

# Structure and Properties of Polypropylene/Low-Density Polyethylene Blends Grafted with Itaconic Acid in the Course of Reactive Extrusion

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Received 10 March 2005; accepted 16 November 2005

DOI 10.1002/app.23998

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** This study was concerned with the structural features and mechanical properties of polypropylene (PP)/low-density polyethylene (LDPE) blends, which after compounding were modified by the free-radical grafting of itaconic acid (IA) to produce [PP/LDPE]-g-IA in the course of reactive extrusion. To analyze the structural features of the [PP/LDPE]-g-IA systems, differential scanning calorimetry and relaxation spectrometry techniques were used. The data were indicative of the incompatibility of PP and LDPE in the [PP/LDPE]-g-IA systems on the level of crystalline phases; however, favorable interactions were observed within the amorphous phases of the polymers. Because of these interactions, the crystallization temperature of PP increased by 5–11°C, and that of LDPE increased by 1.3–2.7°C. The rapprochement of

their glass-transition temperatures was observed. The single  $\beta$ -relaxation peak for the [PP/LDPE]-g-IA systems showed that compatibility on the level of structural units was responsible for  $\beta$  relaxation in the homopolymers used. Variations in the ratios of the polymers in the [PP/LDPE]-g-IA systems led to both nonadditive and complex changes in the viscoelastic properties as well as mechanical characteristics for the composites. Additions of up to 5 wt % PP strengthened the [PP/LDPE]-g-IA blended systems between the glass-transition temperatures of LDPE and PP. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1746–1754, 2006

**Key words:** mechanical properties; polyethylene (PE); poly(propylene) (PP); reactive processing

## INTRODUCTION

Recently, considerable progress has been made in the development and application of composite materials based on blends of engineering plastics (polyamide, polyalkylene terephthalates, polycarbonate, etc.) and polyolefins (POs).<sup>1–4</sup> This allows us to obtain improved processability, increased low-temperature resistance, better impact strength, and so forth.

When blend systems similar to those previously mentioned are being designed, the major task is to ensure compatibility between unlike polymers.<sup>1–5</sup> One of the factors that hinder the direct mixing of POs with engineering plastics is the nonpolar nature of the PO component. In this connection, when commercially valuable composites are being prepared by reactive processing with PO addition, much attention is paid to the chemical modification of the latter; such

modification is based on the introduction of polar functional groups into PO chains.<sup>5–8</sup> The most efficient route for increasing PO polarity is grafting onto its chains monomers containing functional groups of one or another origin. Among chemically reactive monomers, the most important for PO modification by free-radical mechanisms are unsaturated organic compounds that have oxygen-containing functional groups [maleic anhydride and its derivatives, glycidyl methacrylate, itaconic acid (IA), etc.].<sup>9–14</sup>

To obtain the most commercially valuable composites with increased durability or impact strength, for instance, it is advantageous, in many situations, to use modifiers such as complex, multicomponent systems based on polypropylene (PP)/polyethylene (PE), PP/ethylene–propylene rubber (EPR), and PE/EPR.<sup>15,16</sup> These blends have to be subjected to intended functionalization by polar monomers of the required functionality being grafted onto them. There is, however, a lack of information on the details of monomer grafting onto such systems and on their structures and properties.

A description of IA grafting onto PP/low-density polyethylene (LDPE) blends in the course of reactive extrusion while the component ratios are varied over

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Contract grant sponsors: Mianowski Fund, Foundation of Polish Science, Belarussian Republic Fund of Fundamental Investigations; contract grant number: T04-013.

a wide concentration range has been reported elsewhere.<sup>17</sup> Some attention is paid there to the study of the rheological properties of the molten [PP/LDPE]-g-IA produced.

On the basis of the obtained data, a conclusion has been made about the complex nature of the mutual interactions of the components in the course of free-radical transformations in polymers during reactive extrusion. For relatively small additions of LDPE (up to 25 wt %), a nonlinear rise (most evident in comparison with the additive dependence) in the grafting efficiency of IA onto a PP/LDPE blend has been found. For 25–95 wt % LDPE, the grafting efficiency increases monotonously with increasing LDPE concentration. The introduction of small amounts of one or another polymer leads to unusual changes in the rheological properties of the molten blends: an addition of up to 25 wt % LDPE, which undergoes crosslinking during functionalization, increases the melt flow index (MFI; reduces the melt viscosity) of [PP/LDPE]-g-IA systems in comparison with that of PP-g-IA. The relatively low grafting efficiency, which is typical of both the initial PP and PP/LDPE blends containing between 75 and 99 wt % PP, can be explained<sup>17</sup> by a rate of  $\beta$  scission of PP chains higher than the IA grafting rate. The higher rate of  $\beta$  scission is indicated by a marked increase in MFI for PP-g-IA and [PP/LDPE]-g-IA systems with increasing PP concentrations up to 75 wt % in comparison with MFI for the initial PP.

