X-RD, SEM and conductivity of ethylene carbonate added PVC polymer films

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Abstract. The films of PVC were prepared by mixing ethylene carbonate (EC) and by employing the solution casting method. The samples that were prepared were characterized for their structural, morphological, functional, and electrical properties by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and AC impedance analysis, respectively. The XRD patterns illustrated that the pure PVC was having sharp crystalline broad peaks at 17.45° and 19.25° which gradually disappeared with the increasing concentration of EC showing a gradual transition to the amorphous nature. The best combination PVC with EC showed the highest amorphous character with the suppressed crystalline peaks, which is indicative of the good miscibility of PVC and EC. The SEM results revealed that the surface of PVC with EC was smooth and homogeneous. The FTIR spectra showed significant polymer-plasticizer interactions in the form of O-H and C=O stretching vibrations and also decreased C-Cl intensity indicating the disruption of PVC crystalline domains. AC conductivity studies revealed that pure PVC had the lowest conductivity ($\sigma = 3.82 \times 10^{-8}$ S/cm), however, the conductivity increased enormously with the addition of the EC. The PVC with 30% EC had the lowest resistance and highest conductivity due to increased chain flexibility and free volume, however, the performance was degraded by the excess EC.

1 Introduction

Polymer electrolytes have been attracted a large share of attention in various energy storage and conversion technologies, such as fuel cells, supercapacitors, lithium-ion batteries, and the like, because of their promising applications. Besides, they can be substituted with liquid electrolytes conventionally used in these devices because of their compatibility, simple processing, as well as the capability to limit dendritic growth. Unfortunately, their mechanical instability and low ionic conductivity limit them to be severely [1-3]. Perhaps, to provide cutting-edge solutions to this problem, researchers have experimented many methods, one of which is adding plasticizers in polymer electrolytes matrix. Polymer electrolytes that contain ethyl carbonate (EC) as the plasticizer can take advantage of EC in terms of both chemistry and structure. In fact, one of the most prominent features of EC as a plasticizer is its semi-crystalline structure, high thermal stability, and the presence of the

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functional groups such as hydroxyl (-OH) and ether (C-O-C), which may interact with each other and form bridges with polymers in the product, thereby changing the physicochemical properties of the polymers. Incorporating EC with PEO, PVC or PVDF etc. can promote the flexibility of the composite materials and simultaneously improve the ionic conductivity. By breaking the crystalline regions of the host polymer matrix where the ions are trapped, EC embraces the role of a plasticizer by increasing segmental mobility as well as providing new pathways for ion transport. The result is a consistently mixed polymer electrolyte that is more stable mechanically and has better ionic conductivity. When it comes to electrolyte performance, salt that work well with EC. This compatibility enables for the ions to dissociate.

The investigations on PVC films related to blend with EC is our interest to prepare polymer electrolyte films with various ionic salts for electrochemical application. In this study, we focus on developing and characterizing PVC with EC-based polymer films, where less investigations on plasticizer added PVC polymer films. An analysis is conducted on the structural, morphological, and functional group properties. In order to develop long-lasting and effective polymer electrolytes for future energy storage systems, this research investigates the plasticizing impact of EC and its ability to balance mechanical stability with ionic conductivity.

2 Materials and experimental

Polymer Poly vinyl chloride (PVC) [Sigma – Aldrich, Avg. M.W ~99,000 and purity 99.99%], plasticizer Ethyl Carbonate (EC) [Sigma – Aldrich, purity 98%], and Tetra hydro Furan (THF) procured from sigma Aldrich. PVC and EC used for synthesis without further purification. Plasticized EC based PVC polymer blends are prepared using Solution casting process. We measured the required amounts of PVC and EC as shown in Table1. The PVC and EC were combined with THF and left to dissolve for 12 hours at 40°C with constant stirring. A flawlessly blended polymer film was created by placing a mixture of solvents in separate coded Petri plates and drying them under vacuum. A well-blended polymer film was achieved by pouring a mixture of solvents of varying concentrations into separate coded Petri dishes and then drying them under vacuum. Here are the codes for various concentrations of PVC and EC samples as shown in the table 1. X-ray diffraction, with a wavelength of 1.54 AU and a CuK-α source is used to analyze polymer films using an X-pert Pro diffractometer. Using an FT-IR spectrometer, the SHIMADZU-FTIR (8400S), vibrational spectra of all produced polymer mix films were obtained. By combining scanning electron microscopy with SHIMADZU-XRD (6100/7000), the surface morphology of the sample is examined. AC conductivity of all the films at different frequencies was measured with PSM1700 LCR meter.

