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SHORT COMMUNICATION

Effects of SiC and Si_3N_4 fillers on the electrical properties of $(PEO)_{16}LiClO_4$ electrolytes

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1.Introduction

Addition of fine inorganic fillers to polymer electrolytes leads to an improvement in mechanical properties and electrical conductivity [1–5]. In other composite polymer electrolytes, similar ceramic fillers have been found to have a negligible or small reducing effect on the conductivity [6–8].

The mechanism of conductivity enhancement or reduction can be attributed to various factors such as changes in the segmental motion of the host polymer chain, changes in the volume fraction of the amorphous phase, particle size effects, morphological changes and the polymer–ceramic interfaces. Most reported results are inconsistent with each other mainly because of the presence of many generic parameters which govern the transport of the polymer composite electrolytes.

In this work, the results for $(PEO)_{16}LiClO_4$ complexes modified by adding finely-grained SiC powders (1 and 13 μm) and Si_3N_4 powders (sub-μm) with 2, 5, 10, 15, 20, 30, 40, 50, 60 and 70 wt % are presented. Measurements using impedance spectroscopy and differential scanning calorimetry (DSC) have been carried out.

2.Experimental details

The complexes were prepared by dissolving predetermined amounts of PEO (Aldrich, MW 2×10^6) and lithium perchlorate in acetonitrile. This solution was stirred at room temperature for approximately 24 h. A known amount of SiC or Si_3N_4 powder 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 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 analyser. The complex impedance measured in the frequency range from 100 Hz to 1 MHz allowed the direct current conductivity to be obtained by means of the usual impedance analysis.

A Shimadzu differential scanning calorimeter was used to determine the glass transition temperature and the heat of melting of the electrolytes. 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^{-1} from −110 to 200 °C.

3.Results and discussion

Figure 1 shows typical DSC traces obtained in the heating cycle of $(PEO)_{16}LiClO_4$ complexes with varying weight per cent of SiC (1 μm) and Si_3N_4 contents. 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 may be attributed to the melting of PEO-rich crystalline phase. A broad and weak endothermic peak above T_m is shown in the samples with more than 40 wt % of SiC. The same is observed for the electrolytes filled with SiC(13 μm) powder, while the weak endotherm is nearly absent for the electrolytes with Si_3N_4 fillers. In various PEO-salt electrolytes, the high temperature endotherm is generally observed for higher salt ratio and has been attributed to the melting/dissolution of a stoichiometric crystalline complexes [9]. In the electrolytes with SiC fillers, it indicates a formation of

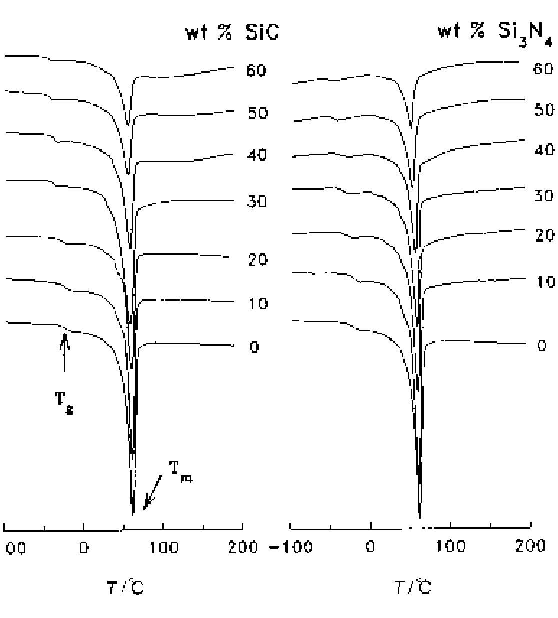

Fig. 1. DSC traces of $(PEO)_{16}LiClO_4$ complexes mixed with SiC and Si_3N_4 fillers.

