

PP/LDPE Blends Produced by Reactive Processing. I. Grafting Efficiency and Rheological and High-Elastic Properties of [PP/LDPE]-*g*-IA Melts

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ABSTRACT: Itaconic acid (IA) was grafted onto polypropylene/low-density polyethylene (PP/LDPE) blends. The ratio of polymeric components was varied from 100 : 0 to 0 : 100. The effect of the variation in the ratios of the components on grafting efficiency and concomitant side processes was studied. Grafting of IA (1 wt %) was initiated by 2,5-dimethyl-2,5-di(*tert*-butyl peroxy)-hexane (0.3 wt %) and was carried out in an extruder reactor equipped with a dynamic mixer. An increase in the PP content of the blend led to a lower yield of the grafted product. With low concentrations of LDPE in the blend (up to 25 wt %), grafting efficiency was observed to increase, and this increase was greater in comparison with the additive rule. Between 25 and 99 wt % of LDPE in the blend,

grafting efficiency rose monotonically with LDPE concentration. At or below an LDPE content of 25 wt %, the melt flow index (MFI) of [PP/LDPE]-*g*-IA would increase unlike with PP-*g*-IA systems. But a small quantity of PP (below 25 wt %) in the [PP/LDPE]-*g*-IA blends would result in a decreased MFI unlike with LDPE-*g*-IA. The dependence of swell index and melt strength on the ratio of polymeric components in [PP/LDPE]-*g*-IA blends also was investigated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5095–5104, 2006

Key words: blends; functionalization of polymers; polyethylene (PE); poly(propylene) (PP); reactive extrusion

INTRODUCTION

Despite great progress in recent years in investigating the chemistry, physics, and technology of grafted polyolefins (GPO),^{1–4} investigations related to the principles and detail mechanisms of particular polyolefins (POs) and PO-based multicomponent systems are of great importance. This is especially true when reactive extrusion is used, which can be advantageous in the production of commercial materials.

Numerous studies^{5–17} of free-radical grafting of polar monomers onto different polyolefins [polypropylene (PP), low-density polyethylene (LDPE), high-density polyethylene (HDPE), ethylene propylene (EPR), etc.] reported that side reactions (crosslinking and degradation of chains, oligomerization of monomer, etc.) occurred simultaneously with the grafting reactions. The side reactions caused some changes in the molecular structure of polymers, depending on the type of PO. Polyethylene (PE)^{5–8,14–16} showed a tendency to branch and crosslink in the course of grafting.

For deep conversion, a gel fraction or a partially insoluble product could result.

For PP, in contrast, degradation usually occurred because of β scission of C—C bonds in the main chain.^{9–11,17} EPR could undergo both crosslinking and degradation.^{12,13}

Data obtained are very important in the development of processes for producing GPO. However, while making use of them, it is not easy to foresee the course of grafting process and the concomitant transformations that may occur in blends of polymers and/or copolymers of olefins. Few studies have been devoted to the grafting of binary systems by the reactive extrusion, still fewer studies have investigated PO-based multicomponent systems.¹⁸

From the information available, it can be presumed that free-radical grafting of polar monomers onto polyolefin blends composed of polymers differing in chemical structure will probably be followed by some changes in the structure of the blends. This assumption has been verified to some extent.¹⁸ It has been shown that PP introduced into LDPE can affect both the amount of maleic anhydride (MA) grafted onto a blend and its rheological behavior. However, grafting of MA onto LDPE/PP blends was studied over a narrow range of concentrations¹⁸ for which the observed influence was negligible. Therefore, these data were

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insufficient to make generalized conclusions about the mutual influence of PP and LDPE on the chemical processes taking place in their blends when polar monomers are grafted onto them.

The above statement suggests the importance of studying the course of grafting of polar monomers onto polyolefin blends during reactive extrusion. The information will be of scientific interest; also, it may be quite useful in finding new applications for multi-component systems such as PP/LDPE, PP/HDPE, PP/EPR, and PP/LDPE/EPR after they have been purposefully grafted.

The present work was devoted to the study of grafting of itaconic acid (IA) onto PP/LDPE blends during reactive extrusion while varying the ratio of polymeric components over a wide range of concentrations. Some attention was focused on studying the rheological features and the high-elastic properties of the resulting materials.

EXPERIMENTAL

Materials

The following POs were investigated in this work: Kaplen isotactic PP, produced at the Moscow Refinery Plant, Moscow, Russia (grade 01030; specification 2211-015-00203521-95; density 0.905 g/cm³; melting point 163°C as defined by DSC; MFI of 4.9 g/min at a temperature of 190°C and a load of 5 kg); LDPE, produced by the Polimir Co., Novopolotsk, Belarus (grade 15803-020, density 0.92 g/cm³, melting point 106°C as defined by DSC; MFI of 7.4 g/mol at a temperature of 190°C and a load of 5 kg). The monomer grafted was IA supplied by Chemical Division Pfizer (New York, NY; MW = 130.1 g/mol, melting point 172°C). The effectiveness of IA use in functionalization of homopolyolefins has been reported in our earlier publications.¹⁴⁻¹⁷ In comparison with other monomers used for such purposes, for example, maleic anhydride, IA is much less toxic. In addition, its production has been set up on a commercial scale, whereas functionalized polyolefins prepared by IA grafting can be allowed to have contact with food.

To initiate the grafting reaction, 2,5-dimethyl-2,5-di(*tert*-butyl peroxy)-hexane (L-101) was used as supplied by Atofine Co. (Paris, France; $\tau_{0.5} = 0.6$ min at 180°C, reactive oxygen concentration 11.03%). The solvents used were acetone (purity of 99.5%) and anhydrous ethanol (purity of 99.9%).