On the contrary, the addition of up to 5 wt % PP increases the viscosity of the [PP/LDPE]-g-IA system in comparison with that of LDPE-g-IA. This can be explained<sup>17</sup> by the fact that macroradicals of PP that form with the grafting of IA cause additional crosslinking of LDPE. Blends containing up to 25 wt % LDPE exhibit an extremely low apparent activation energy of the viscous flow ( $E_a$ ), which reaches even negative values for the [75PP/25LDPE]-g-IA system. Variations in  $E_a$  are related to chemical processes during IA grafting onto PP/LDPE blends and depend on their composition.<sup>17</sup> Rather low magnitudes of  $E_a$  for [PP/LDPE]-g-IA systems containing between 99 and 75 wt % PP can be explained as follows. The reactions related to  $\beta$  scission, in particular, increase the linearity of PP chains at the expense of a reduced number of side substituents (methyl groups). In addition, a considerable quantity of low-molecular-weight oligomers is accumulated in the polymer structure, and chains become more flexible because of the LDPE plasticizing effect. The negative values of  $E_a$  for the [75PP/25LDPE]-g-IA system could obviously have resulted from additional crosslinking or branching of the chains when it was kept in the measuring cylinder of the instrument, whereas MFI was determined at an elevated test temperature.<sup>17</sup>

This study continues a previous one on PP/LDPE blends modified by the free-radical grafting of IA

during reactive extrusion and concerns the investigation of their structure along with the mechanical properties.

## EXPERIMENTAL

### Materials

The following POs were used in this study: isotactic PP (Kaplen) produced at the Moscow Refining Plant [Moscow, Russia; density = 0.905 g/cm<sup>3</sup>; melting point ( $T_m$ ) = 163.2°C as determined by differential scanning calorimetry (DSC); rate of heating ( $\beta$ ) = 16°C/min; MFI = 4.9 g/10 min at 190°C and a 5-kg load] and LDPE produced by Polimir Co. (Novopolotsk, Belarus; density = 0.92 g/cm<sup>3</sup>;  $T_m$  = 105.8°C as determined by DSC;  $\beta$  = 16°C/min; MFI = 7.4 g/10 min at 190°C and a 5-kg load). The grafted monomer was IA supplied by the Chemical Division of Pfizer (New York, NY; molecular weight = 130.1 g/mol;  $T_m$  = 172°C). To initiate the grafting reaction, 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (L-101) was used as supplied by Atofina (France; half-life of a peroxide)  $t_{0.5}$  = 0.6 min at 180°C; reactive oxygen concentration = 11.03%). According to the results of previous works,<sup>18,19</sup> L-101 is an efficient grafting initiator for IA onto PP and LDPE.

The process of making [PP/LDPE]-g-IA blends consisted of two steps. First, PP and LDPE were mixed with component ratios of 100 : 0, 99 : 1, 95 : 5, 75 : 25, 50 : 50, 25 : 75, 5 : 95, 1 : 99, and 0 : 100. The mixing was carried out in the melt at 200°C with a single-screw extruder (screw diameter = 25 mm; length/diameter = 25) with subsequent cooling in water and granulation of the obtained product.

Second, the granulated PP/LDPE blend was treated with L-101 dissolved in acetone and with IA powder. The concentrations of IA and L-101 added to the PP/LDPE mixtures were constant in all the experiments and were 1 and 0.3 wt %, respectively. The mixture thus prepared was run through an extruder reactor assembled on the base of a Brabender plastograph and equipped with a dynamic mixer<sup>17</sup> to provide the following factors: a screw speed of 50 rpm; a shear rate of approximately 100 s<sup>-1</sup>; and temperatures of 160 (zone I), 180 (zones II and III), and 185°C (zone IV). The average residence time for the mixture in the reactor was about 4 min.

Unfunctionalized PP/LDPE blends used for a comparative analysis of the properties were prepared in the same manner as [PP/LDPE]-g-IA, but no IA or L-101 was added to their compositions.

### Characterization of [PP/LDPE]-g-IA

The grafting efficiency and rheological properties of the basic objects of the research, reported in another work,<sup>17</sup> are shown in Table I.

**TABLE I**  
**Properties of the Test Materials**

Test material (wt %)	$\alpha$ (%)	MFI (g/10 min)	$\eta$ (kPa s)	$E_a$ (kJ/mol)
PP	–	4.9	10.36	40.8
PP- <i>g</i> -IA	60.2	15.6	3.06	1.5
[99PP/1LDPE]- <i>g</i> -IA	61.8	16.9	2.96	0.3
[95PP/5LDPE]- <i>g</i> -IA	66.8	17.3	2.92	0.3
[75PP/25LDPE]- <i>g</i> -IA	74.2	16.6	2.91	–7.0
[50PP/50LDPE]- <i>g</i> -IA	78.3	5.7	8.89	53.6
[25PP/75LDPE]- <i>g</i> -IA	85.1	5.5	9.18	53.2
[5PP/95LDPE]- <i>g</i> -IA	89.8	0.1	225.4	77.8
[1PP/99LDPE]- <i>g</i> -IA	90.6	0.2	319.2	62.0
LDPE- <i>g</i> -IA	91.8	0.3	159.3	81.0
LDPE	–	7.4	6.84	43.0

$\alpha$  = grafting efficiency; MFI = melt flow index at 190°C and 5 kg;  $\eta$  = viscosity evaluated with MFI values;<sup>17,22</sup>  $E_a$  = apparent activation energy of the viscous flow evaluated with MFI values determined at two temperatures (190 and 230°C) but with a single load.<sup>17,22</sup>

The structure of the materials was determined with the DSC data. The investigation was performed on a DSM-3A device made at the Institute for Biological Instruments (Russian Academy of Sciences); the specimen weight was 5 mg, and the heating-cooling rate was 16°C/min. The temperature measurement accuracy was  $\pm 1^\circ\text{C}$ . The variations in the crystallinity degree were determined with the crystallinity index ( $\Delta I_{cr}$ ) values, which were determined as the ratio of the areas under the crystallization peaks of functionalized and neat PP and LDPE. For the [PP/LDPE]-*g*-IA system,  $\Delta I_{cr}$  was found from variations in the areas under the crystallization peaks of the PP and PE components with respect to the peaks of the initial (non-blended) components. To eliminate the effect of the specimens' thermal prehistory on the structure, the measurements were performed on specimens that had been preheated up to 200°C in the DSM-3A cell, maintained at this temperature for 60 s, and reused for analysis.

