

Functionalization of Polypropylene with Oxazoline and Reactive Blending of PP with PBT in a Corotating Twin-Screw Extruder

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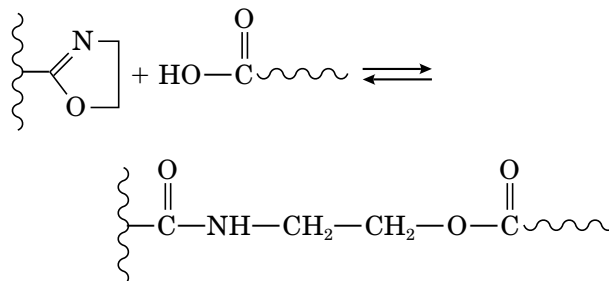
ABSTRACT: The aim of this study was to prepare a compatibilized PP/PBT blend in a twin-screw extruder, using oxazoline-functionalized PP. First we prepared the functionalized PP (PP-*g*-OXA), and then we used it as a compatibilizer in the subsequent reactive blending stage. Polypropylene was successfully functionalized by ricinloxazoline maleinate in a corotating twin-screw extruder using a melt free radical grafting technique. Grafting yields up to 2.1 phr were achieved. This functionalized PP used as a compatibilizer markedly improved the mechanical properties of the uncompatibilized PP/PBT (PBT content 30 wt %) blend. Significant improvements were observed, especially in impact strength (Charpy) and elongation at break of the compatibilized blends. The increased interactions between the phases were characterized by SEM analysis, DMTA, and DSC experiments. The properties of the blend greatly depended on the degradation of the PP during grafting. An optimal content of compatibilizer exists, which is dependent on the degradation of PP, grafting yield of oxazoline monomer, and on the amount of free, ungrafted monomer present in the compatibilizer. These factors can be adjusted by properly choosing the processing conditions and chemical parameters. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 883–894, 1997

Key words: oxazoline; polypropylene; poly(butylene terephthalate); grafting; compatibilization

INTRODUCTION

Graft copolymers of polyolefins are widely used as compatibilizers in blends of polyolefins with engineering plastics such as polyamides and polyesters. Graft copolymers are produced by the melt free radical grafting of monomers onto the polyolefin chain. The most commonly employed monomers are maleic and itaconic anhydrides and vinyl and acrylic monomers containing some reactive functional group.

The oxazoline was of interest because it can react with the carboxylic group to form an esteramide, and, thus, should be effective in the compatibilization of blends in which one polymer contains a carboxylic group.

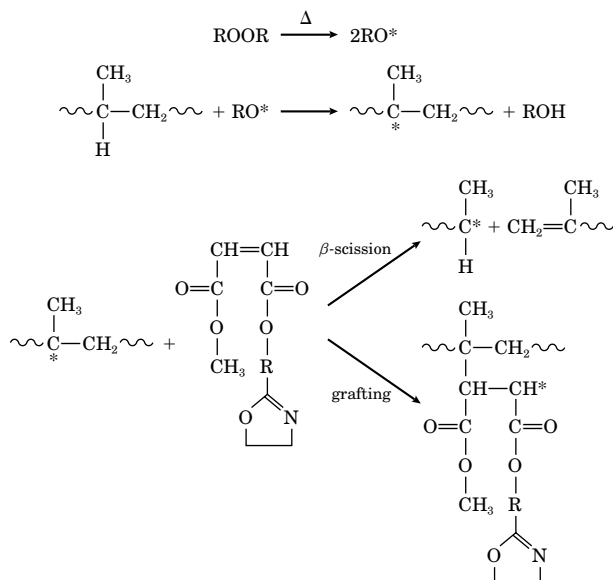


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The oxazoline group can also react with other functional groups such as amine, phenol, and mercaptan. An overview of the reactions and preparation of different oxazolines can be found in the literature.¹

The oxazoline to be grafted onto PP by melt free radical grafting was ricinloxazoline maleinate (OXA). This was also used in our 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 The scheme for grafting the oxazoline monomer onto PP, as used in our study, is presented below:



The oxazoline functionality has already been widely employed in compatibilization studies. For example, PS functionalized with vinyloxazoline has been used in the reactive blending of PS with functionalized PE and NBR.⁶⁻⁹ PP functionalized with 2-isopropenyl-2-oxazoline has been used as a compatibilizer in PP/NBR^{10,11} and in PP/PC¹² blends. We have also applied PP functionalized with OXA as a compatibilizer for a PP/PBT blend in our earlier study carried out in a batch melt mixer.² The aim of this study was to prepare a compatibilized PP/PBT blend in a twin-screw extruder using the oxazoline functionality. First, we prepared the functionalized PP (PP-*g*-OXA), and then we used it as a compatibilizer in the subsequent blending stage. The effect of the amount of residual ungrafted monomer on the blend properties is discussed. As suggested in earlier studies on the free radical grafting of PP^{2, 13-17} the addition of styrene (St) as a comonomer with such

monomers as maleic anhydride and glycidyl methacrylate reduces the degradation of the functionalized PP and enhances the grafting yield of the monomer. Thus, we carried out some experiments with St to determine its effect on the properties of the oxazoline grafted PP.

