# Compatibilization of Polypropylene/Poly(*n*-butylacrylate) Blend: Functionalization of the Poly(*n*-butylacrylate) Phase by Copolymerization

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#### **SYNOPSIS**

Compatibilization of a polypropylene (PP)/polybutylacrylate (PBuA) blend was studied, with the aim of achieving better adhesion at the interphase through modification of both the PP and PBuA phases. The compatibilization involved two separate stages: First, a small amount (2 and 5 mol %) of functional monomer copolymerizable with and soluble in BuA was added to the BuA initiator solution. Then, this solution was impregnated into PP pellets and polymerized inside the pellets by free-radical polymerization in a water suspension. The resulting blend was a thermoplastic elastomer consisting of PP as the matrix and functionalized PBuA as the partly crosslinked dispersed rubbery phase. The functionalities of the monomers were epoxy, oxazoline, hydroxyl, secondary amine, and carboxyl. In the second stage, two commercial graft copolymers of PP (PP grafted with either acrylic acid or maleic acid anhydride) were blended at the melt stage with the PP/ functionalized PBuA blend. Here, the compatibilizing reactions took place between the functionalized components of the blend. The compatilization reactions were detected by FTIR analysis and by changes in mechanical or thermomechanical behavior of the blends. Morphology studies were carried out. As a result, the tensile strength, tensile modulus, elongation at break, and tear strength of the final product were improved by about 15, 20, 160, and 50%, respectively, compared with the unfunctionalized blend. The hardness of the material remained unchanged in the compatibilization. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The thermoplastic elastomer used in this study exhibits a two-phase structure with polypropylene (PP) as the matrix and partially crosslinked polybutylacrylate (PBuA) as the dispersed phase. The interfacial adhesion between the two polymers is poor due to the lack of interfacial interactions and a relatively large difference in polarities (= the ratio of polar component of surface tension to total surface tension,  $x^p$ ). Pure PP is practically nonpolar ( $x^p \approx 0$ ) and has no functionality in the polymer chain, whereas PBuA is slightly polar ( $x^p = 0.127$ ) and not capable of forming strong interactions with PP. As a result, the mechanical properties of the blend are not advantageous.

The two-phase structure (PP/PBuA) itself is prepared by a special solid-state polymerization method described elsewhere.<sup>1-3</sup> In this particular case, the solid-state method involves the impregnation of the solution of liquid monomer(s), initiator (peroxide), and crosslinking agent into the solid PP pellets at elevated temperature yet clearly below the melting point of PP and radical formation temperature of the peroxide. The impregnation takes place in a closed reactor under a nitrogen atmosphere. After the impregnation is complete, hot water is added to the reactor to create a suspension of water and impregnated pellets. When the temperature of the suspension is increased, the impregnated monomer starts to polymerize by a radical polymerization mechanism initiated by the peroxide. As a result, after polymerization, the impregnated monomer forms a finely dispersed, partially crosslinked rubbery phase inside the solid PP pellets. The PP ma-

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**Figure 1** Schematic presentation of the compatibilization in PP/PBuA blend. X and Y are functional groups (see Table I and Fig. 2). *R'*, *R''*, and *R'''* are parts of the functional monomer (I-V). The compatibilization between PP and functional PBuA takes place through addition of functionalized PP which is miscible with the PP phase and also reacts with the functionalized PBuA.

trix and the dispersed PBuA are, respectively, responsible for the thermoplastic and rubbery properties of the material.

The literature gives numerous examples of compatibilization reactions in various blend systems. Examples of important reactions are (a) carboxyl + epoxy,<sup>4</sup> (b) carboxyl + oxazoline,<sup>5</sup> (c) anhydride + amine,<sup>6-10</sup> and (d) ionomeric (based on  $Zn^{2+}$  ions)<sup>11</sup> bonding. The functionalization of the PBuA phase was investigated in many earlier studies as well.<sup>12-16</sup>

Our aim was to achieve better adhesion at the interphase through modification of both the PP and PBuA phases. Small amounts of different functional comonomers (FM) copolymerizable with BuA were added to the monomer solution to functionalize the rubber phase. The commercially known graft copolymers of PP and maleic acid anhydride (MAH) or acrylic acid (AA) were used to functionalize the PP phase.

