Effect of Nanoclay on the Structure and Properties of High Density Polyethylene Composites

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Abstract: In this study we prepared high density polyethylene (HDPE)/ clay nanocomposites by melt compounding in a twin screw extruder with rotational speed of 50rpm and the temperatures of the zones are set to 180-210°C. Different screw configuration have been used to study the effect of screw elements on the properties of nanocomposites. screw configuration changed from dispersive to distributive type. Cloisite 15A was used as the filler and weight percent of clay was fixed to 3wt%. Maleated polyethylene grafted polyolefins supplied from Reliance ltd. A new combination of maleic anhydride grafted polyethylene prepared in our lab through grafting also taken as compatibilizer. the samples were then characterized by XRD, FTIR and DSC. The results showed that PE/clay nanocomposites provide better exfoliation with high dispersive screw configuration. The addition of clay also increased the dispersion and crystallinity of the composite. The clay particles helped the nanocomposites to develop tortuous path that prevent the leakage of gas through it.

Rheological results indicated an increase in the viscosity with the addition of nano clay to PE. wide angle x-ray diffraction shows the better exfoliation of nano particle clays in the polymer matrix. The mechanical, thermal and rheological characteristics were measured by using differential scanning calorimetry (DSC), X-ray diffraction (XRD). XRD indicates that Compatibilizer–nanoclay ratio plays an important role in the exfoliation of clay in the polyethylene.

Keywords – nanocomposites, Cloisite 15A, Maleated polyethylene grafted polyolefins, HDPE.

I. Introduction

Nanocomposites of polyolefin (PO) with nanoscale layered silicates have been studied by many researchers, scientifically and technologically, because these materials offer markedly improved properties as compared to the conventional polymer composites(1-7). Polymer–clay nanocomposites are emerging as a class of advanced engineering materials. Several key properties, such as strength and permeation, can be improved by adding a small amount of clay into the polymeric matrix [8,9]. The properties of polymer–clay nanocomposites depend on the degree of clay dispersion or on the extent of delamination of the individual clay layers in the polymeric matrix [10]. The clay layer is hydrophilic in nature and can be converted to organoclay to promote the wetting of the polymermolecule onto the clay surface [11,12]. By properly controlling the surface properties of the organoclay, various degrees of organoclay dispersion can be achieved to give: (a) conventional composites, (b) intercalated nanocomposites, (c) intercalated-exfoliated nanocomposites and (d) exfoliated nanocomposites [12]. The clay’s surface properties can be modified in various ways. One can use clay with a different layer charge density, control the surfactant surface coverage or vary the kind of intercalated surfactant [13–15].

The packaging industry plays a significant role in a nation economic development; thus, its improvement can help the economic growth by increasing the efficiency of food marketing and other products, and by adding value to exports, for example. In this context, nanocomposites, a new class of materials, have a fundamental role in this improvement, because they have better mechanical, thermal and barrier properties than the pure polymer. The nanocomposites are characterized by the use of a reinforcement agent with nano dimensions, which is added in small quantities compared to the traditional composites.

II. Materials and Methods

2.1 Screw Elements and Configuration

The screw configuration used for the extrusion of nanoclay reinforced HDPE composites are shown in figure1. Two types of screw configurations were used one was dispersive and changed to distributive.
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2.1 Materials
A HDPE (film blowing grade), L60075 from Reliance pvt.ltd. with melt flow index of 8 g/10 min (190 °C, 2.16 kg), weight average molecular weight, Mw, of 420,907 g/mol and molecular weight distribution of 20.89 was chosen as matrix. Two grade of HDPE grafted with maleic anhydride (1%), PEMA, trade name Polybond 3009,Optim,and Fusabond Dupont from Reliance, with melt flow index of 2 g/10 min and 1.5g/10min (190 °C, 2.16 kg) and melting temperature of 127°C was used as compatibility agent. The nanoclay was montmorillonite, MMT, trade name Cloisite15A from Southern Clay, with less than 2% of moisture.

2.2 Mixing Of Materials
The polymer with compatibilizer and nanoclay in the powder form were mixed according to the combination as follows. Nanoclay in each combination was fixed as 3wt%. the blends were mixed with 5kg each in an internal mixer with rotational speed of 1500rpm for 10min.all the batches were preheated @100°C for 8hrs under vacuum condition.

