PII: S0032-3861(97)00584-3

Polymer Vol. 39 No. 12, pp. 2571-2577, 1998
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0032-3861/98/$19.00+0.00

Carboxylation of polypropylene by reactive extrusion with functionalised peroxides

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(Received 25 March 1997; revised 24 June 1997; accepted 1 July 1997)

Variable quantities of functionalised peroxides bearing carboxylic acid groups were reacted with polypropylene in a twin-screw extruder. Systematic variations in the molecular structure of the peroxides were found to significantly affect the grafting efficiency of the carboxylic acid group onto the polypropylene backbone, as well as affect the polymer degradation process. This behaviour was attributed to the relative reactivities of the different free radicals generated by thermal decomposition of the peroxides. The peroxides which yielded reactive methyl radicals were more efficient at producing polymeric radicals, relative to the peroxides which generated less reactive ethyl radicals. Increased grafting efficiency and PP degradation was attributed to this increase in the quantity of polymeric radicals. In addition, the peroxides which yielded radicals bearing double bonds were found to have a higher grafting efficiency. This behaviour was attributed to an increased reactivity of the alkenyl radicals, relative to the alkyl radicals, and to the potential for the polymeric radicals to add across the double bond to create the graft. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: functionalised peroxide; reactive extrusion; polypropylene carboxylation)

INTRODUCTION

Organic peroxides are ideally suited for applications involving modifications of polymer properties via melt-phase chemical reactions performed in an extruder (i.e., reactive extrusion). To optimise the chemical compatibility and/or solubility of the peroxides in a wide variety of polymeric systems, the organic character of these peroxides may be tailored by subtle changes in the molecular structure. Moreover, since applied extrusion conditions (e.g., melt temperatures and zone residence times) vary with polymer type, the structural variables available in the synthesis of organic peroxides are appropriate for the requirements of a wide range of decomposition kinetics and resulting free radical reactivities.

Within the field of reactive extrusion, organic peroxides offer the advantage of a thermally induced decomposition by homolytic cleavage of the labile O–O bonds. This cleavage forms two free radical species which may be able to abstract hydrogen atoms from polymer chains and/or add to double bonds. Furthermore, organic peroxides are generally required in low concentrations and can decompose to complete the chemical reaction during typical extrusion residence times. As a result of these desirable characteristics, a wide variety of organic peroxides have been commercialised for reactive extrusion applications such as: bulk polymerisation[1,2], cross-linking of polyethylene and elastomers[3], production of controlled rheology polypropylene[4–6], and grafting of functional monomers onto polymer chains[7–11].

Functionalisation of polyolefins is often achieved by grafting a polar monomer such as maleic anhydride (MAH) onto the polyolefin backbone using reactive peroxides[9–14]. This reaction can be performed in solution[15], or in the melt[14], and may be an economic way to make these inherently nonpolar polymers more compatible with polar polymers. For example, enhanced minor-phase dispersion and interfacial adhesion has been observed with blends of MAH-functionalised polypropylene with nylon 6[16] and when MAH-functionalised polypropylene was used as a compatibilising agent in blends of polypropylene with nylon 6,6[17].

During a typical melt graft reaction of MAH onto polypropylene, the reactive radicals (i.e., the decomposition products from the peroxide initiators) abstract hydrogens from the polypropylene backbone to form tertiary radicals along the chains. These polymeric radicals then add to the reactive double bond of MAH to form randomly distributed grafts[9]. While the initial product of this free radical addition reaction is another radical, recent ^{13}C n.m.r. studies of MAH-grafted polypropylene[18] have shown that the graft sites of the final product contain predominately single succinic anhydride rings. The possibility for continued MAH homopolymerisation into block sidechains has been suggested to be unlikely based on ceiling temperature considerations[19] (i.e., at typical melt temperatures of ca. 180°C); however, a portion of the grafted MAH groups may form cross-links between polypropylene chains[20].

In addition to the desirable grafting reactions, polypropylene has also been shown to degrade during peroxide-initiated functionalisation by tertiary radical β-scission (i.e., chain scission at the site of the polymeric radicals). At low MAH concentrations, the secondary anhydride radicals have been found to contribute to the formation of tertiary polymeric radicals via intramolecular chain transfer[11]; this rearrangement consequently promotes polypropylene degradation[9,11].

