Research Article

Ionic Conductance, Thermal and Morphological Behavior of PEO-Graphene Oxide-Salts Composites

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Thin films composites of poly(ethylene oxide)-graphene oxide were fabricated with and without lithium salts by solvent cast method. The ionic conductivity of these composites was studied at various concentrations of salt polymer-GO complexes and at different temperatures. The effects of temperature and graphene oxide concentration were measured from Arrhenius conductance plots. It is shown that the addition of salts in pure PEO increases conductance many times. The graphene oxide addition has enhanced the conductance approximately 1000 times as compared to that of pure PEO. The activation energies were determined for all the systems which gave higher values for pure PEO and the value decreased with the addition of LiClO$_4$ and LiCl salts and further decreases with the addition of graphene oxide. The composite has also lowered the activation energy values which mean that incorporation of GO in PEO has decreased crystallinity and the amorphous region has increased the local mobility of polymer chains resulting in lower activation energies. SEM analysis shows uniform distribution of GO in polymer matrix. The thermal stability studies reveal that incorporation of GO has somewhat enhanced the thermal stability of the films.

1. Introduction

Polymer electrolytes have received considerable attention due to their potential uses in solid state electrochemical devices and particularly in lithium batteries [1–4]. Because of their unique mechanical, electrical, optical, and thermal properties, the various allotropes of carbon such as diamond, graphite, graphene, and fullerene with various geometrical shapes (spherical, ellipsoidal, layered, single sheet, tubes, and buds) have attracted enormous interest from both scientific and engineering standpoints. They have extraordinary potential applications in electronics, sensors and actuators, solar cells, data storage, optics, medical applications, biomaterials, and functional nanocomposites. The most recent important discovery in this field is the graphene and graphene based polymer electrolytes. Graphene is a single layered carbon having hexagonal packed structure which has shown a wide variety of applications with better properties such as good optical transparency [5], high carrier mobility at room temperature [6], high Young's modulus [7], and excellent conductivity. Pristine graphene is not compatible with polymers and

does not form homogeneous composites. The pure graphene as such is not very useful because the properties of the composites depend on the distribution of graphene layers in polymer matrix as well as interfacial bonding between the two. In this regard the modified form of graphene where the graphene is modified to graphene oxide (GO) has been found to be more compatible with polymers [8–13]. The GO contains mostly oxygen functional groups like alcohols, carboxylic acid, and epoxides [6]. These functional groups make GO more reactive than the inert graphene and easier to intercalate. Polymer-layered graphene oxide composites are new class of materials where fillers/salts are dispersed in polymer matrix and then GO is also added to prepare composite. These low cost materials show high performance [14–18], so they are attracting more attention from scientists and researchers [19]. The work on this kind of polymer graphene composite has shown that graphene improves the mechanical and electrical properties much better than any other filler like clay or even carbon nanotubes [20–23]. There have been several efforts to prepare useful graphene based polymer composites and important improvement has also

TABLE 1: Composition, conductance, and activation energy values of the samples.

Composition	Conductance (S cm^{-1}) at 303 K	Conductance (S cm^{-1}) at 323 K	Activation energy (KJ/mole)
PEO	1.386×10^{-8}	5.482×10^{-8}	19.887
0.15 wt %GO/PEO	9.885×10^{-7}	1.667×10^{-6}	15.163
0.4 wt %GO/PEO	1.468×10^{-6}	2.421×10^{-6}	14.690
0.7 wt %GO/PEO	2.275×10^{-6}	3.580×10^{-6}	14.216
1.4 wt %GO/PEO	5.188×10^{-6}	1.020×10^{-5}	13.335
PEO:LiCl	3.169×10^{-7}	4.655×10^{-7}	16.386
0.07 wt %GO/PEO:LiCl	7.673×10^{-6}	1.770×10^{-5}	12.811
0.20 wt %GO/PEO:LiCl	1.300×10^{-5}	3.273×10^{-5}	12.263
0.32 wt %GO/PEO:LiCl	2.218×10^{-5}	3.655×10^{-5}	11.764
0.63 wt %GO/PEO:LiCl	2.679×10^{-5}	4.753×10^{-5}	11.550
PEO:LiClO$_4$	6.137×10^{-7}	1.025×10^{-6}	15.688
0.07 wt %GO/PEO:LiClO$_4$	2.041×10^{-5}	3.630×10^{-5}	11.889
0.20 wt %GO/PEO:LiClO$_4$	2.792×10^{-5}	6.039×10^{-5}	11.529
0.32 wt %GO/PEO:LiClO$_4$	3.243×10^{-5}	6.950×10^{-5}	11.356
0.63 wt %GO/PEO:LiClO$_4$	5.105×10^{-5}	1.081×10^{-4}	10.783

been achieved. However, in spite of considerable advances, fundamental research is still necessary to get basic understanding to enable full exploration of their potential. The conducting polymer graphene composites are such composites which have potential applications in various fields like biomedical applications, such as electrical material for electrochromic devices and air craft parts [24].

