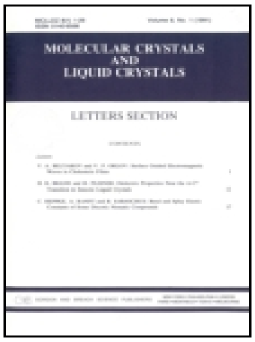

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Effect of $LiCF_3SO_3$ on L-Chitosan/PMMA Blend Polymer Electrolytes

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This paper focuses on the effect of lithium triflate ($LiCF_3SO_3$) on the structural and conduction properties of lauroyl (L)-chitosan/poly(metylmethacryalate) (PMMA)-based polymer electrolytes. Films of L-chitosan/PMMA blends and its complexes were prepared using a solution-casting technique. The ionic conductivity of the system was measured over a wide range of frequency between 50 Hz-1 MHz. Impedance plot for the samples demonstrates two well-defined regions. The disappearance of the high frequency semicircular region led to a conclusion that the current carriers are ions. Sample with 30 wt% of $LiCF_3SO_3$ showed the highest conductivity of $7.59 \pm 3.64 \times 10^{-4}$ Scm^{-1} at room temperature. This is consistent with the results obtained from infrared spectroscopy.

Keywords L-chitosan; PMMA; conductivity; FTIR; polymer electrolytes

1. Introduction

Solid polymer electrolytes (SPE) serve as one alternative to fulfil the demand of inexhaustible sources of derivatives energies such as solar and wind system. They have many advantages such as having high energy density, electrochemical stability and ease in processing [1]. A number of studies have attempted to develop and characterize SPEs from polymers including poly(ethylene oxide) (PEO), poly (vinyl alcohol) (PVA) and strong acids [2]. However due to environmental issues, SPEs based on natural polymer have emerged as an important ionic conductor because these types of polymers are renewable, easily available, cheap and have good physical and chemical properties [2, 3]. Natural polymers, on the other hand, have several disadvantages including their dominant hydrophilic characteristic, fast degradation rate and in some cases, insufficient mechanical properties particularly in ambient temperature [4]. Therefore, in principle, the properties of polymer from natural resources can be improved through blending processes with synthetic polymers. The objective is not to change the properties of the polymer but to capitalize the maximum possible performance of the blend itself.

Chitosan can be considered as one of the natural polymer candidates to act as polymer host for conducting materials. A chitosan monomer consists of hydroxyl and amine

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functional groups which can act as electron donors and could interact with metal salt [5]. However, the applications of chitosan were limited due to the presence of strong intra and intermolecular hydrogen bond [6, 7] from the primary amino groups' residues which resulted in the formation of linear aggregates with extensive crystallinity [8]. This rigid crystalline structure makes chitosan poor in processability and insoluble in aprotic solvent [6, 7]. Therefore, in order to improve its ability, acyl modification of chitosan was carried out in the present study. The presences of lone pair electron in the structure of acylated chitosan such as L-chitosan allowed complexation with the salt. However, since the prepared polymer is very sticky [9] it must be blend with synthetic polymer in order to improve its mechanical stability for the application in lithium based electrochemical devices.

In the present study, L-chitosan was blended with PMMA. PMMA is one of the host polymers previously used in the plasticized polymer electrolyte, which was first reported by Iijima et al. [10]. To the best of the author's knowledge, the report on L-chitosan/PMMA solid polymer electrolytes is still limited. Therefore in an attempt to look for a better lithium ion conducting polymer electrolytes, polymer electrolytes based on L-chitosan/PMMA blend by varying lithium salt concentration is investigated and their characterizations will be discussed in this present paper.

2. Experimental

2.1. Materials

Chitosan flake and PMMA with high molecular weight purchased from Sigma were used without further purification. Pyridine and tetrahydrofuran (THF) purchased from F.S. Chemical with purity of 99.5% were used as solvents. Lauroyl chloride (97.5%, Fluka) was used as the reacting agent. $LiCF_3SO_3$ with purity over 96% obtained from Sigma was used as a doping salt for SPE preparation.

