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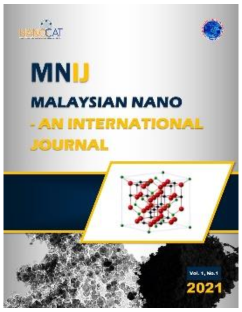

Research Article

Thermal, Structural and Morphology Studies of PEO-LICF$_3$SO$_3$-DBP-ZrO$_2$ Nanocomposite Polymer Electrolytes

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Abstract

This work represents a thermal study of PEO-based polymer electrolyte films that were prepared by the solution cast technique. The melting temperature (T_m), glass transition temperature (T_g) and degree of crystallinity (χ_c) were measured by diffraction scanning calorimetry (DSC). Thermogravimetric (TGA) was used to determine the initial and final degradation temperatures. The structural was also performed to characterize the vibrational wavelength and phase characteristic (crystalline/amorphous). In contrast, the morphological study was emphasized to examine the appearance of the features for pure polymer electrolyte system and after adding salt, plasticizer and filler. The zirconium oxide particles were measured after the milling process using transmission electron microscopy (TEM), and the particles were obtained in the range of 9–54 nm.

Keywords*:* Polymer electrolyte; Ionic conductivity; Thin films, Differential scanning calorimetry

1. Introduction

Solid polymer electrolyte (SPE) plays a role as an electrolyte in secondary lithium batteries and has gained huge attention among researchers all over the world for many years [1], promises as an outstanding source of energy for a wide range of applications in industrial, medical, military and tools of daily use [2]. The poly (ethylene oxide) (PEO) has been acknowledged as a good matrix for dissolving a variety of salts (even in high concentrations) to form polymeric electrolytes [3]. The PEO-based polymer electrolytes can achieve optimal conductivity of 10^{-3} - 10^{-4} S/cm at a temperature of 80 – 100 °C [4]. However, the electrolytes suffered low conductivity of 10^{-7} - 10^{-8} S/cm at a lower temperature due to the high crystallinity behaviour of the PEO [5].

In the previous report, the conductivity of pure PEO achieved 1.58×10^{-9} S/cm and the conductivity of PEO-based salt, lithium trifluoromethanesulfonate electrolyte, increased to 9.26×10^{-6} S/cm [6]. The plasticizer of dibutyl phthalate and inorganic filler of zirconia oxide was introduced into the polymeric electrolyte matrix, increasing the conductivity at room temperature, 4.51×10^{-5} S/cm and 1.38×10^{-4} S/cm, respectively. The plasticization effect reduces the crystallinity of the polymer, increase the amorphous phase of the PEO-base electrolyte, and the polymeric segments become flexible as well as mobile charge carriers. While, the particles of inorganic filler in nanometer size increase the surface ratio to the volume, giving an advantage to the atomic behaviour at the particle's surface compared to the atomic behaviour inside the particle. The reorganization and high degree disorder of the local polymer chain can be prevented and locked. The filler of ZrO_2 is strong. Though ceramic material promotes special properties such as strength, high chemical and heat resistance, offering long-term mechanical stability and increasing the ionic conductivity due to the conducting pathway of Li^+ at the filler surface [7-8].

In the present work, the polymer electrolytes based PEO were further studied to understand the thermal, structural and morphological properties by using several analytical techniques such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray diffraction analysis (XRD), field emission scanning electron microscope (FESEM), Fourier transforms infrared spectroscopy (FTIR) and transmission electron microscope (TEM).

2. Experimental

The materials selection in preparing polymer electrolyte films are poly (ethylene oxide) (PEO) (MW=600,000, Aldrich), lithium trifluoromethanesulfonate ($LiCF_3SO_3$, Aldrich), dibutyl phthalate (DBP, Alfa Aesar) and zirconium oxide (ZrO2, Acros Organics). The sample films were prepared by solution cast technique. Before use, PEO and $LiCF_3SO_3$ were dried at 50 °C for 48 hours and 100°C for 1 hour, respectively, to eliminate the water trace. By per mixture of 1g of PEO and various 14 wt. % of $LiCF_3SO_3$ separately dissolved in acetonitrile (Fisher) and were then mixed and stirred. Next, the 1.0 wt. % of DBP were added to the mixture solution (fix amount of polymer and salt) and stirred. Eventually, the 0.05 wt.% of ZrO_2 were added to the being fixed mixture solution of polymer, salt and plasticizer. The final mixtures were stirred for 24 hours until homogenous solution and then were cast onto a petri dish and allowed slowly evaporating inside a desiccator for four days. The thin films kept storing in dry condition.

