EFFECT OF NANOCLAY ON THE MECHANICAL BEHAVIOR OF COMPATIBILIZED ETHYLENE VINYL ACETATE COPOLYMER / HIGH DENSITY POLYETHYLENE BLENDS

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EFFECT OF NANOCLAY ON THE MECHANICAL BEHAVIOR OF COMPATIBILIZED ETHYLENE VINYL ACETATE COPOLYMER / HIGH DENSITY POLYETHYLENE BLENDS

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ABSTRACT: This paper presents a part of research on the mechanical properties of compatibilized Poly (ethylene-co-vinyl acetate) (EVA)/ high density polyethylene (HDPE)/ organo modified montmorillonite (OMMT) nanocomposites prepared by melt mixing technique. Use of maleic anhydride grafted polyethylene (MA-g-PE) as Compatibilizer improves compatibility of EVA and HDPE. Blends containing EVA/HDPE blend with 2 phr MA-g-PE shows optimum properties. It observes that the addition of nanoclay improves the mechanical properties like tensile strength, flexural modulus, abrasion resistance and hardness of compatibilized nanocomposites systems. The morphology is studied by Scanning Electron Microscopy (SEM). The optimized properties occurs at clay loading levels of 4 phr with MA-g-PE system.

KEYWORDS: Ethylene vinyl acetate copolymer (EVA); High density polyethylene (HDPE); Maleic anhydride grafted polyethylene (MA-g-PE); organophilic Montmorillonite (OMMT); Mechanical Properties; Scanning electron Microscopy

INTRODUCTION

New materials can be prepared by blending with new properties not found in pure polymers. Blends are capable of providing the required properties than synthesizing new polymers. Poly(ethylene-co-vinyl acetate) (EVA) has several advantages such as good mechanical properties, easy processing, low density, low cost, high impact strength, improved elasticity, transparency and compatibility with polar polymers. In addition to these unique characteristics, EVA has a characteristic ability of mixing with a large quantity of fillers to increase the properties of polymer blend. However, there are some drawbacks with EVA including high water absorption characteristic, low hardness and low abrasion resistance, which have restricted its use in some applications. Among the existing polyolefins, high density polyethylene (HDPE) is a suitable polymer for blending with EVA to improve its tensile strength, flexural modulus, abrasion resistance and hardness. Polymer blend based on HDPE and EVA has many good properties because it can combine advantages of both HDPE and EVA [1].

The interfacial tension of HDPE/EVA system is higher than LDPE/EVA [2]. For PE/EVA blends, the minimum mechanical properties have been reported in different blend compositions [3]. Due to different chemical structures of EVA and HDPE, it is difficult to compatibilize EVA with HDPE. Compared to HDPE, EVA is more polar and less crystalline due to polar vinyl acetate (VA) group and leads to better compatibility with polar polymers and fillers [4]. Recently compatibilizers have been added due to their ability to improve both physical and chemical interaction between polymer and filler [5].

It is well established that the organically modified clay can be exfoliated in polyamide using appropriate melt processing techniques. However, exfoliation of organomodified nano clay is not easy in commonly used polyolefins due to their non-polar nature leading to poor interaction with polar aluminosilicate surface of clay [6]. The common technique used is to add small amount of compatibilizer such as maleic anhydride grafted polyolefins. Polar character of the anhydride generates the attraction for the clay in such a way that the maleated polyolefin acts as a compatibilizer between the matrix and filler. Maleic anhydride is found suitable for grafting onto polyethylene because it has low reactivity towards itself and can graft onto the polymer. This functionalization lowers the hydrophobicity of polyethylene, imparting polarity which helps in compatibilizing with hydrophilic clay [7].

Polyethylene/maleic anhydride grafted polyethylene/ organoclay nanocomposites were investigated by Liang et al. [8]. They found that montmorillonite (MMT) intercalation in PE/PE-g-MAH/organo-MMT increased by increasing the content of PE-g-MAH.
In other studies processing of polymer/clay composites using single polymer [9] and blends of polymers [10]. Lee and Goettler [11] reported the effect of sequential addition of nanoclay, PP and EPDM (ethylene propylene diene monomer) on mechanical properties of the composite and found that change in addition sequence of polymer and nanoclay influenced the properties of composite. Ercan et al. studied rheological and barrier properties of HDPE/Clay nanocomposites [12]. Tambe et al. found that there is no appreciable change observed in tensile strength [13]. Hoang et al. investigated the properties of Polyethylene grafted acrylic acid / Ethylene-vinyl acetate copolymer/Calcium carbonate composite using the composition PE-g-AAc/EVA and PE/EVA 30/70 (wt./wt.) [14].

