# Influence of Comonomer Incorporation on Morphology and Thermal and Mechanical Properties of Blends Based upon Isotactic Metallocene–Polypropene and Random Ethene/1-Butene Copolymers

# DIETMAR MÄDER,<sup>1</sup> YI THOMANN,<sup>2</sup> JÜRGEN SUHM,<sup>3</sup> ROLF MÜLHAUPT<sup>2</sup>

<sup>1</sup> Ciba Specialty Chemicals, Inc., R-1055 U114.3, CH-4002 Basel, Switzerland

<sup>2</sup> Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität, Stefan-Meier-Str. 21, D-79104 Freiburg i. Br., Germany

<sup>3</sup> BASF AG, Kunststofflaboratorium, D-67056 Ludwigshafen, Germany

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ABSTRACT: Blends of isotactic polypropene (i-PP) with random ethene/1-butene (EB) copolymers containing 10, 24, 48, 58, 62, 82, and 90 wt % 1-butene were prepared in order to examine the influence of the EB molecular architecture on the morphology development as well as on the thermal and mechanical properties. Compatibility between i-PP and EB increased with increasing 1-butene content in EB to afford single-phase blends at a 1-butene content exceeding 82 wt %. The morphology was investigated using AFM and TEM. Improved compatibility accounted for enhanced EB dispersion and interfacial adhesion. Highly flexible as well as stiff blends with improved toughness were obtained. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 838–848, 1999

**Key words:** polypropene; ethylene-1-butene copolymers; rubber; blend; metallocene; miscibility; impact; dynamic mechanical properties; glass transition; AFM

# **INTRODUCTION**

The recent development of "single-site" metallocene catalysts offers new opportunities for polymer synthesis. Both the stereochemistry of poly(1-olefins) as well as short- and long-chain branching can be varied.<sup>1</sup> In contrast to conventional heterogeneous multisite Ziegler–Natta catalysts, metallocene-catalyzed olefin copolymerization affords copolymers with a narrow molar mass distribution  $(M_u/M_n = 2)$ 

and very uniform comonomer incorporation. The range of tailor-made ethene/1-olefin copolymers include linear low-density polyethene with very low density, highly flexible thermoplastic elastomers, also referred to as plastomers, and rubbers.<sup>2–4</sup> Metallocene-catalyzed copolymerization of ethene with propene,<sup>5</sup> 1-butene,<sup>6,7</sup> 1-hexene,<sup>8</sup> and 1-octene<sup>9</sup> has been reported.

The possibility to vary comonomer incorporation over the entire feasible range offers an attractive potential to understand basic structure/property correlations of blends. Recently, Yamaguchi et al. reported that "1-olefin rich" ethene/1-olefin copolymers were incorporated preferably into the amorphous region of a crystalline propene/ethene copolymer containing 3.2 wt % ethene, thus indicating miscibility.<sup>10,11</sup> The objective of this research was to

Correspondence to: R. Mülhaupt.

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	Abbreviation							
	EB10	EB24	EB48	EB58	EB62	EB82	EB90	
	EB 1-Butene Content							
Contents and Properties	10	24	48	58	62	82	90	i-PP
Ethene content <sup>a</sup> (mol %)	94.6	86.7	68.9	58.8	54.1	30.1	19.0	_
1-Butene content <sup>a</sup> (mol %)	5.4	13.3	31.1	41.2	44.9	69.9	81.0	—
Ethene content <sup>a</sup> (wt %)	89.7	76.4	52.1	41.7	38.0	17.7	10.5	—
1-Butene content <sup>a</sup> (wt %)	10.3	23.6	47.1	58.3	62.0	82.3	89.5	—
$M_n  (\text{kg/mol})^{\text{b}}$	51.0	55.4	60.8	48.2	65.6	40.5	73.9	117.0
$M_w/M_n^{\rm b}$	2.3	2.3	2.2	2.7	2.2	2.2	2.2	2.2
$T_{\sigma}^{(\circ C)^{c,d}}$	Broad/-19.7	-33/-35.2	-55/-60.1	-56/-60.5	-52/-57.1	-32/-41.9	-27/-37.7	5/-2.0
$T_m^{\circ}$ (°C) <sup>c</sup>	98.7	74.4	e	e	e	41.2	56.7	149.5
$\Delta H_m ~(J/g)^c$	82.2	74.5	e	e	e	15.5	26.7	84.5
$T_{\rm cr}$	82.4	67.3	e	e	e	e	e	113

Table I Abbreviations and Physical Properties of the Polymers Used

<sup>a</sup> Determined by <sup>1</sup>H-NMR.

