

# Effects of ceramic fillers on the electrical properties of $(\text{PEO})_{16}\text{LiClO}_4$ electrolytes

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## Abstract

Conductivity and thermal properties on  $(\text{PEO})_{16}\text{LiClO}_4$  complexes mixed with various inert fillers have been studied. Among 22 fillers studied, a composite material with truly exceptional conductivity has not been found. As the inert particles are added, the glass-transition temperature decreases indicating higher flexibility of PEO chain; at the same time the heat of melting increases indicating higher crystallinity of polymer network, which reveals that the ceramic particles act as nucleation centers. The polymer–ceramic grain boundaries are found not to contribute appreciably to ionic conduction. © 1997 Elsevier Science S.A.

*Keywords:* Polymer composite electrolytes; Poly(ethylene oxide); Inorganic fillers

## 1. Introduction

Polymer–ceramic composite electrolytes have recently attracted considerable attention due to their improved mechanical stabilities and enhanced ionic conductivities [1–8]. On the other hand, there are many contrasting reports, in which the fillers of similar types have a negligible or reducing effect on the conductivity [9–14]. It is often ambiguous to compare the reported results since the conductivity is sensitive to many factors such as the salt species and its concentration, particle size, temperature, thermal history, and preparative methods. To examine the effects of various fillers, one needs to measure various physical properties by carefully maintaining the same experimental conditions.

In this work, we present the experimental results for  $(\text{PEO})_{16}\text{LiClO}_4$  complexes modified by adding various ceramic powders such as aluminum nitride (10  $\mu\text{m}$ ), aluminum oxide (0.037 and 0.05  $\mu\text{m}$ ), barium titanate (2  $\mu\text{m}$ ), boron carbide (5  $\mu\text{m}$ ), boron nitride (1  $\mu\text{m}$ ), calcium silicate (25  $\mu\text{m}$ ), fumed silica (0.007 and 0.014  $\mu\text{m}$ ), iron oxide (0.023 and 1  $\mu\text{m}$ ), lead titanate (5  $\mu\text{m}$ ), molybdenum sulfide (2  $\mu\text{m}$ ), silicon carbide (1 and 13  $\mu\text{m}$ ), silicon nitride (1  $\mu\text{m}$ ), titanium boride (10  $\mu\text{m}$ ), titanium oxide (0.032 (Anatase), and 5  $\mu\text{m}$  (Rutile)), tungsten carbide (1  $\mu\text{m}$ ) and zirconium oxide (3  $\mu\text{m}$ ). We have compared 22 different species mixed with 10 wt.% of fillers by carefully maintaining

the same processing conditions. Measurements of impedance spectroscopy and differential scanning calorimetry (DSC) have been carried out.

## 2. Experimental

The complexes were prepared by dissolving predetermined amounts of poly(ethylene oxide) (Aldrich, mol. wt.  $2 \times 10^6$ ) and lithium perchlorate in acetonitrile. This solution was stirred at room temperature for approximately 24 h. A known amount of ceramic powders was then added and the solution was stirred continuously until the mixture appeared to be homogeneous. Films were cast on a Teflon plate by evaporating the solvent in an argon-filled glove box for 24 h and further dried under vacuum at room temperature for 24 h. Finally, the samples were dried under vacuum at 110 °C for a minimum of 48 h.

The complex impedances were determined by means of a HP model 4192A LF impedance analyzer. The complex impedance measured in the frequency range from 100 Hz to 1 MHz allowed us to obtain the direct current conductivity by means of the usual impedance analysis.

The thermal studies were performed by using a Shimadzu DSC. The sample chamber was purged with purified helium at all times. Each hermetically sealed sample was first cooled from room temperature to –120 °C using liquid nitrogen and then measurements were carried out at a heating rate of 10 °C/min from –110 to 200 °C.

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3. Results and discussion

Fig. 1 shows typical DSC traces of several polymer composites. It shows a glass transition at  $T_g$  at which a glassy phase becomes a rubbery amorphous phase on heating. All samples exhibit a relatively sharp endothermic peak at  $T_m$  near 60 °C, which could be attributed to the melting of a PEO-rich crystalline phase. For the composites filled with smaller particles, a broad and weak endotherm appears above  $T_m$  endotherm. It may be attributed to a formation of chemically distinct high-melting complexes due to a specific interaction between polymer complexes and ceramic particles, which is stronger for smaller particles due to their larger surface area.