In the present work an attempt has been made to synthesize thin films of PEO-graphene oxide composites with LiClO$_4$/LiCl salts in order to check their conductance, thermal and morphological properties. PEO is very important thermoplastic polymer which has unique property of solubility in both aqueous and organic solvents. It has polyether chain which can strongly coordinate with cations like Li$^+$, Na$^+$, or Ca^{2+} and so forth, leading to formation of polyelectrolyte for use in battery and other electrochromic devices. It will be interesting to prepare the PEO polyelectrolyte with GO and study their electrochemical behavior. To our knowledge composite materials of PEO with GO are neither quite well reported in the literature nor are known well. Further thin film composites of such system are not discussed elsewhere. This study will add to the knowledge about their potential use in electrochromic devices and so forth.

2. Experimental

2.1. For Conductance Measurement. The graphene based electrolytes were prepared from polyethylene oxide. (Average molecular weight was 300,000 and LiCl and LiClO$_4$ were used as salts and graphene oxide was used as additive.) Samples preparations were carried out in a dry room. The composition of various components is shown in Table 1.

Precisely measured quantities of PEO, GO, LiCl, and LiClO$_4$ were dissolved in a minimum amount of MQ water and the solutions were stirred for 24 hours at room temperature by magnetic stirrer and also further sonication for 1 hr so that homogenous solutions were obtained. The solutions

of various compositions were cast on the identical Teflon Petri Dish and allowed to evaporate off the excess solvent for 24 hrs in evacuated desiccators at 60°C. After partial evaporation of MQ water from the solution, mechanically stable freestanding thin solid polymer electrolyte films were obtained. The resulting thin films were further dried for 24 hrs in vacuum oven to remove any remaining traces of solvent.

The conductance of these prepared samples of graphene based polymer electrolytes systems was subjected to AC impedance. Conductivity of polymer films was evaluated from impedance. Then impedance data was obtained by using LCR HITESTER, Model 3522–50, Hioki, Japan. The graphene based polymer electrolyte samples were cut into pieces with diameter of about 15 mm. The sample films of graphene polymer electrolyte were clipped in between two crocodile clips of the meter and were enclosed in a special vessel, which was immersed in water bath to keep the temperature constant. A digital thermometer was also attached near the film to note the exact temperature of the sample film. The impedance data of these samples were measured. The study was carried out in the frequency range of 1 HZ to 100 KHZ. The temperature dependent conductivity of these samples was performed at 10°C intervals in the temperature range of 10 to 50°C.

2.2. Result and Discussion. The interest in graphene based composites stems from their potential use in electrochromic devices. Conductance is a property that is very important in this regard. Various factors influence ionic conductivity of solid polymer electrolytes. The most important of these factors are concentration of conducting ions, concentration, and their mobility. The mobility of ionic species decreases by the increase in degree of crystallization which causes low ionic conductivity. In the present research work different solid polymer electrolytes of PEO-graphene oxide have been prepared by adding different lithium salts (LiClO$_4$ and LiCl)
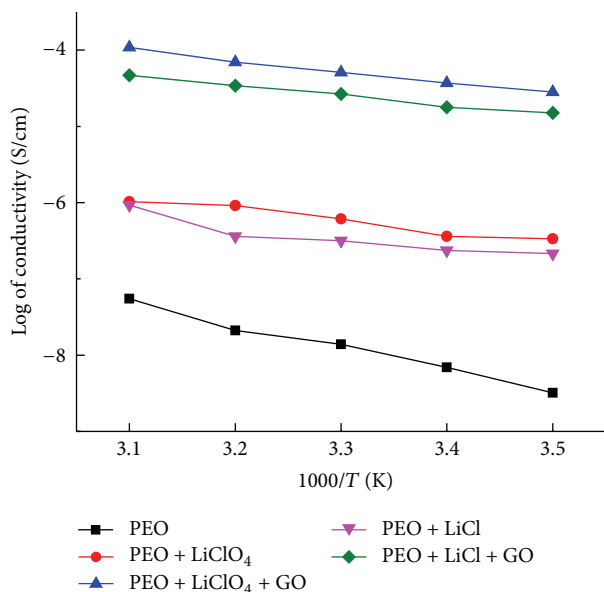
FIGURE 1: Conductance plot for PEO, PEO-LiClO$_4$, PEO-LiCl, PEO-LiClO$_4$-GO, and PEO-LiCl-GO systems.

and graphene oxide into PEO matrix. The graphene based polymer electrolyte films obtained by using this method were very translucent and freestanding. The temperature dependence of conductivities of these systems was determined.

