CHAPTER VI

Composite polymer electrolytes

6.1 PVdF-PVC based composite polymer electrolytes with the addition of TiO\textsubscript{2}

Introduction

It is well known that the composite polymer electrolytes based on high surface area SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}, ZrO\textsubscript{2}, etc., have distinct advantages over plasticized polymer electrolytes. The addition of such fillers with plasticized electrolytes leads to the lowering of the degree of crystallinity, low and stable interfacial resistance across lithium and hence higher conductivity [1-3]. The resulting conductivity purely depends on the concentration of ceramic content and particle size of the inert phase. The increase in conductivity is generally attributed to the formation of a new kinetic path via a thin interphase layer along the interphase itself, or to a concentration enhancement due to space charges in the sub-interface region [4,5].

Experimental

Solid polymer electrolytes composed of PVdF (20) - PVC (5) - LiClO\textsubscript{4} (8) - EC/PC (67) - X\% of (TiO\textsubscript{2}) were prepared using solvent casting technique (where X = (a) 4, (b) 8, (c) 12, (d) 16, (e) 20 wt % in the total polymer’s weight). The obtained polymer films were subjected to FTIR, XRD, TG/DTA and ac electrical conductivity studies. The maximum ionic conductivity value was measured as 7.921x10^{-3} S\text{cm}^{-1} in 12 wt% of TiO\textsubscript{2} complex. The temperature - dependent conductivity plot shows Arrhenius behaviour.
6.1.1 XRD Studies

The XRD spectra of pure PVdF, PVC, LiClO₄ and PVdF (20) - PVC (5) - EC/PC (67) - LiClO₄ (8) with the addition of X % of TiO₂ composite systems (where X = (a) 4, (b) 8, (c) 12, (d) 16, (e) 20) are shown in Fig 6.1. It can be seen that the intensities of the peaks have abruptly reduced up to 75-80 % as compared with pure polymers and salt. It indicates that these polymer complexes have turned to an amorphous phase. The LiClO₄ peaks in the figure are completely minimized in all composite systems. It is well known that mobile lithium ions are necessary for conduction in polymer matrix, so that the dispersed state should be in amorphous phase. Such a phase was induced, only by the addition of plasticizers and salt and these additives induce significant disorder into the original polymer structure.

The diffraction peaks observed at 2θ = 18° and 19.6° in pure PVdF are shifted as one broad peak at 2θ=20.5° with less intensity in the composite complexes. The peak corresponding to PVC is completely reduced in all the complexes. Few more peaks are observed corresponding to the presence of TiO₂ in the polymer complexes. No sharp peaks have been observed corresponding to the salt in the complexes. This indicates the absence of excess salt in the composite system or there may be a complete dissolution of lithium salts in the composite polymer matrices.

