

# Effect of different plasticizer on structural and electrical properties of PEMA-based polymer electrolytes

S. Rajendran · M. Ramesh Prabhu

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**Abstract** Plasticized poly(vinyl chloride)/poly(ethyl methacrylate) PVC/PEMA-based blend polymer electrolyte films containing lithium perchlorate ( $\text{LiClO}_4$ ) as a salt were prepared by solvent casting technique. The effects of the plasticization on structural, thermal and electrical properties of the plasticized polymer blend electrolytes were investigated. The changes in the structural and complex formation properties of the materials were studied by XRD and FTIR techniques. Dielectric relaxation studies of the polymer electrolyte have been undertaken, and the results are discussed. TG/DTA technique is used to study the thermal stability. Complex impedance analysis is used to calculate the bulk resistance of the complexes. The effect of different plasticizer on the structural and physical properties of polymer blend electrolyte is well correlated.

**Keywords** Polymer blends · Plasticization · Complex impedance spectroscopy · XRD · Dielectric relaxation

## 1 Introduction

Gel polymers [1, 2] are promising materials as electrolytes in advanced electrochemical applications, particularly lithium battery technology. Several approaches have been directed to find the optimal combination of host polymer and dopant salt for fast ionic transport because of their potential applications in various electrochemical devices

[3]. The use of a low volatile liquid of high dielectric constant as a plasticizer in the polymer host [4–7] was to enhance the conductivity of polymer electrolytes.

A gel-type membrane is achieved by immobilizing a liquid solution (for instance, propylene carbonate (PC) and/or ethylene carbonate (EC) solutions of a lithium salt) into a polymer matrix. The polymers generally used for these systems are poly(methyl methacrylate) (PMMA) [8–10], poly(acrylonitrile) (PAN) [11], poly(vinylidene fluoride) (PVdF) [12, 13], poly(vinyl chloride) (PVC) [14, 15] and poly(ethyl methacrylate) (PEMA) [16–18].

Recent investigations [19] of PAN-based systems have shown, for example, a clear temperature dependence of the solution of the lithium cations with the plasticizer molecules and with the PAN cyanide group. These electrolytes exhibit sufficient mechanical strength and ionic conductivities of the order of  $10^{-3} \text{ S cm}^{-1}$  [20]. The reasonable conductivity of such plasticized films is offset, however, by their poor mechanical properties at high concentrations of plasticizers such as EC and PC. The problem of poor mechanical strength can be circumvented by blending PEMA with a polymer such as PVC which provides a rather rigid framework in the polymer electrolyte film because of its phase-separated morphology [21].

This article presents the results of a study on plasticized PVC/PEMA blends which contain lithium perchlorate ( $\text{LiClO}_4$ ) as electrolyte salt and PC, EC,  $\gamma$ -butyrolactone ( $\gamma$ -BL) and diethyl carbonate (DEC) as plasticizers.

## 2 Experimental section

### 2.1 Sample preparation

Poly(vinyl chloride) (Aldrich) and poly(ethyl methacrylate) (Aldrich) and  $\text{LiClO}_4$  (Aldrich) were dried under vacuum

S. Rajendran (✉) · M. Ramesh Prabhu  
School of Physics, Alagappa University, Karaikudi 630 003,  
India  
e-mail: srj54alu@gmail.com

M. Ramesh Prabhu  
e-mail: m\_ram83@rediffmail.com

at 100 °C for 10 h. The polymer electrolytes of various blend ratios were prepared by solution casting technique with THF as solvent. The solution thus obtained was cast on a glass plate, and THF was allowed to evaporate slowly in air at room temperature for 48 h. This procedure provides mechanically stable, free standing and flexible films with thickness between 1 and 2 mm. The polymer blends of (PVC:PEMA) blend ratio with constant salt concentration are prepared with different plasticizers (PC, EC, DEC,  $\gamma$ -BL).