<sup>b</sup> Determined using high-temperature GPC based on poly(ethene) standards.

<sup>c</sup> Determined by DSC at a heating rate of 10 K/min.

<sup>d</sup> Determined by DMA at a heating rate of 2 K/min.

<sup>e</sup> Could not be detected.

evaluate the blend formation of isotactic polypropene (i-PP) with ethene/1-butene copolymers (EB) in order to understand the influence of the 1-butene content in EB on the morphology development, toughness/stiffness balance, and, especially, lowtemperature toughness of i-PP/EB blends. Metallocene catalysis was applied to prepare uniform EB copolymers with a 1-butene content varying between 10 and 90 wt % in order to establish structure/property correlations of i-PP/EB blends as a function of both the EB molecular architecture and EB volume fraction.

## **EXPERIMENTAL**

#### **Materials**

The i-PP used in this study was metallocene-PP, Novolen M<sup>®</sup>, supplied by BASF AG. EB10 was Luflexen HS0322 from BASF AG, and EB24 was Tafmer A4085 supplied by Mitsui. The other poly-(ethene-*co*-1-butene)s (EB) were prepared using methylaluminoxane-activated metallocene *rac*-Me<sub>2</sub>Si(2-MeBenz[*e*]Ind)<sub>2</sub>ZrCl<sub>2</sub> (MBI), an isospecific metallocene catalyst.<sup>6</sup> To exclude the influence of MAO or catalyst residues, all MBI-based copolymers were extracted with boiling xylene for 24 h prior to use. The 1-butene content was determined from <sup>1</sup>H-NMR analysis; the accuracy of the determination was about  $\pm 2$  wt %. The molar mass and molar mass distribution were measured by gel permeation chromatography (GPC) in 1,3,5-trichlorobenzene at 135°C, calibrated with polyethene standards. 0.5 wt % Irganox<sup>®</sup> 1010/Irgafos<sup>®</sup> 168 (80/20 wt %) were added as stabilizers during melt processing. Properties of the blend components are listed in Table I.

#### Melt Blending

The melt blends were prepared using a Haake Rheomix 90 twin-screw kneader equipped with a 60 mL mixing chamber which was preheated at 200°C and operated at 60 rpm. The chamber was always charged with 45 mL of the polymer. i-PP was molten in the presence of the stabilizers for 1.5 min. Then, the EB was added within 0.5 min. After another 3 min (total mixing time was 5 min), the sample was quickly recovered and quenched between cooled metal plates. Sheets of 2 and 4 mm thickness were prepared by compression molding: The sample was annealed at 200°C for 10 min in an evacuated press (Schwabenthan Polystat 100) and quenched to ambient temperatures between water-cooled metal plates. Rectangular bars of  $60 \times 10 \times 4$  mm were cut for the evaluation of the impact properties.

## Dynamic Mechanical Analysis (DMA)

The glass transition temperatures,  $T_g$ , were measured by DMA on a Rheometrics Solids Analyzer RSAII at 1 Hz and at a heating rate of 2 K/min using a dual cantilever geometry (50 × 6 × 2 mm), applying a strain of 0.2%. The storage (E'), the loss moduli (E''), and the loss tangent [tan( $\delta$ )] were measured from  $-120^{\circ}$ C to temperatures accessible with the dual cantilever geometry.

## **Thermal Analysis**

Differential scanning calorimetry (DSC) measurements were performed on a Perkin–Elmer DSC-7 at a heating rate and cooling rate of 10 K/min. Prior to the measurement, i-PP and the copolymers were crystallized by cooling from the melt to RT using a cooling rate of 0.1 K/min.

