Mechanical and Morphological Properties of Polypropylene and High Density Polyethylene Matrix Composites Reinforced with Surface Modified Nano Sized TiO$_2$ Particles

Mirigul Altan, Huseyin Yildirim

Abstract—Plastics occupy wide place in the applications of automotive, electronics and house goods. Especially reinforced plastics become popular because of their high strength besides their advantages of low weight and easy manufacturability. In this study, mechanical and morphological properties of polypropylene (PP) and high density polyethylene (HDPE) matrix composites reinforced with surface modified nano titan dioxide (TiO$_2$) particles were investigated. Surface modification was made by coating the nano powders with maleic anhydride grafted styrene ethylene butylene styrene (SEBS-g-MA) and silane, respectively. After surface modification, PP/TiO$_2$ and HDPE/TiO$_2$ composites were obtained by using twin screw extruder at titan dioxide loading of 1 wt.%, 3 wt.% and 5 wt.%. Effects of surface modification were determined by thermal and morphological analysis. SEBS-g-MA provided bridging effect between TiO$_2$ particles and polymer matrix while silane was effective as a dispersant. Depending on that, homogenous structures without agglomeration were obtained. Mechanical tests were performed on the injection moldings of the composites for obtaining the impact strength, tensile strength, stress at break, elongation and mechanical properties. Thermal, morphological studies were done on the composites and reinforcement material for polymers. However, it has polar surface while polymer matrix is non polar which makes the surface adhesion between the matrix and titan dioxide poor. The surface adhesion can be enhanced by the compatibilizers and coupling agents. Maleic anhydride grafted SEBS acts as impact modifier and compatibilizer for these kind of composites. [4]-[5]. Especially, it is used with polypropylene or high density polyethylene as coupling agent due to its compatible structure with olefinic block [6].

In this work, modified nano TiO$_2$ particles with SEBS-g-MA and silane were used for preparing polypropylene and high density polyethylene matrix composites. Thermal, morphological studies were done on the composites and mechanical tests were applied on the injection moldings of reinforced PP and HDPE. Effects of modified nano TiO$_2$ reinforcement on the mechanical and morphological properties were discussed.

II. EXPERIMENTAL STUDY

A. Materials

Polymer materials used in this study were polypropylene copolymer (56M10, Sabic Company) with melt flow index of 6.2 g/10 min, density of 0.902 kg/cm$^3$ and high density polyethylene (Lanufene, HDI-6507UV) with melt flow index...
of 7.5g/10 min and density of 0.965 kg/cm³. Nano material was TiO₂ (Nabond Company, China). SEBS-g-MA (FG1901X, Kraton, Shell Company) and vinyli trimethoxisilane (VTMS, Aldrich) were used for the surface modification of the nano TiO₂ particles.

B. Modification and Characterization of the Nano Powders

The nano titan dioxide particles were modified by coating them with SEBS-g-MA and then silane, respectively. SEBS-g-MA was used as compatibilizer and by coating the powders with it, the coupling agent property of the SEBS-g-MA was thought to be more effective. In this regard, 3 g SEBS-g-MA was dissolved in 200 g toluene in 48 hours at 25 ºC. Then, 100 g nano TiO₂ was added slowly and mixed with a mechanical mixer (IKA RW 20 digital) for 3 hours. SEBS-g-MA coated nano powders were pulverized after drying the mixture at 50 ºC for 8 hours. Then, a new solution was prepared for silane coating with 96% absolute alcohol and 4% distilled water with 1% silane. This solution was mixed for 10 minutes with the mechanical mixer and 100 g SEBS-g-MA coated nano TiO₂ particles was added slowly and mixed for 3 hours. The mixture was dried at 50 ºC for 8 hours and pulverized continuously. The aim of silane coating was to disperse SEBS-g-MA coated nano particles better in the matrix.

The coated powders were analyzed by scanning electron microscope (SEM) JEOL JSM-5910 LV and energy dispersive spectroscopy (EDS).