In this article, we report on the compatibilization of the PP/PBuA blend by copolymerization of the dispersed PBuA phase and functionalization of the PP phase (matrix). The object of our study was to find suitable functional monomers for copolymerization with BuA to increase the chemical reactivity of the rubbery PBuA phase toward the functionalized thermoplastic PP phase. The possible compatilization reactions were followed by FTIR analysis and by changes in mechanical and thermomechanical behavior. A schematic presentation of the compatibilization is shown in Figure 1. The compatibilization between PP and PBuA takes place through addition of functionalized PP which is miscible with PP phase and also reacts with functionalized PBuA. The possible compatibilization reactions between functionalized PP and PBuA are presented in Table I. All these reactions were investigated in the experimental work.

## **EXPERIMENTAL**

#### Materials

The matrix polymer was a nucleated random copolymer of propylene containing 2.5 wt % of ethylene, later referred to as PP (PP XC20 76DNA

Table ICompatibilization Reactions BetweenFunctionalized PP and PBuA; Reaction NumbersRefer to the Numbers in Table II

		F	unction	al Groups		
R	eaction No.	(in	X) PP)	(in PBuA)	R Cher	esulting nical Bond
(1)	R <sub>1</sub> -C=O OH	+	CH2-CH-R	2>	R <sub>1</sub> -C=O O-CH <sub>2</sub> -	сн-к <sub>2</sub> он
(2)	R <sub>1</sub> -C=O OH	+	$\sum_{0}^{N} R_{2}$	>	R <sub>1</sub> -C=O O-CH <sub>2</sub> -	O CH <sub>2</sub> -NH-C-R <sub>2</sub>
(3)	R <sub>1</sub> -C=O OH	+	HO-R <sub>1</sub>	>	O=C-R <sub>2</sub> R <sub>1</sub> -O	+ Н <sub>2</sub> О
(4)	R <sub>1</sub> -C=O OH	+	NH R3	>	R <sub>1</sub> -C=O N-R <sub>2</sub> R <sub>3</sub>	+ Н <sub>2</sub> О
(5)	R <sub>1</sub> -C=O I + Zn OH	<sup>2+</sup> (CH <sub>3</sub> COC	$D_{12}^{O=C-R_2}$	$r_{1} \rightarrow r_{1}$	) -O <sup>-</sup> Zn <sup>2+</sup> <sup>-</sup> O	$C_{-R_2} + C_{+3}COOH$

from Borealis Polymers Oy), having a melt flow rate of 20 g/10 min (230°C, 21.6N). The *n*-butylacrylate monomer (BuA) was stabilized with 10–55 ppm hydroquinone monomethyl ether and was supplied by Aldrich Chemie. 1,6-Hexane diol diacrylate (HDDA) was used as the crosslinking agent (Röhm). The functional comonomers (I-V) and their structure, functionality, and suppliers are listed in Table II.

The initiator in all polymerizations was 2,5bis(*tert*-butylperoxy)-2,5-dimethyl-3-hexyne (Trigonox 145 E 85 from Akzo Chemicals). The half-life of the peroxide is 10 h at 120°C. Sodium dodecyl benzene sulfonate and tricalcium phosphate were used as suspension agents.

Two functionalized PPs (f-PP) were used to impart reactivity to the PP phase. The first was PP grafted with acrylic acid (AA), PP-g-AA (Polybond 1002 from Uniroyal Chemicals, total AA content 6.04 wt %), and the second was PP grafted with maleic acid anhydride (MAH), PP-g-MAH (Exxelor PO 1015 from Exxon, grafted MAH content 0.4 wt %).

## Compatibilization

The experimental steps of the compatibilization procedure are depicted in Figure 2.

