

# Toughened Poly(butylene terephthalate)s and Blends Prepared by Simultaneous Chain Extension, Interfacial Coupling, and Dynamic Vulcanization Using Oxazoline Intermediates

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**ABSTRACT:** Toughness of poly(butylene terephthalate) (PBT) was improved by reactive blending of PBT with 2-substituted 1,3-oxazoline intermediates such as low-molecular-weight bisoxazolines, and oxazoline-functionalized nitrile rubbers derived from both nitrile liquid rubber (Nipol®) and high-molecular-weight hydrogenated nitrile rubber (Therban®). Conversion of 7 mol % of the nitrile groups of Nipol into 1,3-oxazoline, corresponding to less than 1 oxazoline group per chain, was sufficient to afford melt strengthening and substantially improved dispersion and interfacial adhesion of the nitrile rubber microphases in the PBT continuous phase. Also in the case of high molecular weight Therban, oxazoline functionalization significantly improved compatibility with PBT. Best results in terms of toughness/stiffness balance, with impact strength exceeding 200 kJ/m<sup>2</sup>, was achieved when PBT was blended with both oxazoline-functionalized high-molecular-weight hydrogenated nitrile rubber and low-molecular-weight bisoxazoline chain extenders. The outstanding performance of such PBT blends, containing 10 and 20 wt % oxazoline-modified Therban and 0.6–1.1 wt % bisoxazoline chain extender, respectively, was attributed to simultaneous bisoxazoline-mediated PBT chain extension, interfacial coupling and dynamic vulcanization of the oxazoline-functionalized nitrile rubber. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 633–642, 1997

**Key words:** PBT; oxazoline; reactive blending; toughness; polyester; nitrile rubber

## INTRODUCTION

Today, mechanical properties of polymeric materials are tailored by blending immiscible polymers. In order to achieve property synergisms, which are not reflected by the properties of the individual blend components, taking into account their mixing ratios, special blend compatibilizers

such as block and graft copolymers are added to afford dispersion and interfacial adhesion of the blend components.<sup>1</sup> Preferably, such compatibilizers are formed *in situ* by coupling reaction of functionalized polymers. Production of numerous multiphase blends exploit such reactive blending technology.<sup>2</sup> Coupling reactions must proceed in highly viscous polymer melts at temperatures above 200°C within a few minutes holdup time, which is typical for extrusion processes. Moreover, the conversion must be quantitative without extensive byproduct formation because only volatile byproducts can be removed from the polymer melt by vacuum stripping. While maleic anhydride-

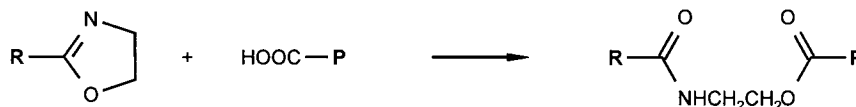
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**Scheme 1** Reaction of oxazoline with carboxylate.

grafted polymers are being used extensively for compatibilizing immiscible polymer blend components, the attractive potential of versatile 2-substituted 1,3-oxazolines has recently been recognized.

Oxazolines are readily available from nitriles and esters which are reacted in solution or bulk with 2-aminoethanol, preferably in the presence of catalysts such as zinc acetate, to form 2-hydroxyethyl-carboxamides, which cyclize upon heating to form oxazolines.<sup>3,4</sup> Hsieh and colleagues reported a solution process for the chemical conversion of nitrile-containing copolymers, [e.g., poly(styrene-*co*-acrylonitrile), poly(butadiene-*co*-acrylonitrile)—referred to as nitrile rubber—and hydrogenated nitrile rubber] into the corresponding oxazoline-functional derivatives.<sup>5,6</sup> Nitrile conversion can also be performed in bulk at much shorter residence times which are suitable for reactive processing, using extruders or internal mixers as reaction vessels.<sup>7</sup> Birnbrich and associates obtained a wide variety of 1,3-oxazolin-2-yl-functionalized polymers by melt grafting of polymers with novel oxazoline-functional maleinates and acrylates, which were derived from fats and plant oils.<sup>8</sup> Their high stability at room temperature combined with high reactivity and selectivity at elevated temperatures qualify 2-substituted 1,3-oxazolines as reactive intermediates for reactive processing applications. As demonstrated by means of low-molecular-weight model reactions, 2-phenyl-1,3-oxazolines react with nucleophiles such as carboxylates at temperatures above 200°C within a few minutes to form esteramide via nucleophilic attack at C-5 position of the oxazoline ring, followed by ring-opening (see Scheme 1).<sup>9</sup> Therefore, oxazoline intermediates offer attractive potential for reactive processing of polymers with carboxylate groups.<sup>10</sup>

