

Reactive Extrusion of Polypropylene with Supercritical Carbon Dioxide: Free Radical Grafting of Maleic Anhydride

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ABSTRACT: A reactive extrusion process for the functionalization of polypropylene with maleic anhydride in the presence of supercritical carbon dioxide was studied. Supercritical carbon dioxide was used in this reactive extrusion system to reduce the viscosity of the polypropylene melt phase by forming a polymer–gas solution in order to promote better mixing of the reactants. Subsequently, the effect of supercritical carbon dioxide on the level of grafting, product homogeneity, and molecular weight was evaluated. Analysis of the products revealed that the use of supercritical carbon dioxide led to improved grafting when high

levels of maleic anhydride were used. The experimental results showed no evidence of an improvement in the homogeneity of the product, while melt flow rate measurements showed a reduction in the degradation of polypropylene during the grafting reaction when low levels of maleic anhydride were employed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1116–1122, 2003

Key words: reactive extrusion; polypropylene; maleic anhydride; supercritical carbon dioxide

INTRODUCTION

The history of graft modification of polypropylene (PP) with maleic anhydride dates back to the mid-1960s¹ when a method was developed for reacting maleic anhydride on particulate isotactic PP below its melting point. Since then studies have included the maleation of both isotactic and atactic polypropylene under a variety of conditions. The functionalization of polypropylene with maleic anhydride has been achieved in melt processes where the molten polymer is mixed with maleic anhydride and with an initiator, such as a suitable peroxide, either in an extruder or in an internal mixer at an elevated temperature. Alternatively, solution processes have been used, where the polymer is dissolved in a suitable solvent at an appropriate temperature and maleic anhydride is added with an initiator. Finally, the functionalization of polypropylene with maleic anhydride has been achieved by a solid phase graft copolymerization process.

Ide et al.² studied the grafting of PP with maleic anhydride in a xylene solution, using benzoyl peroxide as the initiator. Little evidence of degradation of the polymer product was found. Using a Brabender Plasticorder, the grafting reaction was successfully carried out, again in the presence of benzoyl perox-

ide.³ In this case, there was evidence of degradation of the polymer. Sasaki and Ide⁴ used an extruder to graft maleic anhydride onto PP and then used this maleated product as a compatibilizer in the glass-fiber reinforcement of polypropylene. It was shown that mechanical properties and heat resistance of glass-fiber reinforced polypropylene were remarkably improved by the grafting of a small amount of maleic anhydride.

The solid phase graft copolymerization of PP and maleic anhydride was investigated by Rengarajan et al.⁵ The effect of solvent type and amount, catalyst type and amount, and the effect of initiator concentration on the grafting achieved was investigated. They determined that all of these factors had a significant effect on the graft level of the polymer. Borsig and Hřčková⁶ later compared the level of functionalization of isotactic PP using the solid phase method and functionalization in solution. They found no significant differences in the grafting efficiency between the two methods. Isotactic PP was grafted with maleic anhydride in a solution process by Sathe et al.⁷ and the effects of monomer and initiator concentration, reaction time, and reaction temperature on percentage grafting were investigated. Borsig et al.⁸ also studied the reaction in solution but with atactic polypropylene. The focus was on the influence of the separate components of the reaction system on the degradation of the PP. It was concluded that the binding reaction of maleic anhydride onto polypropylene was followed by reactions, leading to degradation or reactions leading to an increase in molecular mass. The functionalization of isotactic PP with maleic anhydride in the

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melt phase was also studied by Gaylord and Mishra,⁹ and a mechanism for the reaction was proposed. Their reactions were carried out in a Brabender Plasticorder and their conclusions were that degradation of the polymer chain is, to a certain extent, a result of the disproportionation of polymer radicals generated by propagating maleic anhydride homopolymer or graft copolymer. Using *N,N*-dialkylamides, the homopolymerization of maleic anhydride was prevented and the polymer degradation was reduced. Ho et al.¹⁰ also studied the reaction in the melt phase, using an internal mixer and dicumyl peroxide as the initiator. Their focus was on the effect of maleic anhydride and dicumyl peroxide levels on the efficiency of the graft reaction and on the extent of the degradation. Regarding the grafting efficiency, the addition of maleic anhydride alone resulted in no grafting. Grafting only occurs in the presence of the peroxide. The optimal composition for their reaction system was at a low dicumyl peroxide level and moderate maleic anhydride level. With regard to degradation, using dicumyl peroxide alone, there was significant degradation of the polymer while chain scission was more extensive when a small amount of maleic anhydride was added. The trend was reversed when more maleic anhydride is added. This result was explained in terms of the competition between chain transfer/ β -scission and combination reactions.

