Free Radical Grafting of Glycidyl Methacrylate onto Polypropylene in a Co-Rotating Twin Screw Extruder

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SYNOPSIS

Free radical grafting of glycidyl methacrylate (GMA) onto molten polypropylene (PP) was studied in a co-rotating twin screw extruder. Grafting yields of GMA obtained under various experimental conditions along the screw length allowed for a good appreciation of the effects of chemical parameters (the presence of styrene and the concentrations of peroxide and monomers) and those of processing parameters (feed rate, screw speed, and specific throughput). Similar to the results obtained in a batch mixer,[1] free radical grafting of GMA carried out in the extruder in the presence or absence of styrene proceeded rapidly, as it was virtually completed half-way down stream of the extruder. Additionally, the presence of styrene as a second monomer increased the GMA grafting yield greatly with reduced PP chain degradation. The ultimate GMA grafting yield increased with increasing concentration of peroxide, 1,3-bis(*tert*-butylperoxyisopropyl)benzene. This similarity between the batch mixer and the extruder is related to the fact that in both cases it is the concentration of the peroxide and its half lifetime that determine the grafting rate and the ultimate grafting yield. On the other hand, the GMA grafting yield decreased with increasing screw speed or feed rate. For a particular specific throughput (the ratio of throughput to screw speed), an increase in throughput with a concomitant increase in screw speed brought about a decrease in GMA grafting yield. It was concluded that the GMA grafting yield is affected primarily by the residence time in the zone in which free radicals are not depleted. The effects of screw speed, feed rate, and specific throughput manifest mainly through this local residence time distribution. Specific energy is not a good measure of the performance of the extruder with respect to the free radical grafting of GMA onto PP. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Recent years have seen increasing research interest in free radical functionalization of polyolefins with monomers containing potentially reactive groups. The driving force behind this has been the need to develop new polymeric engineering materials. Although synthesis of new polymers from new monomers is still a possibility, combination of different polymers with complementary properties has become more attractive. This latter is achieved only when the morphology of the material is controlled in an appropriate manner. As few polymers are miscible, an effective compatibilizer is often necessary. Preformed block or graft copolymers are ideal, but economically making them for an industrial need is often difficult. Thus, people have turned to a radically different route: to create *in situ* these block or graft copolymers during polymer blending through interfacial reaction between selected functional polymers.

When a polymer containing potentially functional groups is to be mixed with another polymer (a polyolefin for example), which is immiscible with the former and chemically inert with respect to its functional groups, *in situ* creation of block or graft
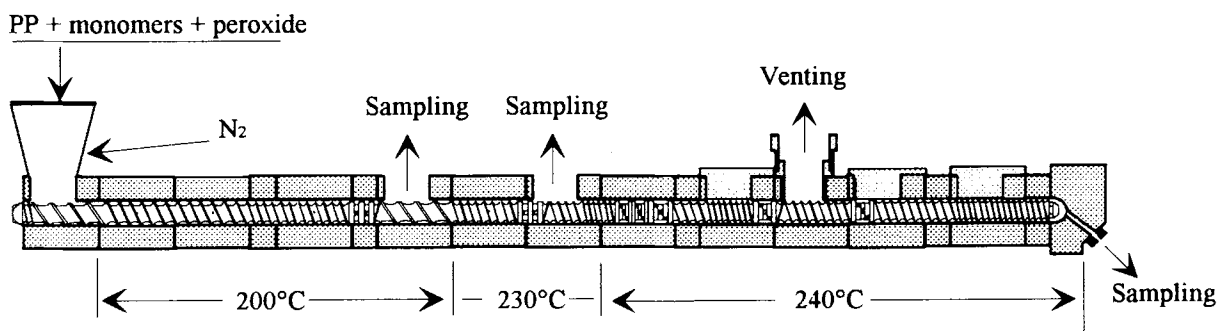

Figure 1   Screw and temperature profiles of the extruder used for the free radical grafting of GMA onto PP.

copolymers during blending through interfacial reaction requires that this polyolefin be functionalized. This is usually done by grafting monomers bearing the desired functional groups onto backbones of the polymer of interest through a free radical mechanism. Some of the most frequently employed functional monomers are unsaturated carboxylic derivatives, such as maleic or itaconic anhydrides, and vinylic or acrylic substances containing a second functionality (acid, epoxide, alcohol, etc.). This functionalized polymer then reacts with the functional polymer to form block or graft copolymers at the interface of these two polymers.

Free radical grafting of functional monomers onto polymer backbones has been investigated mostly in solution or in the melt using a batch reactor.[1-3] Fewer systematic studies on this type of reaction have been conducted in screw extruders. As such, the particular feature of this type of reactor remains poorly understood. To the authors' knowledge, the only systematic study on these problems is some recent work of Janssen and his co-workers[4] who investigated the free radical grafting of maleic anhydride onto a high-density polyethylene in an intermeshing counter-rotating twin screw extruder. To some extent, a lack of understanding on the coupled problem between the free radical chemistry and the inherent characteristics of screw extruders as chemical reactors stems from the various complications involved in the free radical chemistry: crosslinking or degradation of polymer chains, competition between monomer grafting and homopolymerization, limited solubility of monomers, and low initiation efficiency of free radical generators due primarily to their low solubility in highly viscous polymer melts and short half lifetime.

Recently, the chemical aspect of the free radical grafting of glycidyl methacrylate (GMA) onto polypropylene (PP) was studied in a batch mixer.[1] The major result is that the presence of styrene promotes the grafting yield of GMA greatly while reducing the PP chain degradation by β-scission. Another interesting finding is that this free radical chemistry proceeds rapidly: it is completed within about 2 min at 200°C. However, the conversion of GMA into grafted GMA onto PP rarely exceeds 50% because of the various complications mentioned above. The main objective of this article is to show how this free radical grafting behaves in a self-wiping co-rotating twin screw extruder. For that purpose, the effects of chemical parameters (the concentrations of GMA, styrene, and peroxide) and those of processing parameters (screw speed, feed rate, and specific throughput) on the grafting yield of GMA were investigated. As a screw extruder is considered as a special tubular reactor, the effects of chemical and processing parameters on the free radical grafting of GMA were examined along the screw length. Apparently, this is the first time that efforts have been directed towards the understanding of the full picture of free radical grafting along the screw length.

