

A dielectric relaxation study of nanocomposite polymer electrolytes

Benson K. Money^{a,*}, K. Hariharan^b, J. Swenson^a

^a Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

^b Department of Physics, Indian Institute of Technology Madras, Chennai-600036, India

ARTICLE INFO

Article history:

Received 10 September 2011

Received in revised form 19 April 2012

Accepted 23 April 2012

Available online 14 May 2012

Keywords:

Polymer electrolytes

δ -Al₂O₃ nano-fillers

Ionic conductivity

Dielectric relaxations

VTF

ABSTRACT

(PEO)₄:LiClO₄ and the effect of δ -Al₂O₃ nano-fillers on the polymer electrolyte have been investigated by differential scanning calorimetry (DSC) and dielectric relaxation studies. The DSC studies indicated a decrease in the glass transition temperature of (PEO)₄:LiClO₄ in the presence of fillers. The polymer–salt complex exhibited a conductivity of $\sigma_{D.C.} = 4.0 \times 10^{-7} \text{ Scm}^{-1}$ at room temperature (298 K). In the presence of 4 wt% δ -Al₂O₃ fillers, the ionic conductivity increased by almost two orders of magnitude and exhibited a value of $\sigma_{D.C.} = 1.5 \times 10^{-5} \text{ Scm}^{-1}$ (298 K). By comparing the conductivity data with the calorimetric glass transition it is evident that the enhanced conductivity can be attributed to a speeding up of the segmental polymer dynamics. Hence, the combined data indicate a direct coupling between Li⁺ ion motions and polymer segmental dynamics, even when 4 wt% nano-fillers have been introduced. From the temperature dependence of the conductivity relaxation time, which, thus, is coupled to the structural (α) relaxation time, it is understood that the fragility of the polymer electrolytes decreases with increasing filler concentration. The decrease in T_g and fragility suggests that the interaction between the nano-fillers and polymer is mainly non-attractive in nature. Moreover, the dielectric relaxation studies show that the β -relaxation speeds up with increasing concentration of filler particles. However, this speeding up is probably of less importance for the ionic conductivity. It was also found that the activation energy of the β -relaxation of PEO decreases in the presence of δ -Al₂O₃ nano-fillers and lithium salt. The strength of the β -relaxation increases also in the presence of salt ions. The γ -relaxation seems to be unaffected by the salt and fillers.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Poly(ethylene oxide) (PEO) based solid polymer electrolytes (SPE) have received considerable attention for several decades for practical applications such as batteries, fuel cells, supercapacitors, hybrid power sources, sensors etc. However, at ambient temperature, PEO-based electrolytes exhibit very poor ionic conductivity due to their semi-crystalline nature. Most of the ion dynamics are believed to occur predominantly in the amorphous phase, where the transport properties (ionic conductivity, mechanical relaxations, diffusion, spin relaxation etc.) are directly associated with the large-scale segmental motion of the polymer. These SPE systems are considered to be coupled systems i.e. the ionic diffusion is a supported by structural relaxation processes as well as occurs by the migration of ions [1]. However, the semi-crystalline nature of PEO-based electrolytes hinders the ionic conductivity and hampers their performance for device-based applications.

Among various techniques employed in order to reduce crystallinity and enhance the transport properties, the addition of ultrafine inert fillers, like Al₂O₃, BaTiO₃, ZrO₂, MgO, CeO₂ etc. in polymer

electrolyte has attracted considerable research effort [2,3]. This new class of SPE, dispersed with nano- and sub-micron sized inert fillers, or composite polymer electrolytes (CPE), exhibits improved physical and chemical properties. Studies have shown that the size and the nature of the surface groups on the fillers have an important influence on the ionic conductivity and different mechanisms of interactions have been proposed [2,4–11]. The qualitative explanations have been given by considering (i) the interactions of Lewis acid–base type surface groups on alumina grains with ions and provide additional sites creating favourable high conducting pathways in the vicinity of grains for the migration of ions [2,4,8,9], (ii) the surface group of the fillers to attract (via hydrogen bonding) the ions, thus weakens the association between ion pairs and enhance the transference number [10,11] and (iii) the surface activity of the filler particles and the creation of static surface pathways for ionic motions by decoupling the diffusion of ions from the relaxation of the polymer chains [6,7]. The present study is mainly focused on the relaxation processes present in a PEO-based polymer–salt complex system and how the presence of nano-fillers affects these relaxation processes. Previous investigations have shown the presence of three main relaxations i.e. α , β and γ -relaxations in poly(ethylene oxide) (PEO) [12–14]. The α -relaxation is associated with the segmental motions of the polymer chains. The β -relaxation is attributed to the segmental polymer motions in the “interphase” between crystalline and amorphous segments, and is mainly affected by the crystallinity

