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# The Effect of Compatibilizing and Coupling Agents on the Mechanical Properties of Glass Bead Filled PP/PET Blends

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**Summary:** PP/PET blends (95/5) filled with 50 % by weight of glass beads were prepared and studied at morphological and mechanical level, and compared with its analogous samples of glass bead-filled PP. The influence of a compatibilizing agent (maleic anhydride grafted polypropylene) and different silane coupling agents was analysed. It has been found that PET embeds glass bead surface independently on the silane coupling agent employed. Addition of MAPP in PP/PET blends leaded to tensile strength values similar to those of unfilled PP, but rupture takes place in a brittle manner.

## Introduction

One of the most important factors affecting the mechanical behavior of particulate filled polypropylene (PP) is the adhesion degree between this non-polar polymer and the polar surface of the filler particles. Depending of the interfacial adhesion different mechanical behaviors can be observed, from ductile materials with low tensile strength to brittle ones with high tensile strength, even higher than that of the unfilled polymer.

Usually, the way to achieve good adhesion between mineral fillers and PP involves actions concerning both polymer and filler. By one side, PP has to be functionalised in order to increase its polarity. This is usually done by blending PP with maleic anhydride grafted PP (MAPP)[1] or other similar miscible graft copolymer, By the other side, fillers must be surface-treated with silanes[2] or other accurate coupling agents in order to promote bonding with the functionalised polymer.

Ideally, if PP is compatibilized with an accurate functional polymer it could bond directly to the glass surface (through the hydroxyl groups), making then the use of silanes unnecessary. Due to the affinity of PET for the glass surface, we have prepared in this work PP/PET blends (without and with a compatibilizer) filled with glass beads (untreated and silane-treated) to analyse their mechanical behavior and to compare it

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with that of the analogous filled PP samples. Mechanical properties have been correlated with fractographic observations carried out by scanning electron microscopy.

## Materials and compounding

The polypropylene (PP 050) used in this study was provided by Repsol Química,S.A. It is an isotactic homopolymer grade with and MFI (230 °C, 2.16 kg) of 5.0 dg/min. Glass beads with an average particle size of 20 µm were employed as filler, being provided by Sovitec Ibérica, S.A. Eastman Chemical supplied a commercial grade of maleated polypropylene (EPOLENE G-3003), with an acid number of 8. Extrupet EW36 was a copolymer grade of PET manufactured by Catalana de Polímers S.A., with an intrinsic viscosity of 0.8 dl/g. Four different matrix compositions were selected as shown in Table I.

Four different silane coupling agents were employed as glass bead surface treatments (Table I). The following procedure was used to homogeneously coat the glass bead with the silane: a solution containing 30 ml of silane, 250ml of methanol, 60 ml of water and 5 ml of acetic acid was prepared by 1.5 kg of glass beads. This solution was stirred for 20 min to assure silane alkoxy groups hydrolysis. The solution was transferred into a flask and glass beads were then added gradually while stirring. The mixture was then heated up to 40 °C to evaporate the solvent. Stirring was continued as long as the viscosity of the mixture was low enough. The unreacted silane was washed out with methanol.

Table I. Matrix compositions and silane coupling agents employed. Silanes a, c and d supplied by Dow Corning. Silane b supplied by Witco

| Matrix | Silane coupling agents |
|---|---|
| PP (100) | 3-metacryloxypropyl trimethoxy silane [a] |
| PP/MAPP (97/3) | 3-mercaptopropyl trimethoxy silane [b] |
| PP/PET (95/5) | N-(2-aminoethyl)-3-aminopropyl trimethoxy silane [c] |
| PP/MAPP/PET (92/3/5) | 3-N-(2-(vinylbenzylamino)-ethyl)-3-aminopropyl trimethoxy silane[d] |

Compounds containing nominally 50 wt% of glass beads and different matrix blends were prepared using a Collin ZK-35 twin screw extruder with 25 mm screw diameter and L/D ratio equal to 36. In composites containing PET, it was previously dried for a minimum of four hours at 160 °C and air of –40°C dew point. A system of vacuum devolatilizing was employed. Extrusion temperature profile was 150-250-250-250-250-250 °C, screw speed was fixed at 120 rpm. A circular cross-section die of 3-mm diameter was employed, and the extrudate was cooled in a water bath and pelletised. Standard tensile specimens (type "I" according to ASTM D638) were injection-moulded using a Mateu & Solé 440/90 injection moulding machine and a mould (tempered at 60°C), as described in figure 4 of the ASTM D-647 standard. In order to eliminate any residual stresses generated during injection molding process, the dumbbell test specimens were annealed at 110 °C for 24 h.