EXPERIMENTAL

Materials

The PP used in this study was a commercial grade of Valtec CL101D (Himont) in the form of porous pellets. This porous PP was capable of absorbing much larger amounts of liquid monomers than the one in the form of normal pellets, thus facilitating material feeding and reducing monomer loss. The number and weight molecular weights of the PP measured by size exclusion chromatography (SEC) were 141,000 and 654,000 g/mol, respectively, with a melt flow index of 0.3 g/10 min (ASTM 1238L, 230°C and 2.16 kg). GMA and styrene were pur-
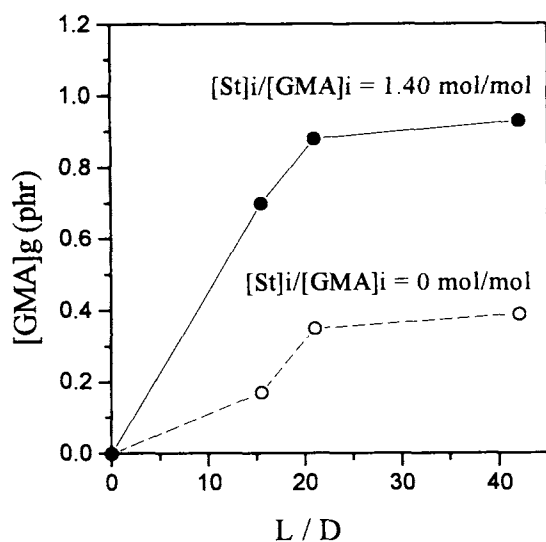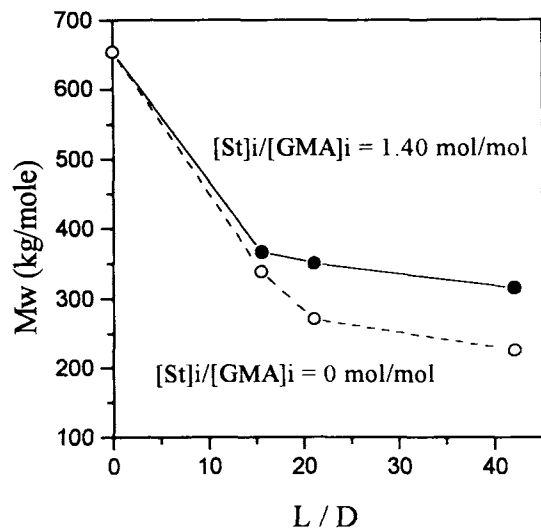
Figure 2 Comparison of the GMA grafting yields and the corresponding PP molecular weights with and without styrene. (a) GMA grafting yields, (b) PP molecular weights. $[GMA]_i$ = 3.0 parts with respect per hundred parts of the PP resins (phr), $[Perk-14]_i$ = 0.30 phr, Q (feed rate of the virgin PP) = 3.5 kg/h, N = 150 turns per minute (rpm).

chased from Aldrich and used as received. 1,3-bis(*tert*-butylperoxyisopropyl)benzene (trade name Perk-14) was chosen as a free radical generator, whose half lifetime was about 30 s at 200°C and 2 s at 240°C. It was a commercial product of Akzo in a liquid state (purity: 90%).

Extruder

A co-rotating self-wiping twin screw extruder of type Werner and Pfleiderer ZSK-30 was used in extrusion (screw diameter D = 30 mm, length-to-diameter ratio L/D = 42). A major feature of this type of machine lies in its modular design in terms of barrel and screw elements. This modularity provides great processing flexibility for feeding, melting, mixing, reaction, devolatilization, temperature control, etc. The temperature of the extruder was regulated by electrical resistance and water circulation in barrels. The screw and temperature profiles used in this study are shown in Figure 1. They were so chosen as to fit a subsequent study on the compatibilization of PP and poly(butylene terephthalate) blends.

Before being fed into the extruder through a weight-loss screw feeder of type K-Tron K10S, the porous PP pellets were moistened with a chosen amount of a liquid mixture of monomers and peroxide at room temperature for about an hour in order that this latter would be absorbed by the porous PP pellets. For all experimental runs, devolatilization was carried out using a vacuum pump. This pump was placed near the die and it created a pressure of about 25 mmHg. The extruder was always starve fed. Thus, the screw speed (N), feed rate (Q), and specific throughput (Q/N) could be varied independently.
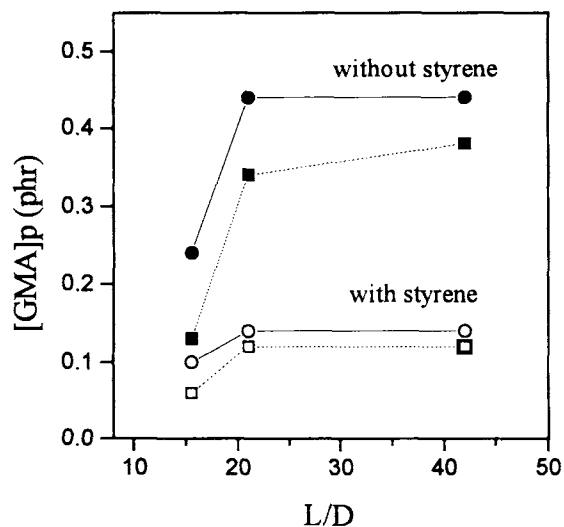

