Comparative study of PP-MA and PP-GMA as compatibilizing agents on polypropylene/nylon 6 blends

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Abstract

Polypropylene (PP) functionalized with maleic anhydride (PP-MA) has been used as compatibilizer for PP/nylon blends. PP functionalized with glycidyl methacrylate (PP-GMA) should be a good alternative due to the reactivity of the epoxy group with –NH₂ and –COOH groups. Blends of PP/PP-MA/nylon 6 or PP-GMA/nylon 6 were prepared using 30% of nylon (Ny6). The effect of the compatibilizers was evaluated by DSC, SEM micrograph and by mechanical properties. The analysis indicated that PP modified with MA showed the best compatibilizing effect in these systems.

Keywords: Polypropylene blends; Nylon; Compatibilization; Reactive blend

1. Introduction

Although polymer blending looks to be a very attractive way to obtain new materials, most of the polymer blends are immiscible and/or incompatible. Reasons for incompatibility are high interfacial tension and, consequently, poor interface adhesion [1,2]. However, the phenomenon of compatibility can be induced into an immiscible binary system by introducing a third component that will either interact chemically with both the phases or will have specific interaction with one phase and physical interaction with the other. The addition of a block or graft copolymer reduces the interfacial tension between the two phases, increases the surface area of the dispersed phase, promotes adhesion between the phase components, and stabilizes the dispersed phase morphology [3–6].

The polyolefins and nylon are two important classes of commercial polymers. However, the direct mixture of nylon and polyolefins leads to incompatible blends that exhibit inadequate properties for their use [7–11].

Functionalization by melt grafting is an interesting method to obtain a compatibilizing agent for these systems [3,8]. Grafting in an extruder involves the reaction of a polymer with a monomer or a mixture of monomers capable of grafting onto the polymer chain through a radical reaction. The extrusion of the nylon with polyolefins functionalized with maleic anhydride [1,7,8], acrylic acid, or with other types of functional groups, epoxy groups for instance, can lead to graft copolymers of polyolefin/nylon, that will act as compatibilizing agents. The success of this process depends on the concentration of the nylon terminal groups that will react with the polar group introduced onto the polyolefin.

Blends of polypropylene (PP) and nylon have received a lot of attention in recent years. PP functionalized with maleic anhydride (MA) has been used as compatibilizing agent in these systems [1,4,9]. In recent years, glycidyl methacrylate (GMA) has been used as monomer to graft onto polyolefins [9,12]. The epoxy group is able to react with either the acid or basic groups and should be a good alternative since the nylon has both –NH₂ and –COOH groups [12].

In the present work, the effects of PP-MA and PP-
GMA as compatibilizing agents will be analyzed based on the morphological, mechanical and thermal properties of PP/nylon 6 blends.

2. Experimental

2.1. Materials and blend preparation

The PP used was a commercial product (PPH301) from OPP Petroquímica with MFI=12 g/10 min (230°C/2.16 kg). Nylon 6 (Ny6) was a commercial product (Nylodur) from De Millus S.A. Company with MFI=6.6 g/10 min (230°C/2.16 kg). The PP-MA used as compatibilizing agent was synthesized in our laboratories [13]. GMA monomer (97%, MW 142, Aldrich) and dycumil peroxide (DCP) (98%, Aldrich) were used as received in grafting reactions.

The grafting reactions were carried out in a Haake Rheomix 600p mixer equipped with two co-rotating rotors. PP pellets, monomer (2.65 wt%) and initiator (0.04 wt%) were dry-blended before being charged into the mixer. The mixer chamber was initially heated to 180°C and saturated with argon. The residence time was 10 min and the rotor speed was fixed at 40 rpm. The unreacted monomer was extracted by reflux with chloroform for 3 h and then the PP-GMA was vacuum dried. The incorporation of GMA onto PP was obtained using a calibration curve [14].

The blends of PP and nylon 6 (all pre-dried at least for three days) were melt mixed at 240°C in a Haake Rheomix internal mixer 600p with rotor speed of 50 rpm for 5 min. The compositions of the blends were PP/Ny6 70/30 and PP/PP-MA or PP-GMA/Ny6 63/7/30.

