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Melt rheology of graft modified polypropylene

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The low frequency rheological behaviour of a family of glycidyl methacrylate and styrene graft modified polypropylenes was studied. Two initiators were examined in the grafting process and were found to produce significantly different copolymers in terms of the degree of grafting, molecular weight, and rheological properties. Rheological evidence that β-scission occurred during the grafting process was found for the PP-g-GMA copolymers. A slight increase in the elastic response was observed for the samples prepared using L 231, most likely due to crosslinking via epoxy ring opening. The elastic response of the styrene grafted copolymers was enhanced significantly, and the copolymers behaved like typical crosslinked materials at higher levels of grafted styrene. The low frequency storage modulus (G') increased, spanning more than 2 decades, with the addition of styrene as a comonomer for the grafting of GMA. At higher levels of grafting, both the PP-g-S and PP-g-(GMA-S) copolymers were sufficiently crosslinked that G' was greater than G'', the loss modulus, over the entire frequency range examined. However, these samples contained no gel material as determined by Soxhlet extraction with xylene. © 1997 Elsevier Science Ltd.

(Keywords: melt rheology; graft modified; glycidyl methacrylate)

INTRODUCTION

The addition of peroxide to polypropylene (PP) is a common technique used to produce controlled rheology resins[1–6] and to prepare graft modified copolymers[7–14]. Commercial PP resins are generally polymerized using Ziegler–Natta catalysts, which produce high molecular weight (MW) polymers with broad molecular weight distributions (MWD)[1]. Small quantities of peroxide are added to PP in post-reactor, extrusion processes to induce β-chain scission, which decreases the MW and narrows the MWD of the polymer. Tzoganakis[1] has examined the effects of chemically induced chain scission on the MW and MWD of branched and linear PP resins in a twin-screw extruder. The polydispersity index obtained through rheological experiments were found to correlate well with those obtained using size exclusion chromatography.

It is also possible to crosslink PP using high levels of peroxide[4–6,15]. Under these conditions, the rate of macroradical combination is much faster than the rate of chain scission. The addition of parabenzoquinone to the PP–peroxide system was found to be a highly efficient method for crosslinking PP, producing up to 90 wt% gel material[15]. Another technique used to crosslink PP involves grafting polyfunctional monomers, in which the grafted unit produces a more stable macroradical site, thereby reducing the probability of fragmentation and increasing the likelihood of undergoing further reaction. Monomers such as divinyl benzene and ethylene glycol dimethacrylate have been used for this purpose[4,5,16].

As mentioned previously, peroxide initiators are also used to promote free radical melt grafting of functional monomers onto polymer molecules. Due to the chemical nature of PP, it has a tendency to undergo β-scission which causes difficulties in producing graft modified PP copolymers having high molecular weights and melt strength; hence, control of the β-scission reaction is desirable during the grafting process. A variety of functional monomers have been grafted onto PP via free radical initiation, and in each case, an increase in the melt flow index and a decrease in the MW were reported[7–14]. The use of styrene as a comonomer in the melt grafting of glycidyl methacrylate (GMA) onto PP was examined by Sun *et al.*[12]. Substantially higher degrees of grafting of GMA were achieved, along with higher molecular weights, than the copolymers prepared without styrene. It was proposed that styrene monomer grafts onto PP first, which is then followed by the addition of GMA. The reactivity of GMA towards the styryl radical is believed to be greater than its reactivity towards the PP macroradical, hence, there is a synergistic effect on the grafting of GMA.

Chen *et al.*[9] examined the effectiveness of various PP-g-GMA copolymers as reactive compatibilizers in PP-nitrile butadiene rubber (NBR) blends, in which the NBR contained 7 wt% acrylic acid functionality. The total concentration of functional groups has been reported to be a key factor in determining the final properties of immiscible polymer blends[9,17]. From this study, it was demonstrated that the degree of grafting (DG) and MW of the graft copolymer also affects the impact performance of the blends. The GMA modified PP copolymers prepared using styrene as a comonomer were less effective as compatibilizers in comparison with the copolymers prepared using only GMA. Hence, in this case, the higher amounts of GMA grafted with the

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addition of styrene were masked by the effects of steric hindrance of the bulky phenyl ring, thus reducing the reactivity of the epoxy group. It was also observed that, in the synthesis of the graft copolymers containing styrene, there was an increase in the mixing torque, suggesting that crosslinking reactions were occurring[9–11]. This increase was unexpected as PP has a natural tendency to undergo chain scission, which would result in a decrease in the mixing torque. This apparent crosslinking of PP, along with the fact that the presence of styrene tended to decrease the efficiency of the graft copolymers as blend compatibilizers, prompted some interest into the structures of these graft modified PP samples.

The low frequency rheological response of polymers is extremely sensitive to molecular structure (refs 18, 19 chap. 2). For uncrosslinked polymers, the values of the storage modulus (G') and loss modulus (G'') decrease to zero ($G' \propto \omega^2$ and $G'' \propto \omega$) at low frequencies, otherwise known as the terminal zone (refs 18, 19 chap. 2). A decrease in the molecular weight tends to shift the terminal zone to higher frequencies. Whereas, the addition of chemical crosslinks results in significant changes in the rates at which the dynamic moduli decrease at low frequencies, and in the case of elastic materials, G' achieves a plateau value, commonly known as the equilibrium modulus, G_e. Kim and Kim[20] examined the effects of crosslinking polyethylene using various reactive ingredients on the rheological properties of the polymer. At a peroxide concentration of 0.3 wt%, G' was greater than G'' over the frequency range examined, indicating the existence of a three dimensional network.

