

# Thermal, Thermomechanical, and Electrochemical Characterization of the Organic–Inorganic Hybrids Poly(ethylene oxide) (PEO)–Silica and PEO–Silica–LiClO<sub>4</sub>

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**ABSTRACT:** To study the effect of the silica content on the properties of the salt-free and salt-added hybrids based on poly(ethylene oxide) (PEO) and silica, two series of hybrids, PEO–silica and PEO–silica–LiClO<sub>4</sub> (O:Li, 9:1) hybrids were prepared via the *in situ* acid-catalyzed sol–gel reactions of the precursors [i.e., PEO functionalized with triethoxysilane and tetraethyl orthosilicate (TEOS)]. The morphology of the hybrids was examined by scanning electron microscopy (SEM) of the fracture surfaces of the hybrid. The results indicated that the discontinuity develops with increasing the weight percent of silica in both hybrids. The differential scanning calorimetric (DSC) analysis indicated that effects of silica content on the glass transition temperatures ( $T_g$ ) of the PEO phase were different in salt-free and salt-added hybrids. The  $T_g$  of PEO phase increased with increasing weight percent of silica in salt-free hybrids, whereas the curve of  $T_g$  of PEO phase and silica content had a maximum at 35 wt % of silica content in salt-added hybrids. For both salt-free and salt-added hybrids, peaks of the loss tangent, determined by dynamic mechanical analysis (DMA) were gradually broadened and lowered with increasing weight percent of silica. The storage modulus,  $E'$ , in the region above  $T_g$  increases with increasing silica content for both PEO–silica and PEO–silica–LiClO<sub>4</sub> hybrids. In the conductivity and composition curves for PEO–silica–LiClO<sub>4</sub> hybrids, the conductivity shows a maximum value of  $3.7 \times 10^{-6}$  S/cm, corresponding to the sample with a 35 wt % of silica. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2471–2479, 2001

**Key words:** organic–inorganic hybrid; poly(ethylene oxide); glass transition temperature; dynamic mechanical properties; ionic conductivity

## INTRODUCTION

Solvent-free polymer electrolytes are currently under intense scrutiny for use in high-energy density batteries and other electrochemical devices.<sup>1,2</sup> Poly(ethylene oxide) (PEO) is the most interesting base material for hosting lithium salts be-

cause it contains ether coordination sites, which assist the dissociation of salts incorporated in the polymer, as well as a flexible macromolecular structure, which promotes facile ionic transport.<sup>1,2</sup> The conductivity at room temperature in pure PEO, however, is limited by partial crystallization,<sup>3,4</sup> and various attempts were undertaken to achieve a more amorphous and plasticized material. Among these attempts, the addition of inorganic filler to polymer electrolytes has been extensively studied because it is useful to

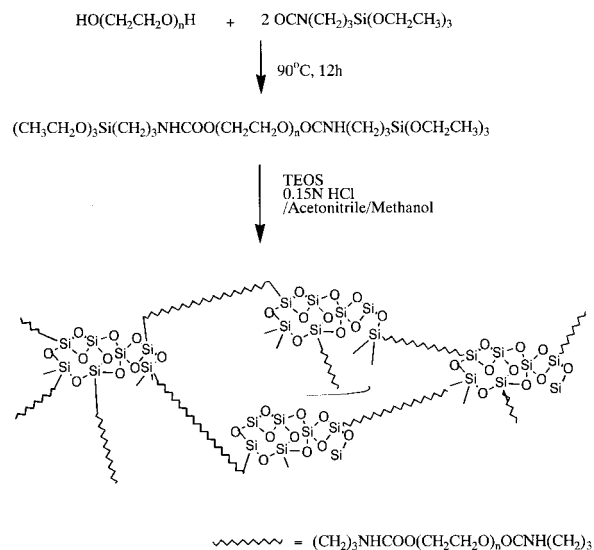
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improve mechanical properties and thermal and electrochemical stability in addition to enhancing ionic conductivity.<sup>5–15</sup>

