

## Compatibilization of PP/PBT and PP/PA6 blends with a new oxazoline-functionalized polypropylene

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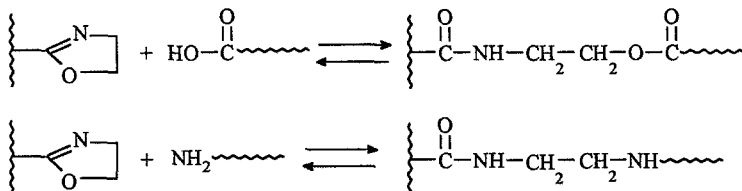
### Summary

Aim of this work was to study the effectiveness of a novel oxazoline-functionalized polypropylene as a compatibilizer for PP/PBT and PP/PA6 blends. This polypropylene-based compatibilizer mixes well with the polypropylene and is capable of reacting with the carboxylic and amine end groups of PBT and PA6. Significant improvements in blend toughness were achieved without reduction in strength and stiffness. These effects were related to stabilized morphology of finely dispersed minor phase well attached to the matrix. The enhanced interfacial interactions between the two phases, in particular at high PBT content were evidenced by increased melt viscosity.

### Introduction

The properties of polyolefins can be widely modified by blending with engineering thermoplastics. Generally such blends of two immiscible polymers are however brittle and special compatibilization is thus needed to improve the toughness. Graft copolymers of polyolefins are widely used as compatibilizers in blends of polyolefins with engineering plastics such as polyamides and polyesters. The most commonly used monomers are maleic and itaconic anhydrides, and vinyl and acrylic monomers containing some reactive functional group.

For this work a novel oxazoline-functionalized polypropylene was prepared with the aim to be used as compatibilizer. The oxazoline functionality was of interest since it can react with the carboxylic and amine groups to form an esteramide bond as shown below. This makes such copolymers potential compatibilizers for blends with polyesters and polyamides.



The oxazoline group can also react with other functional groups such as phenol and mercaptan. An overview of the reactions and preparation of different oxazolines can be found in the literature (1).

The oxazoline to be grafted onto PP by melt free radical grafting was ricinloxazoline maleinate (referred to as OXA). This was also used in an earlier study on the grafting of PP in a batch melt mixer, which indicated that OXA could be successfully grafted onto PP (2). Earlier ricinloxazoline maleinate was also used in the functionalization of PE (3,4) and poly(n-butylacrylate) (5).

Other oxazoline monomers have also been employed in compatibilization studies. For example, PS functionalized with vinylloxazoline has been used in the reactive

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blending of PS with functionalized PE and NBR (6-9). PP functionalized with 2-isopropenyl-2-oxazoline in turn has been used as a compatibilizer in PP/NBR (10, 11) and in PP/PC (12) blends.

The aim of this work was to study the effectiveness of a new oxazoline-functionalized polypropylene as a compatibilizer for PP/PBT and PP/PA6 blends. Compared to the above mentioned oxazoline-functionalized copolymers the present compatibilizer (hereafter referred to as PP-g-OXA) exhibits the following advantages: 1) the oxazoline monomer is grafted directly to the polypropylene (primary blend component), 2) the grafting yield is high, and 3) the monomer consists of relatively long aliphatic chain terminated by the reactive oxazoline group. Compatibilization is based on the fact that the PP-based compatibilizer mixes well with the PP phase and is capable of reacting with the carboxylic and amine end groups of PBT and PA6.

## Experimental

*Materials:* The polybutylene terephthalate (PBT) was Grilpet XE3060 by EMS and polyamide 6 (PA6) Ultramid B3S by BASF. Polypropylenes (VB1950K and VC1233B, supplied by Borealis Polymers) were chosen so that the viscosities of the blended polymers were close to each other (13-15). The former grade was thus blended with PBT and the latter with PA6.

