

Structural properties of poly (Vinyl Chloride)-based polymer electrolytes

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Abstract

Solid polymer electrolyte of poly (vinyl chloride) PVC-sodium iodide (NaI) was prepared using solution casting technique. FTIR results suggested that NaI interacted with PVC. Deconvolution of FTIR spectra region were carried out to estimate the relative percentage of number of free ions at the C-Cl stretching vibration band. This result is in good agreement with the conductivity studies as well as the temperature studies.

Keywords PVC, NaI, FTIR

INTRODUCTION

The development of solid polymer electrolytes (SPE) with high ionic conductivity and energy density is one of the main objectives in electrochemical research. It has been found to have great advantages in replacing conventional liquid electrolytes. In comparison to commercial liquid electrolytes, SPE are safe, mechanically stable, and adaptable in design. [1-2]. Research on lithium salt complexed polymer electrolytes has been extensive. However, very little work has been done on sodium complexed films based on electrolytes. Comparing sodium-based polyelectrolytes to their lithium-based counterparts reveals significant advantages. Sodium is more widely accessible and less expensive than lithium [3].

An essential requirement for a polymer to function as an ionic conductor is the presence of electron donor atoms (atoms with lone pair electrons) in its structure, which allows polymer-salt complexes to form. We have directed our attention to poly (vinyl chloride) PVC as it has lone pair electron of chlorine that can solvate inorganic salt results in the formation of conductive ion solution. PVC also chosen as host polymer due to their easy processibility, less expensive and good compatibility[4-6]. In this paper, structural studies of the polymer electrolytes based on PVC complexes with sodium iodide (NaI) salt were studied using FTIR.

MATERIALS AND METHODS

Films of PVC-based polymer electrolytes were prepared using solution casting method. Poly (vinyl chloride) PVC, (Molecular weight $2.3 \times 10^5 \text{ g mol}^{-1}$) and sodium iodide (NaI) with purity 99% both from Aldrich were used in this work. Tetrahydrofuran (THF) with purity > 99 % obtained from J.T Baker was used as the solvent. The required amount of PVC and NaI concentration ranging from 10 to 40 wt% were dissolved separately in THF. The solutions were mixed and then stirred continuously until a homogenous

solution thus obtained. The solutions were cast in different glass petri dishes and allowed to evaporate slowly at room temperature for the films to form.

Spectroscopic studies were carried out using a FTIR-Is10 Nicolet spectrophotometer in the frequency range from 600 to 4000 cm^{-1} at a resolution of 2 cm^{-1} . The spectral features obtained were analyzed and then fitted with a Gaussian/ Lorentzian function using Origin 8.0 software.

RESULTS AND DISCUSSION

Depicted in Figure 1 (i)-(iv) are the infrared spectra of PVC-NaI complexes for various concentration of NaI in the spectral region 600 to 900 cm^{-1} , 1000 to 1500 cm^{-1} , 1500 to 1800 cm^{-1} and 2700-3000 cm^{-1} , respectively. Details of the corresponding infrared peak assignments are tabulated in the Table 1. For pure PVC film, the absorption peak at 617, 635 and 694 cm^{-1} are assigned to the C-Cl stretching as shown in Figure 1(i). The C-C stretching is observed at 1099 cm^{-1} , C-H rocking deformation and C-H deformation of CHCl are observed at 1244 and 1326 cm^{-1} while CH_2 wagging is observed at 1430 cm^{-1} , respectively as depicted in Figure 1(ii). The C=C stretching vibration can be seen at 1642 cm^{-1} as shown in Figure 1(iii). From Figure 1(iv), The C-H stretching of CH_2 and C-H stretching of CHCl are observed at 2918 and 2967 cm^{-1} , respectively. For NaI salt, the characteristic peaks are observed at 1607, 1621 and 2936 cm^{-1} as shown in Figure 1(iii) and (iv), respectively.

Figure 1(i) shows the weaker C-Cl stretching peak at 617 shifted to 612 with addition of 20 wt.% NaI. Further addition of NaI, these peaks have merged and shifted to 611 cm^{-1} with increase in intensity upon addition of 40 wt.% NaI. The changes of these peaks might be due to the weaker C-Cl stretching indicating a change in environment of the chlorine atoms of PVC, most probably caused by the coordination of Na^+ of the salt. On the other hand, the C-Cl stretching peak of pure PVC at 694 cm^{-1} is shifted to 690 cm^{-1} with addition of 20 wt.% NaI then subsequently shifts to 687 cm^{-1} when 40 wt.% NaI is added. Depicted in Figure 1(ii) the C-C stretching is observed at 1099 cm^{-1} is shifted to lower wavenumber of 1094 cm^{-1} with increases in intensity as increasing salt content to 40 wt.% of NaI. This suggests that the Na^+ ions may be interact with electron donor of the vinyl chloride of the polymer chain- $[\text{CH}_2\text{-CH}_2\text{Cl-}]_n$. [8-9]. The CH_2 rocking deformation at 1244 cm^{-1} shifted in wavenumber at 1248, 1250 and 1252 cm^{-1} with addition of 20, 30 and 40 wt.% of NaI. The relative intensity of the shoulder with reference to CH_2 rocking peak get higher to become a clearer peak as more is present in the complex system. The C-H deformation of CHCl at 1322 and CH_2 wagging at 1427 cm^{-1} seem to increase in intensity and shifted in the wavenumber in all complexes.

