

Nondegradative Melt Functionalization of Polypropylene with Glycidyl Methacrylate

H. HUANG, N. C. LIU

Polymeric Materials Research Institute, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

Received 2 January 1997; accepted 24 August 1997

ABSTRACT: The melt grafting of glycidyl methacrylate (GMA) onto powdered isotactic polypropylene (PP) in a Haake Rheocord RC90 mixer was studied. Grafting degrees were determined by nonaqueous back titration of trichloroacetic acid with sodium hydroxide. The extent of degradation and crosslinking of PP during grafting was indicated by the melt-flow rates (MFR) of the grafted samples. The influences of GMA concentration, initiator type and concentration on grafting degree, reaction efficiency, and degradation were evaluated. A novel method was developed to obtain a high grafting degree with little degradation of PP using acrylamide (AM) as the initiating agent. The grafting process occurred before or during the melting of PP (i.e., solid-state grafting), at which temperature crosslinking is preferred over chain scission. Primary free radicals generated from the rapid decomposition of AM have a higher tendency to attack GMA molecules than PP chains. At the same estimated amount of primary radicals, both grafting degree and grafting efficiency increase with decreasing decomposition temperature of the initiator (for the same decomposition half-life) in the order of AM > benzoyl peroxide (BPO) > 2,5-di(*t*-butylperoxy)-2,5-dimethyl-3-hexyne (LPO). Functionalized PP with the desired grafting degree and little degradation of PP could be obtained by the use of mixed initiators. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1957–1963, 1998

Key words: polypropylene; glycidyl methacrylate; melt functionalization; nondegradative grafting; mechanism

INTRODUCTION

Blending of immiscible polymers offers attractive opportunities for developing new materials with useful combinations of properties.^{1,2} However, most blends are immiscible and often have poor mechanical properties and unstable morphologies. Compatibilization of such blends is necessary. Preformed block or graft copolymers are ideal for such purposes.^{3,4} However, it is often difficult to produce suitable graft or block copolymers for important commercial applications. An alternative

is to generate these copolymers *in situ* during the melt blending of suitably functionalized polymers.^{5,6}

Although there are a number of commercially available polymers containing acidic reactive groups such as maleic anhydride-grafted ethylene-propylene copolymers, styrene-butadiene-styrene block copolymers, polypropylenes, and polyethylenes, few commercially available polymers purposely functionalized with basic reactive groups have been reported. This is in large part due to the scarcity of suitable basic monomers considering their toxicities, difficulties in preparation and handling, instabilities, and cost effectiveness, etc.

Galluci and Going reported the grafting of glycidyl methacrylate (GMA) onto low-density polyethylenes using dicumyl peroxide and benzoyl peroxide as initiators.⁷ They reported that under

Correspondence to: N. C. Liu.

Contract grant sponsors: National Science Foundation of China; State Education Commission of China.

Journal of Applied Polymer Science, Vol. 67, 1957–1963 (1998)

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CCC 0021-8995/98/121957-07

similar grafting conditions GMA could not be grafted onto polypropylene (PP). However, Liu et al. successfully grafted GMA onto PP using peroxide initiators and used the grafted PP in the reactive compatibilization of PP blends with nitrile rubbers.⁸ Sun et al. studied the melt grafting of GMA onto PP in the presence of a comonomer, styrene, which improved the grafting yield and reduced the chain degradation of PP.⁹ They also reported the melt grafting of GMA onto PP in a twin-screw extruder.¹⁰

One of the important issues in the melt functionalization of PP is its degradation during grafting.⁹⁻¹⁵ It is generally agreed that PP degrades extensively during melt functionalization as a result of peroxide-initiated chain-scission reactions.

The purpose of this work was to study the melt functionalization of powered PP with GMA in a batch mixer. A nonaqueous back-titration procedure was developed for the determination of the grafting degree. Factors influencing the grafting degree and the extent of degradation were evaluated. A method for the nondegradative functionalization of PP was discovered.