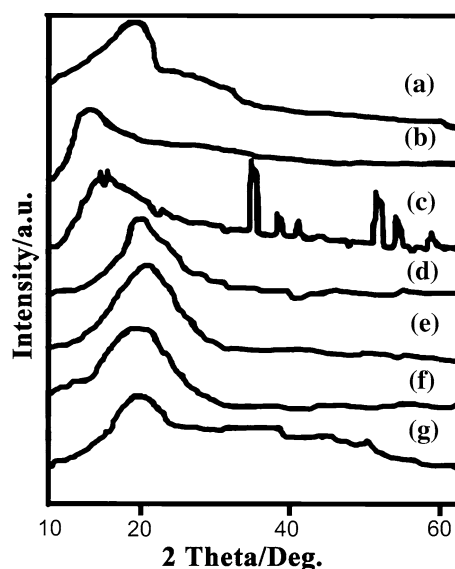
## 2.2 Samples characterization

Ionic conductivities of polymer electrolytes were evaluated from the complex impedance plot in the temperature range (301–341 K) using Keithley 3330 LCZ metre in the frequency range 40 Hz–100 kHz. Also, the dielectric relaxation measurements have been under taken. X-ray diffractograms of the films were studied by Bruker (D8 Advance) diffractometer. FTIR study was made using a Perkin-Elmer (Paragon 500 grating) IR spectrophotometer in the range 400–4000  $\text{cm}^{-1}$ . Thermal stability of the film was also characterized by TG/DTA at heating rate of 10 °C per minute from the room temperature to 400 °C.

## 3 Results and discussion

### 3.1 X-ray diffraction

The X-ray diffraction analysis is a useful tool to determine the structure and crystallization of the polymer matrices. In order to investigate the effect of plasticizers concentration in the PVC–PEMA–LiClO<sub>4</sub> system, XRD analysis has been performed, and their respective diffraction patterns of PVC, PEMA, LiClO<sub>4</sub> and their complexes PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8) with different plasticizer (PC, EC, DEC,  $\gamma$ -BL)-based complexes are shown in Fig. 1a–g. The XRD pattern, Fig. 1c, of LiClO<sub>4</sub> shows intense peaks at angles  $2\theta = 18.36^\circ, 23.2^\circ, 27.5^\circ, 32.99^\circ$  and  $36.58^\circ$ , which reveal the crystalline nature of the ionic salt (JCPDS:30-0751). Figure 1a shows one broad peak at angle  $2\theta = 13^\circ$ , which corresponds to PVC. Figure 1b shows diffraction peak at  $2\theta = 18^\circ$ , which is ascribed to PEMA. The diffractograms (Fig. 1d–g) of PVC–PEMA blend with different plasticizers clearly indicate the fact that the semi-crystalline nature of PVC structure is disturbed by the addition of different plasticizers and salt. The increase in the amorphous nature causes a reduction in the energy barrier to the segmental motion of the polymer electrolyte. The XRD pattern shows that most of the peaks corresponding to pure LiClO<sub>4</sub> disappeared in the blend polymer electrolytes, which reveals the complete dissolution of the salt in the polymer matrix.



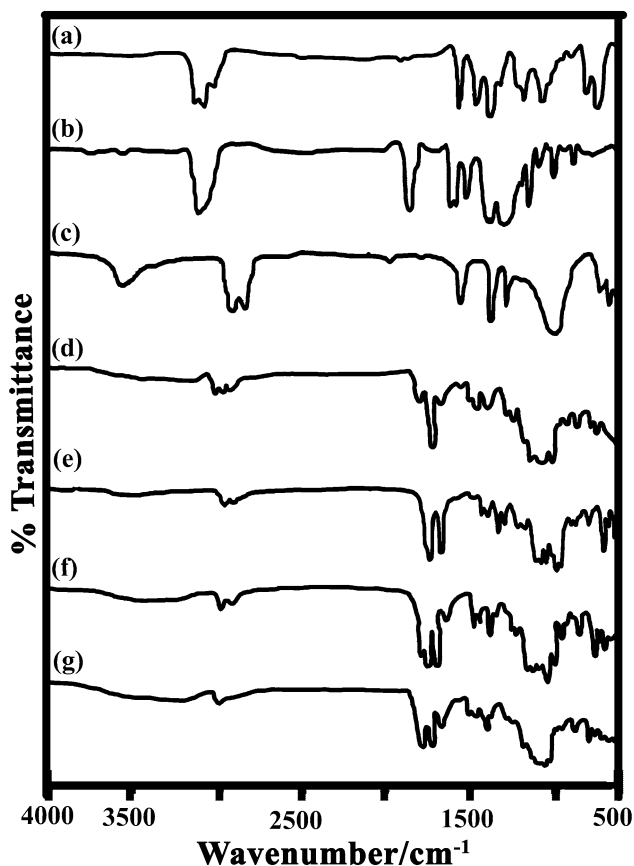
**Fig. 1** X-ray diffraction patterns of (a) pure PVC, (b) pure PEMA, (c) LiClO<sub>4</sub>, (d) PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–EC(67), (e) PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–PC(67), (f) PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–DEC(67), (g) PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–GBL(67)

