PET/PC Blends: Effect of Chain Extender and Impact Strength Modifier on Their Structure and Properties

S. S. Pesetskii,¹ B. Jurkowski,² O. V. Filimonov,³ V. N. Koval,¹ V. V. Golubovich¹

¹Department of Technology of Polymeric Composite Materials and Particles, V.A. Belyi Metal-Polymer Research Institute of National Academy of Sciences of Belarus, 32a Kirov Street, Gomel 246050, Republic of Belarus ²Plastic and Rubber Processing Division, Institute of Materials Technology, Poznan University of Technology, Piotrowo 3, 60-950, Poznan, Poland ³MFK Chemical Corporation, Works on processing of repeated resources, 29, Lazarenko St., Mogilev 212009, Republic

"MFK Chemical Corporation, Works on processing of repeated resources, 29, Lazarenko St., Mogilev 212009, Republic of Belarus

Received 27 November 2009; accepted 25 March 2010 DOI 10.1002/app.32532 Published online 21 July 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Methylene diphenyl diisocyanate (MDI) affects the morphology, rheological, mechanical, and relaxation properties, as well as tendency to crystallize of PET in PET/PC/(PP/EPDM) ternary blends produced by the reactive extrusion. Irrespective of the blend phase structure, the introduction of MDI increases the melt viscosity (MFI dropped), resulting from an increase in the molecular weight of the polymer chains; the PET crystallinity was also reduced. MDI favors compatibility of PET with PC in PET/PC/(PP/EPDM) blends. This is explained by intensified interphase interactions on the level of segments of macromolecules as well as monomer units. The presence of MDI causes a substantial rise in the dynamic shear modulus within the high-elastic region of PET (for temperature range between $T_{g,PET}$ and that of PET cold crystallization); the processes of PET cold crystallization and melt crystallization become retarded; the glass-transition tem-

INTRODUCTION

PET is considered as one of the most important engineering polymers. Despite the fact that its major fields of application are fibers, films, and containers for packing, more and more attention has been paid to finding next spheres for its application, including various engineering composites also those in which post-consumer and industrial wastes are used.^{1–3}

Representatives of such materials are PET/PC blends; their development and study have caused much interest.^{4–8} PET added to PC makes the latter more resistant to organic solvents, provides an opportunity to control the flow viscosity of the molten blend, and reduces the material's cost. PC is helpful in increasing PET's impact strength and improves dimen-

peratures for PET and PC become closer to each other. MDI affects insignificantly the blend morphology or the character of interactions between the disperse PP/EPDM blend and PET/PC as a matrix. PP/EPDM reduces the intensity of interphase interactions in a PET/PC/(PP/ EPDM), but a rise in the degree of material heterogeneity. MDI does not change the mechanism of impact breakdown in the ternary blends mentioned above. Increased impact strength of MDI-modified materials can be explained by higher cohesive strength and resistance to shear flow at impact loading. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 225–234, 2011

Key words: poly(ethylene terephthalate); polycarbonate; chain extender; impact strength modifier; reactive extrusion; compatibility; interphase adhesion; crystallization; hydrolysis

sional stability under operating conditions. PET/PC blends show active interphase interactions, which allows them to be referred to as partly compatible.^{4,9} Improved compatibility of PET and PC in their binary blends results, probably, from transesterification and the interchange reaction, which can also take place between the components (ester-ester) during melt processing at blending of components in the melt.^{10,11}

Nevertheless, melt blending of PET and PC usually results in a two-phase mixture.^{12–14} However, interphase adhesion in mixtures and formation of a "quasi-homogeneous" morphology⁴ reduce the PET/ PC impact strength, which makes them impossible to be considered as impact-resistant materials at temperatures below PET-glass-transition, $T_{g, \text{PET}}$. Only between $T_{g, \text{PET}}$ and $T_{g, \text{PC}}$, the blends show an increased resistance to impact failure and can be considered impact-resistant materials. The reason for this is dissipation of energy of crack propagation in the PET-amorphous phase when PET is in a highelastic state.⁴ For practical applications, therefore, most suitable are PET/PC blends containing impact strength modifiers (ISM).^{9,15}

Correspondence to: B. Jurkowski (BoleslawJurkowski@put. Poznan.pl).

Contract grant sponsor: Fund for Fundamental Research of Belarus; contract grant number: T07A3-0003.

Journal of Applied Polymer Science, Vol. 119, 225–234 (2011) © 2010 Wiley Periodicals, Inc.