## Atomic Force Microscopy (AFM)

AFM measurements were performed on a Nanoscope III scanning probe microscope. The phase images were obtained while operating the instrument in the tapping mode under ambient temperatures. We used a commercial Si cantilever with force constants of 13-70 N/m. Images were taken at the fundamental resonance frequency of the Si cantilevers,  $\omega_0$ , which was typically about 300 kHz. Typical scan speeds during the recording were 0.3-1 line/s using scan heads with a maximum range of  $16 \times 16 \ \mu$ m. All images were taken with a driving amplitude  $A_0 \approx 60$  nm and a setpoint amplitude  $A_{sp} \approx 40-48$  nm. The phase images represented the variations of relative phase shifts (i.e., the phase angle of the interacting cantilever relative to the phase angle to the freely oscillating cantilever at the resonance frequency  $\omega_0$ ). AFM was performed using cryosectioned samples from the microtoming.

## Transmission Electron Microscopy (TEM)

TEM measurements were done with a Zeiss CEM 902 transmission electron microscope applying an acceleration voltage of 80 kV. The samples were cut with an ultramicrotome (Ultracut E, Reichert & Jung, equipped with a diamond knife) at  $-100^{\circ}$ C. Ultrathin sections of approximately 80

nm were stained with  $RuO_4$  prepared from 10 mg  $RuCl_3$  and 1 mL of a 10 wt % NaOCl solution over the gas phase.

## **Tensile Properties**

Tensile properties were measured on an Instron (Model 4202) tensile machine according to the DIN 53455 standard procedure using test specimens of 2 mm thickness and a crosshead speed of 10 mm/min. Notched Izod impact strength values were determined on notched samples according to ISO 180/1A using test specimens of  $60 \times 10 \times 4$  mm. The average standard deviations of the Young's modulus and yield stress were approximately 5%; of impact strength 10%; and of elongation at break 30%. A minimum of five specimens was tested for each blend composition and the average value is reported. All tests were performed at ambient temperature ( $25 \pm 2^{\circ}$ C). In addition, impact properties were measured at  $-28^{\circ}$ C.

# **RESULTS AND DISCUSSION**

Melt blends of i-PP and EB were prepared at 200°C using a Haake Rheomix 90 twin-screw kneader. The 1-butene content in EB was varied at 10, 24, 48, 58, 62, 82, and 90 wt %.

# DMA

All copolymers and corresponding melt blends were investigated using DMA in order to study the  $T_g$  of EB,  $T_g^{\rm EB}$ , and of the matrix i-PP,  $T_g^{\rm i-PP}$ . In Figures 1 and 2, the storage modulus E' (left side) and the loss tangent  $\tan(\delta)$  (right side) of the bulk matrix i-PP (open down triangle), the bulk elastomers EB (open up triangle), and the corresponding blends (80/20 vol %) (solid circle) are shown.

Figure 1(a) depicts the i-PP/EB10 system. EB10 shows a maximum in tan( $\delta$ ) below  $-100^{\circ}$ C which can be assigned to localized molecular relaxation.<sup>6,12,13</sup> The broad transition ranging from 50 to  $+50^{\circ}$ C corresponds to the  $T_g$  of the EB10 phase.<sup>12,14</sup> All ethene copolymers containing low amounts of the comonomer show this typical  $T_g$  broadening.<sup>6</sup> The  $T_g$  of metallocene-based i-PP is about  $+5^{\circ}$ C. The i-PP/EB10 blend exhibits two separated transitions—at -34 and at  $+5^{\circ}$ C—as expected for a two-phase morphology. Figure 1(b) displays DMA traces of i-PP/EB24. The pure EB24 shows a  $T_g$  at  $-33^{\circ}$ C, whereas the  $T_g^{EB24}$  in the blend appears at  $-40^{\circ}$ C. However, the  $T_g^{i-PP}$ 



**Figure 1** DMA traces of i-PP, EB copolymers, and i-PP/EB (80/20 vol %) blends containing different amounts of 1-butene in EB: (a) i-PP/EB10; (b) i-PP/EB24; (c) i-PP/EB48; (d) i-PP/EB58.