2.3 Grafting of Maleic Anhydride onto Polyethylene
The grafting reaction was carried out in a twin-screw extruder. Before extruding, MAH and DCP were dissolved in acetone and then mixed with HDPE granules. After volatilizing the acetone, MAH and DCP adhered onto the granules homogeneously. The temperature profile of the extruder was 140 °C, 160 °C, 180 °C and 200 °C, and the rotation speed of the screws was 60 rpm. The strips from the extruder were cut into granules about 4 mm long after cooling in a water bath.

III. Melt Compounding
For each type of nanocomposite, as well as for the neat polymer, the same processing procedure was applied so that the thermomechanical history of the nanocomposites and that of neat polymers remain similar. The powders were dry blended and fed in a co-rotating twin-screw extruder, Brabender,Germany.The mixing was carried out at a temperature distribution of 180– 200 °C, and speed of 100 rpm. The extruded nanocomposites were pelleted at the die exit. Nanocomposites containing 3wt% clay and different combination compatibilizer have been prepared.

Table 1: Combination of composites

<table>
<thead>
<tr>
<th>No</th>
<th>Designation</th>
<th>Combination</th>
<th>Clay (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HDPE</td>
<td>100/0/0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>HDPE-CLAY</td>
<td>97/3</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>HDPE-FB-CLAY</td>
<td>94/3/3,82/15/3,88/93</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>HDPE-OPT-CLAY</td>
<td>94/3/3,82/15/3,88/93</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>HDPE-FB</td>
<td>1:1:1:5</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>HDPE-OPT</td>
<td>1:1:1:5</td>
<td>0</td>
</tr>
</tbody>
</table>
IV. Characterization

4.1 FTIR Analysis of Maleic Anhydride

Fig. 2 FTIR Peaks of Maleic Anhydride

4.2 XRD Analysis.

Fig. 3 shows the XRD patterns (in the range <10°) of neat 15A and the 15A-included composites. The primary (001) diffraction of neat 15A was evident, indicating an interlayer spacing of 3.15 nm. For the PENC1:3 and PENC1:5 composites, the (001) diffraction position of 15A hardly changed, while the PENC1:1 exhibited a weaker diffraction. These results suggest that, PNC1:1 gives better exfoliation. The 15A’s (001) diffraction was still discernible but became much weaker with the inclusion of the two maleated polyolefins.

Fig. 3 XRD Pattern
4.3 Crystallization Behaviour of Nanocomposites

Sample: HDPE-NC/FB, 1:1  
Size: 4.3000 mg  
Method: H-C-H  
Comment: TACS /31343, N2 atm

DSC

File: C:\TA\Data\DSC\HDPE-31343-1-1 FB.001  
Operator: PBS/PVA  
Run Date: 04-Dec-2013 13:36  
Instrument: DSC Q20 V24.9 Build 121

Fig.4. DSC Curves

Exo Up

Heat Flow (W/g)  
20 40 60 80 100 120 140 160

Temperature (°C)

133.22°C
126.14°C
154.6J/g

Fig.5. DSC Curves
DSC measures the crystallinity of the sample and melting point.

\[
\text{Degree of Crystallinity } X_c = \frac{\Delta H}{\Delta H_m \times X}
\]

- \( \Delta H \) = melting enthalpy of the sample
- \( \Delta H_m \) = melting enthalpy of 100% crystalline form of PE, value is 293J/g.
- \( X \) = weight fraction of HDPE in the sample.
- For 1:1, \( X_c = 52.7\% \)
- For 1:5, \( X_c = 49\% \)
- Increase in crystallinity increases the gas barrier properties.

V. Torque During The Extrusion of Polymer Nanocomposites

Torque developed during the extrusion increased first and decreased with improvement of exfoliation. The torque remains constant when the clays are started to disperse in the polymer matrix.

VI. Conclusion

The XRD analysis ensures the dispersion of clay in the polymer composites. The effect of compatibilizers and clay ratio is clear from the chart. 1:1 ratio gives the most improvement in exfoliation. Crystallinity increases with addition of nanoclay into HDPE DSC curves validates the result. Intercalation or dispersion of HDPE between the gallery improves the thermal stability and mechanical strength with compatibilizers.
References