Figure 3 Effect of styrene on $[GMA]_p$ during the free radical grafting of GMA onto PP. (■) 1.4 phr of GMA without styrene; (●) 3.0 phr of GMA without styrene; (□) 1.4 phr of GMA with styrene; (○) 3.0 phr of GMA with styrene ($[styrene]_i/[GMA]_i$ = 1.4 mol/mol).
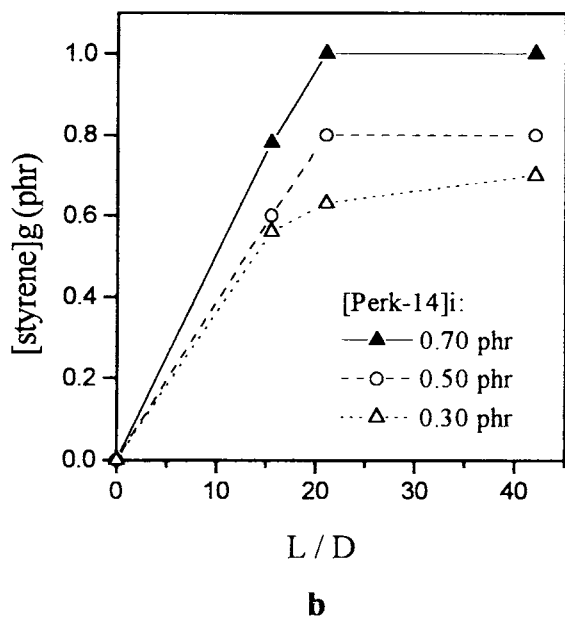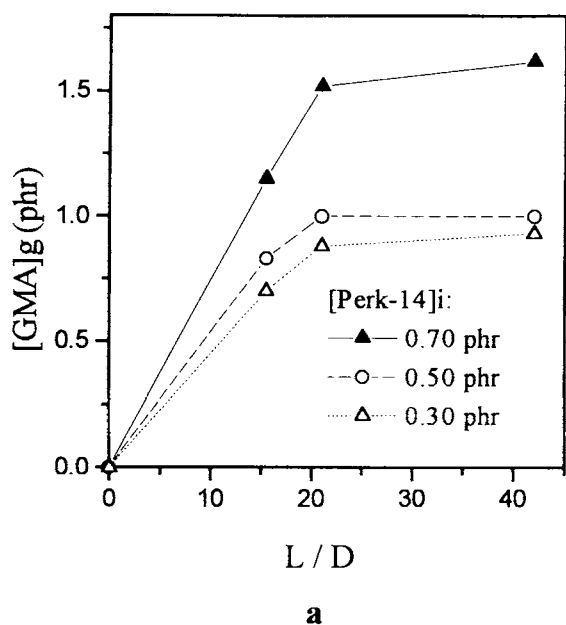
a

b

Figure 4   Grafting yields of GMA (a) and styrene (b) along the screw length at various concentrations of the peroxide. ([GMA]$_i$ = 3.0 phr, [styrene]$_i$/[GMA]$_i$ = 1.40 mol/mol, Q = 3.5 kg/h, N = 150 rpm.)

from the feeding point, respectively. Those holes were closed when the machine was running. After the extrusion process was in a steady state, samples were taken while the machine was running. They were then quenched quickly in liquid nitrogen to stop the reaction.

Characterization of the Grafting Reaction

The grafting reaction was characterized in terms of the grafted, polymerized, and unreacted GMA. Modified PP samples were purified in two ways: they were either dissolved in hot xylene and then precipitated in methanol at room temperature, or they were dissolved in hot xylene and then precipitated in acetone at room temperature. The use of methanol allowed us to precipitate not only the modified PP but also other polymers like poly(glycidyl methacrylate), polystyrene and poly(glycidyl methacrylate-co-styrene) which might be formed during the free radical grafting. On the other hand, acetone precipitated PP well. But it was capable of dissolving certain amounts of poly(glycidyl methacrylate), polystyrene and poly(glycidyl methacrylate-co-styrene). Those two ways of purifying modified PP samples allowed us to determine, with some uncertainties, the relative importance of homo- and/or copolymerization under the said grafting conditions. The grafting yields were determined by FTIR using thin films (100 ~ 120 μm) of purified PP samples. The
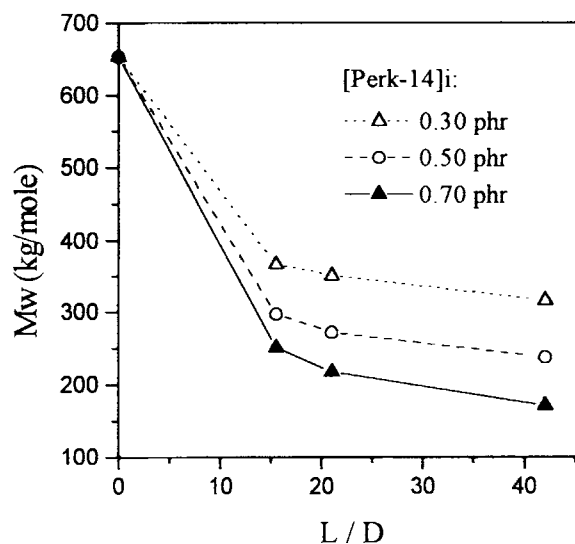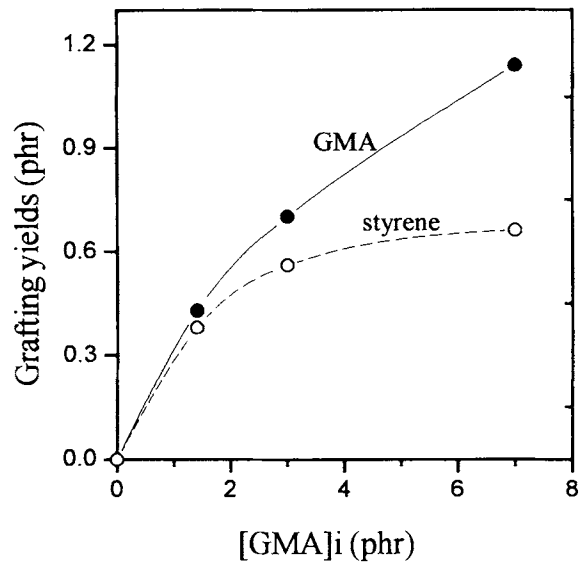

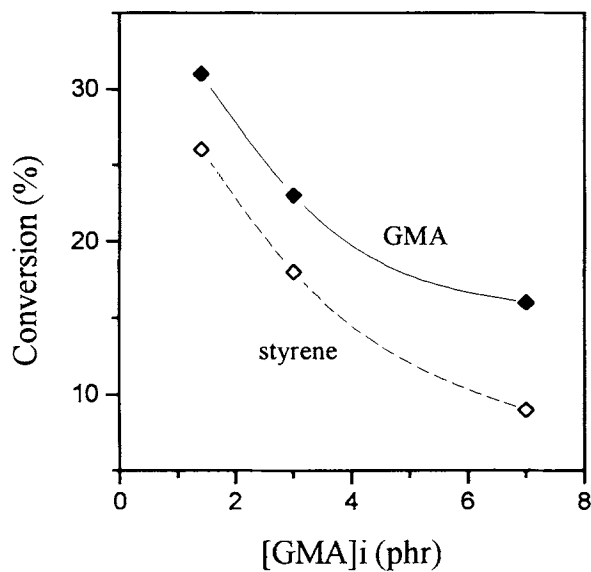**Figure 5**   Decrease in $\bar{M}_w$ of PP during extrusion along the screw length at various initial concentrations of Perk-14. [GMA]$_i$ = 3.0 phr, [styrene]$_i$/[GMA]$_i$ = 1.40 mol/mol, Q = 3.5 kg/h, N = 150 rpm.