Organic–inorganic hybrids or nanocomposite systems are constituted of organic (polymer) and inorganic (silica) phases mixed at the nanometric scale and possess a very high surface-to-volume ratio, leading to materials with new properties, such as transparency and high mechanical strength.<sup>16–21</sup> The sol–gel method<sup>22</sup> has been demonstrated as a practical method for the production of a hybrid of organic and inorganic materials.<sup>23</sup> An application of this process to the synthesis of a solid polymer electrolyte (SPE) has been reported by Ravaine et al.<sup>18</sup> the sol–gel condensation of tetraethoxysilane in the presence of PEO gives a polyether–polysiloxane hybrid, which has been recognized as an excellent matrix of SPE.<sup>24</sup> Fujita et al.<sup>25</sup> reported hybrid polymer electrolyte based on the PEO–silica consisting of interconnected inorganic oxide and organic components through covalent bonds. Bonagamba et al.<sup>26</sup> reported the nuclear magnetic resonance (NMR) study of ion-conducting organic–inorganic nanocomposite PEO–silica–LiClO<sub>4</sub>. Influence of the synthetic conditions for the silica–poly(ethylene glycol) (PEG) hybrids has been studied by Lesort et al.<sup>27</sup> The influence of the composition of hybrids on the thermal and thermomechanical characteristics of the PEO–silica hybrids, which well reflect the change of the polymer chain environment in hybrids and are closely related to the conductivity of the polymer electrolytes, has rarely been studied.

The aim of the present work is the investigation of the influence of the silica content on the thermal and thermomechanical properties of the salt-free and the salt-added PEO–silica hybrids consisting of interconnected inorganic oxide and organic components through covalent bonds. The influence of silica content on the conducting properties and the morphology of the polymer electrolyte based on the PEO–silica–LiClO<sub>4</sub> hybrid is also studied. Salt-free and salt-added PEO–silica hybrids were prepared by the acid-catalyzed sol–gel process of the PEO functionalized with trialkoxysilane moieties to facilitate cross-linking between the polymer and the growing inorganic oxide network and tetraethoxysilane (TEOS). The thermal, dynamic mechanical, and ion conductive properties were determined as a function of the weight percent of silica by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and AC impedance method in both salt-



**Scheme 1**

free and salt-added PEO–silica hybrids, respectively. Scanning electron microscopy (SEM) was also employed to study the freeze-fracture surfaces of various hybrid materials.

## EXPERIMENTAL

### Materials

All chemical reagents are commercially available and were used without further purification. The series of PEO–silica hybrids were prepared by a sol–gel process of the PEO functionalized with triethoxysilane and TEOS catalyzed with 0.15 N HCl in acetonitrile/methanol solution, as shown in Scheme 1. The series of salt-added hybrids, PEO–silica–LiClO<sub>4</sub>, were prepared in the acetonitrile/methanol solution containing lithium perchlorate (LiClO<sub>4</sub>, Aldrich, 95%) under the same conditions with PEO–silica hybrids. Hybrid precursor (OEt)<sub>3</sub>Si–NHCOO–PEG–OOCHN–Si(OEt)<sub>3</sub>, PEO functionalized with triethoxysilane, was prepared by the urethane reaction of 0.5 mol of PEO diol (PEG 2000, Shinyo Pure Chemicals Company, Ltd.) having a number average molecular weight of 2000 and 1 mol of  $\gamma$ -isocyanatopropyl triethoxysilane ( $\gamma$ -IPTEOS, Aldrich, 95%) for 12 h at 90  $\pm$  3 °C. Fourier transform infrared (FTIR) spectra of the product showed no absorption band at 2270 cm<sup>–1</sup> assignable to –NCO groups. This precursor was dissolved in acetonitrile in 10% solution and mixed with TEOS and methanol. Finally, 0.15 N HCl in water was added

**Table I** Characteristics of the Salt-Free PEO/Silica and Salt-Added PEO/Silica/LiClO<sub>4</sub> Hybrids

PEO/Silica Hybrids			PEO/Silica/LiClO <sub>4</sub> [9:1 (O:Li)]		
Sample Abbreviation	SiO <sub>2</sub> (wt %)		Sample Abbreviation	SiO <sub>2</sub> (wt %)	
	Nominal	TGA <sup>a</sup>		Nominal	TGA <sup>b</sup>
P20/Si05	5	5	P20/Si10/Li	10	7
P20/Si15	15	14	P20/Si15/Li	15	12
P20/Si25	25	23	P20/Si25/Li	25	22
P20/Si35	35	32	P20/Si35/Li	35	31
P20/Si45	45	42	P20/Si45/Li	45	40
P20/Si55	55	46	P20/Si55/Li	55	47

<sup>a</sup> Weight percent residue > 900°C in air.

