this study was to investigate the influence of the lithium salt on the mechanical properties of a P(DMS-co-EO)/P(EPI-co-EO) blend. In particular, we examined the correlation between the thermal and



**Figure 2** UV-vis spectroscopy of the P(DMS-co-EO)/P(EPI-co-EO) blend with different concentration percentage of LiClO<sub>4</sub>.



**Figure 3** DSC curves for (a) P(EPI-co-EO), (b) P(DMS-co-EO), (c) P(DMS-co-EO)/P(EPI-co-EO) blend 15/85 ratio containing (d) 2, (e) 6, and (f) 10% wt LiClO<sub>4</sub>.

electrochemical aspects and the tensile properties and morphology of the blends with LiClO<sub>4</sub>.

### EXPERIMENTAL

#### Materials

P(DMS-co-EO) was synthesized by a polycondensation reaction of dimethyldichlorosilane with monoethylene glycol.<sup>12</sup> P(EPI-co-EO) and LiClO<sub>4</sub> were purchased from Aldrich and used as received.

#### Preparation of P(DMS-co-EO)/P(EPI-co-EO)/LiClO<sub>4</sub> blends

The blends were prepared by dissolving the pure polymers and LiClO<sub>4</sub> in tetrahydrofuran. The solvent was evaporated and dried at high vacuum for 72 h. The P(DMS-co-EO)/P(EPI-co-EO) ratio was 15/85 (w/w), with 2, 6, and 10% wt of LiClO<sub>4</sub> added as required.

#### UV-vis spectroscopy

UV-vis spectra were collected on an HP 8453 spectrophotometer. The background signals from the ITO glass substrate were considered 0% absorbance.

#### Thermal analysis

The thermal behavior of the blends was analyzed using a differential scanning calorimeter (DSC 204-NETZSCH). The samples were placed in aluminum pans under a nitrogen atmosphere, heated to 150°C, cooled to -100°C, and then heated to 250°C. The thermograms were recorded at a scan rate of 10°C min<sup>-1</sup>. All DSC experiments were done in duplicate

and the thermograms shown in the next section refer to the final heating.

### Electrochemical impedance spectroscopy

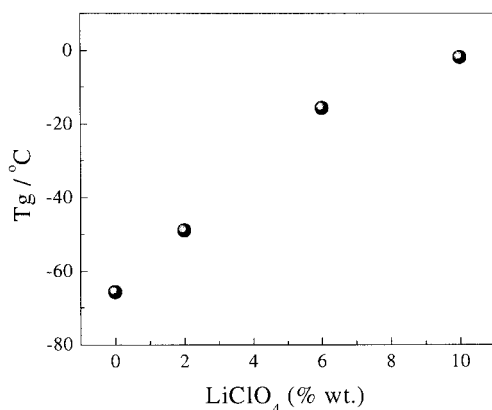
EIS were obtained using an EcoChemie Autolab PG-STAT30 potentiostat with a FRA module. The Li/blend interface behavior was analyzed using two lithium electrodes obtained by pressing lithium foils on the surface of the stainless steel disks ( $1 \text{ cm}^2$ ). An a.c. amplitude of 10 mV was applied and data were collected in the frequency range from  $10^5$  to  $10^{-2}$  Hz after 60 min of stabilization. All electrochemical experiments were done in a dry box under an argon atmosphere. The impedance data were analyzed using Boukamp's fitting software.<sup>13,14</sup>

### Tensile properties

Type IV specimens (ASTM D-638)<sup>15</sup> were studied using a Model DL 2000 NS 5921 universal testing machine (EMIC Equipamentos e Sistemas de Ensaio Ltda., São José dos Pinhais, PR, Brazil). The control program used was MTest LBP, version 3.00, and the load cell had a capacity of 20 kgf. The specimens were initially 25 mm long and the speed of stretching was 50 mm/min.

### Scanning electron microscopy (SEM)

The P(DMS-*co*-EO)/P(EPI-*co*-EO) blend 15/85 containing 0, 2, 6, and 10% wt LiClO<sub>4</sub> were cryofractured in liquid nitrogen and coated with gold in a Bal-tec sputter-coater, Model SCD 50. Photomicrographs of the fracture surfaces of these specimens were obtained using a JEOL Model JSM-5900LV scanning electron microscope (LME/LNLS, Laboratório Nacional de Luz Síncrotron, Campinas, SP, Brazil).



**Figure 4** Variation in the glass transition temperature ( $T_g$ ) as a function of LiClO<sub>4</sub> concentration in P(EPI-*co*-EO)/P(DMS-*co*-EO) blends.

