Influence of PP-g-MAH Compatibilizer Characteristics on Interphase and Mechanical Properties of Glass Fiber Reinforced Polypropylene Composites

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Abstract

Although recent publications have discussed the influence of maleated polypropylene (PP) compatibilizer characteristics, such as molecular weight (MW) and concentration of maleic anhydride (MAH) reactive groups, on the mechanical behaviour of PP composites, many aspects related to the interfacial adhesion and nature of the composite interphase have yet to be elucidated. Therefore, using a composite system of PP reinforced with aminosilane pretreated short GF of varying fiber content, the influence of MW and MAH concentration of different grades of the PP-g-MAH compatibilizer was investigated in this work. The compatibilizer efficiency in the fiber-reinforcement mechanism of these PP/PP-g-MAH/GF composites was determined from ultimate tensile strength (TS) and notched Izod impact strength (IIS) tests; the optimum compatibilizer concentration being defined by maximum mechanical properties enhancement achieved with minimum MAH concentration. For a given PP-g-MAH grade, increase in compatibilizer concentration leads to substantial increase in both the TS and IIS up to a minimum critical concentration, above which both properties tend to level off. This optimum concentration corresponds to a saturation level of the GF surface with the PP-g-siloxane copolymer formed at the interphase. Using this optimum concentration criterion, the PP-g-MAH grade with lowest MW and highest MAH concentration indicated the best compatibilizer efficiency. However, when all experimental data is presented as a function of the MAH concentration per unit surface area of GF (mg/m²), a single master curve is obtained at a given GF content, independently of the grade of the compatibilizer used. This indicates that the increase in the mechanical properties is essentially a function of the effectively reacted MAH concentration. The simultaneous increase in both the TS and IIS with MAH concentration can be attributed to the high interfacial adhesion and a soft and ductile nature of the interphase. These characteristics of the interphase layer were also substantiated by SEM analysis of freeze-fractured composite surfaces.

INTRODUCTION

In glass fiber (GF) reinforced thermoplastics with non-polar polyolefin matrixes, the use of a polyolefin functionalized compatibilizer, in combination with an appropriate silane coupling agent on GF surface, is often recommended for efficient mechanical reinforcement of the composite. In GF-reinforced polypropylene composites (PP/GF), the use of maleic anhydride functionalized PP (PP-g-MAH) as interfacial compatibilizer has been vastly reported in literature and the improved mechanical performance has been associated to the high interfacial adhesion and the nature of the interface/interphase structure achieved [1-6].

During the melt compounding of the PP/PP-g-MAH/GF composites, it is assumed that the compatibilizer migrates to the fiber-polymer interface and its dicarboxylic acid (-COOH) functional groups, originating from the hydrolysis of the cyclic maleic anhydride [(CHCO)₂O] groups, react with the amino functional groups of the silane to form amide bonds and, thereby, resulting in a PP-g-siloxane graft copolymer on the GF surface [3,5-7]. This copolymer is chemically coupled to the GF surface and physically absorbed into the PP matrix, through its interdiffusion and chain-entanglement with the matrix PP polymeric chains and thus generating a multilayer interphase of high interfacial adhesion, composed of graded chemisorbed and physisorbed layers of complex structure [6-9].

The degree of interfacial adhesion achieved and the physical nature and size/thickness of the interphase layer should depend on a number of factors such as the effective reactivity and molar ratio
of the functional co-reactive groups present at the interface and on the molecular weight (MW) of the functionalized PP compatibilizer. Several researchers [1,3-6] have reported on the influence of maleic anhydride concentration and MW of PP-g-MAH compatibilizer on the mechanical properties of GF-reinforced PP composites. Constable et al [1,3], McLoughlin et al [4] and Sousa et al [6] have demonstrated that low MW and high MAH concentration of the PP-g-MAH used leads to the best compatibilizer efficiency, expressed in terms of maximum mechanical properties improvement with the minimum use of the compatibilizer. Furthermore, McLoughlin et al [4] observed that the mechanical properties enhancement of the composite is actually determined by the MAH concentration, and not by the concentration of the PP-g-MAH compatibilizer used or by its melt flow index (MW). On the other hand, Hamada and co-workers [5], using low and high MW PP-g-MAH compatibilizer as binder in the fiber sizing for manufacture of continuous GF-reinforced PP laminates, reported that best results were obtained with low MW compatibilizer.

