

Free Radical Grafting of Itaconic Acid and Glycidyl Methacrylate onto PP Initiated by Organic Peroxides

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ABSTRACT: Comparative analysis was conducted to learn the grafting of itaconic acid (IA) and glycidyl methacrylate (GMA) onto polypropylene (PP) in the course of reactive extrusion. Seven organic peroxides, which satisfactorily dissolve in PP, but do not dissolve in the monomer, were used to initiate free-radical reactions. The grafting of IA and GMA onto PP initiated by certain peroxides gave approximately equal amounts of grafted product. It was learned that the nature of peroxide initiators is decisive for grafting efficiency and degree of macromolecular degradation. To ensure a high yield of grafted product, it is advisable to use peroxides, which have thermodynamic affinity with PP and the temperature range of decomposition of which corresponds to the thermal regime of reactive extrusion. Di(*tert*-

butyl peroxy-isopropyl)-benzene (P-14) appeared to meet for the most these requirements for grafting both GMA and IA. Grafting is accompanied by β -decomposition of the chains irrespective of the type of peroxide and monomer used; hence, the MFI increases. A considerable rise in MFI was observed at a minimum peroxide concentration (0.1wt %). Degradation of PP during modification eases its crystallization from the melt. In this case the crystallization temperature is 5 to 8.5°C higher than of the original PP, and the crystallinity degree increases by 20 to 60%. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 64–72, 2002

Key words: graft copolymers; poly(propylene); reactive processing; initiators

INTRODUCTION

Reactive extrusion is widely used for chemical modification of polymers and their blends by grafting of polar monomers onto macromolecules to improve their adhesional efficiency, and to prepare compatibilizers for polymer/polymer systems.^{1–4} In molten polymers in the extruder some chemical reactions follow the free radical mechanism.^{1–4} These reactions can be best initiated by organic peroxides. Side processes that usually accompany the grafting in a molten polymer like crosslinking and breakdown of the chains are very important.^{2–4} Crosslinking is most typical of polyethylene and copolymers based on ethylene.^{5–11}

The modification of polypropylene (PP) causes breakdown of the chains, which reduces both molecular weight and melt viscosity.^{12–16} This results from hydrogen atom abstraction from the PP main chain, with formation of tertiary macroradicals.¹⁵ The intramolecular transformations of macroradicals are accompanied by disintegration of the polymer chain.^{15,16} Such disintegration, initiated by peroxides, has been

used to produce PP with controllable rheology, using the reactive extrusion method.^{17–19}

It is reasonable to assume that competition between the grafting and side processes, which determine the chemical structure of the product, will largely depend on the nature and concentration of the peroxide used. During rapid processes typical of reactive extrusion, the reactivity of the peroxide initiator and its dissolution in the basic components of the reaction blend, i.e., polymer and monomer, can markedly influence the course of grafting reactions and concomitant conversions.^{8,9,20} The mutual dissolution of the components can be very important under conditions of poor mixing, which can be found, for example, in a single-screw extruder serving as a reactor mixer.⁸

For initiating grafting of itaconic acid (IA) onto low-density polyethylene (LDPE), peroxides, which easily dissolve in molten PE, are preferable.⁹ The closer the peroxide affinity to the monomer, the lower is the grafting efficiency. Assoun et al.²¹ studied the problem of how the peroxide nature influences the kinetics of grafting monomers onto PP. The specific feature of the peroxides used there was their asymmetric structure and, at the same time, they were monomers containing the carboxyl group. That is why breakdown of peroxides was accompanied by their grafting onto polymer chains. It was learned that the peroxides, which after breakdown form methyl radicals, increase the grafting

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efficiency. It was not the case with peroxy-acids, which after breakdown form ethyl radicals.

The grafting reactions of acrylic and polyacrylic acids,^{22–24} maleic anhydride,^{25–29} glycidyl methacrylate,^{13,30,31} and oxaline and its derivatives^{32–34} onto PP are currently well understood. In recent years, however, IA there has been interest in grafting onto polyolefins. A systematic study of the chemical conversions was undertaken only for grafting of IA onto LDPE.^{6–9,35} It was of interest to understand in detail the grafting of IA onto PP with making use of several peroxides characterized by a closer affinity to the polymer. The highest yield of the grafted products could be obtained in that case. In the present work, for comparison, all experiments on grafting of IA onto PP were run in parallel with grafting of GMA, because its interaction with PP had been relatively well understood.