Another problem, at compounding and processing of PET/PC molten blends, is to prevent hydrolytic and thermal degradation of polyesters being blended. This problem results, first of all, from the fact they are usually processed at 270°C or higher because PET's melting temperature is high; at this temperature the rate of reactions leading to degradation is extremely high.¹⁶ Such degradation causes reduction in the molecular weight and thermal stability, and decreases mechanical properties, which reduce the possibility of reprocessing of polyester materials.³

Completion of polycondensation processes that run in a solid phase above $T_{g, \text{PET}}$, but below PET's melting temperature, $T_{m \text{ PET}}$, is one of the ways to prevent a negative effect of macromolecular breakdown on the properties of polycondensation thermoplastics, among them PET and PC.^{2,11–21} High technological expenses required for solid-state additional polycondensation, however, make reprocessing of raw polyester materials unprofitable by this method.

In the recent 20 years, alternative technologies have been developing for polyesters modification; they have essential advantages against solid-state additional polycondensation. These technologies are based on chemical transformations of the polymer chains in molten polyesters; such transformations take place after some bi- or multifunctional chemical compounds have been introduced that act as chain extender (CE).²²⁻²⁸ CEs interact mostly with functional end groups of polyester and link them with one another; the molecular weight does not become lower, it somewhat becomes higher. The interactions of the polymer with CE have been found effective if run in the melt using the reactor-extruder.^{17,29,30} A vacuum treatment and special catalysts is usually employed.31

A similar technology realized using extruders becomes economically advantageous for processing polyester materials. Its capabilities, however, have been investigated mainly for certain types of polyesters or their binary blends.

The effectiveness of MDI as a CE for PET/PC binary blends has been reported elsewhere.⁵ It has been found that MDI may lead to PET/PC copolymers, improve components compatibility and decelerate PET crystallization in the blend. There has been observed some rise in the material impact strength. That work described only PET/PC-30 wt % blended composition in which PET made the disperse phase. The MDI concentration was varied between 0.1 and 1.0 wt %. MDI concentrations between 0.9 and 1.0 wt % were found to give a maximum effect in raising the molecular weight of the components' in blend along with improvements in other properties. It was of interest to understand the role of MDI as CEs in PET/PC blends of a more complex composition that contain ISMs besides the basic components. Another aim was to establish how the phase structure of a blend affects efficiency of modifiers, structural features, and mechanical properties of material when ISM and CE were introduced jointly.

EXPERIMENTAL

Materials and sample preparation

One basic component was PET produced commercially at Mogilev Khimvolokno (Khimvolokno Comp., (Grade Mogilev/Belarus), Belarus PET-8200), designed to make bottles for soft drinks or other types of packages; intrinsic viscosity, 0.882 dL/g; concentration of end carboxyl groups, 22.8 mmol/kg; glass-transition temperature, $T_{g,PET} = 76.5^{\circ}$ C, and solubility parameter 21.2 (J/cm³)^{0.5} (here and below the solubility parameter values have been calculated from the chemical structure of the elementary units of macromolecules).³² Another basic component was PC produced at Zarya, Volgograd/Russia [molecular weight ≈ 35 kg/mol; $T_{g,PC} = 144.5^{\circ}C$, solubility parameter, 19.4 (J/ cm³)^{0.5}]. ISM was an elastomer like PP/EPDM based on a blend of polypropylene and ethylene-propylenediene rubber (solubility parameter, $\approx 16.8 \text{ (J/cm}^3)^{0.5}$, melting temperature of the polypropylene component, $T_{m,PP} = 165^{\circ}C$; crystallization temperature, $T_{cr,PP} =$ 110.5°C; $MFI = 2.8 \text{ g}/10 \text{ min at } T = 190^{\circ}\text{C}, P = 21.6 \text{ N},$ $D_c = 2.095$ mm; tensile strength, 17 MPa; relative elongation at break, 600%; glass-transition temperature, T_{g} = -39° C (elastomeric phase) and T_{g2} = -2° C (PP-component)), Figure 1.

The PP/EPDM concentration in all of the compositions tested was constant, 5 wt %. The CE, as in an earlier work,⁵ was chemically pure MDI (OCN– C_6H_4 – CH_2 – C_6H_4 –OCN, molecular weight, 250 g/mole; solubility parameter, 22.0 (J/cm³)^{0.5}; the NCO



Figure 1 Temperature dependences of mechanical loss tangent (tan δ) and dynamic shear modulus (*G*') for PP/ EPDM.