## Preparation of PP/Functionalized PBuA Blend by Impregnation and Free Radical Copolymerization

The PP pellets, BuA monomer, functional comonomer (FM, in Table II), crosslinking agent, and initiator were mixed and fed to the reactor. Two concentrations of the FM were added: 2 and 5 mol %of the BuA amount. The amounts of initiator and crosslinking agent were 0.2 and 0.1 wt %, respectively, of the monomers. The low viscous monomer solution was impregnated inside the PP pellets at elevated temperature  $(115-124^{\circ}C)$  in the reactor. Before impregnation, the reactor was purged with nitrogen. The free-radical copolymerization of the monomers in the PP pellets was initiated in a nitrogen-purged suspension water phase by increasing the reactor temperature gradually  $(125-132^{\circ}C)$ . The concentration of the initiator decreased from 0.007 to 0.003 mol/L during the copolymerization, so there was residual peroxide in the expanded pellets. The duration of the polymerization was 5.5 h in all experiments. The copolymerizations are listed in Table III.

## Blending of PP/P(BuA+FM) with Functionalized PP

The PP/P(BuA+FM) blends prepared by copolymerization were mixed with 5 wt % of f-PP in a counterrotating twin-screw extruder (Brabender DSK 42/7D) at a melt temperature of  $180^{\circ}C$ , with a screw speed of 50 rpm and a residence time of 120 s. The rubber content [P(BuA+FM)] was equalized in each blend at 42.4 wt % by adding PP together with the functionalized polypropylene (f-PP). Before blending, the components were dried at 70°C for 6 h. The compatibilization reactions (Table I) between the functionalized phases were assumed to take place during this melt-blending stage. The residual peroxide (0.003 mol/L in the rubber phase) was totally decomposed during the blending stage. This was assumed to result in further crosslinking of the rubber phase (initiator was vinyl specific). The blend compositions are presented in Table IV. The blends REF2 and REF3 were prepared as reference samples for the blends containing the functionalized rubber phase.

Table II The Functional Monomers Used to Functionalize PBuA

	Functional Monomer	Chemical Structure	Functionality (Reaction No.)
(I)	Glycidylmethacrylate (GMA) Supplied by Aldrich Chemie	CH <sub>3</sub> =C CH <sub>2</sub> =C O=C+O-CH <sub>2</sub> -CH-CH <sub>2</sub>	Epoxy (1)
(II)	Ricinoloxazoline methylmaleinate (ROMM) Supplied by Henkel KGaA	$\overset{\mathrm{CH}_3 \cdot \mathrm{O}}{\underset{C_6 H_{13}}{\overset{O}{\longrightarrow}}} \overset{O}{\underset{C_6 H_{13}}{\overset{O}{\longrightarrow}}} \overset{O}{\underset{C_6 H_{13}}{\overset{O}{\longrightarrow}}} \overset{O}{\underset{O}{\overset{O}{\longrightarrow}}} \overset{O}{\underset{O}{\longrightarrow}} \overset{O}{\underset{O}{\rightthreetimes}} \overset{O}{\underset{O}{\rightthreetimes}} \overset{O}{\underset{O}{\longrightarrow}} \overset{O}{\underset{O}{\rightthreetimes}} \overset{O}{\underset{O}{\rightthreetimes}} \overset{O}{\underset{O}{\rightthreetimes}} \overset{O}{\underset{O}{\rightthreetimes}} \overset{O}{\underset{O}{\rightthreetimes}} \overset{O}{\underset{O}{{\to}}} \overset{O}{\underset{O}{{\to}}} \overset{O}{\underset{O}{{\to}}} \overset{O}{\underset{O}{{\to}}} \overset{O}{\underset{O}{{\to}}} \overset{O}{{\bullet}} \overset{O}{{\to}}} \overset{O}{{{\bullet}}} \overset{O}{{\to}}} \overset{O}{{{\bullet}}} \overset{O}{{{\bullet}}} \overset{O}{{{\bullet}}} \overset{O}{{{\bullet}}} \overset{O}{{{\bullet}}} \overset{O}{{{\bullet}}}} \overset{O}{{{\bullet}}} \overset{O}{{{\bullet}}} $	Oxazoline (2)
(III)	Polypropyleneglycol monomethacrylate (PPGMM) Supplied by International Specialty Chemicals	сн <sub>2</sub> = с с <del>с с с досн</del> 2 сн3 о	Hydroxyl (3)
(IV)	2- <i>tert</i> -Butylaminoethyl methacrylate (TBAEMA) Supplied by Aldrich Chemie	0 CH2=C-C-O-CH2-CH2-NH-C(CH3)3 CH3	Secondary amine (4)
(V)	Monomethacryloyloxy ethyl phthalate (MMP) Supplied by International Specialty Chemicals	$\underset{c_{H_2=C_{L_2}CH_2}}{\overset{C_{H_3}}{\underset{0}{\leftarrow}}} \underset{c_{H_2=C_{L_2}CH_2}}{\overset{C_{H_2}}{\underset{0}{\leftarrow}}} \underset{c_{H_2}}{\overset{C_{H_3}}{\underset{0}{\leftarrow}}} \underset{c_{H_2}}{\overset{C_{H_3}}{\underset{0}{\leftarrow}}} \underset{c_{H_2}}{\overset{C_{H_3}}{\underset{0}{\leftarrow}}} \underset{c_{H_2}}{\overset{C_{H_3}}{\underset{0}{\leftarrow}}} \underset{c_{H_2}}{\overset{C_{H_3}}{\underset{0}{\leftarrow}}} \underset{c_{H_2}}{\overset{C_{H_3}}{\underset{0}{\leftarrow}}} \underset{c_{H_2}}{\overset{C_{H_3}}{\underset{0}{\leftarrow}}} \underset{c_{H_2}}{\overset{C_{H_3}}{\underset{0}{\leftarrow}}} \underset{c_{H_2}}{\overset{C_{H_3}}{\underset{0}{\leftarrow}}} \underset{c_{H_3}}{\overset{C_{H_3}}{\underset{0}{\leftarrow}}} $	Carboxyl (5)