remains unchanged. Figure 1(c) shows the DMA data of i-PP/EB48. EB48 has a  $T_g$  of  $-55^{\circ}$ C, whereas in the blend its  $T_g^{\rm EB48}$  occurs at  $-65^{\circ}$ C. As apparent from the DMA traces of i-PP/EB58 displayed in Figure 1(d), bulk EB58 has a maximum tan( $\delta$ ) at  $-56^{\circ}$ C, whereas the  $T_g^{\rm EB58}$  is at  $-62^{\circ}$ C in the blend. In all two-phase i-PP/EB blends, a significant depression of the  $T_g^{\rm EB}$  of the dispersed phase ( $\Delta T_g^{\rm EB}$ ) is observed.  $T_g$  shifts toward lower temperatures are reported in the lit-

erature for reactive systems, in which the dispersed phase is covalently bonded to the thermoplastic matrix. For ABS, this behavior was assigned to different thermal expansion coefficients of the components.<sup>15–18</sup> Different thermal shrinking upon cooling accounts for the thermal tensile stress in the dispersed particles, thus causing dilatation in the dispersed phase. Further investigation and a description of this thermal-induced stress was published in a related study.<sup>19</sup>



Figure 2 DMA traces of i-PP, EB copolymers, and i-PP/EB (80/20 vol %) blends containing different amounts of 1-butene in EB: (a) i-PP/EB62; (b) i-PP/EB82; (c) i-PP/EB90.

Blends of i-PP and EB with a 1-butene content higher than 58 wt % exhibit different behavior of the  $T_g$ . From the DMA traces of i-PP/EB62, displayed in Figure 2(a), it is apparent that the  $T_{g}^{\text{EB62}}$  is shifted from  $-52^{\circ}\text{C}$  in the bulk to about  $-41^{\circ}$ C in the blend, that is, the  $T_g^{\text{EB62}}$  is increased. Additionally, the  $T_g^{\text{i-PP}}$  is slightly lowered from +5 in bulk to about  $-4^{\circ}$ C in the blend. This shift of the components toward one another indicates partial miscibility of i-PP with EB62 (which corresponds to a 1-butene content of 45 mol %). This observation is consistent with the results of Yamaguchi et al.<sup>10</sup> Figure 2(b,c) depicts DMA traces of i-PP/EB82 and i-PP/EB90, respectively. Both blends show only one broad single transition. This indicates complete or at least partial miscibility of i-PP with EB82 and EB90.

All observed  $T_g$ 's of the bulk components and the respective blends containing 20 vol % EB are

depicted in Figure 3 (values are summarized in Table II). As evidenced by DMA, the i-PP/EB system shows different miscibility behavior depend-



**Figure 3** Glass transition temperatures of i-PP, EB copolymers, and corresponding i-PP/EB (80/20 vol %) blends as determined by DMA.

EB Type	EB Volume Fraction (vol %)	$T_g^{ m EB}$ in Bulk (°C) <sup>a</sup>	$T_g^{ m EB}$ in Blend $(^{ m o}{ m C})^{ m a}$	$T_g^{ ext{i-PP}}  ext{ in Blend} \ (^\circ ext{C})^{ ext{a}}$	$\Delta T_g^{ m EB}$ (°C)
EB10	20	$-28^{\mathrm{b}}$	-34	5	b
EB24	20	-33	-40	5	-7
EB48	20	-55	-65	5	-10
EB58	20	-56	-62	4	-6
EB62	20	-52	-41	-4	c
EB82	20	-32	-10	-10	c
EB90	20	-27	-9	-9	c

Table II Thermal Properties of the Blends i-PP/EB (80/20 vol %)

<sup>a</sup> Determined by DMA at a heating rate of 2 K/min.

<sup>b</sup> Not detectable with dual cantilever geometry; value is estimated from DSC measurements.

<sup>c</sup> Single  $T_g$  was observed.

ing on the 1-butene content in EB. In Figure 3, two different regimes for the 1-butene content in EB are introduced: regime I for 1-butene contents below 60 wt %, and regime II for 1-butene contents above 60 wt %. In regime I, the phaseseparated blends exhibit two single  $T_g$ 's. The  $T_g^{i-PP}$ (cross) of the matrix remains almost unchanged, whereas the  $T_g^{\rm EB}$  (open circle) of the dispersed EB phase is depressed by -6 to -10 °C with respect to the  $T_{g}$  of the bulk EB (solid circle). In contrast, in regime II, partial miscibility of i-PP with EB can be observed as indicated by a single or an increased  $T_g.$  The  $T_g$  of the bulk i-PP is indicated by a dashed line. In the case of i-PP/EB62, two separate  $T_g$ 's can be detected by DMA but both  $T_{g}$ 's are shifted toward each other, caused by partial miscibility.