EXPERIMENTAL

Materials

In this work we used: thermally stabilized PP (trade name Kaplen) produced by Moscow Refining Plant, Russia (Grade 01030; Specifications 2211-015-00203521-95; density 0.905g/cm³, melting point 169°C as defined by DSC; melt flow index (MFI) was 7 g/10 min at 210°C and load 5 kg); IA supplied by Chemical Division Pfizer Co., USA; GMA (glycidyl methacrylate) supplied by Aldrich-Chemical Co., Germany; organic peroxides having different structures, namely, mono-peroxides such as *tert*-butyl peroxide (TBP), and dicumyl peroxide (DCP) supplied by Orgsintez Co., Russia; diperoxides such as 2,5-dimethyl-2,5-di(*tert*-butyl peroxy)-hexane (L-101) and 2,5-dimethyl-2,5-(*tert*-butyl peroxy)-hexane-3 (L-130), ELF Atochem Co., France; di(*tert*-butyl peroxy-isopropyl)-benzene (Perk-14, P-14), Aldrich-Chemical Co., Germany; 2,2-di(*tert*-butyl peroxy)-5,5,6-trimethyl bicyclo [2.2.1] heptane (D-1) and 2,2-di(3-methyl-1-butylperoxy)-5,5,6-trimethyl bicyclo [2.2.1] heptane (D-2).³⁶ Properties of the peroxides are given in Table I.

Methodology

Solubility parameters (δ) for the peroxides were calculated for 25°C (298 K) following the group contribution principle^{37–39} as in another work.⁹ It is quite clear that δ -values for the peroxides depend on temperature. The patterns of such dependencies for polymers and low molecular weight substances are similar, and can be determined⁴⁰ from the expression:

$$\ln \delta_T = \ln \delta_{298} - k\alpha(T - 298) \quad (1)$$

where δ_T and δ_{298} are values for temperatures T and 298 K; k is the coefficient ($k \approx 1$ for the polyolefin and

$k = 1.25$ for the peroxides and the monomers, IA and GMA); α is the coefficient of linear thermal expansion. Therefore, the solubility of the peroxides, GMA and IA, in LDPE determined at 25°C is objective enough. Such parameters for PP, IA, and GMA at 25°C were 16.3, 26.4, and 20.8 (J · cm⁻³)^{0.5}, respectively.

The viscosity of the molten polymer was estimated from the MFI, which was determined at 210°C and a 2.16-kg load, using the IIRT-AM instrument (Ekodatchik Co., Tula, Russia).

The thermal decomposition of peroxides was examined using the derivatograph Q-1500 (MOM Co., Budapest, Hungary) at a heating rate of 5°C/min, for 100 mg weight of the sample (Table II).

The differential scanning calorimetry (DSC) instrument model DSM-3A (Institute for Biology Instruments, National Academy of Russia) was used to learn the structure of the modified PP. The experiments were performed on a weight of the sample 4 mg and for the heating rate of 16°C/min. The crystallinity indices (I_{cr}) were found as the ratio of the areas under crystallization peaks for the modified PP to that for the initial polymer. The measurements were made on the samples heated up to 200°C in the cell of the calorimeter, maintained at this temperature for 1 min, and then examined repeatedly.

Preparation of test samples

The grafting process was conducted in a single-screw extruder⁴¹ with a screw diameter of 36 mm and L/D = 20 at a rotation speed of the 27 rev/min. The shearing rate was about 30 s⁻¹. The temperature for zone I was 175°C; for zones II, III, and IV, 195°C was used.

Before a reaction blend was prepared, the PP granules were treated by a solution of the peroxide in acetone, stirring thoroughly until all the solvent evaporated. Then the granules were covered by IA powder or mixed with liquid GMA. After that, the granules were charged into the extruder-reactor and grafting process took place. The modified molten PP, coming from the extruder, was cooled in water, and granulated.

Characterization

The grafting efficiency (α_g), i.e., the ratio of the grafted monomer to its total quantity added to the polymer, was accepted as the parameter describing the course of the grafting process.

$$\alpha_g = \frac{D_\tau}{D_0} \times 100 \text{ (wt. \%)} \quad (2)$$

Such efficiency was determined, as in other studies,^{6,8,9} on film samples of thickness between 40 and 60

TABLE I
Characteristics of Peroxide Initiators

| Peroxide | Abbreviated marking | Structural formula | δ , $(\text{J}\cdot\text{cm}^{-3})^{0.5}$ | Concentration of active oxygen, % |
|---|---------------------|--------------------|--|-----------------------------------|
| Dicumyl peroxide | DCP | | 17.4 | 5.92 |
| 2,5-Dimethyl-2,5-di(<i>tert</i> -butyl peroxy)-hexane | L-101 | | 15.5 | 11.03 |
| <i>tert</i> -Butyl peroxide | TBP | | 15.3 | 10.95 |
| 2,2-di(<i>tert</i> -butyl peroxy)-5,5,6-trimethyl bicyclo[2.2.1] heptane | D-1 | | 16.1 | 10.17 |
| 2,2-Di(3-methyl-1-butene-3-ylperoxy)-5,5, 6-trimethyl bicyclo [2.2.1] heptane | D-2 | | 16.3 | 9.57 |
| 2,5-Dimethyl-2,5-di(<i>tert</i> -butyl peroxy)-hexine-3 | L-130 | | 15.0 | 10.2 |
| Di (<i>tert</i> -butyl peroxy-isopropyl)-benzene | P-14 | | 16.4 | 9.0 |