Specimen preparation

Itaconic acid was grafted onto PP/LDPE blends in an extruder-reactor assembled using a Brabender plastograph (Duisburg, Germany) that was equipped with a dynamic mixer (Fig. 1). The grafting reaction was carried out under the following conditions: screw rota-

tion speed of 50 min⁻¹; shear rate of about 100 s⁻¹; and temperatures of 160°C, 180°C, 185°C in zones I, II and III, and IV, respectively. The average residence time in the reactor was about 4 min.

Before grafting was accomplished, blends with component ratios (PP : LDPE) of 99 : 1, 95 : 5, 75 : 25, 50 : 50, 25 : 75, 5 : 95, and 1 : 99 were coextruded in a molten state at 200°C using a single-screw extruder (Termoplastavtomat Plant, Khmelnytsky, Ukraine; screw diameter 25 mm; L/D = 25), with subsequent quenching in water and granulating of the prepared product. Then the granulated PP/LDPE blends were treated with a solution of L-101 peroxide in acetone and covered with powdery IA. The concentrations of both L-101 and IA introduced into the blends were constant (0.3 and 1 wt %, respectively) in all the experiments. The grafting reaction of the blends prepared in this way was carried out in a Brabender plastograph.

The binary unfunctionalized blends of PP and LDPE also were prepared by the additional processing of the blended granules in a Brabender plastograph equipped with a dynamic mixer, with the same temperature regimen as that used for preparing [PP/LDPE]-*g*-IA.

Determination of grafting efficiency

The final products of grafting were [PP/LDPE]-*g*-IA systems containing both grafted and ungrafted IA. The ungrafted IA was easy to remove from the specimens by extraction in ethanol. This procedure was used to determine grafting efficiency (α), which was calculated as the ratio of the grafted monomer to the total quantity of monomer introduced into the blend.¹⁴ For this purpose, film specimens of [PP/LDPE]-*g*-IA systems compressed in the laboratory press to a thickness between 40 and 50 μ m were placed in a temperature-controllable vessel containing anhydrous ethanol at 70°C in order to extract the ungrafted part of the IA. After 18–20 h of soaking in ethanol, the films were removed and examined by IR spectroscopy using a spectrophotometer M-80 (Karl Zeiss, Jena, Germany).

For the analysis, the absorption band for carbonyl groups, which has a maximum at 1720 cm⁻¹, was chosen. To eliminate the effects of variation in film thickness on the optical density of the absorption band, the latter was referred to the optical density of the internal standard, for which the absorption band at 4325 cm⁻¹ was used.¹⁴

The α values were calculated by the expression

$$\alpha = (D_{\tau}/D_o) \times 100 \quad (1)$$

where D_o and D_{τ} are the relative optical densities of carbonyl absorption (found as the ratio of density of the band analyzed to that of the internal standard,

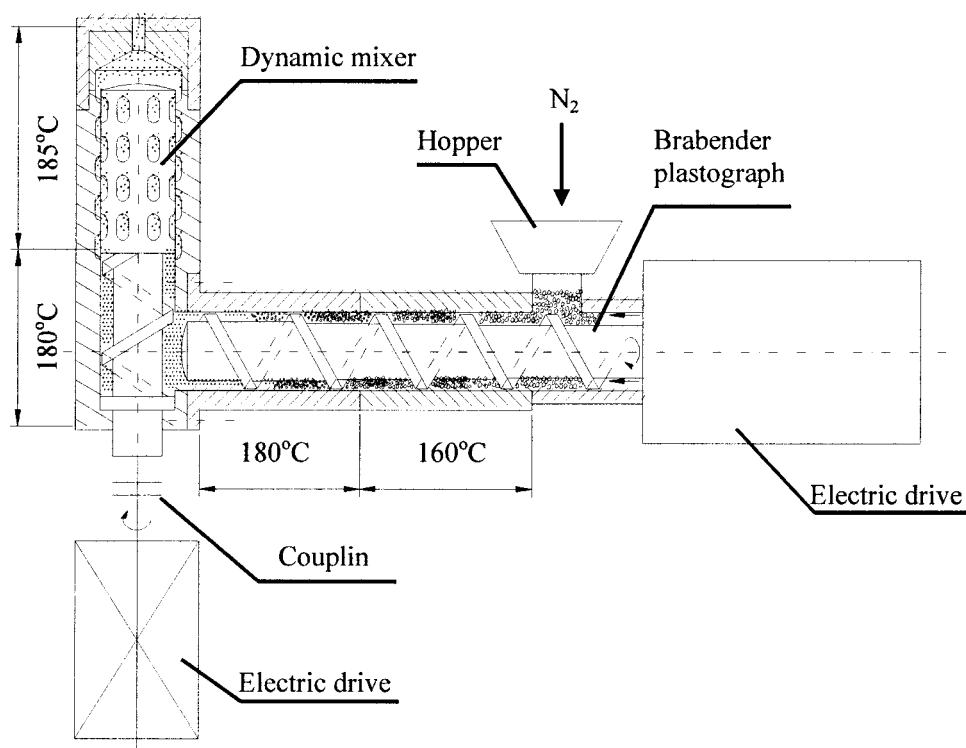


Figure 1 Schematic representation of the extruder reactor used in the study of IA grafting onto PP/LDPE blends.

$v_{c-c} = 4325 \text{ cm}^{-1}$) before and after the films were extracted in ethanol, respectively.