Depicted in Figure 1(iii) is the small shoulder at characteristic peak of PVC at 1583 and 1735 cm^{-1} is shifted in the wavenumber with addition of 10 and 20 wt.% NaI and subsequently disappears as more NaI added to the system. The C=C stretching peak of PVC at 1642 cm^{-1} gradually become more prominent peak with shifted in the wavenumber as increase in salt concentration. This might be due to the overlapped peak with characteristic peaks of NaI at 1623 and 1607 cm^{-1} . Furthermore, C-H stretching of CHCl at 2967 cm^{-1} also shows the similar behaviour as depicted in Figure 1(iv) due to the overlapping with the broad frequency characteristic of NaI at 2936 cm^{-1} . The peak shifted to 2960, 2967, 2970 and 2966 cm^{-1} with addition of 10, 20, 30 and 40 wt.% NaI with increase in intensity. A shift is also noted for the PVC peak due to C-H stretching of CH_2 at 2918 cm^{-1} . This peak has shifted to 2914 cm^{-1} with addition of 40 wt.% NaI and is accompanied with a noticeable decrease in intensity as increasing NaI concentration. The disappearance, shifting of the some peaks and changes in intensity of the peaks in the IR spectra could reflect a possible interaction that occurs between the polymer host, PVC and NaI salt [7].

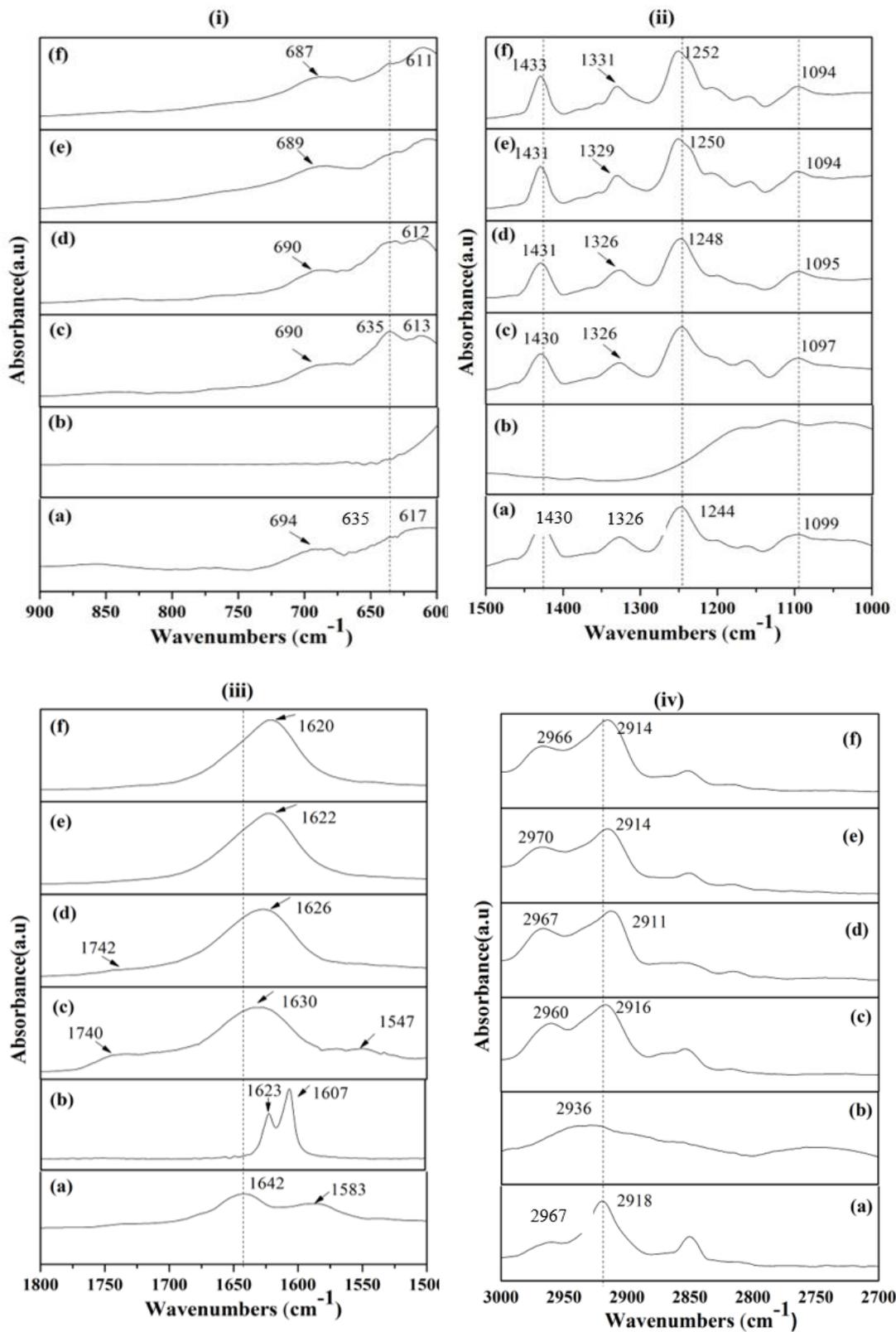
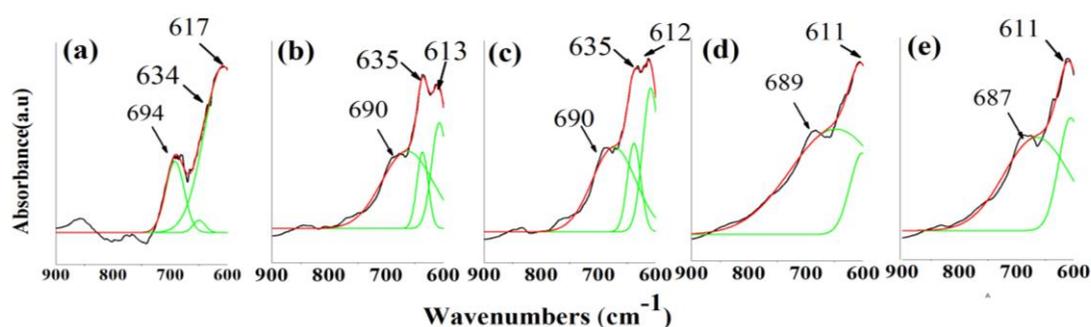