6.1.2 FTIR Studies

FTIR spectra of pure PVdF, PVC, LiClO₄ and PVdF (20) - PVC (5) - EC/PC (67) - LiClO₄ (8) with X% of TiO₂ (where X = (a) 4, (b) 8, (c) 12, (d) 16, (e) 20) in the total polymer weight are displayed in Fig 6.2. FTIR spectra of the composite polymer systems reveal complete information about the molecular interactions between polymers, plasticizers, salt and ceramic (TiO₂). The absorption peaks of pure PVdF (532, 618, 762, 840 and 1407 cm⁻¹), PVC (690, 1096, 1256 and 1333 cm⁻¹),
LiClO₄ (555, 637, 1366 and 1463 cm⁻¹) and TiO₂ (1650 cm⁻¹) are shifted to (522, 623, 778, 832 and 1414 cm⁻¹), (699, 1118, 1238 and 1322 cm⁻¹), (562, 645, 1371 and 1479 cm⁻¹) and (1645 cm⁻¹) in the composite electrolytes. The characteristic peaks observed in PVdF (769, 976 and 1073 cm⁻¹), PVC (494, 961, 2816 and 2849 cm⁻¹) and LiClO₄ (2854 and 2924 cm⁻¹) are disappeared in the complexes. The vibrational peaks occurring in the range of 1000-1300 cm⁻¹ are completely reduced in intensity in all electrolytes except in fig 6.2a, which may be due to the lower concentration of TiO₂ in the polymer matrix. In addition to this, a few new peaks have also occurred in the complexes. It reveals that complex formation has occurred between polymers and additives such as plasticizers, salt and filler (TiO₂). The absorption peak at 623 cm⁻¹ assigned to ClO₄⁻ group, is slightly shifted as a broad band in the complexes. The vibrational band at 840 cm⁻¹ is shifted to 846 cm⁻¹, which is assigned to the C-F compounds of vinylidene group. Peaks at 1265 and 1645 cm⁻¹ are assigned to C-F stretching and C=C skeletal vibrations in the vinylidene group. The vibrational peaks occurring in the range of 1230-1300 cm⁻¹ are assigned to be CH rocking vibrations of EC molecules. The strong carbonyl group vibration of EC has appeared at 1786 cm⁻¹ in all polymer complexes and a characteristic peak at 1479 cm⁻¹ is assigned to CH₂ in-plane bending (scissoring) vibration of propylene carbonate (PC). The absorption peak at 720 cm⁻¹ is assigned to C-Cl stretching vibration of the vinyl group. Peaks at 2964 and 3021 cm⁻¹ are assigned to the C-H stretching bands of methylene or methyl groups, which may be due to EC or PC molecules. As reported by Kwang-Sun ji et.al [6], such changes are expected to minimize the dipole moment when filler is added with the polymer electrolytes. In general it is well known that TiO₂ filler has a higher dielectric constant (ε=80), than that of PVdF (ε=8.4), which contributes to the conduction of lithium ions by providing an inner driving force in addition to the
external driving force due to the applied field. It can therefore be concluded that the composite electrolytes, which contain the inorganic filler, are more sensitive to external electric fields and more efficient for the conduction of lithium ions.

6.1.3 Conductivity studies

Fig 6.3 shows the complex impedance plot of PVdF (20) - PVC (5) - EC/PC (67) -LiClO₄ (8) with 12 wt% of TiO₂ in the total polymer weight at different temperatures. This plot shows linear spikes. This is due to the lack of gel homogeneity due to crystalline separation. In other words, the disappearance of the high frequency semicircular portion in the complex impedance plot indicates that the current carriers are ions and the total conductivity is the result of ion conduction. The bulk resistance of the electrolyte was measured by extrapolating an intercept of this plot on the real axis. The electrical conductivity of the electrolyte was calculated for the known values of bulk resistance (Rₑ), area (A) and the thickness (t) of the film. The improved ionic conductivity is due to the enhancement of ionic mobility and the greater number of carrier ions, as already reported by many researchers [4, 8].

It has been seen that the addition of fine inorganic fillers (grain sizes around 1-3 μm) leads to an increase in the ambient temperature conductivity up to 12 wt% of TiO₂ in the total polymer weight and then the ionic conductivity decreases due to higher concentration of ceramic (Table 6.1). The effect of TiO₂ in the polymer electrolyte on its conductivity values is studied. Fig. 6.4 shows the variation of conductivity with TiO₂ concentration at 303K. This behaviour has also been observed by Rajendran et al., [9] and it reveals that the addition of small particle size ceramic powders enhances the degree of amorphicity of the polymer electrolyte. Indeed, one may surmise that the presence of highly dispersed particles in the polymer matrix may affect the crystallization rate by preventing the agglomeration of the polymer chains.
Further, the particle size and content of the ceramic additive appear to be critical factors. It is also seen that a reasonably high concentration of the filler is also necessary to affect the recrystallization rate of the polymer host.

The temperature-dependence of the ionic conductivity of PVdF (20) - PVC (5) - EC/PC (67) - LiClO$_4$ (8) - X% of TiO$_2$ (where X = (a) 4, (b) 8, (c) 12, (d) 16, (e) 20) in the total polymer weight is shown in Fig 6.5. It indicates that the conductivity of the electrolytes increases with the increase in temperature. According to Watanabe et al [10] and Druger et al [11, 12], the change of ionic conductivity in polymer electrolytes with temperature is to be explained as being due to segmental motion of ions, which results in an increase in the free volume of the system. The increase in free volume would also facilitate the motion of ionic charge [13]. Thus the segmental motion either permits the ions to hop from one site to another site or provides a pathway for ions to move, in other words, the segmental movements of the polymer facilitates transitional ionic motion. In the higher temperatures, the amorphous region progressively increases and the polymer chains acquire faster internal modes in which bond rotations produce segmental motion. The hopping mechanism of ion movement led to greater conductivity in the polymer electrolytes. The overall behaviour of this plot fits with the Arrhenius equation.

