

Ionic conductivity of MG30-PEMA Blend Solid Polymer Electrolyte

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ABSTRACT

This paper presents on ionic conductivity of MG30-PEMA blend solid polymer electrolytes (SPEs) prepared by solution cast technique. The analysis has shown that conductivity increases with the increasing salt composition. It is observed via x-ray diffraction analysis that the crystallinity of the sample decreased with the amount of salt composition as expected. It is also observed that the dielectric value increases with increasing amount of LiCF_3SO_3 in the sample. Surface morphology revealed that ion aggregation occurred after optimum conductivity which has lowered the conductivity.

Keywords: Solid polymer electrolyte; Conductivity; Blend polymer electrolyte; Dielectric; MG30; PEMA.

INTRODUCTION

Polymer electrolytes are potential candidates as a medium for charge transport in electrochemical devices such as lithium polymer battery, super capacitor and fuel cell [1,2,3]. Polymer electrolyte are flexible and have good mechanical properties which lead to good electrode-electrolyte contact hence increased in terms of safety and conductivity. Furthermore, polymer electrolyte has high energy density compared with liquid electrolyte; making it more favorable to be developed than liquid electrolyte. In polymer electrolyte, ionic conduction is contributed from amorphous elastomeric phase. Modified natural rubber such as 30% poly (methyl methacrylate) grafted natural rubber (MG30), 49% poly (methyl methacrylate) grafted natural rubber, and epoxidize natural rubber (ENR) is polymer that has amorphous elastomeric phase below room temperature. Many studies have been conducted based on this modified natural rubber and found that they exhibit high conductivity $\sim 10^{-6}$ to 10^{-3} Scm^{-1} at room temperature [4,5,6]. In addition modified natural rubber has low glass transition T_g , and good elasticity [7]. On the other, hand poly (ethyl methacrylate) has high $T_g \sim 68^\circ\text{C}$ which leads to low conductivity when used as polymer host in polymer electrolytes. Poly (ethyl methacrylate) PEMA, was recently chosen as a polymer host due to its non-taking characteristic, high surface resistance and higher optical properties. The brittleness properties of PEMA have become an obstacle towards its development as polymer electrolyte. Other than the amorphous phase, there are also several properties for ion transport that needs to be considered such as salt concentration and dissociation, dielectric constant of polymer, degree of ion aggregation and the mobility of polymer chains [8]. Addition of lithium salt facilitates increases in amorphous phase and acts as a source of conduction in polymer electrolyte [9]. The understanding of the ion transport behavior and information of ionic and molecular interaction in polymer electrolytes can be done by dielectric relaxation phenomena studies. The dielectric properties of ionically conducting polymer electrolyte give information about the ion association in heterogeneous systems. This heterogeneous system is directly related to

the presence of dipoles. In addition dielectric relaxation and frequency dependent conductivity is sensitive to the motion of charge species and dipoles of polymer [9].

The blend polymer electrolyte is obtained if the mixture of the structurally different polymer interacts without covalent bond formation [10]. By blending different polymer together a desirable property that requires in developing polymer electrolyte can be achieved. Therefore, this paper will cover the dielectric studies and morphology of polymer electrolytes composed of blend MG30-PEMA dope with LiCF_3SO_3 .

METHODOLOGY

30% poly (methyl methacrylate) grafted natural rubber supplied by the Rubber Research Institute of Malaysia, poly (ethyl methacrylate) 50000Mw, solvent tetrahydrofuran and LiCF_3SO_3 was supplied by Sigma Aldrich. The sample was prepared via solvent casting method. Solid polymer electrolyte films were prepared by dissolving MG30-PEMA in tetrahydrofuran (THF), consisting of a selected weight ratio of LiCF_3SO_3 salt. The ratio composition of the prepared films is shown in table 1. All prepared sample was stirred magnetically until homogeneous. The homogeneous mixture was cast onto different petri dishes and left for evaporation of excess solvent to form a thin film. The sample was cut about 1cm^2 for EIS, POM and XRD testing. X-ray Diffraction studies of selected samples were performed by means of the PANalytical X'Pert PRO system under Ni-filtered $\text{CuK}\alpha$ radiation. The impedance of the polymer electrolyte system was determined by HIOKI 3532-50 LCR Hi Tester in the frequency range 100 to 1MHz. Sample conductivity calculated from the equation below:

$$\sigma = t / (R_b \times A) \quad (1)$$

Where t is the thickness of the sample, R_b is bulk resistance and A is the area of the sample. Table 1 shows the composition of the sample and ionic conductivity at room temperature.