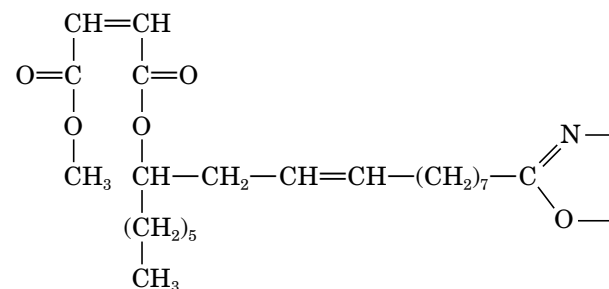
The blend properties were studied in terms of morphology, and mechanical properties such as impact strength, tensile strength, tensile modulus, and elongation at break. Moreover, dynamic-mechanical (DMTA) and thermal (DSC) analysis were applied in order to characterize the changes in compatibility.

EXPERIMENTAL

Materials

The polypropylene (Himont, Valtec CL101D, MFI = 0.3 g/10 min) was a random copolymer of propylene and ethylene (6–12 wt %), supplied in the form of small porous pellets capable of absorbing liquid monomers. The number and weight average molecular weights of the PP were 141,000 and 654,000 g/mol, respectively. The poly(butylene terephthalate) (PBT) used in the blending experiments was Arnite T08-200 from DSM-Akzo ($\bar{M}_n = 28,000$ g/mol, $\bar{M}_w = 65,000$ g/mol). The concentrations of the terminal groups were [—COOH] = 0.040 eq/kg and [—OH] = 0.032 eq/kg.

The monomer containing the oxazoline group was ricinloxazoline maleinate (OXA) supplied by Henkel KGaA. Its structure is presented below.



This monomer is in liquid form and exhibits very low volatility under actual processing conditions (b.p. > 250°C at 0.1 mbar). In addition to the highly reactive oxazoline group, ricinloxazoline maleinate contains a maleinate group that exhibits good grafting properties. The comonomer, styrene (St), was purchased from Aldrich (purity 99%). The peroxide was 1,3-bis(*tert*-butylperoxy-isopropyl)benzene supplied by Akzo (Perk-14, purity 90%). The estimated half-life-

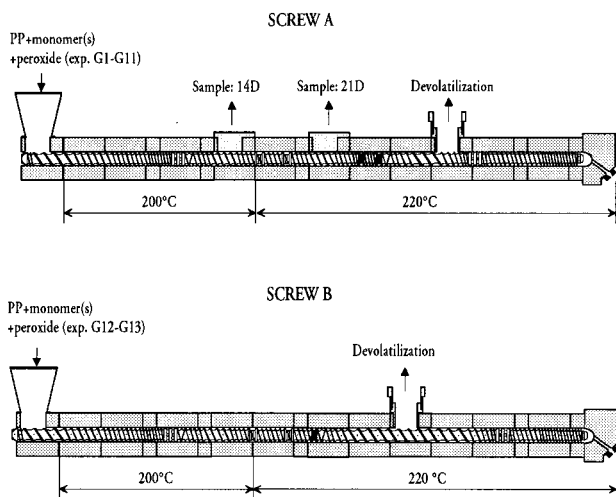


Figure 1 Screw configurations A and B used in grafting experiments.

time at the grafting temperatures (218–220°C) was about 5 to 10 s.

Grafting Procedure

The melt free radical grafting was carried out in a modular, corotating, self-wiping twin-screw extruder (Werner & Pfleiderer ZSK-30 M9, screw diameter $D = 30$ mm, length-to-diameter ratio $L/D = 42$). The screw configurations A and B used in grafting experiments are depicted in Figure 1. Screw A was used in grafting experiments G1-G11 (Table I) and screw B, exhibiting a longer devolatilization zone, was applied in grafting experiments G12 and G13.

The total feed rate was 5.5 kg/h, while the screw speed was 150 rpm in all runs. The mean residence time was about 150 s. Before feeding the materials into the extruder, the monomer(s) and peroxide were allowed to absorb into the small porous PP pellets for 30 min at room temperature. The initial concentration of the OXA varied between 1.5 and 6.0 phr (= grams per 100 g of PP), that of St between 0.72 and 1.44 phr (the molar ratio: $[St]_i/[OXA]_i = 1$) while the initial peroxide concentration was in the range of 0.1 to 0.7 phr. Devolatilization was carried out by vacuum pump in order to remove the residual monomer(s). The hot extrudate was immediately quenched in a water bath and pelletized for further use. In some experiments, upstream samples were taken at two positions (14D and 21D). The sampling was carried out during a steady-state

run by opening the barrel and quenching the emerging hot polymer in liquid nitrogen.

Reactive Blending and Injection Molding Procedures

The reactive blending was carried out in the same twin-screw extruder as was used for grafting. Two different screw configurations were applied for blending (Fig. 2). In screw C, the devolatilization zone was placed just before the final pumping and homogenization zone. In screw D, the devolatilization was placed just after the conveying and melting zone. It was hoped that by devolatilizing at an early stage, the amount of residual monomer present in PP-*g*-OXA could be reduced before the compatibilizing reaction to promote interfacial reactions.

Before blending, PBT was dried at 100°C and PP-*g*-OXA at 60°C under hot air circulation for 12–16 h. The total feed rate was 5.5 kg/h and the screw speed 150 rpm in all blending experiments.

After careful drying the blends and pure polymers were injection molded into the form of test specimens. Injection molding was carried out with a Billion 50 injection-molding machine. The set temperatures of the barrel and the mold were 240 and 50°C, respectively.