Another use of melt rheology is in the determination of the gel point for thermoset and crosslinkable resins[21–29]. At a conversion near the gel point of stoichiometrically balanced networks, as well as in cases where there is excess crosslinker, the storage and loss moduli are congruent over a wide range of frequencies[21–23,27]. In cross-linker deficient systems, the gel point occurs when G' and G'' are parallel to each other[23,27]. The congruency of G' and G'' was used to determine the gel point of ethylene vinyl acetate and ethylene acrylic ester blends, crosslinked via transesterification reactions[28,29], and the results obtained from the rheological studies correlated well with the gel points determined from equilibrium swelling data.

It is the intent of the present work to demonstrate how the low frequency rheological properties of graft modified PP are influenced by the processing conditions used to prepare the copolymers. The GMA and styrene graft copolymers were synthesized in a Haake Rheomix batch mixer at 180°C, and a Rheometrics Dynamic Analyzer II (RDA II) was used to acquire the rheological data. The effects of the initiator type, initiator concentration, monomer concentration(s), and the use of comonomers on the rheological properties of the PP graft copolymers were examined. By comparing the rheological behaviours at low frequencies, the region in which flow is governed by the molecular structure, some inferences regarding the structure of the graft copolymers were made.

EXPERIMENTAL

Materials

The polypropylene homopolymer used in this study was Himont 6823. It is a homopolymer resin with melt flow index of 0.5 (ASTM D1238, 230°C, and 2.16 kg) and a density of 0.90 g cm^{-3}. The number and weight average molecular weight, as determined by high temperature g.p.c., were 87 000 and 750 000, respectively.

Glycidyl methacrylate (97% pure), inhibited with 50 ppm *p*-methoxy phenol (MEHQ), and styrene (99% pure), inhibited with 10–15 ppm 4-*t*-butylcatechol, were supplied by Aldrich and used as received. The two initiators, 1,1-di-(*t*-butylperoxy)-3,3,5-trimethylcyclohexane (L231, 92% minimum) and 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexyne (L130, 91–93% minimum), were supplied by Atochem. The half-lives of L231 and L130 in polyethylene at 180°C are estimated to be 14.3 and 548 s, respectively[30]. Toluene, acetone, methanol, and xylenes used in the purifications and extractions were reagent grade. A chromatographic grade of 1,2,4-trichlorobenzene was used for the high temperature g.p.c. analysis.

Preparation and characterization of graft modified polypropylene

A Haake Buchler Rheomix 600 mixer was used to prepare the graft modified PP. Determined amounts of polymer, monomer(s) and initiator were premixed, by hand in a small container, before being charged into the mixing chamber. The mixing temperature, time, and rotor speed were held constant at 180°C, 6 min, and 90 rev min^{-1} for all runs. The reaction product was removed from the mixing chamber and added to liquid nitrogen to stop any further reaction. Approximately 3.5 g of crude polymer was completely dissolved in 100 ml of hot toluene for approximately 30 min. The grafted polymer was then precipitated by dropwise addition into a 10-fold excess of acetone; the GMA and styrene homopolymers, along with the unreacted monomers and peroxide, remained in solution. The grafted copolymer was filtered and washed with acetone (3 × 100 ml), and dried to a constant weight, under vacuum, prior to rheological evaluation.

The DG was determined via *FT*i.r. spectroscopy, using a Bomem *FT*i.r. spectrophotometer. A small sample, ~ 0.2 g, of the purified polymer was pressed to a thickness of approximately 0.1 mm. Calibration of the *FT*i.r. spectrometer was accomplished by using thin films of PP with known concentrations of GMA and styrene[12]. The peak at 2721 cm^{-1} (combination band, C–H deformation) was used as the PP reference. The ratios of the intensity of carbonyl stretch at 1730 cm^{-1} and the aromatic peak 700 cm^{-1} to the reference peak were used to calculate the DGs of GMA and styrene, respectively. Four spectra were acquired per sample. Further details on the preparation and characterization have been reported earlier[9–11].

Rheological analysis

Rheological data were acquired using a Rheometrics Dynamic Analyzer II (RDA II) equipped with 2K Bendix Spring torque transducer. Parallel plates, 25 mm in diameter and a gap height of 2 mm, were used for the frequency, strain, and time sweeps. The test specimens were cut from a sheet which had been melt pressed to a thickness greater than 2 mm. The temperature was kept constant at 175°C, and a dry nitrogen atmosphere was maintained to suppress degradation of the polymer sample during the experiment.