### 3.2 FTIR analysis

The FTIR spectra of the polymer complexes are presented in Fig. 2. The vibrational peaks at 954 and 630  $\text{cm}^{-1}$  are assigned to *trans*-CH rocking and *cis*-CH wagging of PVC. Peaks at 2963 and 1329  $\text{cm}^{-1}$  are assigned, respectively, to asymmetric C–H methylene group vibration and in-plane CH deformation of PVC. In PEMA, the peak at 1725  $\text{cm}^{-1}$  represents the carbonyl stretching vibration and at 2982, 2939 and 2910  $\text{cm}^{-1}$  are due to the methylene, C(CH<sub>3</sub>), and ethylene, (O) C<sub>2</sub>H<sub>5</sub>, groups which overlap. The peak at 1777  $\text{cm}^{-1}$  represents the CH<sub>3</sub>–C– vibration of PC. The sharp vibrational peaks at 1774 and 1789  $\text{cm}^{-1}$  are assigned to C=O stretching vibrations of EC and PC molecules. The weak intensity peak appearing at 507  $\text{cm}^{-1}$  is assigned to ClO<sub>4</sub><sup>−</sup> [22].

The vibrational peaks at 1219, 1155, 973  $\text{cm}^{-1}$  of EC-based complex; 1340, 951, 849  $\text{cm}^{-1}$  of PC-based complex; 2991, 1757, 1639, 1379, 1272  $\text{cm}^{-1}$  of DEC-based complex and 1767, 1648, 1280, 1036 and 676  $\text{cm}^{-1}$  of GBL-based complex are shifted to 1355, 965, 860; 1236, 1143, 964; 2986, 1773, 1657, 1389, 1269; 1776, 1656, 1266, 1025 and 666  $\text{cm}^{-1}$ , respectively.

It is also found that some of the peaks appearing in the pure polymers, salt and plasticizers disappear in the complexes, i.e. those at 3448, 3514, 2739, 1866, 1077, 543 and 493  $\text{cm}^{-1}$ . In addition to this, new peaks are observed at 3530, 2928, 2905, 1662, 1446, 1024, 963, 718 and 660  $\text{cm}^{-1}$  in the polymer complexes. The shifting of peaks and the formation of new peaks in the electrolyte systems



**Fig. 2** FTIR Spectra of (a) pure PVC, (b) pure PEMA, (c) LiClO<sub>4</sub>, (d) PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–EC(67), (e) PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–PC(67), (f) PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–DEC(67), (g) PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–GBL(67)

indicate the polymer–plasticizer interaction in PVC/PEMA-based hybrid polymer blend electrolytes.