Figure 2 Experimental steps in the compatibilization and testing.

Table III Copolymerization of the Functional Monomers (FM) with BUA in PP	P Pellets <sup>*</sup>	n PP	3uA in	with B	(FM)	Monomers	Inctional	$\mathbf{F}$	of the	rization	Copolymer	ble III
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Run	Functional Monomer	Relative Amounts of FM in BuA (Mol %/wt %)	Total Conversion of Monomers (Wt %)	P(BuA+FM) Content in PP/P(BuA+FM) Blend (Wt %)	Gel Content <sup>b</sup> (Wt %)
REF	c	c	95.4	46.1 (pure BuA)	51
I2	GMA	2/2.2	95.3	46.2	48
I5	GMA	5/5.6	95.0	46.0	50
II2	ROMM	2/6.5	90.0	44.7	50
115	ROMM	5/14.8	d	d	d
III2	PPGMM	2/6.4	95.8	46.2	44
1115	PPGMM	5/14.7	90.2	44.8	43
IV2	TBAEMA	2/2.8	94.4	45.9	42
IV5	TBAEMA	5/6.8	92.2	45.3	36
V2	MMP	2/4.2	96.0	46.3	51
V5	MMP	5/9.9	91.6	45.1	53

\* The amounts of initiator and crosslinking agent (HDDA) were 0.2 and 0.1 wt % of the monomers, respectively.

<sup>b</sup> Determined as the portion of inextractable material in boiling xylene divided by the total weight of the original sample. The accuracy in all gel content determinations was  $\pm 5\%$  units.

<sup>c</sup> Only BuA without FM was used as a monomer.

<sup>d</sup> The polymerization was not successful due to high agglomeration rate.