Purification of Samples and Determination of Grafting Yield

The functionalized PP samples were purified by dissolving them in boiling xylene and then by precipitating in acetone at room temperature. Using this procedure, the possible homo- and copolymers of oxazoline and styrene could be separated, and the real grafting yield could be determined. A more detailed description of the purification is given elsewhere.²

The grafting yield was determined by FTIR (Nicolet SX60) from thin (100–150 μm) compression molded films of the purified PP samples. Three parallel samples were tested for each experiment. The peak at 2722 cm^{-1} , representing the skeleton of the PP chain, was chosen as the reference. The peak at 1671 cm^{-1} was attributed to a complex mode involving C=N stretching and oxazoline ring bending, and was treated as a characteristic peak of the grafted OXA. Another strong peak at 1734 cm^{-1} (resulting from the ester group in OXA) was also treated as a characteristic peak of OXA to verify the results. The peak at 700 cm^{-1} was chosen as the characteristic peak of grafted

Table I The Compositions and Grafting Yields of the Functionalized PPs

Code	[OXA] _i (phr)	[St] _i (phr)	[ROOR] _i (phr)	Torque ^a (%)	[OXA] _σ (phr)	[OXA] _r (phr)
PP	—	—	—	49	—	—
[OXA] _i = 1.5 phr; Screw A						
G1	1.5	—	0.1	31	0.42	0.55
G2	1.5	—	0.3	23	0.57	0.46
G3	1.5	—	0.7	18	0.68	0.42
[OXA] _i = 3.0 phr; Screw A						
G4	3.0	—	0.3	24	0.95	1.13
G5	3.0	—	0.7	17	1.25	0.79
G6	3.0	0.72	0.3	29	0.71	1.44
G7	3.0	0.72	0.7	23	1.13	1.17
[OXA] _i = 6.0 phr; Screw A						
G8	6.0	—	0.3	24	1.30	2.76
G9	6.0	—	0.7	25	2.10	2.07
G10	6.0	1.44	0.3	34	0.94	3.08
G11	6.0	1.44	0.7	31	1.51	2.81
Grafting with Screw B						
G12	3.0	—	0.3	25	0.97	1.10
G13	5.0	—	0.5	24	1.72	1.98

^a The actual percentage torque (= measured torque-idle torque) of the maximum.

St. The grafting yields could be calculated from the ratios of the intensities of the characteristic absorbance peaks using preestablished calibration curves of OXA and St.^{2,15}

Characterization of Blend Morphology

The morphology of the PP/PBT blends was investigated with a scanning electron microscope (SEM, JEOL JXA-840A). The samples were taken straight from the extrudate (=no additional drawing). To prepare a cross-section of the samples they were fractured after liquid nitrogen cooling. Before scanning the fractured surface was coated with a 15 nm layer of gold.

Mechanical, Dynamic-Mechanical, and Thermal Characterization

Tensile properties were measured at room temperature according to ASTM 638–71A with an

Instron 8031 mechanical testing machine. The strain rate was 50 mm/min. The results of the tensile tests are averages of at least five parallel tests. The impact strength was determined for both unnotched (ISO 179/2D) and notched (ISO 179/1A) conditioned test specimens at room temperature. At least seven parallel tests were carried out for each blend sample.

Glass transition temperatures (T_g) of different blends and their components were determined by dynamic-mechanical analysis with a Rheometrics Solids Analyzer RSA II (dual cantilever geometry; bending) as the maxima of the loss modulus (E'') vs. temperature curve. The heating rate was 2°C/min and the frequency 6.28 Hz. The scanned temperature region was from –40 to about +100°C.

The crystallization and melting of the blends was followed using a differential scanning calorimeter (DSC) with heating and cooling rates of 10°C/min. The temperature range from +50 to +250°C was of interest.

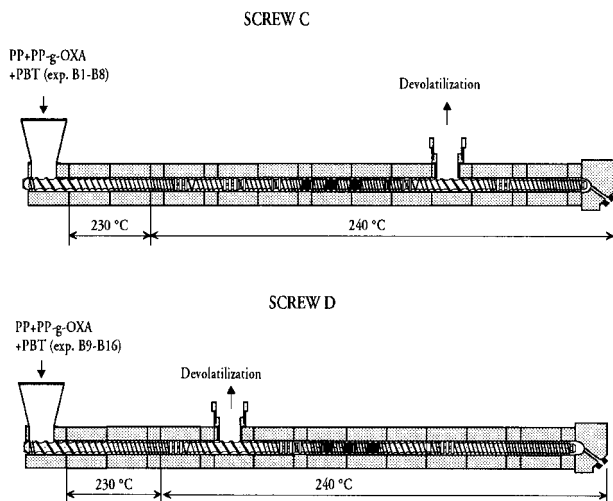


Figure 2 Screw configurations C and D used in reactive blending.

RESULTS AND DISCUSSION

Grafting of PP

The results of grafting experiments carried out in the twin-screw extruder and the corresponding grafting yields are shown in Table I. Under the applied conditions the grafting yield of OXA onto PP varied from about 0.4 to 2.1 phr, while that of St was in the range from 0.3 to 0.6 phr, depending on the concentrations of the monomers and peroxide in the feed. Although a devolatilization zone was installed in the extrusion line in all experiments, some residual monomer was still present in the PP-g-OXA. Even when the length of the devolatilizing zone was increased markedly (Screw B, experiments G12 and G13), only slightly better removal of free monomer was obtained. It was found that about 10–15 wt % of the residual OXA could be removed from the product by the devolatilization system. The accurate amount of devolatilized monomer (by vacuum pump) was difficult to measure, because the devolatilized amounts were very small. The amount of residual OXA in the end product varied from 0.4 to 3.1 phr. It should be noted that if there is too much residual monomer present in the grafted PP, the monomer, exhibiting higher mobility than the polymer chains, will react with the end groups of the PBT, thus preventing the desired compatibilizing reaction.