TABLE I Compositions of Test Materials

Composition No.	Components and their concentration (wt %)
1	PET
2	PC
3	PET/PC – 25%
4	PET/PC - 50%
5	PET/PC – 75%
6	PET/PC – 25%/(PP/EPDM) – 5%
7	PET/PC = 50%/(PP/EPDM) = 5%
8	PET/PC - 75%/(PP/EPDM) - 5%
9	PET/PC - 25%/(PP/EPDM) - 5%/MDI - 1%
10	PET/PC - 50%/(PP/EPDM) - 5%/MDI - 1%
11	PET/PC - 75%/(PP/EPDM) - 5%/MDI - 1%

concentration, 33.6 wt %; density, 1.2 g/cm³; boiling point, 314°C); its concentration was constant, 1 wt %. The compositions of the test materials are listed in Table I.

Both binary and modified blends have been compounded using the extrusion-granulating line based on the twin-screw extruder TSK-35/40 (China); screw diameter 35 mm; L/D = 40; 10 heating zones; one zone for vacuum treatment. The melt temperature in the extrusion zone was 265°C.

To measure mechanical properties of the test materials, samples were injection molded on machine EN-30 (Taiwan); screw diameter, 35 mm; shot volume, 30 cm³. The mold temperature was set at 40° C.

The investigation by relaxation spectrometry was performed on test samples as bars measuring 50 mm \times 5 mm \times 1 mm. They were prepared on the laboratory injection molding machine of plunger type with a shot volume of 2.5 cm³. The mold temperature was 40°C. The central part of plates was also used to prepare samples for testing by the differential scanning calorimetry (DSC) technique .

Granulated components dried to residual moisture content below 0.02% were used to compound the blend materials and make test samples.

Characterization

The mechanical properties of materials under tensile stresses have been determined using dog-bone samples with a neck measuring 50 mm × 5 mm × 3 mm and the Instron 5657 testing machine (Great Britain). The Charpy impact strength has been measured on sharply notched samples as bars in a size of 80 mm × 10 mm × 4 mm using the pendulum hammer PSW-1.5 (Germany). The rheological properties of the melts were judged by *MFI*-values found at *T* = 265°C, *P* = 21.6 N; *D*_c = 2.095 mm (instrument IIRT-AM, Russia).

The structural morphology of the materials was learned from SEM micrographs taken of fractured surface of the central part of the bars after they had been exposed in liquid nitrogen for 30 min. The scanning electron microscope was VEGA II LSH (Czech Republic). The same microscope was also employed for analyzing the failure mode of the bars tested on the pendulum hammer device for impact strength at T = 23°C. SEM micrographs were taken of the notched central part of the working area of bars. The DSC was performed using the instrument DSM-10M (Russia) at a heating/cooling rate of 16°C/min; the weighed samples were 10 mg each.

The dynamic mechanical (relaxation) properties of the materials have been understood in terms of analysis of temperature dependences of mechanical loss tangent (tan δ) and dynamic modulus of samples under shear stresses (*G'*). The tests were conducted similar to other works^{4,33} making use of the reverse torsion pendulum designed at MPRI NAS (Belarus); the pendulum frequency was 1 Hz. The measurement accuracy of temperatures was 0.1°C, that of tan δ , ±3%; and *G'*, ±1%.

The resistance of materials to hydrolysis was found from analyzes of variations in *MFI*-values after the granules of materials under discussion had been soaked in water at 95°C for a definite span of time. *MFI*-values have been measured at $T = 265^{\circ}$ C, P = 21.6 N; $D_c = 2.095$ mm.

RESULTS AND DISCUSSION

Mechanical and rheological properties of the blend

The properties of blends, containing PP/EPDM much differ from properties of PET/PC binary

		TABLE	II	
Mechanical	and	Rheological	Properties	of Materials

Composition No.	MFI (g/10 min)	σ _{HF} (MPa)	σ _{LF} (MPa)	K _{wf} (%)	ε _r (%)	a (кJ/m²)
1	23.0	55	30	100	232	7.4
2	6.1	68	53	98	126	16.6
3	16.9	59	38	97	242	8.7
4	12.5	62	43	97	187	9.9
5	9.8	64	46	98	143	11.7
6	22.1	53	34	87	180	17.7
7	17.0	55	38	84	140	19.6
8	13.3	56	42	86	146	48.3
9	18.0	54	35	95	214	19.0
10	14.1	56	39	94	142	21.4
11	11.2	54	43	90	150	49.5

Here and in subsequent Tables and Figures materials markings are as in Table I; σ_{HF} , σ_{LF} , and ε_r are high and low flow limits, and relative elongation at break, respectively; K_{wf} is weld flow strength coefficient of the weld (melt) flows at injection molding found from expression: $K_{\text{wf}} = \sigma_{\text{HF2}}/\sigma_{\text{HF1}}\cdot100\%$, where σ_{HF1} and σ_{HF2} are, respectively, high flow limit for injection molded the dog-bone samples made by injection at one end and at two ends; *a* is Charpy impact strength measured on sharp-V-notched samples at 23°C.