### 3.3 Conductivity studies

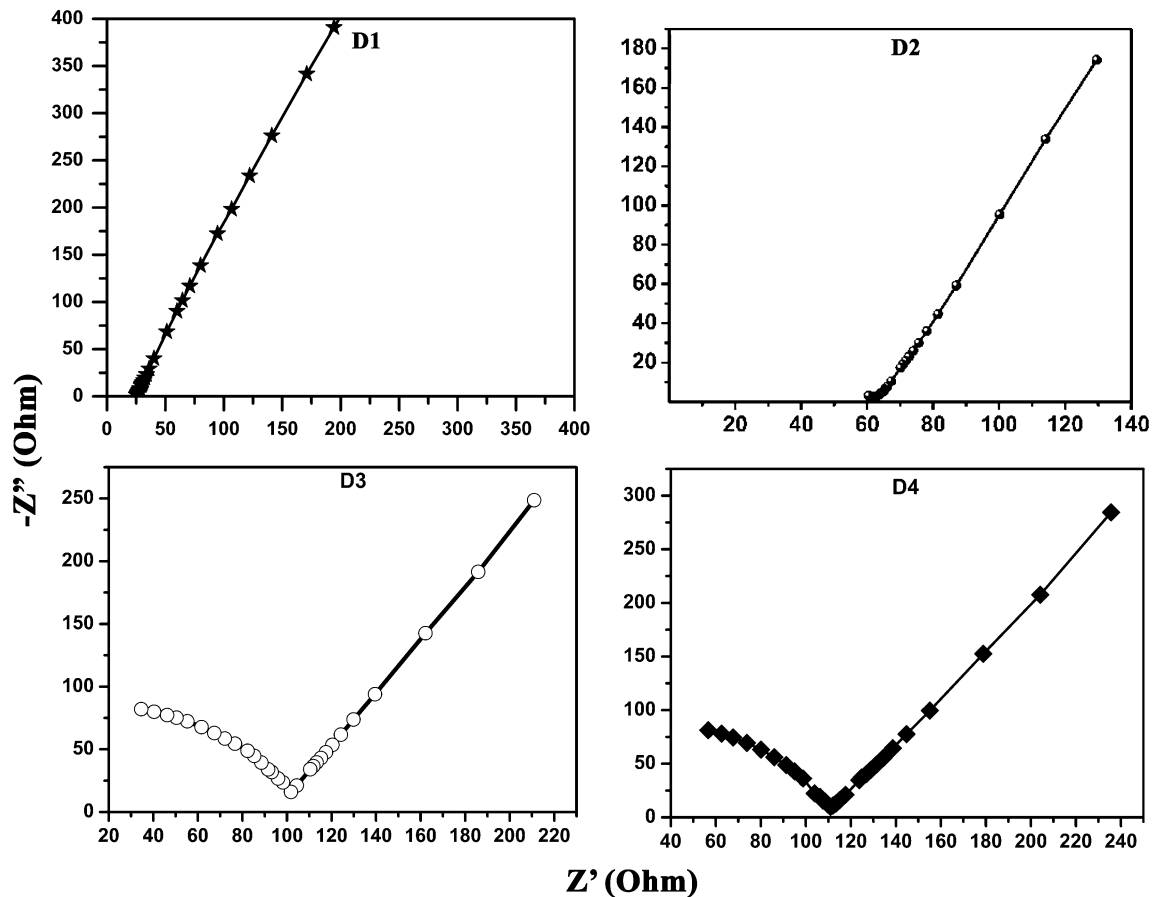
Impedance spectroscopy is employed to establish the conduction mechanism, observing the participation of the polymeric chain, mobility and carrier generation processes. The conductivities of the polymer complexes were calculated from the bulk resistance ( $R_b$ ) obtained by the intercepts of the typical impedance curves for various temperatures. The impedance curve of EC-based PVC–PEMA–LiClO<sub>4</sub> system is shown in Fig. 3 for the room temperature. The disappearance of the semicircular portion in the impedance curve leads to a conclusion that the current carriers are ions and this leads one to further conclude that the total conductivity is mainly the result of ion conduction [23]. The ionic conductivities were calculated using the relation  $\sigma = l/R_b A$ , where  $l$  is the thickness,  $R_b$  is bulk resistance and  $A$  is the known area of the electrolyte film. Table 1 shows the conductivity values of the

