

Reactive Grafting of Glycidyl Methacrylate onto Polypropylene

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ABSTRACT: This work explored the melt-phase grafting of glycidyl methacrylate (GMA) onto polypropylene on a closely intermeshing corotating twin-screw extruder (16-mm screws, 40 : 1 length/diameter ratio). The modification of the base polypropylene to produce GMA-grafted polypropylene was achieved via peroxide-induced hydrogen abstraction from the polypropylene followed by the grafting of the GMA monomer or by the grafting of styrene followed by copolymerization with the GMA. In this study, both the position and order of the reactant addition were investigated as a route to improving graft yields and reducing side reactions (degradation). For the peroxide–GMA system, adding GMA to the melt before the peroxide resulted in significant improvements in the graft levels because of the

improved dispersion of GMA in the melt. The addition of a comonomer (styrene) was explored as a second route to improving the graft yield. Although the addition of the comonomer led to a considerable rise in the level of grafted GMA, altering the order of the reactant addition was not found to contribute to an increase in the grafted GMA levels. However, variable levels of grafted styrene were achieved, and this may play an important role in the development of grafted polymers to suit specific needs. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2707–2714, 2010

Key words: poly(propylene); (PP); reactive extrusion; graft copolymer

INTRODUCTION

The reactive grafting of polar monomers onto non-polar polyolefin backbones via reactive extrusion has received increased attention in recent years as a result of the wide range of functional groups that can be introduced onto a polymer backbone. Common examples of monomers that have been grafted onto polymer backbones in reactive processes include maleic anhydride,^{1–8} glycidyl methacrylate (GMA),^{9–14} oxazolines,¹⁵ and isocyanates (3-isopropenyl- α,α -dimethyl benzene isocyanate TMI).¹⁶ Grafting onto polymers via reactive extrusion is usually carried out by the addition of a free-radical initiator (often an organic peroxide) to a mixture of a monomer and a polyolefin.

The mechanism of the grafting reaction using polypropylene as the base polymer has been previously reviewed and is generally well understood.^{10,17} In brief, the reaction commences with the decomposition of the peroxide, which generates a radical initiator. The radical initiator abstracts a tertiary hydrogen atom from the polypropylene backbone, forming a polymer macroradical (it may also attack the

monomer and cause homopolymerization, reducing the efficiency of the reaction), which may then be consumed via a reaction with the monomer (desirable) or through side reactions (undesirable) that limit the grafting yield. These undesirable side reactions depend much on the polyolefin used: in the case of polyethylene, the main side reaction is enhanced branching and crosslinking of the polymer, whereas in the case of polypropylene, it is degradation of the polymer through β -chain scission, which reduces the molecular weight of the polypropylene and its melt viscosity. To minimize such side reactions, it is necessary to promote reactivity of the polymer macroradicals toward the monomer to ensure that the radicals are consumed mostly by grafting and less so by the side reactions.

This article focuses on the melt grafting of GMA onto polypropylene in a twin-screw extruder. The modification of the base polypropylene to produce GMA-grafted polypropylene (PP-g-GMA) was achieved via organic-peroxide-induced hydrogen abstraction from the polypropylene followed by the grafting of the GMA monomer or by the grafting of styrene followed by copolymerization with the GMA.¹² GMA has been increasingly used as a grafting monomer because of its dual functionality. The presence of its epoxide function means that the grafted polymer is capable of further reaction with a variety of other functional groups such as carboxylic acids (–COOH), amides (–NH), and alcohols

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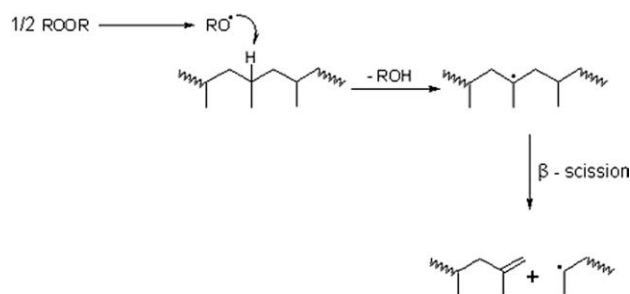


Figure 1 Mechanism of β scission (adapted from Moad¹⁷).

($-\text{OH}$).¹⁸ PP-*g*-GMA is commercially useful as it is an effective compatibilizer for immiscible nonpolar and polar polymers such as polypropylene and poly(ethylene terephthalate).^{19,20}

This study focuses on the addition of reactants to the extruding polymer in two separate stages with a dual-injection technique. Previous experience has shown that it is difficult to co-inject liquid reactants into the extruder barrel during processing as blockages in the tubing can arise from self-reaction of the monomers. The dual-injection system used in this research project not only eliminated this issue but also increased the length of time available for continuous processing and supported the investigation of the order of addition of the reactants.