These contradictory results on the influence of MW of the PP-g-MAH compatibilizer motivated our study, as we believe that the MW of the maleated PP will influence its rate of diffusion through the matrix PP molecules and, therefore, should be sufficiently low in order to facilitate its migration to the fiber-polymer interface to generate chemical bonds. However, the MW should be at the same time sufficiently high in order to assure sufficient chain-entanglements with the polymer matrix molecules; both these factors being important to assure high interfacial adhesion. Furthermore, increase in the MW of the PP-g-siloxane graft copolymer on the GF surface should contribute towards increased thickness of the interphase layer and, thereby, influence on its physical characteristics and on the stress-transfer mechanism at the fiber-polymer interface. Therefore, using a composite system of PP reinforced with aminosilane pretreated short GF of varying fiber content, the influence of MW and MAH concentration of different grades of the PP-g-MAH compatibilizer on mechanical properties of the composites was investigated in this work and from the observed results inferences were drawn on the nature of the fiber-polymer interphase.

**EXPERIMENTAL**

An isotatic polypropylene homopolymer, VM6100K from Polibrasil (\( \rho = 0.91 \) g/cm\(^3\) and MFI = 19.6 g/10 min. at 2.16 kg/230\(^{\circ}\)C), was used as the polymer matrix with adequate antioxidant (0.2% Irganox 1010 - hindered phenol) and phosphite thermal stabilizer (0.4% Irgafos 168) formulation, and a chopped strand E-type glass fiber with aminosilane surface pretreatment from Vetrotex (\( \rho = 2.54 \) g/cm\(^3\), \( D_f = 13 \) \( \mu \)m and \( L_f = 4.5 \) mm,) as the fibrous reinforcement. Three commercial grades of PP-g-MAH compatibilizer supplied by Uniroyal, with distinct MW (high, medium and low MFI values) and MAH concentration as shown in Table 1, were used in this work. The actual MAH concentration (% by weight) in each grade was experimentally determined by acid-base chemical titration [10].

**Table 1 – Physical and chemical characteristics of different PP-g-MAH interfacial compatibilizer used.**

<table>
<thead>
<tr>
<th>PP-g-MAH</th>
<th>MFI * (g/10min)</th>
<th>% MAH (nominal)</th>
<th>% MAH (actual)</th>
<th>Mn (g/mol)</th>
<th>Mw (g/mol)</th>
<th>Mz (g/mol)</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB3001 Virgin</td>
<td>5</td>
<td>0.1</td>
<td>0.09</td>
<td>108,400</td>
<td>385,000</td>
<td>985,000</td>
<td>4</td>
</tr>
<tr>
<td>PB3150 Virgin</td>
<td>50</td>
<td>0.5</td>
<td>0.53</td>
<td>56,600</td>
<td>272,000</td>
<td>914,000</td>
<td>5</td>
</tr>
<tr>
<td>PB3200 Virgin</td>
<td>250</td>
<td>1.0</td>
<td>0.80</td>
<td>51,500</td>
<td>124,000</td>
<td>234,000</td>
<td>2</td>
</tr>
<tr>
<td>PB3200 Degr. A</td>
<td>-</td>
<td>-</td>
<td>0.80</td>
<td>38,100</td>
<td>100,000</td>
<td>189,000</td>
<td>3</td>
</tr>
<tr>
<td>PB3200 Degr. B</td>
<td>-</td>
<td>-</td>
<td>0.80</td>
<td>30,700</td>
<td>83,000</td>
<td>141,000</td>
<td>3</td>
</tr>
</tbody>
</table>

* Melt Flow Index (MFI) in according to ASTM D1218 – g/10 min at 230\(^{\circ}\)C/2.16 Kg.