In addition to sampling the modified PP at the exit of the die, samples were also taken at two other positions upstream. Those two sampling holes were located at 36% and 50% of the total screw length

a

b

Figure 6 (a) Grafting yields of GMA and styrene as a function of the initial concentration of GMA. (b) Conversions of the grafted GMA and styrene as a function of the initial concentration of GMA. $[styrene]_i/[GMA]_i$ = 1.40 mol/mol $[Perk-14]_i$ = 0.30 phr, Q = 3.5 kg/h, N = 150 rpm.

peak of the PP at 2722 cm^{-1} was chosen as the reference, the one at 1730 cm^{-1} corresponding to the grafted GMA and that at 700 cm^{-1} corresponding to the grafted styrene were chosen as the targets.

More details concerning the IR analysis can be found elsewhere.[1] The extent of the degradation of PP was evaluated in terms of the number and weight average molecular weights. These latter were determined by SEC at high temperatures.

RTD Measurement

Residence time distribution (RTD) as a measure of macromixing is an important parameter that characterizes the performance of a continuous chemical reactor. Polystyrene (1240H of Atochem) was chosen as a model polymeric fluid to replace the free radical grafting system of PP/GMA. 1-Aminoanthraquinone was used as a tracer. As pointed out in previous work,[5] this dye as the tracer has the following advantages: fine dispersion in a PS matrix, good thermal and chemical stability, and high sensitivity to ultraviolet (UV) light with a maximum absorption wavelength at 461 nm (the maximum absorption wavelength of an aromatic substance of a single benzene ring like polystyrene is 265 nm).

The RTD of the polystyrene (PS) in the extruder was measured with the same screw configuration as that for the free radical grafting of PP except that the temperature profile of the extruder was 200°C all along the screw length. The tracer (1.0 wt %) was dispersed in the PS using a Haake batch mixer at 200°C, which was then pelletized into small particles having a similar size to the PS pellets. These concentrate pellets were injected into the extruder
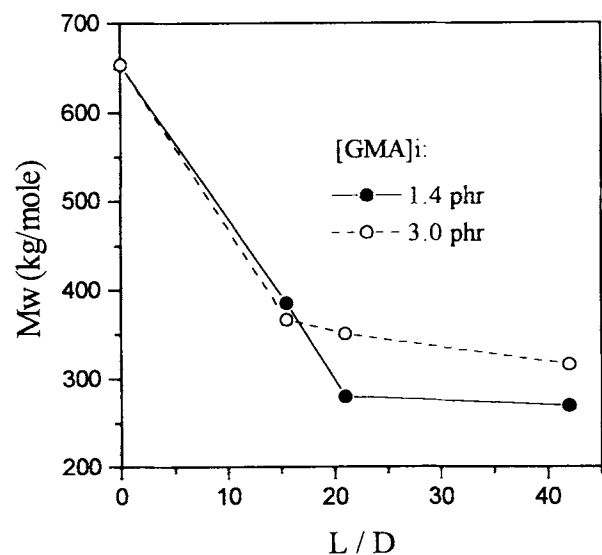

Figure 7 Influence of $[GMA]_i$ on the average molecular weight of grafted PP ($[Perk-14]_i$ = 0.30 phr, $[styrene]_i/[GMA]_i$ = 1.40 mol/mol).
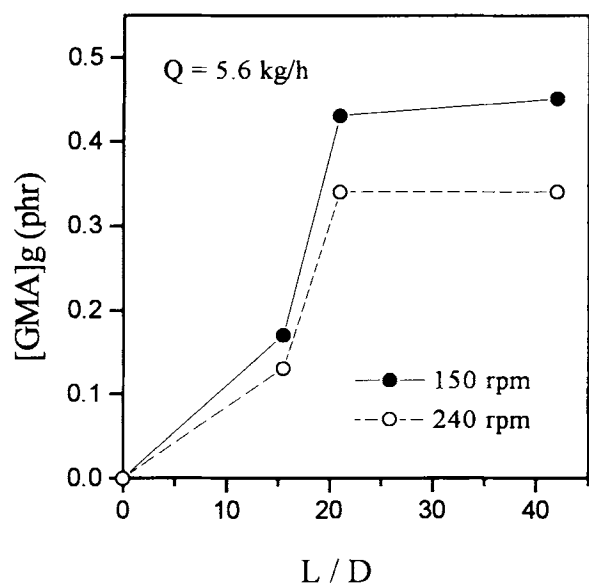
Figure 8   Grafting yield of GMA along the screw length at two different screw speeds (150 and 240 rpm) for a given feed rate of PP (5.6 kg/h).

through the hopper as a pulse after the extrusion process was steady. Samples were collected at the die at chosen time intervals and cut in the direction perpendicular to that of the flow. Tracer concentrations were determined by a UV spectrophotometer. The reproducibility of RTD measurements was found to be good by comparing repeated experiments.

RESULTS AND DISCUSSION

Effect of the Presence of Styrene

The grafting yield of GMA and the molecular weight of the modified PP with and without styrene are shown in Figure 2(a) and (b), respectively. In agreement with the finding reported in previous work[1] concerning the same free radical grafting carried out in a batch mixer, the presence of styrene raises the grafting yield of GMA by a factor of about three [Fig. 2(a)]. The magnitude of increase in the GMA grafting yield should increase with increasing amount of styrene introduced, as was confirmed in the previous work.[1] At the same time, reduction in the molecular weight of the modified PP is much less pronounced [Fig. 2(b)]: the weight average molecular weight of the modified PP is 220,000 g/mol in the absence of styrene and it is increased to 350,000 g/mol in the presence of styrene. As argued