Melt phase functionalization of polypropylene was performed in an extruder by Hogt.¹¹ The effect of maleic anhydride and peroxide catalyst concentrations on the amount of grafts and on the degradation was determined using a twin screw extruder. More grafting occurred when the initial concentrations of peroxide were increased, but the degradation was also increased with increased levels of peroxide. A higher level of grafting occurred with an increased initial concentration of maleic anhydride. Also, chain scission of polypropylene is suppressed at high initial concentrations of maleic anhydride. Callais and Kazmierczak^{12,13} studied the grafting of maleic anhydride onto polypropylene in a single screw extruder. Again, they studied the effects of various organic peroxides and found that the peroxides with the best grafting efficiencies were also the peroxides that had the greatest effect on melt flow. Lupersol 101 was chosen as the preferred peroxide for extruder grafting. Another study of the maleation of polypropylene in a twin screw extruder was completed by Kim and White.¹⁴ The purpose of their work was to study the influence of twin screw design on levels of conversion. Generally, they concluded that the use of kneading disk blocks increased the level of conversion in both corotating and counterrotating modes. In addition, the level of conversion is higher for the corotating machine for all screw configurations.

Heinen et al.¹⁵ used ¹³C-NMR in combination with specific labels in the maleic anhydride monomers to determine the locations of the grafts formed from the radically induced grafting of maleic anhydride onto high- and low-density polyethylenes, isotactic PP, and ethylene-propylene copolymers. This technique showed grafting does occur along the polymer chain. On the high- and low-density polyethylenes, the maleic anhydride was attached in the form of single succinic anhydride rings as well as short oligomers. On the copolymers and isotactic polypropylene, maleic anhydride grafts onto the polymer backbone mainly in the form of single succinic anhydride rings. They suggested that formation of oligomeric graft structures in maleated PP, as described by the mechanism proposed by Gaylord and Mishra,⁹ is of minor importance for high-temperature PP grafting. Furthermore, the presence of single anhydride rings attached to the polypropylene chain end, formed by the addition of maleic anhydride to secondary radicals produced by β -scission of polypropylene does not occur as previously suggested.⁹

Grafting reactions involving the use of free radical initiators, like peroxides, are generally very fast, and the distribution and mixing of the peroxide into the polymer melt is very crucial. It is desirable to optimize the use of peroxide and increase its efficiency, which is limited due to the well-known "cage" effect in free radical reactions. Diffusivities of free radicals under supercritical fluid conditions are typically an order of magnitude greater than in liquids at comparable temperatures.¹⁶ Thus, free radicals under supercritical conditions are able to escape more readily from solvent cages resulting in increased initiation processes. Enhanced initiator diffusion rates will alter the relative reaction and diffusion characteristic time scales for a given initial striation thickness, and therefore will affect mixing and product distribution.¹⁷ For example, it has been theoretically shown that enhanced diffusion may improve product homogeneity in polypropylene degradation operations.¹⁸ One way to improve diffusion of peroxide initiators in polymers could be through the use of supercritical fluids to facilitate reactions in dense polymer melts. Supercritical fluids are used for a variety of applications in polymer processing; particularly, carbon dioxide offers a number of advantages in processing, due to its low toxicity, chemical inertness, and noncombustibility.¹⁹ In the supercritical state, carbon dioxide demonstrates characteristics intermediate between those of liquids and gases having liquid-like high density, giving it good solvating power, yet it has a low viscosity, lack of surface tension, and high diffusivity, providing it with excellent penetrating and mixing power.²⁰ Addition of supercritical carbon dioxide into polymers has been known to lead to significant viscosity reduction,²¹⁻²³ while its effect on polymer blend morphology has been recently evaluated.^{24,25}