<sup>b</sup> Weight percent residue > 900°C in air - salt percent/(100 - salt) × 100.

under vigorous stirring. The sol-gel solution was poured onto a Teflon plate and then cured and slowly dried for 24 h at 60 °C. These films were further dried for 24 h at 90 °C in a vacuum oven. Silica content was adjusted by controlling the added amount of the TEOS. The existence of covalent chemical bonds between the silica network and the polymer chains has been reported for similar materials.<sup>18,20,28</sup> These networks are designated as P20/SiX or P20/SiX/Li, where is the X represents the mass percent of the silica in the hybrids. In the PEO-silica-LiClO<sub>4</sub> hybrid networks, the salt content was maintained as the [EO]/[Li<sup>+</sup>] = 9 mol ratio and the weight percent of silica was represented in view of the PEO and silica composition except the amount of LiClO<sub>4</sub>. All the samples being studied are listed in Table I.

### Measurements

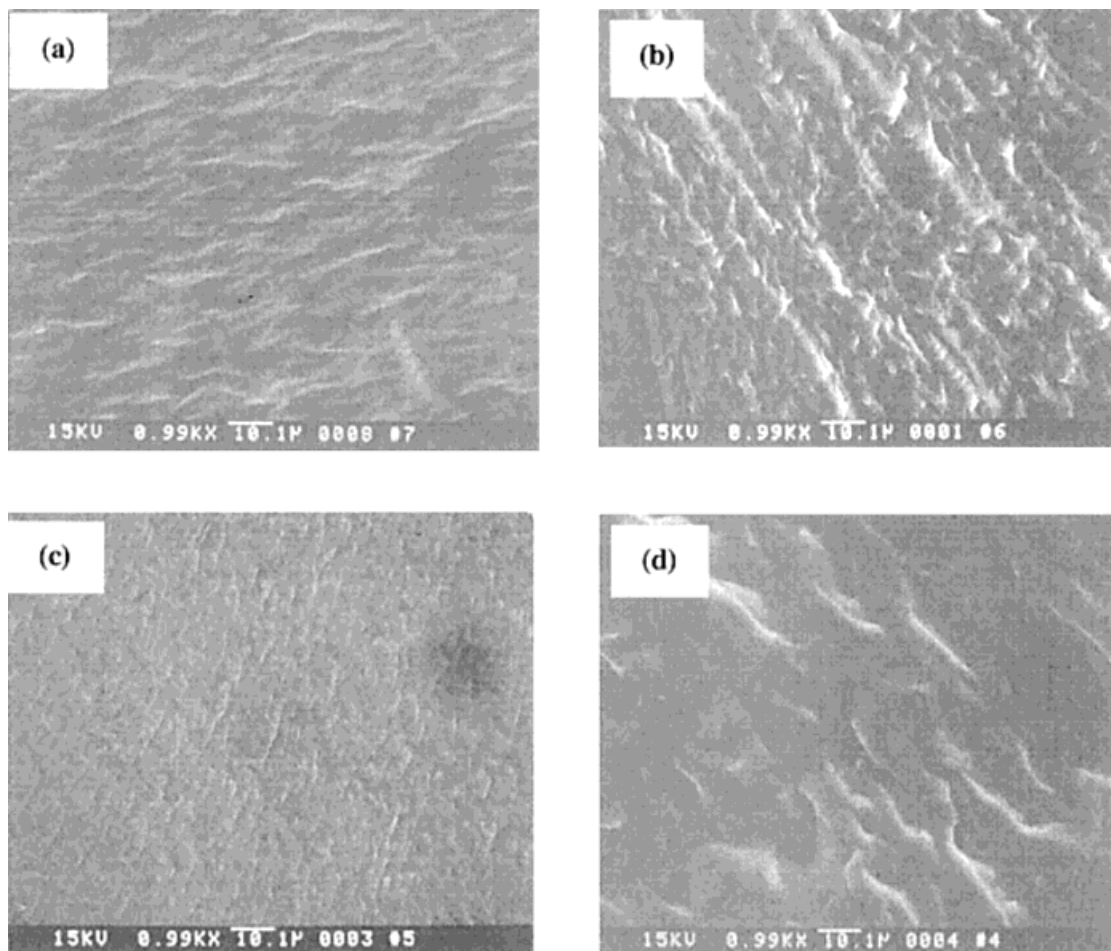
Secondary electron images of the hybrids were obtained in AKASHI WB-6 scanning electron microscope. The samples were fractured in liquid nitrogen and coated with gold by sputtering. DSC (DSC2010, TA instrument) was carried out with annealing at 65 °C for 15 min, slow cooling to -100 °C, and then scanning to 200 °C with a heating rate of 10 °C/min in nitrogen. The glass transition temperatures ( $T_g$ ) were determined as the midpoint of the phase transition temperature region in the DSC thermograms. Dynamic mechanical measurements were performed with a dynamic mechanical analyzer (DMA 2980, TA instrument) operating in the film tension mode, the temperature range of -100-100 °C, with a heating rate of 2 °C/min at constant frequency of 5 Hz. Ionic conductivities of the films of salt-added hy-

brids were measured by the AC impedance method using an HP4194 impedance/gain phase analyzer coupled to an IBM PC. Stainless steel was used as blocking electrodes in both sides. All the samples are equilibrated at the experimental temperatures for 10 min. The ionic conductivity was determined from complex impedance diagram in the frequency range 10<sup>2</sup>-10<sup>6</sup> Hz and the temperature range 25-85 °C.