previously,[1] the enhanced free radical reactivity of GMA with reduced PP chain degradation is due to the fact that when a mixture of GMA and styrene is to be grafted onto the PP, styrene reacts with the PP macroradicals with a greater rate than does GMA, forming styryl radicals attached to the PP
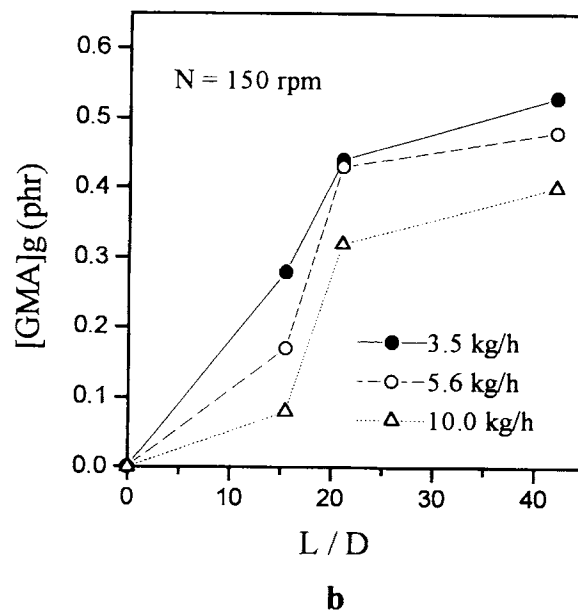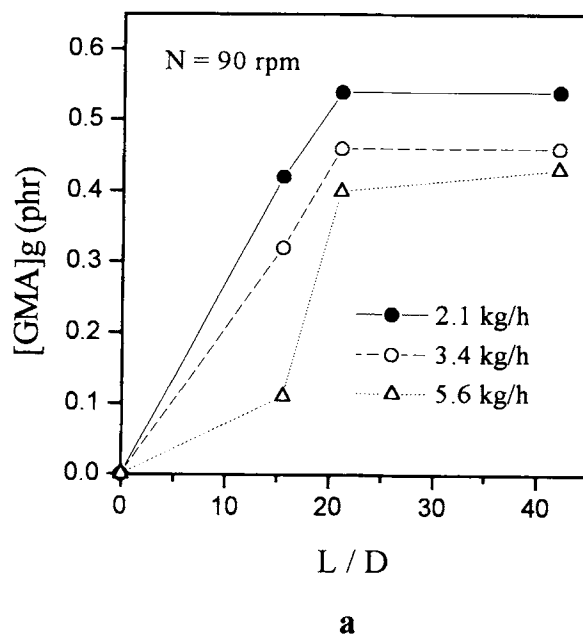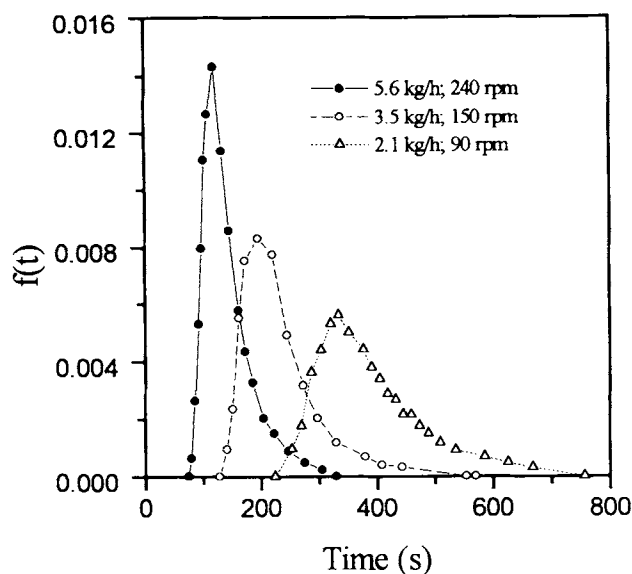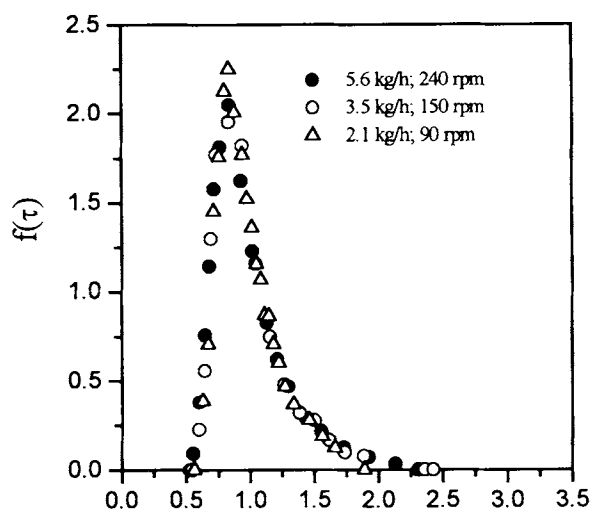

a

b

Figure 9   Grafting yield of GMA along the screw length at various feed rates of PP (varied from 2.1 to 10.0 kg/h) at a given screw speed. (a) N = 90 rpm, (b) = 150 rpm.

Figure 10 Residence time distribution function as a function of time for three different throughputs and screw speeds with a particular Q/N (1/43 kg/h/rpm). Polymeric fluid: polystyrene. (a) $f(t)$ vs. time, (b) $f(\tau)$ vs. τ.

is electronically conjugated with its benzene ring. As a result, its free radical reactivity and that of the corresponding free radical form must be different than a nonconjugated monomer.

Another similarity of the free radical grafting carried out in the twin screw extruder as compared to the one in a batch mixer is that the grafting yield also reaches a plateau beyond a certain screw length downstream: more than 70% of the final grafting yield is already achieved in the first sampling point (36% of the total screw length downstream from the hopper or L/D = 15.5). Almost 100% of the final grafting yield is obtained in the second sampling point (half-way downstream from the hopper or L/D = 21). In other words, the first half screw is already long enough for the grafting yield to reach its ultimate value together with accomplishing solids conveying, melting, and homogenization. But the final grafting yield is far below 100%: even in the presence of styrene, only about one-third of GMA is grafted onto the PP—in fact, as some GMA is lost during the various operation steps, the actual GMA grafting yield should be greater than the reported value. The limited grafting yield is dictated by the concentration of the primary free radicals: this latter decreases considerably along the screw length, as the temperature is 200°C in the first zone between the feeding point and the first sampling point and the corresponding half lifetime of the peroxide used in this study is only about 30 s. The decrease in the concentration of the primary free radicals should be more abrupt beyond the first zone because the temperature is raised to 240°C after the first sampling point. Consequently, the half lifetime of the peroxide is reduced to 2 s. As a result, most of the free radical grafting has proceeded in the first zone. This implies that free radical grafting in a screw extruder is not necessarily characterized by the overall residence time distribution (between the hopper and the exit of the die). To say more precisely, it is related to the residence time in the first zone in which free radicals are not

backbones that are much more stable. They then react with GMA readily. Although the detailed mechanisms by which styrene contributes to the overall free radical grafting of GMA onto the PP remain unknown, they should be related to the particular chemical nature: the double bond of styrene