The first examples of oxazoline-mediated reactive blending involve 1,3-oxazolin-2-yl-functionalized polystyrene, which was produced by copolymerizing styrene with 2-vinyl-1,3-oxazoline.<sup>11</sup> Extensive research was aimed at melt strengthening of polyesters by converting carboxylate end groups into esteramides. This end-capping results in much-improved hydrolytic stability because carboxylic

acids are known to hydrolytically cleave polyesters. Moreover, difunctional oxazolines are very effective chain extenders which afford molecular weight buildup and melt strengthening similar to polyesters prepared in special solid phase polycondensation reactions. As reported by Inata and Matsu-mura<sup>12-14</sup> as well as Loontjens and coworkers,<sup>15,16</sup> chain-extended polyesters exhibit improved mechanical properties, including improved impact strength. Thermal cleavage of polyesters by heating them in the presence of low-molecular-weight dicarboxylic acids and bisoxazolines represents a route to novel families of copolyesteramides.<sup>10</sup> In polyester recycling, chain extension of hydrolytically degraded polyester wastes can account for substantial improvement in the properties of recycled polyesters. Bis(1,3-oxazolin-2-yl)-terminated silicones and oligotetrahydrofurans are high-molecular-weight chain extenders to produce novel segmented copolyesteramides.<sup>17</sup> Douhi and Fradet<sup>18</sup> investigated reactions between carboxylate-terminated oligotetrahydrofurans and bisoxazoline derivatives. Böhme and colleagues<sup>19</sup> applied tri-functional oxazolines as polyester chain extenders to introduce long-chain branching, thus improving mechanical and processing properties of liquid crystalline polyesters. Recently, Hietaoja and colleagues applied oxazoline-grafted polypropylene as blend compatibilizer for reactive blending of polypropylene with polyesters and polyamides.<sup>20</sup> Also, carboxylate side chains of poly(ethylene-*co*-methacrylic acid) are converted quantitatively into the corresponding ethylene copolymers with esteramide side chains.<sup>21</sup> Such esteramide-functional ethylene copolymers would be very difficult to manufacture in high-pressure free radical polymerization because of poor conversion of vinyl-functional esteramides.<sup>9</sup> Moreover, melt phase cationic ring-opening polymerization of 2-phenyl-1,3-oxazoline, initiated by feeding the corresponding oxazolinium ion into the melt, yielded blends of ethylene copolymers with the *in situ* formed poly(*N*-benzoyl-ethyleneimine), which exhibits high molecular weight and glass transition temperature ( $T_g$ ) of 150°C.<sup>9</sup> Another outstanding feature of oxazoline chemistry is the possibility of monitoring oxazoline conversion, including end-group coupling reactions and interfacial reactions,

by means of Fourier transform infrared (FTIR) spectroscopy.<sup>22</sup> In accord with model reactions, FTIR studies confirm that carboxylates react quantitatively with oxazolines to form esteramides via ring-opening reaction subsequent to nucleophilic attack of the oxazoline. Here we report the application of oxazoline-mediated reactive blending technology to improve toughness of polybutyleneterephthalate (PBT) blends with nitrile rubber and hydrogenated nitrile rubber, respectively.

## EXPERIMENTAL

### Materials

Polybutyleneterephthalate, Type RT-4, was purchased from Hoechst AG, Frankfurt/Main, and dried *in vacuo* at 200°C prior to use. Concentration of carboxylic acid chain end groups was 106 mmol/kg, determined by titration analysis. Bis(1,3-oxazolin-2-yl)benzene (OxaPhOxa) and 2-(1,3-oxazolin-2-yl)1,3-oxazoline (OxaOxa) were synthesized according to literature procedures.<sup>17</sup>

### Preparation of NipolOxa7

80.0 g [431 mmol acrylonitrile (AN)] poly(butadiene-*co*-acrylonitrile) (Nipol® 1312) (28.6 wt % AN, 29.0 mol % AN,  $z/(x + y) = 0.29$ ), 1.81 mL 2-aminoethanol, 0.20 g Cd(OAc)<sub>2</sub> · 2H<sub>2</sub>O (2.5 mol % to AN), and 0.1 wt % Irganox® 1010 were stirred for 3 days at 130°C. Gaseous NH<sub>3</sub> evolved from the reaction mixture was removed via a slow argon steam. Residual 2-aminoethanol was removed *in vacuo* at 100°C. The product was soluted in a small amount of CHCl<sub>3</sub> and filtered to remove precipitated catalyst. Yield: 79.7 g (98%).

FTIR (Film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3,073, 2,928, 2,850 (C—H); 2,237 (C≡N); 1,663 (C=N), 1,448, 969 (C—H). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 5.70–5.26 (*m*, HC=); 5.21–4.83 (*m*, H<sub>2</sub>O=); 4.18 (*t*, CH<sub>2</sub>O); 3.81 (*t*, CH<sub>2</sub>N); 2.58 (*s*, CHCN); 2.44 (*s*, CHC=N); 2.40–1.81 (*m*, CH<sub>2</sub>CH=, CHCH=); 1.80–0.70 (*m*, CH<sub>2</sub>, CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  = 170.3 (C=N); 142.4–124.7 (HC=); 121.7 (CN); 117.5–113.9 (CH<sub>2</sub>=); 66.9 (CH<sub>2</sub>O); 54.1 (CH<sub>2</sub>N); 43.4–13.2 (CH, CH<sub>2</sub>, CH<sub>3</sub>).