Table 1. Plasticized PVC polymer compositions.

Sno	Sample code	Polymer PVC	Plasticizer EC
1	PVC	1000mg	0
2	PVCEC1	1000mg	100mg
3	PVCEC2	1000mg	200mg
4	PVCEC3	1000mg	300mg
5	PVCEC4	1000mg	400mg
6	PVCEC5	1000mg	500mg

3 Results and discussion

3.1 Structural analysis by XRD

The important tool to investigate the structural studies of polymer blend is XRD. It confirms the crystalline nature and amorphous nature. Angle of diffraction 2θ Vs intensity of XRD patterns of the pure and polymer blend sample of PVC and EC were shown in Figure 1. The broad peaks corresponding to PVC $17.45^0$and 19.25^0 were representing a part of crystalline nature of PVC. As EC concentration increases in PVC, the peak appears in XRD pattern of PVC intensity decreases due rising of domination of EC. The amorphous nature raising in the polymer blend can be seen from Figure 1(a) to 1(d) with the raising concentration of EC in PVC from 100mg to 300mg and further raising EC concentration i.e., behind 300 mg, a small raising in crystalline nature of PVC and the sample of PVCEC3 indicated best which is given in Figure 1(d). Hence it is being expected that the best supporting sample with better miscibility of formation of polymer blend film [4]. The peak disappearing and reduced intensity of PVC due to raising concentration of EC polymer blending indicate a symbol of interaction between PVC and EC with good miscibility and evidence of converting semicrystalline nature to amorphous nature.

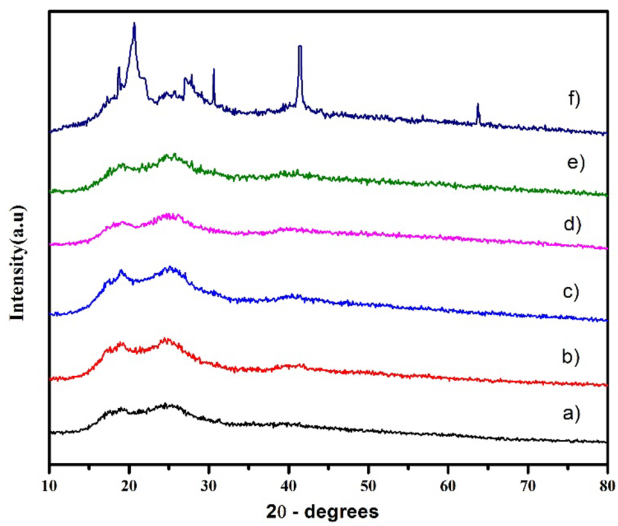

Fig. 1. XRD of PVC added EC films of a) PVC, b) PVCEC1, c) PVCEC2, d) PVCEC3, e) PVCEC4, and (f) PVCEC5.

3.2 Morphological analysis by SEM

The scanning electron microscopy (SEM) image of the PVC-EC system, shown in Figure 2, illustrates the variations in surface morphology. The scanning electron micrograph of polymer PVC reveals a rather uniform background with spots of varying brightness and darkness. The presence of defects, perforations, or variations in density is more likely to be indicated by darker regions. The density of the fillers or reinforcing particles in the PVC matrix may be higher in lighter portions. There may be some minor feature grouping, but overall homogeneity suggests a very steady distribution of material [5-6]. The presence of EC dispersed throughout the PVC matrix is suggested by the larger and more noticeable bright spots in PVCEC1 micrographs compared to pure PVC. As seen in scanning electron microscopy images, amorphous regions or separated phases within the polymer matrix may be produced by increasing EC concentrations. More control over the final properties of the polymer PVC with EC is well mixed without significant phase separation, allowing the mixture to retain high crystallinity in certain places. The polymer blend may seem more uniform and have smoother contours at lower concentrations. The stability and mechanical strength of the material may be compromised when visible features like spots, rough areas, or cracks emerge due to an excess of plasticizer as the EC concentration increases. At optimum concentration of EC (PVCEC3), excellent compatibility and great homogeneity are suggested by the smooth surface shape with minimum flaws or phase separation and the uniform distribution of EC.

