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The Coagulation Impact of 50% Epoxidised Natural Rubber Chain in Ethylene Carbonate-Plasticized Solid Electrolytes

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Summary: In this research, thin, soft and flexible free standing films can be obtained from poly (methyl methacrylate) (PMMA)/50% epoxidised natural rubber (ENR 50)/ lithium triflate ($LiCF_3SO_3$) blends. However, phase separation is observed on the surface of the films which indicates that the blending is not homogeneous. The blend became more homogeneous when ethylene carbonate (EC) plasticizer is introduced into the blend system. However, the anti-plasticization effect of EC on ENR 50 occurs at lower concentration of EC at which the rubber became coagulated due to immiscibility of the rubber with EC plasticizer during solution casting. These ENR 50 coagulates can be observed as large solid structures in the Field Emission Scanning Electron Microscope (FESEM) micrographs of the EC-plasticized rubber-based electrolytes. The presence of these coagulates, hinder the migration of lithium ions in the system and also trap the lithium ions within the coil. This in turn reduced the number of free lithium ions that contribute to the ionic conduction. As a result, the conductivity of the un-plasticized PMMA/ENR 50/$LiCF_3SO_3$ film dropped drastically by two orders of magnitude.

Keywords: blends; conducting polymers; poly(methylmethacrylate); rubber

Introduction

To date poly (methyl methacrylate) (PMMA)-based gel electrolytes have received much attention and have been tested in electrochemical devices.[1,2] These systems exhibit high ionic conductivity at room temperature and gave better interfacial properties towards the lithium electrodes when compared to Polyacrylonitrile (PAN) based gel.[2,3] Following these studies, several systems based on PMMA have been applied on other application such as in electrochromic devices.[4,5] Due to its good optical properties, PMMA has become a good candidate for non-liner optical applications in communicational technology.[6]

The most serious drawback of plasticized gel-based PMMA system is poor mechanical property[7] and to date this problem remains unsolved. Mechanical properties can only be improved by modifying the polymer-solvent ratio. However, these will adversely affect the conductivity of the material. High Ionic conductivity of 10^{-4}S/cm can only be reached at about 100 °C.[8]

Blending the polymer with another polymer can circumvent problems associated with poor mechanical properties. Polymer blending is one of the useful techniques for designing new materials with various properties. Among the advantages of employing this method are simplicity of preparation and easy to control physical properties by compositional change.[9,10] The new polymer blends often exhibit properties that are superior compared to the properties

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of each individual component polymer[11,12]. Rhoo et al.[7] has proven the blend concept in poly(vinyl chloride) (PVC)/PMMA electrolyte system. On the other hand, Kim *et al.*[13] demonstrated the use of PVC/PMMA blend in lithium ion polymer batteries. The mechanical strength of PMMA is increased as the content of PVC is increased. However, the conductivity of the system is decreased due to poor adhesion that leads to the increase of interfacial resistance.

Recently, the use of modified natural rubber in polymer electrolyte systems has received much attention.[13–16] This is due to their distinctive characteristic such as low glass transition temperature, T_g, soft elastomer, good elasticity and adhesion characteristics at room temperature that making them a suitable candidate in polymer electrolyte systems. With these characteristics, it is predicted to give excellent contact between an electrolytic layer and an electrode in batteries. Therefore, in this work 50% epoxidised natural rubber (ENR 50) will be blended with the PMMA host to improve the brittle properties of the PMMA films and therefore, a freestanding film of PMMA can be obtained.

However, ENR has a poor aging resistance[17] that can be improved by introducing a base, a plasticizer or an antioxidant. In polymer electrolytes, plasticizer or mixed plasticizers are added to soften rigid polymers, increase process ability and to lower the glass transition temperature, T_g, of a polymer or polymer blend. Therefore, it will increase the segmental motion of the polymer backbone hence assist the transport of ions along the polymer chain. Furthermore, the addition of plasticizers help to increase the dissolution of salts and dissociation of ion pairs hence increase the number of free ions. The plasticizers impart salt solvating power and high ion mobility to the polymer electrolytes.