There is very limited available information on the effect of the nanoclay addition on the mechanical behavior of compatibilized EVA/HDPE blends having high EVA content. In this paper, the development of high EVA content EVA/HDPE/clay nanocomposites to improve the tensile and flexural properties, hardness and abrasion resistance that are required for footwear sole has been attempted. Maleic anhydride grafted polyethylene (MA-g-PE) and organically modified montmorillonite particles are used as a Compatibilizer and nanofiller respectively for making the nanocomposites.

**EXPERIMENTAL**

**MATERIALS**

The following ingredients were used in the present work:

- Ethylene-co-vinyl acetate copolymer (EVA) (TAISOX 7350 M, Density 0.93 g/cm³, MFI 2.5 g/10 min, VA 18%) supplied by Nippon Unicar. Co. Ltd., Japan was used as the base polymer matrix.
- High density polyethylene (HDPE) (HD 50MA 180, Density 0.95 g/cm³, MFI 20 g/10 min) supplied by Reliance Industries, Hazira, Gujarat, India was used as the base polymer matrix.
- Maleic anhydride grafted polyethylene (MA-g-PE) (E-156, Density 0.92 g/cm³, MFI 1.5 g/10 min.) supplied from Pluss Polymer Pvt Ltd, Faridabad was used as a coupling agent to improve surface adhesion.
- Organo modified montmorillonite (OMMT) clay: Nanomer® 1.31 PS, montmorillonite clay surface modified with 15-35 wt % octadeclamine and 0.5-5 wt% aminopropyl triethoxy silane supplied from Sigma Aldrich, New Delhi was used as reinforcing agent to prepare the nanocomposites.

**COMPONUDING**: Melt blending of EVA (70 vol %), HDPE (30 vol %), MA -g-PE agent of different loading (1, 2, 3 and 4 vol %) and the OMMT of different loading (1, 2, 3, 4 and 5 vol %) was carried out in a Berstorff co-rotating twin screw extruder (screw diameter: 25mm, L/D=48) at a constant rotating speed of 200 rpm. The extrusion temperature was set at 140–180°C from the feeder to the die. Extrudates were cooled with water and pelletized. Table 1 shows sequential addition of EVA, HDPE, compatibilizer and nanoclay.

<table>
<thead>
<tr>
<th>Sample Designator</th>
<th>wt % Polymer</th>
<th>Compatibilizer</th>
<th>Organoclay (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA</td>
<td>HDPE</td>
<td>MA-g-PE</td>
<td>OMMMT</td>
</tr>
<tr>
<td>70/30</td>
<td>70</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>70/30/1MA</td>
<td>70</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>70/30/2MA</td>
<td>70</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>70/30/3MA</td>
<td>70</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>70/30/4MA</td>
<td>70</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>70/30/2MA/1NC</td>
<td>70</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>70/30/2MA/2NC</td>
<td>70</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>70/30/2MA/3NC</td>
<td>70</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>70/30/2MA/4NC</td>
<td>70</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>70/30/2MA/5NC</td>
<td>70</td>
<td>30</td>
<td>2</td>
</tr>
</tbody>
</table>

**SPECIMEN PREPARATION**: The blended samples were injection molded using Injection molding machine (JSW 180H). The barrel temperature was in the range of 140-230°C and injection pressure was 80 MPa.

**EVALUATION OF PROPERTIES**

**TENSILE TESTING**

The tensile properties were evaluated according to ASTM D638 using dumbbell-shaped samples and an Instron universal testing machine Model 3342 tensile tester with a crosshead speed of 50 mm/min.

**FLEXURAL TESTING**

The flexural properties were evaluated according to ASTM D790 using dumbbell-shaped samples and an Instron universal testing machine, Model 3342 with a crosshead speed of 1.3 mm/min. The dimensions of the specimens were 127mm in length, 12.7mm in width and 3mm in thickness.