### Preparation of TherbanOxa6

In 500 mL chlorobenzene, 100.0 g (631 mmol AN) poly(ethene-*co*-1-butene-*co*-acrylonitrile) (Therban®) (33.5 wt % AN, 32.3 mol % AN,  $z/(x + y) = 0.323$ ) was soluted during 8 h at 130°C. After

addition of 2.27 mL (37.9 mmol) 2-aminoethanol and 0.25 g (0.95 mmol) Cd(OAc)<sub>2</sub> · 2H<sub>2</sub>O (2.5 mol % to AN), the resulting mixture was stirred for 3 days at 130°C. Gaseous NH<sub>3</sub> evolved from the reaction mixture was removed via a slow argon steam. The product was soluted in 500 mL CHCl<sub>3</sub>, filtrated and precipitated in MeOH, and cooled at –50°C. Yield: 98.5 g (97%).

FTIR (Film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 2,925, 2,855 (C—H); 2,236 (C≡N); 1,663 (C=N), 1,458. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 4.20 (*t*, CH<sub>2</sub>O); 3.81 (*t*, CH<sub>2</sub>N); 2.58 (*s*, CHCN); 2.38 (*s*, CHC=N); 1.73–0.74 (*m*, CH, CH<sub>2</sub>, CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  = 170.9 (C=N); 122.3 (CN); 66.9 (CH<sub>2</sub>O); 54.1 (CH<sub>2</sub>N); 39.2–23.2; 11.8–8.5 (CH, CH<sub>2</sub>, CH<sub>3</sub>).

## Reactive Processing

### PBT Chain Extension (General Procedures)

*PBT blends with nitrile rubber (Nipol-Oxa, TherbanOxa).* Reactive blending was performed in a Haake Rheomix 90, equipped with a 60-mL double-screw blender which was preheated at 240°C and operated at 100 rpm. Torque and temperature were recorded on-line. From 55.0 to 44.0 g PBT, stabilized with 0.1 wt % Irganox 1010, was melted in the blender at 240°C. After 150 s, *z* wt % rubber was added. After 4 min additional kneading, the obtained materials were removed and compression-molded under *vacuo* at 240°C to produce sheets of 2-mm thickness, using a Schwabenthan Polystat 100 press.

*PBT blends with oxazoline-functional rubber and bisoxazoline chain extenders:* If chain extending with bisoxazolines was performed, *y* wt % OxaOxa or OxaPhOxa was immediately added to the melt when rubber addition was completed, and the blend was kneaded for an additional time of 4 min.

## Polymer Characterization

Vapor pressure osmometry experiments were carried out with a Perkin–Elmer Molecular Weight Apparatus Type 115 with CHCl<sub>3</sub> as solvent at 30°C. The gel permeation chromatography apparatus was equipped with refractive index and ultraviolet (254 nm) detections using polystyrene calibration (column PL-Gel; 10<sup>6</sup>, 10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup> Å; 75 × 300 mm; flow rate 1 mL/min).

For tensile testing, tensile bars (according to DIN 53455) were cut and machined. Tensile tests

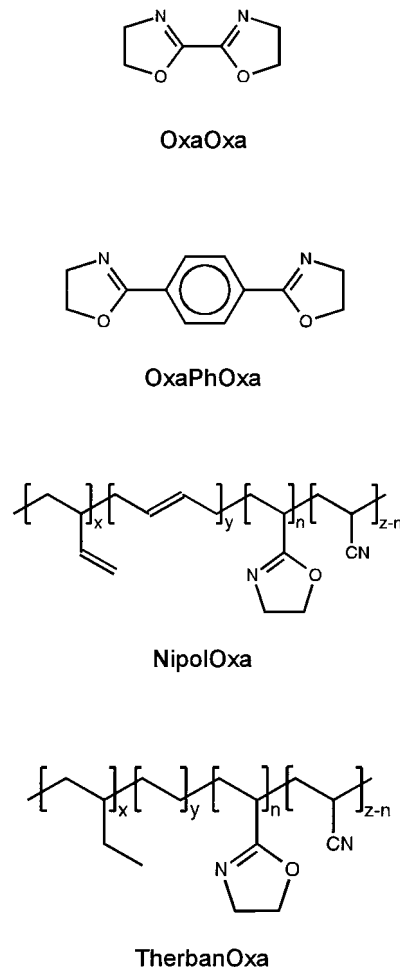
to determine Young's modulus and tensile strength at break were performed at 10 mm/min crosshead speed on an Instron 4204 at 23°C. Scanning electron micrographs of polymer blends were taken on a Zeiss Model DSM 960 microscope. Samples were prepared by fracturing the blend in liquid nitrogen and sputtering it with gold to obtain a surface of 2–3 mm<sup>2</sup>. Micrographs were taken in the magnification range 1,000–10,000.  $T_g$ s were measured by dynamic mechanical analysis (DMA) on a Rheometrics solids analyzer at 1 Hz and a heating rate of 5 K/min, and differential scanning calorimetry (DSC) on a Perkin–Elmer DSC 7 with a heating rate of 20 K/min. <sup>1</sup>H (300 MHz)- and <sup>13</sup>C (75 MHz)-NMR experiments were measured on a Bruker ARX 300, in CDCl<sub>3</sub> with TMS as internal standard.