complexes in the range 301–341 K. It is observed that as the temperature increases, the conductivity also increases for all complexes, and this behaviour is in agreement with the theory established by Armand et al. [24]. This can be rationalized by recognizing the free volume model [25]. When temperature is increased, the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighbouring atoms and creates a small amount of space surrounding its own volume in which vibrational motion can occur [26]. Therefore, the free volume around the polymer chain causes the mobility of ions and polymer segments and hence the conductivity. Hence, the increment of temperature causes the increase in conductivity due to the increased free volume and their respective ionic and segmental mobility. From Table 1, it is depicted that the maximum conductivity value  $4.281 \times 10^{-3} \text{ S cm}^{-1}$  at 301 K is observed for PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–EC(67) complex, which is indeed a higher value than the value of  $10^{-4} \text{ S cm}^{-1}$  reported by Morita et al. [27] for PEO–PMMA complexes with lithium salts and EC as the plasticizer. The effect of plasticizers on the polymer segmental and ionic mobility and conductivity depends on the specific nature of the plasticizer, including viscosity, dielectric constant, polymer–plasticizer interaction and ion–plasticizer interaction. All plasticized electrolyte films exhibit an enhancement in conductivity as compared to the unplasticized electrolytes. Figure 4 shows the variation of log conductivity with inverse absolute temperature for various plasticizer-based PVC–PEMA–LiClO<sub>4</sub> complexes. From the plot, it has been observed that as temperature increases the conductivity values also increase for all the compositions. The non-linearity in Arrhenius plots indicates that ion transport in polymer electrolytes is dependent on polymer segmental motion. The curvature behaviour of the plots suggests that the data can be better described by the Vogel–Tamman–Fulcher (VTF) relation [28–30], which described the transport properties in a viscous matrix. It supports the idea that the ion moves through the plasticizer-rich phase.

### 3.4 Dielectric studies

The dielectric relaxation studies are considered as very useful in understanding the behaviour of polymers and their blends. A broad frequency range of dielectric relaxation spectroscopy is a very useful tool to study the relaxation of dipoles in polymer electrolytes. The variation of real and imaginary parts of the dielectric constant as a function of angular frequency for PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–EC(67) complex is shown in Figs. 5 and 6.

The complex dielectric constant of a system is defined by  $\varepsilon^* = \varepsilon' - i\varepsilon''$ , where  $\varepsilon'$  is real part of dielectric constant,



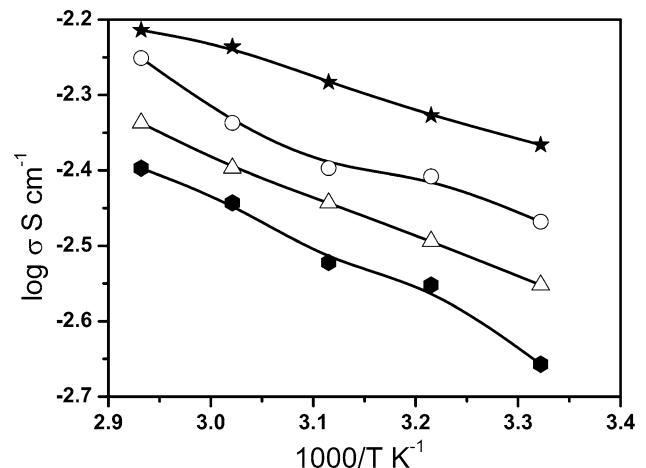
**Fig. 3** Impedance complex spectra of PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–X(67) wt% (where X = EC, PC, DEC, GBL) complexes at 301 K

**Table 1** Ionic conductivity values for EC, PC, DEC and GBL complexed with PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8) system

Film	Plasticizers	Ionic conductivity $\times 10^{-3}$ S cm <sup>-1</sup>				
		28 °C	38 °C	48 °C	58 °C	68 °C
D1	EC	4.3	4.7	5.2	5.8	6.1
D2	PC	3.4	3.9	4.0	4.6	5.6
D3	DEC	2.8	3.2	3.6	4.0	4.6
D4	GBL	2.2	2.8	3.0	3.6	4.0