6.1.4 TG/DTA Analysis

The TG/DTA thermograms of PVdF (20) - PVC (5) - EC/PC (67) - LiClO$_4$ (8) with the addition of X% of TiO$_2$ (where X = (a) 4, (b) 8, (c) 12, (d) 16, (e) 20) composite systems, from room temperature to 400° C are displayed in Fig 6.6. It is observed that there is a weight loss of about 2-3% upto 102° C in all composite polymer electrolytes except in fig 6.6c&e. This initial weight loss reveals the evaporation of moisture in the polymer samples or the volatilization of monomers and
oligomers adsorbed. Above 102° C, the weight of the films becomes almost constant upto 160° C and then a heavy weight loss of about 25-30% is observed, which is attributed to the decomposition of PVdF. The film 6.6c&e (table 6.1) shows heavy weight loss of about 15 – 20%, which is due to the evaporation of moisture.

The initial loss observed in DTA curve is due to the evaporation of moisture at the time of loading the sample. This behaviour is evident from the TG curve and also this result is in agreement with the value reported by Subramania et.al [7]. It is also noted that as the concentration of TiO₂ increases, the initial decomposition temperature increases gradually in all complexes. The exothermic peaks occurring at 280° C and 362° C are due to the evaporation of plasticizers and the first decomposition of the composite electrolytes, respectively. Even after 362° C, films retained more than 40% of their initial weight. It is clear from these observations that the PVdF/PVC based composite polymer electrolytes can be normally operated upto 150° C.
6.2 PVdF-PVC based composite polymer electrolytes with the addition of CeO₂

Plasticized composite polymer electrolytes comprising of poly (vinylidene fluoride) (PVdF) – poly (vinyl chloride) (PVC) – lithium perchlorate (LiClO₄) – ethylene carbonate (EC), propylene carbonate (PC) with different weight percentages of CeO₂ as ceramic were prepared using solvent casting technique. The composite polymer electrolytes obtained were subjected to various characterizations such as FTIR, XRD and TG/DTA analyses. Conductivity studies of these polymer electrolytes were carried out in the temperature range 301-375 K. Higher room temperature conductivity was measured as 4.941 x 10⁻³ S/cm for PVdF (20) – PVC (5) – EC/PC (67) – LiClO₄ (8) – CeO₂ (8) polymer complex.

6.2.1 XRD Studies

X-ray diffraction patterns of pure PVdF, PVC, LiClO₄ and PVdF (20) – PVC (5) – EC/PC (67) – LiClO₄ (8) with X% of CeO₂ (where X = (a) 4, (b) 8, (c) 12, (d) 16, (e) 20) in the total polymer weight are displayed in Fig 6.7. Pure polymers are seen to be highly crystalline (fig 6.7a&b). The crystallinity of the electrolytes is greatly reduced by the addition of salt and plasticizers. The addition of these plasticizers induces significant disorder in the polymer structure, resulting in lower crystallinity. The sharp peaks observed at 2θ=18.4° and 19.5° are shifted to 2θ=20.3° as one broad peak in all composite electrolytes. The nano sized CeO₂ dispersed emulsion can penetrate the space between the polymer chains and consequently, the homogeneously dispersed ceramic filler in the matrix prevents or retards crystallization of polymers due to its large surface area. The intensity of the peaks abruptly decreases in the composite electrolytes. The broad peak centered at 2θ=26.2° is considerably diminished. No peaks have appeared corresponding to the salt in the complexes,
which confirms the amorphicity of the electrolytes. These observations illustrate that the polymer electrolytes have turned to an amorphous phase.