Table I   Peclet Numbers (Pe) and Mean Residence Times t at Various Screw Speeds and Corresponding Throughputs for Q/N = 1/43 (kg/h)/rpm

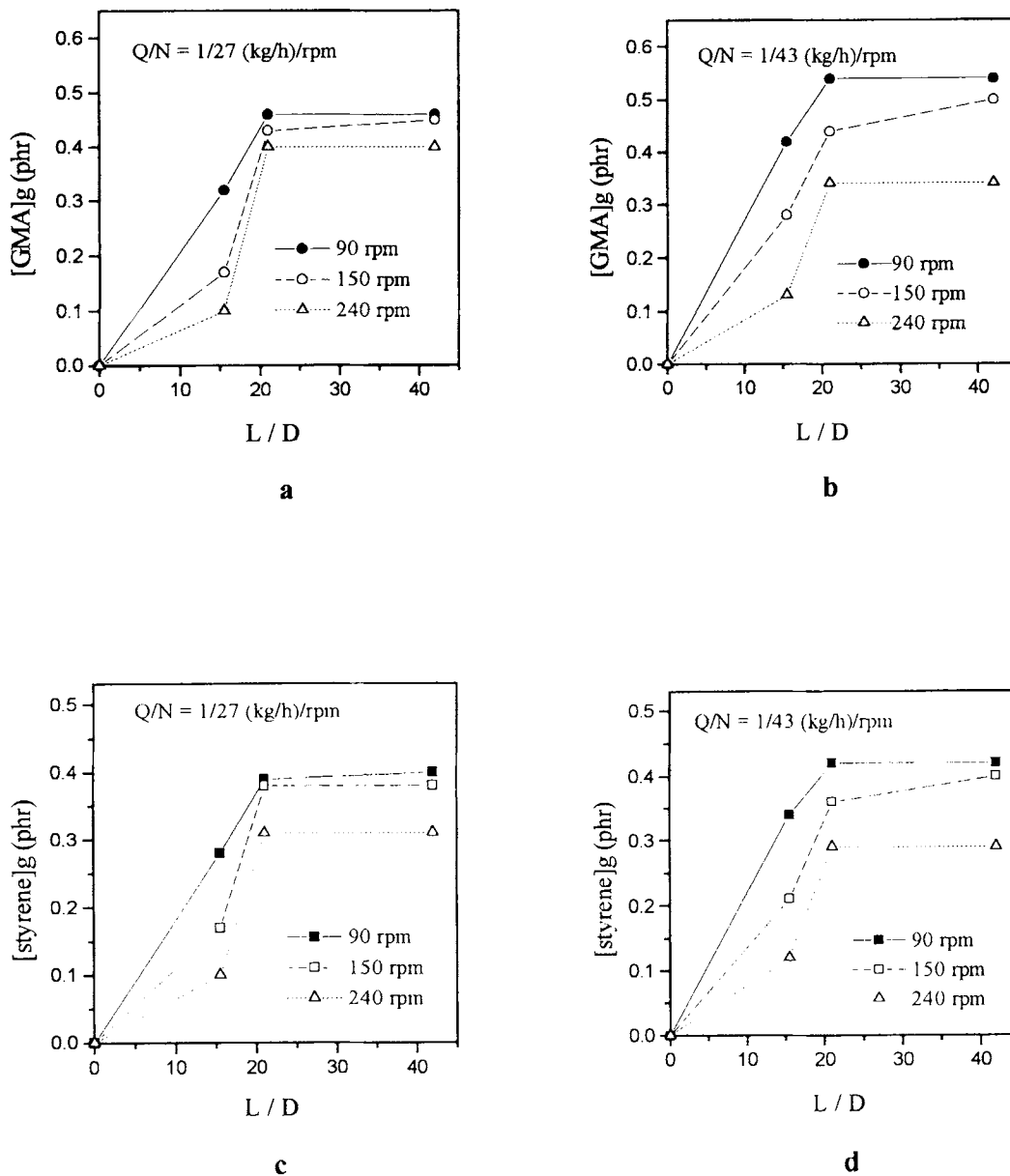|	2.1 kg/h; 90 rpm	3.5 kg/h; 150 rpm	5.6 kg/h; 240 rpm
t (s)	401	235	143
Pe	26.6	23.6	22.2

Figure 11   Grafting yields of GMA and styrene at various screw speeds and throughputs for given specific throughputs. (a) Grafting yields of GMA for Q/N = 1/27; (b) grafting yields of GMA for Q/N = 1/43; (c) grafting yields of styrene for Q/N = 1/27; (d) grafting yields of styrene for Q/N = 1/43.

depleted completely. The length of this zone is determined by the rate of decomposition or roughly the half lifetime of the peroxide under the processing conditions. Put in another way, for a particular zone of interest, if the concentration of the primary free radicals at the exit of this zone is literally greater than zero, the grafting yield of GMA will be affected by the residence time distribution

therein. On the other hand, if the primary free radicals are totally depleted before exiting this zone, the residence time distribution in this particular zone may not have any impact on the grafting yield of GMA. In this case, the grafting yield measured at the exit of the extruder may no longer be an indication of the effect of a processing parameter.
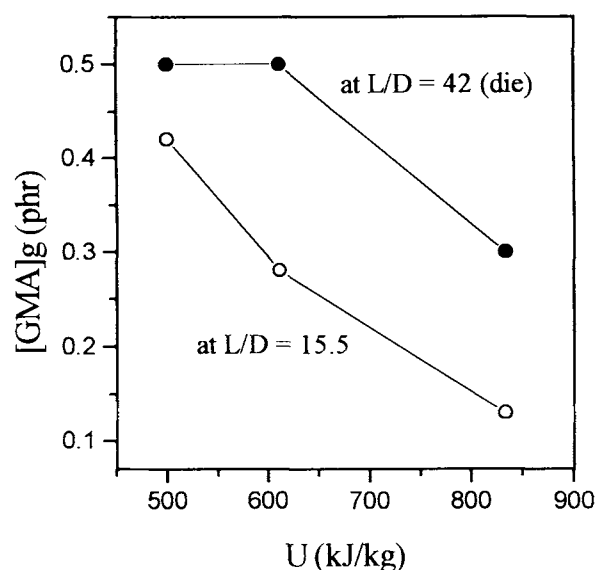
Figure 12 GMA grafting yield as a function of specific energy at a given specific throughput (Q/N = 1/43 kg/rpm). Q = 3.5 kg/h, $[GMA]_i$ = 1.4 phr, $[styrene]_i/[GMA]_i$ = 1.40 mol/mol, $[Perk-14]_i$ = 0.30 phr.