The rate at which the polypropylene macroradical reacts with the GMA monomer is low because of steric and electronic effects,¹² and thus side reactions become important. The β scission (the mechanism of which is shown in Fig. 1) of polypropylene is not necessarily an entirely undesirable reaction; this depends on the properties of the product desired for further processing (e.g., a high melt flow index for injection molding). However, consumption of the polymer macroradical via side reactions means that the rate of production of the grafted product is reduced, and low grafting levels will be achieved; this in turn is undesirable if a high graft yield is desired for use in a secondary process such as adhesion. A method to overcome this problem (i.e., to favor grafting and not side reactions) is to promote the reactivity between the monomer and the macroradicals so that the macroradicals react with the monomer before undergoing recombination/fragmentation.

The dual-injection technique is aimed at promoting the reactivity of the polymer macroradicals toward the GMA monomer and thus overcome some of the problems described previously. For instance, the generation of the macroradical in the absence of the monomer(s) would be expected to reduce homopolymerization yet lower the viscosity as β scission may be predominant. However, the blending of the polymer with the monomer(s) before macroradical generation may potentially reduce chain scission

effects and increase the grafting yield as consumption of the radical would be expected to occur at a faster rate because of the higher concentration of the monomer in the melt.

Another route to achieving higher graft levels involves the use of a comonomer. Choosing a monomer effective at trapping the polyolefin radicals can result in a propagating radical that is highly reactive toward the monomer.¹⁷ The concept of comonomer addition has been shown to be particularly successful for promoting this reactivity in maleic anhydride²¹ and GMA-grafted polyolefin systems.^{11,12,14,22} It has been proposed that the added styrene, which has high reactivity toward the polymer macroradical, reacts first with the polypropylene macroradicals to produce styryl macroradicals, which may then copolymerize with the monomer.¹²

Two systems were investigated during this study. First, the grafting reaction using an organic peroxide and GMA only was examined, and second, the same reaction in the presence of the comonomer styrene was studied.

EXPERIMENTAL

Reagents and solvents

GMA (purum, $\geq 97\%$), styrene (Reagent Plus; $\geq 99\%$), and the organic peroxide Luperox 101 (Lup101; 90%) were purchased from Sigma-Aldrich (Gillingham, UK) and were used as received without further purification. The base resin used throughout this work was Wintec WFX6 polypropylene from Japan Polypropylene Corp. (Mie, Japan). This material is a metallocene-catalyzed polypropylene with a melting point of 125°C and has a melt flow index of 2.0 g/10 min. Solvents used in the purification of PP-*g*-GMA samples (xylene/toluene and acetone) were general purpose reagent (GPR)-grade and were used without further purification.

Reactive grafting apparatus

All experiments were performed in a Thermo Prism Eurolab (Stone, UK) 16-mm corotating twin-screw extruder (length/diameter = 40 : 1) under a nitrogen blanket. The extruder barrel was modified to contain three extra modular feed ports machined with standard 0.5-in. Unified fine (UNF) fittings to allow the introduction of the liquid injectors and devolatilization apparatus. The injectors (Fig. 2) were situated in barrel zones 3 and 4 to coincide with the first and second mixing sections of the screws, respectively (Fig. 3). Volatiles (the solvent and monomers) were removed from the process at barrel zone 9 via a port connected to a vacuum pump (the reverse screw element indicated in Fig. 1 was positioned to build



Figure 2 Dual-Injector Apparatus. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pressure for the removal of the volatiles). The temperature profile used throughout this work is shown in Table I (zone 1 is the water-cooled feed zone), and the experimental setup is shown in Figure 3.

Introduction of the liquid monomers

Liquid reactants were injected into the extruder barrel with in-house designed and manufactured injectors coupled to Isco (Lincoln, NE) 100DX high-precision positive-displacement syringe pumps with a Swagelok (Warrington, UK) valve system and introduced into the extruder barrel with 0.5-in. UNF fittings.