2.2. Sample Preparations

L-chitosan was prepared initially using method found elsewhere [9]. Both L-chitosan and PMMA solution was prepared separately by dissolving each polymer in 100 ml THF. The L-chitosan and PMMA solution were then mixed in different percentage (w/w) to form the blend polymer. (Table 1). Prior to the preparation of SPE, $LiCF_3SO_3$ was added into

Table 1. Various composition of L-chitosan and PMMA

Designation	L-chitosan (wt%)	PMMA (wt%)
PLC	100	0
PLC1	0	100
PLC2	60	40
PLC3	50	50
PLC4	40	60
PLC5	30	70
PLC6	20	80
PLC7	10	90

Table 2. Variation composition of the polymer electrolytes

Designation	Composition (wt%)
LCP	40 wt.% L-chitosan: 60 wt.% PMMA
LCP10	LCP: $LiCF_3SO_3$ (10:90)
LCP20	LCP: $LiCF_3SO_3$ (20:80)
LCP30	LCP: $LiCF_3SO_3$ (30:70)
LCP35	LCP: $LiCF_3SO_3$ (35:65)
LCP40	LCP: $LiCF_3SO_3$ (40:60)
LCP45	LCP: $LiCF_3SO_3$ (45:55)

the homogenous solution of L-chitosan/PMMA with desired amount (Table 2) and stirred continuously for several days. The homogenous and viscous solution obtained were cast in Teflon petri dishes and allowed to evaporate slowly at room temperature for several days. The free standing films obtained were kept in a drying cabinet for continuous drying before further analysis.

2.3. Sample Characterization

The XRD pattern were recorded and scanned on Shimadzu XRD-6000 with a beam of monochromatic CuKα-X-radiation of wavelength $\lambda = 1.5406$Å over the range of $2\theta = 5°$–$80°$. Scanning electron microscopy (SEM) - Philips XL30 was used to analyze the surface morphology of the samples while FTIR studies were carried out using Perkin Elmer model 1650 in the spectral region of 400 cm^{-1} to 4000 cm^{-1} with 1 cm^{-1} resolution to further confirms of complexations in the samples. Conductivity measurement was carried out using the impedance spectroscopy model HIOKI 3532-50 LCR HiTESTER interfaced to a computer. The thin film in which thickness was measured by using a digital micrometer screw gauge was sandwiched between two electrodes of a sample holder with diameter 1.082 cm, under spring pressure. The data was taken over frequency ranges from 50 Hz to 1 MHz at room and elevated temperatures. From the data obtained, imaginary part of the impedance (Z_i) was plotted versus real impedance (Z_r). Bulk resistance (R_b) from intercept at Z_r axis was determined and the conductivity was calculated using equation (1), where A is the area and t is thickness of the sample, respectively

$$\sigma = \frac{t}{R_b A} \tag{1}$$

3. Results and Discussions

Figure 1(a) illustrates the XRD pattern of pure L-chitosan film. The XRD spectrum show a broad reflection centered at $2\theta = 20°$ together with that of strong reflection at $2\theta = 2{\sim}6°$. Similar results have been reported by Winie and co workers [11] who studied on the structure of hexanoyl chitosan based polymer electrolytes. Meanwhile, Figure 1(b) shows the spectrum of pure PMMA that exhibited a semicrystalline feature which is characterized by two halo diffraction pattern centered at $2\theta = 16°$ and $2\theta = 31.5°$ and two distinct peaks at $2\theta = 21.4°$ and $2\theta = 29°$. This is consistent with that reported by Baskaran et al. [12] as well as Rajendran et al. [13]. Figure 1(c–h) illustrates the XRD pattern of L-chitosan/PMMA

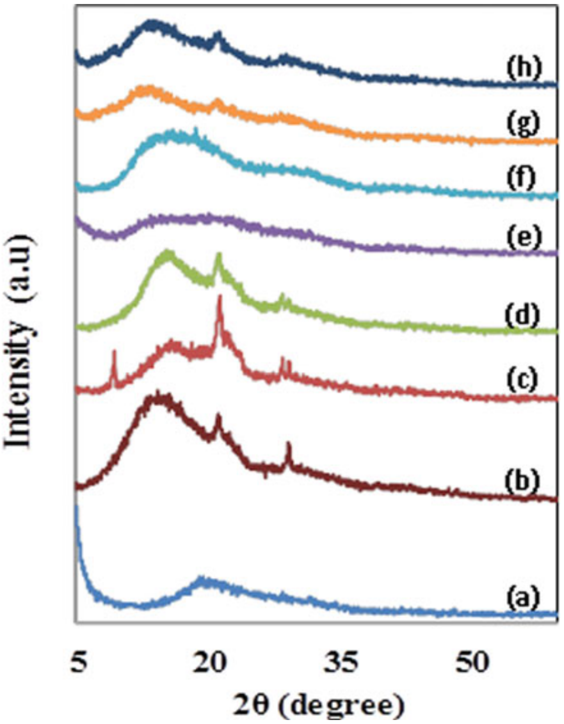

Figure 1. XRD diffraction pattern of samples (a) PLC, (b) PLC1, (c) PLC2, (d) PLC3, (e) PLC4, (f) PLC5, (g) PLC6, and (h) PLC7.

blends at different weight percentages. The intensity of the peaks at $2\theta = 20^0$ decreases with addition of 40% of PMMA and form two halo and the peaks intensity for both halo reduces further when 60% PMMA were added to the blend polymer. This phenomenon shows that introduction of L-chitosan to PMMA has disturbed the semicrystalline nature of PMMA structure.