## RESULTS AND DISCUSSION

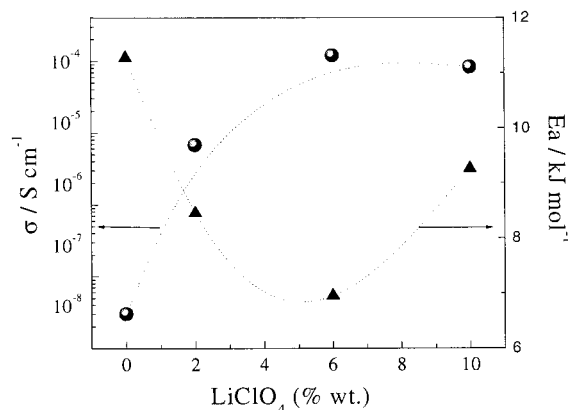
### UV-vis-spectroscopy

Figure 2 shows the UV-vis absorption spectra of the blends. There was no significant absorption in the visible region at the salt concentrations investigated. This requisite is very important when the polymer electrolyte is used in electrochromic applications, in which the color changes of the electrochromic material cannot be affected by polymeric electrolyte coloration.

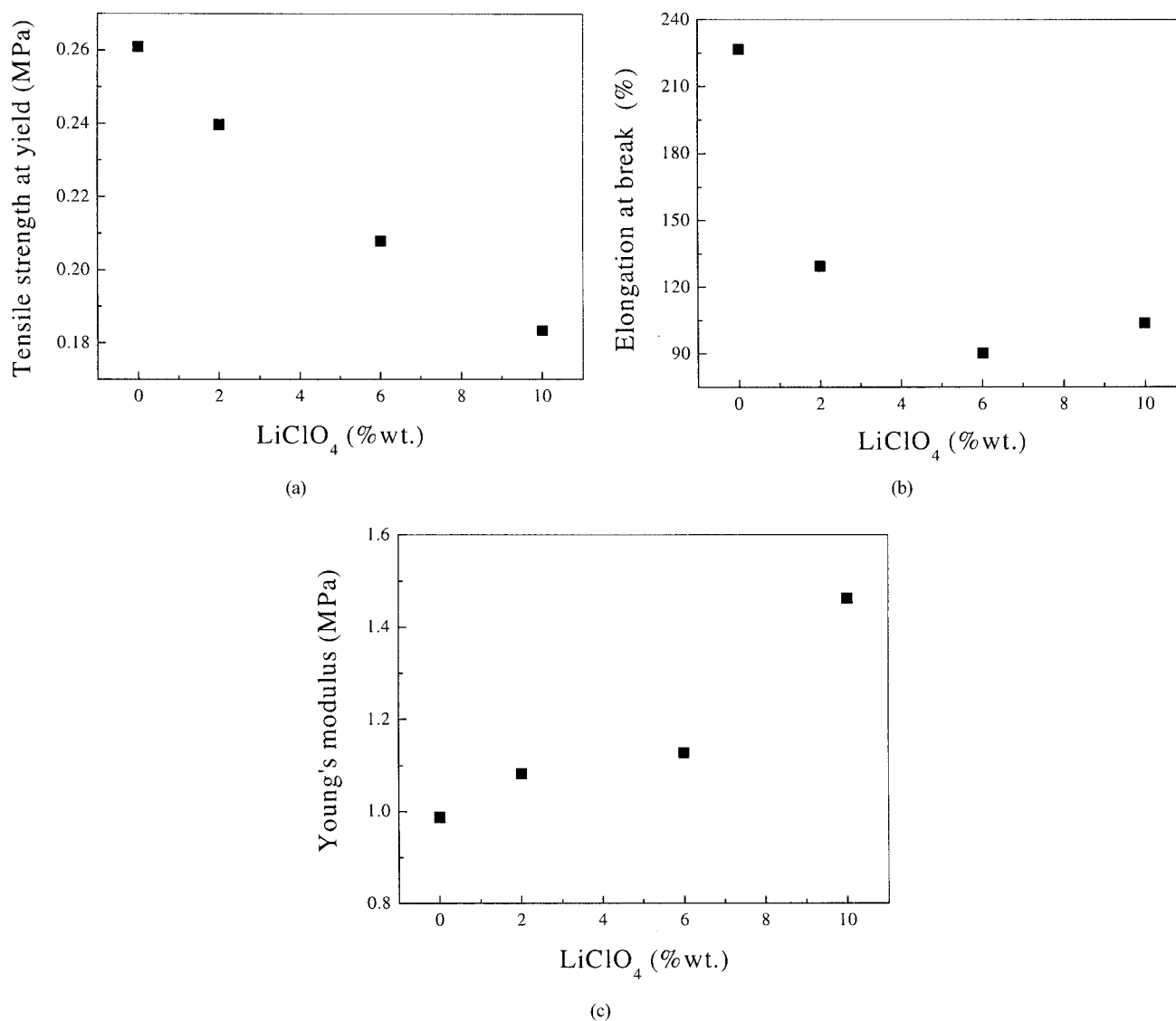
### Thermal analysis

The thermal behavior of the pure copolymers, P(EPI-*co*-EO) (a) and P(DMS-*co*-EO) (b) and P(DMS-*co*-EO)/P(EPI-*co*-EO) blend 15/85 (c) containing 2 (d), 6 (e), and 10% (f) wt LiClO<sub>4</sub> are shown in Figure 3. P(EPI-*co*-EO) showed amorphous characteristics, with a well-defined phase transition at  $-42^\circ\text{C}$ , which was attributed to the  $T_g$  (Figure 3a).<sup>11</sup> P(DMS-*co*-EO) presents a melting process ( $T_m = -12.5^\circ\text{C}$ ), which suggested the presence of a crystalline phase related to melting of the poly(dimethylsiloxane) block. The two-phase transition observed at  $-74.1$  and  $-52.1^\circ\text{C}$  was related to the glass transition temperature of the poly(dimethylsiloxane) block and the poly(ethylene oxide) block, respectively (Fig. 3b).<sup>16</sup>

Two poorly defined phase transitions at  $-69$  and  $-41^\circ\text{C}$  related to the glass transition temperatures of the P(DMS-*co*-EO) and P(EPI-*co*-EO) blocks, respectively, were seen for the blend P(DMS-*co*-EO)/P(EPI-*co*-EO) 15/85 (Figure 3c). The endothermic process observed at  $-10.5^\circ\text{C}$  was attributed to the crystalline phase of P(DMS-*co*-EO) (Figure 3b,  $T_m = -12.5^\circ\text{C}$ ).



