Characterization of Polyvinyl Chloride/Polyethyl Methacrylate Polymer Blend for Use as Polymer Host in Polymer Electrolytes

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ABSTRACT: Polyvinyl chloride (PVC) and polyethyl methacrylate (PEMA) were used to prepare polymer blends for use in solid polymer electrolyte. Dynamic mechanical analysis showed that both the storage modulus (E') and the glass transition temperature (T_g) of the PVC/PEMA blend are intermediate between those of the two component polymers. Scanning electron microscopy proved that addition of PEMA into PVC changed the morphology of the blends. The shifts in Fourier transform infrared bands and X-ray diffraction peaks together with the presence of a single T_g suggest that the blends are partially miscible. The blend with 35 wt % PEMA seems to be the most suitable candidate for use as polymer host in polymer electrolyte, because it has the most suitable mechanical property and is the most amorphous blend system. This blend system also has the highest room temperature conductivity value of 4.74×10^{-10} S cm^{-1} amongst other blend systems. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: polymer blend; polymer electrolyte; storage modulus; glass transition temperature; tan δ

INTRODUCTION

Polymer blending is a promising technique to improve the mechanical strength,[1] thermal stability,[2–4] and ionic conductivity[5,6] of polymer electrolytes. This includes PEO/PAN,[7] PVDF-HFP/PAN,[8] PMMA/PVA,[9] PVA/PMMA,[10] and PVDF/PAN.[11] Recently, blends containing polyvinyl chloride (PVC) and polyethyl methacrylate (PEMA) have drawn the attention of many researchers due to its possible application as an electrolyte in lithium batteries.[1,12,13] Amongst those reported in the literature are PVC/PEO,[14] PVDF-HFP/PEMA,[15] PVC-PMMA,[16] PVDF/PVC,[17] PVC/PEO,[18] etc. Other groups of researchers studied on PVC/PEMA blend system.

Fahmy and Ahmed[19] studied on the compatibility, relaxation behavior, and compensation phenomena in amorphous PVC/PEMA polyblend using thermally stimulated depolarization (TSDC) spectrum. They found out that the blends are not compatible enough, because the TSDC spectrum showed more than one peak with different relaxation modes.

One of the factors that influence the conductivity of polymer blend is the miscibility of the blends. Studies by researchers[20–22] proved that miscible blend showed no phase separation between the two polymers. As a result, charge carriers can be easily transported without the presence of blocking phase hence increasing the conductivity. According to the literature, phase separation eventually will lead to obstruction of the cation in the polymer blend, which in turn reduces the conductivity.[23]

Rajendran et al.[24] investigated the effects of various salts and plasticizers on electrical, structural, and thermal properties of PVC/PEMA blends. The blends exhibited maximum ionic conductivity of 10^{-3} S/cm for plasticized PVC/PEMA polymer electrolytes. They also found that high concentration of PEMA caused the film to become gel-like and physically unstable.

Although many have reported on polymer electrolytes based on PVC/PEMA blends; however, to the best of our knowledge, there has been no report on the basic properties of PVC/PEMA blend itself especially on their suitability for use as host for polymer electrolytes. These basic properties include their physical properties such as its stiffness and relaxation phenomenon and its electrical properties. Hence, this work is focused on the investigation of these basic properties in order to determine the most

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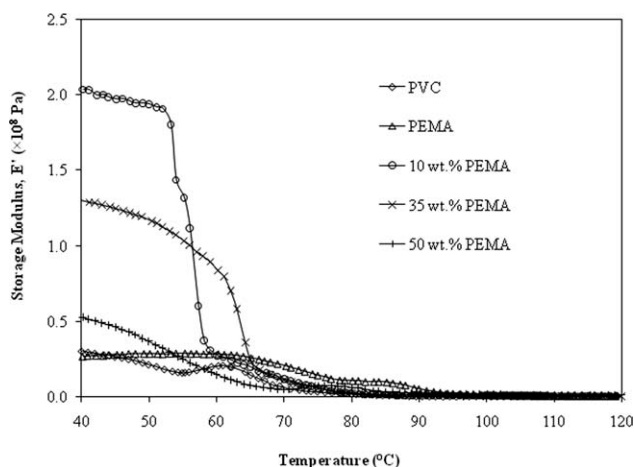
Figure 1 Storage modulus versus temperature for PVC–PEMA blends.

suitable blend ratio to act as polymer host in polymer electrolytes.