EXPERIMENTAL

Materials

The starting material was a powdered isotactic PP supplied by the Shanghai Petrochemical Complex. It has an MFR of 8.5 dg min (ASTM D1238, 230°C, 2,160 g). GMA was redistilled before use. The initiators, 2,5-di(*t*-butylperoxy)-2,5-dimethyl-3-hexyne (LPO, 90% solution) and benzoyl peroxide (BPO), were used as received. The acrylamide (AM) and the solvents were analytical grade and used as received.

Grafting Procedure

The grafting reaction was carried out in a Haake Rheocord 90 batch mixer equipped with roller blades. A 44 g charge of powered PP was dry-blended with the desired amounts of GMA and initiators and then fed into the mixer, which already had been adjusted to the required conditions. The reaction time and mixing speed were maintained at 6 min and 100 rpm, respectively, for all runs. The reaction temperature was 180°C unless otherwise specified.

Analysis

The melt-flow rates (MFRs) of the reaction products were measured at 230°C with a load of 2160 g (ASTM D1238). The reaction products were purified using a precipitation method. About 3 g of the reaction product was dissolved into 100 mL refluxing toluene and precipitated into 600 mL of ethyl acetate with continuous stirring for 1 h, filtered, washed three times, and dried under a vacuum at 85°C overnight.

The grafting degree was determined by a nonaqueous back-titration procedure, developed based on the literature results by Citovicky and Chrastova.¹⁶ About 1 g of the purified product was dissolved in 75 mL of hot toluene, followed by the addition of 5 mL 0.3M trichloroacetic acid solution in toluene. The mixture was kept at 105–110°C for 90 min in order to achieve the complete reaction of the trichloroacetic acid with grafted GMA. The reaction product was then precipitated into 100 mL of ethyl acetate with continuous stirring, filtered, and washed. The filtrate was titrated with 0.1N methanolic NaOH using phenolphthalein as an indicator. Corrections were made based on results with nongrafted PP.

The back-titration procedure was tested using mixtures of nongrafted PP powder with the GMA monomer. When mixtures of 1 g of nongrafted PP powder with 0, 0.03, 0.06, and 0.12 g GMA was titrated using the above procedure, the calculated amounts of GMA from titration were in quantitative agreement with the amounts of GMA initially added in the mixtures.

RESULTS AND DISCUSSION

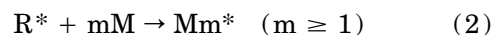
Mechanism of Grafting

The scheme in eqs. (1)–(13) describes some of the main reactions taking place during the melt grafting of a monomer *M* onto PP in the presence of a free-radical initiator.

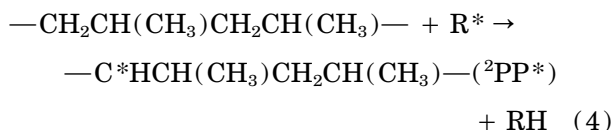
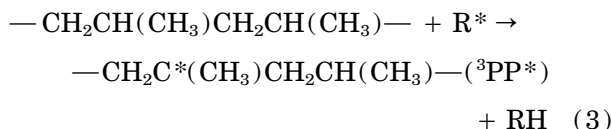
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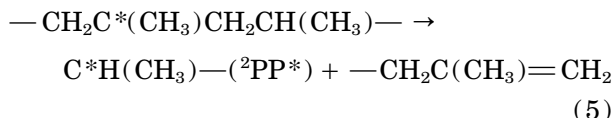
Attacking of monomer and its homopolymerization:



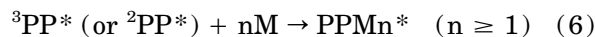
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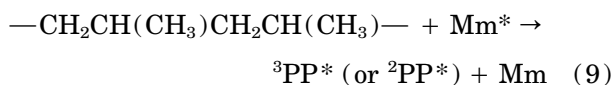
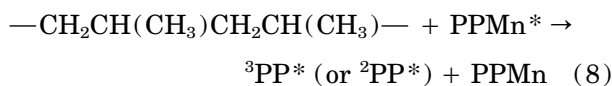
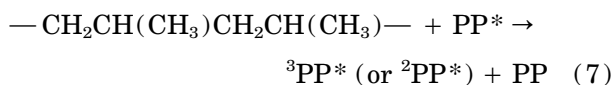
β -Scission:



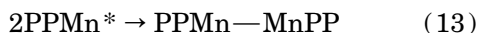
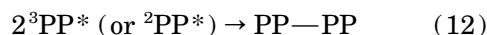
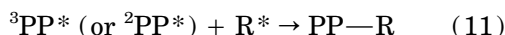
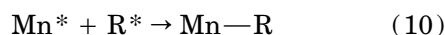
Monomer grafting:



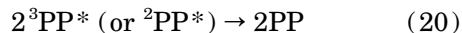
Chain transfer:



Termination by combination:



Termination via disproportionation:



Here, $^3\text{PP}^*$ and $^2\text{PP}^*$ represent, respectively, the tertiary and the secondary radicals from hydrogen abstraction, Mm^* represents the radicals from the attacking of the monomer by primary radical and homopolymerization of the monomer, PPMn^* represents the macroradical after monomer grafting, and Mm , PP , PPMn , $\text{PP}-\text{PP}$, $\text{PPMn}-\text{PP}$, and $\text{PPMn}-\text{MnPP}$ represent the corresponding dead polymers (linear, branched, or crosslinked).

Reactions (5) would obviously result in the degradation of PP while reactions (12)–(14) would cause the crosslinking of PP. Grafting of the monomer may be realized by reactions (8) and (13)–(18).

Figure 1 shows the influence of LPO concentration on the grafting degree and on the reaction efficiency, defined as the molar ratio of grafted GMA to four times the employed LPO, to two times the employed BPO, or to the employed AM. The grafting degree increased slowly with increasing LPO concentration after an initial rapid increase. Meanwhile, the reaction efficiency dropped rapidly initially and leveled off at LPO concentrations above 0.2 wt %. This is probably due to the faster termination rate of free radicals at higher free-radical concentrations, that is, reactions such as (11)–(20) are favored at high free-radical concentrations. It is worth noting that the reaction efficiency at a low LPO concentration of 0.1 wt % was only 3, which is relatively small for free-radical grafting processes.

The influence of GMA concentration on the grafting degree and reaction efficiency is shown in Figure 2. Increasing GMA concentration leads to an increase in grafting degree and reaction ef-

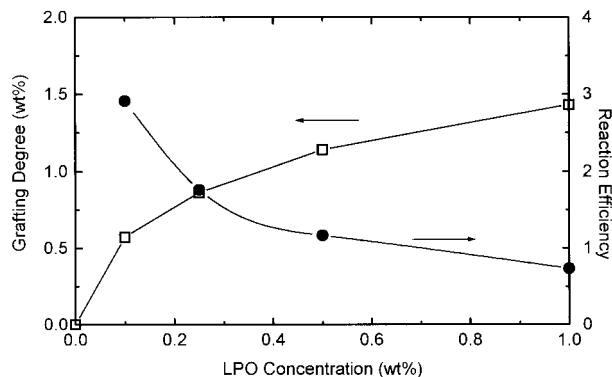


Figure 1 Influence of LPO concentration on the grafting degree and reaction efficiency of grafted PP. GMA concentration: 5 wt %.