The above discussion suggests that the half lifetime and initiation efficiency of a peroxide under actual free radical grafting conditions are the two critical parameters that govern the performance of a particular melt free radical grafting system. Unfortunately, these two parameters are extremely difficult to evaluate under practical processing conditions. As such, it is often difficult to quantify the effects of chemical and processing parameters on the performance of a particular free radical grafting system. An alternative that we propose in this study is to choose a segmental screw length so that the concentration of the primary free radicals at the exit of this zone is not zero. In practice, the end of this zone should be so chosen that the objective function (grafting yield for example) at this location is sensitive to changes in the processing parameters of interest. In our cases, this zone is between the feeding point of the grafting system (PP, monomers, and peroxide) and the first sampling point. This zone will be called later the target zone. In this study, it may be extended to the second sampling point.

Besides an increased grafting yield of GMA and reduced PP chain degradation, the presence of styrene also suppresses the amount of the homo- and/or copolymer of GMA, $[GMA]_p$ (Fig. 3). This implies that when styrene is present, styrenic radicals attached to PP react with GMA more rapidly than do PP macroradicals, generating more grafted GMA with reduced polymerized GMA.

Effect of the Concentration of the Peroxide

The grafting yield of GMA and that of styrene increase with increasing peroxide concentration, as shown in Figure 4(a) and (b), respectively. A plateau for the grafting yield is always observed whatever the initial concentration of the peroxide. The value of the plateau increases with increasing peroxide concentration. This finding supports the above argument that the limited grafting yield of GMA is related to a limited concentration of primary free radicals. This result also agrees with what was found for the same free radical grafting carried out in a batch mixer.[1] The molecular weights of the corresponding modified PP samples are shown in Figure 5. As expected, an increase in the peroxide concentration causes a greater decrease in the molecular weight of PP.

Effect of the Initial Concentration of GMA

At a particular concentration of peroxide (0.3 phr) with a constant ratio of $[styrene]_i/[GMA]_i$ = 1.40 mol/mol, the grafting yields of GMA and styrene increase [Fig. 6(a)] with increasing $[GMA]_i$ while their conversions decrease [Fig. 6(b)]. Interestingly, the conversion and grafting yield of styrene are always lower than those of GMA, possibly due to a greater loss of styrene because of its greater volatility. Additionally, the PP degradation is less pronounced when a higher GMA concentration is added, implying that, indeed, increasing grafting is an effective way of reducing PP degradation (Fig. 7).

To sum up, so far we have shown the effects of the selected chemical parameters (the presence of styrene, the concentration of the peroxide, and the initial concentration of GMA) on the overall free radical grafting of GMA onto PP by reactive extrusion in a co-rotating twin screw extruder. Basically, the results obtained are similar to those obtained in a batch mixer. This is because, although apparently the grafting yield is a function of reaction time in the batch mixer whereas it is a function of screw length in the twin screw extruder, the fundamental basis that governs this free radical grafting is the same: peroxide concentration and its half lifetime. Also noteworthy is the fact that the very fast free radical grafting in a twin screw extruder is probably the most critical factor that has made in situ reactive blending of polymers so successful.[6]

The effects of various processing parameters (screw speed, feed rate, and specific throughput) on this grafting system in the twin screw extruder will

be shown as follows: the composition of the grafting system is always: $[GMA]_i$ = 1.4 phr, $[styrene]_i/[GMA]_i$ = 1.40 mol/mol and $[Perk-14]_i$ = 0.30 phr. As pointed out earlier, besides the modular character of barrel and screw designs, the co-rotating self-wiping twin screw extruder used in this study as a chemical reactor has two additional independent processing parameters: screw speed (N) and feed rate (Q). With particular screw and temperature profiles, variation in N or Q affects not only macromixing characterized by residence time distribution but also micromixing. This latter is related to the intimate contact between reactive species.

In general, the residence time distribution is shifted to a short time domain when N or Q increases. Werner[7] introduced a G factor to characterize the effect of processing parameters on the mechanical mixing in a co-rotating self-wiping twin screw extruder. It has the form:

$$G = \frac{Q_b}{Q_L - Q_b} = \frac{Q_b}{Q}$$

where the Q_L is the axially forward flow rate, Q_b the reverse flow rate, and Q the net axially forward flow rate. The higher the value of G, the higher the mechanical mixing. Usually, G increases when N increases or Q decreases.

Effect of Screw Speed

The grafting yields of GMA along the screw length at two screw speeds (150 and 240 rpm) with a feed rate of PP of 5.6 kg/h are shown in Figure 8. Note that they are consistently higher at the lower screw speed (150 rpm), primarily due to a longer residence time that the reactive species has experienced from the hopper to the second sampling point. On the other hand, a lower screw speed corresponds to a reduced mechanical mixing intensity in the machine. The reduced mechanical mixing intensity apparently has little adverse effect on the overall grafting yield. That the free radical grafting virtually goes to completion at the second sampling point L/D = 21 indicates once again that it is the effective concentration of the primary free radicals that limits the overall grafting yield.

Effect of Feed Rate

The grafting yield of GMA along the screw length at three different feed rates of PP for a given screw speed is shown in Figure 9. With increasing feed

rate, the grafting yield of GMA at a particular location of the screw decreases due to a reduced residence time. Again, a possible reduction in mechanical mixing intensity in the machine does not have a noticeable impact on the overall grafting yield.

The above results indicate that there is an equivalence between an increase in N and an increase in Q, because both bring about a decrease in the grafting yield of GMA. An increase in N or Q shortens the residence time in the target zone. On the other hand, an increase in N enhances mechanical mixing intensity, whereas an increase in Q reduces it. Thus, the equivalence in terms of the grafting yield between N and Q can only be conciliated through residence time in the target zone. In other words, residence time is the primary parameter that affects the overall performance of the extruder with respect to free radical grafting. The effects of N and Q on the free radical grafting are exerted mainly through changes in residence time, and variations in mechanical mixing intensity are apparently unimportant. This latter may imply that the mixing that our free radical grafting is subjected to is good enough under all the processing conditions.

