

# Polypropylene–Phenol Formaldehyde-Based Compatibilizers. I. Preparation and Characterization

K. LARSON BØRVE,<sup>1</sup> H. K. KOTLAR,<sup>2</sup> C.-G. GUSTAFSON<sup>1</sup>

<sup>1</sup> The Norwegian Institute of Science and Technology, Department of Machine Design and Materials Technology, N-7034 Trondheim, Norway

<sup>2</sup> Statoil Research Centre, N-7005 Trondheim, Norway

Received 14 July 1997; accepted 1 October 1997

**ABSTRACT:** This work deals with the synthesis of a new type of compatibilizer suitable for blends or alloys of polypropylene and engineering polymers having aromatic residues or functionality complementary to hydroxyl. Polypropylene–phenol formaldehyde graft copolymers from thermoplastic phenol formaldehyde (PF) resins and functionalized polypropylene (f-PP) were synthesized by reactive extrusion. The content of PF in the graft copolymer was determined by reaction variables like type and density of functionality on PP, molecular weight of PF, and viscosity ratio of f-PP and PF. The results showed that the viscosity ratio is of primary importance for such reactive processing. Also, type and concentration of the functional groups were important variables. The glycidyl methacrylate functionality resulted in higher conversions than did PP-g-maleic anhydride within the available reaction times. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 347–354, 2000

**Key words:** Polypropylene compatibilizers; Phenol Formaldehyde resins; Polypropylene blends; PP-g-Maleic anhydride, PP-g-glycidyl methacrylate; Reactive extrusion

## INTRODUCTION

The field of polymer blends and alloys is growing both industrially and academically. The combination of two or more commercially available polymers through alloying or blending represents an inexpensive route for tailoring of a polymer compound. However, most polymers are immiscible or insoluble in each other due to the very low entropy of mixing for macromolecules. One important way of overcoming this immiscibility and to control the blend morphology is through the use

of compatibilizers. Compatibilizers are often block or graft copolymers that act as interfacial agents in polymer blends.<sup>1–7</sup> The chemical structures of these copolymers are such that one part is miscible with one blend component (polymer 1), and the other part, with the other (polymer 2). Usually, the blocks of the compatibilizer are either identical with the blend components or contain functional groups complementary to the functionality of the components. The compatibilizer is therefore found at the interface between polymer 1 and polymer 2.

The presence of a compatibilizer at the interface will affect both the interfacial adhesion and the interfacial tension,  $\gamma$ .<sup>3,6,7</sup> The former will increase, and the latter, decrease, with addition of a compatibilizer. The domain size of the dispersed polymer phase will reach a certain finite, equilibrium level, as the compatibilizer incorporation

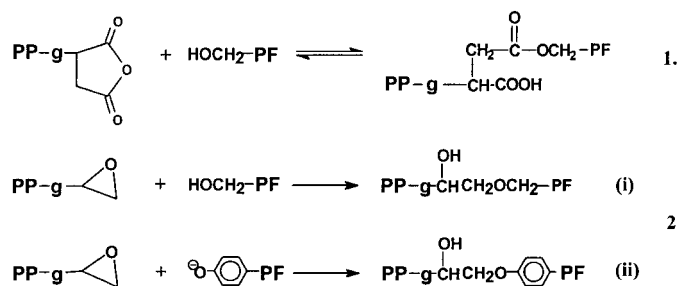
Correspondence to: K. L. Børve, Borealis AS, Department of Polymer Development, Rønningen, N-3960 Stathelle, Norway.

Contract grant sponsors: Norwegian Research Council (NFR); Borealis AS, Bamble.

*Journal of Applied Polymer Science*, Vol. 75, 347–354 (2000)

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CCC 0021-8995/00/030347-08



Scheme 1

increases. However, smaller domain size can also be achieved without considerable reduction of  $\gamma$  by high-energy input, such as very intensive mixing.<sup>5,7–10</sup> A well-compatibilized system results in better than additive improvement in the physical properties such as impact strength and tensile strength.<sup>9–12</sup>

The compatibility of polypropylene (PP) to most polymers is poor due to the lack of polar/functional groups, and blending of PP with other polymers will require addition of a suitable compatibilizer. To prepare a copolymer compatible with PP and engineering polymers like poly(butylene terephthalate) (PBT) and poly(phenylene ether) (PPE), a phenol-like repeating unit as the polar part of the graft copolymer is expected to work. The thermoplastic phenol formaldehyde (PF) resins are characterized by their capability to form hydrogen bonds with polymers containing carbonyl or carbonate groups<sup>13</sup> or by formation of covalent bonding if the polymer contains complementary groups to hydroxyl. In addition, the phenyl ring structure of phenolic resins is capable of forming secondary bonding to specific engineering polymers, by  $\pi$ - $\pi$  overlap.