Table 1 Initial sample compositions and degrees of grafting

	Reactant proportions					Graft levels	
Sample	PP (g)	GMA (g)	S (g)	L 130 (g)	L 231 (g)	DG (GMA)	DG (S)
A1	45.00	1.00	—	0.30	—	0.6	—
A2	45.00	2.00	—	0.30	—	0.9	—
A3	45.00	3.00	—	0.30	—	1.0	—
A4	45.00	4.00	—	0.30	—	1.2	—
A5	45.00	5.00	—	0.30	—	1.3	—
A6	45.00	5.00	—	0.10	—	0.5	—
A7	45.00	5.00	—	0.20	—	0.9	—
A8	45.00	5.00	—	0.40	—	1.6	—
A9	45.00	5.00	—	0.50	—	2.0	—
B1	45.00	1.00	—	—	0.30	0.6	—
B2	45.00	2.00	—	—	0.30	1.1	—
B3	45.00	3.00	—	—	0.30	1.5	—
B4	45.00	4.00	—	—	0.30	2.6	—
B5	45.00	5.00	—	—	0.30	3.0	—
B6	45.00	5.00	—	—	0.10	1.6	—
B7	45.00	5.00	—	—	0.20	2.5	—
B8	45.00	5.00	—	—	0.40	3.6	—
B9	45.00	5.00	—	—	0.50	3.6	—
C1	45.00	—	1.00	0.30	—	—	1.0
C2	45.00	—	2.00	0.30	—	—	1.7
C3	45.00	—	2.93	0.30	—	—	2.6
C4	45.00	—	4.00	0.30	—	—	3.5
C5	45.00	—	5.86	0.30	—	—	4.8
C6	45.00	—	7.33	0.30	—	—	6.2
D1	45.00	4.00	0.37	0.30	—	1.4	0.2
D2	45.00	4.00	0.73	0.30	—	1.8	0.3
D3	45.00	4.00	1.47	0.30	—	2.5	0.6
D4	45.00	4.00	2.93	0.30	—	3.0	1.5
D5	45.00	4.00	4.40	0.30	—	3.2	1.7
E1	45.00	0.50	2.93	0.30	—	0.7	2.2
E2	45.00	1.00	2.93	0.30	—	1.2	2.1
E3	45.00	2.00	2.93	0.30	—	2.1	1.8
E4	45.00	4.00	2.93	0.30	—	3.0	1.5
E5	45.00	6.00	2.93	0.30	—	3.8	1.3

The frequency range and strain used were 0.06 to 300 rad s^{-1} and 5%, respectively, and were confirmed to be within the linear viscoelastic region. The time sweeps were conducted with a strain of 5% and a frequency of 0.1 rad s^{-1} to determine the stability of the PP samples. The samples were stable, as there were no changes in storage modulus up to 1 h, which is triple the time required to complete a frequency sweep.

Gel content analysis

The copolymers containing styrene were analysed to determine if any gel was formed due to the crosslinking of the PP in the grafting procedures using styrene. Approximately 1.5 g of purified sample was cut into small pieces and placed in a cellulose thimble. Soxhlet extraction with xylene was used to determine the relative amounts of gel. The extractions of the grafted PP samples were stopped after 3 and 24 h.

RESULTS AND DISCUSSION

The grafting conditions and degrees of grafting are summarized in *Table 1*. The degree of grafting was strongly influenced by the type of initiator used and the addition of styrene as a comonomer. The temperature was kept constant at 175°C for all of the rheology experiments so the samples could be tested under similar conditions. Some of the copolymers experienced significant amounts of chain scission during the grafting process, and hence, the rheology data obtained at higher temperatures were not reliable as the torque values were out of the transducer limits. The conditions used for the rheological analysis were confirmed to be within the linear viscoelastic region, as the rheological properties were independent of the applied strain. This condition is required as the equations used to calculate the various rheological parameters are based on this assumption[18]. A nitrogen atmosphere was maintained and the sample was stable throughout the duration of the experiment (15 min). The change in the storage modulus was less than 1% over a period of 1 h at 175°C, which was insignificant in comparison to the changes observed for the various copolymers.

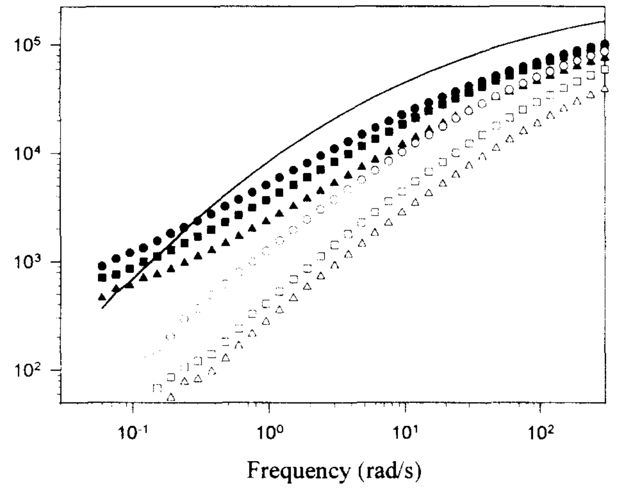

Figure 1 G' vs frequency curves for PP-g-GMA samples prepared with increasing initiator concentration at 175°C and 5% strain. [L 231] (DG wt%) = ● 0.44 (2.5), ■ 0.67 (3.0), ▲ 0.89 (3.6); wt% L 130 = ○ 0.22 (0.5), □ 0.44 (0.9), △ 0.67 (1.3); and — PP

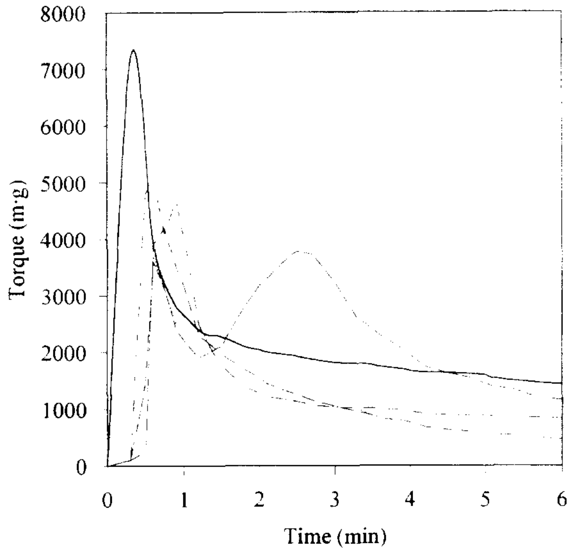

Figure 2 Mixing torque vs time plots: —— PP, · · · · PP + GMA + L 130, – · · · · PP + GMA + L 231, – – · PP + styrene + L 130, ········ PP + GMA + styrene + L 130