The relaxation study was performed with the method of dynamic mechanical losses with a reversion torsion pendulum tester dynamic-mechanical analysis (DMA) designed at the Metal-Polymer Research Institute (Gomel, Belarus).<sup>20</sup> The test specimens were plates measuring 50 mm  $\times$  5 mm  $\times$  0.5 mm. The specimens were heated from  $-150$  to  $+150^\circ\text{C}$  at a rate of 1.5°C/min. The oscillation frequency of the pendulum was about 1 Hz (the measurement accuracy was  $\pm 0.01$  Hz). In the course of the investigation, the dynamic shear modulus ( $G'$ ) and the tangent angle of mechanical loss ( $\tan \delta$ ) were measured. The measurement error for  $G'$  was 3%, and that for  $\tan \delta$  was 5%. The temperature measurement accuracy was  $\pm 0.1^\circ\text{C}$ .

The mechanical properties were determined on samples in the form of dog bones, with the neck measuring 45 mm  $\times$  5 mm  $\times$  2 mm. They were injection-molded at

220°C. The tensile strength was measured on an Instron series 5567 universal testing machine at a loading rate of 50 mm/min. For determining the Charpy impact strength, a PSV-1.5 pendulum hammer (Leipzig, Germany) and unnotched samples as bars measuring 80 mm  $\times$  10 mm  $\times$  4 mm were used. The measurements were performed at 30°C because at higher temperatures the samples could not break down, whereas at lower temperatures the measurement accuracy decreased because of low values. An arithmetic mean value of five parallel tests was accepted as the result of the measurements of the mechanical properties. The error range for the mechanical tests was generally 5–7%.

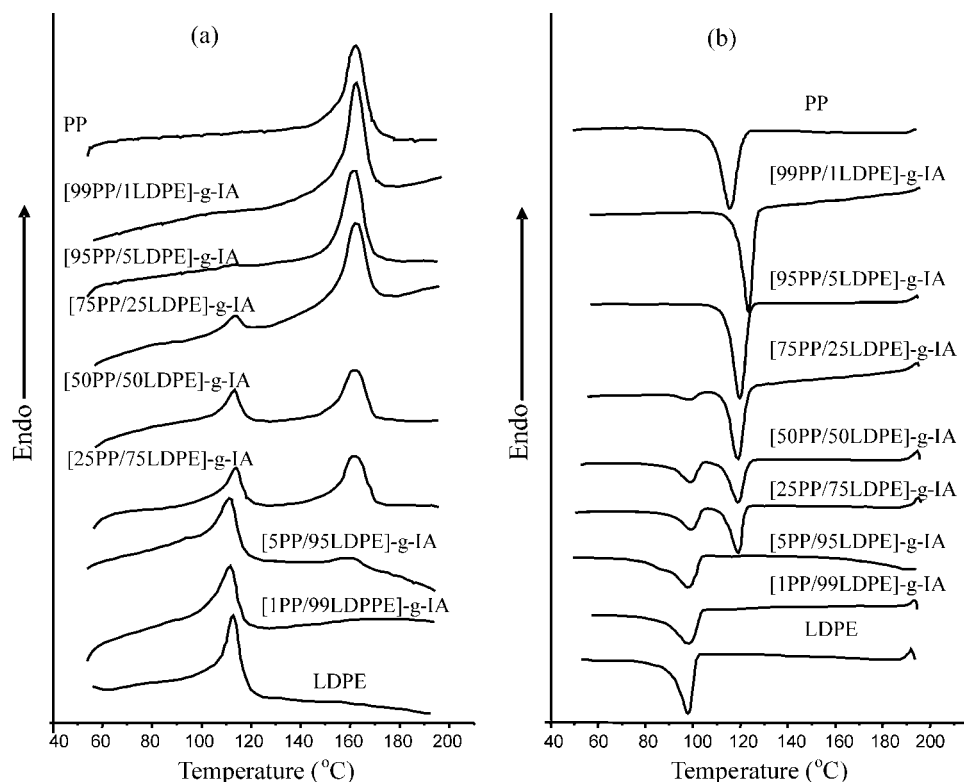
## RESULTS AND DISCUSSION

### Thermal properties of the [PP/LDPE]-*g*-IA systems

Figure 1 shows DSC thermograms for the [PP/LDPE]-*g*-IA systems along with those for initial and modified PP and LDPE. More detailed information, including  $T_m$ , the crystallization temperature ( $T_{cr}$ ), and  $\Delta I_{cr}$  of the tested materials, is given in Table II. Besides, Table II shows the results of the DSC analysis performed for unfunctionalized PP/LDPE blends.