Tensile tests were carried out at a crosshead speeds of 50 mm/min on a GALDABINI (model Sun 2500) universal testing machine and a videoextensometer for elongation measurements. From these tests, Young's modulus (E), tensile strength ($\sigma_{max}$) and elongation at break ($\varepsilon_b$) values were obtained. At least five samples were tested for each composition. Tests were performed at room temperature (23 ± 2 °C) and constant humidity.

In order to investigate the morphological aspects associated with fracture process, fracture surfaces generated in tensile tests were analysed by scanning electron microscopy (SEM), using an electronic microscopy *Jeol JSM-820*, after coating the samples with gold, to achieve an optimal conductivity.

## Results and discussion

### *Young's modulus*

The experimental values of Young's modulus of the studied compounds are presented in Table 2. It is noticed that the addition of glass beads results in a remarkable increase in the rigidity values of the compounds, if compared with that showed by unfilled PP ($E \approx 1.8$ GPa). The presence of PET and/or MAPP does no seem to influence significantly on the experimental rigidity values of the studied formulations. This may be due to the high glass bead content related to the small percentages of PET and MAPP on the compounds, which makes Young's modulus values depend mainly on the amount of glass bead added, hiding aspects related to the matrix modification.

Table 2. Experimental values of Young's modulus

| Matrix | Surface treatment | E (GPa) | Matrix | Surface treatment | E (GPa) |
|---|---|---|---|---|---|
| PP | None | 4.42 | PP/PET | None | 4.69 |
| | Z-6030 | 4.43 | | Z-6030 | 4.60 |
| | A-189 | 4.43 | | A-189 | 4.38 |
| | Z-6020 | 4.04 | | Z-6020 | 4.57 |
| | Z-6032 | 5.03 | | Z-6032 | 4.31 |
| PP/MAPP | None | 4.02 | PP/MAPP/ PET | None | 4.64 |
| | Z-6030 | 4.18 | | Z-6030 | 4.94 |
| | A-189 | 4.52 | | A-189 | 4.58 |
| | Z-6020 | 4.64 | | Z-6020 | 4.92 |
| | Z-6032 | 4.43 | | Z-6032 | 4.43 |

### *Tensile strength and elongation at break*

a) Glass bead filled PP

Tensile strength values (Fig 1a) show three adhesion degree matrix filler in these compounds. Firstly, a low adhesion degree, with a weak matrix/filler interface (Fig. 2a), due to a poor wetting of glass beads by the matrix, leading to a low tensile strengths values, along with ductile rupture (Fig. 2b). The deformation mechanisms in compounds with low matrix/filler interface, comes from the decohesion phenomena, which gives a certain extent of matrix cavitation being an effective way of energy dissipation. This behavior is displayed by the formulations with pure polypropylene-based matrix, except for that with silane Z-6032 treated-glass beads.

Secondly, it can be considered a medium adhesion level, characterized by a less marked tensile strength drop, and brittle rupture. In this case, surface treatment (Fig. 2b) and/or MAPP addition generate a quite more resistant interface (Fig. 2c), but tensile strength values of unfilled PP were not reached.

Finally, two compounds exhibited tensile strength values similar to those of pure PP, revealing a strong matrix filler/interface. These composites contains glass beads with silane treatments of amino nature, which can react with the cyclic anhydride[3-4], creating covalent bonds, an thus a more resistant interface. Due to the deformability constraint of the matrix in these interfacial zones, the deformation extent is small, resulting in brittle rupture (Fig. 2d).