TABLE II
Derivatography Data on Thermal Stability of Peroxides and Their Half-Life Time in Hydrocarbon Environment

| Peroxide | Beginning of decomposition peak (°C) | DTG completion (°C) | Maximum (°C) | TG weight loss (%) | Melting point (°C) | DTA exo-peak (°C) | | Decomposition parameters for peroxide in benzene (0.2 molar) | |
|----------|--------------------------------------|---------------------|------------------|--------------------|--------------------|-------------------|-----------------|--|--------------------|
| | | | | | | Beginning | Maxim | T, °C | $\tau_{0.5}$, min |
| DCP | 131 | 202 | 162 | 74.5 | 43 | 131 | 162 | 177 | 1 |
| L-101 | 118 | 176 | 155 | 94.0 | — | 123 | 162 | 177 | 1 |
| L-130 | 133 | 195 | 177 | 93 | — | 145 | 183 | 193 | 1 |
| P-14 | 148 | 192 | 182 | 82 | 58 | 150 | 185 | 180 | 1 |
| TBP | 15 ^a | 125 ^a | 103 ^a | 96.0 ^a | — | 30 ^a | 98 ^a | 160 | 1 |
| D-1 | 95 | 125 | 117 | 84.0 | 52 | 96 | 118 | 185 | 0.6 |
| D-2 | 85 | 110 | 104 | 86.0 | 40 | 86 | 104 | 192 | 2–2.5 |

^a Parameters characterizing processes of evaporation and partial decomposition of TBP.

μm by the absorptive IR-spectroscopy technique. It is based on analysis of the monomer added to the initial PP and that in the PP, extracted in ethanol at 70°C, or in acetone at 40°C (Fig. 1).

Owing to lower permeability of PP by polar liquids, in comparison with LDPE, the time for complete extraction of the ungrafted monomer portion is much longer than that for PE. When PP films were extracted in ethanol, the increase in time was almost 10-fold (Fig. 1).⁶ In alcohol, the monomer was fully extracted for about 150 h (in the case of LDPE-*g*-IA, it takes 15 to 17 h).⁶ In acetone, extraction process proceeds much faster (Fig. 1). It should be remembered, however, that the correctness of IR-spectroscopy technique, in determining carbonyl absorption of a monomer, might depend on the absorption of the carbonyl group of acetone that was sorbed by the polymer in the course of extraction. That is why the acetone must be removed from the films by drying before spectra are taken.

RESULTS AND DISCUSSION

Grafting of GMA

Peroxides used characterize increased thermodynamic affinity to the polymer (Table I). Peroxides D-1, D-2,

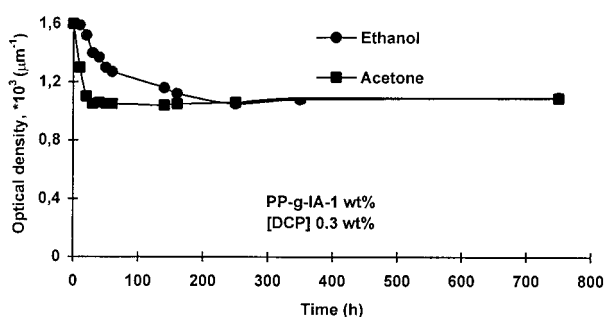


Figure 1 Effect of extraction in ethanol and acetone on relative optical density of the absorption band for carbonyl group.

L-101, and D-14 have solubility parameters similar to that of polypropylene. This implies a high solubility of them in the molten polymer. For systems without strong specific interactions between molecules of the solvent and the dissolved substance, they are miscible⁴² if their solubility parameters differ by less than 2 ($\text{J} \cdot \text{cm}^{-3}$)^{0.5}. Hence, it can be said that none of the peroxides used is miscible with GMA.

The analysis of the data obtained by the derivatography technique (Table II) shows that the peroxides differ much in their thermal stability. However, more accurate data were obtained for solid peroxides such as DCP, D-1, D-2, and P-14, for which a good coincidence in the temperature of the beginning of decomposition and the maximum decomposition rate can be seen on DTG and DTA curves. For the liquid peroxides L-101 and L-130, the maxima on DTG and DTA curves are somewhat shifted towards the higher temperature region. This shifting is most likely related to their volatility. As for TBP, it was rather difficult to obtain reliable data on thermal decomposition, because it became highly volatile during heating. A rather high thermal stability was shown by DCP. The least stable were anticipated to be gem-diperoxides D-1 and D-2; of these two, D-1 was the more thermally stable. The temperature range for fast decomposition of it is between 95 and 125°C; the maximum was observed at 117°C by the DTA technique. As for D-2, it decomposed between 85 and 110°C with a maximum at 104°C.