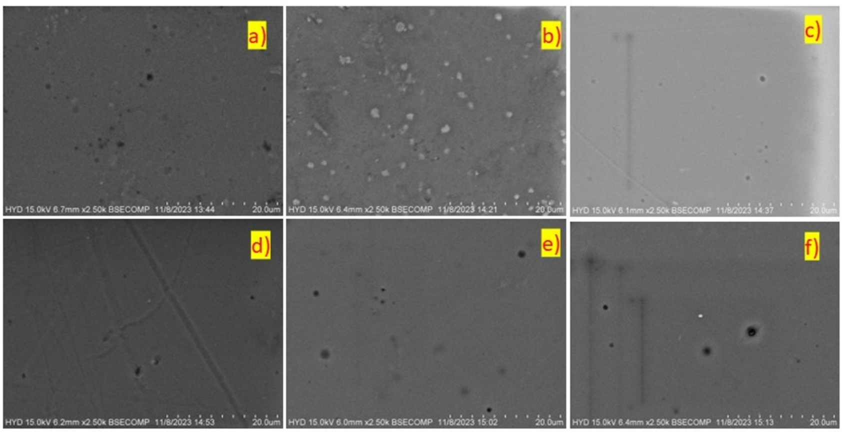

Fig. 2. SEM micrographs of PVC added EC films of a) PVC, b) PVCEC1, c) PVCEC2, d) PVCEC3, e) PVCEC4, and (f) PVCEC5.

3.3 Functional analysis by FTIR

The Fourier transform infrared spectra of pure PVC and a polymer blend based on PVC and Plasticizer EC are shown in Figure 3. FTIR analysis may reveal which functional groups are present in PVC and PVC/EC polymer compositions. The peaks 2800cm^{-1} – 3000cm^{-1} represent the C-H stretching in PVC and this band position shifted to higher wave number by incorporation of plasticizer EC. The PVC with EC films showed well defined band positions are found to be modified where observed of 1600cm^{-1} – 1800cm^{-1} C=O stretching, 600 cm^{-1} – 700 cm^{-1} C-Cl stretching and 3200cm^{-1} -3600cm^{-1} O-H stretching. Increased flexibility and reduced crystallinity in the PVC matrix are both contributed by hydrogen bonding, which is strongly shown by the big O-H peak [7-8]. Incorporating EC into PVC alters the material's structure and improves compatibility by adding functional groups (such as hydroxyl, carbonyl, and ether). The relative intensity of PVC's C-Cl bonds diminishes with increasing EC concentration, suggesting that PVC is becoming more amorphous due to the destruction of its rigid crystalline regions caused by the polymer-plasticizer interaction.

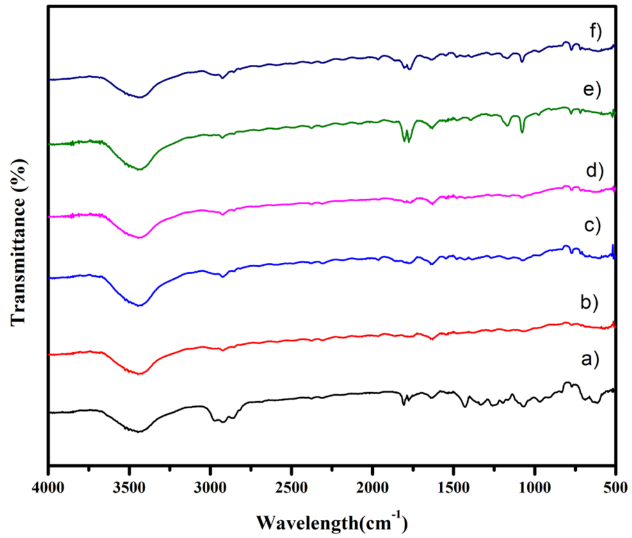

Fig. 3. FTIR of PVC added EC films of a) PVC, b) PVCEC1, c) PVCEC2, d) PVCEC3, e) PVCEC4, and PVCEC5.