Production of the PP-g-GMA samples

Polypropylene was fed into the hopper of the extruder and extruded under the chosen processing conditions. Liquid peroxide diluted in methanol (1 : 9 for an increased rate of injection and to provide improved dispersion in the melt) and GMA were injected separately into the extruding polymer at the chosen weight percentages and injection points. The total throughput was maintained at 0.5 kg/h throughout this study, and the screw speed was varied to assess the effects of different residence times. For experiments involving the addition of the comonomer styrene, the styrene was premixed with GMA

at the desired concentrations, and they were injected together at one injection point.

Upon exiting the die, the extrudate was drawn through water, fan-dried, and pelletized. The extruder was purged with the base polypropylene between experimental runs to minimize potential cross-contamination between samples. A stabilization time of 30 min was observed before collection of the extrudate, allowing the melt temperature and pressure to stabilize to the set parameters and reducing the possibility of residual purge material being present in the sample. As some amount of the added reactants is inevitably consumed via undesirable processes during extrusion (e.g., homopolymerization or loss through volatilization), the total amount of the added reactants will never be consumed solely via the grafting reaction. Therefore, the concentrations of the reactants involved are referred to as initial concentrations and are termed $[Lup101]_i$ and $[GMA]_i$.

Purification of the PP-g-GMA samples was carried out by dissolution-precipitation of the extrudate according to established literature procedures.^{9,11,12,20} A portion of the material (~ 5 g) was dissolved in hot xylene (or toluene; ~ 500 cm³) and reprecipitated with excess acetone. The precipitate containing unmodified PP and PP-g-GMA was isolated by filtration, washed with acetone, and dried *in vacuo* for 24 h at 80°C.

Analysis of the PP-g-GMA samples

Several methods have previously been employed to determine the degree of grafting of monomers onto polyolefins. The most commonly used method for analyzing the graft content is offline IR spectroscopy, which has been employed by many groups for determining the graft levels in maleic anhydride grafted polyolefins,^{1,2,7} oxazoline-grafted polyolefins,¹⁵ and GMA-grafted polyolefins.^{9,12,13,18,22,23–27} The technique can be used as a quantitative tool for functional group/graft level determination when it is calibrated against known levels.

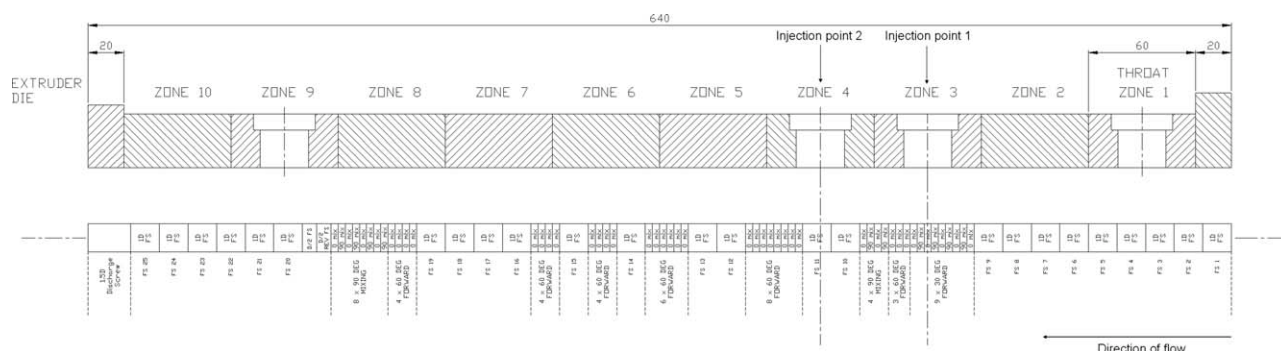


Figure 3 Dual-injection apparatus.

TABLE I
Extruder Barrel Zone Temperatures

| Temperature (°C) | 200 | 200 | 200 | 210 | 210 | 195 | 185 | 185 | 165 | 165 |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Zone | Die | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 |

Purified PP-g-GMA samples were compression-molded into 100- μm films with a Specac (Orpington, UK) constant-thickness film maker. The offline transmission IR spectrum was recorded on a Digilab (Palo Alto, CA) Scimitar S series IR spectrometer using a resolution of 4 cm^{-1} and 64 scans in the wave-number range of 600–4000 cm^{-1} . A background spectrum was taken first, and then the raw data were baseline-corrected with GRAMS/AI32 software. Using IR spectroscopy to determine grafting levels involves determining the intensity of a band due solely to the functionality grafted onto the polymer with respect to the intensity of a band arising from a component of the polymer that remains unchanged during grafting.¹⁷