Table 1: Ionic conductivity at room temperature

Composition of MG30:PEMA- LiCF_3SO_3	σ at 303K
47.5:47.5:5	8.00E-10
45:45:10	4.59E-09
42.5:42.5:15	5.05E-09
40:40:20	8.32E-09
37.5:37.5:25	1.26E-08
35:35:30	9.27E-06
32.50:32.50:35	5.66E-06
30:30:40	6.57E-07

RESULT AND DISCUSSION

Conductivity

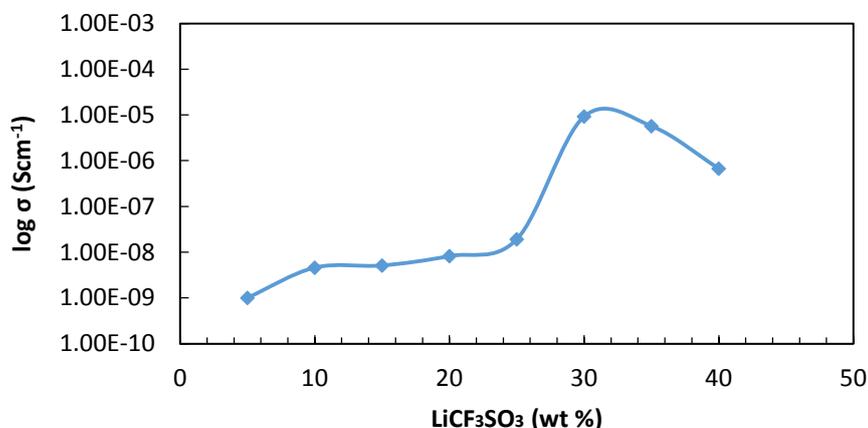


Fig. 1. Conductivity of solid polymer electrolyte as function of LiCF₃SO₃ salt composition.

Fig.1 show conductivity of selected sample at temperature 30°C. While Table I show the conductivity value. It is found that with the increasing composition of LiCF₃SO₃ salt the ionic conductivity increased until it reaches optimum at 30 wt% with the ionic conductivity of $9.27 \times 10^{-6} \text{ Scm}^{-1}$. Increase in conductivity is due to the increase number of conducting species in the electrolyte. The increasing in the number of conducting species is mostly attributed to the ion dissociation of LiCF₃SO₃ into Li⁺ and CF₃SO₃⁻ species. This finding is in good agreement with others previous research on SPEs[1]. Generally, when the composition of salt increased, the more ions dissociate lead to the increasing number of conducting species result in rising of the conductivity value. However, further addition of LiCF₃SO₃ after 30wt% salt, the salt tends to associate more ions hence conductivity value decreasing. Ion association become a hindrance towards the ion conduction by formation of ion cluster thus decreasing the number of conducting species and ion mobility.

Figure 2 depicts the frequency dispersion response in the real part of dielectric constant ϵ' , at different composition of LiCF₃SO₃ at room temperature. At low frequency region, dielectric constant rose sharply is observed. Increase in frequencies demonstrated the dielectric constant decrease continuously and then reaches a constant value. There is no relaxation peak occurred which, shows that the increase in conductivity was primarily due to an increase in the number free ions [11]. This can also be observed that LiCF₃SO₃ composition increases as the dielectric constant is also increased. This is due to fact that the increasing number of charge carriers with the increase of salt composition, hence increases the dielectric constant [12]. At high frequencies region less ionic polarization occurred due to the periodic reversal of electric field occurring so fast and prevent excess ion from accumulating at the interface for long [13]. Hence ionic species become static at their own position resulting to the decrease in dielectric constant.