A small amount of residual monomer present in the grafted PP is not necessarily undesirable. The monomer can react with the end groups of

PBT (= end group capping) increasing the resistance of PBT to hydrolysis at elevated temperatures during extrusion by decreasing the number of carboxylic groups. The higher the concentration of carboxylic groups in the PBT, the more likely is the hydrolysis, which leads to lower molecular weight and worsening of mechanical properties.¹⁸ For end group capping of polyesters, 2-oxazolines have been found to be especially effective.³ Therefore, an appropriate amount of residual monomer might serve as an end group capping agent, and the grafted monomer will link the phases of the blend.

Naturally, it is not only the grafting yield and the amount of residual monomer that describe the total quality of the grafting process. In particular, the molecular weight of the grafted PP and the processability should also be considered when evaluating the different compositions of grafting experiments.

Effect of the Initial Concentrations of Peroxide, St, and OXA on Grafting

As expected, as shown in Figure 3, the higher the initial concentration of the peroxide, the higher the grafting yield achieved. Nevertheless, estimated in terms of the torque of the extruder, a marked decrease in molecular weight of the functionalized PP was observed, as expected. As already found in our earlier study of grafting OXA onto PP,² the addition of styrene as comonomer did not enhance the grafting yield of OXA, but instead reduced the β -scission of the polypropylene chains. This led to slightly higher molecular

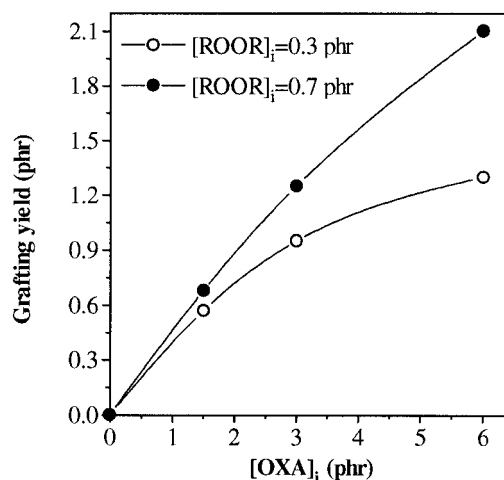


Figure 3 Effect of initial concentrations of peroxide and OXA on the grafting yield.

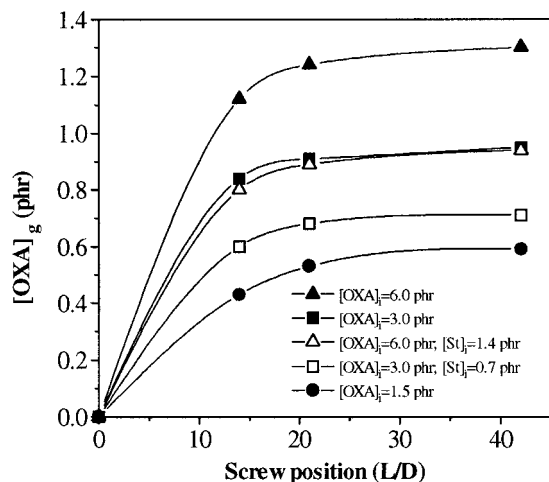


Figure 4 Evolution of grafting yield as a function of screw position. Die exit was at 42 L/D; $[\text{ROOR}]_i = 0.3$ phr.

weights of PP-*g*-OXA as shown by higher values of extruder torque. In fact, a somewhat lower grafting yield of OXA was found with styrene than without it. This effect is due to the high reactivity of styrene towards the PP macroradicals rapidly reducing the amount of free radicals and thus the tendency of PP towards chain scission.

Depending on the application, an optimal initial concentration of OXA should be found, offering the best compromise between grafting yield and residual monomer content. Because the oxazoline-monomer used in this study exhibits very low volatility, the residual monomer content cannot easily be controlled by devolatilization.

Rate of Grafting Reactions

The evolution of grafting yield of OXA along the screw length is shown in Figure 4. Yields of 85–90% at 14D and about 95% at 21D were obtained as percentages of the final grafting yield (at 42D). This implies that the grafting reaction is very fast, mainly due to the short half-life time of the peroxide, and very rapid formation of reactive radicals at the processing temperature. In other words, the residence time of the extruder was clearly longer than needed purely for grafting under the above conditions.

Compatibilized Blends of PP with PBT

The different reactive blends, their compositions, and mechanical properties are listed in Table II.

The viscosity ratio of the pure blend components ($\eta_{\text{PBT}}/\eta_{\text{PP}}$) under actual processing conditions was about 0.6 measured by capillary rheometer (Rosand RH7–2). The viscosity ratio of the compatibilized blends was higher because the compatibilizer PP-*g*-OXA (miscible with pure PP) decreased the viscosity of the matrix.

Impact and Tensile Properties

The impact strength of a blend is very sensitive to changes in interfacial adhesion. Thus, the Charpy impact strength was measured for both unnotched and notched specimens. Most of the compatibilized blends did not fail in the unnotched impact test; hence, the notched impact strength yielded more information on the behavior of the material. The notched impact strengths of the pure PBT and the uncompatibilized PP/PBT blends were about 4.8 and 3.5 kJ/m², respectively. The notched impact strength of pure PP could not be measured, because the samples were only partially broken.