It was impossible to determine the half-life time for the peroxides in the moving molten PP under shearing conditions (the calculated shear rate was 30 s⁻¹ at the screw rotation speed of 27 rev/min). Our experiments were run in the extruder with the reaction zone at 195°C and the melt residence time in this zone was 1.2 min. It could be anticipated that these peroxides could decompose completely during reactive processing. This conclusion is based on mentioned facts, and data in Table II refers to the half-life time for the peroxides

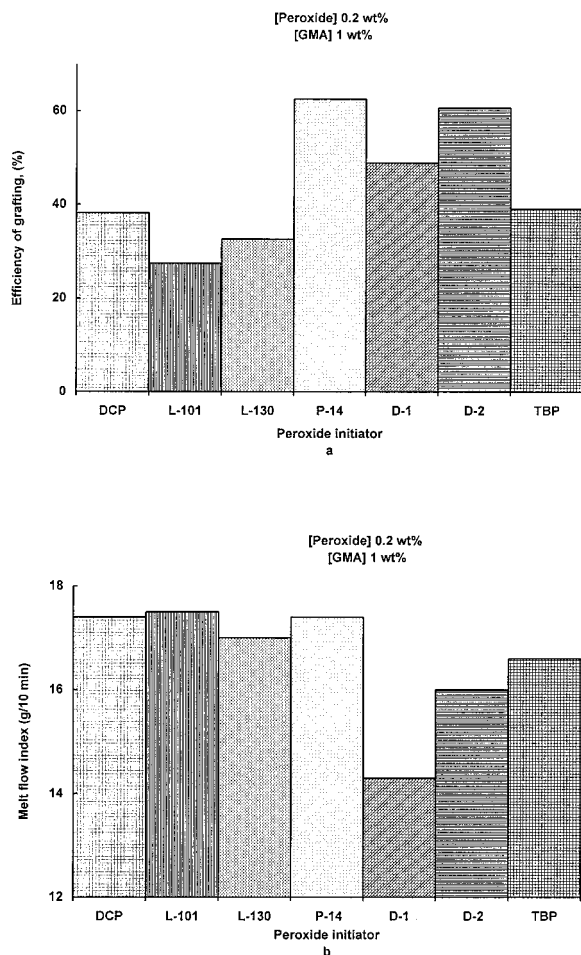


Figure 2 Effect of peroxide on grafting efficiency of GMA (a) and melt-flow index for PP-g-GMA (b).

in benzene, considering that their half-life time change little during thermal decomposition in molten polyolefin.

Figure 2 shows the effect of peroxides on grafting efficiency (α_g) and the MFI. It should be noted that this and further studies were conducted at constant thermal conditions in the extruder-reactor. Chen et al.³¹ revealed that the reaction temperatures between 170 and 200°C influence but little the grafting of GMA, initiated by peroxides. As it was mentioned in the Introduction, the grafting and breakdown of macromolecules compete when monomers are grafted onto PP. Therefore, the main problem, when preparing a modified polymer, is to provide for a maximum grafted product with a high molecular weight. The MFI gives a direct characteristic of the molecular weight for both the initial and modified PP, and is rather sensitive to the reaction of β -break of the PP chain.³¹

We have learned that the nature of peroxides substantially influences the parameters under consideration. It is important to emphasize that maximum α_g were obtained with peroxides P-14, D-1, and D-2 char-

acterized by best solubility in PP. Peroxides D-1 and D-2 were used to prepare PP-g-GMA with minimum breakdown (the lowest MFI). Somewhat lower α_g was obtained with TBP; the MFI were correspondingly higher.

Peroxides D-1, D-2, and TBP are less thermally stable than the other substances examined. These peroxides begin to break down rapidly at 96, 86, and 30°C, respectively, as determined from the beginning of exothermic effects on the DTA curves. Under the chosen conditions, temperature in the charging zone of the extruder-reactor was 175°C. In this zone peroxides and GMA could be dissolved in molten PP and disintegrated to radicals. It could be anticipated that the object for radical attack are PP chains, if we take into consideration closer affinity of D-1, D-2, and TBP to the polymer than to GMA, as well as lower solubility of the latter in PP, if compared with the peroxides. The formed macroradicals react with GMA to give PP-g-GMA and participate in the β -breakdown process, which leads to polymer degradation. Even the most thermally unstable TBP gives a relatively high grafting efficiency; hence, we believe that the formed macroradicals' lifetime is long enough (total residence time for the reactive blend was 1.5 min.). The results obtained support an earlier idea^{9,41} that peroxides with lower thermal stability can be used to initiate grafting of unsaturated monomers onto polyolefin following the reactive extrusion method.