Effects of choice of initiator

As mentioned previously, PP is unstable in the presence of free radicals, and has a tendency to undergo β-scission, leading to difficulties in producing functionalized PP without inducing a significant amount of polymer degradation. The effects of the two initiators on the rheological properties of PP-g-GMA were examined as a function of initiator concentration, while the GMA concentration was kept constant at 11.1 wt%. The estimated half-lives of L 130 and L 231 in polyethylene at 190°C are 213 and 6.6 s, respectively[30]. Observations of the torque during the grafting process gave an indication that β-chain scission was more severe when L 130 was employed to initiate grafting.

The storage modulus plotted as a function of frequency is shown in *Figure 1* for various levels of initiator, with the DG given in parentheses. Rheological data for many of the samples prepared using L 130 are not available since the sample viscosities were too low. It can be seen that the storage modulus was influenced by the amount of initiator used; as the concentration of initiator increased the values of the storage modulus decreased progressively. The increasing concentration of initiator resulted in the production of more free radicals. Since the amount of monomer was kept constant for this series of copolymers, the probability of a macroradical reacting with monomer was decreased, making chain scission more probable and causing further decreases in the molecular weight.

The DG and extent of chain scission were also found to be dependent on the type of initiator used. The storage modulus for the samples prepared using L 231 are higher than for those prepared using L 130, indicating the extent of β-scission was less severe when L 231 was employed; these results were also confirmed by g.p.c. analysis of the copolymers[10,11]. The half life of L 231 is much less than that of L 130 at the processing temperature, hence, L 231 begins to react before it is well dispersed in the PP melt, and the generation of free radicals is 99% complete within 46 s. Since the monomer and initiator were mixed with the PP prior to processing, the monomer was readily accessible to the macroradicals generated by L 231, and grafting is believed to occur, at least in part, on the surface of the PP pellets. L 130 on the other hand continues to produce primary free radicals throughout the grafting process, and the free radicals are dispersed more uniformly in the PP melt. A portion of the monomer has been consumed by grafting and homopolymerization, hence, lowering the effective monomer concentration in the vicinity of the PP macroradicals generated during the latter stages of the melt grafting process. The result is an increase in β-scission of the PP molecules, as indicated by the rheological properties.

Verney *et al.*[31] studied a series of GMA modified PP which were prepared by blending peroxidized PP with GMA monomer. The effect of processing temperature on the viscosity of the grafted PP was examined, and it was concluded that two types of grafting mechanisms were occurring, resulting in different rheological properties. Based on viscosity data, it was proposed that at elevated temperatures β-scission occurs first, followed by grafting on the chain fragment radicals, whereas at low temperatures, grafting takes place before a substantial amount of chain scission occurs.

The rheological behaviour exhibited by the PP-g-GMA copolymers prepared using L 130 were similar to those of the unmodified PP homopolymer, except there was a shift in the curve of similar shape to lower values. For the samples prepared using L 231, the rheological response tended to deviate from that of pure PP at low frequencies. A decrease in the G' vs frequency slope was observed, and G' was shifted to values higher than that of the unmodified PP resin, indicating that there may be some higher molecular weight material present (ref. 19, chap. 13). The presence of the higher molecular weight material is believed to arise from crosslinking of PP via epoxy ring opening reactions of the grafted GMA units, since GMA monomer is capable of forming highly crosslinked networks when polymerized in the bulk[32]. During the grafting process, there was a noticeable rise in the torque shortly after the melting peak (about 1 min), as shown in *Figure 2*, implying a rise in molecular weight. When L 231 was used for graft initiation, the free radicals were generated so rapidly that the monomer and initiator were not well dispersed in the PP melt before reaction occurred. It is believed that grafting was mainly restricted to the surface of the PP pellets, rendering crosslinking reactions between two GMA graft chains more probable.

Effects of monomer concentration

The effect of increasing the initial concentration of GMA, and hence, the level of grafted GMA, on the storage modulus is shown in *Figure 3*. This series of copolymers were prepared with an L 231 concentration of 0.67 wt%. For the samples prepared with a monomer concentration less than 4.4 wt%, the degrees of grafting (less than 1.1 wt%) were low and the extent of polymer degradation was significant, as indicated by the pronounced decrease in the low frequency storage modulus in comparison with the value for the unmodified PP resin. By raising the monomer concentration, the probability of β-scission occurring was reduced and higher levels of GMA were grafted, resulting in an increase in G'. The shape G' vs frequency curve at low frequencies was also affected by the increased levels of grafted GMA. At higher DGs of GMA, the storage modulus was shifted to higher values, and the slope began to decrease in the low frequency range. The DG of GMA for the copolymers prepared with small quantities of monomer was low, hence, crosslinking via epoxy groups on different PP macromolecules was unlikely. However, when higher concentrations of GMA were grafted, the probability of reaction between the graft chains was enhanced, and a change in slope at low frequencies was observed.