Fig. 2 shows the melting temperature  $T_m$  of PEO for 22 different composites. It shows that  $T_m$  is mostly lowered when the ceramic particles are added. The lowering of  $T_m$  upon filler addition is quite general [2,6,14] and it has been attributed to the decrease of spherulite sizes [4]. Hence a lower  $T_m$  in the present work may be attributed to the appearance of smaller crystallites due to the presence of ceramic particles.

The area under the curve for the melting endotherm is related to the crystallinity in the specimens. Fig. 3 shows that the heat of melting ( $H_m$ ) increases when the ceramic particles are added. It reveals that the volume fraction of crystalline phase increases. This is opposite to the suggestions that the inert fillers enhance the formation of amorphous phase [3,4,8]. Recently, however, Kumar et al. [15] reported in their scanning electron microscopy (SEM) graphs that higher concentration of glass particles on the polymeric materials led to well-defined crystallite regions. The preference of crystalline phase in the present work may be possible if the filler grains act as nucleation centers of the crystalline polymer phase. Because ionic conduction takes place primarily

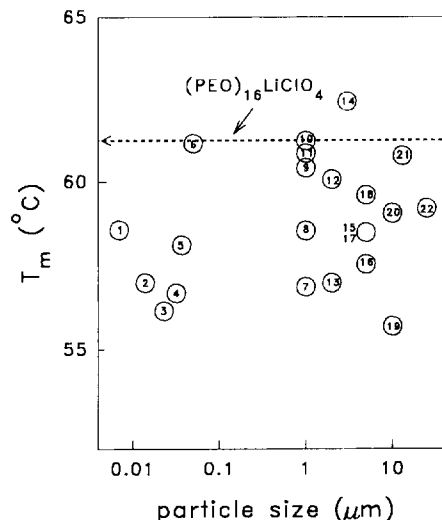


Fig. 2. Melting temperature ( $T_m$ ) of  $(\text{PEO})_{16}\text{LiClO}_4 + 10 \text{ wt \%}$  filler composites. Numbers indicate filler species: (1, 2)  $\text{SiO}_2$ , (3, 8)  $\text{Fe}_2\text{O}_3$ ; (4, 17, 18)  $\text{TiO}_2$ ; (5, 6)  $\text{Al}_2\text{O}_3$ ; (7) BN; (9, 21) SiC; (10)  $\text{Si}_3\text{N}_4$ ; (11) WC (12)  $\text{BaTiO}_3$ ; (13)  $\text{MoS}_2$ ; (14)  $\text{ZrO}_2$ , (15)  $\text{B}_4\text{C}$ ; (16)  $\text{PbTiO}_3$ ; (19) AlN; (20)  $\text{TiB}_2$ , and (22)  $\text{CaSiO}_3$ .

through the amorphous phase of the polymer, high crystallinity is conducive to low conductivity.

Fig. 4 shows  $T_g$  for 22 different composites. The glass transition involves the freezing of large-scale molecular motions without a change in structure. It shows that  $T_g$  is always lowered when the ceramic particles are added. As  $T_g$  lowers, the amorphous phase becomes more flexible and the ionic conductivity is enhanced at room temperature. As a result of more flexible amorphous environment entrapped in or adjacent to the crystalline matrix, the crystalline PEO inside the polymer–ceramic composites melts probably at lower temperature as shown in Fig. 2.

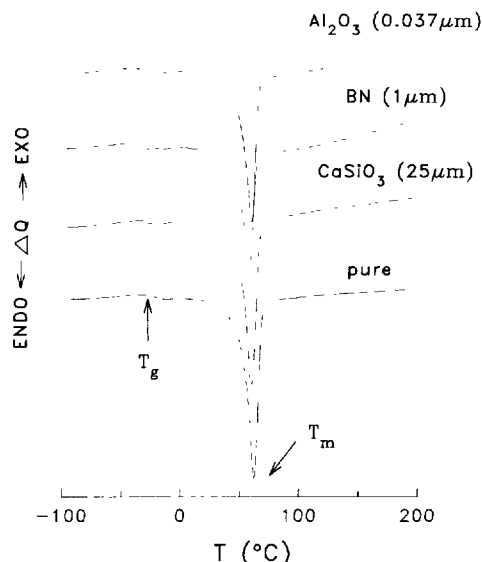


Fig. 1. Differential scanning calorimetric traces of  $(\text{PEO})_{16}\text{LiClO}_4$  complexed with 10 wt.%  $\text{Al}_2\text{O}_3$ , BN and  $\text{CaSiO}_3$  fillers, respectively.