The heating and cooling thermograms of the [PP/LDPE]-*g*-IA systems show the phase transitions typical of the homopolymers. The thermograms of the 99 : 1, 95 : 5, 5 : 95, and 1 : 99 compositions do not show any melting or crystallization peaks for PP and LDPE, and this can be explained by the low concentration of these components in the blends. The temperature-dependent location of the peaks that describe the phase transitions in the [PP/LDPE]-*g*-IA systems changes with the blend composition and does not usually coincide with the respective values for the homopolymers. It should be underlined that  $T_{cr}$  of the PP component in the blends is some 5–11°C higher than that of the PP homopolymer, whereas the typical variations in  $T_m$  of PP are less significant. The [PP/LDPE]-*g*-IA systems of the 99 : 1 ratio show a maximum  $T_{cr}$  value for the PP component. The PE component in the blends shows higher  $T_{cr}$  values than the initial one.  $T_m$  of the LDPE component in the [PP/LDPE]-*g*-IA systems varies but extremely little in comparison with those of the initial LDPE.

The comparison of the experimental and calculated values of  $\Delta I_{cr}$  (Table II) has revealed rather strong variations in the crystallization kinetics of the components in the [PP/LDPE]-*g*-IA systems. For all ratios investigated,  $\Delta I_{cr}$  exceeds its calculated values for the PP phase. The LDPE concentration in the blend increases, and the  $\Delta I_{cr}$  value grows and reaches twice the level for the [25PP/75LDPE]-*g*-IA systems. An obvious and probably major cause of this may be the PP degradation during IA grafting, which is followed



**Figure 1** DSC thermograms of (a) the melting and (b) the crystallization of the initial homopolymers and [PP/LDPE]-g-IA systems.

by a reduced molecular weight of PP, thus making crystallization easier. As  $\Delta I_{cr}$  grows with increasing amounts of LDPE in the blends, it can be assumed that either the degradation degree of PP becomes higher or LDPE present in the melt during PP crystallization favors this process because of, for example, the plasticizing effect or a reduced cooling rate for the crystallizing melt.

Unlike the PP phase, LDPE crystallizes slower more slowly in the [PP/LDPE]-g-IA systems, with up to a 50 wt % concentration against the calculated data (Table II). This is explained by the growing melt viscosity of LDPE during functionalization, thus making the process of crystallization kinetically more difficult. The systems, which give low-viscosity melts, crystallize more easily; therefore, the values of  $\Delta I_{cr}$  differ.

**TABLE II**  
Results of the DSC Analysis of the [PP/LDPE]-g-IA Systems and Unmodified PP/LDPE Blends

Test material (wt %)	PP component				PE component			
	$T_m$ (°C)	$T_{cr}$ (°C)	$\Delta I_{cr}$		$T_m$ (°C)	$T_{cr}$ (°C)	$\Delta I_{cr}$	
			Found	Calcd			Found	Calcd
PP	163.0	113.0	1.0	1.0	—	—	—	—
PP-g-IA	167.0	121.0	1.1	1.0	—	—	—	—
[99PP/1LDPE]-g-IA	163.0	125.0	1.03	0.99	—	—	—	—
[95PP/5LDPE]-g-IA	162.0	119.0	1.1	0.95	—	—	—	—
[75PP/25LDPE]-g-IA	164.0	118.0	1.04	0.75	106.0	93.0	0.5	0.25
[50PP/50LDPE]-g-IA	163.0	119.0	0.9	0.5	106.0	95.0	0.7	0.5
[25PP/75LDPE]-g-IA	163.0	119.0	0.5	0.25	106.0	94.0	0.5	0.75
[5PP/95LDPE]-g-IA	—	—	—	—	103.0	94.0	0.8	0.95
[1PP/99LDPE]-g-IA	—	—	—	—	107.0	95.0	0.9	0.99
LDPE-g-IA	—	—	—	—	107.0	90.5	0.86	1.0
LDPE	—	—	—	—	106.0	92.0	1.0	1.0
75PP/25LDPE	162.0	111.0	0.75	0.75	106.0	90.0	0.2	0.25
50PP/50LDPE	163.0	110.0	0.57	0.5	107.0	91.0	0.5	0.5
25PP/75LDPE	162.0	111.0	0.27	0.25	107.0	92.0	0.7	0.75

The data in Table II indicate that the variations in  $T_m$ ,  $T_{cr}$ , and  $\Delta I_{cr}$  stated previously for the components of the [PP/LDPE]-g-IA blends are due to the specificity of the macromolecular transformations during IA grafting and not due to the simple mutual influence of PP and LDPE during their mixing in the melt. For instance, a comparison of the results in Table II shows that for unmodified PP/LDPE mixtures,  $T_{cr}$  of the PP phase not only increases but, on the contrary, drops somewhat (crystallization is hindered) in comparison with the initial value of PP. The values of  $\Delta I_{cr}$  for PP and LDPE phases are close to the calculated ones. This fact can be explained by the relatively weak mutual influence of LDPE and PP on their crystallizability in unmodified PP/LDPE mixtures and by the fact that neither PP nor LDPE undergoes substantial chemical changes.

Thus, the DSC results allow the assumption that during the cooling of the [PP/LDPE]-g-IA systems, the polymer components undergo crystallization without involving a foreign phase in the crystallites. There is incompatibility between the components on the level of crystalline phases. Variations in the rate of crystallization and in the crystallinity degree of the components along with the  $T_{cr}$  values serve as indirect evidence for rather intensive interactions taking place between the phases in the [PP/LDPE]-g-IA systems.