Pure PEO and PEO-salt systems were first subjected to conductance measurements in order to assess their conductance. The temperature dependence of such systems is shown in Figure 1 and Table 1 at two temperatures. It can be seen that pure PEO system has lowest conductivity values at all temperatures (e.g., at 30°C its value is 1.386×10^{-8} S/cm) which increase with both salts and GO. With 1.4 wt% GO addition, a conductivity of 5.188×10^{-6} S/cm is obtained (10^2 times) and with GO + LiCl it is 2.679×10^{-5} while with LiClO$_4$ addition gives conductivity of 5.105×10^{-5}. This shows enhancement of conductivity with addition of both GO and salts. These results show that not only GO but also the salts were evenly dispersed in the PEO matrix and efficiently made connected conductive channels. As PEO is crystalline polymer, it has low conductance value while the addition of salts increases mobile ions and the conductive channels provide pathways for the movement of ions, so conductance increases. Similarly the interaction of the host polymer backbone and salts is affecting the chain dynamics of PEO. The coordination bonds between ether of PEO and Lithium ion is in a way interrupting the packing of PEO to decrease its crystallinity. This is promoting amorphous phase believed to favor ion transport and hence conductivity.

The GO also seems to enhance conductance due to the fact that it is providing more effective paths for the migration of conducting ions.

From measurement of ionic conductivity values at different temperature, it is found that ionic conductivity values increase with the increase in temperature but the increase in ionic conductivity values is different for different salts depending on ionic size and tendency of ionic association. The increase in ionic conductivity with the increase in temperature is due to the fact that at low temperature ionic mobility and segmental motions of polymer chains are restricted due to strong salt polymer association, while at higher temperature ionic conductivity increases due to decrease in salt polymer association and increased thermal segmental motion of polymer chains. It is found that ionic conductivity of polymer electrolytes PEO:LiClO$_4$ containing LiClO$_4$ salt is higher compared to polymer electrolytes containing other salts. The LiClO$_4$ salt composites show much enhanced conductivity than LiCl systems because it is believed that the association between Li$^+$ and ClO$_4^-$ anion is weaker as compared to Li$^+$ and Cl$^-$. The ClO$_4^-$ ion has smaller size than Cl$^-$ ion, as anions of smaller radius show more mobility with the increase in temperature as compared to that of larger sized cations. Weak pairing of these ions causes easy dissociation and greater mobility. Studies of association between Li$^+$ ions and anions show that ClO$_4^-$ and Cl$^-$ are weekly associated with Li$^+$ ions compared to other anions. Weak ion pairing of these ions causes easy dissociation and greater mobility. The maximum ionic conductivity at 303 K (30°C) temperature is found to be 6.137×10^{-7} S cm^{-1} for PEO:LiClO$_4$ polymer electrolyte system.

The effect of addition of GO is shown in Figure 1 and also in Table 1 with both the salts. The ionic conductivity values are maximum for GO/PEO:LiClO$_4$ composite system as compared to GO/PEO:LiCl system. The maximum ionic conductivity at 30°C was found to be 5.105×10^{-5} S/cm for 0.63 wt% GO/PEO:LiClO$_4$ system. This system contains 0.63 wt% of GO in the composite. This is shown to be much higher than pure PEO (1.386×10^{-8} S/cm); that is, an increase of at least 1000 times in conductivity has occurred. The conductance value by pure graphene is although reported to the higher, but, unlike graphene, GO is electrically insulating so a comparison with pure graphene is not suitable for such composite. The PEO-salt system is acting as conducting material while GO is acting as enhancement agent/filler. It is well known that morphology of conductive filler has significant effect on the formation of conductive network and the electrical properties of the composite [25, 26]. It is believed that in the present PEO/GO-salt system a kind of network has been formed.