The oxazoline-functionalized PP (referred to as PP-g-OXA; grafted oxazoline content: 2.1 wt.%) used as compatibilizer was prepared by melt free radical grafting in a twin-screw extruder as described in ref. (16). The oxazoline monomer was ricinoloxazoline maleinate (supplied by Henkel KGaA) containing a maleinate group which promotes grafting, and a long aliphatic chain terminated by an oxazoline group. In all blend compositions the compatibilizer content was 10 wt.%.

*Blending and injection molding:* Before melt blending PBT was dried for 5 h at 120 °C, PA6 for 16 h at 85 °C, and the compatibilizer for 6 h at 60 °C in a dehumidifying dryer. The materials were melt blended with a Werner & Pfleiderer ZSK 25 M9 co-rotating twin-screw extruder. Melt temperature was 242 °C, screw speed 150 rpm (200 rpm for PA6 blends), and throughput 6 kg/h.

After drying (overnight at 80 °C) the blends were injection molded into the form of test specimens with an Engel ES 200/40 injection molding machine. The melt and mold temperatures were about 240 °C and 40 °C, respectively.

*Characterization:* The injection molded PP/PBT blends were conditioned for at least 48 hours at 23 °C and 50 % relative humidity before mechanical testing. On the contrary, the PP/PA6 specimens were dried overnight at 80 °C before testing due to the sensitivity of PA6 to moisture. Tensile properties were determined with an Instron 4204 testing machine applying ISO 527 with a test speed of 5 mm/min. The Charpy impact strength was determined for unnotched test specimens by using Zwick 5102 pendulum-type testing machine. The dimensions of the test specimens were 112x10x4 mm and the span length was 70 mm (not exactly a standard test).

Morphology of the blends was investigated with a JEOL JXA-840A scanning electron microscope (SEM) of the twin-screw extruded strands. Before scanning the samples were fractured by dipping in liquid nitrogen and plated with a thin layer of gold.

Melt viscosities of some PP/PBT blends were determined with a Göttfert Rheograph 2002 capillary viscosimeter at 240 °C. The blends were dried at 80 °C overnight before the measurements. The L/D ratio of the capillary die was 30 mm/1 mm.

## Results and discussion

*Mechanical properties:* The results of the tensile and impact tests of the injection molded blends are presented in Figures 1 and 2.

Generally, the addition of the oxazoline-functionalized PP improved the toughness of both PP/PBT and PP/PA6 blends which was seen as significantly improved values of

impact strength in all blend compositions (Figures 1a and 2a). Most of the compatibilized blends were extremely ductile i.e. the specimens did not break at all, although the PA6 blends were dried before testing. In addition, all compatibilized blend compositions exhibited markedly enhanced maximal tensile strain. The increased elongation was clearly seen at PBT contents above 30 wt.%, while in PP/PA6 blends the effect was more pronounced at high PA6 contents (60 and 80 wt.%).

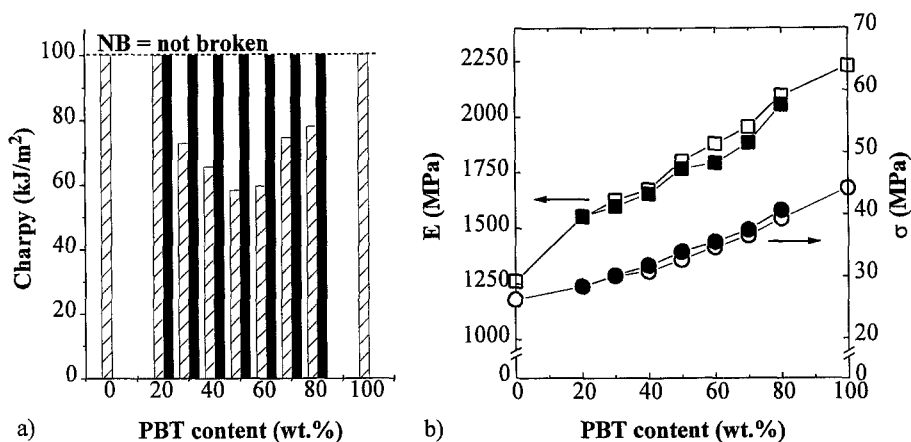


Figure 1. a) Charpy impact strength and b) tensile strength ( $\sigma$ ) and modulus (E) of PP/PBT blends vs. PBT content (white = without compatibilizer, black = compatibilized).