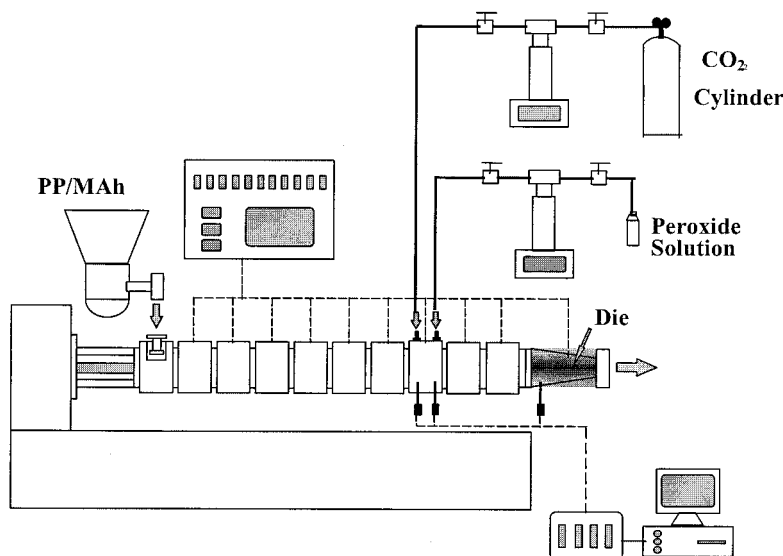


Figure 1 Schematic diagram of the supercritical reactive extrusion system.

The objective of this work was to explore the use of supercritical CO_2 in a reactive extrusion process for the peroxide-initiated functionalization of polypropylene with maleic anhydride. The effect of supercritical CO_2 on the reaction was evaluated, primarily based on the level of grafting achieved, the homogeneity of the product, and the extent of degradation of the grafted material.

EXPERIMENTAL

Materials

The polypropylene used was a high molecular weight isotactic polypropylene (KF6100) supplied in pellet form by Montell Canada (melt flow rate of 3 g/10 min, ASTM D-1238 condition L). Maleic anhydride was supplied by Monsanto in briquette form. The peroxide used in the grafting experiments was Lupersol 101 [2,5-dimethyl-2,5-di-(vol.273, -butylperoxy)hexane], obtained from Elf Atochem. The peroxide was diluted to a 10 wt % solution in acetone. The carbon dioxide (SCF grade) was obtained from Air Products Canada Ltd. It was supplied with a purity of 99.997% and an initial cylinder pressure of about 1900 psi. The cylinder was supplied with a high-pressure helium headspace that helped maintain the high pressure.

Equipment and procedures

The grafting experiments were performed in a corotating intermeshing Leistritz, LSM 30.34 twin screw extruder. First, molten maleic anhydride (Mah) was pumped through a syringe pump and compounded with PP to produce a master batch (6 wt % Mah) that was used in all grafting experiments. In these grafting experiments, the

PP stream flow rate was 80 g/min and the screw speed was 60 rpm. Two levels of maleic anhydride (2 and 4 wt %) and four levels of CO_2 (0, 2, 3, and 4 wt %) were used while the peroxide concentration was kept constant at 2000 ppm. A schematic diagram of the process is shown in Figure 1, illustrating the injection locations of the CO_2 and peroxide streams. A two-strand die was used on the twin screw extruder and the strands were pelletized using a Berlyn pelletizer. During the reaction, melt pressure was measured at three locations, two in the barrel and one in the die as shown in Figure 1, and data were recorded through an Optomux interface (OPTO-22 A/D converter with AC422 serial link).

Determination of grafted maleic anhydride content

The samples collected were first purified to remove the free maleic anhydride. Originally, a previously employed method^{9,12,13} was used. According to this method, samples were dissolved in boiling toluene, or xylene, followed by precipitation in acetone, and subsequent drying in an oven. The purification of the grafted samples using this extraction method was proving to be very time-consuming and costly with all the solvents that had to be used. Therefore, another method¹¹ for removal of the free maleic anhydride was eventually used. According to this method, the sample pellets were purified by being placed in a vacuum oven at 120°C for 24 h. To ensure that all unreacted maleic anhydride, in fact, would be eliminated, a sample of the 6 wt % maleic anhydride/polypropylene master batch material was purified by this method. A Fourier transform infrared (FTIR) spectrum of the sample showed no sign of maleic anhydride after it was purified. FTIR spectroscopy was

