Synthesis and rheological characterization of PEO-Lithium manganate composites

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INTRODUCTION

Polymer electrolyte based on PEO has been on the focus of interest ever since this finding that they can be used as electrolyte (Shin et al., 2005). The most significant drawback of conventional PEO-based electrolytes is their low conductivity (\( \rho < 10^{-5} \text{ S/cm} \)) at ambient temperatures, which is mainly due to the presence of a nonconductive crystalline phase under these conditions (Fauteux et al., 1995). At temperatures above 60 ºC, PEO-based polymer electrolytes show appreciable conductivities (\( \rho > 10^{-4} \) S/cm) as the crystalline phase in PEO melts; however, under these conditions the materials lose their dimensional stability and behave like extremely viscous liquids. Weston and Steele (1982) hence proposed that particulate fillers could be introduced into the polymer matrix to improve its mechanical stability at high temperatures. The fillers not only contribute to enhanced mechanical properties but also lead to superior interfacial stability for the electrolyte in contact with lithium metal, by a mechanism not yet understood (Capuano et al., 1991). In some cases, increases in conductivity have also been observed on addition of filler and have been attributed to a decreased level of polymer crystallinity (Wieczorek, 1992; Wieczorek et al., 1995). It has been reported that the addition of nanoparticles such as TiO\(_2\), Al\(_2\)O\(_3\), SiO\(_2\), and ZnO to polymer electrolytes raises the conductivity in the solid state without losing mechanical and interfacial properties (Faers, 2003). Moreover; it has been found that PEO nanocomposite filled with nanoclay show quite a bit of potential for use as polymer electrolytes (Liao and Ye, 2004; Long et al., 2004; Loyens et al., 2005). It is well known fact that particle–particle interactions, particle–polymer interactions, the dispersion state of particles, and the shape and orientation of dispersed particles are reflected in the rheological properties (Luckham and Ukeje, 1999). The rheological behavior of polymeric material can indicate an internal structure of material and depends on dispersion state, shape, loading and surface condition of fillers in a polymer system (Mitchell et al, 1999).
Lithium manganate is a promising material to be used as cathode because it has advantages of lower cost, higher abundance of Mn in earth, good safety and non-toxicity (Tucker et al., 2002; Im and Manthiram, 2003). Our objective in this study is to determine rheological properties of PEO-LiMn$_2$O$_4$ systems to understand the effect of polymer on flow properties of Lithium Manganate for its potential use in various applications in the form of polyelectrolyte composite. We made our study on a wide range of PEO composites with lithium manganate to see the effect of concentration of LiMn$_2$O$_4$. To the best of our knowledge, no rheological investigations have been performed previously using such system of PEO-LiMn$_2$O$_4$ composite.
EXPERIMENTAL

Materials: PEO, with a weight-average molecular weight of 600,000 g/mol was purchased from BDH chemicals Ltd (Poole, England). Lithium manganese was prepared through molten salt synthesis. Distilled water was used as a solvent.

Synthesis of Lithium Manganate: For the preparation of lithium manganese, analytical grade anhydrous lithium chloride 99% (Loba Chemie, Mumbai, India) and manganese oxide 99% (Loba Chemie, Mumbai, India) powders were used as the starting materials. Stoichiometric quantities of the starting materials were thoroughly mixed and placed in a high purity alumina crucible. Then, the crucible was placed in a programmable electrical resistance furnace and heated at 950°C in air. The heating rate was 4°C min⁻¹ and the heating was continued at this temperature for 5 h. After cooling to room temperature, the product was removed from the crucible and thoroughly washed with 1 M acetic acid followed by triple distilled water for several times to remove the excess lithium salts. The residue was dried in a vacuum oven at 150°C for 1 h and cooled to room temperature. Finally, fine crystalline free-flowing black powders were obtained. Prepared Lithium Manganate was characterized by FTIR and m.pt in order to make sure it was Lithium Manganate.

Preparation of the PEO/LiMn₂O₄ composites

Using gelation method, PEO-LiMn₂O₄ composite gels were prepared by the distribution of lithium manganese salt in an aqueous solution of PEO with the stirring method using a magnetic stirrer. The required amount of lithium manganese was accurately weighed and placed in a beaker. Triple-distilled water (100 mL) was added, and the whole mixture was sonicated for 30 min. Aqueous PEO solution was added to the same beaker. The mixture was again sonicated for 40 minutes and then it was poured in Petri dish and left as such for couple of days for gelation to occur. The PEO/LiMn₂O₄ composite gel samples were designated as PEO/LiMn₂O₄ (4 wt %) or S₁, PEO/LiMn₂O₄ (3 wt %) or S₂, PEO/LiMn₂O₄ (2 wt %) or S₃ and PEO/LiMn₂O₄ (1 wt %) or S₄ depending on the concentration of LiMn₂O₄ (Table 1).