A comparison of the IR absorbance spectra of samples of the unmodified polymer (PP) and the purified PP-g-GMA (Fig. 4) shows that the peak at 1730 cm^{-1} arose solely from grafted GMA. This peak, assigned to the carbonyl stretching ($\nu\text{-C=O}_{\text{GMA}}$), could be normalized to the intensity of the band at 2722 cm^{-1} correlating to C–CH₃ stretching ($\nu\text{-C-CH}_{3\text{PP}}$) of the unchanging polypropylene to yield a ratio that could be used in the quantification of the graft yield.^{12,17,20,28} This ratio (I_{2722}/I_{1730}) was calculated for each PP-g-GMA sample. To quantify the degree of grafting of GMA as a weight percentage, ¹H-NMR analysis was performed (with a JEOL (Tokyo, Japan) ECA600 spectrometer), and the I_{2722}/I_{1730} values were corrected to weight percentages of grafting. The method was applied to the quantitative analysis of PP-g-GMA in previous works by Liu et al.²⁷ and Cartier and Hu.¹³

The peak at approximately 700 cm^{-1} (also shown in Fig. 4) arose from the addition of styrene as the

comonomer.¹² As there was no peak overlap, it could also be normalized to the band at 2722 cm^{-1} [due to the polypropylene ($\nu\text{-CH}_{3\text{PP}}$)] to produce an $I(\delta\text{-CH}_{\text{STY}})/I(\nu\text{-CH}_{3\text{PP}})$ ratio indicative of the level of styrene grafted onto the polymer backbone.¹² Therefore, an increase in the ratio, simplified to I_{700}/I_{2722} , was equivalent to an increase in the styrene content (existing as both bound styrene alone and bound styrene as a comonomer with GMA).

RESULTS AND DISCUSSION

This work explored the effects of adding the liquid reactants (organic peroxide and GMA) in two separate stages to the extruding base polymer for the reactive grafting of GMA onto polypropylene. Both the position and order of the reactant addition were investigated as a route to improving graft yields. Two methods of reactant addition were explored: (1) standard injection and (2) reversed injection. Under standard injection conditions, the peroxide was added to the extruder at barrel zone 3 (injection point 1; see Fig. 3), and the GMA was added at barrel zone 4 (injection point 2). Under reversed injection conditions, the GMA was added at barrel zone 3, and the peroxide was added at barrel zone 4.

Preliminary experiments were used to determine the initial reactant concentrations used in the study. For these experiments, the standard route of reactant injection was adopted, that is, peroxide and then GMA. The screw speed and throughput were maintained at 50 rpm and 0.5 kg/h, respectively, for these preliminary experiments. Figure 5 shows the

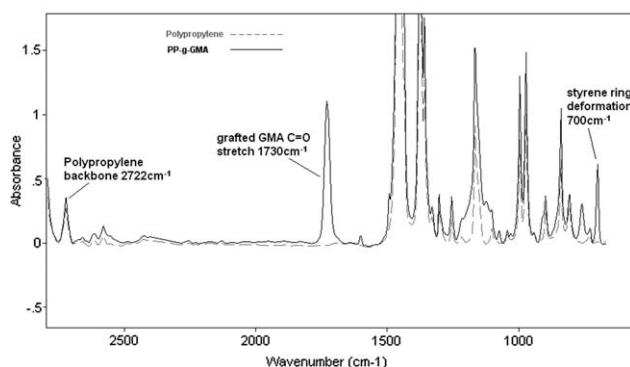


Figure 4 IR absorbance spectra of unmodified WFX6 polypropylene versus PP-g-GMA.

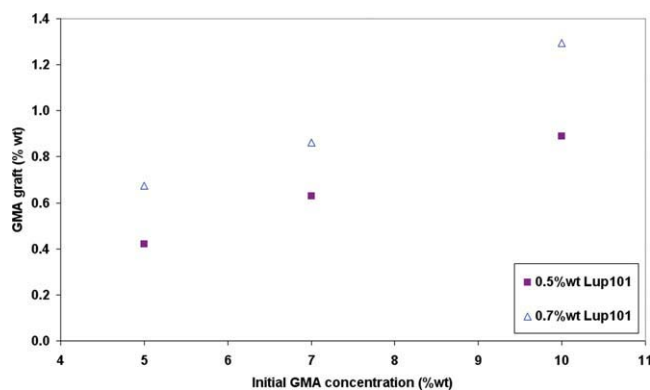


Figure 5 Preliminary study of the optimization of the reactant concentrations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

results of these preliminary experiments. It is clear that for an unchanging value of $[GMA]_i$, increasing $[Lup101]_i$ has a positive effect on the degree of grafting. This is attributable to an increase in the number of polymer macroradicals available for reaction with GMA. This increase in grafting with increasing $[Lup101]_i$ is accompanied by a noticeable drop in the viscosity of the extruded material, a direct result of chain scission reducing the molecular weight of the polymer. Also, for a constant value of $[Lup101]_i$, increasing $[GMA]_i$ yields higher levels of grafting as there is more of the GMA monomer available for consumption by the macroradicals. The highest degree of grafting under these conditions (~ 1.3 wt %) was achieved with 0.7 wt % peroxide and 10 wt % GMA.