Recently, Elf Atochem N.A. has developed a series of

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asymmetric, functional peroxides (peroxyesters) bearing carboxylic groups which may be used to graft acidic functionality *directly* onto polyolefin chains. In addition, DeNicola et al. have demonstrated that unsaturated peroxyacids may be used to functionalise polypropylene in order to increase the interfacial adhesion to glass fiber reinforcement[21]. The original hypothesis in the use of these new peroxides in reactive processing is that highly reactive alkyl radicals from the thermal decomposition of the asymmetric peroxides abstract hydrogens from polypropylene. Subsequently, less reactive radicals (containing the acid functionality) couple with the polymeric radicals to form the grafts. Since these grafts are created during a radical termination step rather than in a chain mechanism, undesirable cross-linking and/or β-scission may be minimised.

In this report, we compare the grafting efficiency of a series of carboxylic acid-containing peroxides in a reactive extrusion process with polypropylene (PP). The focus of this study is on the subtle changes in the chemical structures of these peroxides which differ by only one methylene unit and/or one site of unsaturation. The grafting mechanism is also correlated to other possible free radical mechanisms such as β-scission and cross-linking.

EXPERIMENTAL SECTION

Materials

Polypropylene powder (Pro-Fax 6501) was obtained from Himont Inc. The functional peroxides Luperox PMA, Luperox TA-PMA, Luperco 212-P75 and Lupersol 512 were obtained from Elf Atochem North America. Luperco 212-P75 was obtained and used as a powder of the peroxide on a polypropylene carrier; Lupersol 512 was obtained as a 50 wt% solution in ethyl 3-ethoxypropionate and evaporated onto a PP powder carrier. The structures of these peroxides are represented in *Figure 1*.

Reactive extrusion of PP with the functional peroxides

Polypropylene and the peroxide/PP powders were premixed to obtain samples of 0.5, 1.0 and 2.0 wt% peroxide. The mixture was then extruded in a Haake Rheochord 90 counter-rotating twin-screw extruder with three mixing zones and a rheological slit die. The temperatures of the zones were $T_1 = 150°C$, $T_2 = T_3 = 180°C$, T_4 (die) $= 170°C$. The screw speed was set at 15 rpm corresponding to a residence time of ca. 7 min, and all samples were extruded under a N_2 atmosphere.

Titrimetric assay of the functionalised polypropylene

To eliminate the potential contribution of unreacted peroxide, the extruded products were first purified by reprecipitation. The extrudate was dissolved in xylene at 130°C to a concentration of 5% (w/v) and reprecipitated into methanol. After filtration, the precipitate was washed with pure methanol and dried at 60°C in vacuo. Samples of the purified polypropylene (0.5 g) were dissolved in 100 ml of xylene and titrated to the phenolphthalein endpoint with a standardised solution of benzyltrimethylammonium hydroxide in MeOH. The titrant was standardised with benzoic acid in xylene. All titrations were performed in triplicate at 110°C under a N_2 atmosphere. Due to potential oxidation of PP during melt extrusion, the residual acidity of pure PP (extruded under identical conditions) was assayed as a blank and subtracted from the titrimetric results of the functionalised PP samples. The acid contents and sample standard deviations were calculated in units of equivalents per gram of polymer. The grafting efficiency for the peroxides were then calculated as:

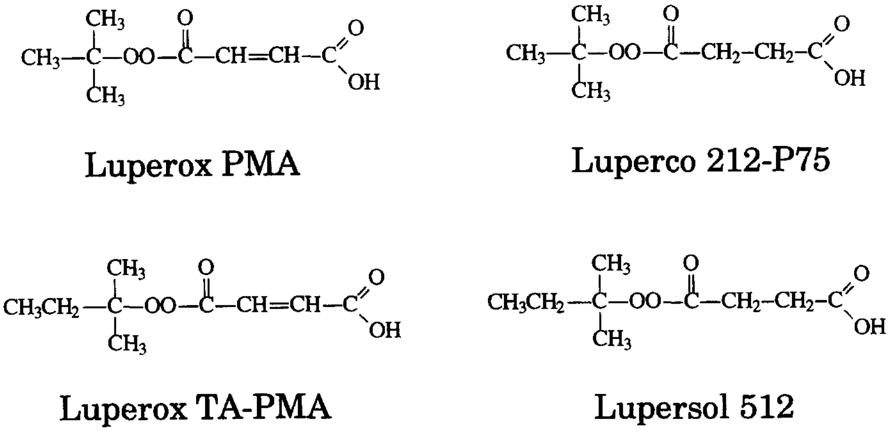
$$\text{grafting efficiency (\%)} = \frac{\text{equiv. f-PP} - \text{equiv. PP}}{\text{equiv. peroxide in feed}} \times 100 \tag{1}$$

where equiv. f-PP is the total acidity of the functionalised PP, equiv. PP is the blank acidity, and equiv. peroxide in feed is the initial concentration of the peroxide/PP mixture.