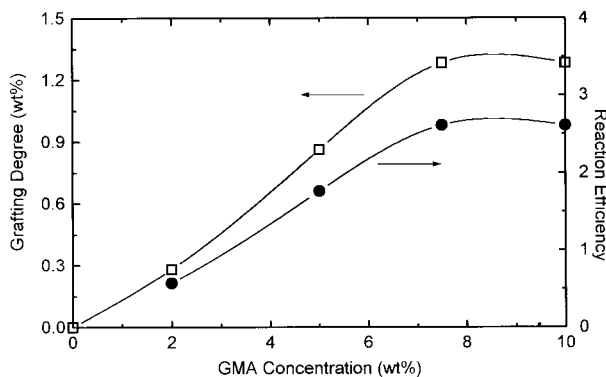


Figure 2 Influence of GMA concentration on the grafting degree and reaction efficiency of grafted PP. LPO concentration: 0.25 wt %.

efficiency. The grafting degree and reaction efficiency reach constant values of 1.3 wt % and 2.6, respectively, at GMA concentrations above 8 wt %.

To improve the reaction efficiency and grafting degree and simultaneously solve the problem of PP degradation during melt grafting, a special initiating agent, AM, was used. AM was reported in the literature to decompose and polymerize vigorously at its melting temperature of about 85°C.^{17,18} However, when only less than 1% of the dissolved AM (in GMA) is well mixed with the PP powder, polymerization is unlikely to occur. Instead, free radicals generated by the decomposition of AM could result in the grafting of GMA.

Figure 3 shows the effect of AM concentration on the grafting degree and reaction efficiency. The grafting degree increases rapidly with increasing AM concentration and reaches a high level of 4.7 wt % at an AM concentration of 0.5 wt %. This is probably because of the structural similarity of

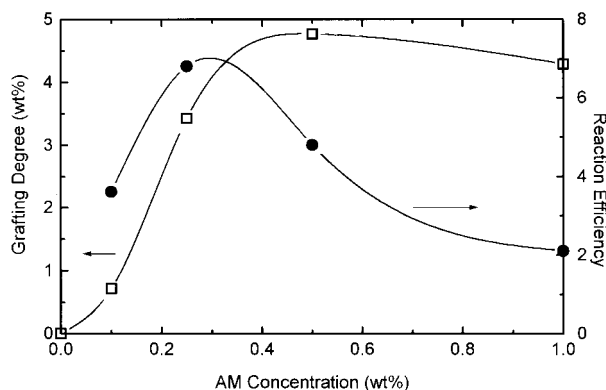


Figure 3 Effect of AM concentration on the grafting degree and reaction efficiency of grafted PP. GMA concentration: 5 wt %.

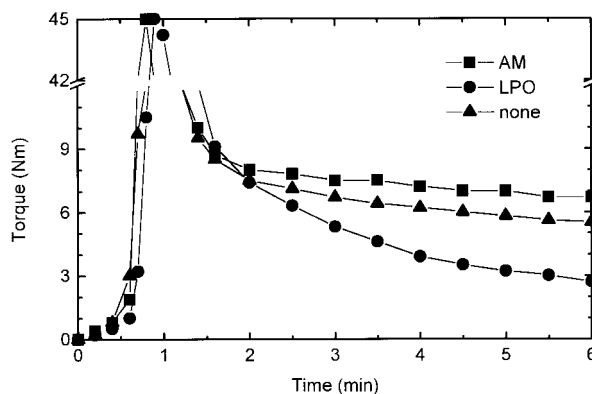


Figure 4 Torque-time relationships for PP grafting reaction with AM and LPO initiators and PP processing without any initiator.

the GMA monomer to the free radicals (most likely carbonyl free radicals) generated from the decomposition of AM, that is, reaction (2) is favored. The grafting degree may be improved by reactions (15), (16), and (19). Furthermore, the grafting reaction could take place during or even before the melting of PP, that is, solid-state grafting, as a result of the early decomposition of AM. At such low temperatures, the free radicals are relatively localized and have a longer lifetime and thus have a lower possibility of termination before grafting. These are in agreement with literature reports for PP grafting in the solid state.^{12,19,20} When the AM concentration is further increased to 1 wt %, a slight decrease in grafting degree is observed. This is probably a result of a large amount of termination and chain transfer without grafting [reactions (9), (10), and (19)] when free-radical concentrations are high. Meanwhile, the reaction efficiency goes through a maximum value of 6.8 at an AM concentration of 0.25 wt %. The relatively low reaction efficiency at a low AM concentration of 0.1 wt % is probably due to the termination of Mm^* by chain transfer [reaction (9)] as a result of a relatively localized reaction. With increasing AM concentrations, reactions (13)–(18), which would lead to grafting, are favored.