### 6.2.2 FTIR Studies

FTIR spectroscopic studies explain the interactions between polymer-polymer, polymer-salt, polymers-salt-plasticizers and ceramic. FTIR spectra of pure PVdF, PVC, LiClO₄, and PVdF (20) - PVC (5) - EC/PC (67) - LiClO₄ (8) with X% of CeO₂ (where X = (a) 4, (b) 8, (c) 12, (d) 16, (e) 20) in the total polymer weight are depicted in Fig 6.8. As noticed from the fig 6.8a-e, there are featureless peaks seen between 3400-3500 cm⁻¹, which shows that the samples are water or moisture free. The absorption of ClO₄⁻ that appeared at 627 cm⁻¹ reveals the dissociation of LiClO₄ [14,15,16] and the intensity of the peak is completely reduced. Around this absorption peak, two small weak intensity peaks have appeared. The lower frequency peak is attributable to the spectroscopically ‘free’ ClO₄⁻ anions, and the higher frequency peak is associated with the bound ClO₄⁻ anions [17]. Two sharp peaks of C-H rocking vibration that occur at 727 and 778 cm⁻¹ are attributed to the vibration of EC molecules, which have shifted from 717 and 772 cm⁻¹. The vibrational peaks that appear at 1328, 1483, 2913 and 3020 cm⁻¹ are assigned to the out-of-plane bending (wagging), in-plane bending (scissoring), asymmetrical stretching and symmetrical stretching vibrations of CH₂ compounds, respectively. The absorption band that occurs at 1396 cm⁻¹ is assigned to the symmetrical bending vibrations of CH₃ (methyl) group in propylene carbonate (PC). The skeletal vibration of C=C of the vinyl group occurs near 1642 cm⁻¹ with a broader shoulder and higher intensity in the complexes. The C-O stretching vibration appearing at 1046 cm⁻¹ in fig 6.8a is minimized in the other films. This may be due to the addition of CeO₂ in higher percentage. The absorption peak appearing at 978 cm⁻¹ in pure PVdF is shifted to 972
cm\(^{-1}\) as a weak band and it is assigned to C-F stretching frequency of PVdF. The carbonyl group (C=O) vibration of EC or PC compounds that occurred at 1772 and 1815 cm\(^{-1}\) in the complexes have reduced intensities as compared with those in pure compounds. This splitting of frequency is considered to be due to the Fermi resonance of the C=O stretching mode with an overtone of the ring breathing mode and the existence of short range ordering of the molecular orientation which originates the dipole-dipole coupling of two EC molecules. The absorption peaks corresponding to plasticizers at around ~1300-1000 cm\(^{-1}\) have completely disappeared i.e., its intensity has become weaker. These results indicate that when Li\(^+\) bonds with oxygen, electrons move from oxygen to the lithium ions and accordingly, weaken the bonding strength between carbon and oxygen. Moreover, as C=O combines with lithium ions, the absorption peaks shift towards a lower or higher wavenumber. These behaviours enhance the complexation between polymer-polymer and polymers-plasticizers-salt-ceramic.

6.2.3 Conductivity studies

The complex impedance diagram of PVdF (20) - PVC (5) - EC/PC (67) - LiClO\(_4\) (8) complexes containing X% of CeO\(_2\) (where X = (a) 4, (b) 8, (c) 12, (d) 16, (e) 20) in the total polymer weight at room temperature is depicted in Fig 6.9. The impedance diagram, which is the plot of Z' and Z", can show the characteristics of the interface, where Z' and Z" are real and imaginary parts of the complex impedance. Since stainless steel was used as blocking electrode in the impedance measurements, the film/electrode interface can be regarded as a capacitance. When this capacitance is ideal, it should have given rise to a vertical spike in the complex impedance plot. However, a spike inclined at an angle less than 90° to Z' axis is generally observed instead of the vertical spike. Here the bulk resistance was measured from the high
frequency intercept on the real axis. The conductivity of the polymer electrolyte was calculated from the measured resistance, known area and thickness of the film. Fig 6.10 exhibits the change of ionic conductivity with the ceramic (CeO₂) content varying from 4 to 20% in steps of 4% in the total polymer weight. Initially, the ionic conductivity increases up to 8% and then decreases, which may be due to the higher concentration of CeO₂. It can be explained that the low concentration of ceramic content leads to an increase in the free volume in the polymer electrolytes, and this enhances higher conductivity. In other words, the enhancement of ionic conductivity is due to the segmental motion of polymers for lithium ion conduction and the increased amorphicity [6]. A high concentration of the filler is also necessary to affect the recrystallization rate of the polymer host. However, the concentration should still remain low enough to prevent phase discontinuities. The room temperature conductivity is found to be 4.941 x 10⁻² S/cm, which is more than the value reported by Kumar et.al [18]. The temperature-dependent conductivities of PVdF - PVC - LiClO₄ - EC/PC - CeO₂ films subjected to various heat treatments are shown in Fig 6.11. It shows that, the conductivity of the composite electrolyte increases markedly with rise in temperature. The curvature of the plots suggests that the data fit the Arrhenius equation,