In general, the impact strength was significantly improved in the blends containing the pre-made PP-*g*-OXA. In particular, the blends (B9–B16) prepared with screw geometry D (devolatilization after melting zone) containing different amounts of functionalized PP-*g*-OXA prepared with screw geometry B (long devolatilization), exhibited an approximate threefold increase in notched impact strength. In addition, up to an eightfold increase in the elongation at break was observed, indicating better interfacial adhesion. This was thought to be due to the better devolatilization and lower amount of residual OXA during the interfacial reaction stage. Thus, efficient devolatilization is one of the key factors in both the preparation of grafted PP and in the reactive blending, as shown previously also elsewhere.¹⁹

It is noteworthy that the higher grafting yield of the PP-*g*-OXA, the better the impact strength and elongation at break of the blend (see blends B5–B8). This observation is depicted in Figure 5. When the amount of PP-*g*-OXA in the blend was increased from 5 to 20 wt %, significant improvements were found in notched impact strength. In addition, the elongation at break was markedly increased (Fig. 6).

The blends (B5–B8) containing 70 wt % of PP-*g*-OXA (matrix composed of PP-*g*-OXA only) showed quite poor properties, mainly due to the

Table II Blend Compositions and Their Mechanical Properties

Code	PP (wt %)	PP-g-OXA (phr)	[OXA] _o (phr)	[OXA] _r (phr)	Screw	Charpy ^a Notched (kJ/m ²)	E (MPa)	σ (MPa)	ϵ_v (%)	ϵ_h (%)
PP	100	—	—	—	C	n.f. ^b	1290 ± 40	28 ± 1	20 ± 0.5	120 ± 20
PBT	—	—	—	—	C	4.8 ± 0.3	2590 ± 70	54 ± 1	6.5 ± 0.3	90 ± 30
REF	70	—	—	—	C	3.5 ± 1.0	1440 ± 40	29 ± 1	10.0 ± 0.2	25 ± 5
PP-g-OXA content: 10 wt %; [OXA] _o = 0.6–2.1 phr										
B1	60	10	0.6	0.5	C	4.7 ± 0.3	1580 ± 10	30 ± 1	12.4 ± 1.2	35 ± 10
B2	60	10	1.0	1.1	C	6.2 ± 1.0	1580 ± 20	31 ± 1	12.4 ± 0.5	70 ± 20
B3	60	10	1.1 ^c	1.2	C	7.7 ± 0.6	1560 ± 20	31 ± 1	12.8 ± 0.9	100 ± 30
B4	60	10	2.1	2.1	C	9.2 ± 0.8	1560 ± 40	31 ± 1	13.3 ± 0.7	100 ± 30
PP-g-OXA content: 70 wt %; [OXA] _o = 0.6–2.1 phr										
B5	—	70	0.6	0.5	C	3.5 ± 0.7	1410 ± 70	27 ± 1	8.3 ± 0.5	25 ± 5
B6	—	70	1.0	1.1	C	6.5 ± 0.7	1370 ± 20	27 ± 1	10.0 ± 0.3	90 ± 20
B7	—	70	1.1 ^c	1.2	C	4.9 ± 0.5	1400 ± 10	27 ± 1	10.7 ± 0.3	30 ± 10
B8	—	70	2.1	2.1	C	4.5 ± 0.5	1290 ± 30	27 ± 1	11.2 ± 1.7	30 ± 10
PP-g-OXA content: 5–20 wt %; [OXA] _o = 1.0 phr										
B9	65	5	1.0	1.1	D	8.7 ± 2.9 ^d	1530 ± 50	34 ± 1	11.9 ± 0.3	35 ± 10
B10	60	10	1.0	1.1	D	10.5 ± 2.8 ^d	1510 ± 50	33 ± 1	12.8 ± 0.5	100 ± 20
B11	55	15	1.0	1.1	D	9.4 ± 0.5 ^d	1540 ± 10	32 ± 1	12.8 ± 0.7	140 ± 30
B12	50	20	1.0	1.1	D	9.1 ± 0.9 ^d	1480 ± 70	32 ± 1	12.8 ± 0.5	190 ± 40 ^c
PP-g-OXA content: 5–20 wt %; [OXA] _o = 1.7 phr										
B13	65	5	1.7	2.0	D	8.5 ± 1.3 ^d	1480 ± 100	32 ± 1	13.5 ± 1.0	100 ± 20
B14	60	10	1.7	2.0	D	9.7 ± 0.5	1550 ± 30	32 ± 1	13.3 ± 0.2	150 ± 40
B15	55	15	1.7	2.0	D	10.7 ± 1.0	1490 ± 80	31 ± 1	13.5 ± 1.2	17 ± 40 ^e
B16	50	20	1.7	2.0	D	11.0 ± 0.9	1450 ± 100	31 ± 1	14.0 ± 0.5	210 ± 40 ^e

PBT content was 30 wt % in all blends. The rest (70 wt %) was composed of PP and/or modified PP as shown in the table. The molecular weights of the different PP-g-OXA grades were about similar evaluated in terms of the torque during grafting (torque = 23–25%).

^a Dimensions of the test specimen were 80 × 10 × 4 mm, notch type according to ISO 179/IA.

^b Partially broken → no value.

^c Contains also grafted styrene 0.4 phr.

^d Skin of the test bar on the opposite side of the notch did not fail in the test.