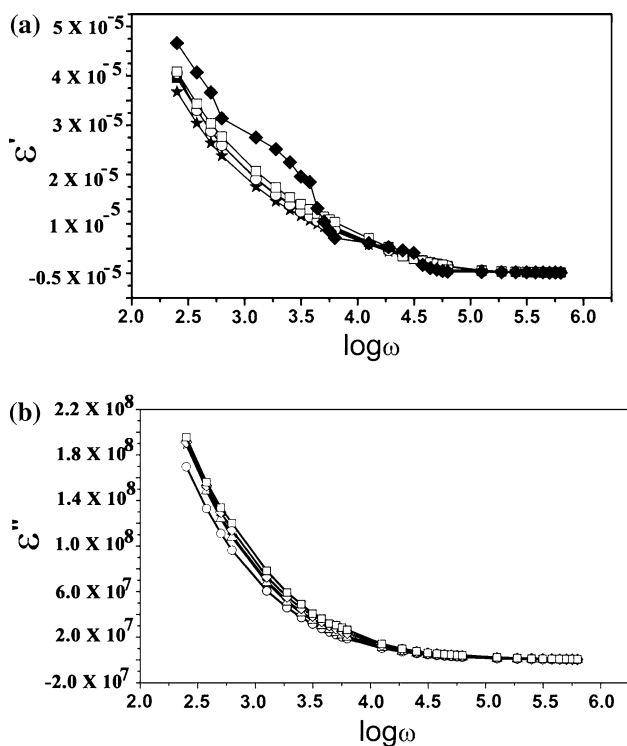
$i\epsilon''$  the imaginary part of dielectric constant of the material. Also, these two real and imaginary parts of the dielectric constants are expressed as  $\epsilon' = Cd/\epsilon_0 A$ ;  $\epsilon'' = \sigma/\omega\epsilon_0$ , where ' $\epsilon_0$ ' is permittivity in free space;  $C$  is parallel capacitance;  $d$  and  $A$  are thickness and known area of the sample, respectively;  $\omega$  is the angular frequency;  $\sigma$  is the conductivity of the sample which may be expressed as  $\sigma = Gd/A$ , where  $G$  is the conductance.

From the Fig. 5a and b, both  $\epsilon'$  and  $\epsilon''$  rise sharply towards low frequencies, and the rise is displaced to higher



**Fig. 4** Arrhenius plot of PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–X(67) wt% (where X = EC, PC, DEC, GBL) complexes

frequencies at higher temperatures. Rather sensitive and sharp rise of the components of the dielectric constant of ( $\epsilon'$  and  $\epsilon''$ ) most probably due to electrode polarization



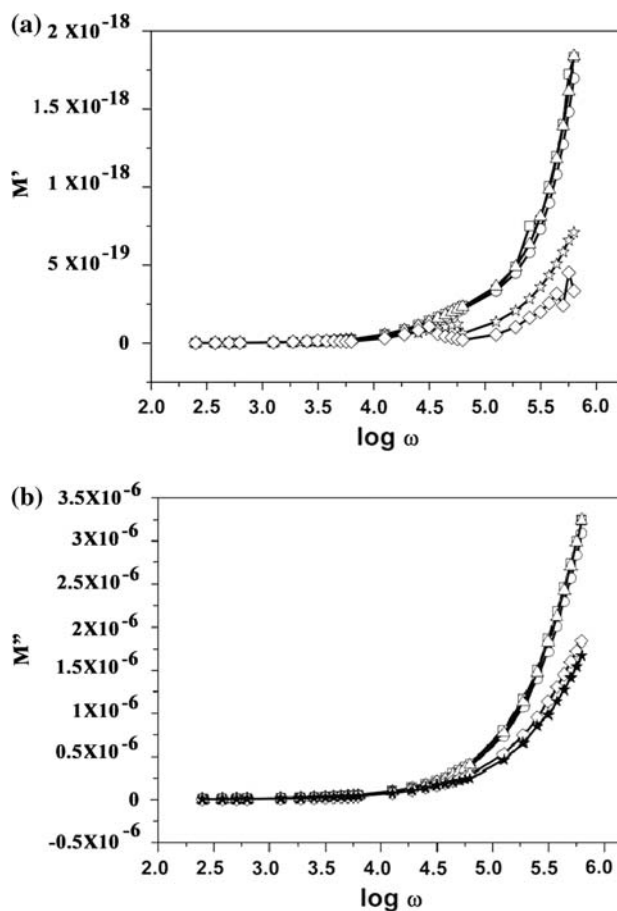
**Fig. 5** Dielectric plot of PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–EC(67) wt% complex at various temperature

effects, and in the Fig. 6a and b, the modulus formalism masks the low frequency dispersion due to electrode polarization effects. The bulk conductivity relaxation in these systems is expected to occur at frequencies higher than the present frequency range of measurement.

