Morphological, Thermal and Mechanical Properties of Nanoclay-Filled Polyethylene Oxide Nanocomposites

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Summary: Polyethylene oxide (PEO) and Nanoclay/Polyethylene oxide nanocomposite films were prepared by solution casting technique. To know about the morphology, scanning electron microscopy (SEM) was performed which indicated that the Nanoclay was dispersed and embedded well within the polymer matrix. The polarized optical micrographs (POM) study of pure PEO showed considerable size of distinct crystalline spherulites. The size of spherulites were decreased by the incorporation of Nanoclay into the polymer matrix. It might be due to the nucleation effect of Nanoclay in Nanoclay/PEO composite which might result small size spherulites. The differential thermal calorimetry (DSC) thermograms presented that the melting temperature (Tm) of pure PEO is about 65 °C while the Tm peak of the nanocomposites were shifted towards slightly lower temperature. It was also observed that the mechanical properties (stress and young’s modulus) of the Nanoclay/PEO nanocomposites were higher than pure PEO. The thermal stability of the Nanoclay/PEO composite was shifted towards higher temperature (about 25 °C higher than pure PEO) by the incorporation of 1 wt. % Nanoclay into the PEO matrix.

Key Words: Nanoclay, Morphology, polyethylene oxide, spherulites, POM, DSC.

Introduction

The combination of organic and inorganic nanocomposite paid great attention because the organic components are flexible, low dielectric constant, and processibility while the inorganic components show rigidity, strength, durability, and thermal stability [1]. Extensive research is going on the nanoclay/polymer composites because they possess unique properties due to their nanometer size features. The minute clay filled polymer nanocomposites show enhanced mechanical properties, ionic conductivity, flammability resistance, thermal properties, and gas barrier properties than pure polymers and conventional microcomposites [2-7]. Due to these significantly enhanced properties, the clay/polymer nanocomposites have wide range of applications in various fields/industries such as automobile, aviation, geotextile, biomedical, and other polymer industries [8]. Ammala et al. [9] prepared Poly(m-xyyleneadipamide)/Kaolininite and Poly(m-xyleneadipamide)/Montmorrillonite by melt-compounded and extruded method. They found that under similar processing conditions, kaolininite resulted in a higher degree of crystallinity. It was also reported that both types of nanocomposites exhibited improved gas-barrier properties than neat resin. Loyens et al. prepared PEO/clay nanocomposites via melt-extrusion and they were found that the exfoliated structure can only be achieved upon melt mixing with a high PEO molar mass. They were also found that the melt temperature and crystallinity was decreased upon the addition of clay, especially in the case of low molar mass PEO matrix. While the mechanical properties were slightly superior based on the high molar mass PEO matrix [10]. Burgaz prepared Poly(ethylene-oxide) PEO/clay/silica nanocomposites and he was found that the properties like thermal stability and stiffness of PEO/clay/silica hybrids were significantly improved than PEO/clay hybrids and pure PEO [11].

The clay/polymer composites are classified structurally into intercalated and exfoliated nanocomposites. The X-ray diffractometry and transmission electron microscopy analyses showed that the polymer chains in intercalated nano-composites are present in between the tactoids layers and are present at regular repeating distance while in exfoliated nanocomposites, clay crystallites are delaminated forming individual layers dispersed within the polymer [12]. Different types of nanoclays like kaolinlite, silica, montmorillonite etc. were used during the preparation of Polymer/nanoclay composites. Among these nanoclays, montmorillonite paid great attraction due to their natural availability, low-cost and with a reactive hydrophilic group –OH.

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on its surface. The montmorillonite is a 2:1 mica type layered silicate, which consists of two dimensional layers. The layer thickness is about 1 nm and lateral dimension is in the range of 300 Å to several microns [13].

In the present study we prepared Nanoclay/PEO nanocomposites films by solution casting technique. PEO is clear, colorless, odorless, inert to many chemical agents, stable against hydrolysis, and nontoxic. It is not only soluble in water but also soluble in many organic solvents. It has various biomedical applications due to its biocompatibility and lack of immunogenicity. It is also serves as electrolytic solvents in polymer lithium cell [14, 15]. The methodology consist the dispersion of Nanoclay in the polymer matrix and the removal/evaporation of solvent at room temperature. The properties of pure PEO and the nanoclay/PEO nanocomposites, have been studied using SEM, DSC, TGA, POM, and a universal tensile machine.