^e Some of the test specimens were not ruptured within the span of the tensile machine (→ $\epsilon_b > 260\%$); the value is based on ruptured specimens.

low molecular weight of the PP-g-OXA. In particular, the impact strength was found to suffer from the degradation of PP during grafting. Another reason for the poor properties of these blends might be the relatively high amount of free monomer (OXA) present in the blends. This free monomer could prevent the compatibilization reaction by reacting with the carboxylic end groups of PBT. Moreover, because the viscosity of the PP-g-OXA was significantly lower than that of pure PP, the

viscosity ratio (viscosity of PBT/viscosity of PP) in these blends was above unity, which was not optimal for the good dispersion of PBT.

The yield strength and modulus did not change significantly in the compatibilization. Nevertheless, a slight increase in yield strength and modulus was observed in blends containing less than 20 wt % of PP-g-OXA. Another observation from the tensile tests is that the elongation at yield of the compatibilized blends was markedly in-

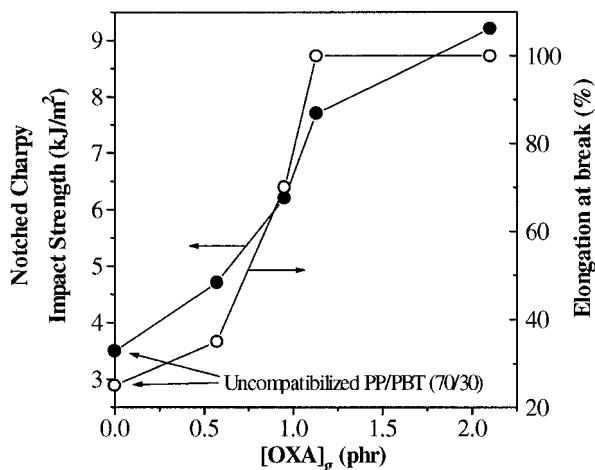


Figure 5 Effect of grafting yield of OXA on the notched impact strength and elongation at break. PP-*g*-OXA content was 10 wt % in all compatibilized blends.

creased in comparison with the uncompatibilized blend (from 10 up to 14%).

Morphology of the Blends

The morphology of the blends was characterized by SEM. The particle size of the dispersed phase (PBT) was reduced from 2–5 to 0.5–1 μm when PP-*g*-OXA was added. The phase boundaries also became less clear when a PP-*g*-OXA was added to the blend. This is typical of compatibilized blends with improved phase cohesion. The increased grafting yield of OXA in the compatibilizer promoted the reduction of phase size as seen in Figure 7.

When the amount of PP-*g*-OXA in the blend was increased the particle size did not change much. Instead, the phase boundaries became less clear, as seen in Figure 8.

Dynamic-Mechanical Analysis

The changes in compatibility of the blends containing different amounts of PP-*g*-OXA were studied by dynamic-mechanical thermal analysis (DMTA). The changes in the glass transition behavior of the blend components were followed by using the peaks of loss modulus (E'') vs. temperature curve. The peaks of the curve were treated as the glass transition temperatures (T_g) of the blend components. Earlier studies suggest that if specific interchain interactions exist, a clear shift in temperature and/or change in the intensity of the peaks of the E'' vs. T-curve may be noted.

In addition, a broadening of the transition region would be observed, especially for the minor phase.^{20–22}

The glass transition temperatures determined by DMTA for pure blend components and blends containing different amounts of PP-*g*-OXA are reported in Table III. The first observation from Table III is that the glass transition temperatures of the blend components in the uncompatibilized blend (REF), and those of the pure PP and PBT are practically equal. Secondly, the T_g of the functionalized PP was 6°C lower than that of the pure PP. The third observation is that when the amount of PP-*g*-OXA in the blend was increased, the T_g of the PBT phase decreased and, at the same time, the T_g of PP or PP/PP-*g*-OXA phase remained practically unchanged. For example, the PP/PBT blend containing 20 wt % of PP-*g*-OXA exhibited a T_g of 42.2°C for the PBT phase, while in the uncompatibilized blend the T_g of the PBT phase was 48.5°C. Also in the blends of pure PP and PP-*g*-OXA the T_g remained practically unchanged in comparison to pure PP. The diminution of the peak intensity related to the glass transition of PBT as the amount of PP-*g*-OXA in the blend was increased is seen in Figure 9. It is seen that the glass transition peak of PBT vanished when the matrix of the blend was composed exclusively of PP-*g*-OXA. For this particular blend, PP-*g*-OXA/PBT (70/30), a clear shift of the peak related to the transition of PP-*g*-OXA was observed (T_g of pure PP-*g*-OXA -8.9°C and T_g of PP-*g*-OXA in blend -2.5°C).