Characterisation of the functionalised PP

The purified polypropylene samples were densified by melting at 190°C in vacuo and then reground into a coarse powder. The melt index of the products was measured with a Custom Scientific Instruments CSI Melt Indexer at 230°C and under a 2.16-kg load as per ASTM D1238.

The molecular weights of the PP samples were measured with high-temperature size-exclusion chromatography (SEC) using a differential refractive index detector. The samples were dissolved in filtered 1,2,4-trichlorobenzene (TCB) at 145°C. A 0.1 wt% antioxidant (butylate hydroxytoluene) was used to stabilise the samples. The SEC column set was heated to 145°C and calibrated using 25 polystyrene standard samples with molecular weights ranging from 950 to 15×10^6 g/mol. The polystyrene calibration curve was converted to one for PP using Mark-Houwink coefficients for polystyrene and PP in TCB.



Luperox PMA

Luperco 212-P75

Luperox TA-PMA

Lupersol 512

Figure 1 Chemical structures of the functionalised peroxides

RESULTS AND DISCUSSION

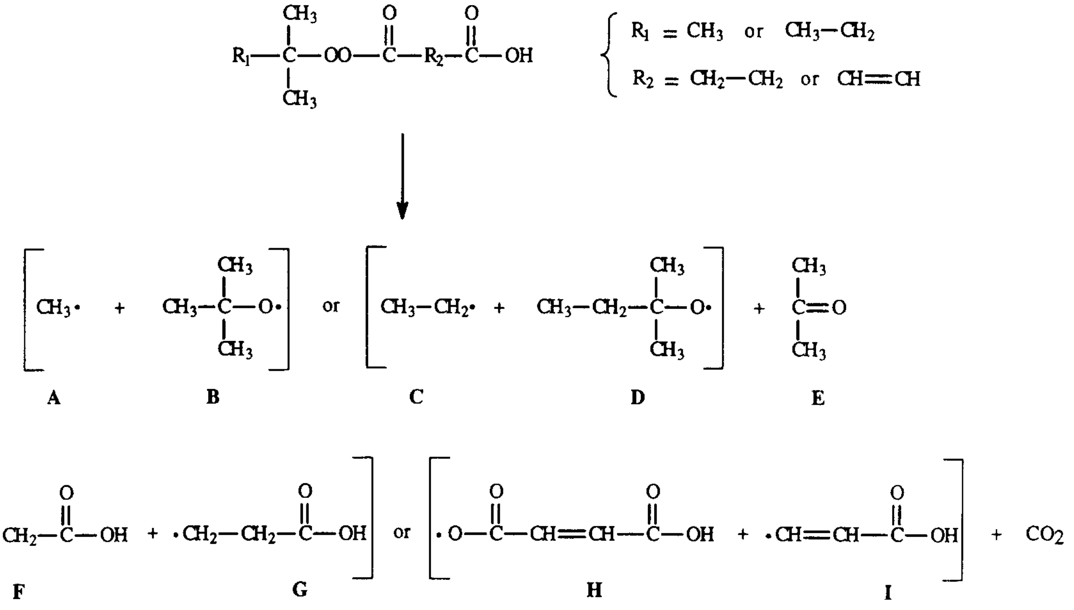
The series of the functional peroxides used in this study (see *Figure 1*) was chosen in order to investigate the effect of systematic changes in the chemical structures on the ability to graft carboxylic acid groups onto a polyolefin backbone. While each of the asymmetric peroxides contain a single carboxylic acid group, they differ in aliphatic character. A cross-comparison of the four peroxides highlights two distinct structural differences. Luperox PMA and Luperco 212-P75 differ from Luperox TA-PMA and Lupersol 512 by one methylene unit. This differentiation will be used to compare the effect of a *t*-butyl group versus a *t*-amyl group on the resulting free radical reactivity. On the other hand, the pair of Luperox peroxides differ from Luperco 212-P75 and Lupersol 512 by a single site of unsaturation. This differentiation will be used to compare the effect of a reactive double bond on the ultimate grafting process. As will be discussed below, these subtle chemical differences affect the respective radical reactivities and yield significant contrast in grafting efficiency during reactive extrusion with polypropylene.