## RESULTS AND DISCUSSION

PBT was blended with bisoxazoline chain extenders such as OxaPhOxa or OxaOxa, oxazoline-functionalized nitrile liquid rubber (NipolOxa) derived from Nipol containing 29 wt % AN units, and oxazoline-functionalized hydrogenated nitrile rubber (TherbanOxa) derived from Therban containing 33 wt % AN units. The structures of the oxazoline intermediates, used in reactive processing of PBT, are displayed in Scheme 2.

Properties of the rubbers and the corresponding oxazoline derivatives, prepared by partial conversion of nitrile groups in processes similar to those reported by Hseih and associates,<sup>6</sup> are listed in Table I. In the case of poly(butadiene-*co*-acrylonitrile) with number average molecular mass  $M_n = 2,100$  g/mol, oxazoline content was varied from 0 to 65 mol % with respect to the total content of polar side chains. This corresponds to an average number varying between 0 and 5.5 oxazoline groups per nitrile rubber chain. The  $T_g$  of the oxazoline-functionalized rubber increases with increasing conversion of the nitrile groups. The higher-molecular-weight poly(ethylene-*co*-butene-1-*co*-acrylonitrile) (Therban) with  $M_n = 58,300$  g/mol was converted into the corresponding oxazoline-functionalized rubber TherbanOxa6 containing 6 mol % oxazoline groups. This corresponds to an average number of 28 oxazolines per one chain of TherbanOxa6.

Reactive processing of PBT with various oxazolines was performed at 240°C in bulk, using a twin-screw blender. In order to study the role of oxazoline coupling reaction with carboxylate end



**Scheme 2** Oxazoline components.

groups of PBT, three systems were investigated: (1) PBT chain extended with bisoxazolines such as OxaOxa and OxaPhOxa, (2) PBT blended with oxazoline-functionalized rubbers NipolOxa and TherbanOxa, and (3) PBT blended with both bisoxazoline chain extender and oxazoline-functionalized rubbers.

Similar to reports by Inata and Matsumura<sup>12–14</sup> and Loontjens and colleagues,<sup>15,16</sup> bisoxazolines are very effective chain extenders which react with PBT carboxylate end groups (according to Scheme 3) to afford end-group coupling via esteramides. When stoichiometric amounts of OxaOxa (1 mol COOH/1 mol oxazoline) were added to PBT, molecular mass increased from 23,600 to 52,600 g/mol. However, this molecular weight increase was followed by chain scission, which could result from thermal decomposition of the resulting oxalic amide units. As demonstrated in a previous communication,<sup>10</sup> esteramides formed

**Table I Oxazoline-Functionalized Rubber**

Sample No.	$M_n^a$ (g/mol)	$M_w/M_n^b$	Oxa/(Oxa + CN)	Number of Oxazoline Groups per Chain (mol/mol)	$T_g^c$ (°C)
Nipol®	2,100	1.9	0	0	-44.0
NipolOxa7	2,140	2.0	0.07	0.5	-41.5
NipolOxa27	2,390	2.3	0.27	2.3	-40.2
NipolOxa47	2,570	2.4	0.47	3.9	-38.6
NipolOxa65	2,600	2.2	0.65	5.5	-36.7
Therban®	58,300	3.1	0	0	-26.2
TherbanOxa6	60,100	3.2	0.06	28	-25.6

<sup>a</sup> Determined by means of vapor pressure osmometry with  $\text{CHCl}_3$  as solvent.

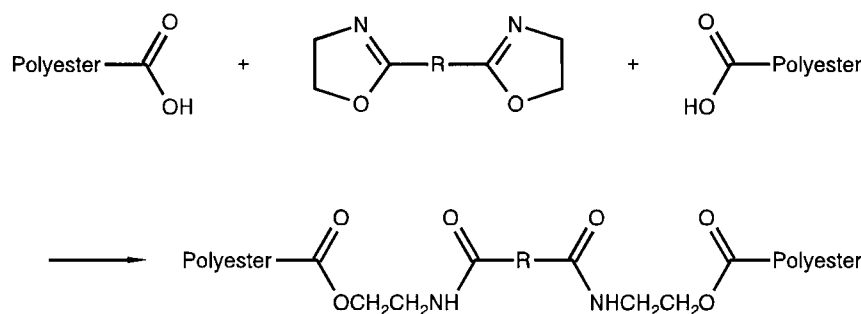
<sup>b</sup> Determined by means of GPC with  $\text{CHCl}_3$  as solvent.

<sup>c</sup> Glass transition temperature, determined by means of DSC.

by chain extension with OxaPhOxa are stable. When OxaPhOxa was added, PBT molecular mass increased to 36,200 g/mol and did not decrease upon further thermal treatment. Stoichiometry of bisoxazoline addition, preferably 1 mol carboxylic acid per 1 mol oxazoline, is an important requirement for both OxaOxa and OxaPhOxa chain extenders. Properties of PBT, chain-extended with either OxaOxa or OxaPhOxa, are listed in Table II. Bisoxazoline chain extenders are very useful additives to stabilize PBT during processing. As shown in Figure 1, thermal treatment of PBT in the blender causes degradation and embrittlement, reflected by substantial losses of modulus, stiffness, and notched impact strength of PBT processed in the blender. When bisoxazoline chain extension takes place, the notched Charpy impact strength increases from 10 to 35  $\text{kJ/m}^2$  for OxaOxa and is only marginally improved for OxaPhOxa, while Young's modulus of approximately 2,000 MPa is retained. Obviously, increasing PBT molecular mass during melt processing represents a very attractive route to improve PBT toughness without sacrificing stiffness.