## RESULTS AND DISCUSSION

### Morphology

SEM was employed to study the fracture surfaces of various hybrid materials. In two series of hybrids, SEM provided no signs of phase separation within the limits of the instrument resolution. The morphology of several hybrids observed by SEM are shown in Figure 1: (a) P20/Si20/Li; (b) P20/Si35/Li, (c) P20/Si50/Li, and (d) P20/Si35. Although discontinuity develops with increasing the weight percent of silica in hybrids, any distinct signs of domain structure that may have arisen from the presence of a pure or rich silicate phase was not observed in either salt-free and salt-added hybrids. These data provide evidence for good dispersion of the PEO components within the three-dimensional TEOS self-condensation network, although they certainly do not rule out the possibility of some smaller scale microphase formation. In heterogeneous polymer-silica hybrids prepared by the *in situ* sol-gel process (e.g., the PMMA-silicate systems), separated spherical domains indicating existence of the phase separation were observed.<sup>29</sup> It can be suggested from the



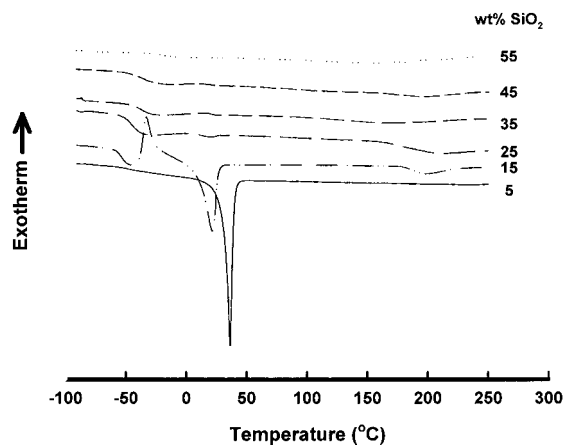
**Figure 1** Scanning electron micrograph of fractured surface of hybrids: (a) P20/Si20/Li, (b) P20/Si35/Li, (c) P20/Si50/Li, and (d) P20/Si35.

good transparency and morphology observed by SEM of the obtained films that homogeneous blending between the PEO and a hydroxylated  $\text{SiO}_2$  network in hybrids under studied was accomplished. The existence of discontinuous boundary developed with increasing weight percent of silica disturbs the ion migration for conduction and thus contributes the decrease of the conductivity in the higher silica concentration.<sup>1</sup>

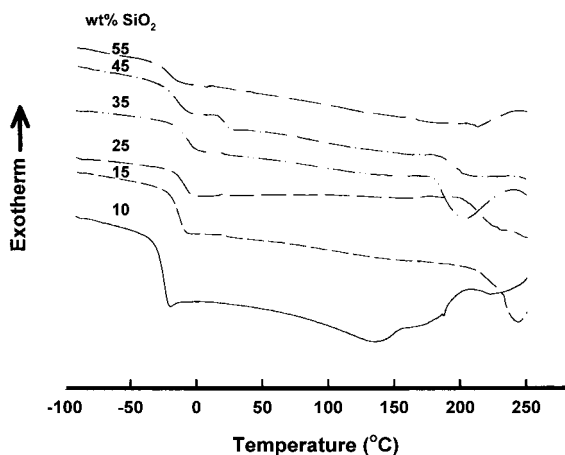
### Thermal Properties

The DSC curves of two series of hybrids, PEO-silica and PEO-silica- $\text{LiClO}_4$ , are shown in Figures 2 and 3, respectively. It can be seen from the DSC measurements that the behavior of the PEO phase is strongly influenced by the silica content in the hybrid materials.

