

Characteristics Of PMMA-Grafted Natural Rubber Doped With LiCF_3SO_3

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Abstract

Varying ratios of polymer electrolyte films containing MG30 doped with LiCF_3SO_3 were prepared using the solution casting method. Pure MG30 with 30 wt. % LiCF_3SO_3 was found to exhibit the highest conductivity at $5.62 \times 10^{-8} \text{ S cm}^{-1}$ at ambient temperature. Analyses by X-ray diffraction (XRD), scanning electron microscope (SEM), fourier transform infrared (FTIR) spectroscopy and electrochemical impedance spectroscopy (EIS) have been carried out to investigate the interaction between the polymer and salt.

Keywords: natural rubber, PMMA

1. INTRODUCTION

In recent years, many research efforts have been devoted to the development of solid-state polymer electrolytes [1,2]. This is because solid polymer electrolytes have promising aspect for applications in solid-state electrochemical devices such as high energy density rechargeable batteries [3], electrochromic windows, fuel cells [4], sensors, photoelectrochemical solar cells and supercapacitors [5]. Solid polymer electrolytes have many advantages such as minimal leakage problem, non-corrosive, non-volatile and easy to form into thin films [6].

In order to improve the mechanical properties and also increase the conductivity of solid polymer electrolytes for applications in electrochemical devices, various techniques have been employed such as blending [7,8], plasticization [9], modification [10] of polymer and incorporation of fillers [11]. Other than that, polymers have been grafted to improve the mechanical properties of polymer, increase adhesion to the electrode, increase solvent intake, change solubility characteristics and enhance the

conductivity of polymer electrolytes [12-14].

In this study, the potential of 30 % poly(methyl methacrylate)-grafted natural rubber (MG30) as the polymer host doped with LiCF_3SO_3 will be investigated. The non-polar natural rubber in MG30 gives the desired properties in its elasticity while PMMA provides the path for ion conduction to occur [15]. Besides that, MG30 also display properties such as good retention at elevated temperatures and good electrical properties [16]. MG30 was mixed with LiCF_3SO_3 in different ratios in a binary solvent system which consists of toluene and tetrahydrofuran (THF) to study the effect of the LiCF_3SO_3 on the MG30.

2. EXPERIMENTAL

2.1 Sample Preparation

All polymer electrolyte samples were prepared by using solvent casting method. The rubber MG30 was obtained commercially and lithium trifluoromethanesulfonate (LiCF_3SO_3) was purchased from Aldrich. Toluene and tetrahydrofuran (THF) both purchased from J.T. Baker

were used as solvents. Samples of MG30-LiCF₃SO₃ films with wt. % ratios of 100/0, 95/5, 90/10, 85/15, 80/20, 75/25, 70/30, 65/35, 60/40 and 55/45 were prepared. MG30 and LiCF₃SO₃ were dissolved in toluene and THF, respectively before being mixed together. The solutions prepared were stirred for 72 hours at ambient temperature. The homogeneous solutions were then cast onto glass petri dishes and allowed to dry to form films at room temperature.

2.2 X-ray Diffraction (XRD)

X-ray diffraction was carried out to determine the amorphous/crystalline nature of the materials. The diffraction intensity of MG30-DBC- LiCF₃SO₃ films was measured by using X-ray diffractometer (Siemens D5000) with operating voltage and current of 40 kV and 40 mA, respectively. The X-ray wavelength is 1.5406 Å at 2 theta angles between 5° and 80° with a step size of 0.04°.

2.3 Scanning Electron Microscopy (SEM)

The surface morphology of the samples was characterized using S 440-Leica Scanning Electron Microscope (SEM) instrument.

2.4 Fourier Transform Infrared Spectroscopy

Infrared spectra of the resultant films were recorded using Thermo Scientific/ Nicolet iS10 at ambient temperature in the wave numbers region between 4000-650 cm⁻¹ to verify the occurrence of complexation between the MG30 and LiCF₃SO₃.

2.5 Electrochemical Impedance Spectroscopy (EIS)

The ionic conductivity of the films was measured by ac impedance method using HIOKI 3531-01 LCR Hi-Tester, in the frequency range of 50 Hz to 1 MHz. Each film was sandwiched between two stainless

steel disc electrodes, and the conductivity was performed at ambient temperature.

3. RESULTS AND DISCUSSION

Fig. 1 depicts the X-ray diffractograms for pure MG30 and LiCF₃SO₃ doped MG30 films. It can be inferred that the samples are amorphous. Broad peaks are observed between $2\theta = 10^\circ$ to 25° . There is no significant crystalline peak in the XRD data and this could probably be due to the good capability of the MG30 polymer to retain the salt within its structure [17]. This implies that the carbonyl (C=O) and carboxyl (-COO) groups of PMMA have interacted with Li⁺ from the salt.