OOOO6OOO6OOO7OOO8OOO10OOO20 μm20 μmOO

Figure 2 SEM micrographs of impact fractured blend surfaces at 23°C.

blends (Table II). Binary blends are characterized by higher strengths and strength coefficients of weld flows, K_{wf} , approaching 100% at injection molding. However, they show a much lower value of impact strength (*a*) for the notched samples.

Properties of PET/PC/(PP/EPDM) - blends altered noticeably after MDI-1 wt % had been added, irrespective of the phase structure. It should be mentioned that in PET/PC blends containing PC-25 wt %, PET creates the disperse medium; with PC-50 wt %, there exist two continuous phases - PET and PC; whereas with PC-75 wt %, PC makes the disperse medium in the blend.⁹ Blends modified with MDI have a somewhat higher level of mechanical properties — $\sigma_{\rm HF}$, $\sigma_{\rm LF}$, ε_r , and a — against ternary blends, Table II. There is a fall in MFI-values for all of the compositions. This fact is indicative of MDI-efficiency as a CE in the blends under consideration.⁵ Consequently, the absence of PP/EPDM in PET/PC blends is not harmful for MDI activity as a CE for polyester materials. It is worth noting that despite a lower MFI (higher melt viscosity), MDImodified blends show a higher K_{wf} . As this property much depend on both the melt viscosity and inten-

Journal of Applied Polymer Science DOI 10.1002/app

sity of adhesional interactions between the phases in thermodynamically immiscible (or partly miscible) polymers, it can be assumed that MDI decreases *MFI* and intensifies interphase adhesion in PET/PC blends leading to better components miscibility.

The analysis of dependence between impact strength and composition, Table II, has shown that MDI raises a-values irrespective of the phase structure of blends. According to SEM findings, Figure 2, the failure character of samples under impact loading does not virtually change with addition of MDI: the appearance of failed surfaces changed negligibly - independently of *a*-values. Folds appear on the fractured surface, which is typical of materials that fail by the shear flow mechanism.⁴ These folds are formed by the quasi-homogeneous PET and PC phase; ISM (PP/EPDM phase) in the fracture zone becomes agglomerated into spherulite-like particles having the size of tenths of a micrometer up to several micrometers. It is clear that ISM particles do not break-down by crack propagation.

The whitened zone resulting from multiple crazes generated by impact loading occupies only a small area ($\leq 10\%$) of the fractured surface. In view of this,



Figure 3 DSC-curves for polyester materials: (a) heated and (b) cooled samples.

it can be assumed that failure follows the mechanism of shear flow and not multiple crazing.^{4,33} Consequently, enhanced impact strength of the blends containing MDI results, probably, from enhanced mechanical strength and resistance of PET/PC blend matrix to shearing strain. PP/EPDM-particles dispersed in the blend matrix volume favor dissipation of impact failure energy, also at the expense of a larger area of the fractured surface.

Differential scanning calorimetry

Mechanical properties of PET-based blend materials largely depend on crystallizing tendency of PET. A higher rate of its crystallization and higher crystallinity may reduce blend plasticity as well as impact strength.⁴

Figure 3 and Table III show analytical results on PET crystallizability in tested blend materials against neat polyester. The main finding is that MDI in a blend decelerates the crystallization rate and decreases crystallinity of PET in ternary blends. The extent to which MDI affects PET crystallizing tendency depend on blend composition: the higher PC concentration, the greater the role of MDI. This can be explained by the fact that in PET/PC/(PP/ EPDM) ternary blends, PET undergoes slower crystallization - compared with neat polyester - owing to its interactions with PC.4 The growing effect of MDI upon PET crystallizability with increasing PC concentration in PET/PC/(PP/EPDM) ternary blends is indicative of preferential interactions of MDI with PET macromolecules, and not with PC. A reason for this may be not only a higher reactivity of PET-end groups toward MDI,34 but also improved solubility of MDI in PET, in contrast with PC (because of higher PC melt viscosity and greater difference in solubility parameters between PC and MDI than between PET and MDI). That is why, with increasing PC concentration in a blend, diisocyanate concentration in PET-phase increases.