In DSC thermograms for the PEO-silica hybrids, an endothermic peak corresponding to



**Figure 2** DSC heating scans for salt-free hybrids, PEO-silica.

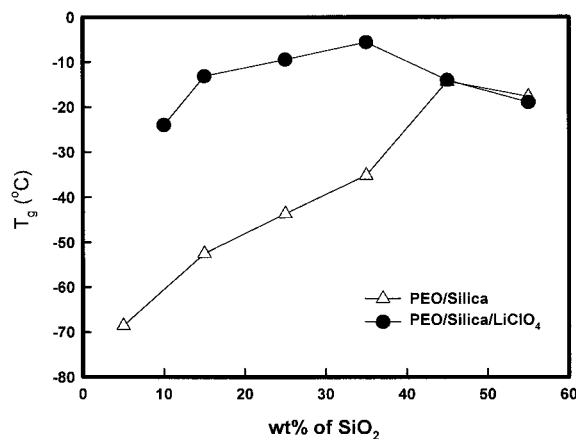


**Figure 3** DSC heating scans for salt-added hybrids, PEO-silica-LiClO<sub>4</sub>.

melting of PEO phase appears in the 5 and 15 wt % silica content cases and is not observed in the case of the 25 wt % and the higher silica content. This result suggests that the incorporation of the silica effectively suppresses the crystallization of the PEO chain and that the threshold weight percent of silica for the complete suppression of the crystallization of PEO is in the range 15–25 wt % for hybrids under study. The melting of PEO phases observed in PEO-silica samples containing 5 and 15 wt % SiO<sub>2</sub> is at ~35 °C, whereas for pure PEO, the melting peak generally appears at ~60 °C, and the crystallinity of PEO reduces from 0.86 for pure PEO to ~0.4 for PEO-silica samples containing 5 wt % SiO<sub>2</sub>. These drastic changes in  $T_m$  and crystallinity are due to the junction point and silica network disturbing the crystalline formation and acting as a defect in the crystalline form. The increase of the content of SiO<sub>2</sub> in PEO-silica samples enhances this effect and results in the disappearance of the crystalline phase in high weight percent SiO<sub>2</sub> hybrids. The  $T_g$  of the PEO phase is shifted to higher temperature and broadened with the increasing silica content. The influence of the silica content on  $T_g$  can be seen more clearly in Figure 4, which shows the  $T_g$  variations from DSC as a function of silica weight percent in the hybrids for PEO-silica and PEO-silica-LiClO<sub>4</sub>. It can be seen from Figure 4 that the  $T_g$  of the PEO phase linearly increases with the silica content in hybrids. These effects are due to the increase in rigidity of the PEO chains as the number and the strength of the silica-polymer interaction increase. This phenomenon can be related to the increase in the growth of the silica surface

by increasing the silica content in these materials. The broadening of the glass transition range indicates a large distribution of the relaxation time of the PEG inside the silica structure that is due to the increase of interaction between the PEO and silica with increasing silica content in hybrids.

In DSC scans of PEO-silica-LiClO<sub>4</sub> hybrids, a low-temperature endothermic peak corresponding to melting of the PEO phase is no longer detectable but a high-temperature endothermic peak presumably corresponding to melting of PEO-salt complex is observed at ~200–250 °C, as shown in Figure 3. It was difficult to obtain PEO-silica-LiClO<sub>4</sub> samples containing 5 wt % SiO<sub>2</sub> with reproducible properties, as in the case of the PEO-silica hybrids. The weight percent of SiO<sub>2</sub> means the relative quantity to the PEO content. Therefore, the precursor concentration for sol-gel reaction in the reaction mixture for the PEO-silica-LiClO<sub>4</sub> system is relatively low compared with the case of the PEO-silica system. This would be the cause the inappropriate reaction conditions for the sol-gel reaction in the reaction mixture for PEO-silica-LiClO<sub>4</sub> system. So, we start from 10 wt % SiO<sub>2</sub> in PEO-silica-LiClO<sub>4</sub> system. In salt-added hybrids with low silica content, disappearance of a low temperature endothermic peak contrasting with salt-free hybrids is due to an additional restriction caused by dipole interaction of oxygen from the ether and the Li cation. The influence of the silica content on  $T_g$  of PEO phase in salt-added hybrids was more clearly represented in Figure 4. Below the 45 wt % concentration of silica in hybrids, the  $T_g$  of the PEO phase in the salt-added hybrids is higher