Thermal decomposition of the functional peroxides

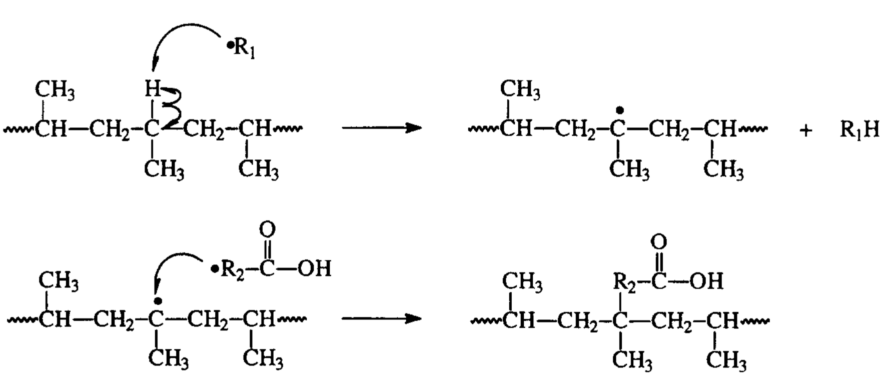
At 180°C (i.e., the temperature of the melt-mixing zones in the extruder), the thermal decomposition half-times of the two Luperox peroxides are approximately the same ($t_{1/2} =$ *ca.* 0.27 min) and only slightly less than that of the Luperco and Lupersol peroxides ($t_{1/2} =$ *ca.* 0.31 min). Nevertheless, based on these $t_{1/2}$ data and given the 7-min residence time in the extruder, all of the peroxides are assumed to decompose completely by the time the melt enters the rheological slit die. Thus, any differences in the overall grafting efficiencies are not considered to be a simple function of the peroxide decomposition kinetics.

The thermal decomposition of the peroxides proceeds by the general reaction shown below in *Scheme 1*. As a result of the asymmetric structures of the functionalised peroxides, two free radicals with distinctly different reactivities are formed by the homolytic cleavage of the peroxide linkage. Note that this reaction includes a number of possible rearrangement products which are a consequence of free radical stabilisation processes. Throughout the context of this paper, the initiating radicals (**A–D**) in *Scheme 1* will be referred to as R_1 radicals and the coupling radicals bearing the acid functionality (**F–I**), will be referred to as R_2 radicals.

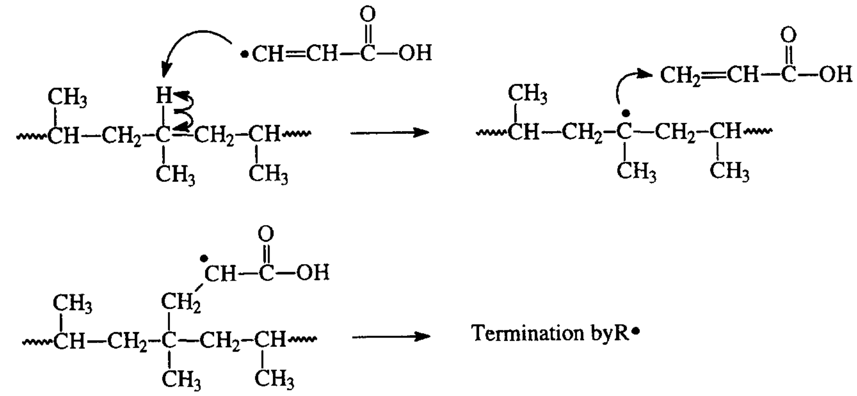
In order to understand the role of these decomposition products in the ultimate grafting process, it is necessary to first rationalise the relative reactivities of each of the radical species. For the *t*-alkyloxy radicals, **B** and **D**, rearrangement by *β*-scission and elimination of a molecule of acetone is



Scheme 1 Peroxide decomposition scheme



Scheme 2 H-abstraction followed by coupling



Scheme 3 H-abstraction followed by addition

also possible. However, the kinetics of this β-scission reaction differ significantly between the *t*-butoxy, **B**, and *t*-amyloxy, **D**, radicals[22]. The *t*-butoxy radicals can slowly rearrange to yield methyl radicals, **A**, of about the same reactivity as the *t*-butoxy radicals (corresponding bond dissociation energies of 105 and 104 kcal/mol, respectively). Furthermore, both the *t*-butoxy and methyl radicals are quite capable of abstracting hydrogen atoms off of the PP backbone. In contrast to the *t*-butoxy radicals, there is a strong thermodynamic driving force for β-scission of the *t*-amyloxy radicals[22]. This stabilisation process yields an ethyl radical, **C**, which is a weaker hydrogen abstractor relative to the methyl radical as suggested by the lower corresponding bond dissociation energy of 98 kcal/mol.