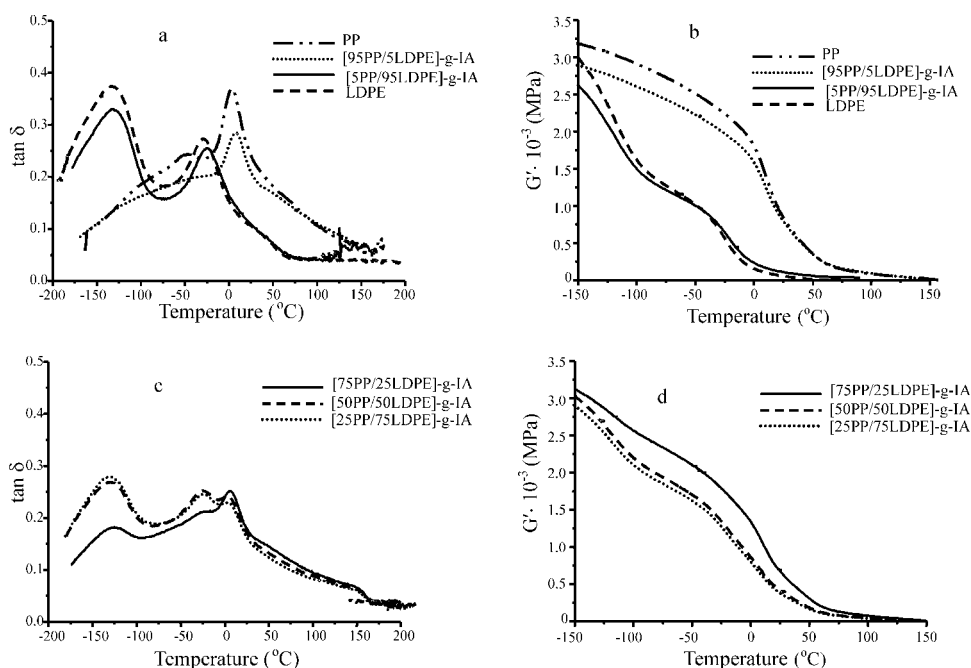
### Relaxation properties of the [PP/LDPE]-g-IA systems

Figure 2(a,c) and Table III show data on  $\tan \delta$  measured for both the initial homopolymers and [PP/

LDPE]-g-IA systems versus the temperature. For the PP homopolymer, over the temperature range of  $-150$  to  $+150^\circ\text{C}$ , there are two maxima: an intensive  $\alpha$  peak at a glass-transition temperature ( $T_g$ ) of  $7.3^\circ\text{C}$ , related to the glass transition of its amorphous phase, and a less intensive  $\beta$  peak at the  $\beta$ -peak temperature ( $T_\beta$ ) of  $-47.5^\circ\text{C}$ , related to the mobility devitrification of  $-\text{CH}_2-$  groups in the main chain.<sup>21</sup> The temperature dependence of  $\tan \delta$  for the LDPE homopolymer also shows two intensive peaks related to  $\alpha$ - and  $\beta$ -relaxation transitions ( $T_g = -29.8^\circ\text{C}$  and  $T_\beta = -132.7^\circ\text{C}$ ); their maxima are in a lower temperature region in comparison with that for PP.

A plot of  $\tan \delta$  versus the temperature for the [PP/LDPE]-g-IA systems with 95:5 and 5:95 polymer ratios shows only one glass-transition peak of the homopolymer, the concentration of which prevails [Fig. 2(a) and Table III]. The lack of a second peak can be explained by a low concentration of one of the polymers. The  $\alpha$ -peak intensities of both PP and LDPE decrease in both instances in comparison with that of the initial homopolymer. An obvious cause for this may be a decreased portion of the amorphous phase of each of the components in the blend. The location of the  $\alpha$  peak on the temperature scale, in the case of PP, differs insignificantly from  $T_g$  of the initial PP, whereas for LDPE, it shifts somewhat into a higher temperature region (Table III).

For [PP/LDPE]-g-IA systems of intermediate ratios [Fig. 2(c) and Table III], the plots of  $\tan \delta$  versus the temperature show two peaks of mechanical losses related to the glass transition of each of the components. Of interest is the fact that for these blends the



**Figure 2** Temperature dependence of (a,c)  $\tan \delta$  and (b,d)  $G'$  for the homopolymers and [PP/LDPE]-g-IA systems.

TABLE III  
Results of the Relaxation Analysis of the [PP/LDPE]-g-IA Systems and Unmodified PP/LDPE Blends

Test material (wt %)	PP component		PE component		$\Delta T_g$ (°C)
	$\beta$ transition (°C)	$\alpha$ transition (°C)	$\beta$ transition (°C)	$\alpha$ transition (°C)	
PP	-47.5	7.3	-	-	-
PP-g-IA	-46.6	7.4	-	-	-
[95PP/5LDPE]-g-IA	-	7.4	-	-	-
[75PP/25LDPE]-g-IA	-	5.1	-125.5	-25.2	30.3
[50PP/50LDPE]-g-IA	-	2.4	-130.6	-25.1	27.5
[25PP/75LDPE]-g-IA	-	1.8	-131.6	-25.2	27.0
[5PP/95LDPE]-g-IA	-	-	-132.4	-25.6	-
LDPE-g-IA	-	-	-131.5	-28.2	-
LDPE	-	-	-132.7	-29.8	-
25PP/75LDPE	-	3.6	-128.6	-24.6	28.2
50PP/50LDPE	-	4.3	-129.3	-24.8	29.1
75PP/25LDPE	-	5.6	-129.0	-25.8	31.4

distance between the glass-transition peaks of the two polymers on the temperature scale decreases noticeably, whereas the  $\alpha$  peaks approach each other. Moreover, a general level of mechanical losses for the blends of intermediate ratios in the lower temperature region depends mainly on the mechanical losses of LDPE. All the blends tested are characterized by an absence of the  $\beta$ -relaxation peak for PP. Those blends show single  $\beta$ -relaxation peaks that shift into the higher temperature zone, whereas the height drops with an increasing PP concentration in the blends.