There are several plasticizers that had been used as a plasticizer for the above mentioned purposes in order to enhance the ionic conductivity of PMMA-based electrolytes such as 1,3-dioxolan-2-one (ethylene carbonate, EC),[18] 4-Methyl-1,3-dioxolan-2-one (propylene carbonate, PC),[19] dimethyl carbonates (DMC),[20] dimethyl phthalate (DMP),[20] dibuthyl phthalate (DBP),[21] N,N-dimethylmethanamide (DMF),[22] *etc*. Among them, the most widely used plasticizers are EC and PC due to their low molecular weight, low viscosity, high dielectric constant and high boiling point.

Experimental Part

Materials

PMMA (ALDRICH, Mw = 120,000), tetrahydrofuran, THF (MERCK), lithium triflate $LiCF_3SO_3$ (ALDRICH) and EC (MERCK) were used without further purification. ENR 50 was obtained from Guthrie Polymer Sdn. Bhd. Siliau, Negeri Sembilan, Malaysia.

Preparation of Blends

PMMA and ENR 50 stock solutions were prepared separately by dissolving the polymers in THF by continuous stirring with a magnetic stirrer. The two polymer solutions were then mixed in a beaker together with $LiCF_3SO_3$ salt. The concentration of PMMA, rubber and salt were fixed in all samples preparation. Solutions were stirred for about 24 hours. All the preparations steps were done in a glove box (MBraun UNIlab) to avoid the presence of moisture that will The electrolyte solutions were then cast into glass petri dishes and left to dry by solvent evaporation at room temperature. The films obtained were further dried in an oven at 50 °C for another 48 h. The solvent free films were then kept at ambient conditions in a desiccator containing fused silica gel until further use.

Measurements

Scanning Electron Microscopy

The surface morphology of the samples prepared were observed by using Leo Fourier Extended scanning electron microscope at

Faculty of Mechanical Engineering, UiTM Shah Alam.

Impedance Spectroscopy

To measure the impedance of the films, the samples were cut into round shape that fit the size of the electrodes. The samples were then sandwiched between the two stainless steel blocking electrodes with a diameter of 2 cm. A Hioki 3532-50 LCR HiTester was used to perform the impedance (Z) measurement for each electrolyte films over the frequency range of 100 Hz to 1 MHz. The conductivity measurements were carried out from room temperature (26 °C) to 86 °C. From the Cole-Cole plots (plot of imaginary part of the impedance (Zi) versus the real part of the impedance (Zr)) obtained, the bulk resistance, R_b of each sample was determined by extrapolating the plot until it touches the x-axis (Figure 6). The conductivity (σ) of the samples were then calculated using the following equation:

$$\sigma = l/\mathrm{R_b A}$$

where l = sample thickness (cm), A = effective contact area of the electrode and the electrolyte (cm^2) and R_b = bulk resistance (Ohm).

Results and Discussion

The Formation of PMMA/ENR 50/LiCF$_3$SO$_3$/EC Electrolytes Films

Thin, soft and flexible free standing films were obtained from both un-plasticized and plasticized PMMA/ENR 50/LiCF$_3$SO$_3$ electrolytes. Phase separation can be observed on the surface of the films which indicate the immicibility of the polymers and the in-homogeineity of the blending. However, it was almost diminishing and insignificant when EC plasticizer was added into the blend suggesting the role of EC plasticizer in enhancing the mobility (viscosity) of the ENR 50 hence allowing it to extend into the PMMA phase. Thus, the blend became more homogeneous and hence no obvious phase separation can be observed as illustrated in Figure 1.

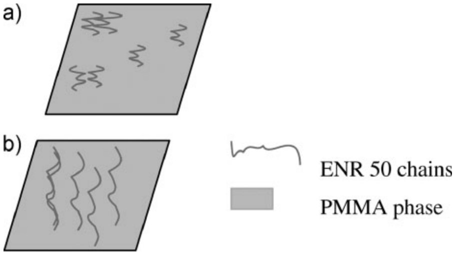

Figure 1.
ENR 50 chains in PMMA phase (a) without plasticizer and (b) with plasticizer.