Increasing $[Lup101]_i$ beyond 0.7 wt % resulted in a further drop in the melt viscosity (a result of chain scission) significant enough to limit the handling of the material. Therefore, at this stage, the initial weight percentages of the reactants were not further increased even though the results pointed to the likelihood of this increasing the graft yield.

Figure 6 shows the results for the main focus of the study, the importance of the order of reactant injection. The two routes explored, termed standard and reversed injection, were investigated under identical processing conditions for screw speeds of 25, 50, 75, 100, and 200 rpm and a throughput of 0.5 kg/h. With the standard injection route, an increase in the grafting of GMA was observed with a decrease in the screw speed, and this was consistent with an increased mean residence time (i.e., increased reaction time) at the lower screw speed. However, it is evident that even at the lowest screw speed studied (25 rpm), the conversion of the GMA monomer to grafted GMA was poor, a maximum conversion of 19% (1.9 wt % grafting) being achieved. As the reactivity of polypropylene macroradicals toward GMA is relatively low, the melt grafting of GMA onto polypropylene is quite inefficient, leading to the poor conversion and high degree of chain scission observed.

Looking next at the effect of reversal of the injection positions, we can see that this route is more efficient at promoting the grafting reaction. A significant increase in grafting was observed upon the reversal of the injection order (GMA being injected first and followed by peroxide) in the experiments run at 75, 100, and 200 rpm. In fact, almost the same degree of grafting (~ 1.85 wt %) was achieved at 75 rpm (i.e., a shorter residence time) under the reversed injection conditions as at 25 rpm with the standard injection route (1.9 wt %).

The addition of GMA before the peroxide generates a melt blend of the polymer and GMA resulting in an increased distribution/surface area of GMA in

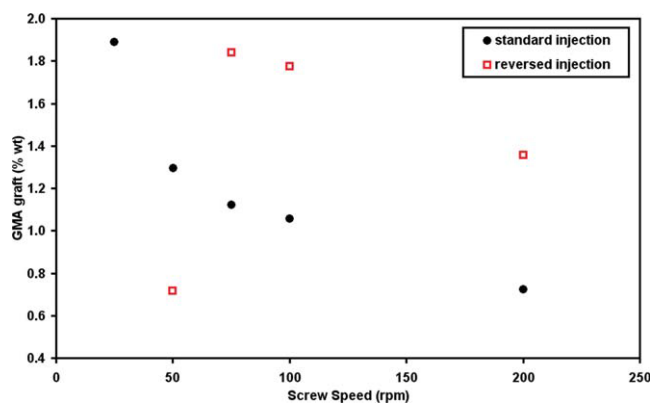


Figure 6 Effect of reversing the order of the reactant injection on the degree of grafted GMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the melt if we assume that the injection zones are well filled. Upon the addition of the peroxide (and generation of the polymer macroradical), the pre-distributed GMA in the melt is able to trap the macroradical faster than in the standard injection route, and this allows a higher proportion of macroradicals to be consumed via the grafting reaction and a lower proportion to be consumed by chain scission reactions. This was evidenced by the production of a more viscous extrudate and an increase in the extruder torque. The point at 50 rpm demonstrated a lowering in the graft yield upon reversal of the injectors. It is believed that this was due to the entrapment of volatiles at the slow screw speed (high barrel fill), which restricted the grafting reaction. It was not possible to process below a screw speed of 50 rpm because of extruder torque limitations. In a larger scale extrusion setup (e.g., for industrial-scale manufacture), dilution of the peroxide would be unnecessary, and this problem would likely not arise. The trend of an increase in the degree of grafting with increased residence time would then be allowed to continue to lower screw speeds and higher residence times.

The results are remarkable given that the difference between the two injection points is a single barrel zone length (the distance from injection points 1 to 2 being 6 cm). They demonstrate that when the peroxide is injected first, the short time lapse incurred before the addition of the GMA is sufficient for a significant proportion of the peroxide to be consumed by side reactions before the grafting reaction is able to occur.