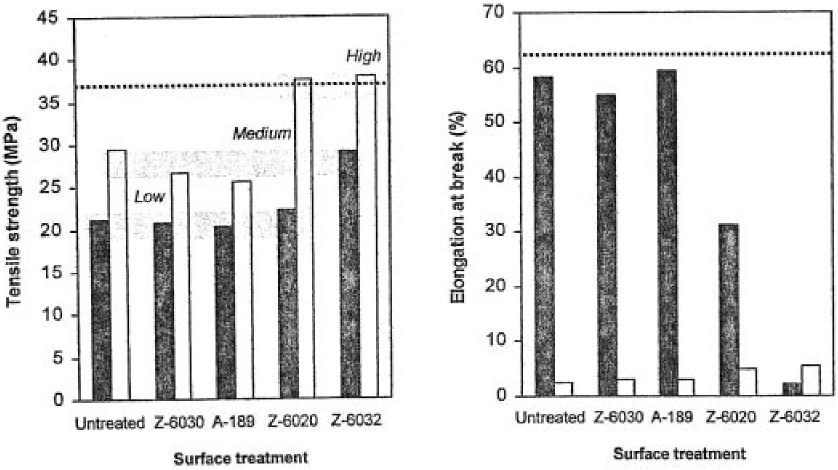

Fig. 1. Tensile strength and elongation at break of (■) PP and (□) PP/MAPP filled composites. Dashed line represents unfilled PP value. Shadowed zones refer to different matrix/glass adhesion degrees.

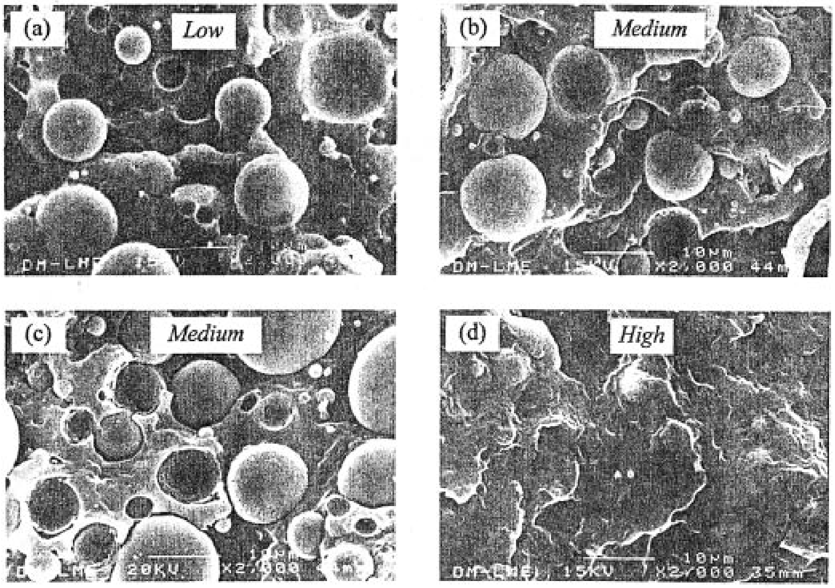

Fig. 2. SEM micrographs of the fracture surface with different adhesion degrees: (a) PP filled with untreated GB, (b) PP filled with Z-6032 treated GB, (c) PP/MAPP filled with A-189 treated GB and (d) PP/MAPP filled with Z-6032 treated GB.

b) Glass bead filled PP/PET blends

These formulations display two completely different behaviors (Fig. 3). Firstly, the absence of MAPP in the compounds leads to low tensile strength values. SEM micrographs (Fig. 4a) reveals that glass beads are debonded from matrix, but its surface is covered by a layer of polymer. Extraction with trifluoroacetic acid (Fig. 4c) gave a smooth glass bead surface, revealing that PET embeds glass bead surface. It is probably that hidroxy and carboxyl PET groups interact with hydroxyl groups of glass surface, and thus PET tends to embed glass beads. These formulations break in a ductile manner, but with lower values than those of PP (100) based formulations, which could be due to the poor PP/PET compatibility[5], leading to smaller elongation at break values It is noticed that any surface treatment reduces the dramatic fall in tensile strength.