The findings of a previous work¹⁹ led us to presume that the extinction coefficient of absorption for the $>C=O$ groups in the carboxyl groups of grafted and ungrafted IA remained unchanged. Mean grafting efficiency was calculated using the results obtained for nine specimens. The relative error of a single measurement did not exceed 8%.

Rheological testing

The viscosity of molten materials was indirectly evaluated by using MFI values. The analysis was conducted making use of the IIRT instrument (Ekodatchik Co., Tula, Russia) at a load of 5 kg, a capillary diameter of $2.095 \pm 0.005 \text{ mm}$, and temperatures of 190°C and 230°C . The test material, which was in granular form, was charged in the heated cylinder of the instrument and held for 4 min. The MFI was determined at 190°C and 230°C and a load of 5 kg; it was used to calculate the apparent activation energy of the viscous flow (E_a) by the equation²⁰

$$E_a = -R \ln k \frac{T_1 T_2}{T_2 - T_1} \quad (2)$$

where R , $8.31 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$, is the universal gas constant; T_1 and T_2 are the test temperatures ($T_1 < T_2$; K); and k is the coefficient found by the expression

$$k = \frac{\text{MFI}_{T_1}}{\text{MFI}_{T_2}} \quad (3)$$

Using the MFI values, the Newtonian viscosity (η) could be roughly evaluated as follows:²⁰

$$\eta = \frac{P r_c^4 \rho t_c}{2D_p^2 (L_c + v r_c) \text{MFI}} \quad (4)$$

where P is the load (N), t_c (600 s) is the time constant, r_c is the capillary radius (m), L_c is the capillary length (m), D_p is the piston diameter (m), ρ is the polymer density (kg/cm^3), and v is the correction factor (not accounted for in the calculations).

The procedure used to determine MFI (temperature, T , and load, P , were stated) showed that for materials of different viscosity, the shear rate (γ) changed somewhat. At a given T and P , however, the variation in viscosity, which was a consequence of the pseudoplasticity of the test materials resulting from a changeable shear rate, was not substantial. When determining MFI values for the [PP/LDPE]-*g*-IA blends at $T = 190^\circ\text{C}$, the shear rate varied from 0.13 to 14.1 s^{-1} (Table I); marked deviations from Newtonian flow were detected for PP and LDPE at $\gamma \geq 10^2 \text{ s}^{-1}$.^{20,21}

The shear rate was calculated from eq. (5):²⁰

$$\gamma = \frac{4\text{MFI}}{t_c \pi r_c^3 \rho} \quad (5)$$

TABLE I
Dependence of Properties of Initial Polyolefins and Functionalized [PP/LDPE]-*g*-IA Blends
on Ratio of POLYMER COMPONENTS

Test material (wt %)	α (%)	T (°C)				E_a (kJ/mol)	Gel content (%)	σ_m (kPa)	K_m (rel.un)
		190°C		230°C					
		MFI (g/min)	γ (s ⁻¹)	MFI (g/min)	γ (s ⁻¹)				
PP	—	4.9	4.0	11.4	9.5	40.8	0	2.3	2.5
PP- <i>g</i> -IA	60.2	15.6	13.4	16.2	14.3	1.5	0	0.4	1.5
[99PP/1LDPE]- <i>g</i> -IA	61.8	16.9	13.9	17.0	14.2	0.3	0	0.3	1.5
[95PP/5LDPE]- <i>g</i> -IA	66.8	17.3	14.1	17.4	14.2	0.3	0	0.5	1.6
[75PP/25LDPE]- <i>g</i> -IA	74.2	16.6	14.1	16.2	13.6	-7.0	0	2.0	2.1
[50PP/50LDPE]- <i>g</i> -IA	78.3	5.7	4.6	17.1	13.4	53.6	3.4	13.6	3.0
[25PP/75LDPE]- <i>g</i> -IA	85.1	5.5	4.5	16.5	14.2	53.2	5.7	20.2	2.2
[5PP/95LDPE]- <i>g</i> -IA	89.8	0.1	0.18	0.5	0.63	77.8	27.4	21.3	2.1
[1PP/99LDPE]- <i>g</i> -IA	90.6	0.2	0.13	0.7	0.92	62.0	22.1	32.6	2.0
LDPE- <i>g</i> -IA	91.8	0.3	0.26	1.6	1.33	81.0	16.7	35.0	1.9
LDPE	—	7.4	6.0	18.0	14.2	43.0	0	3.1	3.0

where t_c (600 s) is the time constant, r_c is the capillary radius (m), and ρ is the polymer density (kg/cm³).

Determination of strength and swelling of molten material

The highly elastic behavior of [PP/LDPE]-*g*-IA systems was judged by the strength (σ_m) and swell index (K_m) of a molten jet. To investigate these, a device based on the piston-type laboratory injection-molding machine designed at MPRI NAS (Belarus) was used. It was equipped with a capillary 1.45 mm in diameter and 2 mm in length. The cylinder and nozzle of the machine were assembled vertically. To determine σ_m , a force was exerted on the molten material in the machine, so that the applied velocity to move the piston and hence the velocity of the melt leaving the capillary was constant, which was 3.5 g/min. Having reached a certain length, the extrudate broke off under the effect of its own weight.

The values of σ_m were calculated by the expression²⁰

$$\sigma_m = \frac{G_m}{S_c} \quad (6)$$

where G_m is the critical weight of a molten extrudate forced to flow through the capillary (when this weight was exceeded, the jet was separated from the capillary) and S_c is the surface area of the capillary cross section.

The ratio of G_m to the cross-sectional area of the capillary made it possible to eliminate otherwise unavoidable inaccuracies caused by the difficulty of measuring a true cross-sectional area of the extrudate the moment it started to break off.