**Figure 5** Ionic conductivity ( $\sigma$ ) and energy of activation ( $E_a$ ) of the P(EPI-*co*-EO)/P(DMS-*co*-EO) 15/85 blend polymer in the presence of 2, 6, and 10% wt LiClO<sub>4</sub>.



**Figure 6** Mechanical properties of the P(EPI-*co*-EO)/P(DMS-*co*-EO) 15/85 blend in the presence of 2, 6, and 10% wt LiClO<sub>4</sub>. (a) Tensile strength at yield; (b) elongation at break; and (c) Young's modulus.

The addition of salt to the P(DMS-*co*-EO)/P(EPI-*co*-EO) 15/85 blend abolished the crystalline phase of the pure blend (Figure 3e and f). This result has already been reported for P(EPI-*co*-EO) electrolytes<sup>11</sup> and is caused by ion complexation that acts as cross-linking nodes to decrease the degree of crystallinity. At high salt concentration (10% LiClO<sub>4</sub>), incomplete dissociation of the salt was observed, with a broad melting peak at  $T_m = 125^\circ\text{C}$  (Figure 3f), indicating the formation of a crystalline phase.

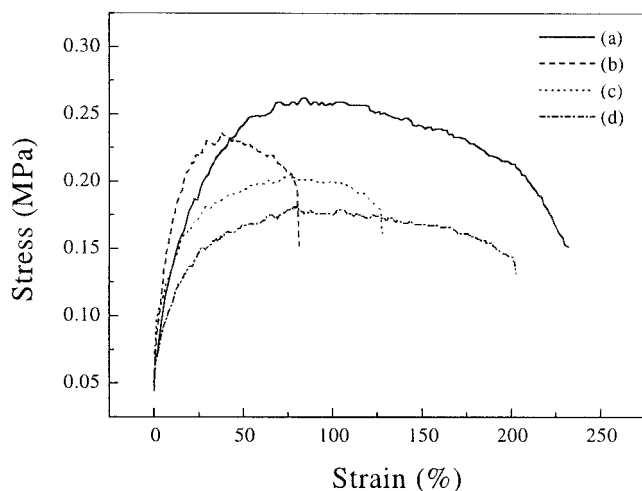
Figure 4 shows the glass transition temperature of the blends as a function of salt concentration. Chain movement decreased with increasing salt concentration as shown by the increase in  $T_g$ . This result reflects the increased oxygen coordination of the chain with salt, as well as the incomplete dissociation of the salt. The degree of chain movement decreased the ionic conductivity of the polymer electrolyte.