\[ \sigma = \sigma_0 \exp \left(-\frac{E_a}{kT}\right) \]  

(1)

where \( \sigma_0 \) is the pre-exponential factor, \( k \) is Boltzmann constant and \( E_a \) is the activation energy.

In general, the ionic conductivity of solid polymer electrolytes increases with temperature due to the higher segmental motion of polymer chains in the amorphous phase. Under these conditions, the filler's role in assisting lithium ion conduction is
significant as shown in fig 6.11 for all temperatures. Increasing conductivity has focused on two points, namely, dielectric properties and the degree of crystallization.

\[ \sigma = \sum |Z| C_i \mu_i \]  

(2)

The conductivity of a solid-state electrolyte has many determinants, such as carrier concentration \(C_i\), mobility \(\mu_i\) and so on [19], as depicted in equation (2). The enhancement in ionic conductivity when adding high dielectric ceramic filler (TiO\(_2\), BaTiO\(_2\), etc.) to a polymer complex might be due to the fact that the active dissociation of the Li salt results in an increased concentration of mobile carriers \(C_i\). Many experiments have been performed not only with normal oxides but also with ferroelectric materials [20]. The assumption does not hold well for the present use of CeO\(_2\) because, the dielectric constant of CeO\(_2\) (dielectric constant \(\varepsilon=3.9\)) is less than the dielectric constant of PVdF (dielectric constant \(\varepsilon=8.4\)). CeO\(_2\) based composite electrolytes exhibit better ionic conductivity \(x10^{-3}\text{ S cm}^{-1}\) than ZrO\(_2\) based composite electrolytes [7]. Hence, it is concluded that the enhancement of conductivity, may be due to the segmental motion of ions in the free volume. Furthermore, it is confirmed that an increase in mobility would be more effective than the concentration of ceramic in the polymer matrix.

**6.2.4 TG/DTA Analysis**

The thermal stability of the composite polymer electrolytes is analyzed using TG/DTA thermograph. TG/DTA thermograms of PVdF (20) - PVC (5) - EC/PC (67) - LiClO\(_4\) (8) with X% of CeO\(_2\) (where X = (a) 4, (b) 8, (c) 12, (d) 16, (e) 20) in the total polymer weight are shown in Fig 6.12. It can be seen that there is no weight loss observed up to 162°C in all the composite electrolytes. After this temperature, there is a heavy weight loss of about 25-30% observed up to 182°C and then the TG curve remains constant up to 270°C. The first decomposition is attributed to the melting
temperature of PVdF. It indicates that the TG curves remain stable up to 160°C without losing any weight demonstrating that the films used to measure the conductivity are water free sample. This is also evidenced by the FTIR spectra (Fig 6.8). The weight loss centered at ~280°C and 360°C are attributed to the evaporation of plasticizers and the second decomposition of polymer electrolytes, respectively. Even after this temperature, 40% of the sample remains stable in these electrolytes. In addition to that, films 6.9a,b&c show a small weight loss at around 65-70°C, which indicates the evaporation of volatile impurities present in these electrolytes.