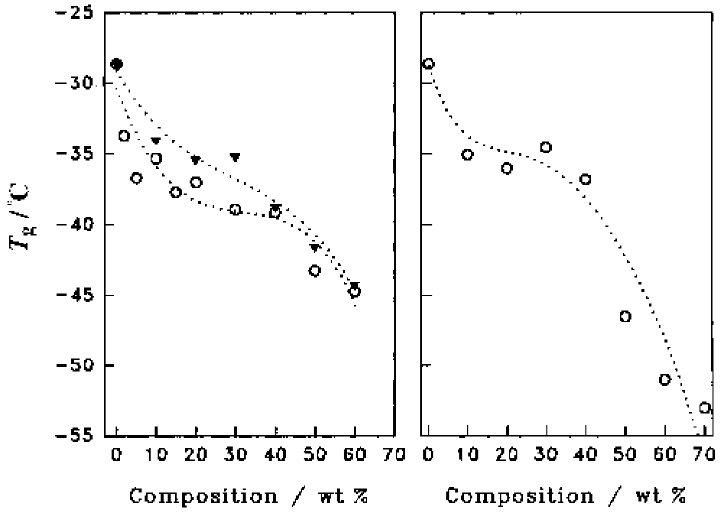

Fig. 2. Glass transition temperature against filler concentration of $(PEO)_{16}LiClO_4$ complexes. (a): (○) SiC, 1 μm; (▼) SiC, 13 μm; (b) (○) Si_3N_4.

a chemically distinct polymer-salt complexes due to a specific interaction between PEO and ceramic particles. The formation of a high-melting complex suggests an increase in the crystalline phase at a higher filler ratio.

Figure 2 shows the variation of glass transition temperature with varying contents of SiC and Si_3N_4 fillers. The T_g first decreases considerably and then reaches a plateau beyond which it drops further. The glass transition involves the freezing of large–scale molecular motion without a change in structure. The lower the value of T_g, the higher the mobility of the polymer segments in the amorphous phase. Present results show that flexibility of the polymer increases considerably with the addition of inorganic particles.

The area under the curve for the melting endotherm in DSC data is related to the crystallinity in the specimens. The heat of melting (H_m) normalized by the mass fraction of pure $(PEO)_{16}LiClO_4$ complexes, including the weak endotherm above T_m, is shown in Fig. 3. In the case of SiC fillers, the normalized H_m increases continuously for all wt %. In the case of Si_3N_4 fillers, it also increases as compared with that of pristine $(PEO)_{16}LiClO_4$ electrolyte, but is nearly constant above 10 wt %. This shows that the volume fraction of crystalline complex increases with filler addition, in contrast to suggestions that inert fillers enhance the formation of an amorphous phase [2, 5]. The preference of the crystalline phase may be possible if the filler grains act as nucleation centres of a crystalline polymer phase. It is considered that the nucleation effect is sufficient to overcome the crystallization hindrance due to the enhancement of the segmental motion of PEO.

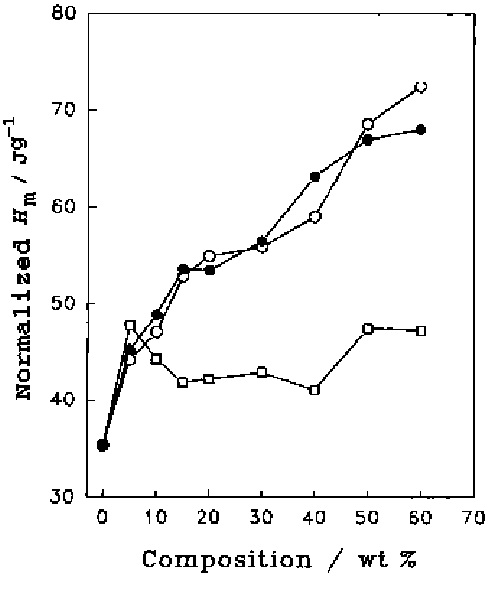

Fig. 3. Heat of melting normalized by the mass fraction of pure $(PEO)_{16}LiClO_4$ complexes against filler concentration. Key: (○) SiC, 1 μm; (●) SiC, 13 μm; (□) Si_3N_4.