When the swell index was being determined, short segments of the extrudate (about 15.0 mm) were forced through the capillary at a rate of 10.8 g/min, then cut off with a scalpel. The piston of the injection-molding machine was pulled backward to reduce the

diameter of the extrudate at the point it was cut off. The separated segment was immediately put into water preheated to 70°C; it was removed from the water after 3–5 min. Measurements were conducted after 10–12 h.

K_m was calculated by the formula^{20,21}

$$K_m = \frac{d_m}{d_c} \quad (7)$$

where d_m is the greatest diameter of a short piece of the extrudate and d_c is the capillary diameter.

The experiments to determine σ_m and K_m were carried out at 230°C. All the parameters examined for the [PP/LDPE]-*g*-IA systems were compared with those of the functionalized homopolypropylene (PP-*g*-IA) and homopolyethylene (LDPE-*g*-IA), which were obtained and tested according to the methods described above.

Determination of gel content

Samples of [PP/LDPE]-*g*-IA each weighing 1 g were packed in a metal net that had been previously weighed and then were placed in a flask containing xylene. Antioxidant Irganox 1010 (1 wt %) was added to the solution. The soluble fraction was extracted at the boiling temperature of xylene for 12 h. After extraction was complete, the net with the samples was removed and placed into a porcelain cup to dry in a vacuum chamber at 80°C to a constant weight. The gel content was calculated as the weight ratio of the insoluble fraction to the initial weight of the sample.^{22,23}

RESULTS AND DISCUSSION

Effect of PP and LDPE ratios on grafting efficiency

Data on the course of the grafting reactions of IA onto PP, LDPE, and PP/LDPE blends are presented in

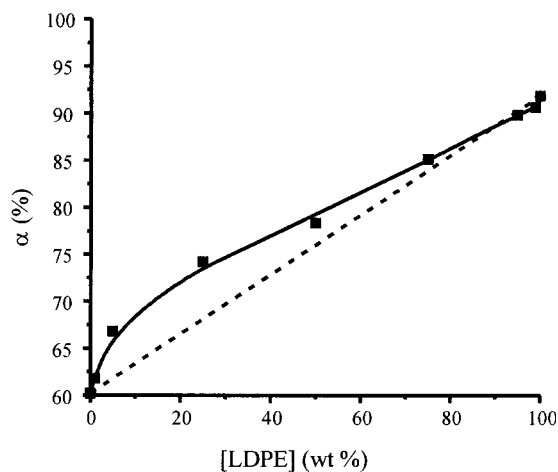


Figure 2 Effect of LDPE concentration in PP/LDPE blends on IA grafting efficiency (α) (solid line). In Figs. 2–5, 7 dotted lines stand for additive values of the tested variables calculated as the sum of values for initial PP and LDPE with account for their concentrations in blends under consideration.

Table I and Figure 2. The ratios of PP and LDPE in the reaction mixture strongly influenced the grafting efficiency (α). The higher the LDPE concentration in the PP/LDPE blends, the greater was the grafting efficiency, whereas a higher PP concentration caused the α value to decrease. The extent to which the addition of LDPE or PP influenced the α value depended on their concentrations. For LDPE added at relatively low concentrations (up to 25 wt %), the α value increased at a higher rate and the relationship was nonlinear. For LDPE concentrations between 25 and 95 wt %, the association approached a linear pattern, that is, α rose monotonically with LDPE concentration.

Thus, low concentrations (up to 25 wt %) of LDPE affected the increase in the α value more significantly

than low amounts of PP affected the decrease in the α value in cases in which IA was grafted onto a PP/LDPE blend.

The increased grafting efficiency of IA, in contrast with the additive one, at LDPE concentrations below 25 wt %—the continuous phase in PP/LDPE blends is formed by the PP phase—could be a result of the LDPE \cdot macroradicals formed being initiated by PP \cdot macroradicals. Judging by the MFI values, LDPE participated chiefly in the grafting reaction of IA and did not undergo recombination between them. It is quite probable, therefore, that at LDPE concentrations below 25 wt %, the increase in the α values, in contrast with the additive ones, resulted from the prevailing grafting of the monomer onto LDPE macromolecules and not onto PP macromolecules.

Of all the materials tested, the functionalized homopolymer PP (PP-*g*-IA) showed the lowest α values. The highest α values were found for LDPE grafted with IA (LDPE-*g*-IA). Similar results were obtained in previous studies,^{11,23} which showed higher yields of the grafted products when maleic anhydride was grafted onto LDPE than when it was grafted onto PP. It should be noted that the concentration dependence of the α value was nonadditive because this relationship was nonlinear at relatively low concentrations of LDPE (up to 25 wt %).

The magnitude of α exceeded the additive value for LDPE concentrations between 1 and 90 wt %.

Effect of PP and LDPE ratios on melt behavior of [PP/LDPE]-*g*-IA systems and gel content

The MFI determined at $T = 190^\circ\text{C}$ and $P = 5$ kg was found to depend on blend composition in a more complicated manner than did grafting efficiency [Table I, Fig. 3(a)]. The data shown in Table I and Figure 3(a) allowed distinguishing three groups of blends with