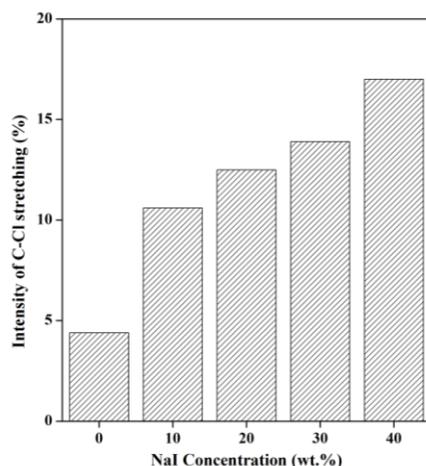
Figure 1 FTIR spectra between (i) 600 and 900 cm^{-1} , (ii) 1000-1500 cm^{-1} , (iii) 1500-1800 cm^{-1} and (iv) 2700-3000 cm^{-1} of (a) PVC, (b) NaI and PVC-NaI SPEs containing (c) 10 wt.%, (d) 20 wt.%, (e) 30 wt.% and (f) 40 wt.% NaI.

Table 1: FTIR vibrational modes of PVC polymer electrolytes with different wt.% of NaI concentration

Assignment of bands	Wavenumbers (cm ⁻¹) / wt.% NaI			
	Pure PVC	20 wt.%	30 wt.%	40 wt.%
Stretching C-H of CHCl	2967	2967	2970	2966
Stretching C-H of CH ₂	2918	2911	2914	2914
C-C stretching	1642	1626	1622	1620
CH ₂ wagging	1430	1431	1431	1433
Deformation C-H of CHCl	1326	1326	1329	1331
C-H rocking	1244	1248	1250	1252
C-C stretching	1099	1095	1094	1094
C-Cl stretching	694	690	689	687
	635	-	-	-
	617	612	612	611

**Figure 2** Band fitting of IR spectra in the wavenumber between 600 and 900 cm⁻¹ (a) PVC, PVC-NaI SPEs containing (b) 10 wt.%, (c) 20 wt.%, (d) 30 wt.% and (e) 40 wt.% NaI.