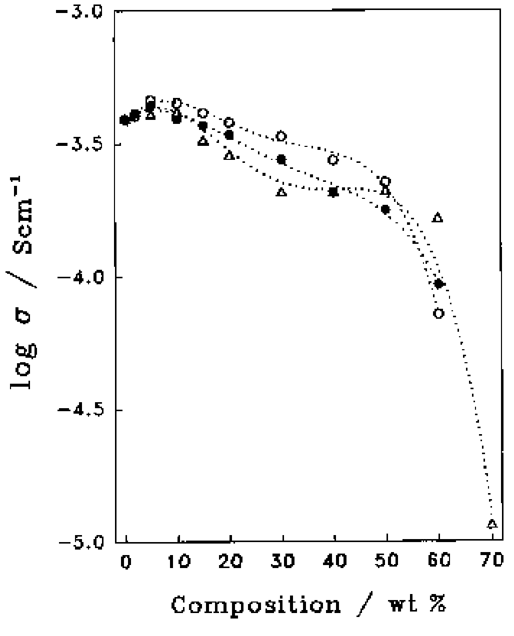

Fig. 4. Ionic conductivity at 100 °C against filler concentration of $(PEO)_{16}LiClO_4$ complexes. Key: (○) SiC, 1 μm; (●) SiC, 13 μm; (△) Si_3N_4.

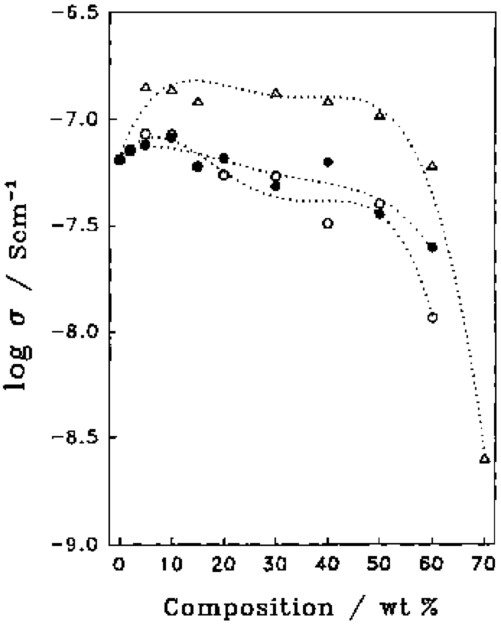

Fig. 5. Ionic conductivity at 30 °C against filler concentration of $(PEO)_{16}LiClO_4$ complexes. Key: (○) SiC, 1 μm; (●) SiC, 13 μm; (△) Si_3N_4.

The effect of SiC and Si_3N_4 additives on the conductivity at 100 °C is shown in Fig. 4. The best values for the ionic conductivity are found near 10 wt %. At 100 °C above T_m, only a small enhancement of conductivity is observed. Appreciable enhancement of conductivity is observed only for Si_3N_4 fillers at ambient temperature as shown in Fig. 5. This is because the particle size of Si_3N_4 powder is smaller than that of SiC. For higher filler contents, the conductivity decreases since the blocking effects become dominant. At very high contents additive of near 60 wt %, a threshold for ion migration occurs, possibly caused by a decrease in the ionic pathway due to the agglomeration of nonconducting dispersoids.

The enhancement of the conductivity in a polymer–ceramic composite electrolyte can be estimated at least by two factors, that is, changes in the proportion of amorphous phase and changes in the segmental motion of the polymer chains. In the case of SiC fillers, the decrease in T_g means an increase in segmental polymer motion, hence conductivity enhancement. However, the increase in the normalized H_m means an increase in the volume fraction of crystallinity, hence conductivity reduction. These two factors have a contrasting effect on the conductivity, this possibly accounts for the small enhancement in conductivity at ambient temperature.

In the case of Si_3N_4 fillers, the conductivity is significantly enhanced at ambient temperature as shown in Fig. 5. Since the crystallinity is nearly constant over all wt % of Si_3N_4 particles as shown in Fig. 3, the enhanced conductivity is related primarily to the enhancement of the polymer chain assisted motion of the conducting ion, which is signified by the decrease in T_g. Higher levels of filler concentration lead to detrimental effects on the conductivity, even though there is further enhancement of the segmental motion of PEO.

In several polymer electrolytes showing enhanced conductivity by adding SiO_2, amorphous Al_2O_3 or zeolite fillers, T_g is increased [2, 5, 10]. In several other systems showing enhanced conductivity adding lithium glass or β-Al_2O_3 fillers, the T_g is nearly constant [3]. For a few systems showing reduced conductivity by adding α-Al_2O_3 filler, the T_g is nearly constant [6] or lowered [11].

Recently it has been suggested that the structure and chemistry of the polymer–ceramic grain boundaries may have an even more important role than the formation of an amorphous phase in the electrolyte [4, 9, 12]. In polymer composite electrolytes, there are too many other factors simultaneously involved. More systematic work is needed before any general conclusions on the effect of inert fillers can be reached.

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