Blends comprising PBT and 10 wt % nitrile rubber Nipol or the corresponding oxazoline derivatives NipolOxa were processed at 240°C. Composition and properties are listed in Table II. Mechanical properties are displayed in Figure 1. Only NipolOxa7 with low oxazoline content, corresponding to an average of 0.5 mol oxazoline/1 mol elastomer, was processable. At higher oxazoline content with more than one oxazoline group incorporated in the nitrile rubber chain, crosslinking occurred and caused very large increases of melt viscosity. Melt viscosity increase, reflected by torque measurement, of PBT/NipolOxa7 was very similar to that of PBT, chain-extended with OxaOxa. While PBT/Nipol did not contain gel fractions and was soluble in phenol/tetrachloroethane (6/4), the corresponding PBT/NipolOxa7 was not soluble. This indicates that oxazoline groups reacted with carboxylate groups, thus causing grafting, branching, and, to some extent, crosslinking of the rubber, especially the small fraction containing more than one oxazoline group.

As illustrated in Figure 2 by scanning electron microscopic (SEM) images of fracture surfaces,

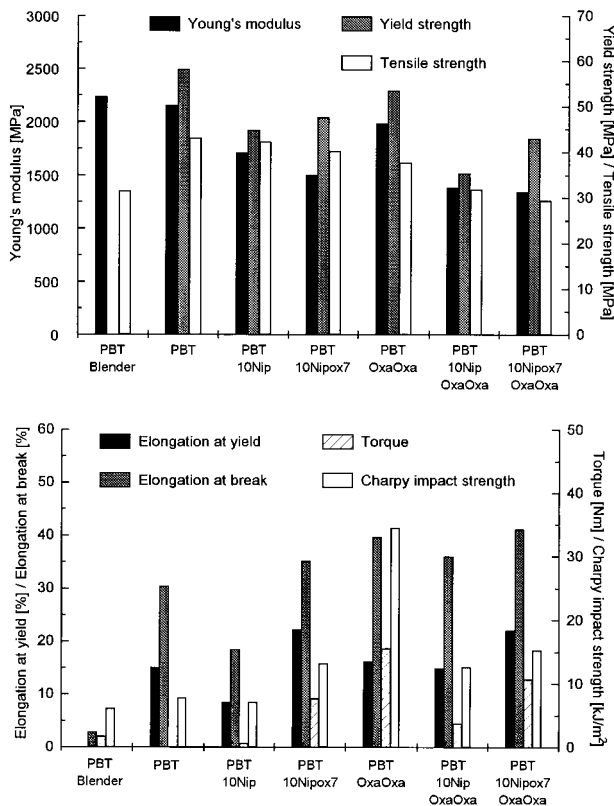


**Scheme 3** Chain extension reaction of PBT with bisoxazolines.

**Table II Blend Compositions and Properties**

Sample	y Extender Type <sup>a</sup> (wt %)		z Rubber Type <sup>b</sup> (wt %)		$T_g$ Rubber/PBT (°C)	$T_m/\Delta H_m^d$ (°C)/(J/g)	Particle Size <sup>e</sup> ( $\mu\text{m}$ )	Young's Modulus (MPa)	Yield Stress (MPa)	Elongation at Yield (%)	Elongation at Break (%)	Impact Strength <sup>f</sup> (kJ/m <sup>2</sup> )
PBT	—	0	—	—	-/53.8	224.6/51.2	—	2,150	58.2	15.1	30.4	7.8
PBT	—	0	—	—	-/54.0	226.6/48.2	—	2,230	—	31.5	2.9	6.1
Blender												
PBT	A	1.1	—	—	-/52.0	222.9/34.3	—	2,040	52.6	17.9	37.2	9.7
OxaPhOxa												
PBT	B	0.6	—	—	-/51.0	219.9/30.7	—	1,980	53.5	16.2	39.6	34.5
OxaOxa												
PBT10Nip	—	—	Nip	10	-39.2/53.0	223.0/41.4	1–5	1,710	44.8	8.5	18.5	7.1
PBT10Nipox7	—	—	Nipox	10	-25.7/47.7	222.4/37.6	—	1,500	47.6	22.2	35.1	13.2
PBT10Nip	B	0.6	Nip	10	-38.4/52.1	219.9/33.2	0.5–3	1,380	35.4	14.9	36.0	12.6
OxaOxa												
PBT10Nipox7	B	0.6	Nipox	10	-25.1/47.7	220.1/31.5	—	1,340	43.0	22.1	41.4	15.3
OxaOxa												
PBT10Th	—	—	Th	10	-29.4/51.2	224.7/38.3	0.5–2	1,810	41.0	7.1	20.4	17.1
PBT10Thox6	—	—	Thox	10	-16.8/52.0	223.3/36.4	—	1,690	38.0	35.7	55.0	22.4
PBT10Th	B	0.6	Th	10	-29.5/50.5	219.4/32.1	0.3–1	1,650	37.6	9.4	35.8	30.5
OxaOxa												
PBT10Thox6	B	0.6	Thox	10	-19.5/50.5	219.1/30.5	—	1,560	35.5	36.1	76.8	62.7
OxaOxa												
PBT20Th	—	—	Th	20	-29.3/52.1	224.2/35.4	1–4	1,460	32.5	6.5	15.0	30.1
PBT20Thox6	—	—	Thox	20	-16.4/51.1	223.5/32.5	—	1,140	30.6	63.6	72.7	38.4
PBT20Th	B	0.6	Th	20	-29.0/51.3	221.1/28.5	0.5–2	1,370	31.9	8.9	31.3	115
OxaOxa												
PBT20Thox6	B	0.6	Thox	20	-19.7/51.2	220.9/28.3	—	1,100	29.4	59.9	140.7	190
OxaOxa												