Because TBP is highly volatile, a portion of this substance will evaporate from the charging zone of the extruder. Its real concentration in PP at the beginning of grafting will be, therefore, lower than that of the other peroxides. Once TBP decomposes, however, there are more $\cdot\text{CH}_3$ and $\cdot\text{OC}(\text{CH}_3)_3$ reactive radicals generated than with the other peroxides.⁴³ Consequently, a great quantity of macroradicals can be formed as early as in the charging zone. Because no perfect molecular contact is possible between the reactive macroradicals and the monomer is in this zone, a large portion of them can become deactivated in the reactions of macromolecular β -breakdown. Probably, for these reasons, TBP-initiated PP-g-GMA has lower α_g and higher the MFI in comparison with D-1 and D-2 (Fig. 2).

The differences in the initiating capacity of gem-diperoxide D-2 and its saturated analogue D-1 could be explained as follows. It was reported^{9,43} that breakdown of a D-1 molecule gives a low-reactive biradical A (Fig. 3), and two $\cdot\text{OC}(\text{CH}_3)_3$ radicals, which, during fragmentation, produce methyl reactive radicals $\cdot\text{CH}_3$.

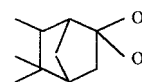


Figure 3 Biradical A.

The broken down D-2 molecule leads to biradical A and two $\cdot\text{OC}(\text{CH}_3)_2\text{C}\equiv\text{CH}$ radicals, which are less reactive than $\cdot\text{CH}_3$.⁴³ Despite increased concentration of reactive oxygen in D-1 and higher yield of reactive radicals during its thermal decomposition as compared with D-2, the latter ensures a higher grafting efficiency and deeper chain degradation [Fig. 2(a) and (b)]. This is indicative of the fact that chemical activity of peroxides may not be decisive in the yield of grafted and secondary products. In this case, because the tested PP is a commercial-grade product containing low molecular weight fractions and a stabilizer, although the solubility parameters of D-1 and D-2 are similar, the latter seems to be easier dissolved in molten PP. This would explain why initiation of grafting and degradation of D-2 macromolecules is more efficient than of D-1. The molecular weight of PP-g-GMA decreased less with D-1 and D-2 than with the other peroxides. This difference may be explained by interaction of tertiary macroradicals of PP with biradical A, when stable products are formed.

Peroxide P-14 appeared to be the most reactive initiator for both the basic and secondary processes [Fig. 2(a) and (b)]. P-14 differs from the other peroxides in better solubility in PP and in higher thermal stability (Table II). The temperature range for P-14 breakdown is most favorable for GMA grafting. A maximum quantity of free radicals from P-14 must be formed by the moment, when PP is completely melted and the monomer is thoroughly homogenized in this melt. Thus, solubility of peroxide in the polymer and its thermal stability are the most important factors that determine the course of GMA grafting reaction and macromolecular breakdown.

The decrease in α_g , when peroxides L-101 and L-130 whose structures resemble that of P-14 [Fig. 2(a)], initiate grafting can obviously, be explained by their poorer dissolution in PP. The concentration of formed macroradicals, therefore, is not enough to initiate grafting. They are mainly consumed in reactions of macromolecular β -breakdown [Fig. 2(b)].

The yield of PP-g-GMA, when DCP was the initiator, was approximately the same as with L-101, al-

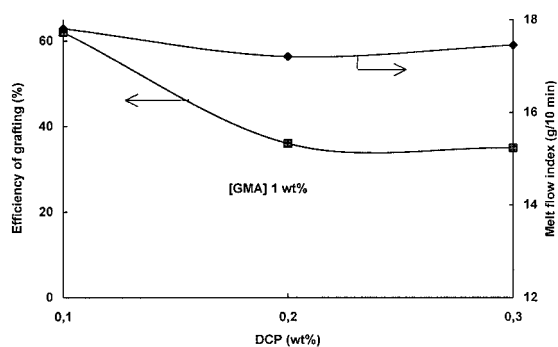


Figure 4 Effect of DCP concentration on grafting efficiency of GMA and melt-flow index for PP-g-GMA.