The speculation that grafting with AM as an initiator occurs during or even before the melting of PP is supported by the torque results shown in Figure 4. After the melting peak, the torque curve for the AM initiator has the same trend as that without any initiator, indicating that no reaction occurs after the melting peak. However, when the LPO initiator is used, the torque continues to drop with processing time, indicating that the reaction takes place after the melting of PP.

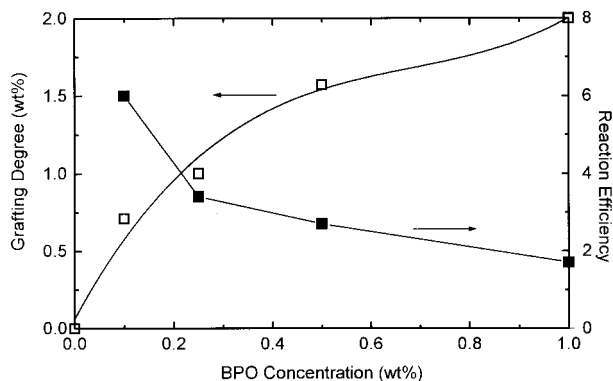


Figure 5 Influence of BPO concentration on the grafting degree and reaction efficiency of grafted PP. GMA concentration: 5 wt %.

To support the above suggestion of a low-temperature grafting reaction, BPO, an initiator with a decomposition temperature in the middle of LPO and AM, is used and the results are shown in Figure 5. The grafting degree with the BPO initiator is significantly higher than that with the LPO initiator. Meanwhile, the reaction efficiency is much higher, close to that when AM is used. This is, again, probably is the result of the grafting reaction during or before the melting of PP. The effectiveness comparison for grafting among the three initiators is more clearly seen in Table I. At the same estimated amount of primary radicals of 3.5 mmol per 100 g of PP, both the grafting degree and grafting efficiency increase with decreasing decomposition temperature of the initiator.

Degradation and Crosslinking of PP

PP degrades extensively during melt functionalization as a result of peroxide-initiated chain-scission reactions.⁹⁻¹⁵ Crosslinking of PP could only be possible in the presence of multifunctional ad-

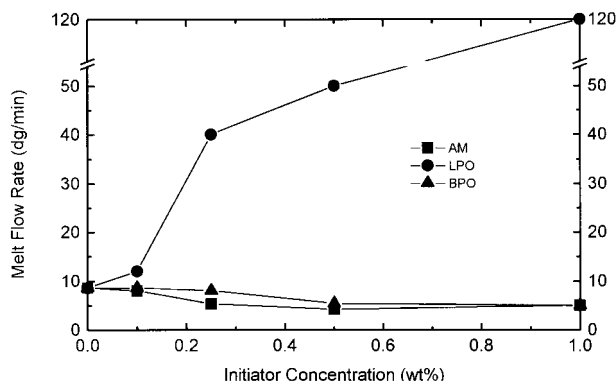


Figure 6 Influence of initiator concentration on the MFRs of PP grafted using different types of initiator.