For the decomposition products containing the R_2 moiety, spontaneous decarboxylation will occur if the carboxy radical is thermodynamically unstable relative to the functionalised alkyl, **G**, or alkenyl, **I**, radicals. Based on bond dissociation energy considerations, decarboxylation is assumed to occur for all of the saturated carboxy radicals, **F**, used in this study. However, due to the relatively high energy of the alkenyl radical (corresponding bond dissociation energy of ca. 104 kcal/mol), the thermodynamic driving force for decarboxylation of the 2-carboxy acryloyloxy radical, **H**, is significantly lower compared to that of the **F** radical. Therefore, alkenyl radicals and 2-carboxy acryloyloxy radicals are both expected to participate in the reactive process. The functionalised alkyl radicals are expected to be low-energy radicals (ca. 98 kcal/mol) which mainly participate in coupling reactions with the generated polymeric radicals, while the alkenyl and 2-carboxy acryloyloxy radicals possess reactivities which are capable of hydrogen abstraction as well as coupling reactions.

Formation of the functional graft

In light of the relative reactivities of the radicals in *Scheme 1*, it is reasonable to expect that the overall efficiency of grafting carboxylic acid groups onto PP will be governed by: (1) the ability of radical species to abstract hydrogens from the PP backbone and (2) the ability of the functionalised radicals to couple to the new polymeric radicals. One possible grafting mechanism is shown in 2 2 as a two-step process of hydrogen abstraction by the $R_1^{\cdot}$ radical (i.e., an initiation step) followed by a single radical coupling between $R_2^{\cdot}$ and the polymeric radical (i.e., the termination step) to form the functionalised graft.

Once the polymeric radicals are formed by hydrogen abstraction, it is important to note that several other radical reactions are possible which do not lead directly to graft formation. For example, in the presence of free radicals, PP is know to degrade via β-scission[4–6] to yield terminal double bonds and terminal free radicals. Under the conditions of reactive extrusion, the β-scission of PP is expected to be a parallel reaction with the coupling reaction shown in *Scheme 2*.

While all of the peroxides used in this study yield radicals capable of coupling to the polymeric radical (as per *Scheme 2*), it is important to note that the *unsaturated* $R_2^{\cdot}$ radicals from the two Luperox peroxides are further capable of both H-abstraction and free radical addition reactions. *Scheme 3* illustrates a possible mechanism for grafting the functionalised alkenyl radical onto PP in the absence of the $R_1^{\cdot}$ initiation step shown in *Scheme 2*. First, the functionalised alkenyl radical abstracts a hydrogen from PP to yield the polymeric radical. Then, within the same 'solvent-cage,' the polymeric radical adds across the vinyl group of the newly formed acrylic acid molecule to form the desired acid graft. Note that while this mechanism is shown specifically with radical **I** it is likely that radical **H** could participate in a similar manner; this would yield a diacid graft.

Effect of peroxide structure on reactive functionalisation

Figure 2 shows the titrimetric results of the functionalised polypropylene (f-PP) after reactive extrusion and sample purification. For each peroxide used, there is a slight

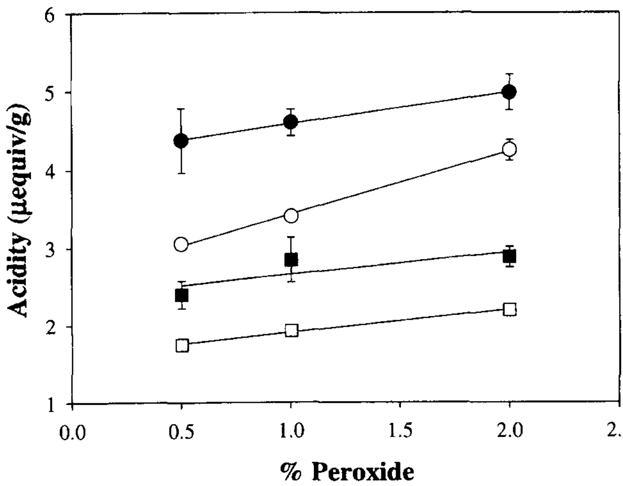


Figure 2 Titrimetric results for the acid content of the functionalised PP versus the peroxide concentration in the feed: (●) Luperox PMA; (○) Luperox TA-PMA; (■) Luperco 212-P75; (□) Lupersol 512