Similar observations are also arrived at from the DTA curve. The endothermic peaks noticed at about ~70°C and 158°C indicated the evaporation of moisture and the melting temperature of PVdF in the electrolytes respectively. The melting temperature of PVdF has shifted towards a lower temperature, which enhances higher conductivity. The exothermic peaks that occur at ~287°C and 368°C exhibit good agreement with the decomposition temperature shown in TG. This indicates that the composite polymer electrolytes are highly stable in the temperature range usually used in rechargeable batteries.

6.2.5 SEM Studies

Fig 6.13 shows the SEM micrographs of PVdF/PVC based blend electrolytes containing ceramic added polymer complexes. The pores size is found to increase by the addition of plasticizers and free volume is developed by the incorporation of fillers (Fig 6.13a,c). The ceramic containing films show uniform dispersion of pores and the size of which is about 1-2 μm, which is also evident from cross sectional micrograph of this electrolyte. The formation of the pores structure is a complex process that depends on the interaction of the solvent and plasticizers with the polymer / ceramic and is kinetically controlled by the relative rates of evaporation of
the components. While comparing all these micrographs, it is observed that the grains are well dispersed in ceramic added systems than unplasticized (fig 4.21a) electrolytes. This rapid decrease in the degree of crystallinity of the polymer is only due to the addition of ceramic, plasticizers and salt.

Conclusion

Composite solid polymer electrolytes comprising of PVdF (20) – PVC (5) – EC/PC (67) – LiClO₄ (8) with X % of ceramic (where X = 4, 8, 12, 16, 20) were prepared and their ionic conductivities are measured for different compositions of the nano sized ceramic filler. The structure and complexation behaviour of these electrolytes are confirmed by XRD and FTIR spectroscopic techniques. It is clear from table 6.1 and 6.2 that the ionic conductivity increases with the increase in the concentration of TiO₂ and CeO₂ upto 12 wt% and 8 wt% respectively, and then decreases. It is confirmed that the filler disrupts ion aggregation, probably by interaction directly with the ionic species. The overall performance of the CeO₂ based composite electrolyte systems is poor, when compared to that of TiO₂ based composite electrolytes. This confirms that the dielectric constant of the ceramic material could induce an amorphicity and hence higher conductivity.
Fig 6.1. XRD spectra of pure PVC, PVdF, LiClO$_4$ and PVdF (20)-PVC (5)-EC/PC (67) - LiClO$_4$(8) with X% of TiO$_2$ [X = (a) 4, (b) 8, (c) 12, (d) 16 (e) 20] in the total polymer weight.
Fig 6.2. FTIR spectra of pure PVdF (20)-PVC (5)- EC/PC (67) - LiClO$_4$ (8) with X% of TiO$_2$ [X = (a) 4, (b) 8, (c) 12, (d) 16 (e) 20] in the total polymers weight.
Fig 6.3. Impedance diagram of PVdF (20)-PVC (5)- EC/PC (67) - LiClO$_4$ (8) with X% of TiO$_2$ (X = 4, 8, 12, 16, 20) in the total polymers weight at different temperatures.

Fig 6.4. Dependence of ionic conductivity on ceramic concentration of PVdF (20)-PVC (5)- EC/PC (67) - LiClO$_4$ (8) with X% of TiO$_2$ (X = 4, 8, 12, 16, 20) in the total polymers weight.
Fig 6.5. Arrhenius plot of Log (σ) against reciprocal temperature of PVdF (20)-PVC (5)- EC/PC (67) - LiClO₄(8) with X% of TiO₂ [X = (a) 4, (b) 8, (c) 12, (d) 16 (e) 20] in the total polymers weight.
Fig 6.6. TG/DTA spectra of PVdF (20)-PVC (5)-EC/PC (67) - LiClO₄ (8) with X% of TiO₂ [X = (a) 4, (b) 8, (c) 12, (d) 16 (e) 20] in the total polymers weight.
Fig 6.7. XRD spectra of pure PVC, PVdF, LiClO₄ and PVdF (20)-PVC (5)- EC/PC (67) - LiClO₄ (8) with X% of CeO₂ \( X = (a) 4, (b) 8, (c) 12, (d) 16 (e) 20 \) in the total polymer weight.
Fig 6.8. FTIR spectra of pure PVdF (20)-PVC (5)- EC/PC (67) - LiClO₄(8) with X% of CeO₂ [X = (a) 4, (b) 8, (c) 12, (d) 16 (e) 20] in the total polymer weight.
Fig 6.9. Impedance diagram of PVdF (20)-PVC (5) - EC/PC (67) - LiClO₄ (8) with X% of CeO₂ (where X = (a) 4; (b) 8; (c) 12; (d) 16; (e) 20) in the total polymer weight at different temperatures.