Effect of Specific Throughput

In order to further support the argument that residence time is the key parameter that controls the overall grafting yield, the effect of specific throughput is examined. Specific throughput is defined as the ratio of throughput to screw speed, Q/N. As discussed elsewhere,[8] it has a unit of kg/turn and measures, to some extent, the pumping capacity of a particular twin screw extruder: the amount of material each turn of the screw can pump. It also characterizes the degree of fill of the twin screw extruder for partly filled zones. The reverse of Q/N, N/Q, has a unit of turns/kg and can be viewed as the number of screw rotations a unit material has experienced. Thus, it measures the intensity of mixing the material has experienced through the partly filled zones. If the pressure flow in a twin screw machine due to the die and/or other pressure consumers is unimportant, Q/N and N/Q are expected to characterize the degree of fill and the intensity of mixing of the overall machine, respectively. If so, unlike a change in Q or N that affects not only macromixing but micromixing as well, variations in Q and N at the same time for a particular Q/N will change residence time distribution only. The residence time distribution functions $f(t)$ as a function of time for three

different throughputs and screw speeds at a given Q/N (1/43 kg/h/rpm) are shown in Figure 10(a). The corresponding dimensionless residence distribution functions $f(\tau)$ as a function of dimensionless time τ (time divided by the mean residence time, $t/\bar{t}$) are shown in Figure 10(b). The $f(t)$ curve is shifted to a short time domain when Q and N are increased [Fig. 10(a)]. Interestingly, the three $f(t)$ curves in Figure 10(a) superimpose well when they are converted to the $f(\tau) - \tau$ form. This supports the above argument that mechanical mixing intensity and associated longitudinal flow pattern (longitudinal micromixing) do not vary much upon varying Q with a concomitant change in N for a particular Q/N, and only residence time distribution (macromixing) changes. The values of the mean residence time and the Peclet number are shown in Table I. The Peclet number is defined as $\bar{u}L/D$, which measures the relative importance of convective mixing compared to dispersion of a flow passing through a tube. The data in Table I show that, indeed, when Q/N is constant, the Peclet number does not vary much with concomitant variations in Q and N.

The grafting yields of GMA along the screw length at three different screw speeds for two given Q/N ratios (1/27 and 1/43 kg/h/rpm) are shown in Figure 11(a) and (b) and those of styrene in Figure 11(c) and (d). When the ratio of Q/N is constant, the grafting yield of GMA increases with decreasing Q and N due only to longer residence times in the zone of 200°C. This is also true for the grafting yield of styrene.

Criterion of Specific Energy (U)

In what follows, we examine whether the specific energy that an extruder imparts to the material can be used as a measure of the performance of this extruder with respect to the free radical grafting of GMA onto PP. The power consumed by the motor of an extruder can be expressed as follows:

$$\text{power} = \text{shear rate} \times \text{viscosity} \times \text{shear area}$$
$$\times \text{radius} \times \text{screw speed}$$
$$= \text{torque} \times \text{screw speed}$$

The specific energy (U) is defined as power divided by throughput. On our ZSK-30 co-rotating intermeshing twin screw extruder, it is percentage torque rather than torque itself that is measured. As the percentage torque is not zero when the extruder is running empty (i.e., without material inside the extruder), the actual percentage torque the material exerts onto the screw shafts for a particular screw speed is:

$$\text{actual percentage torque} = \text{percentage torque}$$
$$\text{of the actual extrusion process}$$
$$- \text{percentage torque when the extruder}$$
$$\text{is running empty at the same screw speed.}$$

According to the ZSK-30 twin screw extruder operations manual, the power at 100 percent torque is equal to 64.8 (kJ/h) × screw speed (rpm). Thus, the specific energy can be calculated from

$$U = (\text{actual percentage torque}) \ (64.8)$$
$$(\text{screw speed})/\text{throughput}$$
$$= (64.8) \ (\text{actual percentage torque})$$
$$N \ (\text{rpm})/Q \ (\text{kg/h})] \quad [\text{kJ/kg}]$$

Interestingly, the GMA grafting yield decreases with increasing specific energy regardless of variations in Q or N, being in contradiction to one's intuition. An example is given in Figure 12, which shows the GMA grafting yield as a function of specific energy at a given specific throughput. This finding indicates that specific energy is not a measure of the performance of the extruder with respect to the free radical grafting of GMA onto PP. The reason is that it is residence time that is the critical parameter. The decrease in the GMA grafting yield in Figure 12 indicates that, in our case, an increase in specific energy is concomitant with a decrease in residence time.

CONCLUSION

This article concerns the performance of a co-rotating twin screw extruder as a chemical reactor for the free radical grafting of glycidyl methacrylate (GMA) onto molten polypropylene (PP). The effects of chemical and processing parameters have been discussed. Basically, the behavior of this free radical grafting system is similar to that in a batch mixer:[1] the GMA grafting in the presence or absence of styrene proceeds rapidly as it has gone to completion half-way downstream of the extruder. Additionally, the presence of styrene as a second monomer increases the GMA grafting yield greatly with a significant reduction in PP chain degradation.

The GMA grafting yield increases with increasing concentration of the peroxide, 1,3-bis(*tert*-butyl-peroxy-isopropyl)benzene. This similarity is related to the fact that it is the peroxide concentration and its half lifetime that govern the overall grafting rate and ultimate yield, regardless of the reactor (the batch mixer or the screw extruder). On the other hand, it is through the residence time distribution that the processing parameters (screw speed, feed rate, and specific throughput) impart their effects on the GMA grafting yield. Strictly speaking, this residence time distribution should correspond to the zone where the peroxide has not depleted completely. An increase in screw speed or feed rate causes a decrease in GMA grafting yield due to a decrease in residence time distribution. At a particular specific throughput (the ratio of throughput to screw speed), an increase in throughput with a concomitant increase in screw speed brings about a decrease in GMA grafting yield. This is again due to a corresponding decrease in residence time distribution. Specific energy is not a good measure of the performance of the extruder with respect to the free radical grafting of GMA onto PP.

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