Thus, the two glass-transition peaks found in the plots of  $\tan \delta$  versus the temperature for the [PP/LDPE]-g-IA systems support a lack of compatibility between PP and LDPE as well as a two-phase structure for the [PP/LDPE]-g-IA systems. However, the approaching values of  $T_g$ , unlike those of the initial components, allow us to believe that in the [PP/LDPE]-g-IA systems, interactions between PP and LDPE lead to partial mutual dissolution.

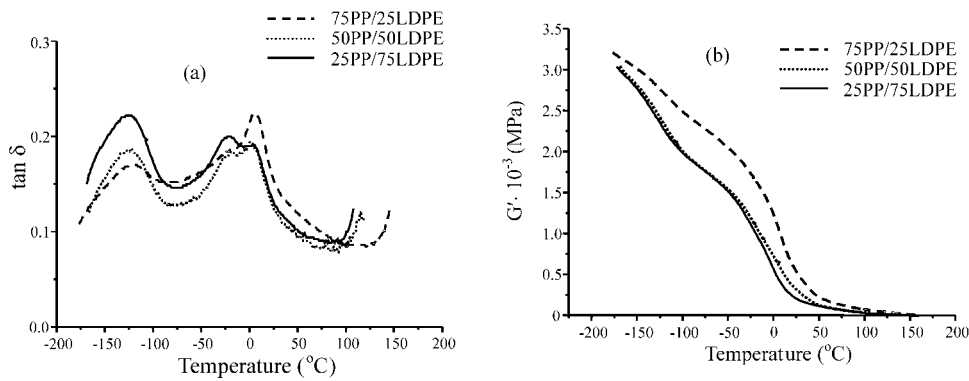
The single  $\beta$ -relaxation peak found for the systems points out that the compatibility on the level of small structural units is responsible for  $\beta$  relaxation in the homopolymers. On the basis of the relaxation spectrometry data, one can infer that the grafting of IA onto a PP/LDPE blend may lead to the formation of certain amounts of copolymers because of cross reactions among the macroradicals of the two homopolymers, which seem to favor compatibility.<sup>1-3,15</sup>

Figure 2(b,d) shows  $G'$  for the initial components and their functionalized blends. For the initial PP and [PP/LDPE]-g-IA system containing 5 wt % LDPE [Fig. 2(b)], the  $G'$  values drop sharply within the temperature range from 0 to 50°C; this is related to the mobility of the devitrified chain segments in the amorphous region of PP. In blends containing between 25 and 95 wt % LDPE, two temperature zones are clearly visible, within which  $G'$  drops considerably [Fig. 2(d)]. One region (at ca. -100°C) is related to the devitrifica-

tion of the mobility of  $-\text{CH}_2-$  groups in the main chain and side branches of LDPE. The other, at about -30°C and above this temperature, refers to the devitrification of both LDPE and PP.

The analysis of the results in Figure 2(b,d) shows that increased quantities of LDPE in the [PP/LDPE]-g-IA blends result in lower  $G'$  values. Then, the  $G'$  values for most of the PP/LDPE ratios over the whole temperature range lie within limited values of the moduli of the initial components. An exception is the [PP/LDPE]-g-IA system with a 5 : 95 ratio, the PP concentration being low [5 wt %; Fig. 2(b)]. This system, at temperatures below that of the glass transition for the initial LDPE, shows a lower modulus than that for the homopolymer before processing. For instance, for [5PP/95LDPE]-g-IA at -80°C,  $G'$  is 1268 MPa, whereas for LDPE, it is 1330 MPa. At about  $T_g$  of LDPE and higher temperatures, the  $G'$  value of the [PP/LDPE]-g-IA system containing 5 wt % PP becomes larger than that of the initial LDPE (at 10°C, for [5PP/95LDPE]-g-IA and LDPE,  $G'$  is 185 and 107 MPa, respectively). This variation in  $G'$  can be explained by the special supermolecular arrangement of the amorphous regions in the [PP/LDPE]-g-IA systems with a ratio of polymer components of 5 : 95. From its MFI values (Table I), it can be determined that this blend contains some definite quantity of crosslinks that can strengthen the material in its rubbery state, and this leads to larger  $G'$  values. Besides, the PP phase can increase the differences in the segmental mobility of the blend components. At the  $T_g$  of LDPE and higher ones, when its amorphous phase is in a rubbery state, the PP amorphous portion in the [PP/LDPE]-g-IA system remains in a glassy state, because of which its  $G'$  value is much higher than that of the initial LDPE. Most likely, because of this, the effect of reinforcement is noticeable within the range of small additions of PP.

Lower  $G'$  values of the [5PP/95LDPE]-g-IA systems, compared with those of the initial LDPE over



**Figure 3** Temperature dependence of (a)  $\tan \delta$  and (b)  $G'$  for the unmodified PP/LDPE blends.

a temperature range below  $T_g$  for PE, result most likely from the imperfect structure of the blend; the imperfection could result from the incompatibility of the polymer components.

The temperature dependence of  $\tan \delta$  and  $G'$  for unmodified PP/LDPE blends correlates with that for [PP/LDPE]-*g*-IA [Figs. 2(a–d) and 3(a,b)]. However, the opposing shifting of  $T_g$  for PP/LDPE blends is somewhat less than that for [PP/LDPE]-*g*-IA (Table III). Consequently, macromolecular transformations, including the possible formation of grafted copolymers, occurring during the stage of blend preparation in the case of [PP/LDPE]-*g*-IA,<sup>17</sup> are favorable for stimulated partial compatibility of the components.