## EIE

Figure 5 shows the ionic conductivity of the P(DMS-*co*-EO)/P(EPI-*co*-EO) 15/85 blend with 0, 2, 6, and 10% wt LiClO<sub>4</sub> at room temperature. The maximum ionic conductivity ( $\sigma = 1.2 \times 10^{-4} \text{ S cm}^{-1}$ ) was obtained for P(DMS-*co*-EO)/P(EPI-*co*-EO) 15/85 with 6% wt LiClO<sub>4</sub>. This value was 1 order of magnitude higher than for P(EPI-*co*-EO) electrolyte<sup>11</sup> and was the same magnitude as for P(DMS-*co*-EO) gel electrolyte.<sup>12</sup> The decrease in ionic conductivity beyond the maximum may reflect factors such as the presence of a crystalline phase, an increase in the macromolecular rigidity of the amorphous phase, and the appearance of ion pairs.

The activation energy of the P(DMS-*co*-EO)/P(EPI-*co*-EO) 15/85 blend with 0, 2, 6, and 10% wt LiClO<sub>4</sub> shown in Figure 5 was obtained by VTF fitting.<sup>17</sup> An energy minimum was observed for all blends with 6% wt





**Figure 7** Strain–strength curves for the P(EPI-*co*-EO)/P(DMS-*co*-EO) 15/85 blend in the presence of (a) 0, (b) 2, (c) 6, and (d) 10% wt LiClO<sub>4</sub>.

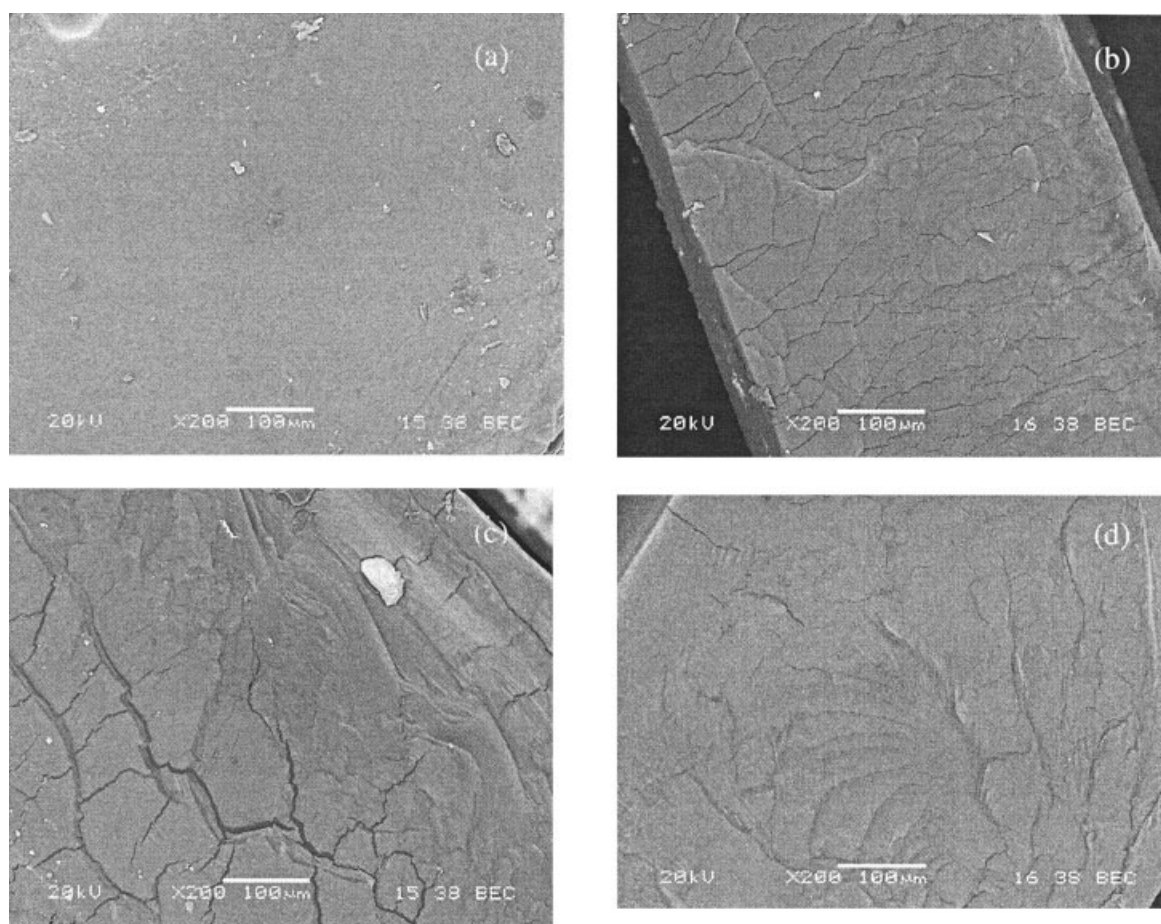
LiClO<sub>4</sub>. In this case, the activation energy was lower than that for the pure P(EPI-*co*-EO)/LiClO<sub>4</sub> system,<sup>11</sup> indicating that the addition of P(DMS-*co*-EO) increased the segmental movement and flexibility of the blend.