FESEM Study on the Morphology of PMMA/ENR 50/LiCF$_3$SO$_3$/EC Electrolytes Films

The FESEM micrograph for un-doped PMMA (Figure 2) exhibits rough bulging structures of various sizes and shapes. However, these bulging structures were suppressed when a viscous phase of ENR 50 was introduced into the system hence resulting in the formation of craters (Figure 3). Phase separation can also be observed from the FESEM micrographs of the blends which confirm the in-homogeneity of the blending. The absence of craters produced a smoother surface of the blends when LiCF$_3$SO$_3$ salt was doped into the blend system (Figure 4).

Large solid structures were noted in the FESEM micrograph of the plasticized PMMA/ENR 50/LiCF$_3$SO$_3$ electrolyte as

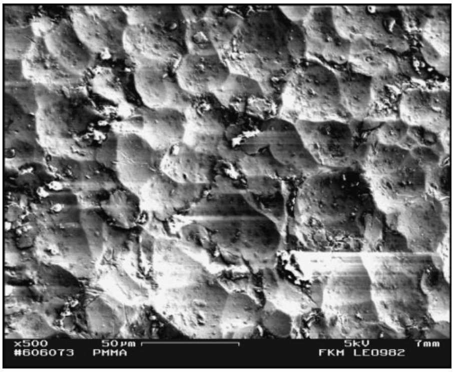

Figure 2.
FESEM micrograph for pure PMMA.

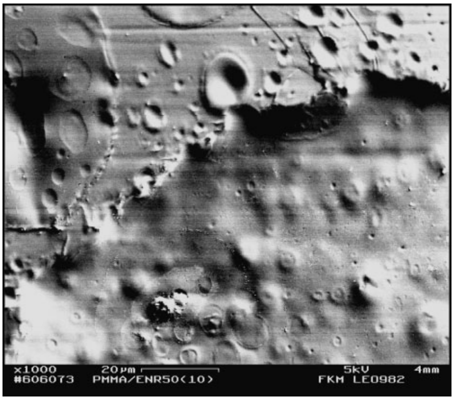

Figure 3.
FESEM micrograph for PMMA/ENR 50 blend.

soon as 20% of EC plasticizer was introduced in the system (Figure 5(a)). This large solid structure may be due to the formation of ENR 50 coagulates that is formed due to immiscibility of the rubber with EC plasticizer during solution casting. However, as the amount of EC was increased up to 60%, the morphology of the system was improved in which the large solid structure of ENR 50 coagulates were almost diminishing (Figure 5(b)–(c)). As the amount of EC was increased, the viscosity of ENR 50 chain may be reduced and therefore, the coagulated ENR 50 chain became disentangle hence eliminating the structure of ENR 50 coagulates.

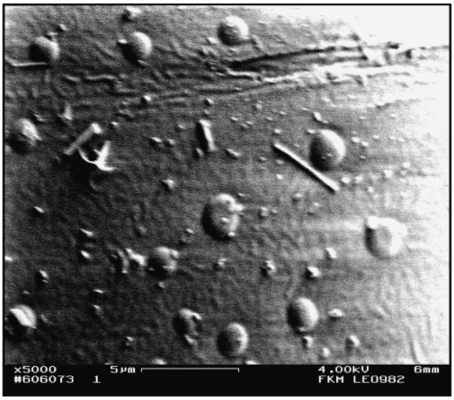

Figure 4.
FESEM micrograph for FESEM micrograph for PMMA/ENR 50/$LiCF_3SO_3$ electrolyte.