The influence of MDI in PET crystallization becomes clear when the DSC-curves of heating/cooling procedure have been analyzed, Figure 3, TableIII. The PET cold crystallization temperature rises by 3–9°C with respect to the ratio of basic components; when crystallized from the melt, the extent of melt overcooling is 12.3–19.2°C to ensure PET crystallization. The crystallinity drops 1.1–2.1 times, Table III.

It should be mentioned that MDI little affects $T_{m,PET}$ — values, which evidences to unchanged crystallization mechanism for PET in the tested materials. In PET/PC binary blends, PET's crystallization also somewhat decelerates against ternary blends, PET/PC/(PP/EPDM). A reason for this may be

TABLE III DSC-Results Obtained for Polyester Materials

				5				
Composition No	Cold crystallization at heating		Melting		Crystallization at melt cooling			
	$T_{c,\mathrm{cr}}$ (°C)	$\Delta H_{c,cr} (J/g)$	T_m (°C)	$\Delta H_m (J/g)$	$T_{\rm cr}$ (°C)	$\Delta H_{\rm cr}$ (J/g)	α (%)	
1	130.4	28.2	253.3	44.1	194.4	27.7	11.0	
3	144.9	8.0	251.1	26.6	177.4	32.7	17.2	
4	145.2	6.3	248.6	17.8	168.7	15.5	16.0	
5	148.1	1.9	249.5	7.6	170.0	13.8	16.0	
6	139.5	15.5	251	25.2	177.8	25.9	9.5	
7	143.6	13.1	252.8	18.8	182.3	25.8	8.2	
8	139.0	7.4	249.5	9.2	179.9	8.6	5.5	
9	145.3	12.0	250	21.1	165.5	29.3	8.9	
10	146.6	10.8	248.9	13.4	169.0	14.5	3.9	
11	148.0	4.5	252.5	5.7	160.7	8.5	3.4	

Crystallinity $\alpha = (\Delta H_m - \Delta H_{c_c \text{ cr}})\dot{c}100\%/(k\cdot\Delta H_m^*)$, where ΔH_m is latent melting heat; $\Delta H_{\alpha,\text{cr}}$ is latent heat of cold crystallization, $\Delta H_m^* = 144.664 \text{ J/g}$ is latent melting heat for 100%-crystallinity PET; *k* is PET content in material, wt parts.

plasticization caused by PP/EPDM. $T_{m,PP/EPDM}$ is 165°C, which is lower than $T_{cr,PET}$ in the blends. Very likely, that PP/EPDM melt being incompatible with any of the basic components of the blend — owing to a great difference in solubility parameters — gets concentrated in zones of interphase contact and promotes PET-higher molecular mobility, thus making PET crystallize easier in ternary blends than in binary ones.

It can be concluded, therefore, that in MDI-modified blends diisocyanate acts as a CE and increases PET's molecular weight; also it evidently helps to form copolymers by interacting with chain end groups of PET and PC.⁵ As a result, molecular mobility of PET becomes restricted, and its crystallization is decelerated. Addition of MDI to PET/PC/ (PP/EPDM) ternary blends can be one of the effective ways to make PET amorphous in blend materials.

Dynamic mechanical properties and interphase events in blends

The relaxation spectrometry technique appears useful for studying changes in dynamic mechanical properties of blends over a wide temperature range for obtaining experimental data that could show compatibility as well as specificity of interphase interactions in the blends.^{4,9,33–36}

The analysis of Figure 4 and Table IV has allowed to make important inferences about the MDI effect on relaxation behavior, compatibility, and interphase interactions in PET/PC/(PP/EPDM) ternary blends.

For example, Table IV shows that addition of MDI causes values of $T_{g, \text{PET}}$ and $T_{g, \text{PC}}$ to approach each other. A decrease in ΔT_g results mainly at the expense of lower $T_{g, \text{PC}}$ and not of higher $T_{g, \text{PET}}$. This can be explained by enhanced components compatibility because of MDI and by the fact that PET-amorphous phase has plasticized PC, because PET has lower T_g -values.