The electrolyte for pure PEO, PEO-$LiCF_3SO_3$, PEO-$LiCF_3SO_3$-DBP and PEO- $LiCF_3SO_3$-DBP-ZrO_2 was carried out for thermal investigation using Mettler DSC 820 under nitrogen flow at a heating rate of 20 °C/min for temperature range 100 to 100 °C. The dynamic weight losses were measured using TGA/SDTA 851 Mettler Toledo over a temperature range of 20 °C to 1000 °C with a scan rate of 10 °C/min. The structural properties were determined by using Philips X' Pert MRD X-ray diffractometer system. The infrared spectra were obtained using a Perkin Elmer FTIR spectrophotometer in the wave region 4000 and 500 cm-1. The morphology observations were carried out by FESEM, JSM 5410LV JEOL Japan and the particles sizes of ZrO_2 were determined by TEM (LIBRA® 120).

3. Result and discussion

3.1. Thermal Study

3.1.1. DSC analysis

Figure 2 show two endothermic peaks except for the pure PEO system. Figure 2(a) show the melting temperature T_m of pure PEO obtained at 72 °C, indicating the melting-rich crystalline phase [9]. Upon adding salt, the T_m of PEO-$LiCF_3SO_3$electrolyte system was observed to lower temperature, 64 °C, and the second endothermic peak appeared at temperature range 100 – 120 °C, indicating the melting of the crystalline phase.

The T_m decreased to 61°C upon addition of DBP to the PEO- $LiCF_3SO_3$ electrolyte system as shown in Figure. 2(c), and slightly transition to 59 °C by the addition of ZrO_2. By adding filler lowering the glass transition temperature (T_g) according to the increment of volume fraction of amorphous phase due to the modification of polymer structure [10]. Therefore, it suggests a significant contribution to the conductivity enhancement due to the structural modification in the PEO-$LiCF_3SO_3$-DBP-ZrO_2 electrolyte system. The relative crystalline (χ_c) was calculated by using the relationship [11] where ΔH_m^{sample} is the melting enthalpy of the sample and ΔH_m^o is the melting enthalpy of the 100 % crystalline of PEO (213.7 Jg-1) [12].

$$\chi_c = \frac{\Delta H_m^{\text{sample}} \times 100}{\Delta H_m^o} \quad (1)$$

Table 1 shows the T_m, T_g and χ_c values were decreased gradually by the presence of salt, plasticizer and filler to the PEO-base electrolyte. The decrement attributed to the favoring anionic and cationic transportation in the polymer matrix due to the segmental motion enhancement of polymer host, thus improving the PEO's conductivity $LiCF_3SO_3$-DBP-ZrO_2 electrolyte system.

Table 1: Thermal properties of PEO-based electrolytes

Sample	**T_m (°C)**	**ΔH_m (J g^{-1})**	**χ_c (%)**	**T_g (°C)**	**Conductivity ($Scam^{-1}$)**
PEO	72.20	178.53	83.54	-64.01	1.58×10^{-9}
PEO- $LiCF_3SO_3$	64.21	64.77	30.31	-68.01	9.24×10^{-6}
PEO- $LiCF_3SO_3$-DBP	61.08	58.52	27.38	-70.00	4.51×10^{-5}
PEO- $LiCF_3SO_3$-DBP-ZrO_2	59.33	58.10	27.19	-72.21	1.38×10^{-4}