* Corresponding author. Tel.: +46 76 4448540; fax: +46 31 772 2090.
E-mail address: moneyb@chalmers.se (B. K. Money).

content present in the polymer. The γ -relaxation peak may be associated with the local twisting motion of the ethylene ($-\text{CH}_2-\text{CH}_2-$) part or chain ends of polymer segments [14].

In this paper we report results from differential scanning calorimetry (DSC) and dielectric spectroscopy on $(\text{PEO})_4:\text{LiClO}_4$ with $\delta\text{-Al}_2\text{O}_3$ nano-fillers. It should here be noted that previous studies have indicated that different aluminium oxides, such as α - and $\gamma\text{-Al}_2\text{O}_3$ nanoparticles, have different effects on polymer electrolytes [4,8,15]. Although the ionic transport in the $\text{PEO}:\text{LiClO}_4$ system and similar systems has been well studied [5,10,16–18], the studies related to the dielectric relaxations in the system and the influence of nano-fillers on these dielectric relaxations have drawn much less attention.

2. Experimental techniques

The polymer electrolyte samples were prepared by mixing appropriate quantities of PEO ($M_w = 5 \times 10^5$; Polysciences, Inc.) and LiClO_4 salt in acetonitrile solution. High pure, fumed $\delta\text{-Al}_2\text{O}_3$ (Aluminiumoxid C, Degussa AG; size ~ 13 nm) fillers were added to acetonitrile and stirred and sonicated for 2 h for proper dispersion. The final solution of PEO, salt and fillers was sonicated and vigorously stirred for 72 h, until the fillers were uniformly dispersed and the whole solution appeared translucent (agglomeration of fillers were not observed). The solution was poured on PTFE petri dish and vacuum dried at 320 K for 48 h to remove all the traces of solvent. In this way free-standing thin polymer electrolyte films, of thickness of 100–150 μm , were obtained. The preparation conditions can greatly influence the final properties of CPE, thus systematic and careful procedures should be adopted during preparation of all polymer electrolyte samples [19].

For thermal characterisation, DSC measurements have been carried out on polymer sample encapsulated in aluminium pans, using TA instruments Q1000 DSC. The measurements were carried out from 160 K–430 K with a heating rate of 10 K min^{-1} , under nitrogen atmosphere. In the present analysis, the glass transition temperature (T_g) is defined as the onset of change in rate of heat flow in the DSC curves.

Dielectric measurements were performed on a Novocontrol GmbH Broadband Dielectric spectrometer system with a Quatro Cryosystem temperature control unit. Polymer film samples were placed between two gold plated electrodes in a ZGS active sample cell and the measurements were performed in the frequency and temperature ranges 10^{-2} – 10^7 Hz and 135 K–365 K, respectively.

3. Results and discussions

3.1. Thermal characterisation

Fig. 1 shows the DSC curves of $(\text{PEO})_4:\text{LiClO}_4$ and $(\text{PEO})_4:\text{LiClO}_4$ with 4 wt% $\delta\text{-Al}_2\text{O}_3$ during heating and cooling cycle. The melting temperature of pure PEO is around 338 K. During the cooling cycle of the polymer electrolyte, no phase transition is observed in the measured temperature range. However, in the presence of fillers an exothermic crystallisation peak is observed around 335 K, as these fillers act as multiple nucleation sites for the rapid growth of poorly developed spherulites [20]. During the heating cycle, the DSC curve of $(\text{PEO})_4:\text{LiClO}_4$ exhibits an exothermic crystallisation peak at 326 K and an endothermic melting peak at 380 K [16,21]. However, $(\text{PEO})_4:\text{LiClO}_4$ with fillers exhibited only a melting peak of 395 K, due to the partial crystallisation during the cooling cycle. The inset of Fig. 1 shows the glass transition of the polymer samples. The glass transition temperature (T_g) of pure PEO is located around 215 K. The polymer–salt complex $(\text{PEO})_4:\text{LiClO}_4$ exhibited a higher T_g around 252 K. The increase in T_g , in the presence of Li^+ salt, can be attributed to a reduction in flexibility of the polymer chains due to the interaction between the ether oxygens of the polymer chains