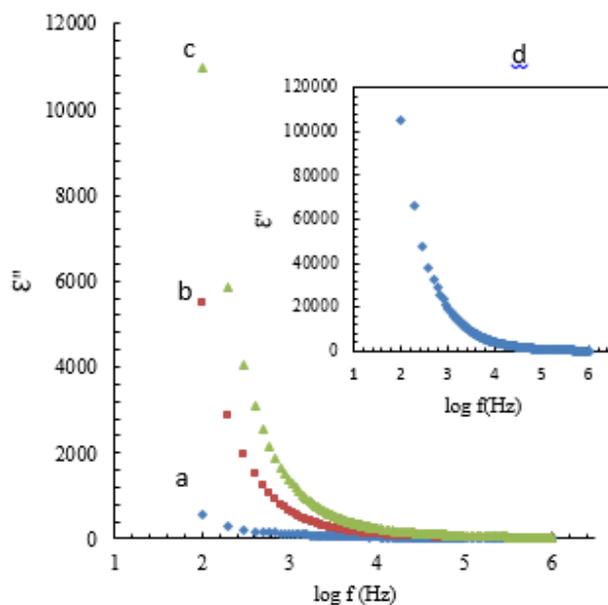


Fig. 2. Dielectric loss versus log f for SPEs at selected temperature.

Fig. 3 shows the response of ϵ' as a function of frequency at various temperature for 30wt% composition of LiCF_3SO_3 . The ϵ' decreases with respect to the increase in frequencies was detected. This behavior agrees with the outputs with other research work [14,15]. The dielectric constant also found to increase with the increasing of temperature at lower frequencies. High value of dielectric constant at low frequencies and high temperature may be due to free charge building up at the interfaces within the bulk of sample and between the electrode electrolytes interfaces [15].

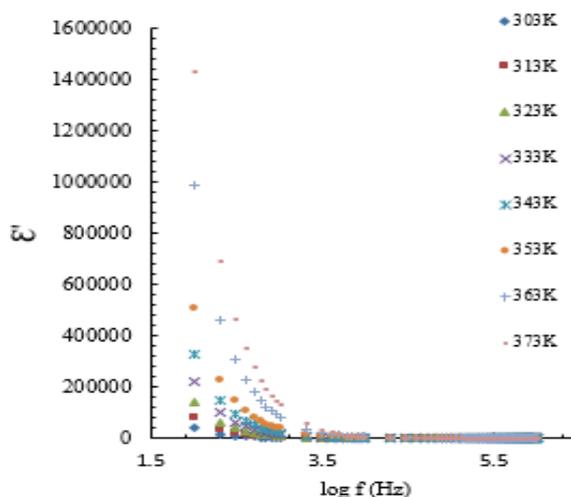


Fig. 3. Plot of dielectric loss with frequency of the SPEs polymer at different temperature.

The phenomenon arises from charge accumulation at the grain boundaries and at the electrode interfaces. At high frequency, charge is well dispersed in the bulk rather than at the interface as the result of unresponsive dipoles at high frequency due to the space charge [13,15]. Hence, the values at high frequency are almost constant. The trend shows high dielectric constant at low frequency region, while it exhibits low dielectric constant value at high frequency; shows that samples are non-Debye type.

Polarized Optical Microscope

Figure 4 shows POM micrographs for pure and salted system of MG30-PEMA. Figure 4(a) show well dispersed surface morphology of pure MG30-PEMA sample at 50wt% PEMA composition. Upon the addition of LiCF_3SO_3 it is observed that co-continuous morphology was observed. At 30wt% of LiCF_3SO_3 salt which is the optimum conductivity of the SPEs system figure 4(c), it was observed that the surface becomes smoother and spherulite structure presence in figure 4(b) vanish. This may be due to LiCF_3SO_3 salt has been well dissolved in polymer matrix. The result may be used to support the interaction between salt and the polymer host. The evidence of ion associate or aggregate can be seen from the formation of roughness surface of the thin film in figure 4(d). Addition of LiCF_3SO_3 salt after optimum conductivity increases the surface roughness. This has caused reduction in conductivity due to the formation of crystalline domain, which has lowered the interaction between Li^+ and polymer matrix. This may support the finding of low ionic conductivity after 30wt% composition of LiCF_3SO_3 .