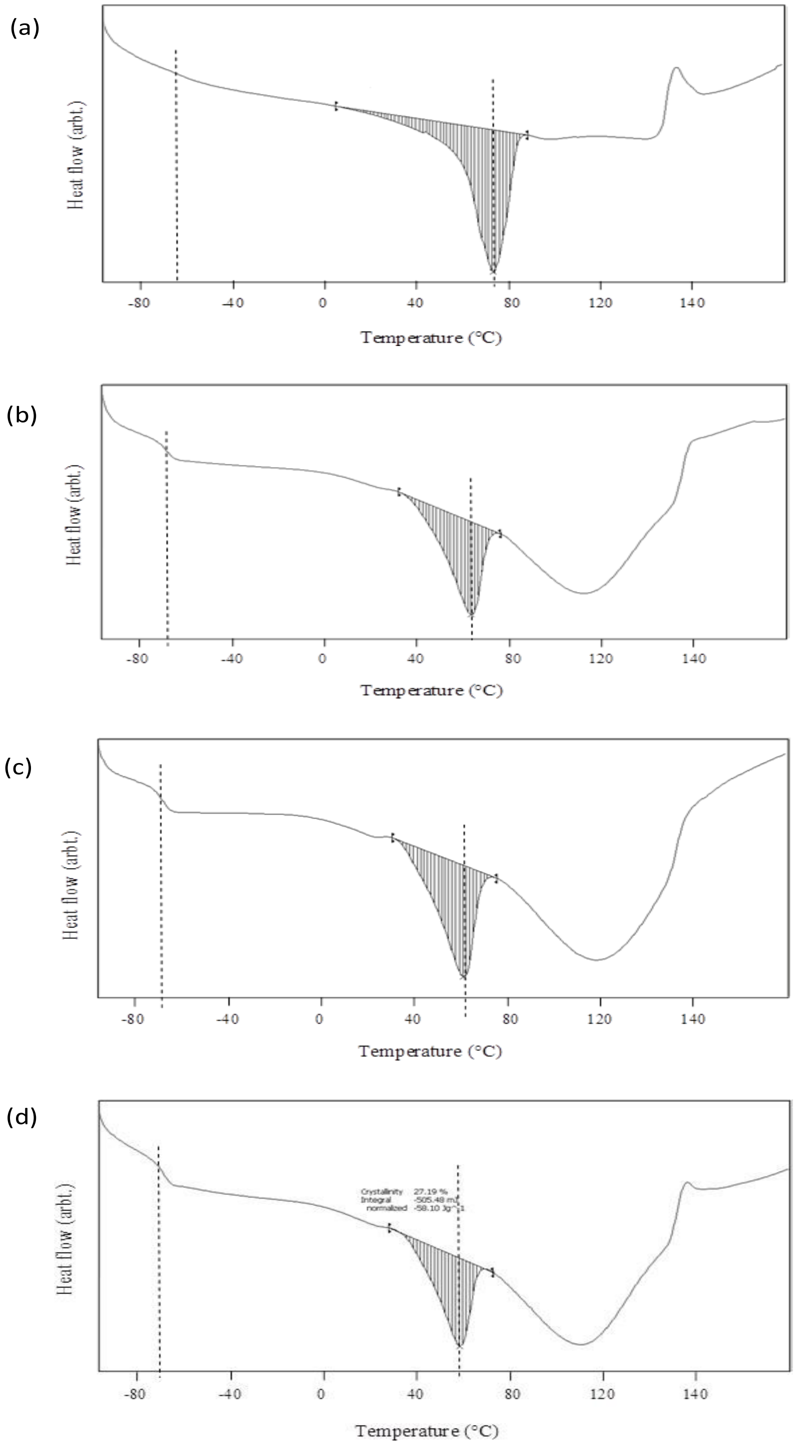

Figure 1: DSC spectra for (a) pure PEO (b) PEO- $LiCF_3SO_3$ (c) PEO- $LiCF_3SO_3$-DBP (d) PEO-$LiCF_3SO_3$-DBP-ZrO_2 polymer electrolyte

3.1.2. TGA analysis

Figure 2 shows the weight loss (TG) and derivative of the weight loss (DTG) curve of PEO-based polymer electrolytes. The TGA curve can determine the initial and final degradation temperatures; meanwhile, the DTG curve can appoint the maximum temperature of weight loss. Figure 2(a) shows the mass loss of pure PEO begins at 176 °C and ends at 469 °C. PEO decomposes at temperatures above 100 °C, forming monomers, small oligomers and other decomposition products [13].

Figure 2(b-d) represents the TGA-DTG curve of salted, plasticized and composite polymer electrolyte, respectively, where the figures exhibit two main weight loss regions. The first region occurred at a lower temperature, which may be due to the evaporation of water content or the loss of absorption solvent. At 200 °C, the $LiCF_3SO_3$, DBP and ZrO_2 began to melt, and the electrolyte systems were no longer stable. As a result, one endothermic curve appeared, indicating the total decomposition of the polymer [14]. It can be noted that the total weight losses were slightly decreased for all electrolyte systems. In contrast, the initial and final decomposition temperature increase indicating the polymer-based electrolyte achieve stability upon the addition of salt, plasticizer and filler.