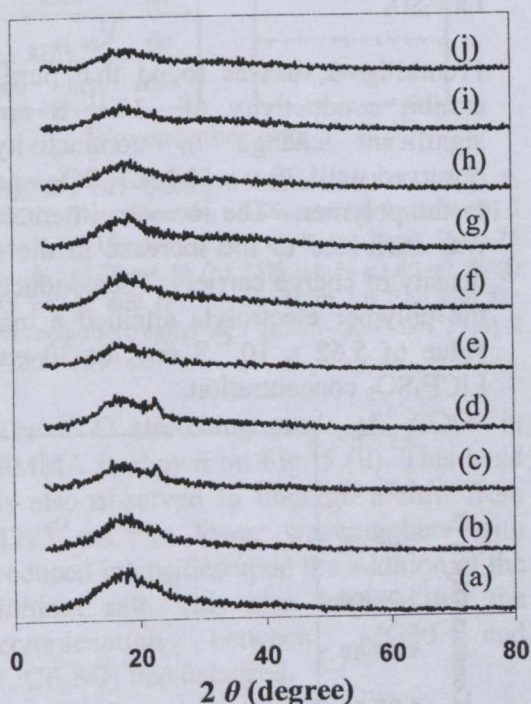


Fig. 1 X-ray diffraction data of the MG30 containing (a) 0 wt. %, (b) 5 wt. %, (c) 10 wt. %, (d) 15 wt. %, (e) 20 wt. %, (f) 25 wt. %, (g) 30 wt. %, (h) 35 wt. %, (i) 40 wt. % and (j) 45 wt. % of LiCF₃SO₃

The semicircle and spike observed in the impedance plots of Fig. 2 indicated the occurrence of ion diffusion [18].

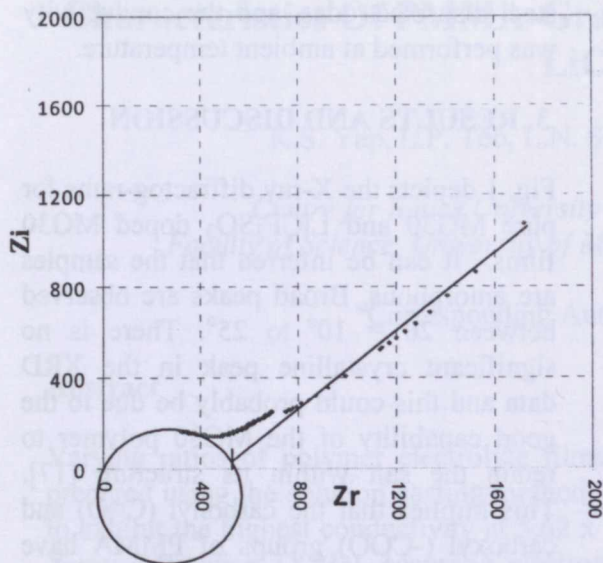


Fig. 2 Impedance plot of MG30 containing 30 wt. % LiCF_3SO_3

From Fig. 3, it was found that pure MG30 exhibit conductivity of $\sim 10^{-11} \text{ S cm}^{-1}$. No significant change in conductivity was observed until 20 wt. % LiCF_3SO_3 was added to the polymer. The increase in conductivity was attributed to the increase in the number density of charge carriers. The conductivity of the polymer electrolyte attained a maximum value of $5.62 \times 10^{-8} \text{ S cm}^{-1}$ at 30 wt. % of LiCF_3SO_3 concentration.

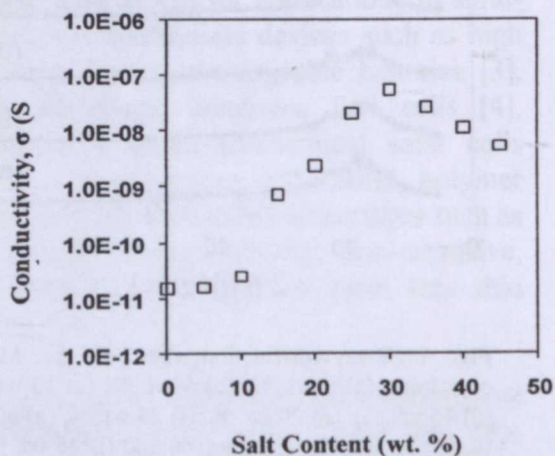


Fig. 3 Ionic conductivity against LiCF_3SO_3 concentration (wt. %)

Further addition of salt led to the decrease in room temperature conductivity. This could be due to the occurrence of ion association into neutral ion aggregates and/or due to the viscosity of the samples, which could have taken effect at high salt concentration. Fig. 4 (a) to (h) depict SEM micrographs of

LiCF_3SO_3 doped MG30 at 1000 magnification.