All the PP/PP-g-MAH/GF composites, with 20, 30 and 40 weight percent of GF, were extrusion compounded in a corotating twin-screw extruder, ZSK-30 from Werner & Pfleiderer (D = 30 mm & L/D = 35), fitted with K-Tron gravimetric feeders. At each fiber content in the PP/PP-g-MAH/GF composite, the compatibilizer was employed in the concentrations of 0, 0.5, 1, 2, 5 and 10 % by weight in the composite. The choice of the screw profile and the optimum extrusion processing conditions used in this work were established in a previous work reported by the authors [11], where
conditions for uniform fiber dispersion and wetting by the matrix polymer were sought at minimal fiber attrition. Similarly, the test-specimens for mechanical properties evaluation were prepared in an automatic injection moulding machine (Arburg Allrounder 270V/300-120) in previously optimized conditions [11], maintaining the same processing conditions for all moulded composites. Tensile and Izod Impact tests were carried out in accordance with the specifications of ASTM D-638 (Type 1) and ASTM D-256 (V notched) respectively, in order to determine the mechanical performance of the PP composites.

In order to analyze the influence of the MW of the PP-g-MAH, at a given constant MAH concentration, on the compatibilizer efficiency in PP/PP-g-MAH/GF composites, it was necessary to resort to shear induced degradation (chain scission) of the functionalized PP compatibilizer in a Haake torque rheometer, as no appropriate samples of maleated PP were commercially available for this purpose. The PP-g-MAH used for this study was the PB3200 grade (0.8 % MAH), which showed the best compatibilizer efficiency as demonstrated in the next item on mechanical results. The controlled MW reduction conditions in the Haake mixer were 190 °C at 75 RPM for 90 minutes (Condition A) and 240 °C at 150 RPM for 45 minutes (Condition B). Both MW reduction conditions were conducted for shear time periods up to nearly “zero” torque registration in the Haake mixer. All PP-g-MAH compatibilizer grades, along with the degraded samples, were subjected to gel permeation chromatography in a Waters’ HPLC at high temperature for MW characterization. The degree of chain scission achieved in the degraded compatibilizer samples is reported in Table 1.

In order to evaluate the influence of the compatibilizer characteristics on the polymer-fiber interfacial adhesion and also on the nature of the interphase layer, scanning electron microscopy (SEM) of freeze-fractured composite surfaces, obtained from both unstrained and pre-strained (at stress level of 70 % of its ultimate tensile strength) tensile test-specimen, was carried out in order to analyze the fiber "pull-out", fiber surface characteristics and degree of interfacial adhesion.

RESULTS AND DISCUSSIONS

Influence of MW and MAH Concentration on Mechanical Properties

Figure 1 presents the tensile strength (TS) and notched Izod impact strength (IIS) data of the PP/PP-g-MAH/GF composites, with 30 % by weight of GF, as a function of PP-g-MAH concentration (wt. % in the composite) for the three grades of interfacial compatibilizer used in this work. Analyzing the data of TS and IIS for a given grade of PP-g-MAH, it can be observed that an increase in the compatibilizer concentration leads to a substantial increase in both properties up to an optimum concentration of the compatibilizer, above which these properties tend to level off. However, the compatibilizer with the lowest MAH concentration (0.09 %) does not attain the maximum IIS value even at its highest concentration of 10 % by weight in the composite. Considering that the compatibilizer efficiency in the mechanical reinforcement mechanism of these PP/PP-g-MAH/GF composites can be defined as a function of maximum TS and IIS properties improvement achieved with minimum PP-g-MAH concentration, a preliminary analysis of the data presented in Figure 1 indicates that the PP-g-MAH grade (PB3200) with lowest MW and highest MAH concentration showed the best compatibilizer efficiency. Constable et al [1, 3] also reported similar results.