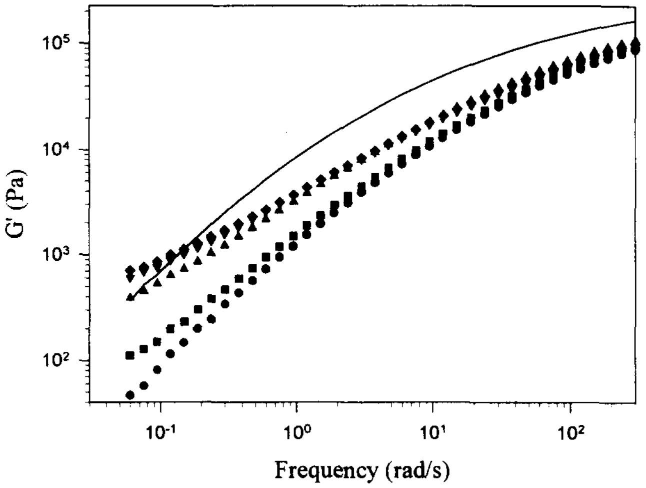

Figure 3 G' vs frequency curves for PP-g-GMA samples prepared with increasing initial GMA concentration at 175°C and 5% strain. $[\mathrm{GMA}]_0$ (DG) = ● 2.2 (0.6), ■ 4.4 (1.1), ▲ 6.7 (1.5), ▼ 8.9 (2.6), ◆ 11.1 (3.0) wt%, and PP (—)

Melt rheology of styrene modified PP

During the melt grafting of GMA onto PP a substantial amount of polymer chain scission occurred, as indicated by the rheological properties of the materials, and it is not unreasonable to expect a similar type of behaviour to occur when melt grafting styrene onto PP. However, during the preparation of these styrene grafted samples, an unexpected rise in the mixing torque was observed (see *Figure 2*) in the 2–3 min range. This type of behaviour is typically reported when graft modifying PE, which is capable of crosslinking in the presence of free radicals. It was, therefore, assumed that crosslinking of PP had occurred during the grafting process, though this appears to be an unlikely reaction owing to the chemical nature of PP.

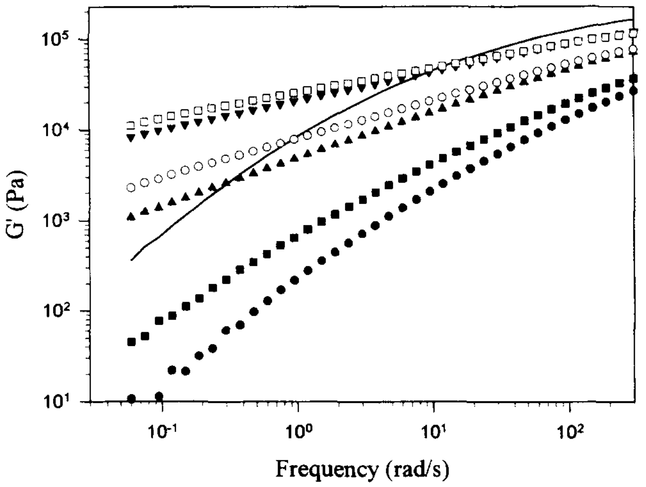

Figure 4 G' vs frequency curves for PP-g-S samples prepared with increasing styrene concentration at 175°C and 5% strain. $[\mathrm{S}]_0$ (DG) = ● 2.2 (1.0), ■ 4.4 (1.7), ▲ 6.5 (2.6), ○ 8.9 (3.5), ▼ 13.0 (4.8), □ 16.3 (6.2) wt%, and — PP

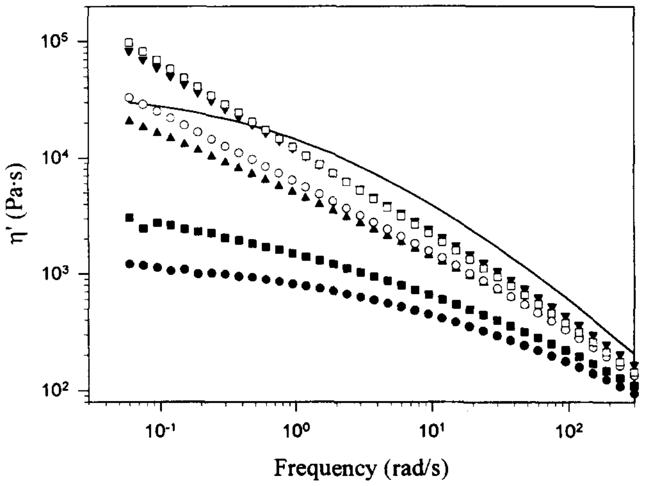

Figure 5 η' vs frequency curves for a series of PP-g-S samples prepared with increasing styrene concentration at 175°C and 5% strain. $[\mathrm{S}]_0$ (DG) = ● 2.2 (1.0), ■ 4.4 (1.7), ▲ 6.5 (2.6), ○ 8.9 (3.5), ▼ 13.0 (4.8), □ 16.3 (6.2) wt%, and — PP

To investigate the extent to which crosslinking had occurred, the rheological properties in the low frequency range were observed; it is in this region that molecular structure governs the rheological behaviour (refs 18, 19 chap. 2). *Figure 4* illustrates how the storage modulus, as a function of frequency, changed as the level of grafted styrene increased. The samples were prepared by progressively increasing the initial concentration of styrene, while keeping the L 130 concentration constant at 0.67 wt%. The shape of the G' vs frequency curve for the samples prepared with an initial styrene concentration less than 4.4 wt% (or DG < 1.7 wt%) resembled the curve for the unmodified PP resin. As the concentration of styrene was raised beyond 6.5 wt% (DG > 2.6), the low frequency storage modulus increased beyond the value for the unmodified PP resin and tended towards a plateau value, indicating an increased elastic response for these materials (refs 18, 19 chaps 2, 10, 14, 20, 31). It was also observed that the PP-g-S samples retracted upon