Blend	Composition <sup>b</sup> (in Wt %)	Reaction (No.)
REF1	<b>REF</b> (100)	None
REF2	REF(95) + PP-g-MAH(5)	None
REF3	$\operatorname{REF}(95) + \operatorname{PP}-g-\operatorname{AA}(5)$	None
CI2	I2(95) + PP-g-AA(5)	Carboxyl + epoxy(1)
CI5	I5(95) + PP-g-AA(5)	Carboxyl + epoxy(1)
CII2	II2(95) + PP-g-AA(5)	Carboxyl + oxazoline (2)
CIII2	III2(95) + PP-g-AA(5)	Carboxyl + hydroxyl (3)
CIII5	III5(95) + PP-g-AA(5)	Carboxyl + hydroxyl (3)
CIV2	IV2(95) + PP-g-MAH(5)	Anhydride $+$ secondary amine (4)
CIV5	IV5(95) + PP-g-MAH(5)	Anhydride + secondary amine (4)
CV2	V2(94.3) + ZnAc(0.7) + PP-g-AA(5)	Ionomeric bonding (5)
CV5	V5(94.3) + ZnAc(0.7) + PP-g-AA(5)	Ionomeric bonding (5)

Table IV Blending of PP/P(BuA+FM) with f-PP in a Counterrotating Extruder<sup>a</sup>

<sup>a</sup> Melt temperature 180°C, screw speed 50 rpm, output 1.5 kg/h, mean residence time 120 s. ZnAc = zinc acetate.

<sup>b</sup> The rubber content [P(BuA + FM)] in the blends was equalized at 42.4 wt % by adding PP together with the functionalized polypropylene f-PP.

# **Preparation of Test Samples**

The compatibilized blends in Table IV were injection-molded with an Engel ES 200/40 injectionmolding machine at a melt temperature of  $180^{\circ}$ C using a mold temperature of  $30^{\circ}$ C. The dimensions of the molded test plate were  $80 \times 80 \times 2$  mm. Before the injection molding, the blends were dried 16 h at 70°C. The tensile and tear test bars were cut from the injection-molded plates.

## Characterization

## Tensile and Tear Tests

Tensile and tear properties were measured with an Instron 4204 testing machine. Tensile tests were made on the test bars at a test speed of 500 mm/ min according to ISO 37 (Type 2). The tear strength was determined according to ISO 34 (trouser test). Before testing, the samples were conditioned for 16 h at 23°C (50% RH).

#### Thermomechanical Analysis

The thermomechanical properties of the blends were characterized with Perkin-Elmer DMTA equipment. The measurements were carried out by using the three-point bending method. The frequency was 1 Hz, the rate of heating  $5^{\circ}$ C/min, and the scanned temperature range -80 to  $+150^{\circ}$ C.

# Gel Content

The degree of crosslinking (i.e., gel content) of the polymerized blend was measured by extracting the soluble PP phase in boiling xylene (135°C) for 20 h. The gel content was determined as the portion of the inextractable material divided by the total weight of the original sample. Two parallel extractions were done for each sample.

#### FTIR Analysis

The possible compatibilization reactions were investigated by FTIR (Nicolet 5DXC). Before measurement, the pellets were compression-molded to thin films ( $\approx 20 \,\mu$ m) at 180°C. Special attention in the IR analysis was paid to changes in the original absorbance peaks (new chemical bonds).

#### Transmission Electron Microscope Studies

The morphology of the blends was investigated by a transmission electron microscope (JEOL JEM-1200 EX-2). Photos were taken of the samples both after polymerization and after the subsequent blending stage to verify the changes in the rubber particle size. The sample (film) preparation was sometimes very difficult due to the elastomeric behavior of the blends. Samples cut with a microtome (Reichert Ultracut E) at -50 to  $-67^{\circ}$ C were stained with ruthenium hypochloride or osmium tetroxide vapor. The PBuA phase turned dark in the staining process, while the PP phase remained unchanged.

# **RESULTS AND DISCUSSION**

#### **Impregnations and Polymerizations**

Depending on the amount and type of FM used, the impregnation temperature was varied between 115 and 124 °C. During the impregnation, the pellet size changed from approximately 2.5 to 4.5 mm. The polymerizations were successful with all the comonomers used in the study. The yield of monomers to the pellets varied from 90 to 96 wt %, which means that, in the worst case (II2), only 10 wt % of the monomers was polymerized elsewhere than inside the pellets. Usually, the unimpregnated monomers were polymerized to the metal parts of the reactor (walls, agitator, etc.). After the polymerization, the pellet-water suspension was stable and the pellets were loose.