In conclusion, we found a shift in the T_g of the

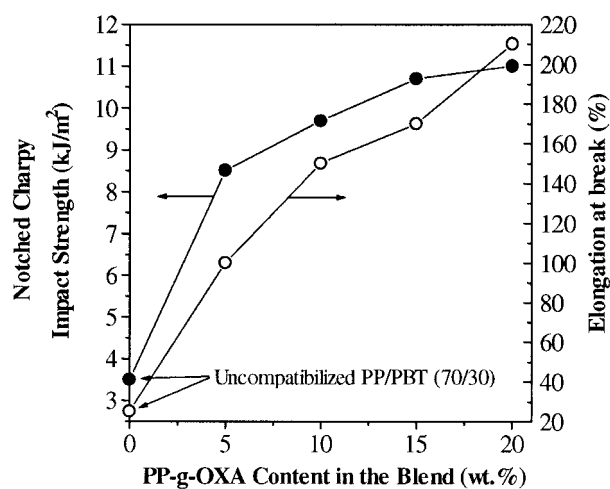
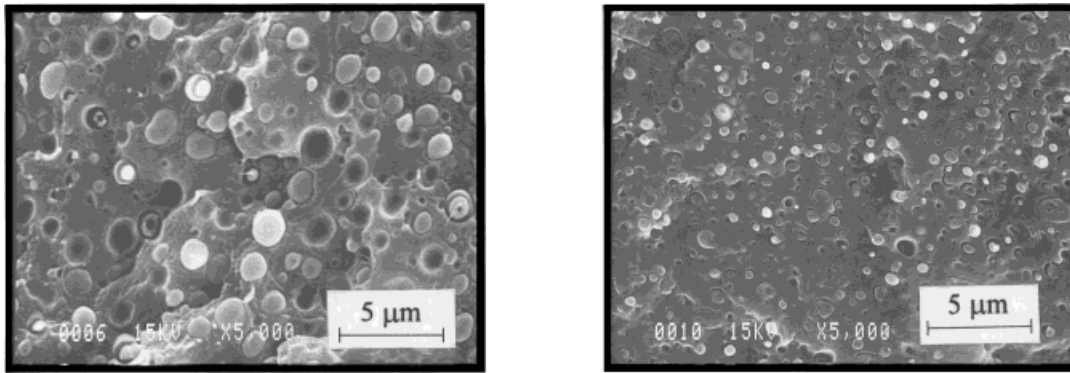


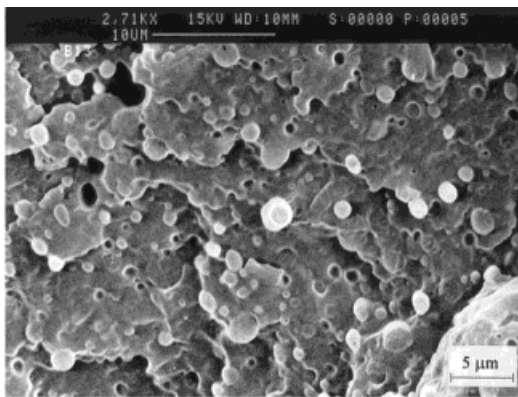
Figure 6 Effect of PP-*g*-OXA content on the notched impact strength and elongation at break. Grafting yield of OXA was 1.7 phr.



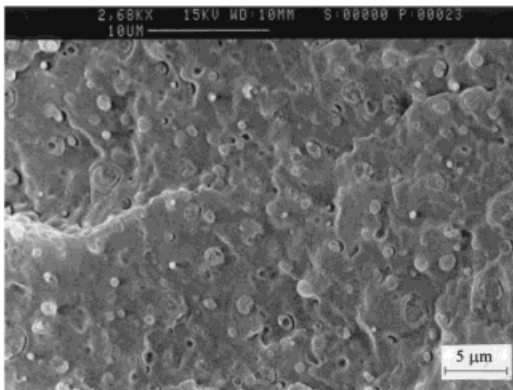
(a)

(b)

Figure 7 Effect of grafting yield of OXA on the morphology of PP/PP-*g*-OXA/PBT (60/10/30) blends. In (a) the grafting yield $[OXA]_g = 0.6$ phr and in (b) $[OXA]_g = 2.1$ phr.



(a)



(b)

Figure 8 SEM micrographs of (a) PP/PP-*g*-OXA/PBT (65/5/30) and (b) PP/PP-*g*-OXA/PBT (50/20/30) blends. The grafting yield was $[OXA]_g = 1.0$ phr.

PBT phase and a diminution of the intensity of the peak of the E'' vs. T -curve related to the PBT phase, when a compatibilizer was added to the system. Thus, these observations can be treated as evidence of improved interactions between the phases. However, it should be kept in mind that the improved interactions suggested by, for example, thermomechanical analysis are not always reflected in improved mechanical properties if other factors, such as molecular weight, are more dominant than the increased interactions between the phases. Hence, for example, the mechanical properties of different PP-*g*-OXA/PBT (70/30) blends were not as good as suggested by the DMTA analysis, because the molecular weight of the matrix in blends was too low.

DSC Analysis

The DSC analysis was carried out by first heating the sample to 250°C and then cooling it down to 50°C. Moreover, to verify the changes in crystallinity the sample was reheated from 50 to 250°C. These experiments showed that the position of the crystallization peak of the PBT phase shifted to lower temperatures when the PP-*g*-OXA was added to the blend. The crystallization peak of PBT in the uncompatibilized PP/PBT blend was at 197°C, while in the compatibilized blend containing 20 wt % of PP-*g*-OXA it was at 189°C. The crystallization region of PBT also became broader and its intensity decreased dramatically in the compatibilized blends. The PBT was, however, slowly crystallized in the compatibilized

Table III Glass Transition Temperatures (T_g) of Different Blends and Their Components Determined by Dynamic-Mechanical Analysis with Dual Cantilever Geometry as the Maxima of Loss Modulus (E'') vs. Temperature Curve

Sample	Glass Transition Temperature (°C)	
	PP or PP- <i>g</i> -OXA Phase	PBT Phase
PP	-2.9	—
PBT	—	+48.6
Grafted PP		
PP- <i>g</i> -OXA (G13)	-8.9	—
PP/PP- <i>g</i> -OXA (93/7) ^a	-2.7	—
PP/PP- <i>g</i> -OXA (71/29) ^b	-2.6	—
PP/PBT Blends		
REF: PP70/PBT30	-2.7	+48.5
REF; PP70/PBT30	-2.7	+48.5
B13; PP/PP- <i>g</i> -OXA/PBT (65/5/30)	-2.6	+45.3
B16; PP/PP- <i>g</i> -OXA/PBT (50/20/30)	-2.6	+42.2
B8; PP- <i>g</i> -OXA/PBT (70/30)	-2.5	peak not observed

^a Blend of PP and PP-*g*-OXA corresponding the composition of matrix in blend B17.