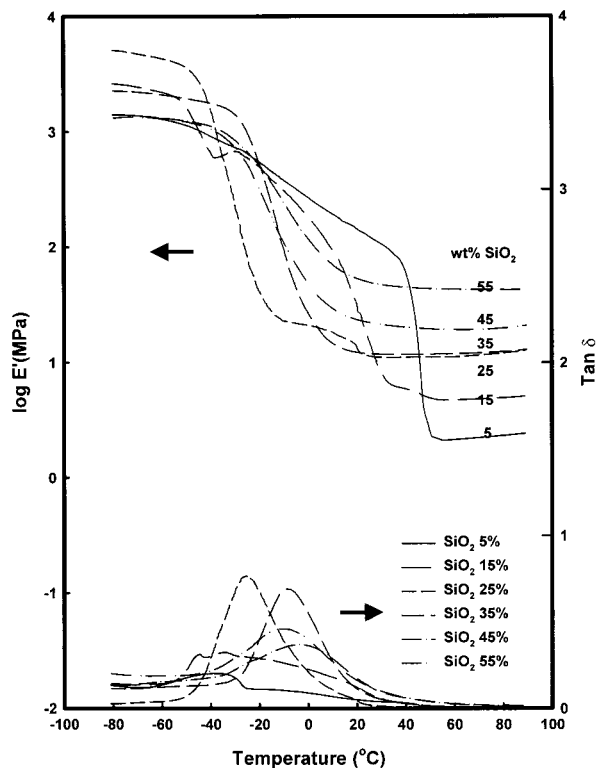


**Figure 4** Variations in  $T_g$  as a function of the silica content for the hybrids.

than that of the salt-free hybrids. An increase in the  $T_g$  in the salt-added polyether system is a commonly observed property that is due to the dipole cation interactions between polyether segments and dissociated ions (i.e., lithium ions).<sup>30</sup> Cation–dipole interaction is due to ionic bonding and may act as the transient crosslinks point in the polymer electrolytes. This interaction considerably reduces the segmental mobility of polyether and results in the increase of  $T_g$ . In salt-added hybrids, the  $T_g$  variation behavior as a function of silica weight percent is different from that of the salt-free hybrids, as shown in Figure 4. The  $T_g$  of the salt-added PEO–silica hybrids was not largely influenced by silica content like in the salt-free PEO–silica hybrids. Between 35 wt % and the lower weight percent of silica, the  $T_g$  of the PEO phase increased with increasing the weight percent of silica; however, this increase in  $T_g$  with increasing silica content is less than that of the salt-free hybrids. Furthermore, the  $T_g$  and composition curves of the salt-added hybrids reach a maximum at 35 wt % silica, and the  $T_g$  decreases when the silicate network increases above the 35 wt % silicate content. These observations suggest the existence of a decreasing factor for  $T_g$  of the PEO phase. In salt-added hybrids, the increasing factor of the  $T_g$  of the PEO phase followed by an increase in the silica network is the increase of the interaction between the PEO chain and silicate network, like the case of salt-free hybrids. Considering the restriction for the PEO chain imposed by the PEO–Li cation interaction and the PEO–silicate interaction in salt-added hybrids, the decrease of  $T_g$  with increasing silicate content could be due to one of the following reasons: (a) decrease in the amount or strength of interaction between the PEO chain and the silicate networks with increasing weight percent of silica or (b) decrease of the interaction between  $\text{Li}^+$  and PEO with increasing silicate networks in hybrids. Considering the fact that the  $T_g$  of the PEO phase in the salt-added hybrids containing 45 and 55 wt % of silica is similar to that of the salt-free hybrids and the added salt-effect on  $T_g$  is observed in those hybrids, the second reason could be true.