C. Blending

The chemical composition of the blends and their coded names are given in Table I. The dried powders and the polymer were loaded into a twin screw extruder (Rondol MicroLab, England) with L/D ratio of 20. The operation temperature was set as 220, 200, 180, 120 and 75 ºC. The speed of the screw was 60 rpm. The extrudate strands were granulized and dried at 80° C under vacuum for two hours.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ratio of TiO₂ (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original PP</td>
<td>0</td>
</tr>
<tr>
<td>Original HDPE</td>
<td>0</td>
</tr>
<tr>
<td>PP/1TiO₂</td>
<td>1</td>
</tr>
<tr>
<td>PP/3TiO₂</td>
<td>3</td>
</tr>
<tr>
<td>PP/5TiO₂</td>
<td>5</td>
</tr>
<tr>
<td>HDPE/1TiO₂</td>
<td>1</td>
</tr>
<tr>
<td>HDPE/3TiO₂</td>
<td>3</td>
</tr>
<tr>
<td>HDPE/5TiO₂</td>
<td>5</td>
</tr>
</tbody>
</table>

D. Differential Scanning Calorimetry (DSC)

The melting and crystallization behaviors were studied by differential scanning calorimetry (DSC, Perkin Elmer DSC-7) in nitrogen atmosphere. The samples (4-5 mg) were heated from 40 °C to 180 °C at 10 °C/min and held at 180 °C for 5 min and then cooled back to 40 °C at 10 °C /min and held 5 min at 40 °C. Then, second heating cycle was performed to delete the thermal history of the samples. The melting temperature (Tm), crystallization temperature (Tc) and degree of the crystallization (Xc) were obtained. The fusion enthalpy of 100 % crystalline phase of PP and HDPE were taken as 209 J/g and 290 J/g in calculating the degree of the crystallization of the blends, respectively [7].

E. Injection Molding

The dried granules of the composites were injection molded with a 40 tone injection molding machine. Tensile test and impact test specimens were obtained for mechanical tests. The mold temperature was 40 °C, injection pressure was 65 MPa, holding pressure 45 MPa, holding time 15 s and cooling time was taken as 10 s.

F. Mechanical Characterization

Tensile test was carried out by universal tensile machine (Zwick Z010) at room temperature according to ISO 527. The speed of the cross head was 50 mm/min. The izod impact test was performed on the notched specimens by using a 5.4 J pendulum hammer on the Zwick Impact test machine according to ISO 180.

G. Scanning Electron Microscope (SEM)

Morphology of the fracture surface of the each specimen was analyzed by scanning electron microscope (JEOL JSM-5910 LV). The fracture surfaces obtained from the impact tests were etched with tetrahydrofuran (THF) and then washed with acetone and dried under vacuum. Finally, all the specimens were coated with gold.

III. RESULTS AND DISCUSSION

A. Characterization of the powders

The SEM images of the original and coated titan dioxide particles are given in Fig.1. The EDS results are given in Fig. 2. The increments in carbon and oxygen peaks of the coated particles are obvious which is related to the coating with SEBS-g-MA and silane.
B. Thermal Characterization

The DSC results of the composites are given in Table II and DSC cooling scans of the composites are given in Fig. 3. Melt temperature of the PP matrix composites did not change very much with the addition of TiO$_2$ which indicates that TiO$_2$ particles did not influence the stability of the PP. On the other hand, the crystallization temperature and degree of crystallinity of these composites decreased slightly due to the retarding effect of the titan dioxide on PP crystals and physical hindrance of TiO$_2$ particles to the motion of polymer molecular chains. For HDPE matrix composites, the melt temperature and the crystallization temperature did not change very much by the addition of the TiO$_2$ particles as given in Table II. However, increase in degree of crystallinity was seen about 25-30% for HDPE/TiO$_2$ composites. This increment was probably due to the nucleating agent effect of the TiO$_2$ as seen in some earlier studies on similar inorganic fillers used with polyethylene [8]-[9]. Also, the presence of the SEBS-g-MA might favor the crystallization of the HDPE.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Tm (°C)</th>
<th>Tc (°C)</th>
<th>Enthalpy (J/g)</th>
<th>Xc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original PP</td>
<td>166.3</td>
<td>124.9</td>
<td>85.4</td>
<td>40.86</td>
</tr>
<tr>
<td>PP/1 TiO$_2$</td>
<td>165.8</td>
<td>122.9</td>
<td>82.7</td>
<td>39.57</td>
</tr>
<tr>
<td>PP/3 TiO$_2$</td>
<td>166.1</td>
<td>124.5</td>
<td>81.2</td>
<td>38.85</td>
</tr>
<tr>
<td>PP/5 TiO$_2$</td>
<td>166.5</td>
<td>125.1</td>
<td>83.1</td>
<td>39.76</td>
</tr>
<tr>
<td>Original HDPE</td>
<td>136.1</td>
<td>118.2</td>
<td>171</td>
<td>58.97</td>
</tr>
<tr>
<td>HDPE/1 TiO$_2$</td>
<td>136.5</td>
<td>118</td>
<td>219</td>
<td>75.52</td>
</tr>
<tr>
<td>HDPE/3 TiO$_2$</td>
<td>136.6</td>
<td>117.8</td>
<td>212</td>
<td>73.10</td>
</tr>
<tr>
<td>HDPE/5 TiO$_2$</td>
<td>134</td>
<td>118.1</td>
<td>208</td>
<td>71.72</td>
</tr>
</tbody>
</table>
C. Mechanical Properties