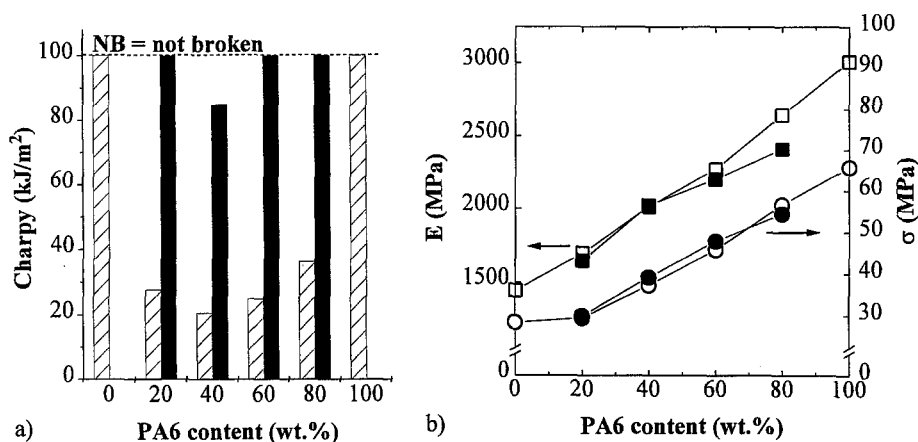


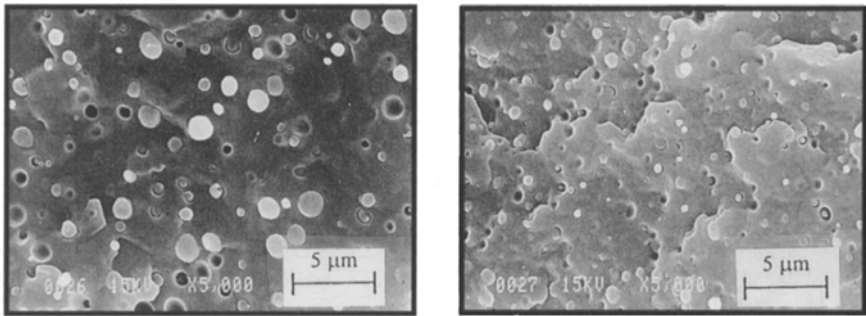
Figure 2. a) Charpy impact strength and b) tensile strength ( $\sigma$ ) and modulus (E) of dried PP/PA6 blends vs. PA6 content (white = without compatibilizer, black = compatibilized).

Tensile properties presented in Figures 1b and 2b show that the PP-g-OXA compatibilizer did not reduce the level of strength and stiffness at all like most of the reactive compatibilizers do (e.g. ref. 17). Very often the compatibilizers promoting improvements in toughness are soft elastomeric materials, whose addition leads to a dramatic decrease in the blend stiffness. In fact in the present study, even slight

improvements were observed in tensile strength, especially at PBT and PA6-rich compositions. Hence, a good balance between toughness and stiffness was achieved.

**Morphology:** The improvement in toughness was based on changes in blend morphology evidenced by SEM micrographs. The uncompatibilized blends exhibited a clear dispersion of spherical particles of the minor phase without indications of particular adhesion. Addition of the PP-g-OXA compatibilizer significantly reduced the particle size and made the dispersed phase well embedded to the matrix.