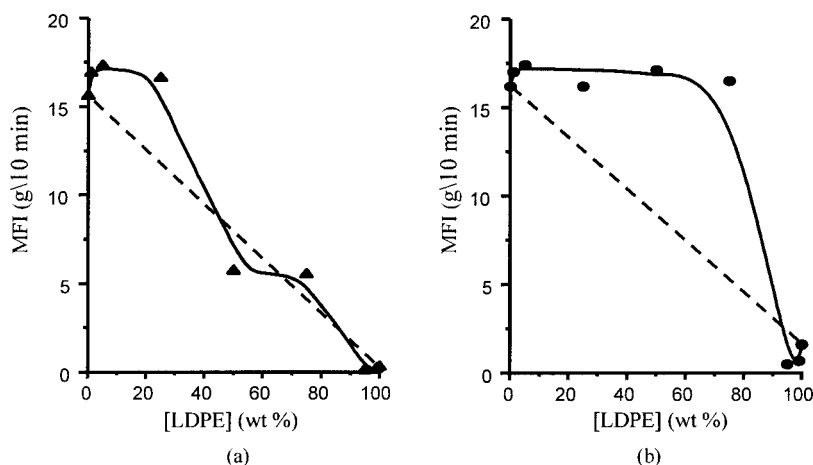


Figure 3 Effect of LDPE content on MFI of the test materials at (a) 190°C and (b) 230°C (solid lines). For dotted lines, see Figure 2.

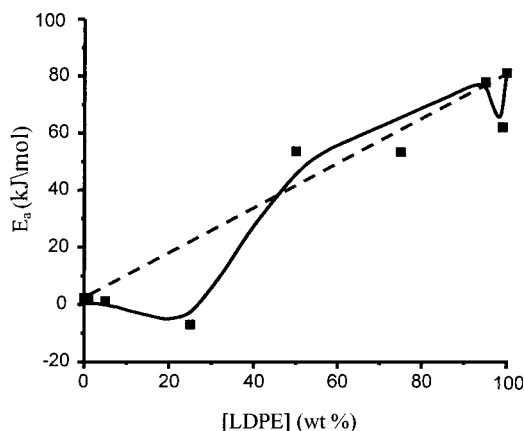


Figure 4 Effect of LDPE concentration on apparent activation energy of viscous flow (E_a) for [PP/LDPE]-g-IA systems (solid line). For dotted lines, see Figure 2.

different rheological behavior depending on the concentrations of PP and LDPE.

The [PP/LDPE]-g-IA systems, for example, which contained 75–99 wt % PP (the continuous phase in the PP/LDPE blends was formed by the PP phase) had higher MFI values, more than three times that of the initial PP. The maximum MFIs were typical of [95PP/5LDPE]-g-IA systems. Moreover, these blends showed a sharp decrease in the apparent activation energy of the viscous flow, down to the negative values for the [75PP/25LDPE]-g-IA system [Table I, Fig. 3(a)].

PP/LDPE blends with polymer component ratios of 50 : 50 and 25 : 75 most likely formed a continuous phase of the two components in the blend. As a result, the apparent viscosity was observed to rise sharply (MFI decreased). These blends had MFIs close to those of the initial PP and LDPE.

Further increases in LDPE concentration (compositions of 5 : 95 and 1 : 99 in which LDPE made the continuous phase) led to still lower MFI values. At the same time, E_a was observed to grow (Fig. 4). It was noticeable that the [PP/LDPE]-g-IA systems containing 1 and 5 wt % PP had lower MFIs than did the LDPE-g-IA systems.

The pattern of dependence of MFI at $T = 230^\circ\text{C}$ and $P = 5$ kg on the composition of the [PP/LDPE]-g-IA systems was roughly the same as that at $T = 190^\circ\text{C}$ and $P = 5$ kg [Table I, Fig. 3(a,b)]. The only difference was that a greater number of systems differing in composition showed higher MFIs (several times exceeding the MFIs of the PP-g-IA and LDPE-g-IA), whereas the viscosity began to increase sharply only when the PP concentration was less than 25 wt %. It is quite probable that at $T = 230^\circ\text{C}$, a low-viscosity PP-g-IA melt formed a continuous phase up to a concentration of 25 wt %. This occurred only after a phase inversion at a PP of less than 25 wt % because the viscosity of blended systems depended on the viscosity of LDPE-g-IA, which formed a continuous phase. The related viscosity of the materials varied inversely to the variation in MFI (Fig. 5).

The variations observed when IA was grafted onto PP/LDPE blends can be explained by the mechanisms of free-radical processes (initiated by organic peroxides) occurring in molten PP and LDPE (Fig. 6). Peroxide produces macroradicals by abstracting a hydrogen atom from the polymer substrate when the substrate interacts with free radicals, which have been formed by thermolysis of the peroxide used.^{4-7,11,23,24}

The macroradicals can participate in subsequent chemical reactions such as grafting of a monomer, crosslinking of the chains, and their degradation. The tendency of macroradicals to participate in one or

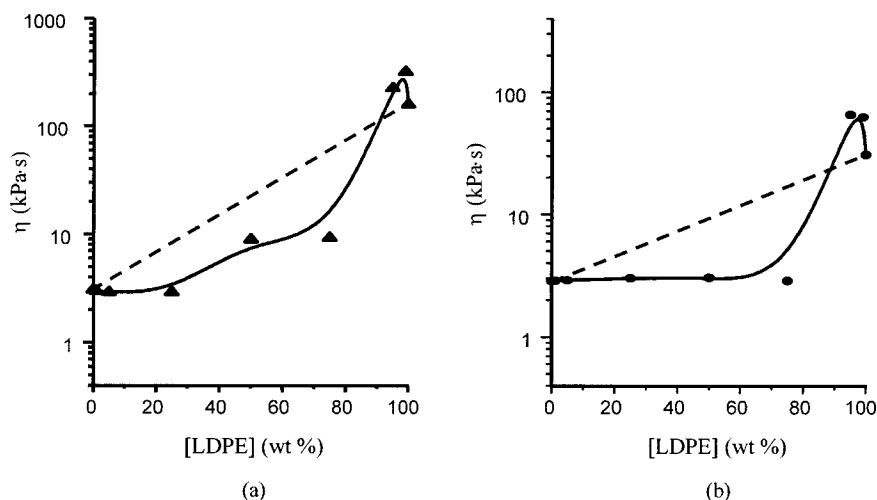


Figure 5 Effect of LDPE concentration in [PP/LDPE]-g-IA systems on their viscosity (η) at (a) 190°C and (b) 230°C (solid lines). For dotted lines, see Figure 2.