^b Blend of PP and PP-*g*-OXA corresponding the composition of matrix in blend B20.

blends during the cooling stage, as shown by a clear melting peak of PBT obtained in the subsequent reheating. In compatibilized blends, a shift to lower temperatures of the crystallization peak of the PP phase was also observed. The main re-

sults of the DSC analysis are shown in Table IV and Figure 10.

These DSC results led us to conclude that the increased interactions between the phases modi-

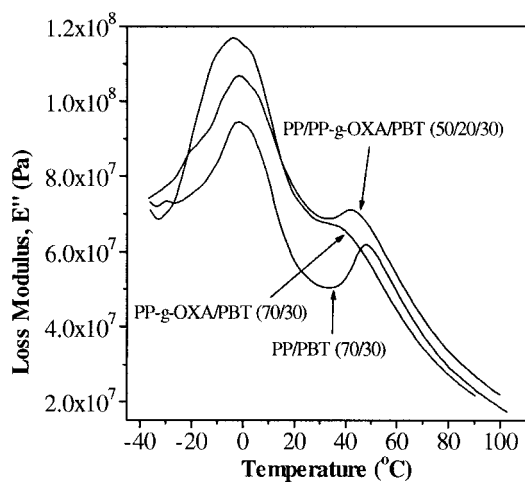


Figure 9 The loss modulus (E'') vs. temperature curves of PP/PBT blends containing different amounts of PP-*g*-OXA.

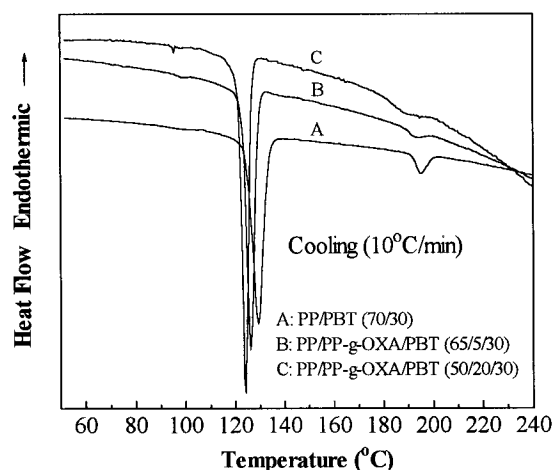


Figure 10 DSC thermograms of uncompatibilized and compatibilized blends obtained in cooling from 250 to 50°C (10°C/min). Before the cooling samples were heated from 50 to 250°C (10°C/min).

Table IV The Melting and Crystallization Temperatures of Different Blends after Melt Blending

Sample	$T_m/T_c/T_m$ (°C)	
	Matrix	PBT Phase
REF; PP70/PBT30	167/129/166	226/196/225
B13; PP/PP- <i>g</i> -OXA/PBT (65/5/30)	164/126/163	222/193/223
B16; PP/PP- <i>g</i> -OXA/PBT (50/20/30)	166/124/161	223/189/223

The heating and cooling rates were 10°C/min.

fied the crystallization behavior of the blend components. In particular, the crystallization of the dispersed PBT phase was greatly affected by the addition of oxazoline-modified PP.

CONCLUSIONS

The following main conclusions could be drawn on the basis of this study:

1. Polypropylene was successfully functionalized by ricinloxazoline maleinate in a corotating twin-screw extruder using melt free radical grafting. Grafting yields up to 2.1 phr were achieved.
2. This functionalized PP used as a compatibilizer markedly improved the mechanical properties of the uncompatibilized PP/PBT (PBT content 30 wt %) blend. Significant improvements were observed especially in impact strength (notched Charpy) and elongation at break of the compatibilized blends. The increased interactions between the phases were characterized by SEM analysis, DMTA, and DSC experiments.
3. The properties of the blend greatly depend on the degradation of the PP during grafting. An optimal content of compatibilizer exists, which is dependent on the degradation of PP, grafting yield of oxazoline monomer, and on the amount of free, ungrafted monomer present in the compatibilizer. These factors can be adjusted by properly choosing the processing conditions and chemical parameters.

SYMBOLS

[x]	concentration of x (phr)
E''	loss modulus (Pa)
I	intensity (-)
\bar{M}_n	number average molecular weight (g/mol)
\bar{M}_w	weight average molecular weight (g/mol)
phr	g/100 g of PP
T_c	crystallization temperature (°C)
T_g	glass transition temperature (°C)
T_m	melting temperature (°C)
DMTA	dynamic-mechanical thermal analysis
DSC	differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
GMA	glycidyl methacrylate
MAH	maleic anhydride
NBR	nitrile butadiene rubber
OXA	ricinloxazoline maleinate
PBT	poly(butylene terephthalate)
PE	polyethylene
PP	polypropylene
PP- <i>g</i> -OXA	PP grafted with OXA
PP- <i>g</i> -St	PP grafted with styrene
PS	polystyrene
SEM	scanning electron microscope
St	styrene

subscripts

g	grafted
i	initial, at feed
r	residual, ungrafted

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