### 3.5 TG/DTA analysis

TG/DTA has been used widely to study all physical processes involving the weight changes and as such has been used to measure the diffusion characteristics and the moisture uptake. Also, it is used to investigate the thermal degradation, phase transitions and crystallization of the polymers. Figure 7a–d shows the TG/DTA curves of EC-, PC-, DEC- and GBL-based PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8) system.

The film starts decomposing at 40, 35, 33 and 50 °C with a weight loss of 3–10 wt% of EC, PC, DEC, GBL complexes, respectively (Fig. 7a–d). This is attributed to the presence of moisture at the time of loading the samples. A second decomposition takes place at 260, 254, 230 and 275 °C with a rapid weight loss of 75, 80, 50 and 70 wt% of EC, PC, DEC and GBL complexes, respectively. This indicates that the film is stable up to 260, 254, 230 and 275 °C.

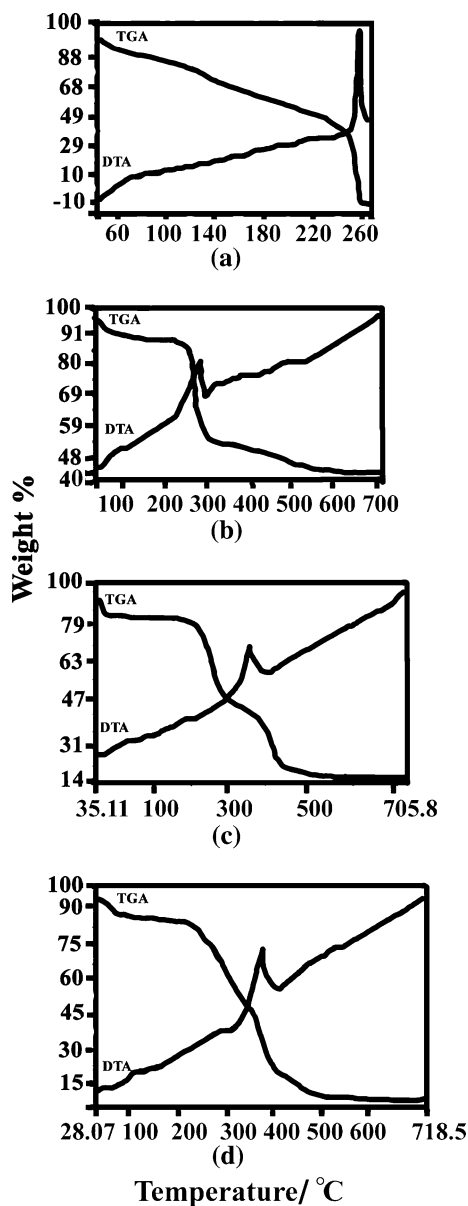


**Fig. 6** Dielectric moduli plot of PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8)–EC(67) wt% complex at various temperature

The DTA trace shows that an endothermic peaks at around 275, 280, 250 and 290 °C, respectively. It is clear that the decomposition temperature for EC-based complex is found to be 260 °C, which is slightly lower than that GBL-based complex even though the conductivity is found to be maximum for this electrolyte film.

### 4 Conclusion

Polymer electrolytes comprising EC, PC, DEC and GBL complexed with PVC(5)–PEMA(20)–LiClO<sub>4</sub>(8) wt% systems were prepared using solvent casting technique. Complexation of the polymer matrices has been ascertained by XRD and FTIR analyses. Ionic conductivity of the polymer electrolytes has been measured in the range of 301–341 K. The maximum ionic conductivity value has been obtained for EC-based complex because of the high dielectric constant as compared to the other plasticizers used in this study. The temperature-dependant ionic conductivity plot of the electrolyte films seems to obey



**Fig. 7** TG/DTA curves of PVC(5)–PEMA(20)–LiBF<sub>4</sub>(8)–PC(67) complex

the VTF relation. The dielectric relaxation behaviour of the samples is also discussed. A sustained increase in the thermal stability (260 °C) is observed for EC-based complex as compared to pure PEMA.

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