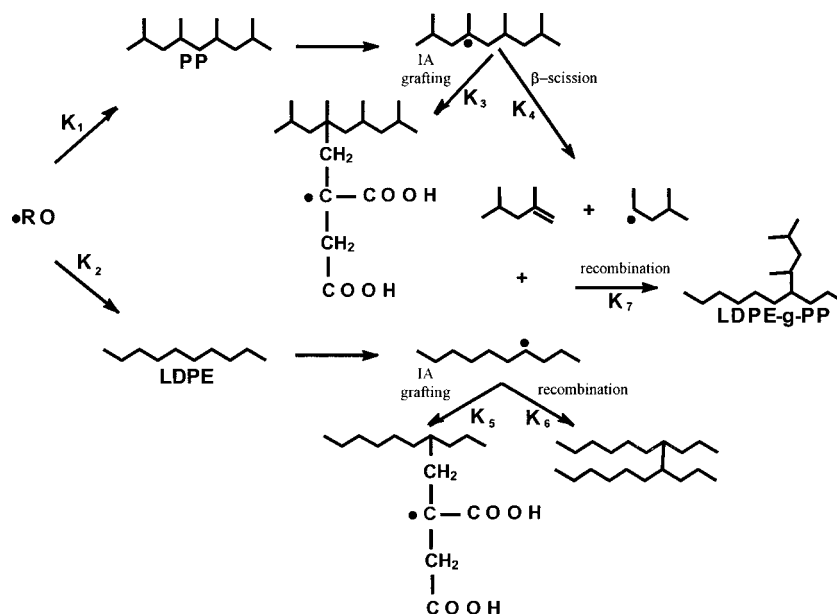


Figure 6 Scheme of probable chemical reactions occurring at free radical grafting of IA onto PP/LDPE blends.

another reaction depends on their chemical structure as well as on the composition of the reaction medium and technological factors.

PP• macroradicals result from the H atom abstracted mostly from tertiary carbon atoms in a polymer chain.^{4,11,23,24} Subsequently, these macroradicals may participate either in β scission (resulting in chain degradation) or in the joining reaction of a monomer (Fig. 6). A relatively low grafting efficiency typical of both the initial PP and PP/LDPE blends (containing between 75 and 99 wt % PP) can be explained by a higher rate of β scission of PP chains than in the IA-grafting rate.^{11,23,24} The higher rate of β -scission was indicated by a marked increase in the MFI for PP-g-IA and [PP/LDPE]-g-IA systems with a high PP content, compared with the MFI for the initial PP (Table I).

The methyl group,²⁵ present near the reaction center, created extra steric obstacles to interaction of the grafted monomer with the PP macroradicals, thereby hindering grafting and promoting β scission.

For LDPE, macroradicals formed with the participation of secondary carbon atoms have no such obstacles to grafting reactions; as a result, higher grafting efficiency was observed for IA grafting onto LDPE chains than for PP.

Grafting efficiency could also be increased by introducing LDPE into PP. Apart from the interaction with the monomer, LDPE macroradicals were involved in recombination reactions leading to crosslinking, branching, or chain extension, which increased the apparent viscosity (and decreased the related MFI) of LDPE-g-IA as well as [PP/LDPE]-g-IA systems containing higher amounts of LDPE.

Figure 6 illustrates that β scission of PP macroradicals resulted in other (new) macroradicals belonging to a secondary carbon atom. However, some authors^{11,23,24} believe such radicals do not markedly affect the grafting process because of their fast termination.

β Scission of macroradicals and their recombination, which take place during monomer grafting onto PP and LDPE, are side reactions. They are undesirable in many situations because they are harmful for the grafted product yield and can cause unfavorable changes in the rheological properties of GPO (and some other properties). In PP and LDPE during grafting, opposing side reactions (degradation and crosslinking of chains) occurred. It was assumed, therefore, that certain quantities of one or another polymeric component introduced into a PP/LDPE blend could control the extent of macromolecular transformations and rheological behavior of polymer melts. However, it is evident from Table I and Figures 3–5 that a small quantity of PP did not produce an increase; on the contrary, it led to a lower MFI for [PP/LDPE]-g-IA systems relative to that for LDPE-g-IA. In turn, a small quantity of LDPE, despite expectations, appeared to increase the MFI of GPO blends against PP-g-IA.

In our opinion, knowing these facts is important when attempts are made to understand the general mechanisms of the transformations observed.

It is obvious that for [PP/LDPE]-g-IA blends containing LDPE below a concentration of 25 wt % when PP is a continuous phase, degradation of PP chains prevailed over macroradical recombination, and the former proceeded faster in comparison with PP-g-IA. This can be explained as follows. First, it is quite probable that the rate of reaction between PP chains and

free radicals (formed during decomposition of the peroxide initiator) was higher for PP than for LDPE. For PP, an H atom was abstracted from a tertiary carbon atom, not from a secondary one, as occurred with LDPE. The formed radical would tend to undergo β scission than recombination. Most likely because of this, it was difficult to produce grafted copolymers such as LDPE-*g*-PP, the presence of which could influence the rheological properties of the materials. Another obstacle to obtaining LDPE-*g*-PP copolymers, as reported previously,²⁶ could be the two-phase structure of PP/LDPE blends. This type of structure is also found in their melts. As a result, each of the polymers studied may have been involved in free-radical processes independently of each other. For such a situation, however, additive variation in the MFI should be anticipated.