A single  $T_g$  in DMA provides good evidence for miscibility. However, this criterion does not hold for nanophase-separated systems because they can also show single  $T_g$ 's in DMA. Therefore, AFM and TEM were employed to study the blend morphology.

#### AFM

The morphologies of the blends under investigation were studied using AFM. Figure 4(a–g) depicts AFM phase images of the i-PP/EB blends (80/20 vol %) with the 1-butene content in EB varying at 10, 24, 48, 58, 62, 82, and 90 wt %. The images are recorded on ultramicrotomed surfaces. Phase imaging of the tapping mode AFM gives a contrast due to different material compliances. The more compliant material, that is, the EB phase, leads to a negative phase shift, corresponding to darker areas in the micrographs.<sup>20–22</sup>

Figure 4(a) depicts the i-PP/EB10 blend. The dispersed EB10 phase appears as dark areas in the AFM micrograph. The particle size ranges from about 0.2 to 2 microns. In a higher magnification, the lamellae of the i-PP matrix can be clearly identified. The i-PP/EB10 interface is quite sharp. However, there is no debonding of the EB10 particles detectable which might be induced during cryosectioning. Figure 4(b) shows an AFM micrograph of the i-PP/EB24 blend. The rubber domains show elongated shapes due to shearing during preparation. In the case of i-PP/ EB48, the AFM image [Fig. 4(c)] clearly indicates that the particle size is significantly decreased when compared to those of the EB blends with a lower 1-butene content. The particle size ranges from 50 to 400 nm. This is experimental evidence for the enhanced compatibility of i-PP with EB48.

As apparent from Figure 4(d), the i-PP/EB58 blend exhibits a similar morphology when compared with Figure 4(c). Although the 1-butene content is only sligthly higher compared to the previous system, the morphology of i-PP/EB62 [Fig. 4(e)] is completely different. The rubber/matrix interface is very diffuse, indicating the formation of an i-PP/EB62 interphase. It appears that EB62 is partially dissolved in i-PP and vice versa.

Figure 4(f) displays the AFM image of i-PP/ EB82 in which the dark rubber phase is more finely dispersed compared to the previous investigated systems, forming nano-scaled particles of 20-80 nm. The fraction of the dark area is smaller than the 20 vol % from the given mixing ratio. The i-PP/EB90 blend exhibits a single phase, reflecting complete miscibility of both components [Fig. 4(g)].



**Figure 4** AFM phase images of i-PP/EB (80/20 vol %): (a) i-PP/EB10; (b) i-PP/EB24; (c) i-PP/EB48; (d) i-PP/EB58; (e) i-PP /EB62; (f) i-PP/EB82; (g) i-PP/EB90. The micrograph width corresponds to 12  $\mu$ m.

The morphology development of the i-PP/EB blends depends on the 1-butene content in EB. In regime II, the preparation of miscible i-PP/EB blends is possible. Similar observations were reported recently by Thomann et al. who investigated the morphology development of i-PP/EB solution blends with another mixing ratio (50/50 wt %).<sup>22</sup>

# TEM

The morphology of the phase-separated blends (regime I) was confirmed by TEM. Figure 5 depicts the TEM morphologies of the i-PP/EB (80/20 vol %) blends with 1-butene contents in EB above 48 wt %. TEM gives additional information concerning the morphology. The i-PP/EB58 blend [Fig. 5(a)] shows elongated particles (dark) with black spherical inclusions. These particles consist of an EB58-rich i-PP/EB58. The inclusions are only detectable by TEM. We assume that these inclusions might be the result of a demixing process in the dispersed EB58rich phase. These inclusions appear dark due to intense staining of the i-PP/EB58 interface between the i-PP lamellae and the surrounding EB58. A more detailed investigation is in progress.<sup>23</sup> The matrix phase shows also a pattern of a demixing process similar to that of a spinodal decomposition. This indicates that the blend i-PP/EB58 is a very complex system.