MATERIALS AND METHODS

The preparation of PVC-PEMA blends was carried out using solution cast technique. Both PVC and PEMA were purchased from Sigma-Aldrich, USA, with M_w of 233,000 and 515,000 g mol^{-1}, respectively. The mixtures of the two polymers at different ratios were stirred continuously with a suitable solvent for several hours at room temperature until the solutions were formed. The solutions were then cast into different glass petri dishes and allowed to dry in an evacuated glove box. The resulting films were then placed in a vacuum oven for further drying before characterization. All samples were characterized by X-ray diffraction (XRD) using Pro Panalytical XRD spectrometer while Fourier transform infrared (FTIR) was done using FTIR Variant Excalibur 1300 at a resolution of 1 cm^{-1}. The surface morphology was studied by using JEOL JSM-7600F scanning electron microscope. Dynamic mechanical thermal analysis was measured using PERKIN ELMER Dynamic Mechanical Analyzer 8000 under tension mode from 40 to 120°C at heating rate of 1°C/min at a frequency of 1 Hz, and electrochemical impedance spectroscopy was carried out using HIOKI 3532-50 LCR Hi-Tester.

RESULTS AND DISCUSSION

Dynamic mechanical properties

The mechanical properties of both pure polymers and their blends at selected blend ratios are pre-

sented in a plot of storage modulus (E') versus temperature as shown in Figure 1. Storage modulus can be defined as the ratio of stress over strain, and it indicates the stiffness of the material. Pure PVC and PEMA have storage modulus values of 3.8×10^7 and 3.5×10^7 Pa, respectively, at 40°C. The lower storage modulus value of PEMA could possibly be attributed to the fact that PEMA moieties have much higher free volume with ample room for threading or interpenetration of the linear chains of PEMA[25] making it less stiff. From the figure, it can be observed that the values of the storage modulus for all the blends are higher compared to those of either pure polymer. The highest value is obtained for the film with 10 wt % PEMA. This means that this blend ratio has the highest stiffness compared to other blend ratios. The storage modulus is observed to increase with the increase in PVC content. This increase is due to the increase in number of electron acceptors at α-hydrogen of PVC, which facilitates dipole–dipole interaction between carbonyl group of the methacrylate ester moieties of PEMA resulting in close packing of the molecules in the blends.[3] As the temperature increases, the free volume in the blends increases leading to a decrease in storage modulus, indicating that the physical properties of the material change drastically as it goes from hard glassy to a rubbery state. This transition in behavior gives an indication of the presence of glass transition temperature.[26] At this temperature, the large segments of polymer chains start to move in the amorphous regions resulting in loosening of the close packing of molecules thus reducing the storage modulus.

Tan δ of pure PVC and its blends with various compositions of PEMA are shown in Figure 2. When the temperature increases, the values of tan δ increase sharply up to a maximum before decreasing
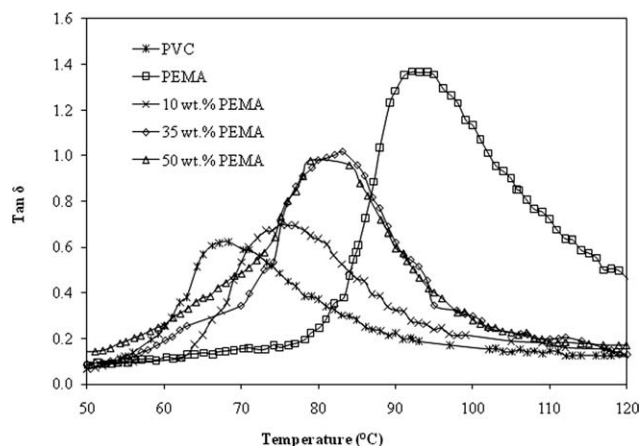
Figure 2 Tan δ versus temperature for PVC–PEMA blends at various blend ratios.