Exploring the comonomer effect with the dual-injection technique

The reactive processing conditions employed up until this point in the study yielded PP-g-GMA with

a maximum GMA content of approximately 1.9 wt %; this is low and inefficient with respect to the conversion of the GMA monomer to grafted GMA (19% conversion). The subsequent experiments investigated the effects of the addition of a comonomer, styrene, to the extrusion process with the dual-injection technique. The addition of styrene as a comonomer has been highly successful for promoting the grafting of maleic anhydride onto polyolefins,²¹ and styrene has been shown to be a promoter for the reactive grafting of GMA onto polypropylene.^{9,11,12,29} Styrene was first added to the process in a 0.5 molar ratio (R_m) with respect to $[GMA]_i$ (termed 0.5- R_m styrene/GMA). The styrene ratios were selected on the basis of work previously reported in the literature.^{12,29} The effect of the comonomer was first studied under the standard injection route, which involved injecting the diluted peroxide into barrel zone 3 of the extruder and then injecting an undiluted mixture of the GMA and styrene into barrel zone 4.

Figure 7 demonstrates the comonomer effect for the addition of 0.5- R_m styrene/GMA at 3 screw speeds (25, 75, and 200 rpm). When 0.5- R_m styrene/GMA was added, the degree of grafting in each case was approximately doubled in comparison with the peroxide-GMA-only system. The results of varying the screw speed are consistent with the residence time effects reported for peroxide-GMA-only systems; an increased residence time (a lower screw speed) results in an increase in the degree of grafting. A maximum of 3.7 wt % grafting was achieved at the lowest screw speed (25 rpm). It is evident that the rate of reaction is much faster in the presence of styrene in comparison with GMA only. For the GMA-only system, a maximum degree of grafting (~ 1.9 wt %) was achieved when the screw speed was 25 rpm and the residence time was longest. However, under the same reaction conditions, in the presence of 0.5- R_m styrene/GMA, a slightly higher

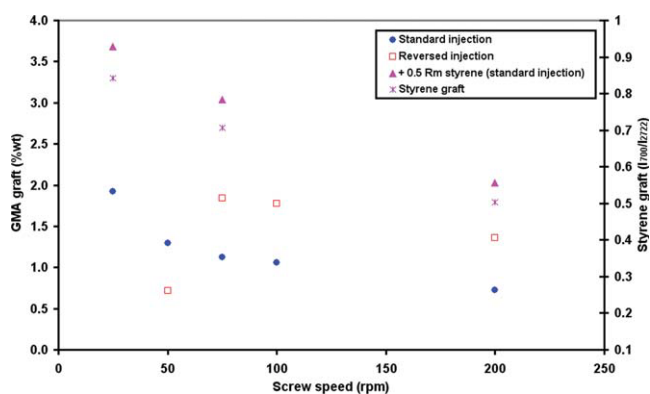


Figure 7 Effect of the addition of the comonomer (styrene) under standard injection conditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

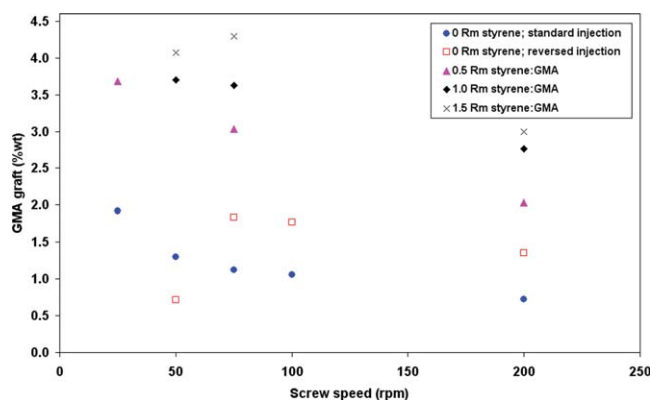


Figure 8 Effect of the addition of higher concentrations of the comonomer (styrene) under standard injection conditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

degree of grafting (~ 2 wt %) was achieved in the shortest residence time under study when the screw speed was 200 rpm.