It is important to note that the glass-transition temperature (T_g) values, determined with the reverse torsion pendulum device, characterize the temperature of mechanical glass-transition.³⁵ Temperature values of the mechanical glass-transition are always somewhat higher than those of the structural glass-transition, which in their turn depend on the heating/cooling rate of the sample. The temperature values of the mechanical or structural glass-transition may be equally used in comparative testing of identical samples under identical thermal conditions.³⁵

On introducing MDI, the values of the main maximum of β -relaxation shift noticeably (by 3.5 to 5.4°C) to the lower-temperature region. The kink in the peak maximum of β -relaxation at T = -40°C follows from superposition of PP/EPDM elastomeric phase

glass-transition on β-relaxation in basic components of the blend ($T_{g, PP/EPDM} = -39^{\circ}$ C, Figure 1). This is supported by the fact that no kinks have been observed in temperature dependences of tan δ for PET/PC binary blends. The shift of T_{β} -values to the lower-temperature region (toward $T_{g, PC}$) for MDIcontaining blends, unlike that for PET/PC/(PP/ EPDM) ternary blends, is indicative of intensified interphase interactions at the level of monomer units caused by diisocyanate. Lower T_{β} -values predetermine a possibility for designing more frost-resistant materials — with lower brittleness temperature based on MDI-modified blends.

As MDI causes a strong effect on location of the glass-transition peak for basic blend components (PET and PC), it is quite evident that diisocyanate in the tested blends affects interphase interactions at the level of polymer chain units, along with segmental interactions that are of cooperative nature.

The most important consequence of MDI in PET/ PC/(PP/EPDM) ternary blends is much higher dynamic shear modulus in the region where PET is in a high-elastic state (between $T_{g, \text{PET}}$ and PET cold crystallization temperature in the blend being $\approx 120^{\circ}$ C). For quantative estimation of this effect, Table IV lists $\Delta G'_{100}$ -values approximately equal to G'-values of the materials when PET undergoes devitrification in the blends.

After PET has undergone devitrification and blend is heated up to $\approx 120^{\circ}$ C, the PET-amorphous phase undergoes cold crystallization, which leads to higher values of G', Figure 4(b,d,f,h); Table IV. The addition of MDI to the blend material causes sharp deceleration in PET cold crystallization down to its complete suppression in PET/PC - 75%/(PP/EPDM) - 5%/MDI - 1%; for this blend $\Delta G'_{CC} = 0$, Table. III. Higher values of $\Delta G'_{100}$ result evidently from intensified interphase (segmental) interactions between amorphous PC and amorphous phase of devitrified PET. It is because of increased interphase adhesion, along with reciprocal partial components dissolution - which restricts segmental mobility — that PET cold crystallization in MDI-containing blends becomes retarded (or suppressed). Earlier works9,37,38 had reported about decisive influence of segmental mobility on crystallizability of partly crystalline thermoplastics.

The data analysis of Figure 4 and Table IV shows that PP/EPDM weakens the interphase interactions in PET/PC blends: ΔT_g for binary blends are much lower than those for ternary ones; besides, T_β for binary blends are shifted by 1.7 to 3.2°C to the lowertemperature region (closer to $T_{\beta, PC}$). This results in enhanced impact strength of ternary blends against binary ones. Binary blends of thermoplastics with strong interphase interactions have quasi-homogeneous structure and cannot dissipate energy under impact stresses.^{4,9}



Figure 4 Temperature dependences of tan δ and *G*' for PET and PC (a, b), and blends containing PC-25 wt % (c,d); 5 wt % (e,f), and 75 wt % (g,h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Structural morphology

Fracture of samples of the blend materials was done under liquid nitrogen; next SEM micrographs were analyzed to see that morphologically all of the blends looked identical. PP/EPDM forms spherical particles in the PET/PC quasi-homogeneous matrix; the particle size varies from fractions of a micrometer to 3 to 4 μ m.

Journal of Applied Polymer Science DOI 10.1002/app

TABLE IV	
Parameters Characterizing Relaxation Properties of Polyester Materials	
	-

Composition No.	$T_{g, \text{ PET}}$ (°C)	$T_{g, PC}$ (°C)	ΔT_g (°C)	T_{β} (°C)	G'_{100} (MPa)	$\Delta G'_{\rm CC}$ (MPa)
1	76.5			-61.3	8	82
2		144.5		-87.28	795	
3	75,6	132.3	56.7	-71,0	107	52
4	76,6	136.2	59.6	-72,8	311	45
5	77,1	138.4	61.3	-80,0	473	0
6	76.8	141.0	64.2	-66.8	43	93
7	78.0	141.2	63.2	-71.7	136	166
8	77.6	141.6	64.0	-76.9	308	84
9	74.3	132.0	57.7	-70.4	65	60
10	78.0	135.0	57.0	-74.2	158	59
11	78.2	138.0	59.8	-82.3	437	0

 $\Delta T_g = T_{g,PC} - T_{g,PET}$; T_β is temperature of main maximum in β -relaxation temperature region; G' is dynamic shear modulus at 100°C; $\Delta G'_{CC}$ is increase in G'-values against G'_{100} caused by PET cold crystallization.