Rheometry

In this study, rheometry was used to characterize the shear rate - shear stress performance of the system. The rheometer employed was Anton Paar’s Physica MCR 301 rheometer. Samples were mixed in glass flasks with 25 ml of distilled water as a solvent. For calculation of PEO and LiMn₂O₄ a weight-weight proportion was used. The rheological measurements were carried out at 10°C, 20°C, 30°C, 40°C and 50°C on Anton Paar’s MCR 301 Rheometer using plate-plate geometry with automatic gap setting, organize and common force computing sensors. Furthermore it consists of the air bearing-supported synchronous motor and a PP25 measuring system was also connected to rheometer. Rheoplus software installed in the system is used to run the instrument, data compilation and study. It has also got a pump attached to it for generating high pressure as well as an inter cooling system in order to maintain the temperature within a range of -150 to 1000°C.

RESULTS AND DISCUSSION

Flow curves

The composites with changeable concentrations of solute and solvent were regarded as typical samples and rheograms of these samples were acquired at different temperatures. Presentation for rheograms of such system is given for low and high concentration samples of PEO-LiMn₂O₄ in figure 1 & figure 2. The maximum shear stress is recorded in S₃ having highest amount of Lithium manganese oxide and the lowest shear stress is examined in S₁ which has smallest amount of Lithium manganese oxide. It is evident from these observations that shear stress values increases with the increase in Lithium manganese oxide concentrations and as such depend strongly on the amount of the filler added to PEO matrix. From figure 1 and figure 2 it is clear that the highest shear stress value decreases to lower shear stress value gradually as temperature increases. This may be because, with the rise in temperature the bonds within the gels are broken down and so the shear stress decreases. The viscosity-shear rate profile for our samples is given in figure 3-6. Figures 3 and 4 explain viscosity-shear rate relationship of sample S₁ and S₂ at different temperatures. This shows that viscosity decreases as temperature increases because with the rise in temperature, the bonds within hydro gels are broken down easily and so the fluidity of sample increases which in turn decreases the viscosity. For all temperatures maximum viscosity is recorded in case of Sample S₁. This is due to higher loadings of lithium manganese oxide while the minimum viscosity is recorded in case of sample S₂ which is due to lower loadings of lithium manganese oxide. Each

Table 1: Composition of composite gels

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Molecular weight PEO/gmol⁻¹</th>
<th>PEO (%)</th>
<th>%LiMn₂O₄ to PEO</th>
<th>Weight of LiMn₂O₄ to PEO</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁</td>
<td>600,000</td>
<td>1</td>
<td>1%</td>
<td>0.005g</td>
</tr>
<tr>
<td>S₂</td>
<td>600,000</td>
<td>2</td>
<td>2%</td>
<td>0.01g</td>
</tr>
<tr>
<td>S₃</td>
<td>600,000</td>
<td>3</td>
<td>3%</td>
<td>0.015g</td>
</tr>
<tr>
<td>S₄</td>
<td>600,000</td>
<td>4</td>
<td>4%</td>
<td>0.02g</td>
</tr>
<tr>
<td>S₅</td>
<td>600,000</td>
<td>5</td>
<td>5%</td>
<td>0.025g</td>
</tr>
</tbody>
</table>
curve represents power law model between shear rate ($\gamma$) and viscosity ($\eta$).

It is obvious that non-Newtonian flow system is noticeable in both cases of higher and lower shear rates. Initially the viscosity values at low shear rates decreases quickly then decrease is slow at higher shear rate in case of all compositions and at all temperatures. This is due to intermolecular forces and hydrogen bonds which in the start are strong enough to keep the gel viscous but for higher shear rates and temperatures the hydrogen bonds are broken down and the gel’s viscosity decreases (Malana et al., 2012). Finally the gels get deformed and lineup in the track of flow and so behaves like pseudo plastics. It can also be seen that all the compositions show shear thinning behavior which is typical of polymer system.

Diagram also show that at constant temperatures the initial values of viscosity are higher at lower shear rate values while viscosity decreases with increase in shear rate values.

**Flow curve modeling**

Some famous rheological models were also employed to test flow behavior of the prepared materials.

Ostwald’s Model: Two famous forms of Ostwald’s model i.e. $\tau = K_o \gamma^n$ and $\eta = K_o \gamma^{n-1}$ were used to examine the flow data: where $K_o$ is frequently recognized as the consistency co-efficient. The exponent $n$ is known as the Power Law Index or Rate Index or the Fluidity Index. The value of $n$ should be $0 < n < 1$ for a shear thinning fluid. As long as the shear thinning gets higher, the value of $n$ gets closer to 0. At different temperatures (10, 20, 30, and 40 °C) the magnitude of $n$ was calculated from the plot of “$\tau$” or “$\eta$” versus shear rate (“$\gamma$”) and the values obtained are given in the Table 2. The table plainly proves that our composite gels are presenting the shear thinning behavior according to the Ostwald’s model. The Ostwald’s model gives no yield stress for our system. This means