### Mechanical properties of the [PP/LDPE]-*g*-IA systems

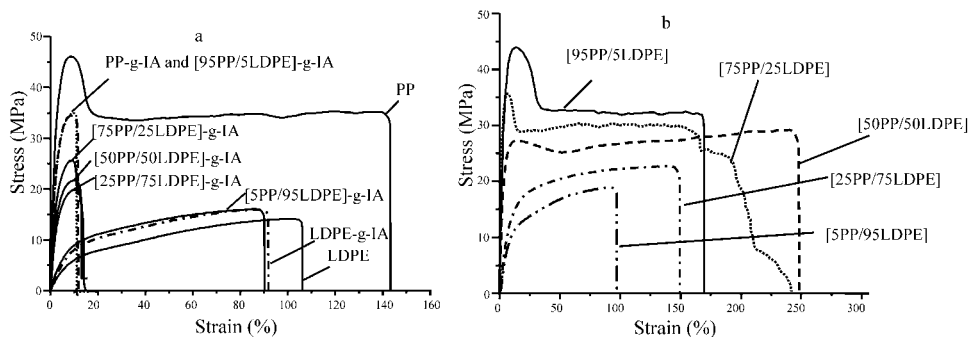
The stress–strain curves for initial POs, PP-*g*-IA, LDPE-*g*-IA, [PP/LDPE]-*g*-IA systems, and unmodified PP/LDPE blends are shown in Figure 4(a,b). For the [PP/LDPE]-*g*-IA systems, except for [5PP/95LDPE]-*g*-IA, there are some significant changes in the pattern of curves from that for the initial homopolymers. Of interest is the fact that most of the [PP/LDPE]-*g*-IA systems and PP-*g*-IA, unlike the initial homopolymers and unmodified PP/LDPE blends, lose their capacity for large deformations.

The data of Figure 5(c) show that even [PP/LDPE]-*g*-IA systems containing 75 wt % LDPE exhibit rather low relative elongations at break. A sharp rise in the elongation has been observed for a ratio of 5 : 95 PP/LDPE in the blends. This can probably be explained by the two-phase nature of the [PP/LDPE]-*g*-IA systems, the imperfection of contact zones between the phases, and the prevailing degradation of PP chains that follows IA grafting onto PP and PP/LDPE blends.<sup>17</sup>

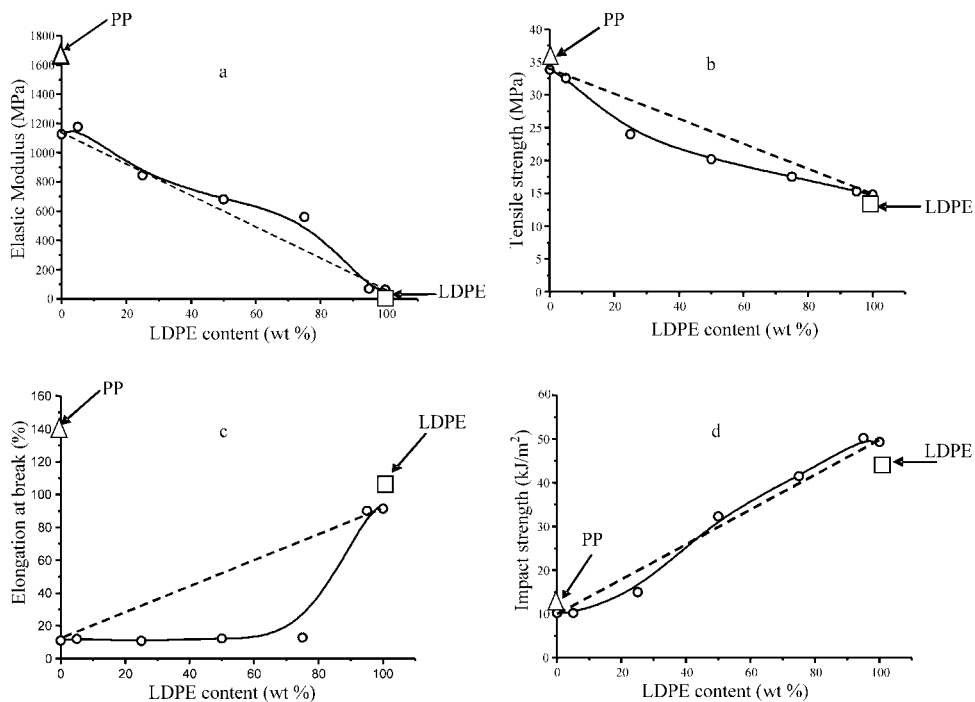
An analysis of the relationship between the elastic modulus and tensile strength and the blend composition shows that their growth depends on the contribution of the higher modulus PP [Fig. 5(a,b)].

A significant increase in the elastic modulus can be observed even with 25 wt % PP in the blend. With lower PP concentrations, the elastic modulus depends on the LDPE component. Similar is the situation with the tensile strength; it increases with higher PP concentrations in the [PP/LDPE]-*g*-IA systems. However, the strength growth is monotonous with increasing PP concentration [Fig. 5(b)]. The comparison of all the mechanical properties on the PP and LDPE ratios in the [PP/LDPE]-*g*-IA systems shows a lack of additivity for these relationships [Fig. 5(a–c)]. This fact could result from some structural changes in the polymer components caused by chemical processes taking place at IA grafting.