Figure 5 SEM micrographs of fractured surfaced of blend samples after they had been cooled in liquid nitrogen. *Journal of Applied Polymer Science* DOI 10.1002/app

TABLE V Effect of Blend Soaking in 950°C – Water on MFI Variation						
$\begin{array}{rl} MFI, g/10 \mbox{ min } (T=265^{\circ}\text{C}; P=21.6 \mbox{ M}\\ \mbox{ capillary, } 2.095 \mbox{ mm) } \mbox{ versust}_{H_2O}, \mbox{ day}\\ \mbox{ (1 } \mbox{ day}=24 \mbox{ h}) \end{array}$						
No.	0	2	6	15		
6	22	18	23	24		
7	17	15	22	23		
8	13	12	14	15		
9	18	13	19	20		
10	14	13	18	18		
11	11	10	13	13		

There are few larger particles. No traces of foreign matter are present on PP/EPDM particles, which means an absence of strong interactions between the modifier of impact strength and the blend matrix-PET/PC – irrespective of type and phase structure of the blend. Consequently, MDI mostly modifies the basic components of PET/PC matrix and not PP/EPDM or its interactions with the polyester matrix.

Effect of MDI on resistance of polyester blends to hydrolysis

Table V lists the estimated data on the effect of water soaking at 95°C on MFI for ternary and MDI-modified polyester blends.

It is clear that at an early stage of hydrolysis (τ_{H_2O} = 2 days) MDI decreased somewhat independently of blend composition. One of the causes is that water washes out the low-molecular-weight products from the bulk material. *MFI*-values rose with longer τ_{H_2O} . This is explained by hydrolytic degradation of polyester (evidently, mostly PET). *MFI*-values for MDIcontaining compositions are lower than those for MDI-free materials irrespective of hydrolysis duration. This observation is explained by an increased resistance to hydrolysis of MDI-modified blends.

CONCLUSIONS

Reactive blending of PET, PC, and PP/EPDM-5 wt % (used as ISM) plus MDI-1 wt % causes considerable variations in molecular structure and major properties of resultant materials.

Irrespective of the blend phase structure, MDI rises melt viscosity (decreases *MFI*-values) of materials, which is explained by increased molecular weight of the chains and, probably, by PET-PC copolymers formed, as well as by decelerated crystallization and decreased crystallinity of PET. MDI favors better compatibility of PET with PC in PET/PC/(PP/EPDM) ternary blends. This results from intensified interphase interactions at the level of ele-

mentary units of the polymer chains along with segmental interactions, which are of cooperative nature. MDI causes the dynamic shear modulus to rise in the PET high-elastic region (between $T_{g,PET}$ and PET cold crystallization temperature); PET cold crystallization proceeds at a slower rate as well as its melt crystallization; glass-transition temperatures of PET and PC come nearer to each other. MDI doesn't change much the blend morphology or character of interactions between PP/EPDM disperse phase and PET/PC blend matrix.

PP/EPDM, when in PET/PC/(PP/EPDM) ternary blends, makes the interphase interactions less intensive and increases heterogeneity of the material unlike the case with PET/PC binary blends. MDI does not change the impact failure mechanism for ternary systems. Enhanced impact strength of MDImodified materials comes from higher cohesion strength and resistance to shear flow. MDI-modified blends show increased resistance to hydrolysis at temperatures close to the water boiling point, irrespective of their phase structure.