The GO is dispersed evenly and uniformly which is confirmed by the activation energy values calculated for the systems from Arrhenius equation as given in Table 1 and also from SEM analysis. The values of activation energy decrease with the increase in contents of GO in all the three kinds of system which we have studied, that is, GO/PEO, GO/PEO:LiCl, and GO/PEO:LiClO$_4$. A mobile Li$^+$ ion within the polymer matrix requires low energy and hence increases the conductivity. It is also possible that GO is lowering the percolation threshold of the composites and a continuous network is being formed by the GO. It is a kind of segregated network. The GO acting as conducting enhancer distributes itself along specified pathways in the polymer matrix. Thus they have more contacting probability decreasing contact resistance. As a consequence the composites with more GO
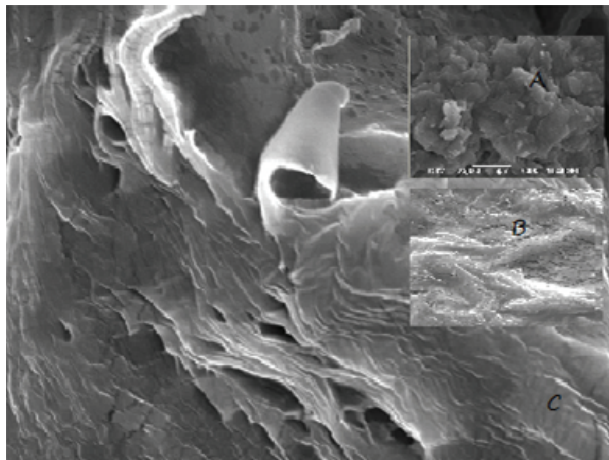
FIGURE 2: SEM of (A) pure PEO, (B) pure graphene, and (C) 1.4 wt% GO/PEO system.

FIGURE 3: TGA of pure PEO with different GO concentration.

FIGURE 4: TGA of PEO:LiCl and also with different GO concentration.

have lower percolation threshold and hence conductance values increase with GO contents.

The ionic mobility and viscosity of polymer electrolyte depend on chain flexibility which in a way can be judged by glass transition temperature (T_g). At this temperature (T_g) without a change in structure the sample becomes a rubbery amorphous phase on heating. Glass transition temperature of a polymer is concerned with the mobility of the polymer chain [27]. The effect of addition of fillers like graphene in polymer matrix or polymer electrolytes towards T_g is rather controversial. Keddie et al. reported about increase of T_g of atactic poly(methyl methacrylate) thin films on neat surfaces but showed decrease on low adhesive surfaces [28]. Ellison and Torkelson showed that (T_g) changed near the interfaces between fillers and polymer matrix [29]. The graphene loading of 0.05 wt% was shown to increase (T_g) by Ramanathan et al. [30], while other reports did not find any change in (T_g) at even higher graphene amount [31, 32]. In recent study by Liao et al. it was shown that in polyelectrolyte formed by physical blending process there is no change in T_g with graphene addition [33]. Furthermore it is well known that hydrogen bonds are highly temperature dependent. It has been reported by Noro et al. [34] that in poly(vinyl pyridine) only 40% of the hydrogen bonds are active at 125°C compared to the bonds at 64°C. So keeping the fact that PEO usually shows T_g at around −66°C, there will be more hydrogen bonds to interact with graphene, so it is reasonable to assume that our solution blended PEO-graphene system will show no change in T_g. Due to this reason the T_g studies were not undertaken.

2.3. SEM Studies. The SEM micrograph of pure PEO shown in Figure 2(A) is having crystalline flat lamellar leaf-like structure. Some spaces between the leaf-like structures are available throughout the structure. The figure of SEM of pure graphene oxide is given in Figure 2(B). It is a kind of layered structure or somewhat crumpled paper-like morphology.
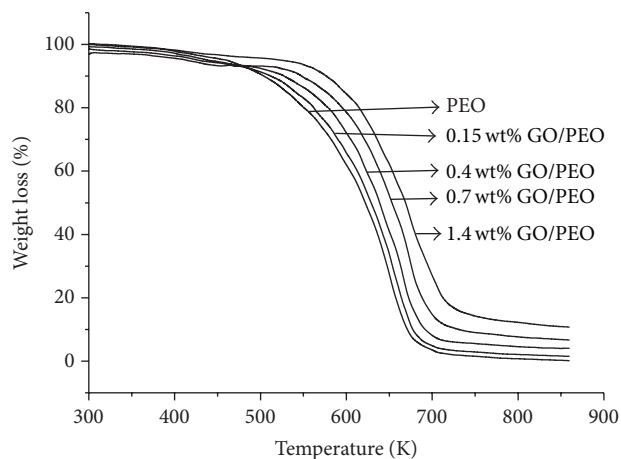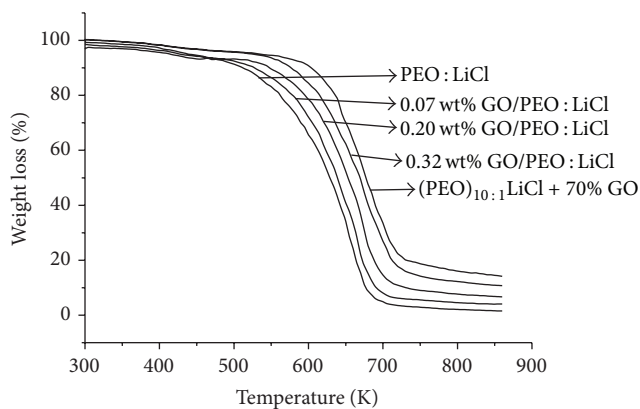
The SEM of 1.4 wt% GO/PEO as given in Figure 2(C) shows the incorporation of GO in PEO. This micrograph shows that the exfoliation of GO crumpled paper-like structure is being opened by PEO leaf-like structure. This micrograph is a combined structure of both the components and shows that both the components are homogeneously integrated within each other and no separate entity is seen. A complete mixing is thus confirmed.