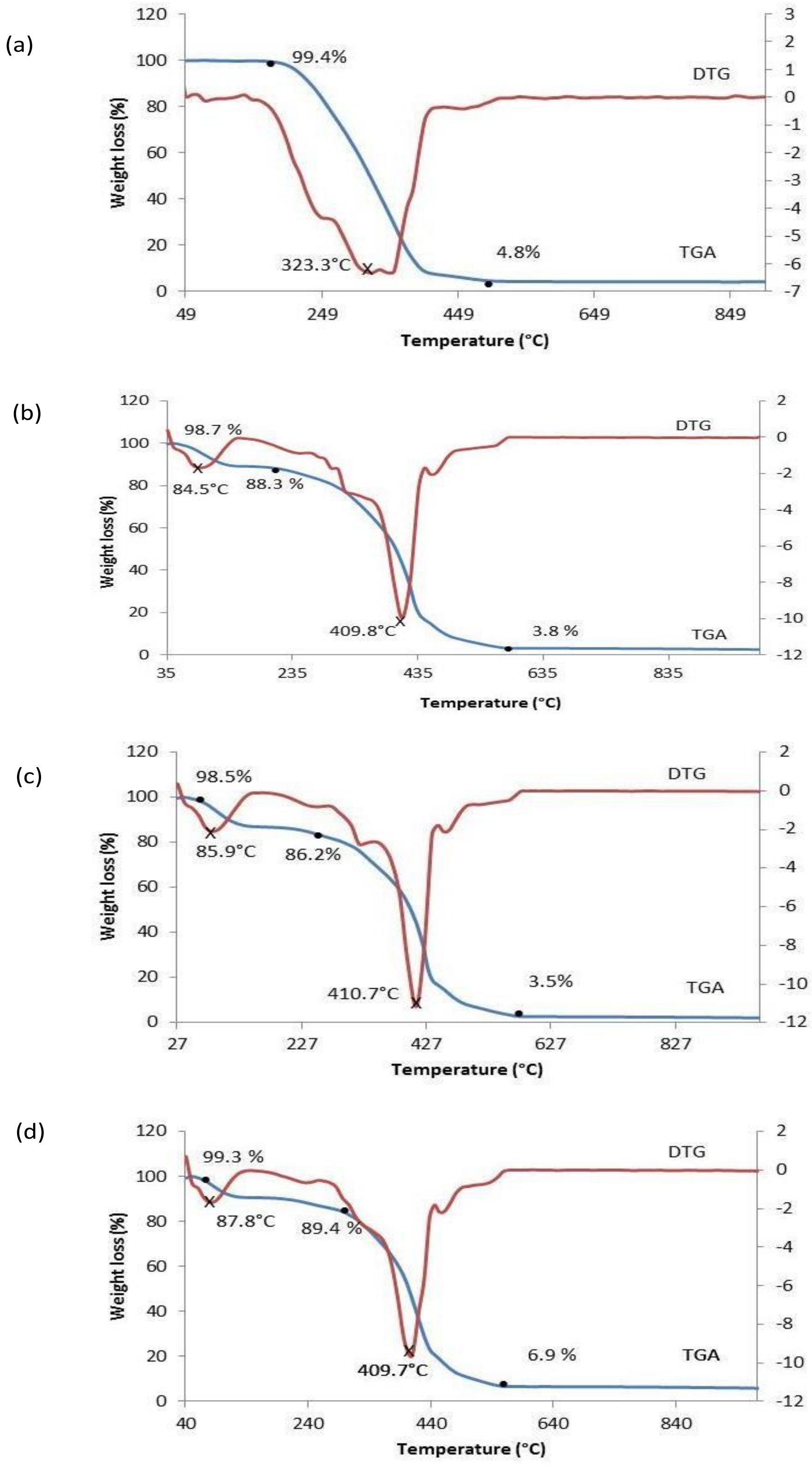

Figure 2: TGA-DTG curve for (a) pure PEO (b) PEO- $LiCF_3SO_3$ (c) PEO- $LiCF_3SO_3$-DBP (d) PEO $LiCF_3SO_3$-DBP-ZrO_2 polymer electrolyte.

3.2. *Structural study*

3.2.1. *XRD analysis*

Figure 3 shows the XRD pattern consist of both sharp crystalline and broad region that indicates the electrolyte films in a combination of a crystalline and amorphous phase, respectively [15].