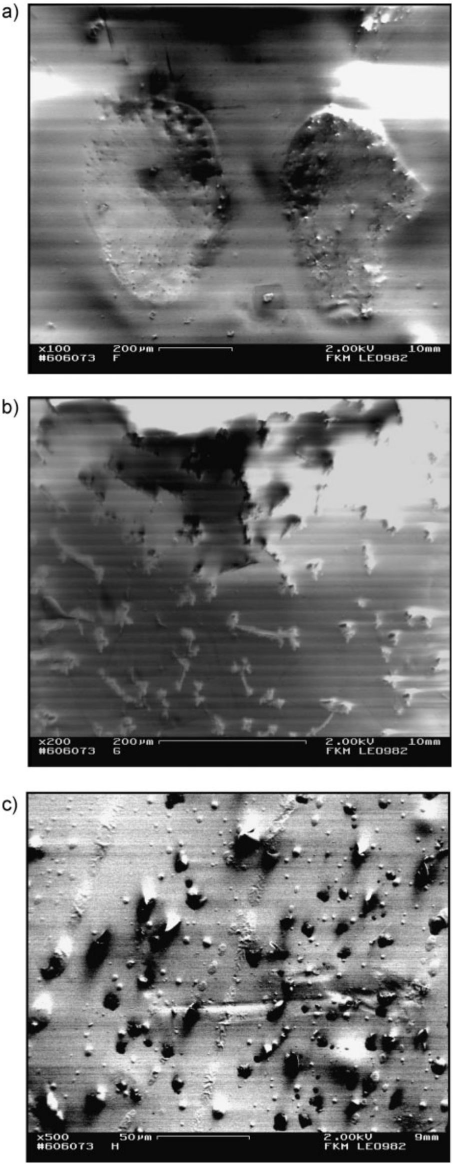

Figure 5.
FESEM micrographs for PMMA/ENR 50/$LiCF_3SO_3$ electrolytes when plasticized with (a) 20% (b) 40% and (c) 60% of EC.

This may also explained why the morphology of the films were improved at higher concentration of EC the.

Ionic Conductivity

The Cole-Cole plots for both un-plasticized and plasticized PMMA/ENR 50/$LiCF_3SO_3$ systems display a depressed semi-circle

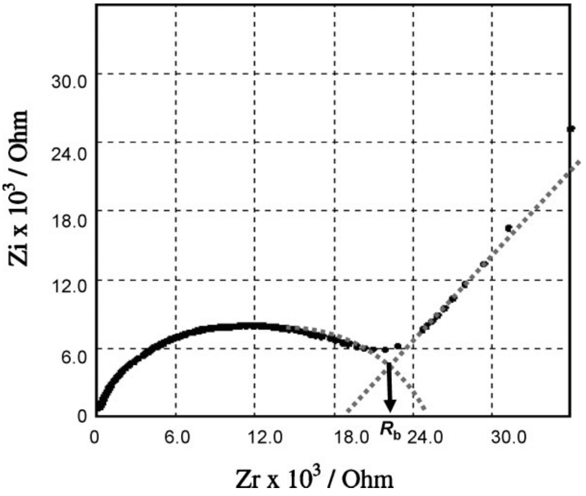

Figure 6.
Cole-Cole plots for PMMA/ENR 50/$LiCF_3SO_3$ films when plasticized with 60% of EC.

(Figure 6) which confirms that the films is an ionic conductor.[23] The appearance of the tail on the right side of the semi-circle indicates the existence of the constant phase element. However, for a non-ionic conducting system, like the un-doped PMMA and ENR 50 films, the depressed semi-circle pattern was not appeared in their Cole-Cole plots (Figure 7).

Figure 8 represents the average conductivity of PMMA/ENR 50/$LiCF_3SO_3$/EC system as a function of temperature. It was noted that the conductivity of the un-plasticized PMMA/ENR 50/$LiCF_3SO_3$ film dropped drastically as soon as EC plasticizer was added into the electrolyte system.