PVC/PEMA blend concentration in wt %	Glass transition temperature, T_g (°C)
100/0	68
90/10	76
65/35	81
50/50	81
0/100	92

with further increase in temperature. The temperature corresponding to the maximum peak of tan δ is attributed to T_g. Because the secondary relaxations of PVC (β-relaxation) in the blends are not evident,[27] the study was focused on the α-relaxation of PVC that corresponds to the rubbery plateau transitions of the amorphous portions. From the graph, it can be seen that the T_g for pure PVC and PEMA is 68 and 92°C, respectively. The glass transition temperatures for all the blends lie between these two values. Although the blends show a single T_g, it does not definitely mean that mixing has occurred on the molecular scale. However, according to Ahmad et al.,[28] the presence of a single T_g indicates possible uniform distribution at the microscopic level of the polymers. The T_g values determined from the plots are listed in Table I. These values were found to increase with the increase in PEMA concentration. The variation in T_g is consistent with earlier reported works.[29,30] It is also observed in this study that the intensity of tan δ increases as the concentration of PEMA increases. According to Senake et al.,[31] the intensity of the tan δ peak at the glass transition temperature reflects the extent of mobility of the macromolecular chain segment at that temperature. Hence, this implies that the mobility of the molecules is increased with PEMA concentration in the blends.

Morphology studies

Scanning electron microscopy (SEM) images of pure PVC, pure PEMA, and their blends for different ratios of PEMA are depicted in Figure 3(a–e). PVC exhibits a brittle surface with fractures, which is consistent with its mechanical properties as observed by Oksan et al.[32] It can be observed that the morphology of pure PEMA consists of pores with an average spherical size of around 10 μm. Upon addition of 10 wt % PEMA into PVC, the average size of the pores increases to about 14 μm. The shape of the pores changed from spherical to rectangular when PEMA is added into PVC, suggesting that PVC and PEMA tend to join together.[23] This proves that PEMA is coordinated with PVC to form complexes. The average pore size increases further to 23 μm when 35 wt