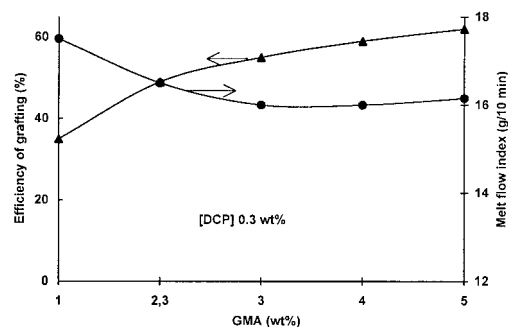


Figure 5 Effect of GMA concentration on its grafting efficiency and melt-flow index for PP-g-GMA.

though DCP contains a lower quantity of active oxygen and have a weaker affinity with PP (Table I). This fact could be explained, most likely, by thermal behavior of DCP. Peroxides DCP and P-14 are optimal for initiating grafting, in view of the breakdown temperature range, under experimental conditions. Chen et al.³¹ reported that increased concentration of a peroxide initiator is followed by higher α_g and the MFI; then PP undergoes degradation at a higher rate. At our experimental conditions, concentration increase of DCP from 0.1wt % to 0.3 wt % did not cause much change in the MFI, whereas α_g somewhat decreased (Fig. 4). Unlike Chen et al.,³¹ in our experiments the concentration of grafted GMA is much lower (1 wt % against 6-10 wt %); the initiator concentration was also lower and varied within a narrower range. Data in Figure 4 indicate that grafting was more efficiently initiated at the concentration $C[\text{DCP}] = 0.1$ wt %. Hence, when small quantities of GMA are to be grafted onto PP, it is not advisable to increase the initiator concentration. The excessive free radicals, formed from the decomposed peroxide, are obviously involved in oligomerization of the ungrafted GMA; this oligomerization occurs along with monomer grafting and PP degradation.³¹

Increased concentrations of GMA in the reaction blend lead, as it was expected,³¹ to higher grafting efficiencies and lower degree of chain degradation (Fig. 5). However, the monomer was not as powerful in suppressing degradation of chains as peroxide D-1 [Figs. 2(b) and 5]. That is why it is more advisable to use a peroxide of a certain composition and concentration, and not to vary the concentration of the monomer, to reach a most favorable relation between grafting and breakdown of the chains.

Grafting of IA

The comparison of data in Figures 2 and 4 reveals a marked effect of monomer's nature on the yield of products from the basic chemical processes, namely, monomer grafting and chain degradation. Grafting of

IA, initiated by P-14, L-101, and DCP, proceeds efficiently enough, the same as of GMA. In both instances, P-14 is the best initiator among the tested peroxides for the grafting reaction.

The reasons of high efficiency of P-14 have already been mentioned. They are an easy dissolution of this peroxide in molten PP and coincidence of the temperature range of its thermal decomposition and the temperature regime at which reactive extrusion was performed (Table II). Similar to the grafting of IA onto LDPE, the lowest yield of PP-g-IA can be achieved by using thermally unstable peroxides D-1, D-2, and TBP. In comparison with GMA, these peroxides gave lower yields of PP-g-IA, namely, by 1.8, 2.9, and 1.3 times, respectively [Figs. 2(a) and 6(a)]. The lower thermal stability of the peroxides and the fact that initial IA is a solid substance, unlike GMA, are the major factors that gave the present result.

The decreased thermal stability leads to lower concentrations of D-1, D-2, and TBP peroxides than the initial magnitude by the moment when grafting and β -breakdown started. This results in lower concentrations of reactive radicals in the reaction zone. In the

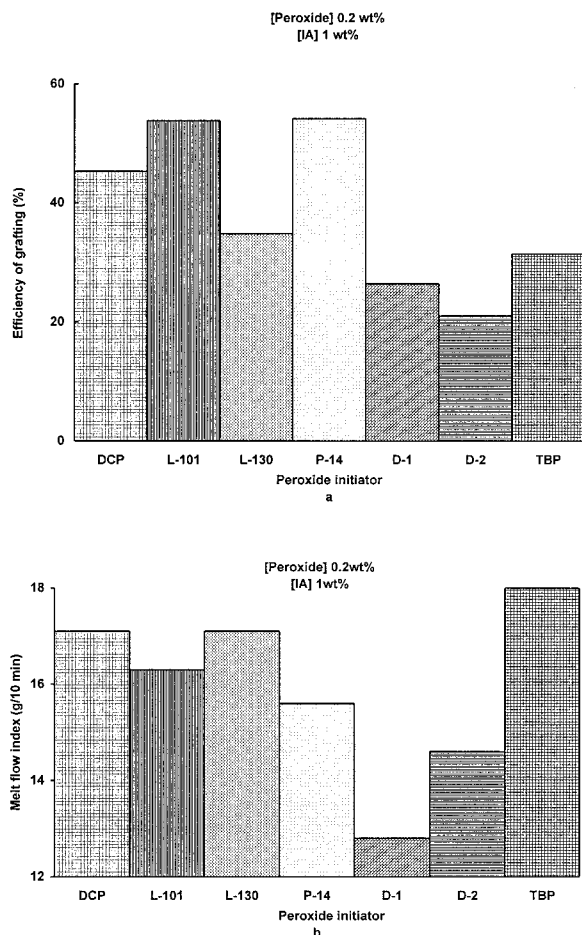


Figure 6 Effect of peroxides on grafting efficiency of IA (a) and melt-flow index for PP-g-IA (b).