<sup>a</sup> A: OxaPhOxa; B: OxaOxa.<sup>b</sup> Nip: Nipol®; Nipox: NipolOxa7; Th: Therban®; Thox: TherbanOxa6.<sup>c</sup> Glass transition temperature, determined by means of DSC.<sup>d</sup> Determined by means of DSC.<sup>e</sup> Determined by means of REM.<sup>f</sup> Notched Charpy impact strength.

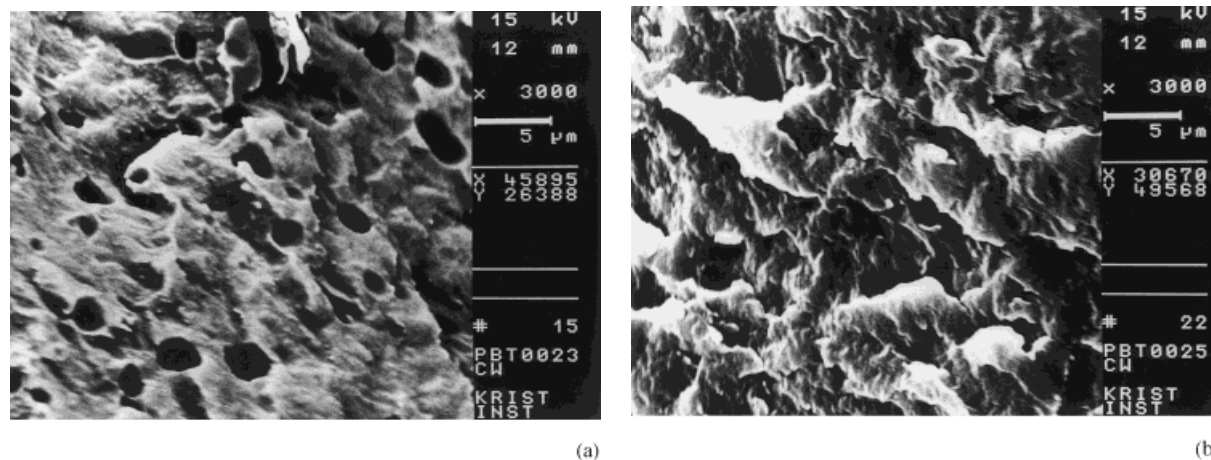


**Figure 1** PBT chain extended with OxaOxa and PBT blended together with nitrile rubber.

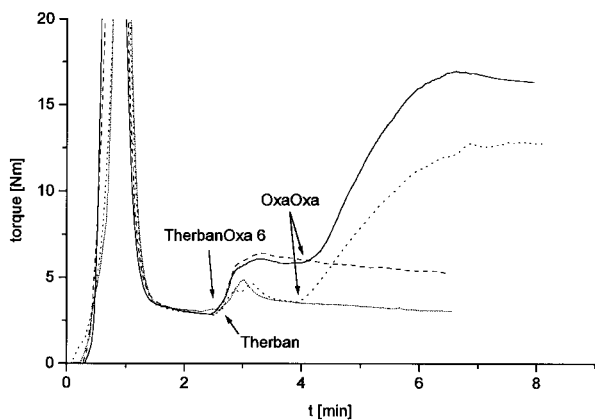
noncompatibilized Nipol is dispersed as a separate microphase of 1- to 5- $\mu\text{m}$  average diameter in the continuous PBT matrix. No such particles were visible when NipolOxa7 was used as blend component. However, DMA revealed two distinct  $T_g$ s of  $-39^\circ\text{C}$ , typical for nitrile rubber, and  $53^\circ\text{C}$ ,