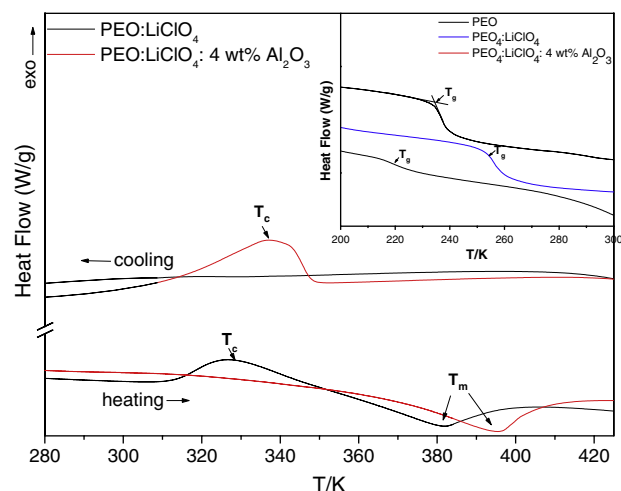


Fig. 1. DSC plots of $(\text{PEO})_4:\text{LiClO}_4$; x wt% $\delta\text{-Al}_2\text{O}_3$ ($x=0$ & 4). Inset: glass transition of PEO, $(\text{PEO})_4:\text{LiClO}_4$; x wt% $\delta\text{-Al}_2\text{O}_3$ ($x=0$ & 4). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and the Li^+ ions. This also confirms the complexation of the polymer and the salt. Previous studies of CPE have indicated that, in the presence of fillers, the increase or decrease in T_g depends on how the fillers surface interactions affect the dynamics of polymers within an interfacial layer near fillers surfaces [22–24], i.e. a slowing down (increased T_g) or an acceleration of dynamics (decreased T_g) when the polymer–filler interactions are attractive or repulsive, respectively. Fig. 1 shows that T_g tends to decrease with increasing filler content (to ~ 230 K with 4 wt% $\delta\text{-Al}_2\text{O}_3$), which indicates that the interaction at the filler–polymer interface may be repulsive in nature and the structural (α) relaxation of the polymer chains speeds up with increasing filler concentration, at least at temperatures around the glass transition temperature.

3.2. Temperature dependence of the D.C. conductivity

The effect of the Al_2O_3 filler concentration on the temperature dependent conductivity for $(\text{PEO})_4:\text{LiClO}_4$; x wt% $\delta\text{-Al}_2\text{O}_3$ ($x=0, 2, 4$) has been studied. The polymer–salt ($x=0$ wt%) complex exhibited a D.C. conductivity of $\sigma_{\text{D.C.}} = 4.0 \times 10^{-7} \text{ Scm}^{-1}$ at room temperature (298 K) and the ionic conduction process is mainly determined by the structural (i.e. segmental) polymer relaxation process. In the presence of 4 wt% $\delta\text{-Al}_2\text{O}_3$ fillers, the electrolyte exhibited an increase of the ionic conductivity to $\sigma_{\text{D.C.}} = 1.5 \times 10^{-5} \text{ Scm}^{-1}$ at 298 K. At lower temperatures the increase in ionic conductivity was even higher. The temperature dependence of the conductivity exhibited a Vogel–Fulcher–Tammann (VFT) behaviour for all electrolytes, similar to the temperature dependence of conductivity relaxation (discussed below).

3.3. Dielectric relaxations

The analysis of dielectric relaxation spectra provides important information regarding the behaviour of polymer electrolytes and the effect of nano-fillers on the polymer relaxations. The imaginary part of the dielectric spectra (ϵ'') was fitted by the sum of a conductivity term, the Havriliak–Negami function [25] for the α -process and the Cole–Cole function [26] for the β and γ processes. Thus, the total fitting function is given by Eq. (1):

$$\epsilon''(\omega) = \frac{\sigma_{\text{D.C.}}}{\epsilon_0 \omega} + \text{Im} \left[\frac{\Delta\epsilon_\alpha}{(1 + (i\omega\tau_\alpha)^a)^b} + \frac{\Delta\epsilon_\beta}{1 + (i\omega\tau_\beta)^a} + \frac{\Delta\epsilon_\gamma}{1 + (i\omega\tau_\gamma)^a} \right] \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/7747121>

Download Persian Version:

<https://daneshyari.com/article/7747121>

[Daneshyari.com](https://daneshyari.com)