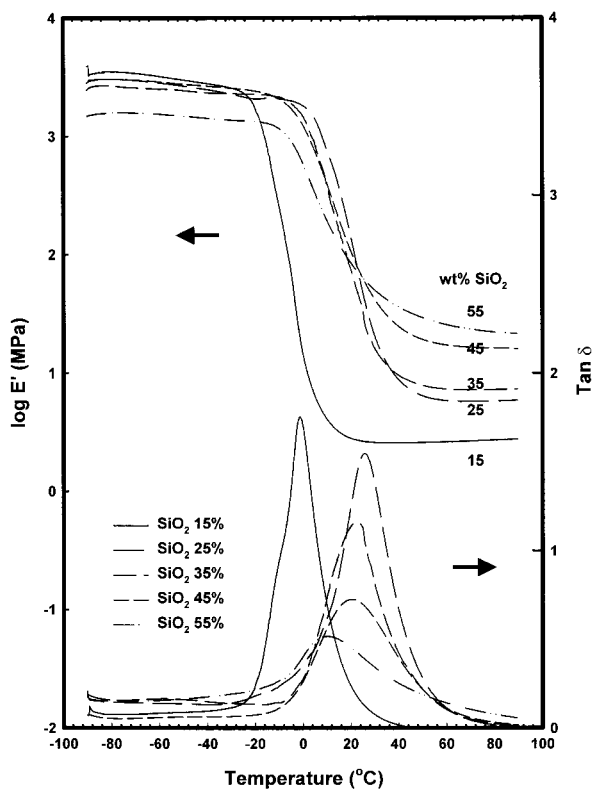
### Dynamic Mechanical Properties

The storage modulus ( $E'$ ) and  $\tan \delta$  variations with temperature for salt-free PEO–silica and salt-added PEO–silica– $\text{LiClO}_4$  hybrids are shown in Figures 5 and 6, respectively. The storage mod-



**Figure 5** Dynamic mechanical spectra (i.e., storage modulus and  $\tan \delta$  versus temperature) of PEO–silica hybrids at 5 Hz.

ulus,  $E'$ , of the hybrids in the region above  $T_g$  increases with increasing silica content for both PEO–silica and PEO–silica– $\text{LiClO}_4$  hybrids. The variation tendency of  $T_g$  from the loss tangent according to the silica content in the hybrids is in good agreement with the DSC analysis in which the  $T_g$  increases with increasing salt-free hybrids but has a maximum in salt-added hybrids. The widening of the loss tangent peak is due to increasing interactions of the PEO chain and silica. The widening of the loss tangent peak from DMA analysis (Figures 5 and 6) with increasing silica content is observed for both hybrids, with the exception of the salt-free PEO–silica hybrids with 5 and 15 wt % silica with a crystalline phase, as deduced from the DSC curves. This result suggests that the amount of interaction between the PEO and silicate increases with increasing the silicate content in both hybrids. From this result we can exclude the decreasing of the  $T_g$  of the PEO phase in salt-added PEO–silica hybrids from the decrease in the amount or strength of interaction between the PEO chain and silica network in higher mass percent of silica. This exclusion supports the suggestion from DSC analysis that



**Figure 6** Dynamic mechanical spectra (i.e., storage modulus and  $\tan \delta$  versus temperature) of PEO-silica-LiClO<sub>4</sub> hybrids at 5 Hz.

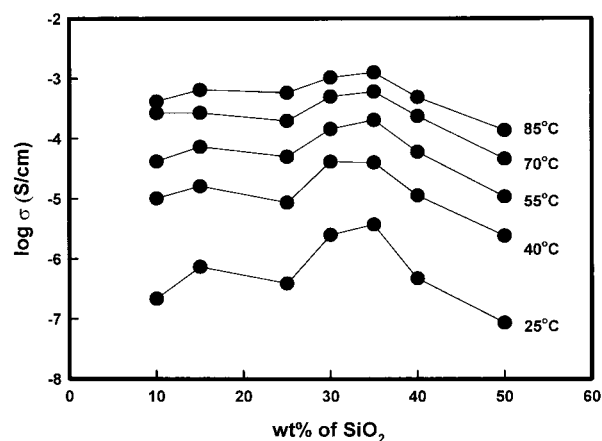
the decreasing factor of the  $T_g$  of the PEO phase in salt-added PEO-silica hybrids could be due to a decrease of the interaction between Li<sup>+</sup> and PEO with increasing silicate networks in hybrids.

### Conductive Properties

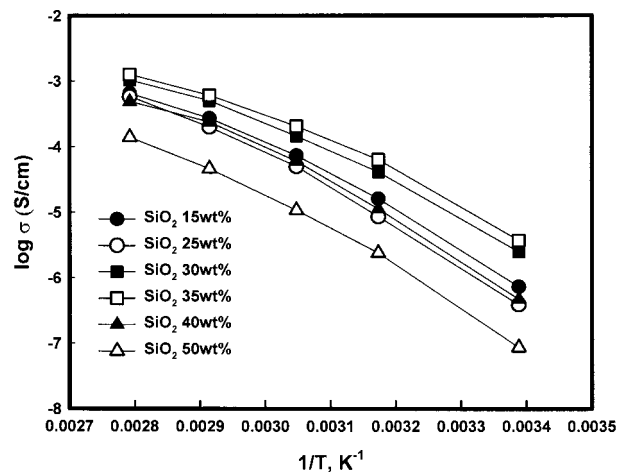
The dependence of ionic conductivity on the silica content at various temperatures for PEO-silica-LiClO<sub>4</sub> hybrids is shown in Figure 7. The conductivity shows a maximum value of  $3.7 \times 10^{-6}$  s/cm corresponding to the sample with a 35 wt % of silica for the PEO-silica-LiClO<sub>4</sub> system. The results obtained are similar to those of earlier studies on composite electrolytes.<sup>31-33</sup> The increase in conductivity is generally explained<sup>34-36</sup> to be due either to the formation of a new kinetic path via a thin interphase layer along the interface itself, or to a concentration enhancement caused by space charges in the sub-interface region that has been found to depend on the concentration and particle size of the inert phase matrix.<sup>32-34</sup> It has been shown that mechanical and electrochemical properties of electrolytes increase with decreasing the