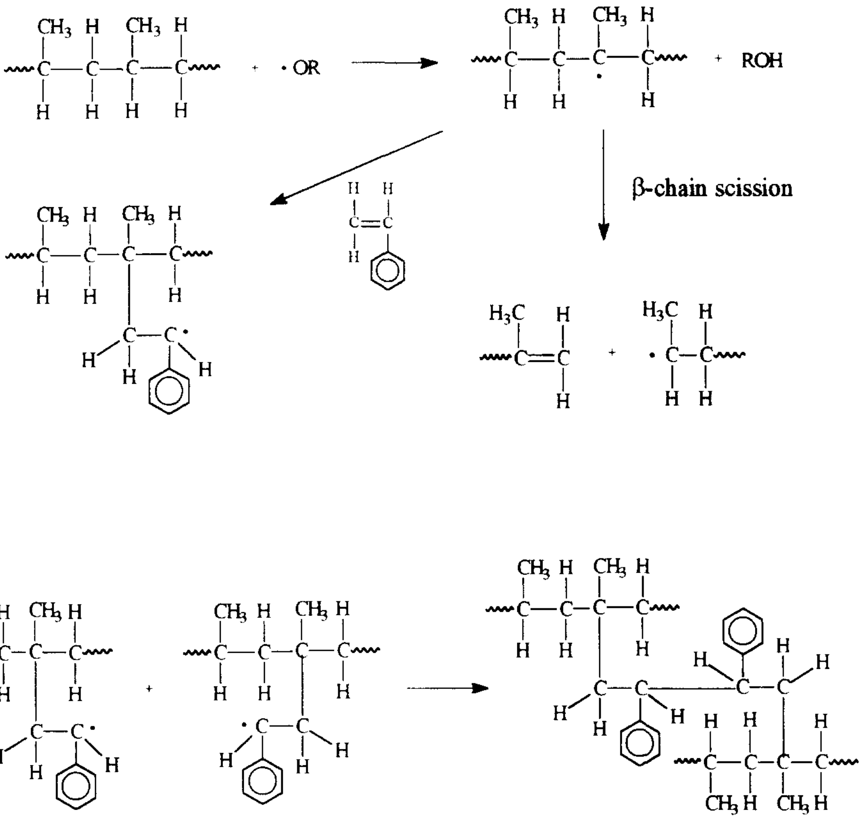

Figure 6 Crosslinking reactions of PP in the presence of styrene monomer and L 130

heating. This type of behaviour is typically reported for elastomers and crosslinked materials, indicating an unexpected behaviour for these styrene grafted copolymers.

Further evidence of crosslinking in the PP-g-styrene samples was found by examining the effect of increasing grafted styrene levels on the dynamic viscosity, η' as shown in *Figure 5*. The curves for PP and PP grafted with low levels of grafted styrene, DG < 1.7 wt%, leads to the presence of a plateau at low frequencies, as η' approaches the limit of the zero shear viscosity, η_o, which is solely dependent on the weight average molecular weight. However, at grafted levels higher than 2.6 wt% styrene, the dynamic viscosity continues to increase linearly as the frequency decreases, with no signs of levelling off in the frequency range tested.

In the bulk polymerization of styrene, termination by combination occurs readily[33]; therefore, it is possible for two styrene graft chain radicals to combine, resulting in the formation of a crosslink as shown in *Figure 6*. The dynamic viscosity curves for the copolymers prepared with small amounts of styrene fall below the curve for the unmodified PP resin, signifying that the effect of chain scission is more dominant than the crosslinking reactions. The low monomer concentration results in the production of fewer PP-S · radicals, making crosslinking less probable. Also, the homopolymerization and grafting reactions, which compete with the chain scission reaction, were reduced due to the limiting amount of available monomer, resulting in a decreased molecular weight. The dynamic viscosity continued to increase linearly at low frequencies for the samples containing higher levels of grafted styrene, indicating that the weight average molecular weights of these samples were higher. The elevated levels of styrene allow the grafting reactions to compete more effectively with chain scission, while producing more PP-S · radicals. The increase in η' may partially be due to the suppression of β-scission, but the fact that the dynamic viscosity shows no evidence of plateauing implies that the material was crosslinked. Similar trends were observed by Kim and Kim[20], who examined a series of HDPE samples, crosslinked via reactive extrusion. They correlated the increase in complex viscosity, and a decrease in melt flow index,with an increase in initiator concentration. As the MFI approached zero, the levelling off of η' was no longer apparent in the frequency range tested. The MFI of the graft copolymers containing styrene were found to decrease rapidly to zero as the degree of grafted styrene increased[9].

The storage and loss moduli plotted as a function of frequency for PP-g-S samples with different degrees of grafted styrene are shown in *Figure 7*. At low frequencies, deformation is generally more viscous than elastic for most thermoplastics, hence G'' is greater than G'; the reverse is true for elastomeric materials[18]. The curves for PP and samples with less than 1.7 wt% grafted styrene exhibited rheological properties that are typical for amorphous polymers. At a DG of 2.6 wt% styrene, the values of G' approached those of G'', and beyond this level of grafting, the storage modulus was greater than the loss modulus, indicating that the material was crosslinked.