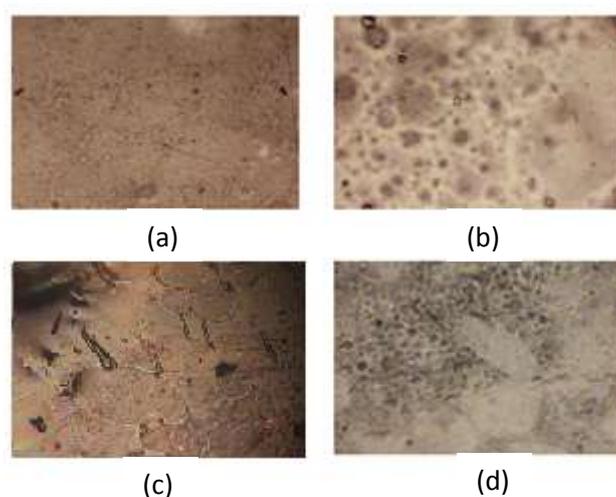


Fig. 3. POM image of SPE membrane for a) Pure MG30-PEMA, b) MG30-PEMA-20% LiCF_3SO_3 c) MG30-PEMA-30% LiCF_3SO_3 d) MG30-PEMA-35% LiCF_3SO_3

XRD

Structural elucidation of the sample was analyzed by X-ray diffraction. Figure 5 shows the XRD diffraction pattern of pure MG30-PEMA, LiCF_3SO_3 and MG30-PEMA- LiCF_3SO_3 films at selected composition. Peak pertaining to LiCF_3SO_3 disappeared in the complexed. The absence of corresponding lithium salt diffraction peak in complexed polymer indicates the complete dissolution of the salt in the polymer salt complexed system. The polymer hump

becomes wider upon addition of LiCF_3SO_3 up to 30 wt% of salt. These suggest that the sample become more amorphous. Recrystallization of LiCF_3SO_3 occurred at high content of salt has reduced the conductivity of the sample. The same phenomenon was reported in [17]. The phenomenon is called ion aggregation, which occurred after 30wt% LiCF_3SO_3 salt composition.

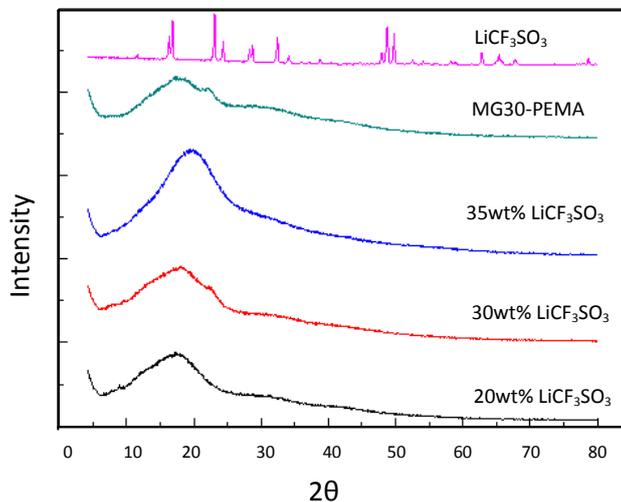


Fig. 4. XRD pattern for MG30-PEMA, pure LiCF_3SO_3 and MG30-PEMA with selected LiCF_3SO_3 salt composition.

CONCLUSION

Addition of salt composition has witnessed the dielectric value to increase with the increase of LiCF_3SO_3 composition. Dielectric constant value is high at low frequency and almost constant at high frequency concluded that the sample exhibits non-Debye type. The POM image analysis supports the conductivity studies. The conductivity reduces after optimum conductivity due to ion association. Complexation between polymer and salt was supported by XRD analysis.

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