### Mechanical properties

Figure 6 shows the tensile strength at yield, elongation at break, and Young's modulus, and Figure 7 shows representative strain–strength curves obtained for the P(DMS-*co*-EO)/P(EPI-*co*-EO) blend with 0, 2, 6, and 10% wt LiClO<sub>4</sub>.

The addition of lithium salt decreased the tensile strength at yield when compared with the pure P(DMS-*co*-EO)/P(EPI-*co*-EO) blend (Figure 6a). Reductions of 8, 20, and 30% were observed in the presence of 2, 6, and 10% wt LiClO<sub>4</sub>, respectively, suggesting an incompatibility of the blends with LiClO<sub>4</sub>. This conclusion was supported by the disappearance of the crystalline phase of the P(DMS-*co*-EO)/P(EPI-*co*-EO) 15/85 blend upon the addition of salt, as discussed above for the thermal analysis.

Figure 6b shows that the elongation decreased with increasing LiClO<sub>4</sub> content. This reduction suggested that the lithium salt behaved as a rigid filler when added to the polymeric matrix and that an incompatible system was produced since the addition of LiClO<sub>4</sub> reduced below of the linear level.



**Figure 8** Electron micrograph of the P(EPI-*co*-EO)/P(DMS-*co*-EO) 15/85 blend containing (a) 0, (b) 2, (c) 6, and (d) 10% wt LiClO<sub>4</sub>.

The addition of LiClO<sub>4</sub> increased Young's modulus by 10, 14, and 48% with the addition of 2, 6, and 10% wt LiClO<sub>4</sub>, respectively (Figure 6c). These values of Young's modulus further suggested incompatibility of the blends. The pure P(DMS-*co*-EO)/P(EPI-*co*-EO) 15/85 blend was more rigid than blends containing LiClO<sub>4</sub>, as shown by the greater crystalline phase of these blends, seen in EIE analysis.

### Morphology

Phase separation between PEPI and P(DMS-*co*-EO) was seen in the pure P(DMS-*co*-EO)/P(EPI-*co*-EO) 15/85 blend (Figure 8a).

The presence of LiClO<sub>4</sub> produced a polymer blend with a homogeneous dispersion but showed various fissures, the number of which increased with increasing LiClO<sub>4</sub> concentration (Figure 8b, c, and d). These results agree with the decreasing values of tensile strength and elongation. The morphological alterations also showed a decrease in the organization of the chains, i.e., a reduction in crystallinity.

### CONCLUSION

These results show that it is possible to produce a polymeric electrolyte by mixing two copolymers of very different mechanical and electrochemical properties. The addition of P(DMS-*co*-EO) to P(EPI-*co*-EO) significantly affected the electrochemical properties, although the flexibility and autosupport of the polymer electrolyte film (a characteristic of P(EPI-*co*-EO)) were maintained. The increase in ionic conductivity and in the electrochemical stability window reflected the enhanced segmental motion of the polymeric chain and the flexibility of blend polymer with the addition of P(DMS-*co*-EO). Thus, blends consisting of P(DMS-*co*-EO)/P(EPI-*co*-EO) can be used as solid state polymeric electrolytes. The addition of lithium salt to the P(DMS-EO)/P(EPI-EO) 15/85 blend reduced the

tensile strength and elongation at break, but increased Young's modulus. These mechanical properties were indicative of an incompatible system. Morphological analysis revealed that the blends showed phase separation of P(DMS-*co*-EO) and P(EPI-*co*-EO) and that LiClO<sub>4</sub> made the blends more susceptible to fissures.

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