TABLE I
FTIR Peak Height Averages and Variances

Run	CO ₂ added (wt %)	MAh added (wt %)	Relative peak height average	Relative peak height variance	Overall average	Overall variance
81	2	2	2.090	1.51×10^{-3}		
82	2	2	2.218	3.85×10^{-3}		
83	2	2	2.383	6.10×10^{-4}		
88	2	2	2.468	5.27×10^{-3}		
89	2	2	2.714	4.89×10^{-3}	2.378	4.59×10^{-2}
84	3	2	2.336	2.37×10^{-3}		
85	3	2	2.541	6.48×10^{-3}		
90	3	2	2.661	1.28×10^{-4}		
91	3	2	2.824	2.15×10^{-3}		
92	3	2	2.688	2.78×10^{-3}	2.610	3.36×10^{-2}
86	4	2	2.759	6.86×10^{-4}		
87	4	2	2.489	6.65×10^{-3}		
93	4	2	2.589	4.77×10^{-3}		
94	4	2	2.805	2.02×10^{-3}		
95	4	2	2.632	3.41×10^{-3}	2.655	1.64×10^{-2}
116	0	2	2.905	2.77×10^{-3}		
117	0	2	3.081	5.90×10^{-3}		
118	0	2	3.354	1.91×10^{-2}		
119	0	2	3.149	7.37×10^{-3}		
120	0	2	3.388	8.75×10^{-3}	3.175	4.00×10^{-2}
96	2	4	3.094	1.70×10^{-4}		
97	2	4	3.059	5.28×10^{-3}		
103	2	4	3.184	2.23×10^{-3}		
104	2	4	3.092	1.23×10^{-2}		
105	2	4	2.919	2.69×10^{-2}	3.070	9.24×10^{-3}
98	3	4	3.592	3.9×10^{-3}		
99	3	4	3.400	1.67×10^{-3}		
106	3	4	3.669	5.50×10^{-3}		
107	3	4	2.961	8.66×10^{-4}		
108	3	4	3.473	1.74×10^{-3}	3.419	7.64×10^{-2}
100	4	4	3.041	4.97×10^{-2}		
101	4	4	4.000	1.74×10^{-2}		
102	4	4	3.198	2.04×10^{-3}		
109	4	4	3.829	2.29×10^{-2}		
110	4	4	3.329	2.22×10^{-3}	3.479	1.72×10^{-1}
111	0	4	2.699	1.91×10^{-3}		
112	0	4	2.837	2.33×10^{-3}		
113	0	4	2.942	4.36×10^{-3}		
114	0	4	3.466	7.45×10^{-4}		
115	0	4	3.304	1.35×10^{-3}	3.050	1.04×10^{-1}

used to determine the relative amount of maleic anhydride grafted to the polypropylene. Films were prepared for FTIR by compression molding between two Teflon sheets using a hot press. Each sample was pressed at a temperature of 215°C and at a pressure of 7000 psi for 15 s after melting at this temperature for 5 min under no load. Sample film thickness ranged between 0.3 and 0.5 mm. Using the FTIR spectrometer, the spectra were recorded from 4000 to 400 cm⁻¹ and the grafting amount was determined by monitoring the band at 1785 cm⁻¹ (due to mechanical coupling of carbonyl vibrations within the anhydride).²⁵ Relative peak heights of the anhydride located at 1785 cm⁻¹ were calculated using a peak at 459 cm⁻¹ as an internal reference. This internal reference peak is due to polymer backbone triple carbon bending.

A titration method was used to develop a calibration curve for determining the absolute maleic anhydride content from the relative peak heights obtained from FTIR analysis of the product. The samples were placed in a vacuum oven overnight to remove the volatiles. Each sample was then pressed into a film using the hot press, in the same manner as mentioned above. The films were analyzed by FTIR spectroscopy and then dissolved in a xylene-butanol solution for the titration. The samples were titrated with a potassium hydroxide solution using 1% thymol blue in *N,N*-dimethylformamide as indicator.