increase in the acid content of the f-PP samples with an increase in the peroxide concentration (i.e., feed concentration, wt%). Moreover, the four peroxides yield significant differences in the quantity of acidic groups grafted onto the polypropylene. These differences in acidities can be attributed to the distinct contrast in relative reactivities of the radicals originating from the different chemical structures of the peroxides.

Of the four peroxides used in this study, the highest acidity was obtained with Luperox PMA. As discussed above, this peroxide yields both $\dot{R}_1$ and $\dot{R}_2$ radicals with the highest relative reactivities. The $\dot{R}_1$ methyl radicals of Luperox PMA are very efficient at producing polymeric radicals, while the $\dot{R}_2$ radicals are capable of grafting onto PP by *Scheme 2* and/or *Scheme 3*. The lowest acidity of f-PP (*Figure 2*) was obtained with Lupersol 512. In contrast to Luperox PMA, this peroxide yields both $\dot{R}_1$ and $\dot{R}_2$ radicals with the lowest relative reactivities. The $\dot{R}_1$ ethyl radicals of Lupersol 512 are inefficient at producing polymeric radicals, and the $\dot{R}_2$ species are likely to graft onto PP only by the process shown in *Scheme 2*.

The intermediate acidities observed with Luperox TA-PMA and Luperco 212 can be attributed to the peroxides yielding a combination of $\dot{R}_1$ and $\dot{R}_2$ radicals with high and low relative reactivities. For example, Luperco 212 yields reactive methyl $\dot{R}_1$ radicals and less-reactive $\dot{R}_2$ radicals. This peroxide is the ideal case for grafting by *Scheme 2*, and actually demonstrates the principle of the original hypothesis of this work. In comparing the observed acidity from Luperco 212 to that from Luperox TA-PMA, it is important to note that the $\dot{R}_1$ radical of Luperox TA-PMA is less reactive than the methyl radical from Luperco 212; however, Luperox TA-PMA yields the very reactive alkenyl $\dot{R}_2$ radical. Since Luperox TA-PMA yields an acidity which is significantly greater than that observed with Luperco 212, these data suggest that the grafting process shown in *Scheme 3* is not only likely, but that the reactivity of the $\dot{R}_2$ radical is quite important in the overall grafting process.

Figure 3 compares the overall grafting efficiency of the four peroxides with respect to the feed concentration. For each feed concentration, the relative grafting efficiencies follow the trends in acidity (*Figure 2*); the greater the relative radical reactivities, the higher the grafting efficiency. The systematic decrease in grafting efficiency is correlated to the low slopes observed in the plots of *Figure 2*. A significant increase in peroxide feed concentration only yields a slight increase in acidity, and thus the grafting efficiency (as calculated with equation (1)) diminishes at high peroxide concentrations.

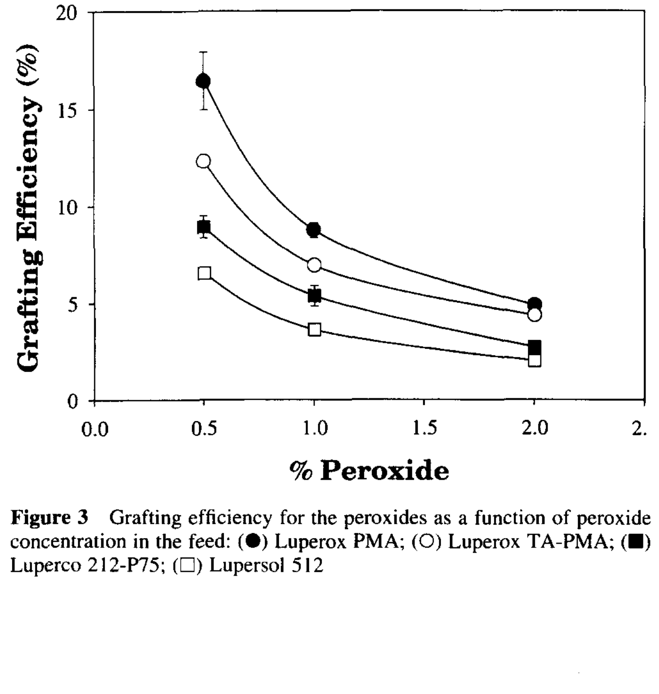


Figure 3 Grafting efficiency for the peroxides as a function of peroxide concentration in the feed: (●) Luperox PMA; (○) Luperox TA-PMA; (■) Luperco 212-P75; (□) Lupersol 512