As the addition of styrene to the process benefited the grafting yield, the addition of two higher concentrations of styrene was investigated: 1.0 and 1.5 mol with respect to $[GMA]_i$. Runs were attempted at 25 rpm to maintain consistency with the 0.5- R_m tests; however, the extruder torque was too high for stable processing, so the screw speed was adjusted to 50 rpm, at which stable processing was achievable. The results of these tests are shown in Figure 8 versus the GMA-only system and the 0.5- R_m styrene/GMA system. In both cases, an increase in the degree of grafting was observed; however, the increase was less significant than that in the 0.5- R_m styrene experiments. A maximum of 4.3 wt % grafting (43% conversion of GMA to grafted GMA) was achieved when 1.5- R_m styrene was added and the screw speed for processing was 75 rpm. Again, the trend of a decreasing screw speed resulting in increased grafting was generally observed, and this was supportive of an increased reaction time yielding a greater conversion of GMA to grafted GMA.

However, the test performed at 50 rpm in the presence of 1.5- R_m styrene demonstrated a slight decrease in the degree of grafting (cf. the experimental run at 75 rpm). The viscosity of the extrudate was seen to increase as the amount of styrene added increased, and this was consistent with the findings of Cartier and Hu,¹² who reported that the molecular weight of grafted polypropylene increased with an increased amount of styrene added; that is, degradation via chain scission was reduced. It is possible that the increase in the viscosity of the extrudate with an increasing amount of styrene resulted in poorer mixing of the reactants at the low screw speed and thus the reduction in the grafting yield.

Examining the relative amount of grafted styrene with increased R_m values of styrene, we observed

the results shown in Figure 9. For each screw speed, an increase in the molar amount of styrene results in an increase in the quantity of styrene bound to the polymer. In fact, the amount of styrene grafted approximately doubles with each 0.5- R_m increase in styrene added to the reaction. The creation of more styryl radicals would have been expected to result in greater increases in the grafting of GMA than are evidenced in Figure 7, and as this has not been observed, it is likely that consumption of the GMA via other routes such as homopolymerization occurs (instead of a reaction with the styryl macroradicals). Cartier and Hu¹² previously demonstrated that although increasing the molar quantity of styrene increases the grafting of GMA, it also raises the amount of polymerized GMA exponentially. It is also possible that the increase in the molecular weight through suppression of the chain scission results in poorer mixing of the melt, so less surface area of GMA is presented to the styryl radicals.

Effect of reversing the order of the reactant injection for experiments using the comonomer

The results for the peroxide/GMA system demonstrated a significant increase in the degree of grafting when the order of the reactant addition was reversed (Fig. 6). The next experiments in this study were designed to evaluate whether this effect would also be seen in the peroxide/GMA/styrene system. Under reversed injection conditions, a mixture of styrene and GMA was injected into the extruder at barrel zone 3, and this was followed by the injection of the peroxide at zone 4 (see Fig. 3).

The results shown in Figure 10 contrast with those achieved for the peroxide/GMA-only system, showing no significant change in the degree of grafting of GMA under the reversed injection conditions (the

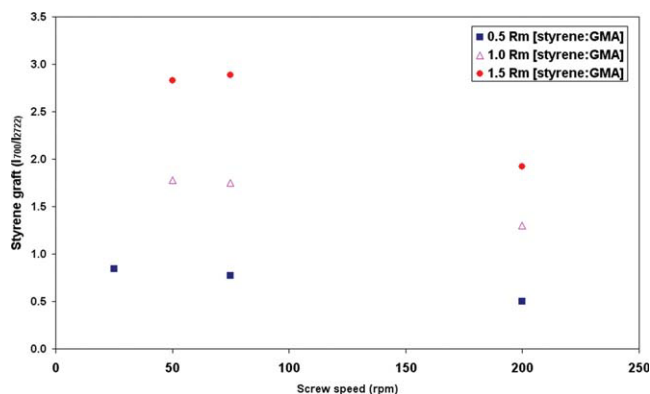


Figure 9 Comparison of grafted styrene (relative IR ratio I_{700}/I_{2722}) with the addition of styrene in three styrene/GMA ratios ($R_m = 0.5$, $R_m = 1.0$, and $R_m = 1.5$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