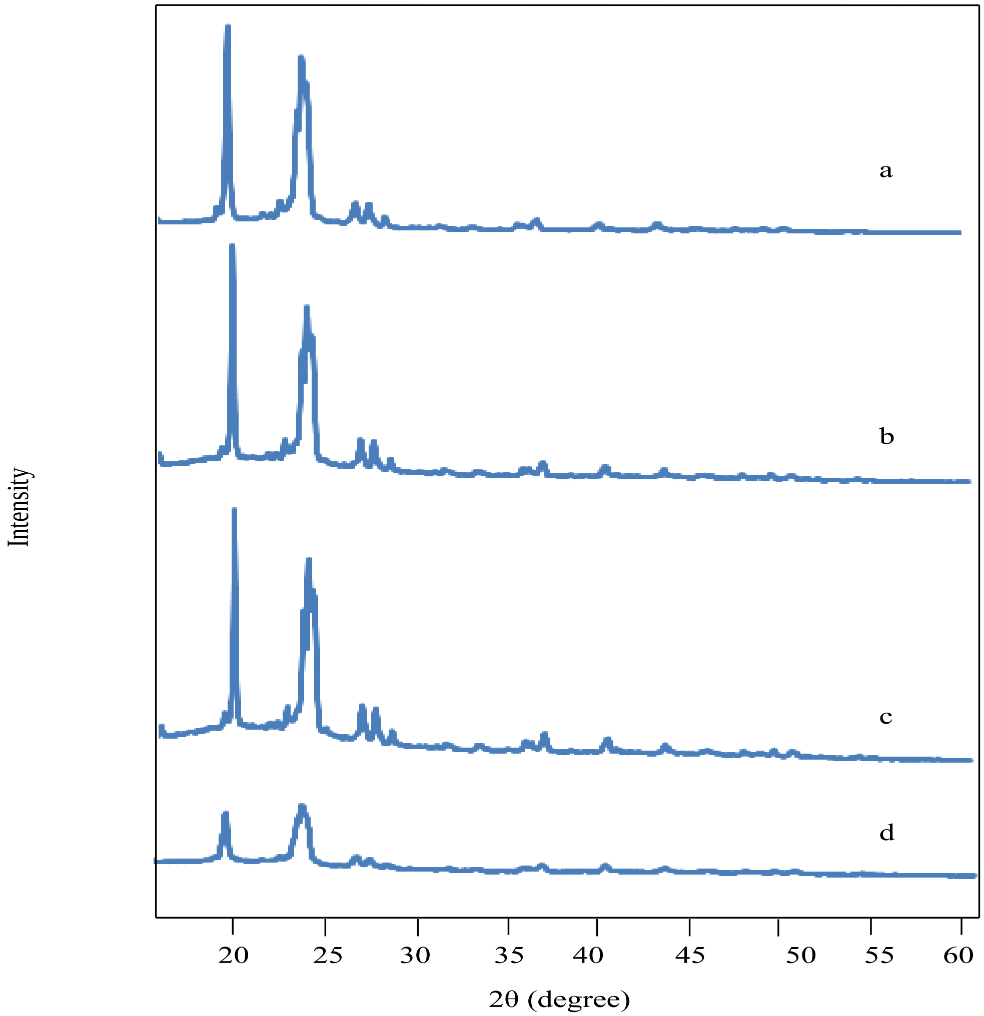

Figure 3: XRD patterns for (a) pure PEO (b) PEO- $LiCF_3SO_3$ (c) PEO- $LiCF_3SO_3$-DBP (d) PEO- $LiCF_3SO_3$-DBP-ZrO_2 polymer electrolyte.

The dominance diffraction peaks appeared at 2θ = 19.4° and 23.5°, indicating the presence of a crystalline phase originating from the ordering of polyether side chain of PEO, which is in good agreement with the report by Kuila et al. [16]. Meanwhile, the peaks are also present for salted, plasticized and composite filler electrolyte systems. There were no significant differences between the PEO-based electrolyte and pure PEO system. The addition of $LiCF_3SO_3$ and DBP did not affect the degree of crystallinity of PEO. However, by addition of ZrO_2 showed notable changes, which indicated the degree of crystallinity of polymer decrease and influenced the crystallization kinetics of the polymer chains. This phenomenon exhibits the localization of the amorphous region and thus enhancing ionic conductivity at room temperature.

3.2.2. FTIR analysis

Figure 4 depicts the FTIR spectra for pure PEO, $LiCF_3SO_3$, DBP and ZrO_2. The assignment of the vibrational features of PEO was observed at 959.89 cm^{-1} for vibrational CH_2 twisting, the strongest peak found at 1096.28 cm^{-1} (C-O-C stretching) and CH_2 scissoring and asymmetric stretching was observed at 1466.47 and 1684.15 cm^{-1}, respectively [17-18]. Characteristic frequencies of $LiCF_3SO_3$ were assigned at 1227.05 cm^{-1} (vs (CF_3)), 1191.44 cm^{-1} (vas(CF_3)), 1039.37 cm^{-1} (vs(SO_3)) and 640.31 cm^{-1} (δs(CF_3)) [19]. The presence of water can be identified by observing a broad peak at 3400 – 3600 cm^{-1}, which is the characteristic of –OH stretching of hydrogen bonding [20]. This was observed at a frequency of 3528.47 cm^{-1} for the $LiCF_3SO_3$ spectrum. The peak at 1579.63 cm^{-1} and 1721.59 cm^{-1} were assigned as C=C sketching and C=O for pure DBP, respectively [21]. The filler spectrum shows bands at 500-1000 cm^{-1} according to the Zr-O bond [7].