Melt flow rate testing

The melt flow rate (MFR) of a select number of samples was tested to determine if the inclusion of CO₂ in

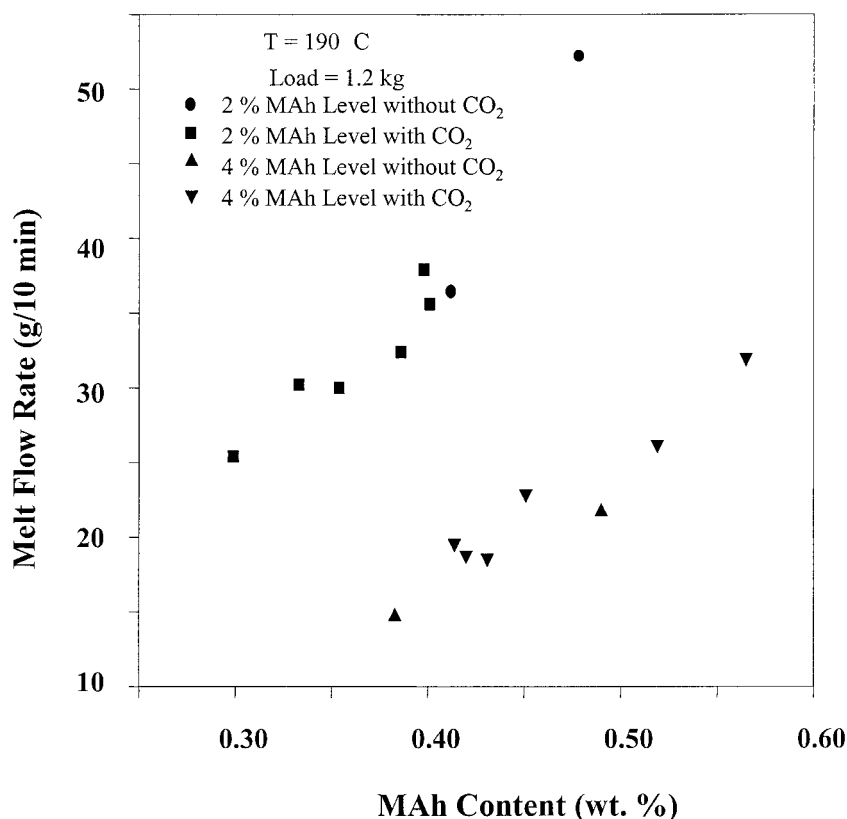


Figure 2 Relationship between melt flow rate and amount of grafted MAh. Effects of supercritical CO₂ and MAh feed level (2 and 4 wt %).

the reacting system had an effect on the molecular weight of the final polymer product. The MFR measurements were carried out using a Kayeness Galaxy V capillary rheometer. Due to the low viscosity of the samples, the MFR could not be measured in accordance with the standard ASTM D1238 test method. Instead, a lower temperature of 190°C and a smaller load of 1.20 kg had to be used. The test was repeated four times for each sample.

RESULTS AND DISCUSSION

Experimental results from randomized runs are listed in Table I. Each line represents a separate extrusion experiment and each block (e.g., 81–89) represents five experimental runs repeated at the same conditions. In terms of FTIR product analysis, three samples were analyzed from each product run, and two films were pressed for each sample, thus resulting in six measurements per run. The sample averages from each run, sample variance, overall average relative peak height for the runs performed at the same reaction conditions, and the run variance were calculated, and the results are given in Table I. The sample variance and overall variance in the relative peak heights for each set of reaction conditions performed were all of the same order of magnitude, indicating that CO₂ did not have an effect on the homogeneity of the product.