## **Mechanical Properties**

The mechanical properties of the compatibilized blends are presented in Table V in both flow and transverse directions (MD/TD). The hardness of the blends remained practically unchanged in the compatibilization reactions. Thus, the changes in the mechanical properties can be attributed to changes in the rubber phase or in the interfacial adhesion between the rubber phase and PP.

The tensile strength was improved in all compatibilized blends by 10-15% compared to the un-

Table	V	Mecha	nical	Pro	perties	of	the	Blend	$\mathbf{s}^{a}$
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compatibilized reference samples (REF1, REF2, REF3). The elongations at break were usually increased by about 20-25% and 100-150% in flow and transverse directions, respectively. Improved tear strength is thought to reflect improved adhesion between the rubber and matrix. The best improvements in tear strength (up to 50%) were achieved with CI and CIV2 blends. These simultaneous improvements in tensile and tear strength and in elongations at break are indirect indications of better adhesion between the blend components or improvement of rubber properties, since the PP matrix itself has remained unchanged. The changes in MD and TD elongations of samples REF3 and REF2 compared to sample REF1 maybe due to the added PP-g-AA and PP-g-MAH in REF3 and REF2, respectively. Added compatibilizer might cause changes in their morphologies, and, on the other hand, elongations (MD and TD) are very sensitive to changes in morphology.

## Gel Content

The gel content was measured after the polymerization stage, before compatibilization (Table III). The gel content of the polymerized PP/P(BuA+FM) was quite close to the total rubber content of the product, which indicates that almost total crosslinking of the rubber phase was achieved during the polymerization. Evidently, TBAEMA interferes to some extent with the crosslinking, since the gel con-

Blend	Tensile Strength MD/TD (MPa)	Elongation at Break MD/TD (%)	Tear Strength MD (kN/m)	Tensile Modulus MD/TD (MPa)	Hardness <sup>b</sup> (°/Shore D)
REF1	$10.7 \pm 0.5/8.9 \pm 0.1$	$170 \pm 80/90 \pm 20$	$35 \pm 3$	$250 \pm 20/220 \pm 10$	38
REF2	$11.1 \pm 0.2/9.1 \pm 0.2$	$90 \pm 20/120 \pm 30$	$34 \pm 3$	$290 \pm 20/250 \pm 10$	39
REF3	$11.3 \pm 0.1/9.1 \pm 0.1$	$80 \pm 30/160 \pm 40$	$29 \pm 4$	$290 \pm 20/230 \pm 10$	40
CI2	$12.3 \pm 0.4/10.4 \pm 0.1$	$80 \pm 20/70 \pm 10$	$52 \pm 10$	$300 \pm 10/330 \pm 30$	40
CI5	$12.2 \pm 0.5/10.5 \pm 0.1$	$200 \pm 80/100 \pm 20$	$47 \pm 10$	$330 \pm 30/300 \pm 30$	40
CII2	$12.6 \pm 0.1/10.8 \pm 0.1$	$120 \pm 90/250 \pm 20$	$38 \pm 1$	$360 \pm 40/340 \pm 0$	42
CIII2	$11.3 \pm 0.3/9.6 \pm 0.4$	$200 \pm 90/170 \pm 30$	$38 \pm 6$	$290 \pm 20/260 \pm 10$	39
CIII5	$11.9 \pm 0.4/9.9 \pm 0.1$	$200 \pm 110/110 \pm 40$	$36 \pm 1$	$320 \pm 30/300 \pm 10$	40
CIV2	$12.1 \pm 0.4/10.0 \pm 0.3$	$180 \pm 110/230 \pm 20$	$52 \pm 9$	$340 \pm 10/280 \pm 20$	40
CIV5	$11.8 \pm 0.1/10.1 \pm 0.2$	$210 \pm 70/230 \pm 20$	$40 \pm 3$	$330 \pm 20/290 \pm 20$	40
CV2	$11.8 \pm 0.4/10.3 \pm 0.4$	$140 \pm 90/220 \pm 40$	$36 \pm 2$	$300 \pm 30/280 \pm 30$	41
CV5	$12.2 \pm 1.1/10.3 \pm 0.3$	$160 \pm 70/180 \pm 30$	$32 \pm 3$	$250 \pm 20/230 \pm 10$	40

\* The polyacrylate (= rubber) content in each blend was 42.4 wt %.