2.2. Thermal analysis

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Thermal Analyser 2100, under nitrogen atmosphere. The samples were heated from 30 to 240°C at a heating rate of 10°C min⁻¹. The melting temperatures ($T_m$) values were taken from the second heating curve. Crystallinities were calculated using an extrapolated value of enthalpy corresponding to the melting of 100% crystalline samples: $\Delta H_{mp}=137.9$ J g⁻¹ and $\Delta H_{Ny6}=190$ J g⁻¹ [4].

2.3. Mechanical properties

The tensile properties were measured at room temperature in accordance with ASTM D882-83 using a Wolpert TZZ Test Machine, at crosshead speeds of 10 and 2 mm min⁻¹. At least seven specimens of each copolymer were tested.

The films were prepared using a hydraulic press, Carver series Monarch model 3710-ASTM, at 240°C for 15 min without pressure to melt the sample, followed by using a pressure of 9 kN for 3 min. The films were 1 cm wide and were stored under vacuum.

2.4. Blend morphology

The morphology was studied using a scanning electron microscope (JEOL JSM 5800). Samples were fractured under liquid nitrogen and the fractured surfaces were coated with gold.

3. Results and discussion

The samples were characterized by DSC. The results of crystallization temperatures ($T_c$), melt temperatures ($T_m$) and the crystallinity percentages ($\lambda_c$) of PP and Ny6, of the pure components and of the blends, are shown in Table 1.

The rise in crystallization temperature of PP in the blends was provoked by the presence of nylon with higher $T_c$, and by the nucleating agent-like behavior of the already crystallized minor component [9]. The crystallinity of the components of the PP/PP-GMA/Ny6 blend was virtually unchanged indicating that the presence of PP-GMA did not disturb the crystalline structure of the blend components.

Fig. 1a shows the cooling thermograms of the investigated samples. PP-GMA did not interfere in the crystallization peak of Ny6 but the presence of PP-MA caused its disappearance. The crystallization process of Ny6 in the blends may happen in two steps, one at the usual $T_c$ of nylon and the other at that of PP. The disappearance of the crystallization peak at the usual $T_c$ for Ny6 suggested that the whole Ny6 crystallization coincidentally took place at the usual $T_c$ for PP. This crystallization behavior did not mean that Ny6 co-crystallized with PP, since each component showed separated a melting endotherm (Fig. 1b). Hence, the coincident crystallization of Ny6 with PP is a concurrent crystallization and it is due to the reduction of the particle sizes of Ny6 in the PP/PP-MA/Ny6 blend [8].

The results of the tensile properties are presented in Table 1. The error limits correspond to the measurement standard deviations from seven samples.

The mixture of PP and Ny6, in the proportion 70/30 reduced the mechanical properties in relation to the pure components, indicating an incompatible mixture. The addition of 7% by weight of PP-GMA in the blends did not show an increase in their properties compared with the PP/Ny6 system.

PP/PP-MA/Ny6 presented an improvement in properties when compared with PP/PP-GMA/Ny6 and PP/Ny6; this may be attributed to the improvement in compatibility of the system. The elongation percentage value of the blend with PP-MA was higher than for the others.
Table 1
Thermal and mechanical behavior of pure PP, Ny6 and their blends

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_c$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\lambda_c$ (%)</th>
<th>Ultimate tensile strength (MPa)</th>
<th>Elongation-at-break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>112</td>
<td>163</td>
<td>64.8</td>
<td>28.0±1.8$^a$</td>
<td>10.3±0.9$^a$</td>
</tr>
<tr>
<td>Ny6</td>
<td>184</td>
<td>219</td>
<td>26.3</td>
<td>32.7±2.2$^a$</td>
<td>20.6±5.8$^a$</td>
</tr>
<tr>
<td>PP/Ny6</td>
<td>119</td>
<td>162</td>
<td>68.7</td>
<td>14.7±1.4$^a$</td>
<td>4.0±0.8$^a$</td>
</tr>
<tr>
<td>PP/Ny6</td>
<td>185</td>
<td>219</td>
<td>28.5</td>
<td>90.8±15.6$^b$</td>
<td>4.1±0.9$^b$</td>
</tr>
<tr>
<td>PP/PP-GMA/Ny6$^c$</td>
<td>119</td>
<td>183</td>
<td>66.1</td>
<td>14.5±2.6$^a$</td>
<td>3.0±0.6$^c$</td>
</tr>
<tr>
<td>PP/PP-MA/Ny6$^d$</td>
<td>121</td>
<td>164</td>
<td>73.1</td>
<td>250.3±9.9$^b$</td>
<td>15.8±1.6$^b$</td>
</tr>
</tbody>
</table>