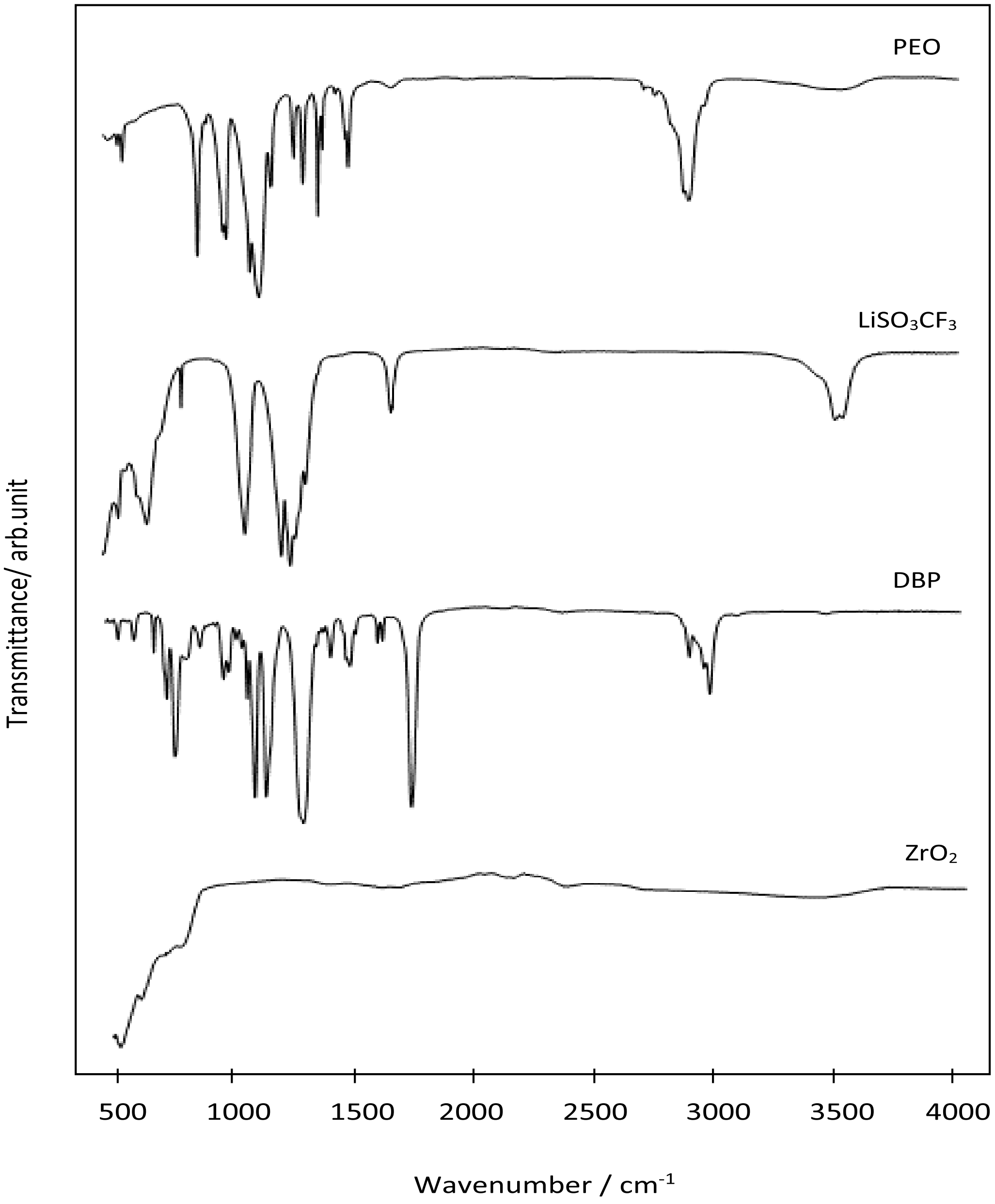

Figure 4: FTIR spectra for pure PEO, $LiSO_3CF_3$, DBP and ZrO_2

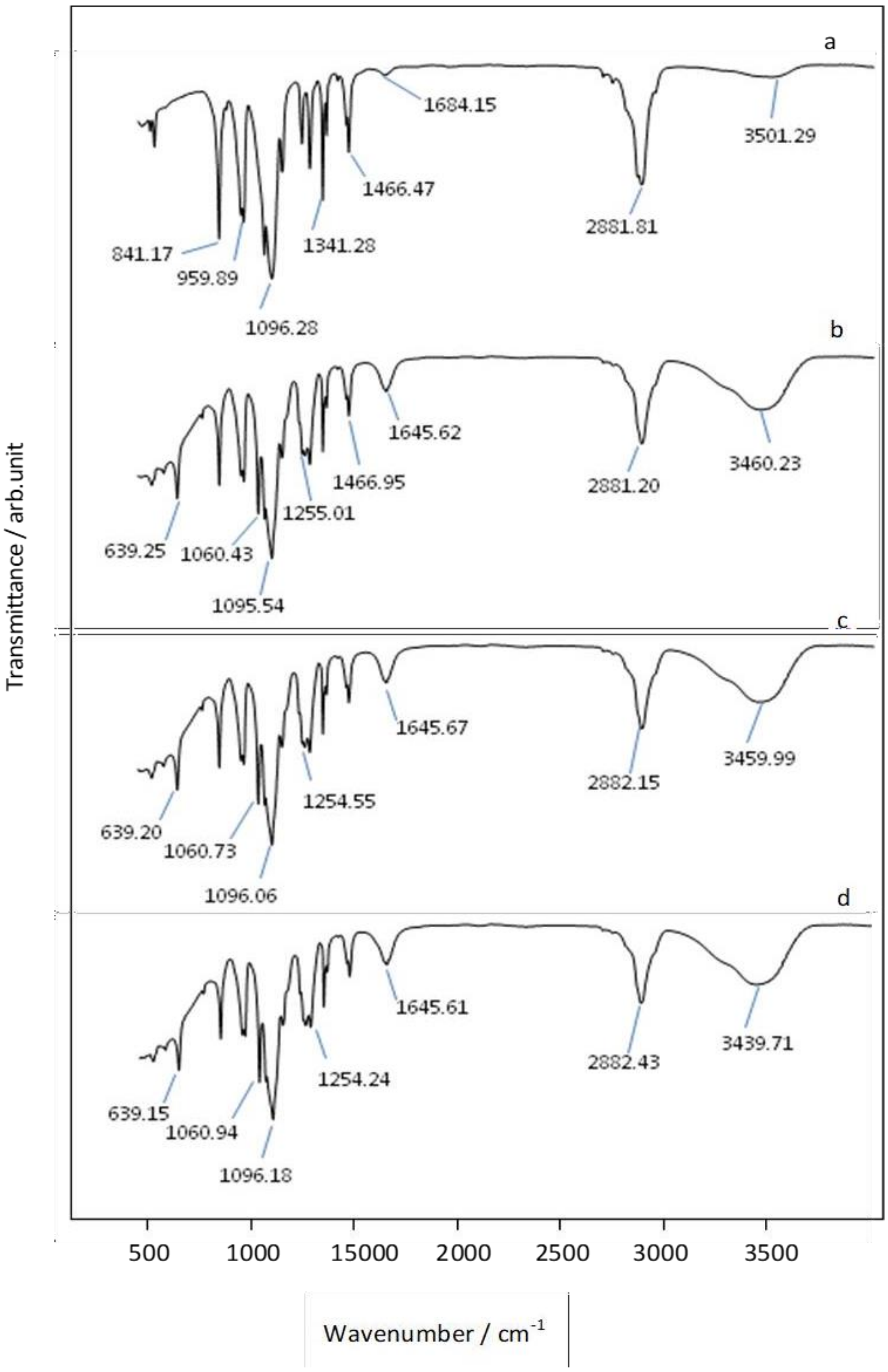

Figure 5: FTIR spectra for (a) pure PEO (b) PEO-$LiSO_3CF_3$ (c) PEO-$LiSO_3CF_3$-DBP (d) PEO-$LiSO_3CF_3$-DBP-ZrO_2

Figure 5 depicts the IR spectra of PEO-based electrolytes. The spectra show a similar trend of peaks but have different wavenumbers due to the Li-ions bounded in all electrolyte systems. The significance peaks for DBP and ZrO_2 were disappeared due to the vibrational role of the dominancy of polymer and salt. In the PEO-$LiCF_3SO_3$ complex, the peaks at 1277.05 cm^{-1} ($\nu_s(CF_3)$) shifted to 1255.01 cm^{-1}. The characteristic frequencies of PEO at 1096.28 and 1466.47 cm^{-1} were shifted to 1095.54 and 1466.95 cm^{-1}, respectively, which conforming the $LiCF_3SO_3$ complexation in the polymer matrix.

3.3 Morphology study

3.3.1 FESEM and TEM analysis

Figure 6(a) shows the pure PEO image that the surface comprises a joint polygon-like shape with definite boundaries where the inside of polygon are vein-like structures originating from the centre. By adding salt to the polymer host, the polygon-shapes were less centralized, and the spherulitic structures start to close and attach to each other means reducing the crystalline phase, as shown in Figure 6(b). Figure 6(c) shows the boundaries continued to be less by the addition of plasticizer. The surface exhibits both rough and smooth features, indicating the degree of crystallization and amorphous regions were stand together in the PEO-$LiCF_3SO_3$-DBP matrix. The addition of ceramic filler exhibits no boundaries, and the surface becomes smooth, indicating the amorphous phase increase. This means the modifications of the internal structure occurred due to the filler interacted with the polymer chain and reducing the crystallinity degree of PEO, as shown in Figure 6(d).