A basic distinction between the concentration dependence of the properties found in a tensile test of



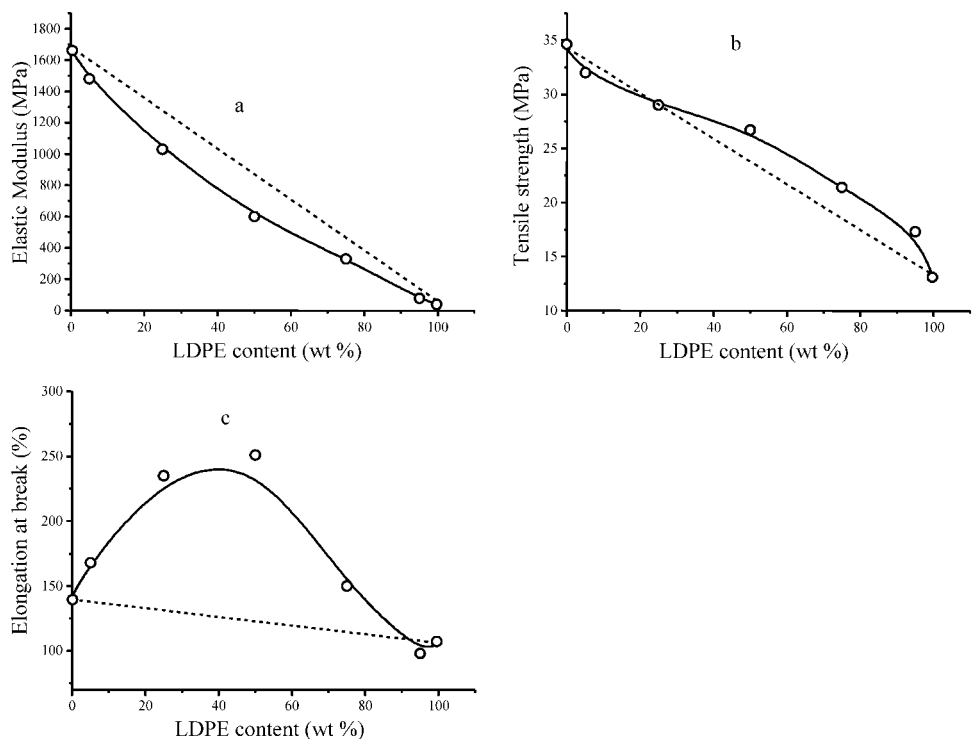
**Figure 4** Tensile diagrams for (a) the [PP/LDPE]-*g*-IA systems and (b) the unmodified PP/LDPE blends.



**Figure 5** Effect of the LDPE concentration in functionalized [PP/LDPE]-g-IA blends on (a) the elastic modulus, (b) the tensile strength, (c) the elongation at break, and (d) the Charpy impact strength (unnotched samples; test temperature =  $-30^{\circ}\text{C}$ ): ( $\Delta$ ) initial PP and ( $\square$ ) initial LDPE.

unmodified PP/LDPE blends containing initial polymers [Fig. 6(a-c)] and functionalized [PP/LDPE]-g-IA blends [Fig. 5(a-c)] is that the former show a greater elongation in comparison with the initial

component. Besides, the mode of deviation from the additive dependence of the elastic modulus and tensile strength depends on the types of blends. Obviously, this difference in the mode of the concentra-



**Figure 6** Effect of the LDPE concentration in unmodified PP/LDPE blends on (a) the elastic modulus, (b) the tensile strength, and (c) the elongation at break.



tion dependence of the properties for the [PP/LDPE]-*g*-IA systems and unmodified PP/LDPE blends results from specific chemical transformations in the polymer components at functionalization and their mutual influence on the structure and interphase interactions in the blends.

The concentration dependence of the Charpy impact strength at  $-30^{\circ}\text{C}$  is closer to the additive one than the other mechanical properties. The highest impact strength at  $-30^{\circ}\text{C}$  has been found for the [5PP/95 LDPE]-*g*-IA blend [Fig. 5(d)]. As this property greatly depends on the degree of microheterogeneity of the polymer material,<sup>23</sup> it can be assumed that the functionalization of the PP/LDPE blends by the grafting of IA under our experimental conditions does not cause any significant morphological changes in its influence on the impact strength.

### CONCLUSIONS

The results of DSC and relaxation spectrometry evidence a lack of compatibility on the level of the crystalline structures in the [PP/LDPE]-*g*-IA systems and efficient interactions in the amorphous phases of the polymer components. Because of these interactions,  $T_{cr}$  of these components rises ( $T_{cr}$  of PP rises by 5–11 $^{\circ}\text{C}$ , and that of LDPE rises by 1.3–2.7 $^{\circ}\text{C}$ ). In addition, the  $T_g$  values of the polymer components approach. The single  $\beta$ -relaxation peak found for the [PP/LDPE]-*g*-IA systems as well as the unmodified PP/LDPE blends points out that the compatibility on the level of small structural units is responsible for  $\beta$  relaxation in the homopolymer.

Variations in the ratio of the polymer components in the [PP/LDPE]-*g*-IA systems cause some nonadditive and complex changes in the viscoelastic properties and mechanical characteristics of the blend materials.

Small (up to 5 wt %) additions of PP strengthen the [PP/LDPE]-*g*-IA system over the temperature range from  $T_g$  of LDPE to  $T_g$  of PP.

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