Comparing the overall average relative peak height results at each level of CO₂ used with the CO₂-free results at the 2 wt % level of maleic anhydride used

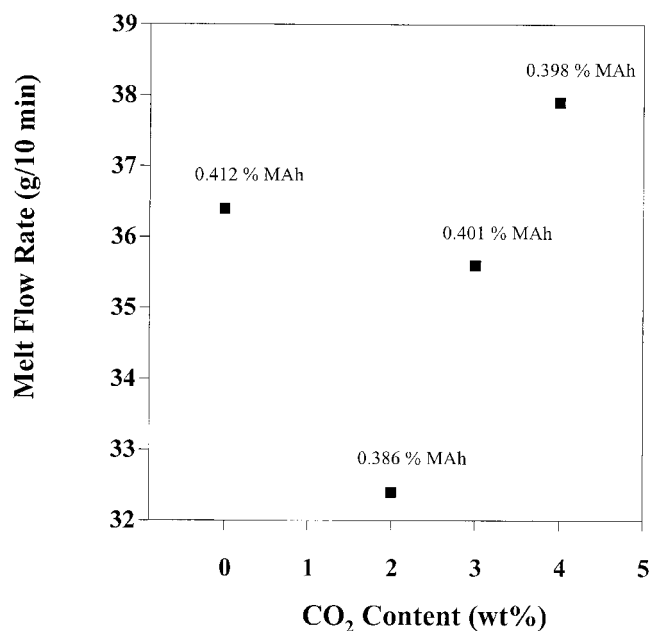


Figure 3 Effect of supercritical CO₂ on the melt flow rate using a 2 wt % MAh feed. Numbers next to the data points represent the amount of grafted MAh.

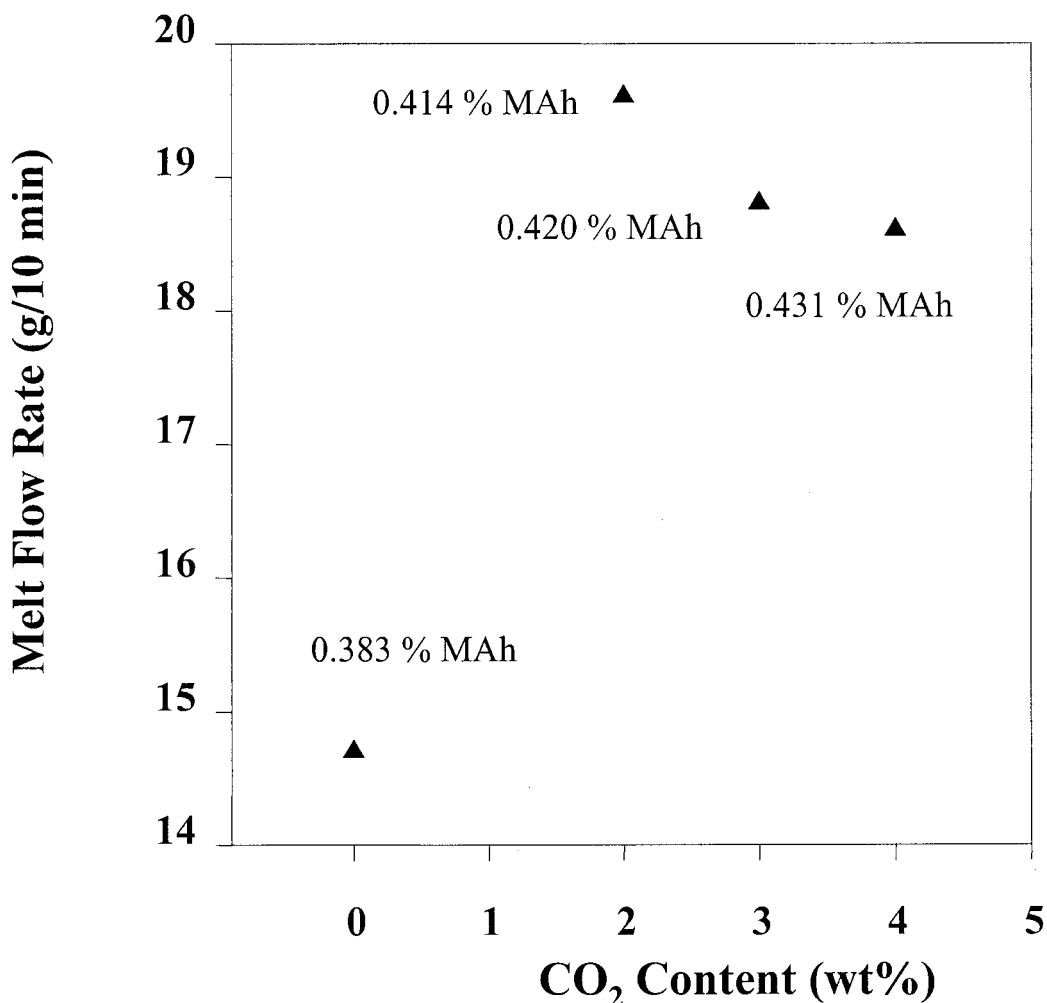


Figure 4 Effect of supercritical CO₂ on the melt flow rate using a 4 wt % MAh feed. Numbers next to the data points represent the amount of grafted MAh.