However, when all experimental data shown in Figure 1 are now presented as a function of the MAH concentration of PP-g-MAH, expressed in terms of milligrams of MAH per unit surface area of GF (mg/m²), a single master curve is obtained at a given GF content in the composite, as shown in Figure 2. Again, it can be observed that an increase in MAH concentration leads to a substantial gains in both TS and IIS properties up to an optimum MAH concentration, above which both properties tend to level off. This minimum critical MAH concentration corresponds to the saturation level of the GF surface with the in-situ formed PP-g-siloxane copolymer. Figure 2 indicates that the minimum critical MAH concentration required for optimum IIS (0.1 mg/m²) is double of that for optimum TS (0.05 mg/m²). This leads us to infer that the minimum interphase layer thickness required for maximum impact energy dissipation should be much higher than that required for efficient stress transfer at the
fiber-polymer interface for tensile strength enhancement.

Also, the fact that all experimental data shown in Figure 2 fall within a single master curve, independently of the MW of the compatibilizer grade used, indicates, at a first instance, that the increase in the mechanical properties is essentially a function of the MAH concentration effectively reacted with the aminosilane functional groups on the GF surface. Similar results were also previously reported by McLoughlin et al [4]. However, in order to confirm these results, it would be necessary to analyze the above mechanical properties as a function of MW of PP-g-MAH at a given constant MAH concentration in the compatibilizer. This can be now verified by analyzing the mechanical properties data of the PP composites shown in Figure 3, where the MAH concentration of PP-g-MAH was maintained constant at 0.8 % by using the non-degraded (virgin) and two degraded samples (conditions A and B). Table 1 indicates the MW reduction data of these three compatibilizer samples.

From Figure 3, it can be seen that the data curves of TS and IIS are slightly shifted to the left with reduction in MW of the compatibilizer. At a given relative concentration of MAH/GF (mg/m²) below the optimum concentration, it can be clearly seen that MW reduction of PP-g-MAH, at constant

**Figure 1** - Tensile strength (a) and Izod impact strength (b) of PP/PP-g-MAH/GF composites with 30 % by weight of glass fiber as a function of PP-g-MAH concentration (% by weight).

**Figure 2** – Tensile strength (a) and Izod impact strength (b) of PP/PP-g-MAH/GF composites (30 % GF) as a function of the MAH concentration, expressed in terms of mg of MAH per unit surface area (m²) of GF surface.
MAH concentration, leads to a slight increase in the property analysed. This minor property enhancement can be attributed to the higher diffusion of the lower molecular weight PP-g-MAH chains through the polymer matrix and its easier penetration into the polysiloxane network formed at the GF surface, during its quest for amino-functional groups to form amide bonds [5, 8, 12]. Apparently, the limited influence of MW of PP-g-MAH on the compatibilizer efficiency as verified in the present work, can be credited to the difficulties encountered in MW reduction to sufficiently low values in the range of the critical molecular weight ($M_C = 6,890$) for chain-entanglement of PP molecules, as cited in the literature [13].

As the mechanical strength of fiber-reinforced thermoplastics depends, amongst other factors, on the degree of interfacial adhesion necessary for efficient stress transfer at the fiber-polymer interface, and also on the volume fraction of the fiber reinforcement, in Figure 4 are shown the TS and IIS properties for the three GF concentration (20-30-40 wt. %) used in this work. In this analysis, the PP composites were prepared using PP-g-MAH grade (0,8 % MAH) that showed the best compatibilizer efficiency.

**Figure 3** – Tensile strength and notched Izod impact strength of PP/PP-g-MAH/GF composites (30 wt. % of GF) as a function of relative concentration of MAH/GF (mg/m$^2$), for three different MW of compatibilizer at constant MAH concentration (0.8 %).