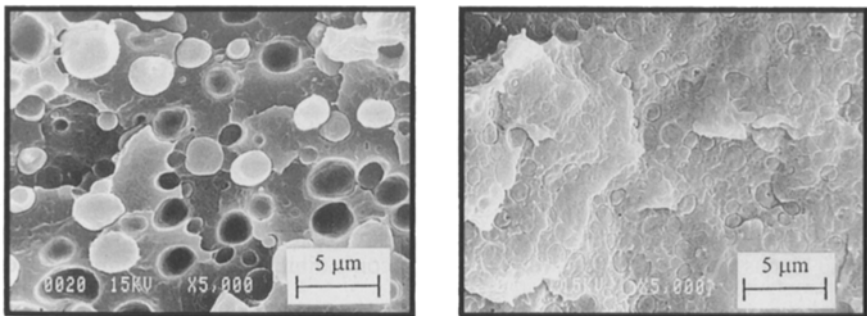
Examples of the effects of the compatibilizer on the blend morphology are shown in Figures 3-6. In the uncompatibilized PP/PBT blends with PP as the matrix the average size of the PBT domains was of the order of 0.5-1.5  $\mu\text{m}$ , while in the compatibilized blends it decreased to 0.2-0.5  $\mu\text{m}$  (see Fig. 3). In PBT-rich compositions the size of the PP particles decreased from the level of 2-3  $\mu\text{m}$  to 0.5-1.5  $\mu\text{m}$ , respectively (Fig. 4). Moreover, in the latter case the dispersed PP domains were well embedded and attached to the PBT matrix. This was supposed to be due to the higher amount of carboxylic end groups available to react with the oxazoline-functionalized PP. Such reactions between PP-g-OXA and PBT were confirmed in the earlier studies by DMTA, DSC and a kinetic analysis (2,16). In addition, the compatibilizer stabilized the morphology of the blend compositions also in the phase inversion region.



a)

b)

Figure 3. SEM micrographs of a) uncompatibilized and b) compatibilized (with 10 wt.% PP-g-OXA) PP/PBT blends containing 20 wt.% PBT.



a)

b)

Figure 4. SEM micrographs of a) uncompatibilized and b) compatibilized (with 10 wt.% PP-g-OXA) PP/PBT blends containing 80 wt.% PBT.

Although similar trends were observed in PP/PA6 blends, they showed however more pronounced reduction in particle size of the dispersed phase than the corresponding PP/PBT blends. In addition, clearly improved interfacial adhesion was seen also in the PP-rich PP/PA6 compositions. The particle size of the blends containing 20 wt.% PA6 diminished from 3-5  $\mu\text{m}$  to 1-2  $\mu\text{m}$  as seen in Figure 5. Again the compatibilizer addition homogenized the coarse blend morphology found near the phase inversion leading to narrower particle size distribution (Fig. 6). In the PA6-rich blends containing 80 wt.% of PA6 the reduction was even more significant, from the level of about 10  $\mu\text{m}$  to 1-2  $\mu\text{m}$ .

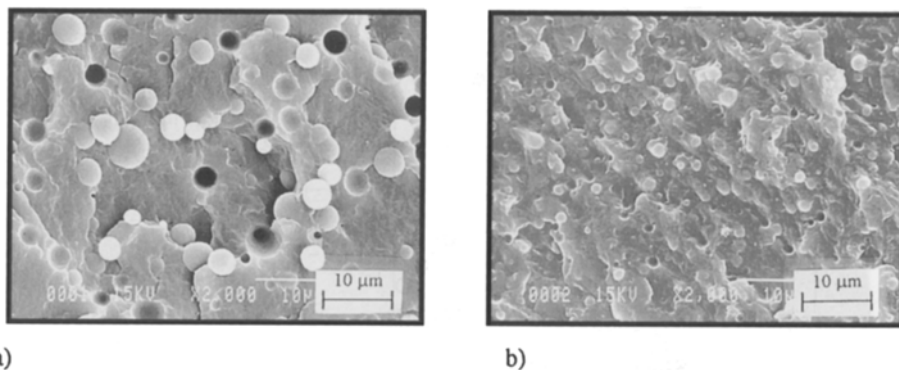


Figure 5. SEM micrographs of a) uncompatibilized and b) compatibilized (with 10 wt.% PP-g-OXA) PP/PA6 blends containing 20 wt.% PA6.