2.4. Thermal Studies. Thermal stability is very important for polymeric materials because end use and processability of these depend on it. The thermal stability studies were undertaken by thermogravimetric analysis (TGA). The thermograms of the three kinds of systems, that is, GO/PEO, GO/PEO:LiCl, and GO/PEO:LiClO$_4$, are given in Figures 3, 4, and 5. The PEO/GO thermogram (Figure 3) shows that with the increase of GO contents the major weight loss (onset of degradation) temperature value increases showing more thermal stability with more GO. The pure PEO degrades at approximately 450 K (177°C) while 1.4 wt% GO/PEO composite onset temperature is 600 K (327°C) showing an increased thermal stability. This means that there is strong
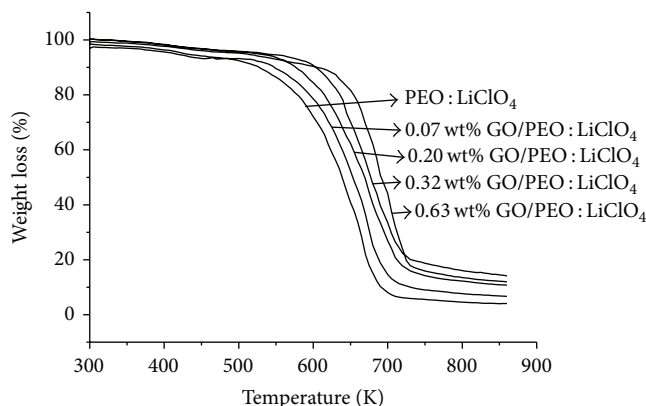
FIGURE 5: TGA of PEO:LiClO$_4$ and also with different GO concentration.

interaction between polymer matrix and GO which decreases the chain mobility at the interface and enhances the thermal stability.

The GO/PEO:LiCl thermogram is given in Figure 4. LiCl salt is enhancing thermal stability with higher onset temperature. The composite with higher GO is even more stable and degrades at 640 K (367°C).

The third thermogram of GO/PEO:-LiClO$_4$ (Figure 5) is seen to be the best and highest stable in terms of thermal behavior. It can be concluded that GO along with salts has enhanced the thermal stability of the films. If we see the effect of GO addition separately then it is clear that GO containing composites have more and significant improvement in thermal stability compared with neat PEO. While the content of GO in the composite is as low as 0.63 wt%, the onset of degradation temperature has risen from 177°C of pure PEO to 377°C for 0.63 wt% GO containing composite. This means that an improvement of about 200°C has been given to the system by GO. Again this may be due to uniform distribution and well exfoliation of GO which is hindering the thermally degraded volatile products and slowing the degradation. Such important increase widens the spectrum of application of GO/PEO:salt composites whenever thermal stability is a key factor. This increased high thermal stability with GO makes these polymer-GO composites promising materials as flame retardant materials which delay the time of ignition or resist the spread of fire [35].
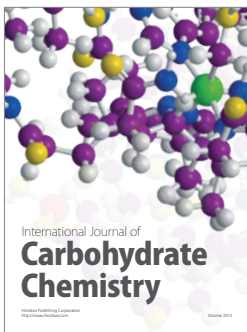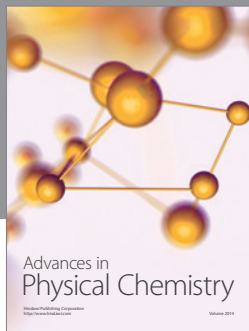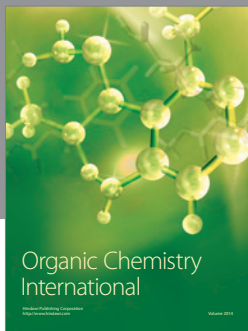
Conflict of Interests

The authors declare that they have no conflict of interests.

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