**HARDNESS TESTING**

The hardness property (shore A) was evaluated according to ASTM D2240 using a Durometer hardness tester using truncated cone.

**ABRASION TESTING**

The abrasion test was evaluated according to ASTM D1044 using a Taber abraser (Model 5131). The dimensions of the specimens were 100 mm in diameter and 3 mm in thickness. Calibrated abrasive wheel H-18 and Standard load 1000g were used for this purpose.
Effect of Nanoclay on the Mechanical Behavior of Compatibilized Ethylene Vinyl Acetate Copolymer / High Density Polyethylene Blends

SCANNING ELECTRON MICROSCOPY (SEM)

The samples of EVA/HDPE blend, Compatibilized EVA/HDPE blend and compatibilized EVA/HDPE/OMMT nanocomposites were fractured and sputtered with thin gold-palladium layer to prevent charging by Polaron Sputter Coater. The fracture surfaces were observed by SEM microscope (LEO 430), using secondary electrons detector.

RESULTS AND DISCUSSIONS

Effect of Addition of Compatibilizer on Mechanical Properties

Figures 1a and 1b show effect of compatibilizer, MA-g-PE, on the tensile strength and Flexural modulus of 70/30 system respectively.

![Figure 1a](image1a.png)

**Figure 1a.** Effect of compatibilizer on tensile strength of the 70/30 system.

It is found that the mechanical properties like tensile strength and flexural modulus of EVA/HDPE blends increase up to 2 phr of MA-g-PE addition. Above 2phr of MA-g-PE these properties are not affected. It is likely that the addition of MA-g-PE yields stronger adhesion between EVA and HDPE phases, contributing to the improvement of the tensile and flexural properties of the compatibilized blends.

![Figure 1b](image1b.png)

**Figure 1b.** Effect of compatibilizer on flexural modulus of the 70/30 system.

Similar improvement after addition of compatibilizer was also reported by previous researchers in their works on other polymer blend like PBT/HDPE [15]. In the polymer matrix, the addition of MA-g-PE tends to decrease the free volume, which showed its compatibilizing effect [16]. This can be explained in terms of the penetration of both polar and non polar segments in the compatibilizer. On the basis of above study 2 phr compatibilizer composition is selected. In this compatibilized blend concentration of nanoclay was varied and mechanical properties were evaluated.

Effect of Addition of Nanoclay on Physico-mechanical Properties

![Figure 2a](image2a.png)

**Figure 2a.** Effect of nanoclay on tensile strength of the 70/30/2MA system.
Figures 2a and 2b show the effect of nanoclay on the tensile strength and flexural modulus of 70/30/2MA system respectively. It is found that tensile strength and flexural modulus began to increase up to 4 phr of OMMT. As clay loading exceeds 4 phr, these properties are found to level off. Similar improvement was also reported by previous researchers in their works on any polymer/organo clay nanocomposites [17].

The primary causes for such improvement is attributed to the presence of immobilized or partially mobilized polymer phases as a consequence of interaction of polymer chains with organic modification of the clays, which is similar to earlier reported result [18]. Since, the molecular structure of MA-g-PE contains anhydride group which is highly attracted to OMMT sheets and a longer non polar fragment attracted to the EVA/HDPE matrix. This reason for the improvement of tensile and flexural properties is also reported earlier [18]. There is no appreciable change observed in tensile strength. Similar study was carried out by Lee and Goettler [11] on effect of blending sequence of PP and EPDM with Closite 20A and they have reported that blending ratio and sequence affect the tensile properties of the composites. It has been reported by Chows et al. [19] that the tensile strength of the nanoclay filled composites depends on several factors such as dispersion of nanoclay in the skin and core layers, interaction of polymer with nanoclay, compatibility of polar polymer with non-polar component of the polymer blend. The results of hardness and abrasion resistance are shown in table 2.

Table 2. Hardness and Abrasion resistance of 70/30/2MA system and their nanocomposite systems.