Although the PP-g-S samples did display increased elasticity with increasing levels of grafted styrene, Soxhlet extraction of these samples with xylene for 24 h indicated that there was no gel material in any of the samples. The copolymers were purified prior to extraction to remove the unreacted initiator and monomer so that the extraction process would not be complicated by

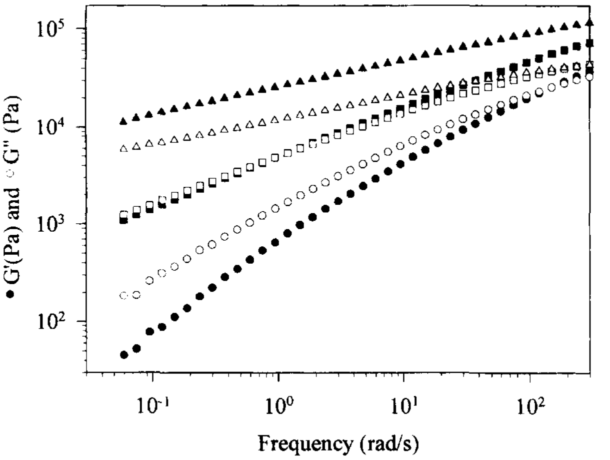

Figure 7 G' and G'' vs frequency curves for a series of PP-g-S samples prepared with increasing styrene concentration at 175°C and 5% strain. $[S]_0$ (DG) = ● 2.2 (1.0), ■ 6.5 (2.6), ▲ 13.0 (4.8) wt%, and — PP

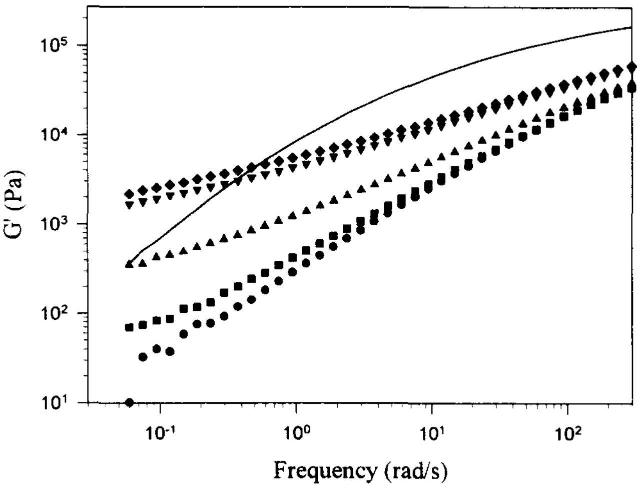

Figure 8 G' vs frequency for a series of PP-g-(GMA-S) samples prepared with increasing styrene concentration at 175°C and 5% strain. S : GMA molar ratio = ● 0.125, ■ 0.250, ▲ 0.50, ▼ 1.00, ◆ 1.50, and (—) PP

any further grafting reactions occurring in the system. There are two possible explanations for the discrepancy between the rheological data and the results of the Soxhlet extractions. One possible explanation could be that the PP degraded during the extractions by thermal heating, as the extractions were performed in air at high temperature and no stabilizer was added to the system. If β-scission of the PP molecules occurs between two S–S bridges, the number of effective network segments decreases, resulting in a less crosslinked material that is more readily dissolved.

The second explanation could be that the level of crosslinking was not severe enough to form an insoluble three-dimensional network. PP has been crosslinked, with gel contents as high as 90 wt%, in the presence of high levels of peroxides (up to 4 wt%) and polyfunctional monomers or other additives[5,6,14,15]. The concentration of initiator used in this grafting process was much lower than the levels used to achieve high amounts of gel material, 0.67 wt% in comparison to 4 wt%. Hence the crosslink density may have been too low, resulting in long chain branching rather than the formation of a three-dimensional, insoluble network. The effects of long chain branching on the rheological properties are similar to those of crosslinking, and it is difficult to separate the two contributions. However,the fact the PP-g-styrene copolymers exhibited increased elastic properties and molecular weight[10,11] implies that PP was crosslinked to some degree as the result of grafting.

Melt rheology of GMA–styrene modified PP

Only low levels of grafted of GMA (1.3 wt%) were achieved, even when high monomer and L 130 concentrations were used, 11.1 and 0.67 wt%, respectively. The addition of styrene to the PP-GMA system significantly enhanced the DG of GMA by providing a more stable macroradical for graft propagation. With the addition of an equimolar amount of styrene, the DG of GMA increased to 4.0 from 1.3 wt%. It is believed that the graft chains consist of both GMA and styrene units, as the reactivity ratios of styrene and GMA are approximately 0.29 and 0.78, respectively[35]. Sun *et al.*[12] not only observed an increase in the DG but also in the molecular weight of the graft modified PP copolymers with the addition of styrene. The retention in molecular weight was attributed to the higher reactivity of styrene, in comparison to GMA, towards the PP macroradicals, thus reducing the amount of β-scission by consuming more PP macroradicals for graft initiation. If this were the case, the rheological response of these polymers in the low frequency range would be similar to that of unmodified PP, but with G' and η' shifted to lower values as a consequence of β-scission. However, the addition of styrene was found to have a significant impact on the low frequency behaviour of these polymers, implying that the retention in molecular weight could have been partially due to crosslinking reactions.