Scherer length, *L* which is a method of calculating crystallite size using data from XRD was calculated using the equation as follows:

$$L = \frac{k\lambda}{\Delta 2\theta_b \cos\theta_b} \qquad (2)$$

where *k* is the Scherer constant value (0.94), $\lambda = 1.5418$ Å, θ_b is the glancing angle of the peak, $\Delta 2\theta_b$ is the full width at half maximum. The peak at $2\theta = 21.4^\circ$ is chosen to determine *L*. The plot of *L* variation against the percentage blend is shown in Figure 2. It was observed that sample with 40% of L-chitosan and 60% of PMMA has the shortest value of Scherer length thus having the least crystallite size was further chosen for the SPE preparation. Samples with lower crystallite size has lower crystallinity is expected to exhibit higher ionic conductivity [14].

Figure 3 depicts the infrared spectra of the samples in the spectral region ranging from 500 cm^{-1} to 4000 cm^{-1}. Upon addition of 10 wt.% of salt, a broad peak at 3488 cm^{-1} which is characteristic of $LiCF_3SO_3$ was observed to appear confirming that lithium ion has been introduced to the sample. The peaks attributed to L-chitosan and PMMA in the blend at 842 cm^{-1}, 983 cm^{-1}, 1065 cm^{-1}, 1386 cm^{-1}, 1443 cm^{-1}, 1723 cm^{-1}, 2857 cm^{-1}

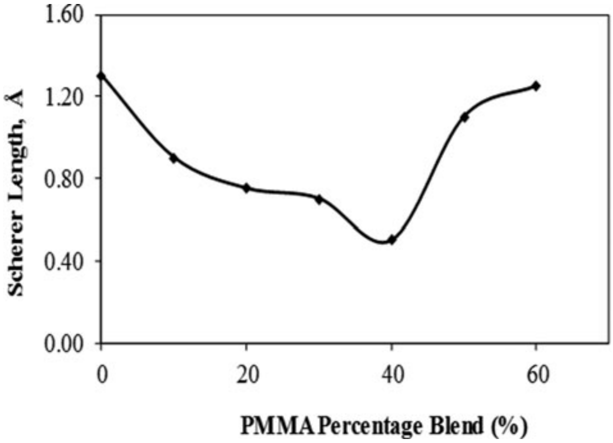

Figure 2. Scherer length for L-chitosan/PMMA blend.

and 2928 cm^{-1} was also observed to shift to 846 cm^{-1}, 977 cm^{-1}, 1035 cm^{-1}, 1385 cm^{-1}, 1447 cm^{-1}, 1719 cm^{-1}, 2856 cm^{-1} and 2926 cm^{-1}, respectively. Other peaks including symmetric SO_3 deformation mode, δ_a (SO_3) of $LiCF_3SO_3$ at 640 cm^{-1} was observed to decrease in intensity with increasing salt content while a small shoulder which appears at