<table>
<thead>
<tr>
<th>Sample Designator</th>
<th>Hardness (ShoreA)</th>
<th>Abrasion resistance (mg of weight loss/1000 revs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70/30/2MA</td>
<td>55</td>
<td>32</td>
</tr>
<tr>
<td>70/30/2MA/1NC</td>
<td>56.5</td>
<td>30</td>
</tr>
<tr>
<td>70/30/2MA/2NC</td>
<td>58</td>
<td>28</td>
</tr>
<tr>
<td>70/30/2MA/3NC</td>
<td>59.5</td>
<td>26</td>
</tr>
<tr>
<td>70/30/2MA/4NC</td>
<td>61.5</td>
<td>24.5</td>
</tr>
</tbody>
</table>

The incorporation of nanoclay improves the hardness of nanocomposites. This result is similar to tensile and flexural properties. Hardness test gives an idea of variation in mechanical properties [20]. Table 2 shows the weight loss of the specimens due to abrasion after 1000 strokes. It is evident from the results that incorporation of nanoclay improves the abrasion resistance of nanocomposites. The higher abrasion resistance of the nanocomposites may be due to the mechanical reinforcement of specimens by nanoclay. Similar improvement is also reported by previous researcher in their work on EVA/LDPE/nanoclay nanocomposites [13].

Morphology of the EVA/HDPE blend, modified EVA/HDPE blend and modified EVA/HDPE/OMMT nanocomposite

In the Figures 3a and 3b, the scanning electron micrographs (SEM) for 70/30 and 70/30/2MA systems indicate that grafting maleic anhydride on to HDPE improves dispersion of HDPE into EVA; HDPE disperses into EVA more regularly.
Effect of Nanoclay on the Mechanical Behavior of Compatibilized Ethylene Vinyl Acetate Copolymer / High Density Polyethylene Blends

The SEM of the nanocomposite sample of 70/30/2MA/4NC demonstrates that the adhesion of the particles of nanoclay and polymer blend of EVA and HDPE in the presence of MA-g-PE compatibilizer is improved (Fig. 3C).

The morphology of the 7030, 70/30/MA and 70/30/MA/4NC samples is studied using scanning electron microscopy. It is well known that the volume ratio of the blending components forms the disperse phase and the matrix phase.

From Figure 3(a), it can be seen that EVA acts as the continuous phase, while HDPE serves as the dispersed phase because the content of EVA was 70 wt%. This SEM micrograph shows non compatible EVA and HDPE phases. The 70/30 system shows low value of mechanical property, as a consequence of the poor interfacial adhesion (Figure 1a and 1b). The addition of MA-g-PE increases the values of mechanical properties in EVA/HDPE blends (Figures 1a and 1b). The good interfacial interaction between EVA and HDPE can be achieved, as shown in Fig. 3(b). The reasons of these results are as follows: (A) For uncompatibilized blends, EVA has a great number of acetate groups and HDPE is hydrophobic polymer, consisting nearly completely methylene groups, which will lead to low chemical adhesion between the HDPE and EVA. (B) By adding compatibilizer, MA-g-PE has the hydrophobic segment and the hydroxyl segment, which will result in strong physical interaction between HDPE and EVA on the interface. In a word, SEM results indicate that MA-g-PE can improve the compatibility of EVA/HDPE blend.

Figure 3(c) may confirm that MA-g-PE not only enhances the compatibility of HDPE with EVA but also improves adhesion of the particles of nanoclay and EVA/HDPE blend. Addition of 4 phr OMMT nanoclay in MA-g-PE modified EVA/HDPE blends improves mechanical properties and the values of these properties were higher than that of the neat MA-g-PE modified EVA/HDPE blend (Figure 2 a, b). Therefore, it can be concluded that the organoclay can have its maximum compatibilizing effect, only in the presence of the MA-g-PE compatibilizer.

CONCLUSIONS

The present study shows the effect of nanoclay on mechanical properties. Nanocomposites with 4 phr nanoclay showed maximum tensile strength and flexural modulus compared to other nanocomposites. SEM results show that MA-g-PE can improve the compatibility of EVA/HDPE blends. Interfacial adhesion and dispersion of the particles of nanoclay into modified EVA/HDPE/OMMT nanocomposite is better than that of neat modified EVA/HDPE blend. The best finer morphology was also obtained by the addition of nanoclay at 4 phr in nanocomposite. In view of good mechanical properties of 70/30/MA/4NC, it can be concluded that this composition can be used for many industrial application.
REFERENCES