Obviously, with equal concentrations of the components (1 : 1 ratio), at which two cocontinuous phases are likely to form, their effect on MFI depends on the degree of conversion in each of the blended components.

The MFI for [PP/LDPE]-*g*-IA systems containing small quantities of PP, when LDPE is a continuous phase, could decrease compared to the MFI for LDPE-*g*-IA because of a higher concentration of LDPE macroradicals that could have been initiated by products of PP chain degradation through a radical mechanism. In addition, in the presence of PP there was a greater probability that LDPE macroradicals would be formed through mechanochemical reactions, also typical of the reactive extrusion process.³ Also, the possibility of some additional changes in the rheological properties of materials, when [PP/LDPE]-*g*-IA systems are tested to determine their MFI should be considered. Naturally, these variations also will depend on the test temperature.

Variations in E_a are also related to chemical processes of IA grafting onto PP/LDPE blends and depend on their composition (Table I, Fig. 4). The rather small E_a values for [PP/LDPE]-*g*-IA systems containing a concentration of PP between 99 and 75 wt % could be explained as follows. The reaction of β scission, in particular, increased the linearity of the PP chains at the expense of a reduced number of side substituents (methyl groups). In addition, a consider-

able quantity of low-molecular-weight oligomers were accumulated in the polymer structure, and the chains became more flexible because of the plasticizing effect of LDPE.^{21,27} The negative values of E_a for the [75PP/25LDPE]-*g*-IA system obviously could have resulted from additional crosslinking or branching of the material when it was kept at an elevated test temperature in the measuring cylinder of the instrument while the MFI was being determined. Because of this, in particular, the MFI values were lower at 230°C than at 190°C (Table I).

For [PP/LDPE]-*g*-IA systems containing at least 50 wt % LDPE, an increase in E_a resulted from macroradicals recombination. This led to a greater number of side branches, thus restricting the flexibility of chains and creating obstacles to their conformable rearrangement at flowing.

Thus, the analysis of rheological behavior of [PP/LDPE]-*g*-IA blends revealed a complex mutual influence of the polymeric components on the course of free-radical transformations in chains during reactive extrusion. The joint analysis of data related to the dependence of grafting efficiency and MFI on concentration was advantageous for formulating a substantiated opinion about the tendency of reactions that take place in such systems.

The information on the MFI and E_a values determined for the original, that is, the unfunctionalized blends of PP/LDPE (Table II), provide evidence of the prevailing effect (within the range of values examined) of specific chemical transformations that occur during grafting of IA. When the ratio of the components in a mixture of PP/LDPE was varied, MFI and E_a varied between those typical of the original components independently of the phase structure of the materials. This shows the absence of any specific interactions in the PP/LDPE blended systems prepared in our experimental conditions.

The above reasoning is logically supported by data on gel content in the initial PP/LDPE as well as functionalized [PP/LDPE]-*g*-IA blends (Table I). It was found that in functionalized blends with a prevailing PP component, crosslinking of LDPE was completely suppressed. The functionalized blends to which small concentrations of PP (between 1 and 5 wt %) had been added were characterized by a higher gel content

TABLE II
Values of Properties of Binary Blends of Initial PP and LDPE

Test material (wt %)	MFI (g/min)		E_a (kJ/mol)	σ_m (kPa)	Km (rel.un.)
	190°C	230°C			
95PP/5LDPE	5.2	13.3	45.4	1.5	1.8
75PP/25LDPE	6.1	15.5	45.1	1.7	2.1
50PP/50LDPE	6.6	15.7	42.0	2.2	2.2
25PP/75LDPE	6.8	16.0	45.1	2.4	2.1
5PP/95LDPE	7.1	17.1	42.6	2.7	2.0

compared with that in the [PP/LDPE]-*g*-IA. These data corroborated our supposition about the possibility of initiating grafting and crosslinking of LDPE macromolecules at the expense of PP macroradicals formed in the course of macromolecular transformations. It is worth mentioning that a maximum gel content (27.4%) was found in the [5PP/95LDPE]-*g*-IA composition. Table I shows that this proper composition had the lowest MFI (0.1 g/min) and the highest E_a (77.8 kJ/mol) of all the blends tested.

As should have been expected in the experimental conditions, when the initial PP and LDPE were mixed, no crosslinked structures were formed that would characterize the absence of a gel fraction.

High elasticity of molten [PP/LDPE]-*g*-IA systems

The strength of molten material, as well as its swell index, influences the processing of PP and LDPE.^{20,21,28} These properties are of paramount importance when films, hollow vessels, and so forth are made by blow extrusion. As PP is a linear polymer, it has low-strength molten material unlike that of LDPE, so that the former finds limited applications. To increase the strength of the molten material, PP is subjected to chemical modification in order for longer side branches to form, or it is mixed with high-molecular-weight polymers.²⁸ There is little information about the effect of grafting on the strength of the molten material and extrudate swelling of POs or their blends.²⁸ It was of interest, therefore, to study changes in these properties caused by IA-grafting onto PP/LDPE blends.