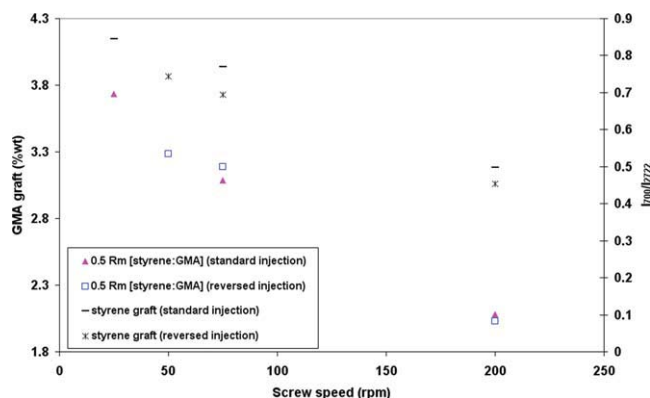


Figure 10 Effect of the reversed injection conditions for the addition of styrene (R_m for styrene/GMA = 0.5). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

experiment at 25 rpm was not possible under reversed conditions because of increased extruder torque, so the experiment was run at 50 rpm). It is, however, clear that less styrene is grafted onto the polymer by this reversed injection route in comparison with the route in which the peroxide is injected first. It is likely that a significant proportion of the styrene is consumed by side reactions before the formation of the polymer macroradical. This, however, would suggest that less GMA is likely to graft as fewer, more reactive styryl radicals have been generated. The results suggest otherwise, as the amount of GMA grafted is little different from that with the standard injection route. This indicates that although a proportion of styrene is consumed before the reaction with the polymer macroradical, the increase in the surface area of GMA blended before macroradical formation results in an increased degree of reaction of the polypropylene macroradical with GMA only.

CONCLUSIONS

This study adopted a dual-injection methodology, with the reactants being injected separately into consecutive barrel zones of the extruder. Experiments to determine the effect of the order/method of reactant addition have provided important insights into process development.

The order of injection of the reactants was found to play an important role in achieving an increase in the degree of grafting. In the initial experiments, the peroxide (Lup101) was injected at barrel zone 3, and it was followed by GMA at barrel zone 4. In determining the reaction conditions, we found that 0.7 wt % [Lup101]_i and 10 wt % [GMA]_i produced the highest degree of grafting (1.3 wt %). In this case, a significant proportion of the polymer macroradicals that formed were likely to have been consumed by

side reactions before the GMA was mixed sufficiently for a reaction to occur; therefore, the level of conversion of the monomer to the grafted monomer was low (13%).

The reversal of the order of the reactant injection led to a significant increase in grafted GMA. Under the reversed injection conditions, when GMA was injected before the peroxide, a melt blend of the polymer and GMA was formed. This increased the surface area of the monomer in the melt before macroradical formation and resulted in the macroradical being trapped more quickly, leading to a considerable increase in grafting and a reduction in chain scission.

The effect of adding styrene as a comonomer was investigated in this study for styrene/GMA R_m values of 0.5, 1.0, and 1.5. As in the initial tests, the peroxide was injected at point 1 and was followed by a mixture of GMA and styrene at point 2.

- The addition of 0.5- R_m styrene/GMA to the 0.7 wt % Lup101/10 wt % GMA system resulted in more than a 2-fold increase in the degree of grafting.
- The grafting reaction was clearly faster in the presence of the comonomer. For the 0.7 wt % Lup101/10 wt % GMA system, a maximum of 1.9 wt % grafting was achieved with processing with the longest residence time (25 rpm). When 0.5- R_m styrene was added to this system, 2 wt % grafting was achieved in the shortest residence time (200 rpm).
- Further increasing the styrene/GMA R_m value (to 1.0 and 1.5) led to further increases in the degree of grafting; however, the increase was to a lesser extent than that with the 0.5- R_m addition, likely because of an increase in the consumption of the GMA monomer through homopolymerization.¹²
- Increasing the amount of the comonomer resulted in an increase in grafted styrene (ca. 2-fold for each increase from 0.5 R_m to 1.0 R_m to 1.5 R_m).

The effect of reversing the order of the injection of the reactants was investigated for the comonomer system (0.5- R_m experiments). A mixture of GMA and styrene was injected at barrel zone 3, and it was followed by the peroxide at zone 4.

- Although no increase in grafting was observed, no decrease was evident either.
- A decrease in the amount of grafted styrene was evident from the results of this part of the study.
- The consistency of the quantity of grafted GMA from the two different methods of reactant addition can likely be explained by the increase in the surface area of the monomer in the polypropylene due to the reversed injection order.

Therefore, when the comonomer is added to the system, it is preferable to add the styrene as a mix with the GMA. This avoids consumption of the styrene before macroradical formation and is suggestive of product tailoring through various styrene contents; that is, careful control of the reactant concentrations along with ordering of the addition may offer ways of tailoring the properties of grafted polymers to meet specific needs.

The results of this study were used to file a successful patent application (WO/2008/003946 A1). The authors acknowledge the support of their collaborators in this work: Fuji Seal International, Inc. (Japan), and Fuji Seal Europe (United Kingdom).

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