It is known that inorganic nano particles improve the mechanical properties of the polymers [2]-[10]. Generally tensile strength, elastic modulus, stress at break increase while impact strength and elongation decrease. The mechanical properties obtained from tensile test are given in Fig. 4. Tensile strength of both polymers increased while elongation reduced because of the hardness of TiO₂ (Fig. 4a). Stress at break for all the compositions except HDPE/1TiO₂ increased slightly (Fig. 4b).

For HDPE/1TiO₂, SEBS-g-MA was found more effective than in other compositions because elongation of this composition was higher than the original HDPE as seen in Fig. 4(c). This result was also compatible with the results of lower tensile strength and stress at break. Elastic modulus of PP matrix composites increased parallel with the addition of the TiO₂ while HDPE was not affected that much (Fig. 4d).
The results of the impact strength are given in Fig. 5. The main problem about nano composites is the reduction of the toughness [3]-[11]. Some researchers used elastomeric materials to increase the impact strength of rigid and stiff structure of the reinforced polymers [12]-[13]. In this study, very small amount of SEBS-g-MA was used for better surface adhesion between TiO$_2$ and polymer matrix. Therefore, an apparent increase in impact strength was not observed but the elastomeric nature of the SEBS was probably effective in minimizing the reduction of the impact strength. As a consequence, impact strength reduced according to the increment of TiO$_2$ ratio (Fig. 5). The decrease in the impact strength of the HDPE composites was higher than that of PP, probably due to the increased degree of crystallinity parallel with the addition of TiO$_2$.

![Fig. 5 Impact strength of nano TiO$_2$ reinforced PP (a) and HDPE (b) injection moldings](image)

**D. Morphology**

The SEM images of the fracture surfaces of PP/TiO$_2$ and HDPE/ TiO$_2$ are given in Fig. 6 and Fig. 7. The bridging effect between the polymer and nano particle is provided by SEBS-g-MA. The high polarity of the MA group of SEBS-g-MA enhanced the compatibility between the filler and the polymer matrix. The interface between the polymer matrix and SEBS is strong due to the compatibility of their phases because SEBS could diffuse into the polymer under the formation of miscelles [6]. However, the interaction between TiO$_2$ and matrix is limited because TiO$_2$ has polar surface and polymer is non polar. The SEM photographs of the PP given in Fig. 6 indicate strong bonding developed between TiO$_2$ and PP. TiO$_2$ particles are almost dispersed in the matrix and they behave like one phase which shows the good compatibility of the two materials.

This chemical bonding is due to the fact that MA functional groups grafted to the ethylene butylenes (EB) mid block of SEBS. Then, it becomes easier for the molecular chains of SEBS-g-MA and the polymer to bond with TiO$_2$. Besides, the surface energy of the SEBS-g-MA coated TiO$_2$ is higher than that of polymer matrix. In order to reduce the surface energy difference, silane coating was applied. Final chemical bonding was resulted in the reactions of the methoxy groups of the silane with the polymer matrix and hydroxyl groups with SEBS-g-MA coated TiO$_2$. For HPDE matrix composites, chemical bonding of TiO$_2$ and HDPE can be seen by the HDPE covering of the individual TiO$_2$ surface in Fig. 7.

![Fig. 6 SEM images of fracture surface of nano TiO$_2$ reinforced PP](image)
IV. CONCLUSION

Polypropylene and high density polyethylene were reinforced with surface modified nano sized TiO_2 particles. Modification was made by coating the powders with SEBS-g-MA and silane, respectively. According to the DSC results of the HDPE matrix composites, TiO_2 behaved like nucleating agent and SEBS-g-MA favored degree of crystallization while degree of crystallization decreased for PP matrix composites due to the hindering effect of TiO_2. SEM results revealed that the presence of SEBS-g-MA and silane increased the surface adhesion and dispersion without agglomeration. Depending on that noteworthy increments were obtained in tensile strength, elastic modulus although small amount of TiO_2 additions were applied. Elongation at break decreased and impact strength reduced normally due to the stiff and rigid structure of TiO_2. Elastomeric nature of the SEBS-g-MA was thought to minimize the reduction of the impact strength besides its strong bridging effect between the inorganic filler and the polymer matrix.

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REFERENCES


Fig. 7 SEM images of fracture surface of nano TiO_2 reinforced HDPE