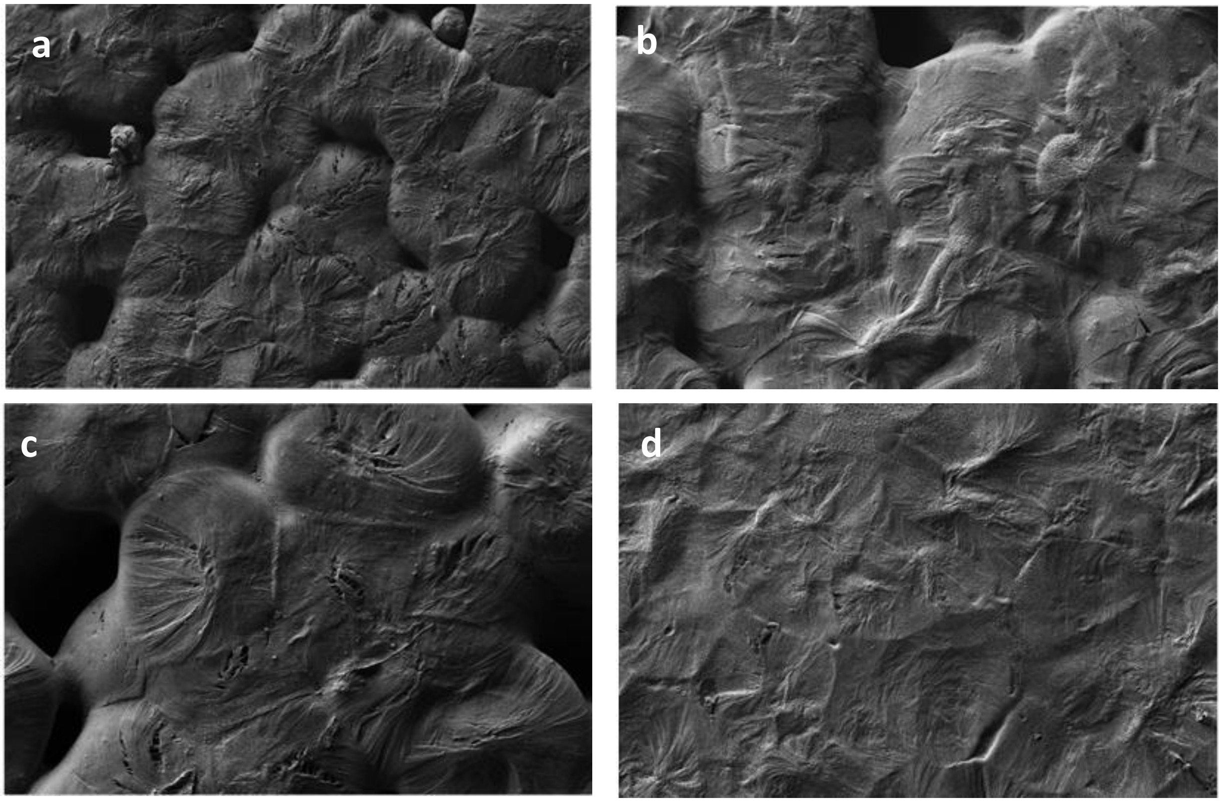

Figure 6: FESEM images for (a) PEO (b) PEO-$LiCF_3SO_3$ (c) PEO-$LiCF_3SO_3$-DBP (d) PEO-$LiCF_3SO_3$-DBP-ZrO_2

Figure 7 shows the TEM image of ZrO_2 after the milling procedure. The ZrO_2 particles size was obtained in non-uniform with the size range of 9-54 nm. The ceramic filler in nanometer size exhibits a large surface area to the volume ratio, contributing to the conductivity enhancement of PEO-$LiCF_3SO_3$ based polymer electrolyte.

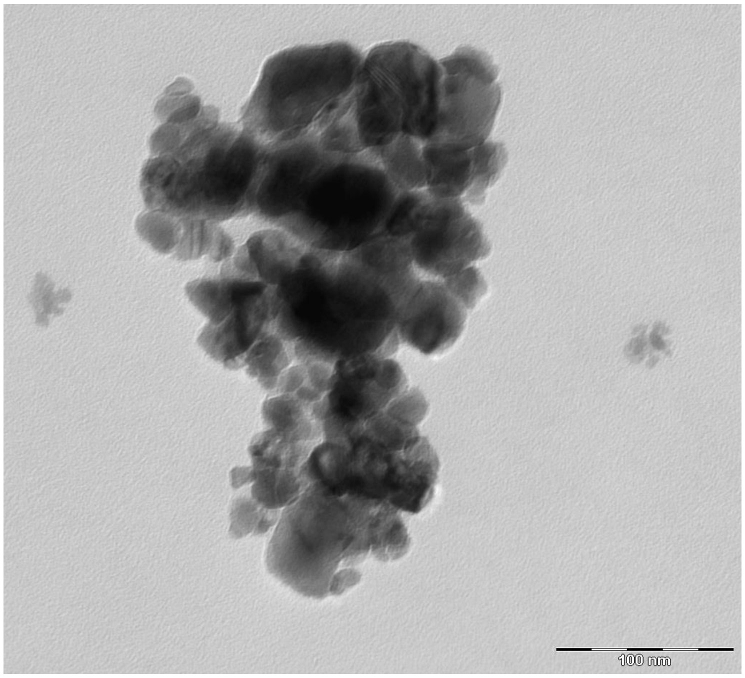

Figure 7: TEM image of ZrO_2 nanoparticle

4. Conclusion

Four PEO-based polymer electrolyte systems were prepared (PEO, PEO-$LiSO_3CF_3$, PEO-$LiSO_3CF_3$-DBP-ZrO_2) by using the solution casting technique. The melting temperature, glass transition temperature and degree of crystallinity of PEO were continuous decreases by the added salt, plasticizer and nanoceramic filler. This thermal behaviour is caused by the increase of volume fraction of the amorphous phase. While the decomposition temperatures increased, indicating the electrolyte system achieve higher stability. The diffraction peaks for polymer complex nanocomposite electrolytes were less intense due to the crystalline phase was decrease. It also slightly different in wavelength for vibrational assignment peaks, indicating an interaction between polymer host, salt, plasticizer, and nanoceramic filler. By morphological evidence, it was definite boundaries of polygons in the complexed electrolyte compared to the pure system indicating an increase of amorphous behaviour; therefore, the complex nanofiller electrolyte system achieving the optimum thermal, structural and conductivity enhancement.

Conflicts of Interest

There are no conflicts to declare

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