typical for PBT. When oxazoline-functional NipolOxa7 was used, the nitrile rubber  $T_g$  was raised from  $-39^\circ\text{C}$  to  $-25^\circ\text{C}$ , whereas PBT  $T_g$  was lowered from  $53$  to  $48^\circ\text{C}$  and PBT melting temperature decreased by  $4^\circ\text{C}$ . The DMA clearly indicates that NipolOxa7 is much more compatible with PBT with respect to Nipol. This improved compatibility translates into the modified mechanical properties listed in Table II and displayed in Figure 1. For comparison, both nonfunctionalized and oxazoline-functionalized nitrile rubber were also combined with OxaOxa chain extender. Again oxazoline addition improved the properties of PBT after processing in the blender because chain scission was prevented. Notched Charpy impact strength improved when oxazoline was incorporated either into the nitrile rubber backbone or added as chain extender together with nitrile rubber. Decrease of Young's modulus is much larger for oxazoline-functional nitrile rubber with respect to nonfunctionalized nitrile rubber. However, the toughness improvement was only marginal, with highest toughness and best toughness/stiffness balance observed for PBT, chain-extended with OxaOxa without rubber addition. Therefore, compatibilized oxazoline-functionalized nitrile liquid rubbers are not suited as PBT toughening agents.

Similar results were obtained for PBT blends containing 10 and 20 wt % of high-molecular-weight poly(ethylene-*co*-butene-1-*co*-acrylonitrile) without (Therban) and with oxazoline functionality (TherbanOxa6). For comparison with both rubbers, OxaOxa was added as chain extender. According to torque measurement displayed in



**Figure 2** SEM images of fracture surfaces of PBT/Nipol (left) and PBT/NipolOxa7 (right).



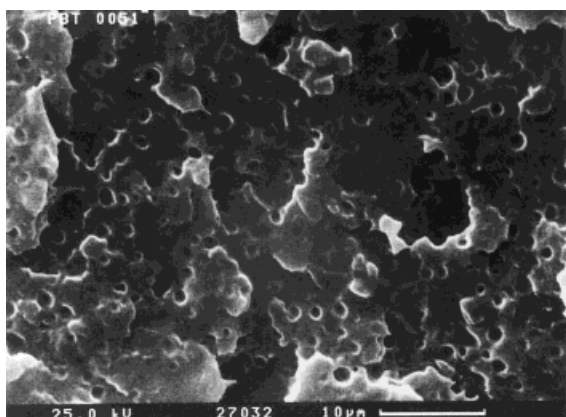
**Figure 3** Torque of PBT blends containing 10 wt % hydrogenated nitrile rubber: Therban (·····), Therban/OxaOxa (-·-·-), TherbanOxa6 (- - -), TherbanOxa6/OxaOxa (—).

Figure 3, the addition of oxazoline-functionalized rubber gave higher melt viscosities. Interestingly, for both rubber types, OxaOxa chain extender caused a substantial additional increase of melt viscosity. When the TherbanOxa6 content was increased to 20 wt %, this molecular weight increase was much more pronounced in the presence and absence of OxaOxa. While PBT/Therban (90/10) blends were soluble in phenol/tetrachloroethane (6/4), the corresponding PBT/TherbanOxa6 (90/10) blend contained gel fractions. This is experimental evidence for dynamic vulcanization of poly(ethylene-*co*-butene-1-*co*-acrylonitrile) where crosslinking takes place via reaction of oxazoline groups with carboxylate end groups of PBT.

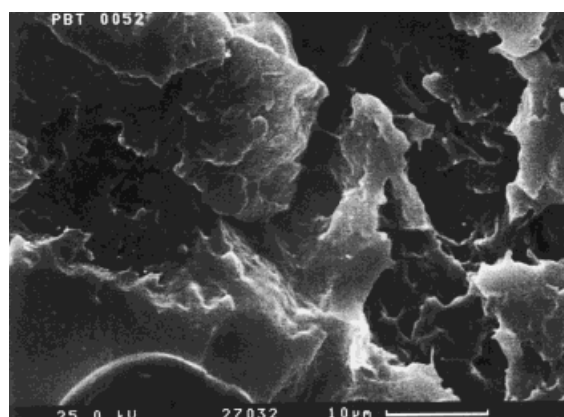
Fracture surface analyses of PBT blends with

Therban shown in Figure 4 shows dispersed rubber phase of average sizes of 0.5–2  $\mu\text{m}$  for blends containing 10 wt % Therban and 1–4  $\mu\text{m}$  for blends containing 20 wt % Therban. OxaOxa addition does not appear to influence morphology. Again, SEM was not able to reveal microphases corresponding to TherbanOxa6, although the DMA supports the evidence for the presence of two phases. As is apparent from the DMA traces in Figure 5, neither Therban nor TherbanOxa6 influence the glass transition of the PBT matrix. Also, the melting temperature of PBT was unchanged and decreased by 6°C when OxaOxa was added. However, the  $T_g$  corresponding to poly(ethylene-*co*-butene-1-*co*-acrylonitrile) was shifted from -29°C to -17°C and the intensity of the  $\tan \delta$  curve at the nitrile rubber phase transition also increased substantially. Most likely, PBT is incorporated into the nitrile rubber phase and accounts for dynamic vulcanization of the nitrile rubber during processing.