<sup>b</sup> Hardness was measured according to ISO 48; standard deviation in all measurements was  $\pm 2^{\circ}$ .

tent was clearly lower in the polymerization made with TBAEMA at higher concentration (IV5).

#### **Thermomechanical Properties**

The glass transition temperatures  $(T_g)$  of the blend components determined by DMTA are shown in Table VI. The  $T_g$  values of the blend components were determined as the maximum of the tan  $\delta$  vs. temperature curve.

We assumed in this study that better compatibility is achieved if the glass transition temperatures of two separate phases move closer to each other.<sup>17</sup> All the blends gave two separate  $T_g$  values, which means that they exhibit two separate phases. The first observation from the results is that the  $T_e$  values of REF2 and REF3 are almost the same as those of the uncompatibilized REF1, which shows that no compatibilization is achieved by adding functional groups only to the PP phase. The second observation is that copolymerization of BuA with ROMM or PPGMM (blends CII and CIII) decreased the  $T_e$ value of the rubber phase while the use of other functional monomers tended to increase the  $T_g$  value of the rubber phase. The higher the amount of the functional comonomer used in the copolymerization, the bigger the change in the  $T_g$  values of the rubber phase observed. The  $T_g$  values of the PP phase in the compatibilized blends were generally unchanged compared to the uncompatibilized blend. The third observation from the thermomechanical analysis is that a slight shift of  $T_{\epsilon}$  values of the phases closer to each other was found in CI, CIV, and CV blends, which might be an indication of increased interactions between the phases.

## **FTIR Results**

Infrared absorptions were determined for the PP+PP-g-AA/P(BuA+PPGMM) [Fig. 3(c)] blend, with primary attention paid to changes in the acrylic acid carbonyl (C=0) absorption peak at  $1720 \text{ cm}^{-1}$ . To verify the possible reactions between the matrix and rubbery phases, two reference samples were prepared: PP-g-AA [Fig. 3(a)] and PP/P(BuA+PPGMM) [Fig. 3(b)]. The ester carbonyl peaks (at 1740 cm<sup>-1</sup>) of PP+PP-g-AA/ P(BuA+PPGMM) and PP/P(BuA+PPGMM) blends were equalized to the same value. To discover whether there was a reaction between the carboxyl group (in AA) and the hydroxyl group (in PPGMM) of the PP+PP-g-AA/P(BuA+PPGMM) blend, the IR curve of the PP/P(BuA+PPGMM) blend was subtracted from the curve of the PP+PP-g-AA/

Table VI	Glass Transition Temperatures
of the Blei	nd Components Measured by DMTA
(1 Hz, 5°C	/min, Flexing Mode)

Blend	P(BuA+FM) $T_g/(^{\circ}C)$	$\frac{\rm PP}{T_g/(^{\circ}\rm C)}$	Difference in $T_g$ (°C)
Pure PP		-0.5	
REF1	-46.5	-2.0	43.3
REF2	-45.4	-3.3	42.1
REF3	-45.8	-2.4	43.4
CI2	-43.5	-2.7	40.8
CI5	-41.6	-2.0	39.6
CII2	-48.3	-2.9	45.4
CIII2	-47.9	-2.3	45.6
CIII5	-48.4	-2.7	45.7
CIV2	-44.0	-1.9	42.1
CIV5	-41.7	-1.2	40.5
CV2	-44.8	-4.9	39.9
CV5	-42.3	-2.5	39.8

P(BuA+PPGMM) blend. It was assumed that if the reactions had not occurred between the carboxyl and hydroxyl group in the PP+PP-g-AA/ P(BuA+PPGMM) blend, the residual curve should correspond to the curve of the sample PP-g-AA.