% of PEMA is blended to PVC. Because the presence of pores in the blends indicates the occurrence of phase separation[33] and that larger pore size is an indication of reduced segregation,[20,23] it therefore implies that the blend with 35 wt % PEMA is the most homogeneous with reduced segregation when compared with other blend ratios. Hence, the blend with 35 wt % PEMA is partially miscible.[20,23] The phase separation in the micrographs is indicated by the dark phase, which belongs to PEMA, while the bright phase containing high-atomic weight atoms (Cl)[34] corresponds to PVC. Studies by Wimolmala et al.[34] revealed that miscibility between PVC and (meth)acrylate depends on the length of the ester side chain and the blending method. When 50 wt % of PEMA is blended into PVC, the morphology is completely homogenous and well distributed [Fig. 3(e)]. This kind of behavior is concurrent with the morphological model proposed by Pielichouski and Hamerton.[35]
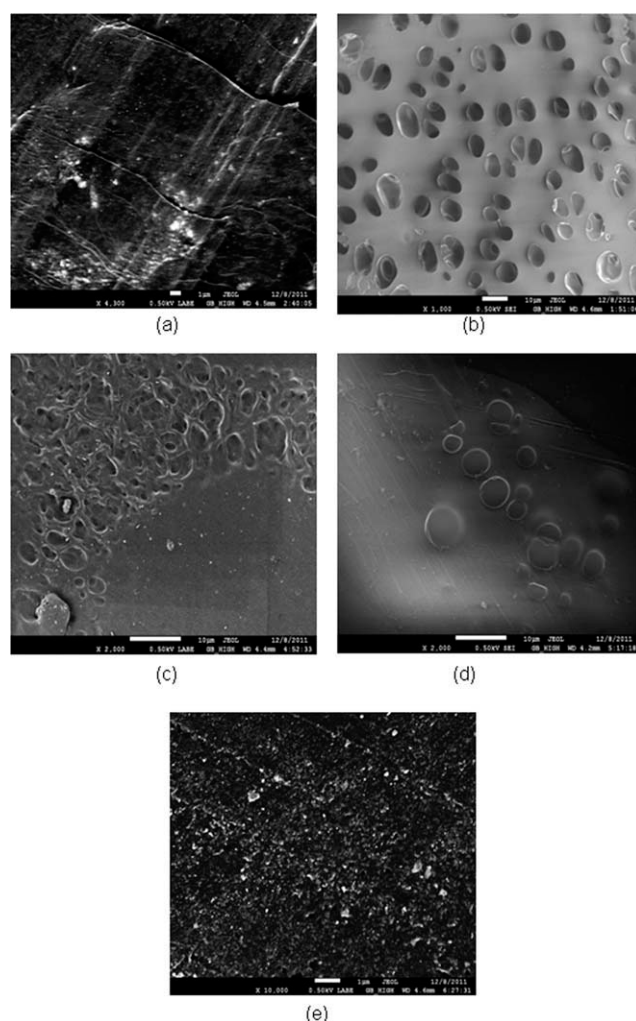
Figure 3 SEM images of (a) pure PVC, (b) pure PEMA, (c) 10 wt % PEMA, (d) 35 wt % PEMA, and (e) 50 wt % PEMA.
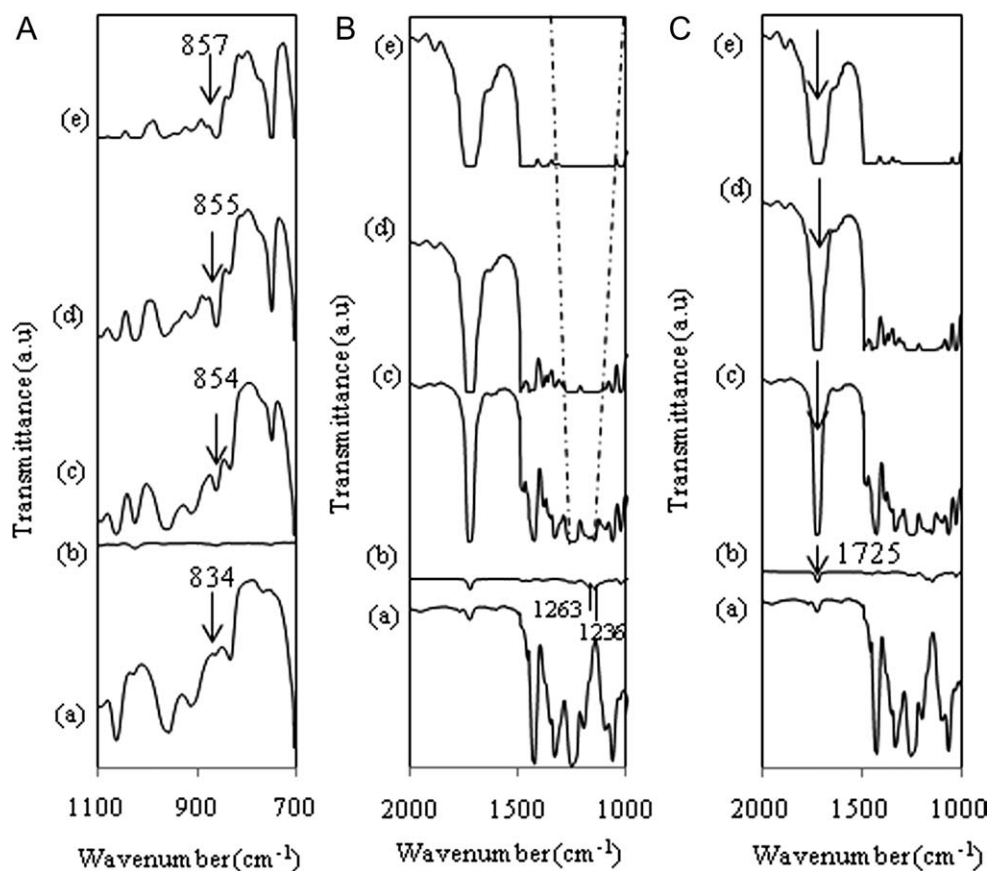
Figure 4 (A) FTIR spectra of (a) pure PVC, (b) pure PEMA, (c) 90 wt % PVC–10 wt % PEMA, (d) 65 wt % PVC-35 wt % PEMA, (e) 50 wt % PVC-50 wt % PEMA for wavelength region 700–1100 cm^{-1}. (B) FTIR spectra of (a) pure PVC, (b) pure PEMA, (c) 90 wt % PVC–10 wt % PEMA, (d) 65 wt % PVC–35 wt % PEMA, (e) 50 wt % PVC–50 wt % PEMA for wavelength region 1000–2000 cm^{-1}. (C) FTIR spectra of (a) pure PVC, (b) pure PEMA, (c) 90 wt % PVC–10 wt % PEMA, (d) 65 wt % PVC–35 wt % PEMA, and (e) 50 wt % PVC–50 wt % PEMA for wavelength region 1000–2000 cm^{-1}.