indicated that the use of CO₂ negatively affected the grafting level. The difference in the overall average relative peak heights between the CO₂-free runs and each of the CO₂ runs was significant based on a 5% significance level. At the 4 wt % maleic anhydride level, there was no significant improvement in the overall relative peak height averages with the use of 2 and 4 wt % CO₂, but there was an improvement in the level of grafting with the use of 3 wt % CO₂, based on a 5% significance level.

The relative peak heights were only useful for making relative comparisons. A calibration curve had to be developed to relate the relative peak heights obtained from the FTIR analysis to the actual maleic anhydride content. The method is outlined in the experimental section. The calibration curve developed was

$$\text{wt \% MAh} = 0.139 \left(\frac{\text{Relative Peak Height}}{\text{Peak Height}} \right) + 0.007$$

Using this expression, the wt % grafted maleic anhydride levels for the samples obtained were determined.

The use of peroxide as one of the reactants resulted in degradation of the PP chain. The polymer product, therefore, had a lower molecular weight and its viscosity was drastically reduced from that of the unreacted PP polymer. Figure 2 is a plot of melt flow rate vs maleic anhydride content. It should be pointed out that the level of MAh grafting was very small and therefore its effect on MFR through free volume changes would be negligible in comparison to the effect of chain scission on MFR. The data plotted in Figure 2 clearly show a distinction between samples produced using 2 wt % maleic anhydride and those produced using 4 wt % maleic anhydride. The samples produced with less maleic anhydride in the feed had a higher melt flow rate—therefore, a lower molecular weight. There has been more degradation of the polymer chain when less maleic anhydride was

used in agreement with other literature reports. Figure 2 also indicates that, for each maleic anhydride level, the samples with a higher grafted maleic anhydride content had experienced more degradation as indicated by their higher melt flow rate. The degradation may be less when less maleic anhydride molecules were being consumed by the grafting reaction and were able to act as chain transfer agents, attaching to the radicals before the radicals could attack the polymer chain. This would suppress the chain scission reactions caused by the peroxide radicals. More degradation occurs when more of the maleic anhydride molecules are being consumed in the grafting reaction and there are less available to suppress the chain scission reactions. Figures 3 and 4 are plots of melt flow rate vs the level of CO₂ used in the production of the grafted material at the 2 and 4 wt % feed levels of maleic anhydride, respectively. Indicated on the plots, next to each data point, is the grafted maleic anhydride content of the sample. Figure 3 shows an increase in the melt flow rate, hence, a decrease in molecular weight, with an increase in the level of CO₂ used, with the exception of the case where no CO₂ is used. The sample from the CO₂-free run had a higher melt flow rate than the 2 and 3 wt % CO₂ cases. At the lower level of maleic anhydride used, therefore, there was a reduction in the amount of degradation that occurred with the use of either 2 or 3 wt % CO₂. Using the higher level of maleic anhydride, Figure 4 shows a slight decrease in the amount of degradation with an increase in the CO₂ level used for the samples produced with CO₂. The sample from the CO₂-free run had the lowest melt flow rate and, therefore, had the higher molecular weight. It should be noted, however, that it was also the sample with the lowest maleic anhydride content, which would explain its low melt flow rate.

CONCLUSION

The results of the present study indicate that the use of supercritical CO₂ during free radical grafting of maleic anhydride onto PP in an extruder had the following effects on the functionalized PP properties:

1. No significant improvement of product homogeneity was observed due to the supercritical CO₂ presence.

2. An improvement in the level of grafting was observed when high levels of maleic anhydride were fed to the extruder in the presence of CO₂.
3. When lower levels of maleic anhydride were fed to the extruder, a reduction in the amount of degradation was observed with the use of either 2 or 3 wt % CO₂.

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