Fig 6.10. Dependence of ionic conductivity on ceramic concentration of PVdF (20)-PVC (5)-EC/PC (67) - LiClO₄ (8) with X% of CeO₂ (X = 4, 8, 12, 16, 20) in the total polymer weight.
Fig 6.11. Arrhenius plot of Log (σ) against reciprocal temperature of PVdF (20)-PVC (5)- EC/PC (67) - LiClO₄ (8) with X% of CeO₂ [X = (a) 4, (b) 8, (c) 12, (d) 16 (e) 20] in the total polymer weight.
Fig 6.12. TG/DTA spectra of PVdF (20)-PVC (5)- EC/PC (67) - LiClO₄ (8) with X% of CeO₂ [X = (a) 4, (b) 8, (c) 12, (d) 16 (e) 20] in the total polymer weight.
Fig. 6.13. Surface and Cross sectional morphology of

(a), (b) PVdF (20) – PVC (5) – EC/PC (67) – LiClO$_4$ (8) – TiO$_2$ (12%)

(c), (d) PVdF (20) – PVC (5) – EC/PC (67) – LiClO$_4$ (8) – CeO$_2$ (8%)
Table 6.1
Conductivity values of PVdF(20) – PVC(5) - EC/PC(67) – LiClO₄(8) with X% of TiO₂ in the total polymers weight.

<table>
<thead>
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<th>Film content wt%</th>
<th>303 K</th>
<th>313 K</th>
<th>323 K</th>
<th>333 K</th>
<th>343 K</th>
<th>353 K</th>
<th>363 K</th>
<th>373 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 4</td>
<td>1.380</td>
<td>2.363</td>
<td>3.714</td>
<td>5.303</td>
<td>6.318</td>
<td>9.864</td>
<td>11.820</td>
<td>13.152</td>
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<td>(b) 8</td>
<td>3.582</td>
<td>4.702</td>
<td>4.786</td>
<td>6.642</td>
<td>7.792</td>
<td>12.690</td>
<td>13.541</td>
<td>13.794</td>
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<tr>
<td>(e) 20</td>
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<td>1.548</td>
<td>2.782</td>
<td>5.128</td>
<td>5.333</td>
<td>6.825</td>
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</tbody>
</table>
Table 6.2
Conductivity values of PVdF(20) – PVC(5) - EC/PC(67) – LiClO₄(8) with X% of CeO₂ in the total polymer weight.

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<tr>
<th>CeO₂ content</th>
<th>303K</th>
<th>313K</th>
<th>323K</th>
<th>333K</th>
<th>343K</th>
<th>353K</th>
<th>363K</th>
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<tbody>
<tr>
<td>Film wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) 4</td>
<td>1.442</td>
<td>1.764</td>
<td>2.117</td>
<td>2.903</td>
<td>4.500</td>
<td>5.590</td>
<td>6.014</td>
<td>6.667</td>
</tr>
<tr>
<td>(c) 12</td>
<td>2.049</td>
<td>2.451</td>
<td>3.846</td>
<td>4.971</td>
<td>5.556</td>
<td>8.632</td>
<td>11.36</td>
<td>15.214</td>
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<tr>
<td>(d) 16</td>
<td>0.725</td>
<td>0.765</td>
<td>0.875</td>
<td>1.027</td>
<td>1.460</td>
<td>3.752</td>
<td>4.623</td>
<td>4.385</td>
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<tr>
<td>(e) 20</td>
<td>0.262</td>
<td>0.297</td>
<td>0.338</td>
<td>0.649</td>
<td>1.153</td>
<td>2.011</td>
<td>2.832</td>
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References