On the contrary, the addition of MAPP in these PP/PET composites, leads in all cases to tensile strength levels similar to those of pure PP. By one hand, the maleated PP could act as compatibilizer of PP/PET blend[6-7] and/or interact with the functional groups of the silanes employed as surface treatments, which results in strong interfaces (Fig. 4b). A large amount of PET is located at the polymer filler interface (Fig. 4d). All these materials, displayed brittle rupture.

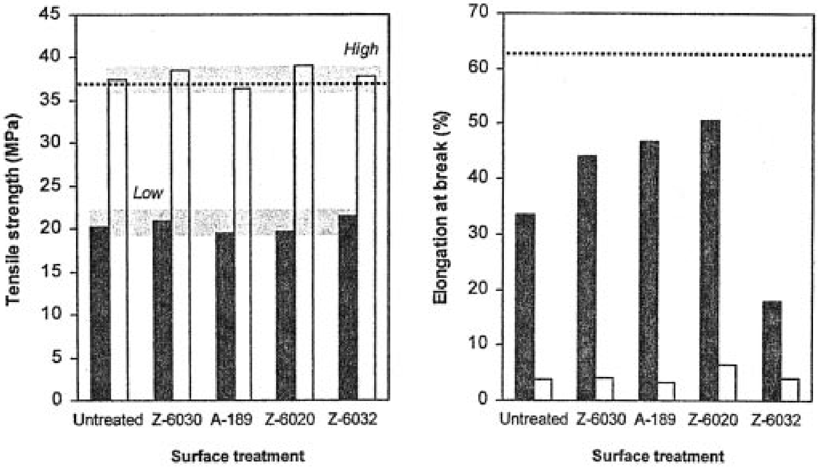

Fig. 3. Tensile strength and elongation at break of (■) PP/PET and (□) PP/MAPP/PET filled composites. Dashed line represents unfilled PP value. Shadowed zones refer to different matrix/filler adhesion degrees.

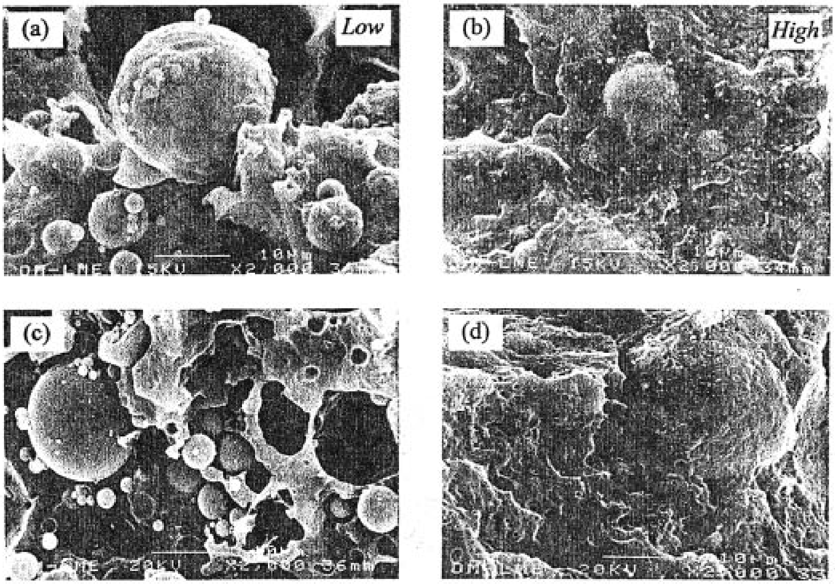

Fig. 4. SEM micrographs of fracture surfaces of (a) PP/PET filled with untreated GB, (b) PP/MAPP/PET filled with untreated GB. (c) and (d) show fracture surfaces of the same composites than (a) and (b) after extracting PET with $CF_3COOH$.

## Conclusion

Different mechanical properties have been obtained in glass bead-filled PP by using or not MAPP and depending on the type of silane coupling agent employed for filler surface treatment. Good interfacial adhesion makes the composite tensile strength to be high, even higher than that of unfilled PP. This was only achieved when both MAPP and an accurate silane coupling agent (Z-6020 or Z-6032) were used.

Instead of the use of silanes on the glass surface, an alternative way to generate good adhesion in filled PP has been found. It involves melt blending PP with a small percentage of PET, using MAPP as a compatibilizing agent.

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