ditives such as triacrylates.²¹ Figure 6 shows the effects of various initiators on the MFR of grafted PP. The MFR increases rapidly with increasing LPO concentration, whereas the MFR decreases slowly with increasing BPO and AM concentration. In the case of the LPO initiator, the MFR increases rapidly with increasing LPO concentration at low LPO concentrations; then, the increase becomes relatively slow and reached a value of 120/dg min at 1 wt % LPO concentration, indicating a severe degradation of PP during grafting. On the one hand, increasing the LPO concentration results in increased chances of degradation and grafting; on the other hand, high LPO concentration leads to low reaction efficiency and a high probability of termination by a combination involving macroradicals and termination by a combination involving PP* macroradicals before chain scission. The balance of these influences results in the slower increase of the MFR at a higher LPO concentration. In the case of the AM and BPO initiators, the MFR decreased slightly from 8.6 to about 5 dg/min, indicating some crosslinking. First, it is because the reactions occur at lower temperatures, at which chain scission takes

Table I Effectiveness Comparison of Different Initiators for Grafting at the Same Estimated Amount of Primary Radicals of 3.5 mmol per 100 g of PP

| Type of Initiator | Temperature (Half-life : 1 min) (°C) | Grafting Degree (wt %) | Reaction Efficiency | GMA Conversion (wt %) | MFR (dg/min) |
|-------------------|--------------------------------------|------------------------|---------------------|-----------------------|--------------|
| LPO | 190 | 0.9 | 1.2 | 17 | 40 |
| BPO | 135 | 1.5 | 3.0 | 30 | 5.7 |
| AM | 85 ^a | 3.4 | 6.8 | 68 | 5.3 |

^a AM decomposes vigorously at its melting temperature of 85°C.

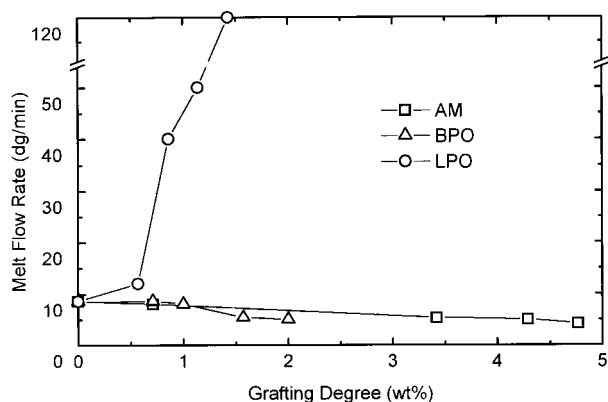


Figure 7 Relationship between the MFRs and grafting degree.

place to a much lesser extent since it is a monomolecular reaction and has a higher activation energy than do the other reactions.²² Second, termination by combination of macroradicals would result in the crosslinking of PP, which is not obvious in the case of the LPO initiator. Third, the interpolymer polar interaction between glycidyl groups in the grafted PP may play some part in the decrease of the MFR.

To determine if there is any relationship between the MFR and the grafting degree, the MFRs of grafted samples prepared with various initiators are plotted versus their grafting degree in Figure 7. It is obvious that the MFR is controlled by the reaction mechanism, that is, the decomposition properties of the initiators. There is no clear relationship between the MFR and the grafting degree.

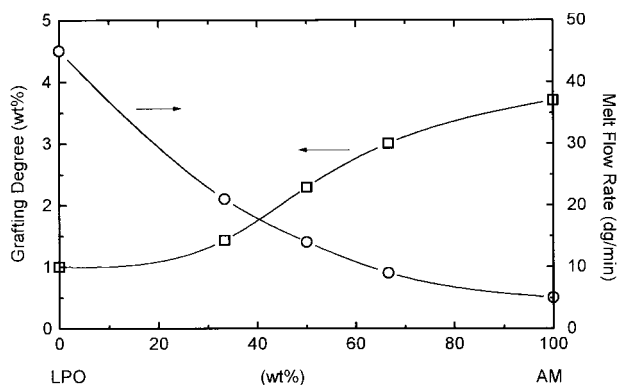


Figure 8 Influence of mixed initiators (LPO + AM) on the grafting degree and MFR of grafted PP. GMA concentration: 5 wt %; total initiator concentration: 0.3 wt %.