**Figure 4** - Tensile strength (a) and notched Izod impact strength (b) as a function of the MAH (mg/m$^2$) for PP/PP-g-0.8 % MAH/GF composites with 20, 30 and 40 % by weight of GF.
Analyzing the data presented in Figure 4, it becomes obvious that with increase in the relative concentration of MAH/GF, both TS and IIS values increase up to its optimum concentration and then tend to level-off in a similar manner as shown in the previous Figure 2. At a given GF concentration, the TS and IIS values increase substantially with MAH concentration, indicating clearly that the critical GF length is significantly reduced with increasing interfacial shear strength achieved with the PP-g-siloxane graft copolymer layer formed at the interphase. At the optimum MAH concentration, the entire GF surface is saturated with the PP-g-siloxane copolymer and thus tends to the leveling of the mechanical properties.

Another important observation verified in Figure 4 is the inverse relation between optimum MAH concentration with GF content in the composite, where increase in fiber concentration leads to a reduction in its optimum value. As the MAH concentration has been expressed in terms of milligrams of MAH per unit surface area of GF (mg/m²), it would be expected that its optimum value should not vary with GF content. The fact that it does vary with increase in the GF concentration is a clear indication that the GF surface saturation level with PP-g-siloxane copolymer is actually dependent on the probability of the compatibilizer migrating to the GF surface. Thus, higher the GF content, higher will be the available GF surface for the migrating compatibilizer molecules and, therefore, higher will be the statistical probability of attaining the saturation level of GF surface with less MAH concentration in the composite, as demonstrated in Figure 4.

Interphase Morphology

The simultaneous increase in both the tensile (TS) and Izod impact (IIS) strengths, verified in PP/PP-g-MAH/GF composites and as evidenced in the Figures 2 and 4 shown above, is in direct contradiction with the micromechanics of the classical theory of fiber reinforced polymer (FRP) composites. This “restrained monolayer interface” theory [14] stipulates that perfect interfacial adhesion leads to tensile/flexural strength enhancement at the cost of reduced impact/toughness resistance of the composite, and experimental results with both long and short glass fiber reinforced PP composites has been reported in published literature [15, 16]. However, several recent studies [1-3, 6, 17] have also reported the simultaneous increase in both tensile/flexural and impact/fatigue resistance properties of PP/PP-g-MAH/GF composites and this singular behaviour has been attributed to the multilayer interphase of high interfacial adhesion.

Sousa and Lopes [17], analyzing tensile modulus, ultimate tensile strength and strain data, along with Izod impact data of PP/PP-g-MAH/GF composites, have argued that substantial gains in both TS and IIS with unaltered tensile modulus and slight increased elongation at rupture, can only be achieved with high interfacial adhesion of a thick interphase of soft and ductile nature, which can be associated to the “deformable interphase layer” theory cited in the literature [8, 9, 14]. In order to elucidate this hypothesis, in Figure 5 are shown the details of the interphase morphology of freeze-fractured surfaces of PP/PP-g-MAH/GF composites with 30 % GF, as viewed by SEM.

In Figure 5 are shown the photomicrographs of PP composite samples with (Fig. 5-b, 5-d and 5-f) and without (Fig. 5-a, 5-c and 5-e) PP-g-siloxane interphase layer. Analyzing the “pulled-out” fiber surface characteristics, Fig. 5-a indicates low polymer wetting and interfacial adhesion of the GF surface with only aminosilane pretreatment, as verified by the presence of slight superficial ridges. In contrast, the photomicrograph in Fig. 5-b shows a thick interphase layer covering the GF surface of the same aminosilane-pretreated GF in the presence of PP-g-MAH compatibilizer, at the optimum MAH/GF concentration of 0.1 mg/m².