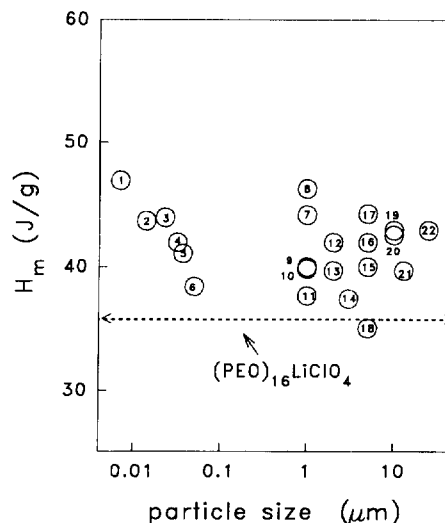


Fig. 3. Heat of melting ( $H_m$ ) of  $(\text{PEO})_{16}\text{LiClO}_4 + 10 \text{ wt \%}$  filler composites

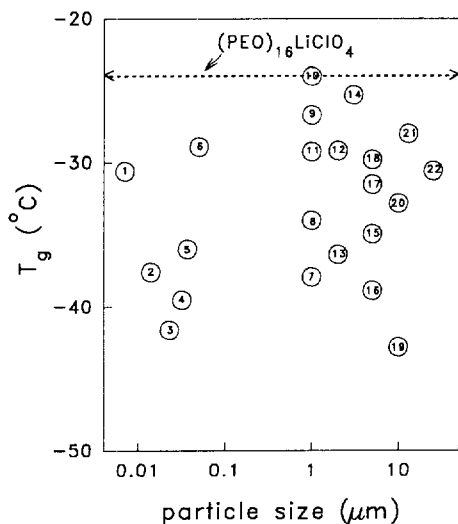


Fig. 4. Glass-transition temperature ( $T_g$ ) of  $(\text{PEO})_{16}\text{LiClO}_4 + 10$  wt.% filler composites

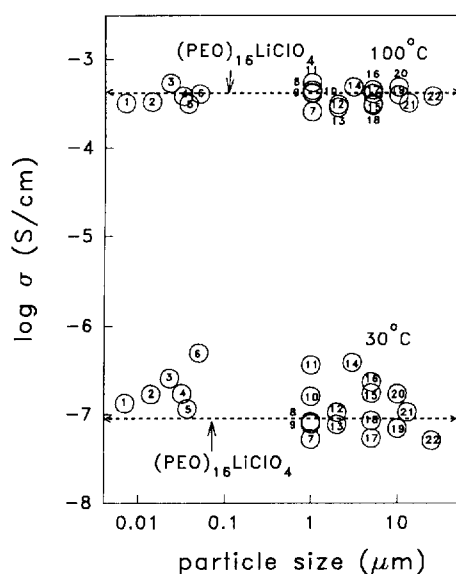


Fig. 5. Ionic conductivity at 30 and 100 °C for  $(\text{PEO})_{16}\text{LiClO}_4 + 10$  wt.% filler composites.

Fig. 5 shows the ionic conductivity of 22 different composites. At 30 °C, the electrical conductivity is slightly enhanced or reduced according to the filler species. At room temperature, there appear two competing effects for ionic conduction. The lowering of  $T_g$  means an increase in segmental motion of the polymer, hence conductivity enhancement. Whereas, the increase of  $H_m$  means an increase in the crystallinity, hence conductivity reduction. Due to these contrasting effects, which appear more or less according to the filler species, the conductivity may be enhanced or reduced at ambient temperature.

At 100 °C, where the polymer electrolytes are mostly amorphous, the ionic conductivity is nearly constant irrespective of big differences in particle sizes as well as in chemical species. It indicates that the interfaces between ceramic particles and polymer/salt electrolyte do not have a crucial importance for ionic conduction. It has been suggested that the formation of a new kinetic path via polymer–ceramic grain boundaries may be most important for ionic conduction [7,13,16]. Present results may rule out this conjecture since the conductivity at 100 °C does not increase considerably though the area of the polymer–ceramic interfaces increases greatly for the composites filled with smaller particles.

#### 4. Conclusions

Concerning to the conductivity enhancement due to the additives, there were two suggestions frequently quoted, that the inert fillers enhance the formation of the amorphous phase and the high conductivity path would extend along polymer–ceramic grain boundaries. Present results rule out these conjectures. From the thermal studies, we found that the ceramic particles act as nucleation centers, enhancing the crystallinity. From the conductivity measurements, we found that polymer–ceramic grain boundaries do not contribute appreciably to ionic conduction.

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