The mechanical properties of PBT/Therban and PBT/TherbanOxa are listed in Table II and graphically presented in Figure 6. Although Young's modulus, yield stress, and tensile strength decreased when nonfunctionalized and oxazoline-functionalized nitrile rubber was blended together with PBT, the oxazoline appeared to improve compatibility significantly. In contrast to low-molecular-weight Nipol and NipolOxa liquid rubbers, the high-molecular-weight poly(ethylene-*co*-butene-1-*co*-acrylonitrile) rubbers are much more effective as toughening agents. This is reflected by increased elongation at break and substantially improved notched



(a)



(b)

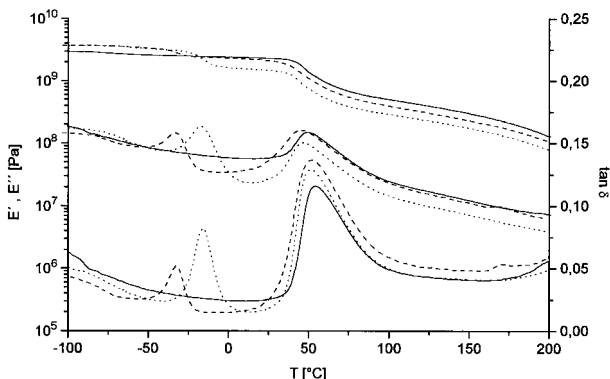
**Figure 4** SEM images of fracture surfaces of PBT blends containing 10 wt % Therban (left) or 10 wt % TherbanOxa6 (right).



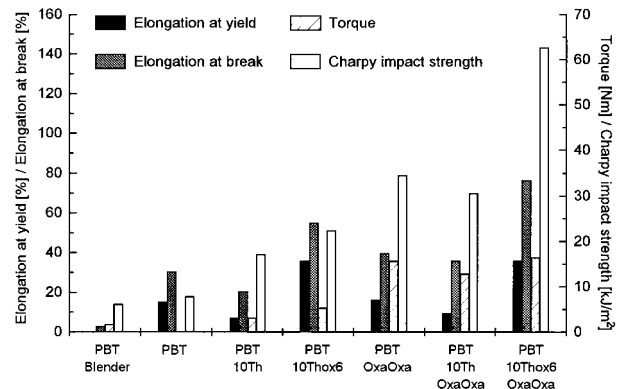
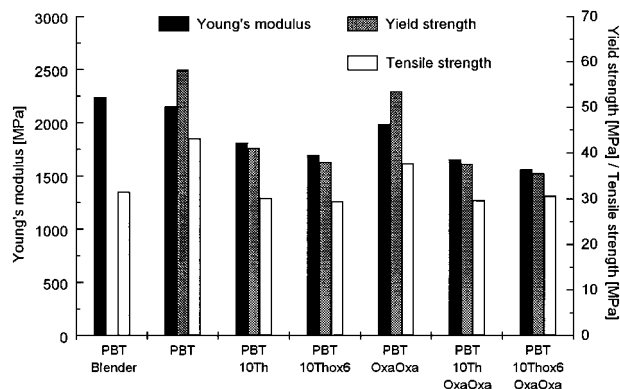
Charpy impact strength of  $200 \text{ kJ/m}^2$  corresponding to more than 30-fold increase with respect to PBT when TherbanOxa6 is used in conjunction with OxaOxa chain extender. All samples with impact strength larger than  $30 \text{ kJ/m}^2$  exhibit stress-whitening. In fact, very high impact resistance and efficient energy dissipation prevented breaking of the samples and propagating cracks were stopped within the samples.

## CONCLUSION

Oxazoline intermediates such as low-molecular-weight bisoxazoline chain extenders and high-molecular-weight oxazoline-functionalized nitrile rubbers are attractive blend components to modify properties of polyesters such as PBT. On the one hand, oxazoline coupling reaction with carboxylate end groups affords esteramide-coupled segmented polymers which are efficient compatibilizing agents, facilitating dispersion of the rubber in the polyester matrix. Moreover, the covalent esteramide bond formation at the rubber/polyester interface also affords excellent interfacial adhesion, which is an elementary requirement for efficient stress transfer between microphases. Since the oxazoline-functionalized poly(ethylene-*co*-butene-1-*co*-acrylonitrile) contains more than one oxazoline group per chain, the PBT-dicarboxylic acids can crosslink the oxazoline-functional rubber during processing. Most likely, part of the nitrile rubber is also incorporated into the polyester matrix, thus promoting the possibility for entanglements. When, simultaneously, the molecular weight of the polyester matrix is built up by chain-extending polyester with



**Figure 5** Dynamic mechanical analysis of PBT (—) and PBT blends containing 20 wt % Therban (---) or 20 wt % TherbanOxa6 (· · · · ·).



**Figure 6** Mechanical properties of PBT and PBT blends containing 10 wt % Therban or TherbanOxa6, respectively, and also corresponding blends with OxaOxa chain extender.

bisoxazolines such as OxaOxa, impact resistance is enhanced by more than one order of magnitude. In conclusion, oxazolines are very versatile intermediates which give excellent control on morphology development and help to improve plastic deformation processes which contribute to energy dissipation during impact. Oxazoline intermediates can be tailored to meet the demands of reactive blending applications.

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