The system i-PP and isotactic poly(1-butene) (i-PB) exhibits an UCST behavior.<sup>24</sup> Assuming UCST behavior for i-PP/EB58, the sample is phase-separated in the melt at temperatures below the UCST. The melt consists of an i-PP rich and an i-PP poor i-PP/EB58 mixed phase. Upon cooling from the melt (exhibiting a two-phase morphology), another phase separation within each phase can be expected. This cascade of twophase separation processes could explain the detected multiphase morphology. Additionally, crystallization processes might influence the morphology development during quenching.<sup>25</sup>

In contrast to AFM, TEM shows phase-separated particles in the i-PP/EB62 blend [Fig. 5(b)]. The morphology of i-PP/EB62 resembles the morphology of i-PP/EB58. However, the contrast between the matrix and particles is strongly decreased compared to the previous system. Furthermore, the number of inclusions (dark) is slightly higher than the one in i-PP/EB58.

In the i-PP/EB82 blend [Fig. 5(c)], only particles are visible which resemble the inclusion from Figure 5(a,b). These observations are consistent with AFM.

#### **Mechanical Properties**

The mechanical properties of the i-PP/EB blends were examined as a function of the 1-butene con-





(c)

 $\label{eq:Figure 5} \begin{array}{l} \text{TEM images of $i$-PP/EB$ blends (80/20 vol \%): (a) $i$-PP/EB58 (the inclusions are indicated by an arrow); (b) $i$-PP/EB62; (c) $i$-PP/EB82. \end{array}$ 

ЕВ Туре	EB Content (vol %)	Young's Modulus (MPa)	Yield Stress (MPa)	Elongation at Break (%)	Notched Izod Impact Strength at RT (kJ/m <sup>2</sup> )	Notched Izod Impact Strength at -28°C (kJ/m <sup>2</sup> )
i-PP	_	900	27.8	700	3.6	2.0
EB10	5	868	26.3	728	5.0	2.1
	10	817	24.8	685	6.7	2.4
	15	780	23.5	630	6.8	2.6
	20	720	22.5	598	7.4	2.7
EB24	5	831	26.6	610	4.7	2.4
	10	797	24.4	640	9.5	2.4
	15	770	22.2	610	12.8	2.6
	20	709	21.3	647	16.2	2.9
EB48	5	825	25.1	620	6.0	3.5
	10	779	22.9	620	11.8	3.5
	15	710	20.5	580	n.b.ª	3.8
	20	645	18.9	540	n.b.ª	7.9
EB58	5	804	25.8	716	7.5	2.4
	10	750	23.2	665	11.9	2.6
	15	695	20.0	531	n.b.ª	3.6
	20	610	17.7	624	n.b.ª	3.9
EB62	5	752	24.3	699	4.5	2.4
	10	635	21.1	676	8.8	2.3
	15	549	19.8	643	14.2	2.5
	20	453	17.5	643	20.4	2.6
EB82	5	878	26.3	694	5.2	2.0
	10	773	25.0	740	7.3	2.0
	15	601	22.2	867	10.2	2.0
	20	517	17.8	894	12.9	2.0
EB90	5	783	24.6	717	3.5	2.0
	10	710	22.0	760	5.8	1.9
	15	626	20.0	702	8.1	2.1
	20	537	18.4	960	10.2	2.0

Table III Mechanical Properties of the Blends i-PP/EB

<sup>a</sup> Sample did not break.

tent in EB and of the EB volume fraction. The 1-butene content in EB is varied at 10, 24, 48, 58, 62, 82, and 90 wt %. The Young's modulus, yield stress, elongation at break, and notched Izod impact strength at 25 and at  $-28^{\circ}$ C are listed in Table III. The influence of 1-butene content in EB on the Young's modulus and yield stress of the i-PP/EB blends (80/20 vol %) is shown in Figure 6.

The moduli of all blends are smaller with respect to i-PP. The mechanical properties indicate, analogously to the morphological and thermal properties, a different behavior for copolymers within regime I (low 1-butene content) and regime II (high 1-butene content). In regime I, the Young's modulus decreases with increasing 1-butene content. The decrease for i-PP/EB10 and i-PP/EB24 is less pronounced due to residual crystallinity of EB10 and EB24, that is, enhanced