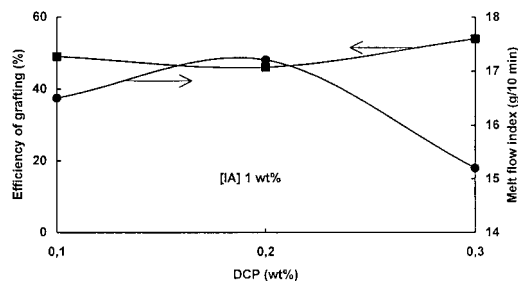


Figure 7 Effect of DCP concentration on grafting efficiency of IA and melt-flow index for PP-g-IA.

case of GMA in the liquid form, the peroxide homogenizes to a monomer on the stage where a reaction blend is prepared with a PP granulate. Molecular contact between the peroxide and IA is only made after the latter has melted ($T_m^{IA} = 170^\circ\text{C}$). By the time when the polymer reaches this temperature, the volatile peroxide evaporates, in part, from the reaction blend and it is consumed in the reactions of β -breakdown. It can also be expected that the peroxide evaporates at a lower rate from the liquid GMA, in comparison with free evaporation.

The MFI for PP-g-GMA and PP-g-IA prepared with the help of D-1, D-2, and TBP, differ but little [Figs. 2(b) and 6(b)]. The MFI for PP-g-IA prepared with TBP was the highest among the tested systems. This result confirms the assumption that most reactive free radicals are consumed on the early stage of IA grafting to initiate reactions of β -breakdown of the chain.

The data obtained emphasize the importance of the aggregate condition of the reaction blend components, i.e., the monomer and the initiator nature, when designing an optimum blend composition. Most advisable are liquid-phase components, or those that can change to the liquid phase during the initial step of reactive extrusion.

The effect of monomer as well as peroxide concentrations on the course of the major and secondary reactions is more complex when IA was grafted than

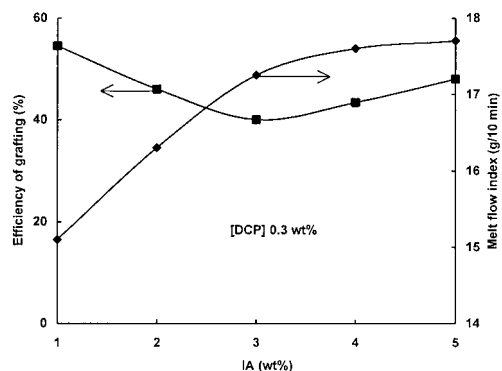


Figure 8 Effect of IA concentration on its grafting efficiency and melt-flow index for PP-g-IA.

TABLE III
Structural Characteristics of Modified PP Using DSC Data

| Composition PP | $T_{m'}$, °C | T_{cr} , °C | $\Delta T = T_m - T_{cr}$ | I_{cr} |
|--------------------------------|---------------|---------------|---------------------------|----------|
| PP | 169.0 | 110.0 | 59.0 | 1.0 |
| PP + IA 1wt. % + PDC 0.1wt. % | 166.5 | 116.1 | 50.4 | 1.25 |
| PP + IA 1wt. % + PDC 0.2wt. % | 165.5 | 115.0 | 51.5 | 1.6 |
| PP + IA 1wt. % + PDC 0.3wt. % | 164.5 | 117.5 | 47.0 | 1.42 |
| PP + IA 2wt. % + PDC 0.3wt. % | 164.5 | 116.0 | 48.5 | 1.23 |
| PP + IA 3wt. % + PDC 0.3wt. % | 165.0 | 117.0 | 48.0 | 1.46 |
| PP + IA 5wt. % + PDC 0.3wt. % | 165.0 | 116.6 | 48.4 | 1.34 |
| PP + GMA 1wt. %+ PDC 0.1 wt. % | 168.5 | 118.5 | 50.0 | 1.32 |
| PP + GMA 1wt. %+ PDC 0.2wt. % | 164.5 | 117.5 | 47.0 | 1.37 |
| PP + GMA 1wt. %+ PDC 0.3wt. % | 164.0 | 115.5 | 48.5 | 1.27 |
| PP + GMA 2wt. %+ PDC 0.3wt. % | 165.0 | 117.0 | 48.0 | 1.23 |
| PP + GMA 3wt. %+ PDC 0.3wt. % | 163.5 | 117.0 | 46.0 | 1.4 |
| PP + GMA 5wt. %+ PDC 0.3wt. % | 165.8 | 117.5 | 48.3 | 0.93 |