The intensity of the C-Cl peak has been related to the number of free ions present in the polymer electrolyte [8]. In this work, the stretching C-Cl vibration mode at 617 cm⁻¹ in the region 600 to 900 cm⁻¹ has been deconvoluted to quantify the number of free ions as shown in Figure 2. Gaussian-Lorentz function was chosen with nonlinear least square fitting for peak deconvolution. Figure 3 shows the graph of intensity of C-Cl stretching vibration mode with respect to NaI concentration for salted PVC systems. It is observed that the intensity of the stretching C-Cl vibration mode at 617 cm⁻¹ increase with increasing concentration of NaI salt up to 40 wt.% of NaI indicating the increase in the number of free ions.

**Figure 3** Intensity of C-Cl stretching of PVC with respect to the NaI concentration

In this study, FTIR spectroscopy dependence on temperature is carried out in order to study the effect of temperature to the structural properties of electrolytes system. The same peak of the stretching C-Cl vibration mode at 617 cm^{-1} in the region 600 to 900 cm^{-1} has been deconvolute to quantify the number of free ions as a function of temperature as shown in Figure 4(a). Figure 4 (b) shows the plot of the intensity of the stretching C-Cl vibration mode with respect to temperature. It is observed from Figure 4 (b) depicted that the percentage (%) of intensity of the stretching C-Cl vibration mode at 617 cm^{-1} band increases with increasing temperature. In other word the number of free ions, n increases with temperature. The increase of n with temperature could be attributed to the greater dissociation of salt at higher temperature. This is due to the fact that at higher temperatures, movement of polymer chain segments is thermally enhanced and the dissociation of salts would increase assisting and resulting in the increase in ionic conductivity [9].

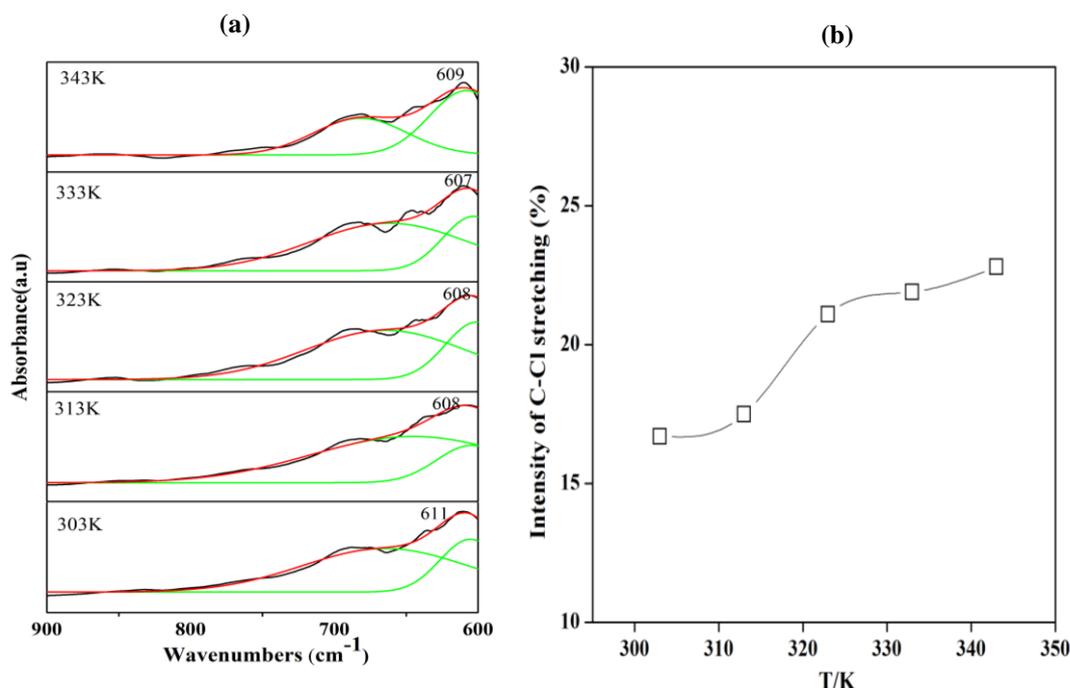


Figure 4 (a) Band fitting of IR spectra between 600 and 900 cm^{-1} for PVC-NaI complexes in temperature range of 303 - 343K and (b) The calculated % of intensity of the stretching C-Cl vibration mode at 617 cm^{-1} band as a function of temperature.

CONCLUSION

The FTIR results showed the addition of NaI to PVC shifts the C-Cl stretching vibration at 694 , 634 and 617 cm^{-1} to the lower wavenumbers. This shift along with changes in band shape and band width indicates that there is interaction between the Na^+ cations of the salt and the chlorine component of the C-Cl bands in PVC. Temperature studies from FTIR suggest that the stretching C-Cl vibration mode increases with increasing temperature indicating that the increase in the number density of free ions.

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