References

- 1. Awaja, F.; Pavel, D. Eur Polym J 2005, 41, 1453.
- Scheirs, J. Polymer recycling, Science, Technology and Application; Wiley: Chichester, 1998
- 3. Karger-Kocsis, J. Handbook of Thermoplastic Polyesters, Fakirov, S., Ed.; Wiley-VCH: Weinheim, 2002; Vol. 2, Chapter 28, p 1291.
- Pesetskii, S. S.; Jurkowski, B.; Koval, V. N. J Appl Polym Sci 2002, 84, 1277.
- 5. Tang, X.; Guo, W.; Yin, G.; Li, B.; Wu, G. J Appl Polym Sci 2007, 104, 2602.
- 6. Samious, C. K.; Kalfoglou, N. K. Polymer 2000, 41, 5759.
- 7. Lee, S.-S.; Jeong, H. M.; Jho, J. Y.; Ahn, T. O. Polymer 2000, 41, 1773.
- 8. Kong, Y.; Hay, J. N. Polymer 2002, 43, 1805.
- 9. Pol, D.; Newman, S. Polymer Blends; Academic Press: New York, San Francisco, London, 1979.
- Wang, L.-H.; Zhihua, H.; Tienxie, H.; Porter, R. S. Macromol Sci 1990, 29, 155.
- 11. Kim, W. N.; Burns, C. M. J Appl Polym Sci 1990, 28, 1409.
- 12. Tan, Q.; Ma, D. Z. J Appl Polym Sci 1993, 48, 747.
- Wu, J. S.; Mai, Y. W.; Cotterell, B. J. Mater Sci 1993, 28, 3373.
- 14. Liao, Z. L.; Chang, F. C. J Appl Polym Sci 1994, 62, 1115.
- 15. Pesetskii, S. S.; Koval, V. N.; Starzhynsky, V. E. Rus. Pat. 2,028,335 (1992).
- 16. Zimmerman, H. Polym Eng Sci 1980, 20, 680.
- 17. Shima, T.; Vrasaki, T.; Oka, I. Adv Chem Sci 1973, 128, 183.
- Buxbaum, L. H. J Appl Polym Sci: Appl Polym Symp 1979, 35, 59.
- Gao, Q.; Nan-Xun, H.; Zhi-Lian, T.; Gerking, I. Chem Eng Sci 1997, 52, 371.
- Karayannidis, G. P.; Kokkalas, D.; Bikiaris, D. J Appl Polym Sci 1993, 50, 2135.
- Karayannidis, G. P.; Kokkalas, D.; Bikiaris, D. J Appl Polym Sci 1995, 56, 405.
- 22. Nata, H.; Matsumura, S. J. Appl Polym Sci 1985, 30, 3325.

- 23. Nata, H.; Matsumura, S. J. Appl Polym Sci 1987, 32, 5193.
- 24. Nata, H.; Matsumura, S. J. Appl Polym Sci 1986, 32, 4581.
- 25. Nata, H.; Matsumura, S. J. Appl Polym Sci 1987, 33, 3069.
- 26. Japon, S.; Boogh, L.; Leterrier, Y.; Manson, J.-A. E. Polymer 2000, 41, 5809.
- 27. Villalobos, M.; Awojulu, A.; Greeley, T.; Turco, G.; Deeter, G. Energy 2006, 31, 3227.
- Haralabakopoulos, A. A.; Tsiourvas, D.; Paleos, C. M. J Appl Polym Sci 1999, 71, 2121.
- 29. Bikiaris, D. N.; Karayannidis, G. P. J Appl Polym Sci 1996, 60, 55.
- Bikiaris, D. N.; Karayannidis, G. P. J Polym Sci Part A: Polym Chem 1995, 34, 1337.
- 31. Nata, H.; Matsumura, S. J Appl Polym Sci 1987, 34, 2609.

- Matveev, Y. I.; Askadsky, A. A. Chemical Structure and Physical Properties of Polymers; Khimia: Moscow, 1983 (in Russian).
- Pesetskii, S. S.; Jurkowski, B.; Koval, V. N.; Storozhuk, I. P. J Appl Polym Sci 1999, 73, 1823.
- Torres, N.; Robin, J. J.; Boutevin, B. J Appl Polym Sci 2004, 79, 1816.
- 35. Bartenev, G. M.; Barteneva, A. G. Relaxation Spectroscopy of Polymers; Khimia: Moscow, 1992 (in Russian).
- Yu, Z. Z.; Yang, M. S.; Dai, S. C.; Mai, Y. W. J Appl Polym Sci 2004, 93, 146.
- Pesetskii, S. S.; Jurkowski, B.; Olkhov, Y. A.; Bogdanovich, S. P.; Koval, V. N. Eur Polym J 2005, 41, 1380.
- Pesetskii, S. S.; Bogdanovich, S. P.; Koval, V. N. Mater Technol Instrum 2006, 11, 29 (in Russian).