Results and Discussion

Morphological Study of PEO and Clay/PEO Nanocomposites

The morphological study of composite materials is necessary in order to confirm the embedment as well as the dispersion of the reinforcing materials in the polymeric materials. The SEM micrographs of fractured surface (broken in liquid nitrogen) of pure PEO and nanoclay (5 wt. %)/PEO composite are shown in Fig. 1. Fig. 1b show some white spots with diameter below 60 nm clay plates while such type of spots are not present in pure PEO (Fig. 1a). These white spots might be due to clay platelets. The SEM analyses also presented that the clay is dispersed well in the PEO matrix.

Crystallization of PEO and Clay/PEO

The POM microphotographs for pure PEO and Clay/PEO nanocomposites, are shown in Fig. 2. The samples were prepared by cooling from the melt state. Fig. 2a presented that pure PEO upon crystallization showed large size of distinct crystalline spherulites, which are similar to the reported pattern [16, 17]. The size of spherulites of pure PEO were in the range of 40-70 μm. The POM images showed that the Nanoclay(5 wt %)/PEO composite (Fig. 2b) have much smaller size spherulites as compared to the pure PEO. The smaller size of spherulites of the nanocomposite might be due to the nucleation effect, which hinder the spherulites of pure PEO. Various research groups reported the crystallization behavior for different types of nanocomposite material. Loyens et al. [18] studied the crystallization behavior for clay/PEO nanocomposites and they were also found that the size of PEO spherulites was decreased even by incorporation of small amount of clay (less than 1 wt. %). Saeed and Park observed that the size of PCL spherulites was decreased when the carbon nanotubes were incorporation into polymer [19].

The DSC analyses of pure PEO and the nanoclay/PEO composites are shown in Fig. 3. The DSC thermogram (Fig. 3a) presented that the melting temperature (Tm) of pure PEO is about 65 °C while the Tm of the nanocomposites were decreased gradually as increased the quantity of nanoclay in the polymer matrix. The Tm of 1, 3 and 5 wt. % clay/PEO nanocomposites were about 59, 52 and 48 °C, respectively. Maria et al. [20] also reported that the Tm of Clay/Poly(ethylene terephthalate) (PET) nanocomposites were decrease when nanoclay was incorporated into the PET. They suggested that less stable crystals were formed during the crystallization from the melt state, due to the nanoscale interactions between the clay surface and the polymer. The Ou et al. and Burnside et al. also reported that the melting temperature of Poly(ethylene terephthalate) slightly decreased in the presence of nanoparticles and further no reduction in the Tm was found when the amount of nanoclay was exceeded (more than 1wt. %) [21, 22].
Fig. 3: DSC $T_m$ of PEO and Nanoclay/PEO nanocomposites, clay wt. % (i) 0, (ii) 1, (iii) 3, and (iv) 5.

TGA Study of Nanoclay/PEO Composite

The TGA (Thermo gravimetric analysis) curves of the pure PEO and Nanoclay (1 and 5 wt. %)/PEO composite are shown in Fig. 4. The TG curve of pure PEO shows that initially the mass remained constant up to 188 °C, and then reduced abruptly. The PEO started weight loss at about 195 °C and completely decomposed at about 350 °C. The thermogram of the nanoclay (1 wt. %)/PEO composite shows that the composite started weight at about 220 °C, which is about 25 °C higher than pure PEO. The Nanoclay (5 wt %)/PEO composite started weight loss comparatively at slightly low temperature than pure PEO, which might be due to the formation of low molecular chain when high quantity of the nanoclay were incorporated into the PEO. The TGA thermogram also presented that Nanoclay/PEO composite decomposed completely at about 350 °C. The residual amount, which was contributed by the nanoclay in the composite, remained at higher temperatures. The TGA thermograms showed that the incorporation of Nanoclay improved the thermal degradation of PEO.