GMA (Figs. 7 and 8). The concentration dependencies of α_g and the MFI on DCP content are inverse (Fig.7), resulting from competition of two processes, viz., IA grafting and β -breakdown of the chain. Inverse dependencies were not observed, when GMA was grafted, most likely because the monomer was simultaneously undergoing oligomerization (Fig. 4). No oligomerization of IA was detected when it was grafted onto polyolefin macromolecules.^{9,41}

The extreme nature of α_g vs. IA concentration relationship with a minimum could be explained by an active participation of the monomer in generation of primary free radicals. Antonovskii⁴³ reported that ingredients, particularly organic acids, could accelerate peroxide decomposition. It can be expected that on increasing IA concentration up to a certain value (e.g., 3 wt % in Fig. 8), the additionally formed free radicals will be mainly consumed in the reactions of β -breakdown of the chains. These, on the other hand, cause a decrease in α_g and an increase in the MFI (Fig. 8). A further increase in IA concentration up to 5 wt % is followed by the conversions ensuring primary yield of PP-g-IA grafted product. Hence, the best balance between grafting of IA and degradation of PP, when peroxide P-14 was the initiator, as one possessing a high solubility in the polymer and optimum parameters for thermal breakdown. When optimizing compositions for reaction blends, the ambiguous effect of IA concentration on the course of both the major and secondary processes should be taken into consideration. The maximum efficiencies of IA and GMA grafted onto PP by the reactive extrusion process were similar.

DSC data

Grafting of IA onto LDPE does not cause any marked change in polymer crystallinity.⁶ Only at relatively high concentrations of the peroxide initiator, when

LDPE-g-IA changes to a highly viscous partly crosslinked product, the process of crystallization becomes somewhat retarded, and the crystallinity decreases by 8 to 12%, as was revealed by the DSC technique.

Unlike LDPE, PP degrades at the conditions when a monomer is grafted with the help of peroxides. Considering a higher crystallization rate in PP, as well as its dependence on the polymer melt viscosity,⁴⁴ more deep structural changes could be anticipated for this polymer in the course of grafting. Indeed, grafting of the two monomers results in modified PP with a higher crystallinity in comparison with the initial polymer (Table III). Only PP-g-GMA, prepared with GMA 5 wt % and DCP 0.3 wt %, has lower crystallinity ($I_{cr} = 0.93$). For all the tested compositions, grafting reduces the melting point but leads to higher crystallization temperatures for the polymer. The extent of variations in these parameters depends a little on the composition. For example, $\Delta T = T_m - T_{cr}$ for PP is 59°C; it varies between 47 and 51.5°C for PP-g-IA; between 46 and 50°C for PP-g-GMA. It follows from the above that even at a minimal peroxide concentration (0.1 wt %) the melt viscosity and molecular weight of the polymer change so much that the crystallization proceeds at a much higher rate.

Peroxide concentration vs. I_{cr} dependencies are extreme with a maximum for the two polymers; the dependencies on monomer concentrations are more complex (Table III). These changes are caused by variations in the melt viscosity, grafting efficiency, and probably, the degree of monomer oligomerization (when GMA was grafted). Obviously, the monomer oligomerization makes I_{cr} decrease in a case of PP-g-GMA prepared with GMA 5 wt % and DCP 0.3 wt %. Oligo-GMA, similar to other high molecular weight agents, can interfere with crystallization and restrict macromolecular mobility.

CONCLUSIONS

Grafting of IA onto PP initiated by certain peroxides gives grafted product nearly to the same extent as with GMA. The nature of the peroxide initiator determines the grafting efficiency and in the degree of chain degradation, estimated from changes in the MFI of the polymer. To reach a high yield of a grafted product, peroxides are recommended that have thermodynamic affinity to PP, the temperature range for thermal decomposition that coincides with the thermal regime of reactive extrusion. Di(*tert*-butylperoxy-isopropyl)-benzene (P-14) was found most suitable for grafting both GMA and IA.

To reach a desirable balance between the grafting efficiency and the degree of degradation, variations in the type and concentration of peroxide initiator are recommended for grafting both IA and GMA monomers. To initiate monomer grafting, those peroxides can be useful that decompose at temperatures much lower than the IA melting point, or the temperature in the major reaction zone. This observation supports the known fact that radicals generated from decomposed peroxides first interact with polyolefin chains, then the formed macroradicals initiate grafting reaction for the monomer.

Regardless of the type of peroxide and monomer employed, the grafting reaction causes β -decomposition of macromolecules resulting in higher MFI. A substantial rise in the MFI can be observed at a minimum peroxide concentration (0.1 wt %).

Degradation of PP during modification makes it easier to crystallize from the melt (it crystallizes at a temperature that is 5 to 8.5°C higher, than the crystallization temperature of the initial PP; the crystallinity increases by 20 to 60%).

At a high concentration of GMA (5 wt %), crystallinity of the modified PP is lower than that of the initial PP, which can, probably, be explained by monomer oligomerization.

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