$^a$ At a speed of 10 mm min$^{-1}$.
$^b$ At a speed of 2 mm min$^{-1}$.
$^c$ PP/PP-GMA/Ny6: (63/7/30) (0.32 mol% GMA).
$^d$ PP/PP-MA/Ny6: (63/7/30) (0.30 mol% MA).

Fig. 1. DSC curves: (a) cooling and (b) heating; for (a) PP; (b) PP/Ny6 (70/30); (c) PP/PP-GMA/Ny6 (63/7/30); (d) PP/PP-MA/Ny6 (63/7/30); and (e) Ny6.

blends. This may be ascribed to the fact that in the PP/Ny6 blend the components were incompatible, without mutual adhesion, and in blend with PP-GMA the adhesion was weak. Moreover, the large size of dispersed particles may cause the premature rupture of the samples, lowering the elongation [7].

The effect of the type of compatibilizer can be seen by comparing the morphologies of the blends. Fig. 2 shows blends without and with the presence of the compatibilizing agent. Fig. 2a displays the micrograph of the noncompatibilized blend (PP/Ny6). The immiscibility of the two components resulted in phase segregation, where the minor phase was dispersed in large spherical domains and the dispersion was poor. The presence of holes evidenced the retreat of particles, indicating that there was no adhesion between the phases.

The poor effect of adhesion of PP-GMA for the blend PP/Ny6 is seen in Fig. 2b. The micrograph showed just a small decrease in the nylon particle size. A large compatilizing effect was observed in the blends with PP-MA, as shown in Fig. 2c. In this blend the particle size was drastically reduced due to the strong adhesion between PP and Ny6 [2].

This behavior is in agreement with the results obtained for thermal and mechanical properties, which can be attributed to the improvement of the homogeneity of the system.

The storage modulus ($E'$) had a smaller value for the nylon at higher temperatures when compared with pure PP and blends, as shown in Fig. 3a. The highest $E'$ value was for pure PP. Apparently, the most compatibilized blend (with PP-MA) presented a small decrease in modulus above 50°C. Fig. 3b shows the nylon tan δ curve. It presented two transitions, at 22.8 and at 83°C that are related to the movement of large chain segments set free by disappearance of hydrogen bonding with increasing temperature [15]. PP presented the β-transition at 15°C and the α-transition at 120°C. Tan δ curves for the blends are quite similar where the nylon β-peak overlaid the PP α-peak. The transitions for the blends with PP-MA, at first sight, displaced to lower temperature.
Fig. 2. The morphology of blend (a) PP/Ny6 (70/30); (b) PP/PP-GMA/Ny6 (63/7/30), GMA=0.32%; and (c) PP/PP-MA/Ny6 (63/7/30), MA=0.30 mol%.

Fig. 3. $E'$ and $\tan \delta$ of PP, Ny6, PP/Ny6 (70/30), PP/PP-GMA/Ny6 (63/7/30) and PP/PP-MA/Ny6 (63/7/30).

4. Conclusions

The compatibilizing effect of the PP-MA for the PP/Ny6 blends was more effective than the PP-GMA. This effect was manifested in the thermal properties, where the PP-GMA essentially did not change the $T_m$, $T_c$ and $\lambda_c$ of the blend components, and on the morphology, with a better dispersion of nylon in the PP matrix. Also, the poorest mechanical properties were obtained when compared with the blends with PP-MA. The compatibilization is due to the presence of PP-$g$-Ny6 formed during the blending. This copolymer results from the reaction of the $-\text{NH}_2$ nylon end groups with the anhydride groups of PP-MA or from the reaction of the $-\text{NH}_2$ and/or $-\text{COOH}$ nylon end groups with the epoxide groups of PP-GMA. In that case, the reactivity of the nylon with the anhydride was more effective than with the epoxide.

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References