The data in *Figure 3* suggest that an increase in the feed concentration leads to high levels of ungrafted R_2 species. This behaviour may be attributed to a combination of limited peroxide solubility (in the polypropylene melt)[24] and/or to a loss of low molecular weight f-PP during the sample purification procedure (see Section Section 2). From group contributions[25], the solubility parameters of the peroxides were calculated to be 16.7, 16.7, 14.1, and 14.3 $(MPa)^{1/2}$ for Luperox PMA, Luperox TA-PMA, Luperco 212, and Lupersol 512, respectively. Due to a lack of correlation, these slight differences among the solubility parameters cannot account for the trends in grafting efficiency at a given concentration. However, with respect to the solubility parameter of PP ($\delta = 19.0\,(MPa)^{1/2}$), it is reasonable to expect rather poor peroxide solubilisation; this behaviour would thus limit the amount of peroxide available for grafting.

The possible link between sample purification and the drop in grafting efficiency with increased peroxide concentration (see *Figure 3*) stems from potential β-scission degradation reactions of PP in the presence of free radicals[4–6]. With this chain-scission reaction, it is possible that a significant fraction of low-MW PP would be produced. Moreover, if these low-MW chains contain grafted carboxylic acid sites, then it is likely that these short f-PP chains would not readily precipitate in methanol. Therefore, the titrimetric results may be more representative of grafting onto high-MW f-PP chains. To test for this possibility, a sample of f-PP (prepared with 0.5 wt% Luperox PAU) was reprecipitated following the purification procedure described in Section 2. The filtrate was evaporated and found to contain *ca.* 2% of the original sample mass. Moreover, FTIR analysis of this filtrate sample (after soxhlet extraction with water) indicated the presence of polypropylene with a high acid content. Therefore, as the peroxide concentration in the feed increases, more chain-scission reactions occur, more low-MW f-PP is lost in the purification step, and thus the apparent grafting efficiency decreases.

A change in the molecular weight distribution of the extruded samples is evident in the GPC data of *Table 1*. Relative to the pure PP extruded under identical conditions, each of the peroxides caused a significant decrease in the overall molecular weight. Specifically, it is important to note that the *z*-average molecular weight, M_z, which reflects the high-molecular weight tail of the distribution, is most sensitive to the radical-induced chain-scission reactions. As

Table 1 Molecular weights of the functionalised PP samples

Sample	M_n	M_w	M_z
Pure polypropylene	44 400	257 500	686 000
PP + 0.5% Luperox PMA	40 900	196 000	470 000
PP + 1.0% Luperox PMA	34 300	161 700	390 000
PP + 2.0% Luperox PMA	39 300	192 400	470 000
PP + 0.5% Luperco 212-P75	33 900	134 500	280 000
PP + 1.0% Luperco 212-P75	32 600	135 800	290 000
PP + 2.0% Luperco 212-P75	32 100	133 600	287 000
PP + 0.5% Lupersol 512	36 100	147 800	344 000
PP + 1.0% Lupersol 512	38 900	141 800	312 000
PP + 2.0% Lupersol 512	38 100	141 200	311 000

expected from previous studies of controlled molecular weight reduction of PP by the use of peroxides[4,6], the M_z data in *Table 1* show the greatest relative molecular weight reduction. Furthermore, in agreement with the model of Suwanda *et al.*[6], the more reactive methyl radicals from Luperco 212, as compared to the ethyl radicals from Lupersol 512, yielded the highest degree of molecular weight reduction by chain-scission. In contrast, the high-molecular weight tail (as indicated by the M_z data) of the f-PP sample prepared with Luperox PMA was the least affected. Although Luperox PMA yields the reactive methyl radicals, the efficient grafting of the unsaturated R_2 radicals (as discussed above) presents the possibility of further cross-linking reactions between the unsaturated grafts and other polymeric radicals. These cross-linking reactions would thus be expected to maintain a significant presence of high-molecular weight polymer.