Mechanical Properties of PEO and Nanoclay/PEO

The mechanical properties of the neat PEO and Nanoclay/PEO nanocomposites are shown in Table-1. The tensile strength and modulus of the pure PEO was 7.03 and 391 N/mm², respectively. The tensile strength and moduli of the nanocomposites improved significantly by the incorporation of high quantity (7 wt. %) of nanoclay into the PEO polymer. The enhancement of mechanical properties of the nanoclay/PEO composites might be due to good dispersion of Nanoclay in the polymer matrix as well as the improved interfacial adhesion between PEO and Nanoclay particles. The improvement of the mechanical properties indicated that the Nanoclay/PEO nanocomposites are stronger than pure PEO.

![Fig. 4: TGA thermograms of (a) neat PEO and (b) Nanoclay/PEO nanocomposites.](image)

Table-1: Mechanical properties of Pure PEO and Nanoclay/PEO.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (N/mm²)</th>
<th>Modulus (N/mm²)</th>
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<tbody>
<tr>
<td>PEO</td>
<td>7.0 ± 0.6</td>
<td>391.1 ± 9.8</td>
</tr>
<tr>
<td>1 % Nanoclay/PEO</td>
<td>7.9 ± 1.4</td>
<td>374.5 ± 85.7</td>
</tr>
<tr>
<td>3 % Nanoclay/PEO</td>
<td>8.8 ± 1.7</td>
<td>398.9 ± 19.6</td>
</tr>
<tr>
<td>5 % Nanoclay/PEO</td>
<td>8.4 ± 2.1</td>
<td>470.6 ± 58.1</td>
</tr>
<tr>
<td>7 % Nanoclay/PEO</td>
<td>9.9 ± 2.2</td>
<td>515.4 ± 160.9</td>
</tr>
</tbody>
</table>

Experimental

Materials

The PEO (average molecular weight of 600,000) was purchased from Aldrich chemical company. The Nanoclay (Nanocor) was used as reinforcing material in PEO polymer matrix.

Preparation of Nanoclay/PEO Nanocomposites

The PEO (known quantity) was dissolved in 25 mL of distilled water, and then known quantity of nanoclay was added to the polymer solution and stirred for 1 h. For better dispersion, this Nanocaly/PEO solution was sonicated for 30 min. The Nanoclay/PEO solution was then placed in a petri dish, and a thin film of Nanoclay/PEO nanocomposite was obtained after the evaporation of the solvent at room temperature.

Characterization

The SEM images of the gold-coated fractured surfaces (broken in the liquid nitrogen) of the Nanoclay/PEO nanocomposites were analyzed.
using a JEOL JSM-5910 SEM. The POM analyses were done using a BX51 POM. The samples were melted between two glass slides and then squeezed for 10 min.

The thermal properties of the neat PEO and Nanoclay/PEO nanocomposites were studied by TGA and DSC. The DSC analyses were carried out using a Diamond Series DSC Perkin Elmer. A known weight of the sample was sealed in an aluminum sample pan and prepared by compression molding. DSC thermograms of second heating was obtained at rates of 10 °C/min increase in temperature under a nitrogen atmosphere in order to diminish oxidation. The TGA curves of the nanocomposites were obtained in a nitrogen atmosphere at a heating rate of 20 °C/min rise in temperature between 25 °C and 400 °C, using a Diamond TG/DTA PerkinElmer apparatus. The mechanical properties were tested by using a universal testing machine (Model 100-500KN, Testometric Inc., UK). The tests were carried out at room temperature with a crosshead speed of 50 mm/min. The sample dimensions were 70.9 (gauge length) × 27 (width) × 0.1 (thickness) mm.

**Conclusion**

It is concluded that the Nanoclay dispersed well within the PEO polymer matrix, which resulted in the enhancement of the mechanical properties and thermal stability of PEO. The POM micrographs showed that the spherulites size of Nanoclay/PEO nanocomposite are much smaller than pure PEO, which might be due to the nucleation effect of Nanoclay in nanocomposite. The DSC thermograms showed that the T_m of pure PEO is about 65 °C, which was shifted towards slightly lower temperature in the case of Nanoclay/PEO nanocomposites.

**References**