The effect of increasing the level of styrene while keeping the GMA, PP, and L 130 concentrations constant on storage modulus vs frequency curves is shown in *Figure 8*. The DG of both GMA and styrene increased as progressively higher concentrations of styrene were added. The addition of styrene was found to have a pronounced effect on the rheological properties of the PP graft copolymers, resulting in an increase in the low frequency storage modulus that spanned almost 2 decades. As the styrene content was raised, the storage modulus not only increased, but there was also a significant decrease in the slope of the curve at low frequencies. At a styrene : GMA molar ratio of 0.5, there is a significant shift in the curves at low frequencies. As observed for the PP-g-S samples, this sudden increase in the storage modulus also corresponds to the point when G' and G'' crossed over at low frequencies.

To examine better the rheological behaviour of the styrene–GMA graft modified PP samples, another family of copolymers were prepared. In this study, the styrene, PP, and L 130 concentrations were kept constant while the amount of GMA added was varied. The DG of styrene decreased with the addition of GMA due to increased competition for the PP macroradicals[10,11]. The low frequency rheological properties were not significantly altered with increasing levels of GMA, as shown in *Figure 9*; the storage modulus only increased by a factor of ~ 2. The crossover of G' and G'' occurred at a GMA : styrene molar ratio of 0.25.

If the crosslinking of PP occurred only through the combination of 2 PP-S· macroradicals, it would be

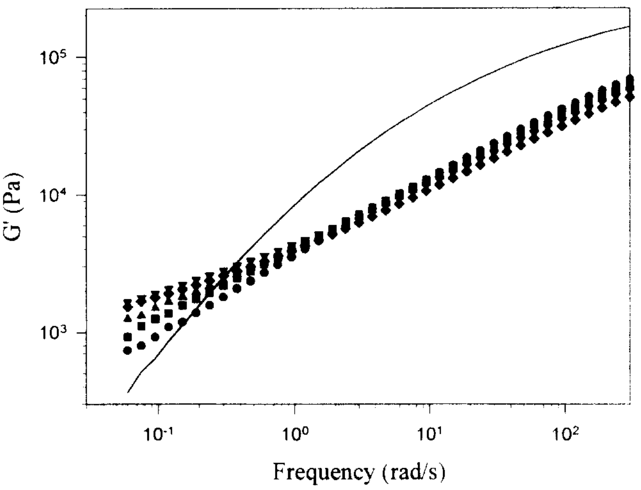

Figure 9 G' vs frequency for a series of PP-g-(GMA-S) samples prepared with increasing GMA concentration at 175°C and 5% strain. GMA:S molar ratio = ● 0.125, ■ 0.250, ▲ 0.50, ▼ 1.00, ◆ 1.50, and (—) PP

expected that the low frequency value of G' would decrease, and the slope would become steeper as more GMA was added. However, the storage modulus increased slightly and the slope decreased with increasing GMA concentration, indicating that the level of crosslinking did in fact increase. In the copolymerization of styrene and methyl methacrylate, termination occurs predominantly by cross-combination at 60°C[34]. It is not unreasonable to assume that termination of GMA and styrene would occur in a similar fashion. The results from the above study indicate that cross termination between graft chains was significant in the dual monomer system, and that the enhanced elastic properties observed for the PP-g-(GMA-S) were not solely dependent on styrene–styrene termination as the DG of styrene decreased when the concentration of GMA was raised. However, these results did reveal that the rheological properties were influenced more by the initial styrene concentration than the GMA concentration.

The retention of the molecular weight of the PP grafted copolymers reported by Sun *et al.*[12], with the addition of styrene, was in part due to the crosslinking of PP, as revealed by the rheological evaluation of the graft copolymers in this study. This point may also help to explain why there was such a pronounced decrease in the efficiency of these copolymers as blend compatibilizers, as reported by Chen *et al.*[9]. The accessibility of the epoxy groups was not only hindered by the presence of bulky phenyl rings, but also by the fact that they are most likely situated in a linkage that bridged two PP macromolecules.

CONCLUSIONS

Melt rheology has proven to be a valuable technique in detecting changes in molecular weight and structure resulting from secondary reactions that occur during the grafting process. The rheological properties of graft modified PP were greatly influenced by the type of initiator, concentration of initiator, concentration of monomer, and the use of comonomers. The grafting of GMA onto PP in the presence of peroxide initiators resulted in a significant amount of β-chain scission, which ultimately reduced the melt strength of the copolymer. The rheological properties of the GMA graft modified PP samples prepared with L 231 suggested that some crosslinking of PP during the grafting process had occurred, most likely due to epoxy ring opening reactions.

Polypropylene was crosslinked via graft modification with styrene using L 130 as the initiator. As the DG of styrene increased, the melt strength was enhanced, and the rheological properties of the samples began to approximate those of a crosslinked polymer. These trends were also apparent for the copolymers prepared with both GMA and styrene; therefore, it is possible to produce highly functionalized PP with good melt strength.

All the grafted samples prepared using styrene exhibited a transition in which G' and G'' crossed over at low frequencies. At a DG greater than 3 wt%, the PP-g-S samples were sufficiently crosslinked that the material behaved as though it were elastic, with G' greater than G'' over the frequency range tested. For the dual monomer system, the DG of styrene must be higher than 1 wt%, and the combined level of grafted material greater than 3 wt% for G' and G'' to cross over. Although rheologically these materials behaved as crosslinked polymers, they contained no gel material as determined by Soxhlet extraction with xylene.

Further work is required to determine if PP can be crosslinked to form an insoluble 3-dimensional network using a mixture of styrene and higher levels of peroxide. Also a more detailed analysis of the low frequency behaviour of these copolymers should be conducted to determine if a gel point can be detected using the model described throughout this paper.

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