(a) 10 wt. %



(b) 15 wt. %



(c) 20 wt. %



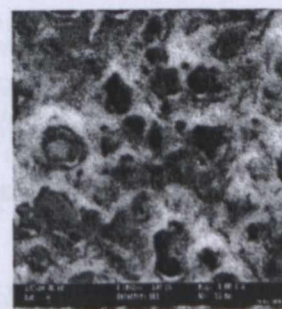
(d) 25 wt. %



(e) 30 wt. % LiCF_3SO_3 MG30



(f) 35 wt. % LiCF_3SO_3 MG30



(g) 40 wt. % LiCF_3SO_3 MG30



(h) 50 wt. % LiCF_3SO_3 MG30

Fig. 4 SEM micrographs of various samples of MG30 doped with different content of LiCF_3SO_3

MG30 films doped up to 30 wt. % LiCF_3SO_3 were observed to have smooth

surface with some burnt marks. The sample which contained 30 wt. % LiCF_3SO_3 has a smooth surface. For the sample doped with 35 wt. % salt, some crystalline structures appear to protrude the surface. These crystalline structures may be attributed to ion aggregates that resulted from the association of ions that usually occurs at high salt concentrations and thus leads to a drop in conductivity. The reason why the ion aggregates were able to protrude the surface was probably due to the increase in viscosity as a result of increment in salt content which delayed the liquid solution from joining together to form a continuing surface. Thus a porous surface may be formed, which is more clearly shown in the micrograph of sample doped with 40 wt. % LiCF_3SO_3 . The porous nature of the surface of the sample with 50 wt. % salt is also obvious.

It has been previously reported that the most prominent feature of the ester group in PMMA appears as a strong and sharp peak of the carbonyl band ($\text{C}=\text{O}$) in the range of $1750 - 1735 \text{ cm}^{-1}$ [19,20]. Fig. 5 (i) and (ii) show the FTIR spectra of pure MG30 and LiCF_3SO_3 -doped MG30 films in the wavenumber range of 1600 to 2000 cm^{-1} , and 1200 to 1600 cm^{-1} , respectively. In Fig. 5 (i), it has been shown that pure MG30 sample displayed the characteristic peak of $\text{C}=\text{O}$ stretch located at 1731 cm^{-1} which is due to the ester group contained in the grafted PMMA side chain. When LiCF_3SO_3 was added into MG30, the FTIR spectra for all doped polymer films showed that the peak of $\text{C}=\text{O}$ band had shifted to lower wavenumbers from the original peak at 1731 cm^{-1} . This is in agreement with literature which reported the shift of $\text{C}=\text{O}$ peak of PMMA to lower wavenumbers in the polymer salt complexes [19,20]. The shift of the $\text{C}=\text{O}$ band indicated that possible complexation between MG30 and LiCF_3SO_3 has occurred through the coordination of Li^+ from the salt with the oxygen atom present in the carbonyl group of PMMA-grafted natural rubber chain [15].

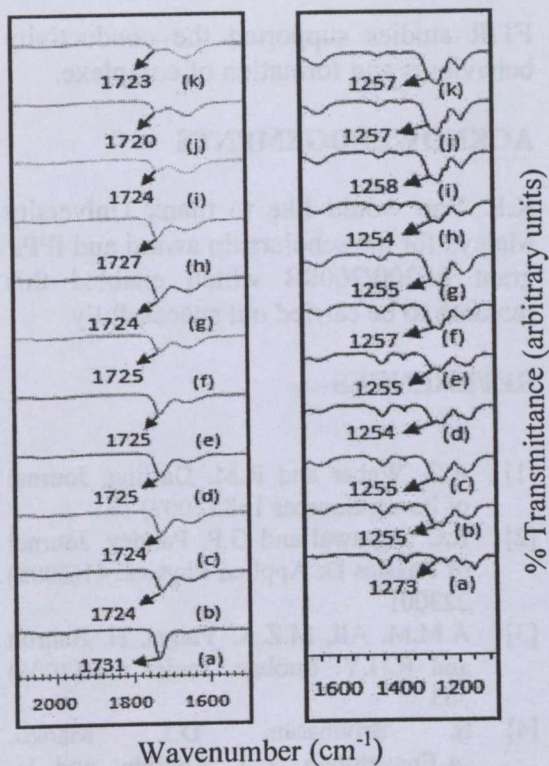


Fig. 5 FTIR spectra which showed the shifts in MG30 films upon the addition of (a) 0 wt. % (b) 5 wt. % (c) 10 wt. % (d) 15 wt. % (e) 20 wt. % (f) 25 wt. % (g) 30 wt. % (h) 35 wt. % (i) 40 wt. % (j) 45 wt. % and (k) 50 wt. % of LiCF_3SO_3 in the wavenumber region of i $1600 - 2000 \text{ cm}^{-1}$, and ii $1200 - 1600 \text{ cm}^{-1}$

The $\text{C}-\text{O}$ stretching mode of $-\text{COO}-$ in PMMA is shown on Fig. 5 (ii). This band is also observed to undergo a shift from 1273 cm^{-1} to lower wavenumbers with reduced intensities upon the addition of the lithium salt. This also implies that the complexation between MG30 and LiCF_3SO_3 had occurred.

4. CONCLUSIONS

It was found that MG30 was still present in the amorphous state with the addition of up to 50 wt. % of LiCF_3SO_3 concentration. Evidence has also been obtained which shows that complexation has occurred between the salt and MG30. The MG30- LiCF_3SO_3 solid polymer electrolyte system with the ratio of 70:30 exhibits the highest room temperature ionic conductivity of $5.615 \times 10^{-8} \text{ S/cm}$. The SEM, XRD and

FTIR studies supported the conductivity behaviours and formation of complexe.

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