size of ceramic particles used and the increase of conductivity is connected with the processes occurring on the grain boundaries.<sup>37</sup>

In the conductivity and composition curves, the existence of the maximum suggest that two factors, one causing an increase in conductivity and the other causing a decrease in conductivity, are competitive. The apparent behavior of the dependence of conductivity on the amount of added filler would reflect the result of the competition of two factors. The increase of the conductivity with the increase of the silica content by 30–35 wt % suggests that the interfacial region is more conductive than the bulk solution increase with the increase of the silica content and the silicate in the PEO-silica hybrid has effective surface properties for conductivity. The increase in the amount of the interaction between the particulate silica and PEO chain was confirmed by the variation of the  $T_g$  and loss tangent behaviors as a function of the silica content. In the higher weight percent region of the silica, the decrease of the ionic conductivity occurs and this may be caused by the decrease of effective ions and the increase of hindrance of ion conduction by silica particle and the discontinuity of hybrids. The temperature dependence of conductivity of the hybrid electrolytes consisting of the LiClO<sub>4</sub> and PEO-silica-hybrid (1:9, Li:O) is shown in Figure 8. It can be seen from Figure 8 that conductivity increased with increasing temperature for both hybrids. This result is generally observed in polymer electrolytes.



**Figure 7** Variations of the ionic conductivity as a function of the silica content of PEO-silica-LiClO<sub>4</sub> hybrids (9:1, O:Li).



**Figure 8** Conductivity temperature dependence of PEO-silica-LiClO<sub>4</sub> hybrids (9:1, O:Li).

## CONCLUSIONS

In both PEO-silica and PEO-silica-LiClO<sub>4</sub> hybrids prepared by the acid-catalyzed sol-gel reaction and consisting of interconnected inorganic oxide and organic components through covalent bonds, the detectable phase separation did not occur in high silica content (55 wt %) according to SEM analysis. Increase of silica content, however, resulted in development of discontinuity of the microstructure, as shown by SEM analysis. This result may be due to shrinkage that is due to a condensation process in the sol-gel reaction.<sup>38</sup> DSC measurements gave further information about the homogeneous blend. In the two series of hybrids, the behavior of the PEO phase measured by DSC and DMA is strongly influenced by the silica content. DSC curves of heterogeneously blended PEO-silica hybrids show an endothermic peak corresponding to melting even though in high salt concentration the  $T_g$  of the PEO phase is rarely influenced by the existence of silica.<sup>27</sup> The variation behaviors of the  $T_g$  of the PEO phase as a function of silica content was different in salt-free PEO-silica and salt-added PEO-silica-LiClO<sub>4</sub> hybrids. In salt-free PEO-silica hybrids,  $T_g$  increased and broadened with the increase of the silica content. In salt-added PEO-silica-LiClO<sub>4</sub> hybrids, however, the  $T_g$  and composition curve reaches a maximum at 35 wt % of silica content. This result indicates the existence of decreasing factors for the  $T_g$  of the PEO chain resulting from the increase of the silica content in the case of salt-added hybrids. The interactions of the PEO and silica increase with increasing the silica con-

tent in both series of salt-free hybrids and salt-added hybrids, which was suggested by the observation that the width of the peak of loss tangent from DMA increased with the increase of the silica content. The  $E'$  of the hybrids in the region  $>T_g$  increases with increasing silica content for both PEO-silica and PEO-silica-LiClO<sub>4</sub> hybrids. The effect of silica content on  $T_g$  behavior and the loss tangent suggests that the decrease of  $T_g$  of the PEO chain with increasing weight percent of silica is caused by the decrease of the interaction between Li<sup>+</sup> and PEO with increasing weight percent of silica in salt-added hybrids. In the conductivity and composition curves, the conductivity shows a maximum value of  $3.7 \times 10^{-6}$  s/cm, corresponding to the sample with a 35 weight ratio of SiO<sub>2</sub> for the PEO-based silica networks-LiClO<sub>4</sub> system.

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