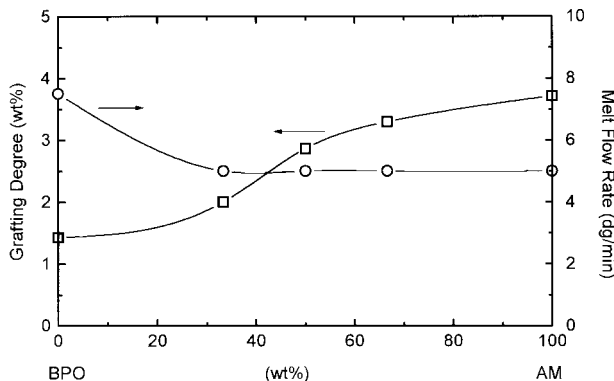


Figure 9 Influence of mixed initiators (BPO + AM) on the grafting degree and MFR of grafted PP. GMA concentration: 5 wt %; total initiator concentration: 0.3 wt %.

Effect of Mixed Initiators

The grafting degree and MFR may be controlled to a large extent simultaneously by using mixed initiators. Figure 8 shows the influence of the LPO and AM proportion on the grafting degree and MFR of grafted PP. When about 70 wt % of LPO and 30 wt % of AM is used, a grafted PP is obtained with the same MFR as that of nongrafted PP but a grafting degree of about 3 wt % of GMA. Figure 9 shows the influence of the BPO and AM proportion on the grafting degree and MFR of grafted PP. At a fixed amount of total initiator concentration of 0.3 wt %, grafting degrees from 1.4 to 3.7 wt % and an MFR from 7.5 to 5 dg/min can be obtained.

The influence of mixed initiator concentration (with the three in equal proportions) on the grafting degree and MFR of grafted PP is shown in Figure 10. When the total initiator concentration

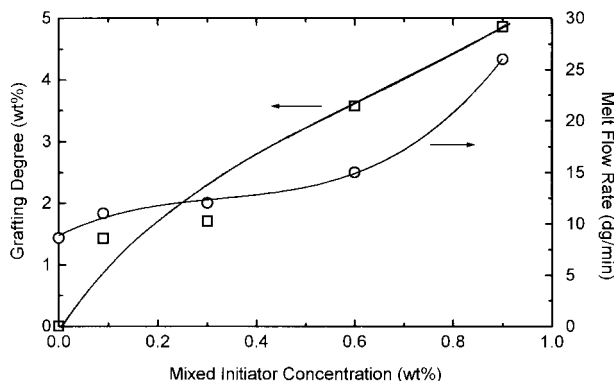


Figure 10 Influence of mixed initiator concentration on the grafting degree and MFR of grafted PP. GMA concentration: 5 wt %; LPO : BPO : AM = 1 : 1 : 1.

is lower than 0.6 wt %, grafted PPs with variable grafting degrees but little degradation can be obtained.

CONCLUSIONS

1. A nonaqueous back-titration method was developed to determine the grafting degree.
2. A novel method was developed to obtain a grafted product with a high grafting degree but little degradation of PP during grafting using AM as the initiating agent. Primary free radicals generated from the rapid decomposition of AM have a higher tendency to attack GMA molecules than PP chains.
3. With benzoyl peroxide as the initiator, the grafting degree is relatively low; however, a little degradation of PP during grafting occurred.
4. The grafting process occurred before or during the melting of PP, that is, solid-state grafting, at which temperature crosslinking is preferred over chain scission.
5. At the same estimated amount of primary radicals, both the grafting degree and grafting efficiency increase with decreasing decomposition temperature of the initiator (for the same decomposition half-life).
6. Functionalized PP with a desired grafting degree and little degradation of PP could be obtained by the use of mixed initiators.

The authors acknowledge the financial support of this project by the National Science Foundation of China and the State Education Commission of China.

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