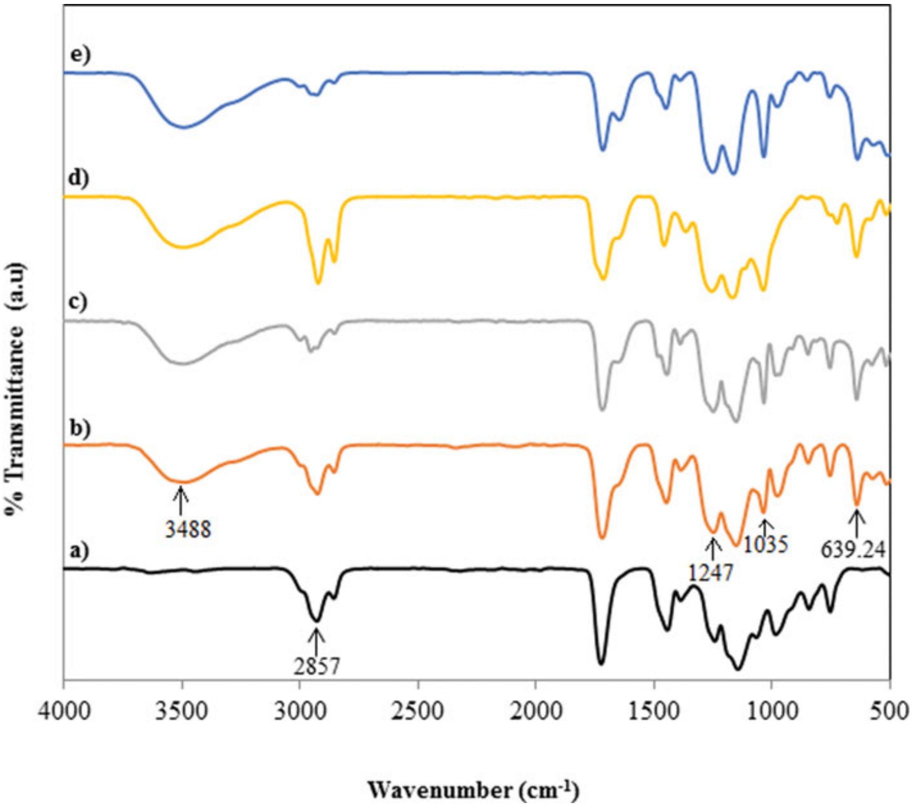

Figure 3. Infrared spectrum of (a) LCP, (b) LCP10, (c) LCP20, (d) LCP30, and (e) LCP40.

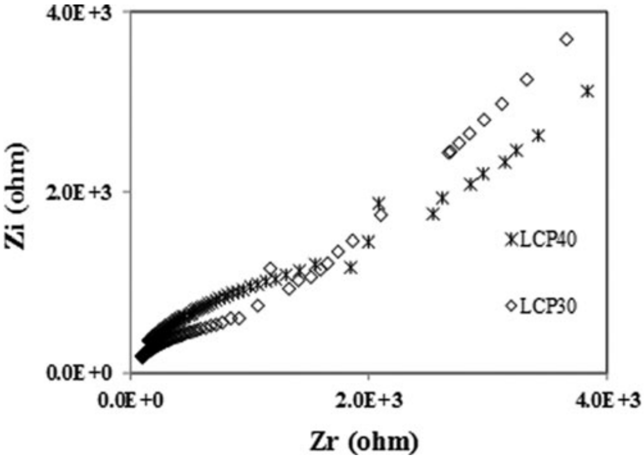

Figure 4. Impedance plot for some selected samples.

1143 cm^{-1} increases with salt content and become a doublet with addition of 40 wt.% of salt. This result may be attributed to the coordination of free lithium ion in the polymer structure [14]. In addition, the presence of the free ions in these complexes could be deduced from the existence of the υ_s (SO$_3$) and υ_s (CF$_3$) peaks at 1035 cm^{-1} and 1247 cm^{-1} which has shifted to 1065 cm^{-1} and 1241 cm^{-1}, respectively. The band at 2857 cm^{-1} assign to υ_s (CH$_2$) vibrations decreases in intensity with salt addition, nevertheless it disappeared when 40 wt.% of salt was added. The disappearance of this peak at 40 wt.% salt could be the result of the overlapping of the 2857 cm^{-1} peak during blending process [15]. All these results support the complexation of lithium ion to the polymer blend.

The impedance plot for some selected samples is shown in Figure 4. The plot consists of both a titled semicircle at high frequency and a spike at low frequency region. The semicircle portion could be observed since both the migration of ion and bulk polarization are physically in parallel. The spike on the other hand is due to the resistive component of the polymer electrolytes which suggest that migration of ions could occur through the free volume of polymer matrix. The bulk resistance R_b was obtained from this plot by taking the intercept at the Z_r-axis. The room temperature electrical conductivity is then calculated using Eq. 1 and the value is tabulated in Table 3.

Table 3. Electrical conductivity at room temperature

Sample	Average conductivity σ (S cm^{-1})
40 wt.% L-chitosan: 60 wt.% PMMA (LCP)	$(6.26 \pm 0.90) \times 10^{-10}$
LCP: LiCF$_3$SO$_3$ (10:90)	$(1.39 \pm 1.06) \times 10^{-09}$
LCP: LiCF$_3$SO$_3$ (20:80)	$(1.47 \pm 0.76) \times 10^{-06}$
LCP: LiCF$_3$SO$_3$ (30:70)	$(7.59 \pm 3.64) \times 10^{-04}$
LCP: LiCF$_3$SO$_3$ (35:65)	$(3.47 \pm 0.52) \times 10^{-05}$

4. Conclusions

In this work, L-chitosan/PMMA based polymer electrolytes films were prepared with the aim of enhancing its ionic conductivity which is suitable for used in further works. This was done by doping the polymer blend with $LiCF_3SO_3$ that causes the conductivity of the complexes to increase by six orders of magnitude. FTIR confirms that complexation has occurred between the polymer blend and the doping salt.

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