In Figure 3(d) can be seen powerful absorptions of aliphatic C—H bonds but no AA carbonyl absorption peak at 1720 cm<sup>-1</sup>, and that can be taken as an indirect indication of compatibilization between the phases. It was assumed that lack of the carbonyl peak of AA at 1720 cm<sup>-1</sup> in the residual curve [Fig. 3(d)] would indicate reactions between the carboxyl and hydroxyl group in the PP+PP-g-AA/P(BuA+PPGMM) blend. Figure 3(d) shows no carbonyl absorption peak in the residual curve at 1720 cm<sup>-1</sup>, and lack of the peak can be taken as an indirect indication of compatibilization between the phases.

It bears notice, however, that the sensitivity of the IR analysis is quite poor especially at low concentrations of the reactive components. The closeness of the ester and acid carbonyl absorption peaks (1740 and 1720 cm<sup>-1</sup>) could also interfere with the interpretation. To improve the reliability and applicability of the IR analysis, blends with higher concentrations of functional monomers in the rubber phase need to be prepared. In addition, after extracting the PP phase, the interactions between functionalized PP and PBuA phases might be easier to analyze.



**Figure 3** FTIR curves of (a) PP-g-AA, (b) PP/P(BuA+PPGMM) blend, and (c) PP+PP-g-AA/P(BuA+PPGMM) blend, and (d) the residual FTIR curve of PP+PP-g-AA/P(BuA+PPGMM)-PP/P(BuA+PPGMM).

# **Morphology Analysis**

The morphology of the blends was studied by transmission electron microscopy. Owing to the difficulties in sample preparation (cutting and staining), the TEM micrographs were not of high quality and only approximate conclusions about the morphology could be drawn.



Figure 3 (Continued from the previous page)

The rubber particle size for all blends after the polymerization was about 80 nm [Fig. 4(a)]. Melt blending resulted in a clear coalescence of the rubber phase. After the blending, the particle sizes were about 1000 and 500 nm for uncompatibilized and

compatibilized blends, respectively [Fig. 4(b) and (c)]. The higher coalescence rate in the uncompatibilized blends is mainly thought to be due to the higher interfacial tension between the components and softer and stickier nature of the rubber particles.



**Figure 4** TEM micrographs of (a) PP/P(BuA+GMA) blend after polymerization, (b) PP/PBuA blend after melt blending and injection molding, and (c) PP+PP-g-AA/P(BuA+TBAEMA) blend after melt blending and injection molding. In all TEM micrographs, the rubber phase is dark and the PP phase is white.

The elasticity ratio of the components could also have influence on the coalescence as well.

# CONCLUSIONS

Compatibilization and the promotion of interfacial adhesion in PP/PBuA were achieved by incorporating functional components in the PP and PBuA phases. The functionalities of the monomers used to functionalize the rubbery PBuA phase were epoxy, oxazoline, hydroxyl, secondary amine, and carboxyl. The compatibilization reactions between the functional groups of the blends took place in an extruder at the melt stage.

The tensile strength, tensile modulus, elongation at break, and tear strength of the compatibilized blend were improved by about 15, 20, 160, and 50%, respectively, compared to the unfunctionalized blend. The hardness of the material remained unchanged. The glass transition temperatures of the phases were closer to each other for some compatibilized than for uncompatibilized blends, which could indicate better adhesion between the phases. Related to this, the TEM micrographs showed that the compatibilized blends did not agglomerate as much as did the uncompatibilized blends during the processing.

# **SYMBOLS**

D . A

BUA	late
DMTA	dynamic mechanical ther- moanalysis
f-PP	functionalized polypropylene
FM	functional monomer
FTIR	Fourier transform infrared spectroscopy
GMA	glycidylmethacrylate
MMP	monomethacryloyloxy ethyl phthalate
PBuA	polybutylacrylate
PP	polypropylene
PP-g-AA	polypropylene grafted with acrylic acid

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PP-g-MAH	polypropylene grafted with
	maleic acid anhydride
PP/P(BuA+FM)	blend of PP and copolymer of
	BuA and FM
PPGMM	polypropyleneglycol mono-
	methacrylate
ROMM	ricinoloxazoline methylmal-
	einate
TBAEMA	2-tert-butylaminoethyl meth-
	acrylate
ZnAc	zinc acetate
$x^p$	polarity []

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