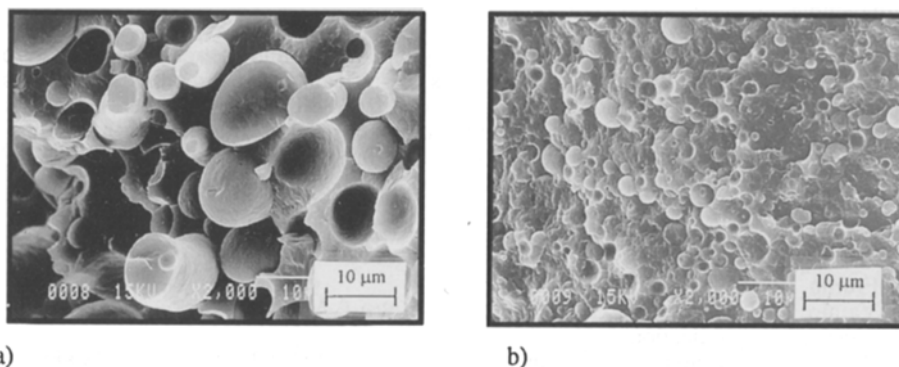


Figure 6. SEM micrographs of a) uncompatibilized and b) compatibilized (with 10 wt.% PP-g-OXA) PP/PA6 blends containing 60 wt.% PA6.

**Viscosity increase:** The effects of the compatibilizer on the melt viscosities of PP/PBT blends containing 20 or 80 wt.% PBT are shown in Figure 7. The viscosity of the compatibilized PBT-rich blend was clearly increased after the compatibilizer addition. Although not shown here, the viscosity of the compatibilizer itself is very low, which lets us to conclude that the increase in viscosity was probably due to reactions between the oxazoline groups in the compatibilizer and carboxylic end groups of PBT as suggested above. At the lower PBT content (20 wt.%) such increase in viscosity was not found, most probably due to insufficient amount of carboxylic end groups available.

Nevertheless, it should be noted that significant interactions between the discrete PP and PBT phases were achieved through the compatibilizer also at this composition evidenced by SEM and impact tests.

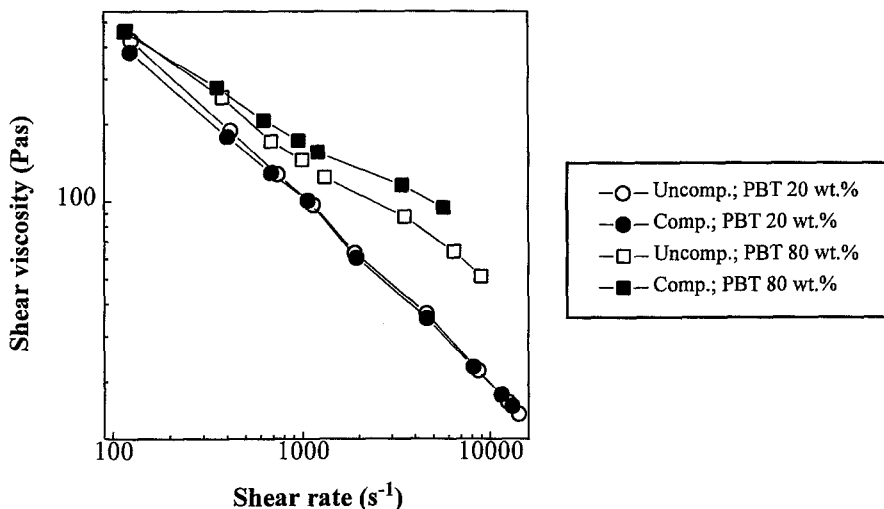


Figure 7. Melt viscosities of uncompatibilized and compatibilized PP/PBT blends containing 20 or 80 wt.% of PBT.

## Conclusions

New oxazoline-functionalized polypropylene was found to act as an effective compatibilizer for PP/PBT and PP/PA6 blends. Significant improvements in toughness were achieved without reduction in strength and stiffness. These effects were related to stabilized morphology of finely dispersed minor phase well attached to the matrix. Increase in melt viscosity induced by the compatibilizer, in particular at high PBT content, evidenced the enhanced interfacial interactions between the two phases.

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