The effect of changes in the molecular weight distribution of the f-PP samples during the reactive extrusion process is further evident by comparing the melt indices of the extruded products. *Figure 4* shows clear differences in the melt indices of the f-PP samples prepared with the four peroxides. In agreement with the GPC data in *Table 1*, the f-PP sample prepared with Luperco 212 yields the highest melt index. As the $R_1^{\cdot}$ radical is changed to the less reactive ethyl species (i.e., with Lupersol 512), less chain scission is induced, and the melt index drops.

The two Luperox peroxides yield the lowest melt indices (*Figure 4*). Again, due to less chain scission, the peroxide which yields the weakest $R_1^{\cdot}$ radical (i.e., Luperox TA-PMA) shows the lowest melt index. In comparing the Luperox pair to Lupersol 512 and Luperco 212, it is clear that the chemical nature of the $R_2^{\cdot}$ radical is an important factor in affecting the melt index. As noted above, the unsaturated group of the R_2 species apparently contributes to cross-linking. In fact, the melt indices for the f-PP samples extruded with Luperox TA-PMA are all lower than for the pure PP sample. This behaviour provides strong support for potential cross-linking reactions. While Luperox PMA renders more efficient grafting and is also capable of yielding cross-links, the more reactive $R_1^{\cdot}$ radicals induce significant chain scission, which apparently counteracts the effects of cross-linking.

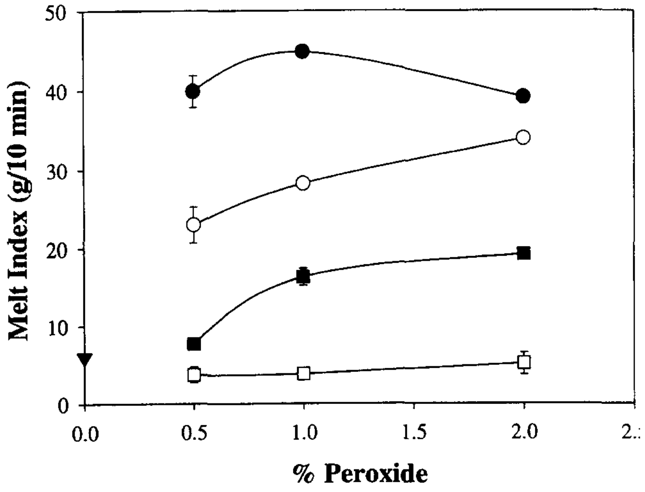


Figure 4 Melt index of the functionalised PP as a function of peroxide concentration in the feed: (●) Luperco 212; (○) Lupersol 512; (■) Luperox PMA; (□) Luperox TA-PMA. The melt index of pure polypropylene (▼) is shown for comparison

CONCLUSIONS

Polypropylene can be functionalised to contain grafted carboxylic acid groups via a reactive extrusion process using functional peroxides. Moreover, the specific grafting process can be tailored and optimised by systematically altering the molecular structure of the peroxides. By affecting the reactivities of the radicals generated from the peroxides, the grafting efficiency of the carboxylic acid group onto the polypropylene backbone, and the polymer degradation process may be controlled.

Based on bond dissociation energy considerations, the relative reactivities of the free radicals fall in the order: methyl $\approx$ functional alkenyl $>$ ethyl $\approx$ functional alkyl. The peroxides which yield reactive methyl radicals are more efficient at producing polymeric radicals, relative to the peroxides which generate less-reactive ethyl radicals. An increase in the grafting efficiency and PP degradation is apparently attributable to this increase in the production of polymeric radicals. With respect to the functional radicals, the peroxides which yield radicals bearing double bonds have a higher grafting efficiency. This behaviour may be partially attributed to an increase in the reactivity of the alkenyl radicals, relative to the alkyl radicals. In addition, the increased grafting efficiency may be further attributed to the potential for the polymeric radicals to add across the double bond of the alkenyl groups. Therefore, this study clearly demonstrates that subtle changes in the molecular structure of peroxides can yield a range of radical reactivities which may be exploited in the precise control of chemical reactions within a twin-screw extruder.

ACKNOWLEDGEMENTS

Support for this work was provided by Elf Atochem North America, Inc. We gratefully thank Professor A. Rudin for the high-temperature GPC results.

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