This contradictory result may be due to the anti-plasticization effect of the EC plasticizer[24] to the electrolyte system. In the presence of only 20% of EC, the ENR 50 begins to coagulate due to immiscibility of the rubber with the plasticizer. The

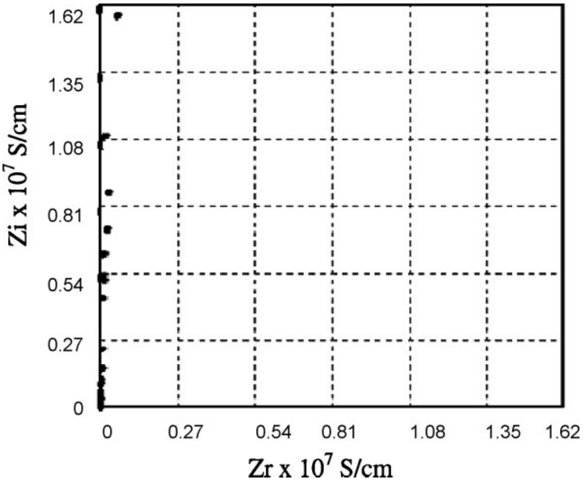

Figure 7.
Cole-Cole plot for pure PMMA film at room temperature.

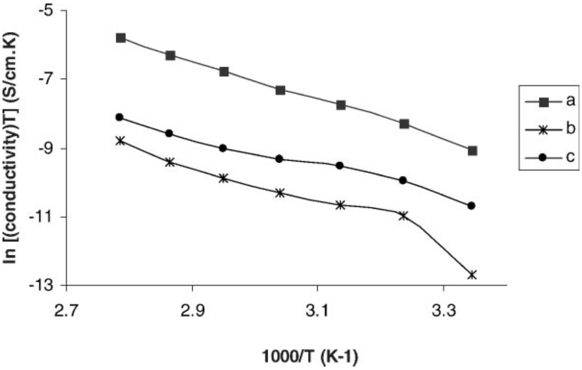

Figure 8.
Plot of log conductivity versus temperature for PMMA/ENR 50/LiCF$_3$SO$_3$ films when plasticized with (a) 20%; (b) 40% and (c) 60% of EC.

presence of such coagulates can be observed from the FESEM micrographs of these EC-plasticized rubber-based systems (Figure 5). These ENR 50 coagulates can be visualized as ''solid'' like medium that occupying the polymer blend matrix thus hinder the transport of lithium ion. Therefore the ions have to move indirectly along a convoluted path (Figure 7(a)). The presence of ENR 50 coagulates may also trap the lithium ions within the coil (Figure 7(b)) hence decreased the number of free ions.

However, according to Jackson and Caldwell,[25] beyond certain concentration, the anti-plasticizer may reverts to a plasticizer and thereafter exhibits normal plasticizer behaviour. As in this case, the plasticization effect of EC plasticizer starts to occur when more than 20% of EC was added into the system. Above this concentration, it was able to increase the ENR 50 chain flexibility and hence facilitate the coagulated ENR 50 chains to disentangle. Therefore it reduced the structure of ENR 50 coagulates in the system thus improved the morphology of the blend. As a result a more favourable medium for ion migration was created and subsequently increased the conductivity of the plasticized system.

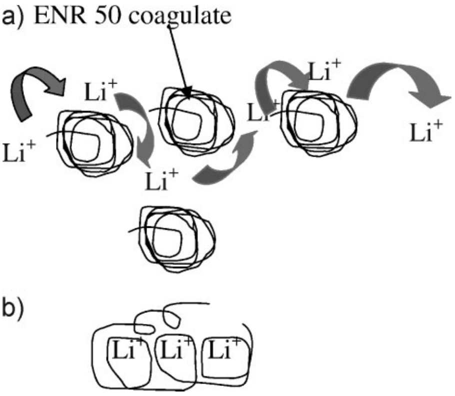

Figure 9.
Illustrations on (a) The transport of lithium ion along a convoluted path and (b) Lithium ion trapped in the ENR 50 coil.

Conclusions

The addition of EC plasticizer was observed to improve the phase separation of the un-plasticized PMMA/ENR 50/LiCF$_3$SO$_3$ electrolyte. However, it was found that ENR 50 chain coagulated due to its incompatibility with the EC plasticizer at lower concentration of plasticizer hence causing a significant drop in their conductivity. Therefore, it can be concluded that EC plasticizer is not a suitable plasticizer for an electrolyte system containg rubber.

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