In order to analyze the degree of “fiber pull-out” and interfacial adhesion of these PP composite surfaces, in the following sequence of photomicrographs are shown the polymer-fiber interface region at the base of the pulled-out fibers, where Fig. 5-c and 5-d correspond to the “unstrained” and Fig. 5-e and 5-f to the “pre-strained” PP composite samples, according to the experimental procedure explained earlier. Although the unstressed samples do not indicate fiber debonding, it can be clearly seen in Fig. 5-d that the presence of the compatibilizer contributes to extensive polymer matrix wetting of the fiber surface.
Figure 5 - SEM photomicrographs of freeze-fractured surfaces of PP/PP-g-MAH/GF composites (30 wt. % GF), where (a), (c) and (e) correspond to samples without PP-g-MAH compatibilizer and (b), (d) and (f) to samples with PP-g-MAH compatibilizer (0.1 mg/m² of MAH/GF).
In Fig. 5-e, the absence of the PP-g-MAH compatibilizer leads to extensive fiber debonding and fiber “pull-out” voids can now be seen clearly on the matrix surface, once the existing poor interfacial interactions have been overcome by the induced pre-strain. In contrast, the presence of the compatibilizer in the composite leads to extensive plastic deformation at the fiber-polymer interface and little fiber pullout is evident on the matrix surface, as shown in Fig. 5-f, even at the high strain level used in the pre-strained PP composite, well above the elongation at break of the glass fiber by itself. These two observations are clear indications of the high interfacial adhesion achieved in the PP/PP-g-MAH/GF composites and of the soft and ductile nature of the multilayer interphase of PP-g-siloxane graft copolymer formed at the GF surface, in accordance with the above stipulated “deformable interphase” theory.

CONCLUSIONS

The influence of molecular weight and MAH concentration of several grades of PP-g-MAH interfacial compatibilizer on the mechanical properties of aminosilane pretreated short glass fiber reinforced polypropylene composites of varying glass content was analysed in this work. The compatibilizer efficiency in the fiber-reinforcement mechanism of these PP/PP-g-MAH/GF composites was determined from ultimate tensile strength (TS) and notched Izod impact strength (IIS) tests; the optimum compatibilizer concentration being defined by maximum mechanical properties enhancement achieved with minimum MAH concentration. The following main conclusions can be drawn from this work:

(i) At a given GF concentration, increase in compatibilizer concentration leads to substantial increase in both the TS and IIS up to a minimum critical concentration, above which both properties tend to level off. This optimum concentration corresponds to the saturation level of the GF surface with the PP-g-siloxane graft copolymer formed at the interphase.

(ii) Using this optimum concentration criterion, the PP-g-MAH grade with lowest MW and highest MAH concentration indicated the best compatibilizer efficiency. However, when all experimental data is presented as a function of the MAH concentration per unit surface area of GF (mg/m²), a single master curve is obtained independently of the grade of the compatibilizer used, indicating that the increase in the mechanical properties is essentially a function of the effectively reacted MAH concentration.

(iii) At a given constant MAH concentration, MW reduction of PP-g-MAH leads to a slight increase in TS and IIS properties. This minor property enhancement can be attributed to the higher diffusion of the lower molecular weight PP-g-MAH chains through the polymer matrix and its easier penetration into the polysiloxane network formed at the GF surface, during its quest for amino-functional groups to form amide bonds.

(iv) At the optimum relative MAH/GF concentration (mg/m²), substantial gains in both the TS and IIS are achieved with increase of glass fiber concentration (20-30-40 wt. %), in comparison with the same composites without the PP-g-MAH compatibilizer. Also, this optimum compatibilizer concentration is reduced with increase in GF content in the composite, indicating that the compatibilizer efficiency is also dependent on the statistical probability of PP-g-MAH molecules migrating to the GF surface, such that higher the GF content, higher will be the statistical probability of achieving interfacial compatibilization in the composite.

(v) The simultaneous increase in both the TS and IIS with MAH concentration can be attributed to the high interfacial adhesion and to a soft and ductile nature of the interphase, the characteristics of which were confirmed by SEM analysis of freeze-fractured composite surfaces.

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