**Figure 6** Young's modulus and yield stress of i-PP/EB (80/20 vol %) blends as a function of 1-butene content in EB.

stiffness, with respect to amorphous EB48 and EB58. In regime II, partial or full miscibility accounts for flexibilization of the polymer matrix. In the case of EB82 and EB90, which exhibit low crystallinity, the Young's moduli are somewhat larger with respect to that of the corresponding blend containing amorphous EB62. The transition from immiscibility to partial miscibility between i-PP and EB with increasing 1-butene content at a 1-butene content of 62 wt % is also demonstrated by the mechanical data. The yield stresses of i-PP/EB (80/20 vol %) blends decrease with increasing 1-butene content (regime I) and are almost constant for miscible blends at high 1-butene content (regime II). The higher flexibility of miscible blends is associated with lower yield stress. Again, this provides good evidence that miscible EB with a high 1-butene content acts as high molecular weight diluent or plasticizer for i-PP.

In Figure 7, the Izod impact strength [(a) at RT and (b) at -28 °C] is plotted versus the EB volume fraction (5, 10, 15, 20 vol %) and the 1-butene content in EB. As indicated by the arrow, the toughness behavior differs between regimes I and II. In regime II, (partial) miscibility causes singlephase blends with poor toughness. In regime I, the toughness reaches its maximum at a 1-butene content of approximately 48 wt %. At this 1-butene content, the compatibility of i-PP and EB are adjusted to afford phase separation with a fine EB dispersion and excellent interfacial adhesion at the same time. The optimum toughness/ stiffness balance is reached.

The appropriate balance of compatibility between i-PP and EB affects the morphology and the toughness of the resulting i-PP/EB blends. The dispersed EB48 rubber phase improves resistance against failure by means of efficient energy dissipation, as evidenced by substantially improved notched Izod impact strength at room temperature and at  $-28^{\circ}$ C. The i-PP/EB48 blends exhibit a very attractive toughness/stiffness balance similar to that of i-PP blends with polystyrene-*block*-poly(ethene-*co*-1-butene)-*block*-polystyrene (SEBS) blends.<sup>26</sup>

#### **CONCLUSIONS**

The 1-butene content in EB plays the key role in blend properties of i-PP with metallocene-based random ethene/1-butene copolymers and governs the morphology development as well as the thermal



**Figure 7** Notched Izod impact strength of i-PP/EB blends as a function of EB volume fraction and 1-butene content in EB (a) at  $25^{\circ}$ C and (b) at  $-28^{\circ}$ C.

behavior and toughness/stiffness balance. At a 1-butene content above 82 wt %, single-phase blends are formed as demonstrated by AFM and TEM (regime II). Surprisingly, the system i-PP/EB exhibits a miscibility window at high 1-butene contents. As expected, immiscibility is observed in regime I, that is, from PE (EB00) to EB58. Complete miscibility is observed for EB90, whereas i-PP is only partially miscible with i-PB.<sup>24</sup> A similar behavior was found for poly(ethylene/ethylethylene) by Bates et al.<sup>27</sup> These copolymers, synthesized via hydrogenation of polybutadiene containing different amounts of 1,2- and 1,4-units, are often referred to as model poly(ethene-co-1-butene)s. Due to the anionic polymerization procedure, these polyethylethylenes exhibit different characteristics compared to metallocene-based copolymers, such as different stereoregularity. Furthermore, the poly(ethylene/ethylethylene) exhibits a completely different microstructure. Due to the polymerization procedure, the BEB triad is absent. It is not yet clarified in which way the microstructure influences the miscibility of i-PP with EB or other copolymers.<sup>28</sup>

Two-phase blends (regime I) exhibited lowered  $T_g$ 's of the dispersed EB with respect to those of the corresponding bulk EB. While stiffness decreases with increasing 1-butene content, unexpected toughness/stiffness synergism is observed at a 1-butene content in EB of 48 wt %. In the transition range between regimes I and II, that is, for the i-PP blends with EB58 and EB62, a complex morphology is found.

It has been shown that the scale of dispersion, interfacial adhesion, and thermal behavior of i-PP/EB blends can be controlled via 1-butene incorporation in EB. i-PP/EB48 blends exhibit the best impact properties and the largest  $T_g$  depression  $(\Delta T_g^{\rm EB})$  of all two-phase systems. The control of the morphology and interfacial properties is of particular interest for the preparation of polypropene materials with improved low-temperature toughness. Accurate control of the comonomer incorporation, typical for metallocene catalysts, is the key to tailor polymer blends with an improved property balance.

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