3.4 AC Conductivity

The conductivity of polymer electrolytes is directly related to the bulk resistance (Rb), which can be obtained from Nyquist impedance plots. The conductivity (σ) is given by:

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

where:
- l = thickness of the polymer electrolyte film (cm)
- R_b = bulk resistance from the intercept of the Nyquist plot (Ω)
- A = electrode–electrolyte contact area (cm^2)

This relationship exemplifies the reduction in bulk resistance, which is observed in EC-modified PVC electrolytes leading to increased conductivity. Nyquist plots together with the values of conductivity (σ) are illustrated in Figure 4 & 5. The investigation thus concentrates on the impact of EC concentration in the adjustment of carrier transport with PVCEC3 being the optimum formulation. The Nyquist plots reveal that the pure PVC exhibits the highest resistance, as expected, due to its sturdy structure, which impedes the mobility of the charges and thereby results in low conductivity as illustrated in Figure 4. The addition of ethylene carbonate (EC) to the polymer chains causes them to be softer, the free volume is increased, and it becomes more convenient for the charge to migrate. PVCEC3 is the best composition to be distinguished from the other various mixtures, with the lowest resistance and highest conductivity. The performance, however, is reduced when the EC content is increased (PVCEC4 and PVCEC5) most probably because the excess plasticizer disrupts the structure and hinders the ion transport. It is quite clear that the pure sample of PVC has the lowest conductivity, which is due to the rigid backbone and limited segmental mobility of the polymer chains [9]. The addition of ethylene carbonate (EC) as a plasticizer leads to a marked increase in conductivity and the optimum value is ($\sigma = 3.82 \times 10^{-8}$ S/cm).

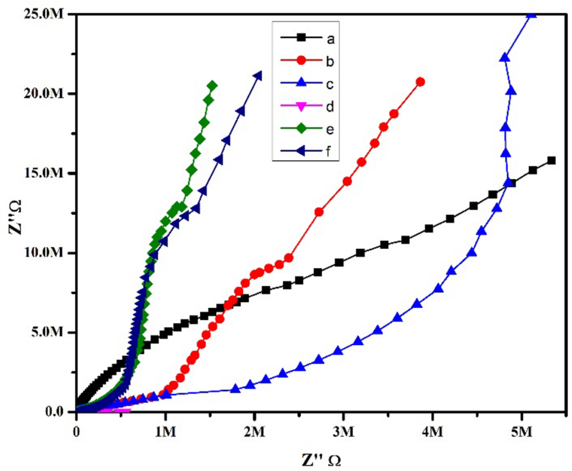

Fig. 4. Nyquist plots of a) PVC, b) PVCEC1, c) PVCEC2, d) PVCEC3, e) PVCEC4, and PVCEC5.

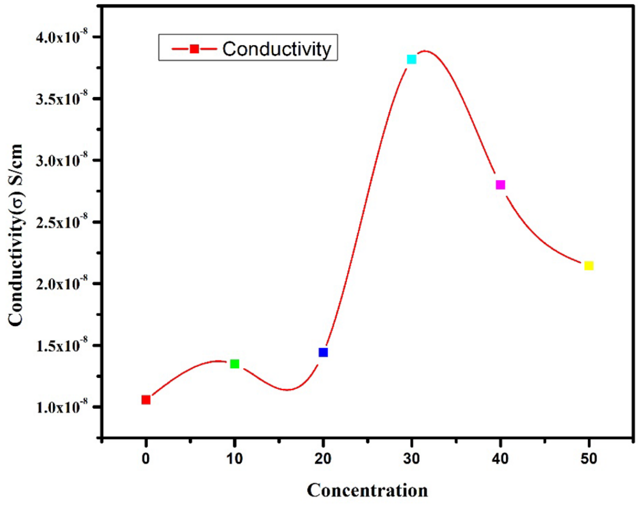

Fig. 5. Concentration vs conductivity of PVC added EC films.

4 Conclusions

The XRD analysis suggested that PVC is partially crystalline and combining it with EC makes the material more flexible and amorphous. The SEM pictures of PVC with EC revealed a smooth, uniform surface with no fissures or phase separation. The FTIR study revealed a favorable interaction between PVC and EC, with changes appeared in OH and CO stretching band positions and lower C-Cl band intensity. Electrical conductivity of PVC with EC studies confirmed that PVCEC3 film had the lowest resistance and the high ionic conductivity ($\sigma = 3.82 \times 10^{-8}$ S/cm). Conductivity decreased again at higher EC values due to structural disruption caused by too much plasticizer. The film PVCEC3 had the best mix of structure and conductivity, making it the most viable choice for solid polymer electrolyte applications and further investigations are in-progress.

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