### Table 2: Thermo rheological properties of composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fluidity index (“$n$”)</th>
<th>($K_o$) (Pa.s)</th>
<th>Correlation Coefficient R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0°C</td>
<td>10°C</td>
<td>20°C</td>
</tr>
<tr>
<td>S1</td>
<td>0.42</td>
<td>0.33</td>
<td>0.29</td>
</tr>
<tr>
<td>S2</td>
<td>0.074</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>S3</td>
<td>0.129</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>S4</td>
<td>0.08</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>S5</td>
<td>0.72</td>
<td>0.6</td>
<td>0.52</td>
</tr>
</tbody>
</table>

### Table 3: $\tau_B$ values at different temperatures (Bingham model and modified Bingham model)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Sample</th>
<th>Bingham Model</th>
<th>Modified Bingham Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>($R^2$)</td>
<td>($\tau_B$)</td>
</tr>
<tr>
<td>10 °C</td>
<td>S1</td>
<td>0.92</td>
<td>47.7</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>0.93</td>
<td>36.9</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>0.95</td>
<td>27.9</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>0.93</td>
<td>34.7</td>
</tr>
<tr>
<td></td>
<td>S5</td>
<td>0.85</td>
<td>94.23</td>
</tr>
<tr>
<td>20 °C</td>
<td>S1</td>
<td>0.97</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>0.97</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>0.98</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>0.94</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>S5</td>
<td>0.88</td>
<td>71.95</td>
</tr>
<tr>
<td>30 °C</td>
<td>S1</td>
<td>0.98</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>0.98</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>0.97</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>0.93</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>S5</td>
<td>0.89</td>
<td>61.9</td>
</tr>
<tr>
<td>40 °C</td>
<td>S1</td>
<td>0.97</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>0.98</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>0.97</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>0.93</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>S5</td>
<td>0.89</td>
<td>71.26</td>
</tr>
</tbody>
</table>
that the Ostwald Model is not fully applicable here on our gel systems.

Considering the consistency coefficient ($K_s$), the Table 2 show that the sample $S_1$ and $S_2$ has higher consistency at all the temperatures. In addition, it is noted from the Table 2 that for all samples except sample $S_1$, the consistency coefficient ($K_s$) increases mostly with increasing solute content and become lesser with increasing temperature for almost all the samples.

**Yield stress**

The least stress applied before the material begins to flow is termed as yield stress (Barners, 1999). It is taken as a fine indicator for description of semisolid systems, upsetting their spread- ability and retention (Keiweg et al., 2004). Normally, small values of the yield stress enhance spread ability but reduce retention. The yield stress showed by our system is in fact caused by intermolecular and intra-molecular hydrogen bonding and additional valence forces. Significance of hydrogen bond as a molecular interaction on gel formation is also discussed by different authors (Guan et al., 2010; Khutoryanskiy et al., 2004).

Bingham yield stress ($\tau_B$) shown in Table 3 was found out by means of the Bingham relation for shear stress ($\tau = \tau_B + \mu \gamma$) (Bird et al., 1987). The $\tau$-$\gamma$ association at low shear rates ($\gamma = 0.01$ to $15$ s$^{-1}$) was found to be linear. By extrapolation to zero shear rates, the Bingham yield stress ($\tau_B$) was found equal to the intercept. Bingham yield stress ($\tau_B$) values vary from 2.9 to 94.23 Pa.

The modified Bingham model having its equation is ($\tau = \tau_{MB} + \mu y + C y^2$) (Yahia and Khayat, 2001) was also employed for the purpose to compare yield stress values. The yield stress values given by second order equation is just about half the corresponding Bingham yield stress ($\tau_B$) values for all samples at all temperatures. The yield stress values from Modified Bingham equation ($\tau_{MB}$) are between 0.608 and 37.26 Pa for different samples and at different temperatures. The yield stress values for our system have not been reported so we cannot compare our work with any previous study. But as modified Bingham model is seen to be more applicable with good correlation so it seems to be the best model to show flow behavior for our system.

**CONCLUSIONS**

In present study, attention was kept to rheological studies on composite polymer electrolyte synthesized by dissolving lithium manganate salt in a PEO solution. Rheological studies point out that the composite electrolytes are physical gels due to the existence of a two dimensional, sample-spanning system. The system is created by lithium salt mixing in PEO. It was shown that up to 5% lithium manganate could be dispersed into poly (ethylene oxide) solution. However higher loadings of lithium salt brought enhancement in viscosity and as a result the flow inside the system was slowed. From flow curves acquired at different temperatures it is shown that our composites are having pseudo plastic behavior with power law index ranging from 0.058 at 40 °C to 0.42 at 10 °C. For yield stress we used two relations known as Bingham model and Modified bingham model. The Bingham yield stress values range from 47.7 Pa at 10 °C to 2.9 Pa at 30 °C while for Modified bingham model the yield stress values were in between 0.608 Pa and 18.46 Pa. The consistency coefficient ($K_s$) increases mostly with an increase in solute content up to sample $S_4$ while the consistency co efficient for sample $S_1$ is higher at all temperatures for all samples. It was found that modified Bingham model is more applicable to our system than Bingham model. Viscosity decreased with rise of temperature and with addition of higher amount of lithium manganate.

**REFERENCES**