FTIR studies

Fourier transform infrared (FTIR) spectra of the polymer blends were carried out to study interactions between PVC and PEMA in the blends. The FTIR of pure PVC, pure PEMA, and PVC/PEMA blends is shown in Figure 4(a–c) for various wavenumber regions. The C—Cl stretching mode for pure PVC is observed at 834 cm^{-1}.[16] When PEMA is added to PVC, there is a shift in the C—Cl dipole of PVC to higher wavenumbers with higher intensity up to 35 wt % PEMA concentration and reduced thereafter. The shifting of this peak upon addition of PEMA to PVC can be attributed to the feeble interaction between the C—Cl dipole and β hydrogen of the methacrylate esters of PEMA.[3] Figure 5(b) shows the FTIR spectra in the vicinity of ester group vibration in PEMA at 1236 and 1263 cm^{-1}. When PEMA is blended with PVC, the two peaks merged together into a broad peak, which becomes broader with the increase in PEMA concentration, and disappeared giving another evidence for the complexation between PVC and PEMA in the blends. Interaction

between the two polymers is also shown by the changes in the intensity of the carbonyl stretching peak for PEMA at 1725 cm^{-1} as observed in Figure 4(c). This band is observed to be sharp with high intensity in the blend containing 10 wt % PEMA and shifted to a higher wavenumber. As concentration of PEMA increases, the peak becomes broader and shifts further to higher wavenumbers. The shift of this peak to higher wavenumbers indicates that there is a specific interaction between C=O of
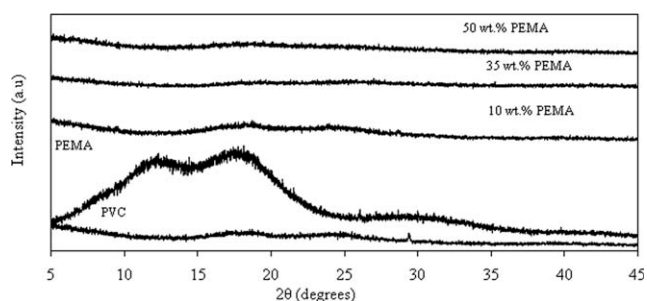
Figure 5 XRD patterns of PVC, PEMA, and its blends.
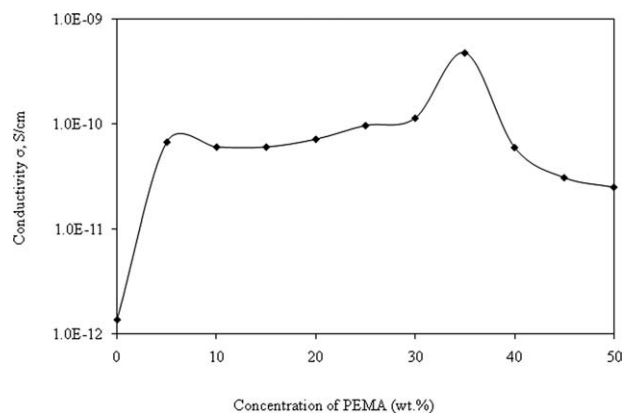
Figure 6 Variation of conductivity in PVC/PEMA blends with concentration of PEMA.