Figure 7 and Table I show the strength behavior of molten [PP/LDPE]-*g*-IA depending on the ratio of PP

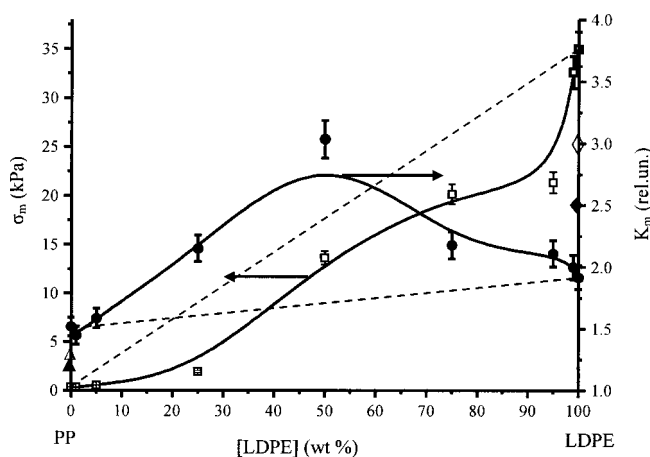


Figure 7 Effect of LDPE concentration in [PP/LDPE]-*g*-IA systems on strength of the molten material (σ_m) and swell index of the molten jet (K_m) of these blends (solid lines). \blacktriangle – strength of the molten material of initial PP; \blacktriangle – strength of the molten material of initial LDPE. \blacklozenge – swell index for initial PP; \blacklozenge – swell index for initial LDPE. For dotted lines, see Figure 2.

to LDPE. A comparison of the systems in which PP was dominant with those in which LDPE was dominant showed a considerable increase in the strength of the molten material with higher LDPE content. The [PP/LDPE]-*g*-IA systems containing a high PP content (between 75 and 100 wt %) showed molten material of extremely low strength in comparison with both the initial PP and [PP/LDPE]-*g*-IA systems containing a high content of LDPE. As the strength of the molten material mostly depended on the molecular characteristics of the polymer materials (molecular weight, MWD, degree of branching, etc.), as well as on intermolecular interactions in the blends and their phase structure, then it was quite possible that low-strength molten [PP/LDPE]-*g*-IA systems containing higher PP concentrations would result from its largely reduced molecular weight caused by degradation processes involved in IA grafting.^{21,28}

The strength of the molten material increased for [PP/LDPE]-*g*-IA systems of equal polymer component ratios and for systems containing higher amounts of LDPE. This can be explained by a continuous phase developed by partially crosslinked LDPE (Table I), which led to increased melt viscosity and, obviously, to intensified interactions of phases in the blends.

Unlike the strength of the molten material, the dependence of the swell index on the ratio of polymeric components in the [PP/LDPE]-*g*-IA systems was extreme in nature (Fig. 7, Table I). The [PP/LDPE]-*g*-IA systems with a polymer component ratio of 1 : 1 showed a maximum swell index. The swelling effect depended on the elastic and relaxation properties of the polymeric materials. Polymers characterized by a wide MWD and a high melt viscosity usually have a higher swell index.^{20,21} It is quite possible that blends with equal weight ratios of the polymer components had the widest MWD because of the reactions involved in IA grafting. On the basis of the experimental data presented, it can be understood that a reduction in molecular weight typical of blends with increased concentrations of PP, same as presence of crosslinked structures typical of blends with increased concentration of LDPE, leads to reduced elasticity of melt, resulting in a reduced swell coefficient for such systems.²¹

It is evident that the σ_m and K_m values for unfunctionalized PP/LDPE blends given in Table II were somewhat lower than the additive ones independently of the phase structure of the blends. An obvious reason for this is the absence of intensive interphase interactions between the components of the PP/LDPE binary blends as well as crosslinked structures. These results, as well as the results for the original and functionalized blends (Tables I and II), prove the determinant role of chemical processes (especially secondary reactions of degradation and crosslinking)—occurring when IA was grafted onto PP/LDPE blends—in the

rheological and highly elastic properties of the molten PP/LDPE blends.

CONCLUSIONS

The ratios of polymeric components in PP/LDPE blends exerted a great influence on the course of IA grafting as well as on the accompanying transformations (side reactions). The major effect of PP on monomer grafting was to reduce the yield of grafted product when the concentration of this component in a blend was increased. This is explained by the tendency of PP to degrade during peroxide-initiated grafting when the formed macroradicals suffer degradation by β scission.

With relatively low concentrations of LDPE in the PP/LDPE blends, a nonlinear (more visible in comparison with additive dependence) rise in the IA-grafting efficiency was observed. For LDPE concentrations between 25 and 95 wt %, the dependence of grafting efficiency on composition approached a linear pattern, that is, α increased monotonously with LDPE concentration.

The data on the rheological behavior of molten [PP/LDPE]-g-IA systems suggested the influence of the polymeric components on the course of free-radical chain transformations taking place during reactive extrusion was complex in nature.

Small amounts of one or another polymeric component introduced into a blend caused some changes in the rheological properties of molten [PP/LDPE]-g-IA systems. For instance, a small (below 25 wt %) quantity of LDPE, contrary to expectations, would increase the MFI, whereas small amounts of PP would decrease the MFI of [PP/LDPE]-g-IA systems compared to LDPE-g-IA systems. Here, blends with LDPE concentrations below 25 wt % were characterized by extremely low apparent activation energy of viscous flow. For [75PP/25LDPE]-g-IA systems, the activation energy could even be negative.

Variations in the ratio of polymeric components in the [PP/LDPE]-g-IA systems cause nonadditive, complex changes in the swell index of a molten jet and in the strength of the molten blended materials under discussion.

The results reported in this article are characteristic not only of grafting of itaconic acid onto PP/LDPE blends carried out in a Brabender plastograph equipped with a dynamic mixer, but also of IA grafting performed

in reactors of other types, particularly, a single-screw extruder.

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