PEMA and the α-hydrogen of CH—Cl of PVC.[28] This interaction is similar to the results reported by other researchers.[28,36,37]

XRD studies

Figure 5 illustrates the X-ray diffraction (XRD) patterns of PVC, PEMA, and their blends. It is obvious that both polymers are amorphous in nature, because no sharp crystalline peaks are observed. The spectrum of pure PEMA has an amorphous hump with two halos at $2\theta = 11°$ and $15°$ while that of PVC is characterized by two broad humps centered at $2\theta = 16°$ and $25°$. When 10 wt % PEMA is blended with PVC, the diffractogram appears to be similar to that of PVC with halos that peak at $2\theta = 17°$ and $23°$ while the peak of PEMA at $2\theta = 11°$ has disappeared. This gives added evidence of the complexation of PVC and PEMA in the blends. The intensity of these peaks also decreases, which implies that the addition of PVC disrupted the arrangement in the polymer backbone of PEMA.[38] The sample with 35 wt % PEMA is the most amorphous, because no obvious peaks are observed. The absence of peaks revealed that a structural modification has occurred in the blends.[38] Further addition of PEMA causes the appearance of a small and broad peak appearing at $2\theta \sim 16°$, indicating that the blend has become more crystalline in nature compared to the blend with 35 wt % PEMA.

Conductivity studies

Figure 6 shows the variation of room temperature conductivity with PEMA concentration. Pure PVC and PEMA have conductivity values of 1.36×10^{-12} and 1.92×10^{-10} S cm^{-1}, respectively. It is noted that the conductivity values of these two pure polymers are comparable to the ones measured by other researchers.[29,39] When PVC is blended with PEMA,

the conductivity is found to be between those of the pure polymers. The conductivity rises to 4.74×10^{-10} S cm^{-1} when PEMA concentration increases up to 35 wt %. Because this value is in the same order of magnitude with that of pure PEMA, it therefore indicates that the blends have conductivity values that lie in the realm of insulator materials, similar to other polymer materials that have served as host for polymer electrolytes. In addition, the blend with 35 wt % PEMA, which has the highest conductivity value, has better mechanical properties when compared with pure PEMA, which is soft and pliable and pure PVC. The increase in conductivity could be attributed to the increase in the amorphicity of this blend as shown by XRD studies and supported by SEM where there is reduced segregation in this blend as a result of less blocking phase.[20]

CONCLUSION

Addition of PEMA into PVC changed the miscibility of the blend from immiscible to partially miscible (35 wt % PEMA) as evidenced by the presence of a single T_g and shifts in the bands in FTIR spectra as well as 2θ positions of peaks in XRD diffractograms, which is supported by SEM micrographs. The results also show that by imparting PEMA into PVC, the mechanical properties of the blends were improved. The blends with 10 wt % PEMA were found to be too stiff, while the blends with 50 wt % PEMA are too rubbery as indicated by their storage modulus values. The blends with 35 wt % PEMA show intermediate storage modulus and flexibility. This blend also yielded the most amorphous film with reduced phase separation, which favors ionic conduction to occur. Therefore, this blend ratio seems to be most suitable candidate to act as a polymer host for the preparation of polymer electrolyte. Works on polymer electrolytes using this polymer blend with this ratio are being carried out in the author's laboratory.

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