In this article, the synthesis and characterization of PP-*graft*-PF polymers are demonstrated. For this synthesis, only high molecular weight PF novolaks (thermoplastic) were considered to meet the viscosity ratio ( $\lambda$ ) requirement for best mixing.<sup>14,15</sup> Special lab grades of thermoplastic PF resins and functionalized polypropylene (f-PP) were used.

The PP-*g*-PF compatibilizer is synthesized from maleic anhydride (MAH) and glycidyl methacrylate (GMA) f-PP according to Scheme 1, where the first reaction (1) indicates the first step in the esterification reaction between PF-OH and PP-*g*-MAH. The second step, the reaction between the remaining carboxylic groups on MAH, is less favored due to steric hindrance. The second reac-

tion indicates that the reaction between PF-OH and PP-*g*-GMA may be conducted by the reaction of the PF-methylol groups or by the phenolic OH. The latter reaction will only take place in the presence of catalysts, like strong bases (e.g., KOH).<sup>16,17</sup>

The present study was aimed at understanding the relationship between the nature of the reactants (f-PP, PF) and the resulting PP-*g*-PF copolymer. In particular, reactive processing of reactants having a different density of functional groups and viscosity ratios were investigated.

## EXPERIMENTAL

### Materials

Four MAH-functionalized materials with low/high MAH content and low/high viscosity provided the polymers and were synthesized by free-radical grafting. The synthesis was conducted by radical-initiated grafting in the molten state. The high functionality grades were synthesized using a styrene comonomer to enhance the MAH content and control the molecular weight. In these grades, a blend of PE/PP (20/80) was also used. One commercially available PP-*g*-MAH with high functionality and low molecular weight (MAH\_VHF) was also evaluated (Eastman Epolene E-43; Eastman Chemical Company, Kingsport, TN).

Three GMA grades were synthesized with low GMA content and low/high viscosity. The synthesis was conducted according to Kotlar and Hansen<sup>18</sup> and Kotlar.<sup>19,20</sup> In addition, two high functionality grades (GMA\_HFLV, GMA\_VHF) were synthesized using styrene comonomer technology and PE/PP (20/80) as the base polymer.<sup>21</sup>

The functionality contents of MAH and GMA were determined by FTIR and titration methods.<sup>19,20</sup> Functionality distributions of the f-PPs

**Table I** Functionalized PP Grades

Functionality	Grade <sup>a</sup>	MFI (g/10 min)	$X_{\text{total}}$ (wt %) <sup>b</sup>	$X_b$ (wt %) <sup>c</sup>
MAH	MAH_LFLV	14	0.5	0.4
MAH	MAH_HFLV <sup>d</sup>	62	2.4	2.1
MAH	MAH_LFHV	11	0.5	0.4
MAH	MAH_HFHV <sup>d</sup>	45	2.1	1.9
MAH	MAH_VHF	—	6.0	3.2
GMA	GMA_LFLV	20	0.3	0.3
GMA	GMA_HFLV <sup>d</sup>	40	2.2	1.8
GMA	GMA_LFHV	14	0.3	0.2
GMA	GMA_VHF <sup>d</sup>	—	3.1	2.5

<sup>a</sup> After the functionality-type description, MAH\_LFLV, where LFLV means Low Functionality/Low Viscosity and so on.

<sup>b</sup> Total functionality content; MAH determined by titration (ICI method), and GMA, by FTIR.

<sup>c</sup> Bound functionality after vacuum drying.

<sup>d</sup> Styrene assisted grafting onto PE/PP blend (20/80).

were determined by combined GPC and FTIR analysis. The results showed that the MAH and GMA functionalities were randomly grafted onto the PP or PE/PP phase and not fractions of high functionality mixed with ungrafted regions. Some properties of the functionalized PP grades are listed in Table I.

The PF polymers used in this study were experimental grades from our own laboratory.<sup>22</sup> Two grades were selected: KLB.002 ( $M_w$  27,550,  $M_n$  3520 g/mol) and KLB.018 ( $M_w$  6300,  $M_n$  890 g/mol). The f-PP and PH polymers were vacuum-dried at 100°C for 12 h before compounding to remove residual monomers and traces of water.

### Synthesis

The preparation of the PP-PF graft copolymers were conducted in a 25-mm Cleextral BC 21 intermeshing corotating twin-screw extruder (TSE) with an  $L/D$  of 44. The extruder screw profile was configured to allow good melting of the polymers followed by efficient mixing and high shear, high residence time in the reaction zone, and venting close to the outlet of the extruder. Neutral, 90°, kneading blocks followed by backmixing screw elements were located after 10  $L/D$  and 25  $L/D$ . The remaining elements of the screw profile were semipitch conveying elements.

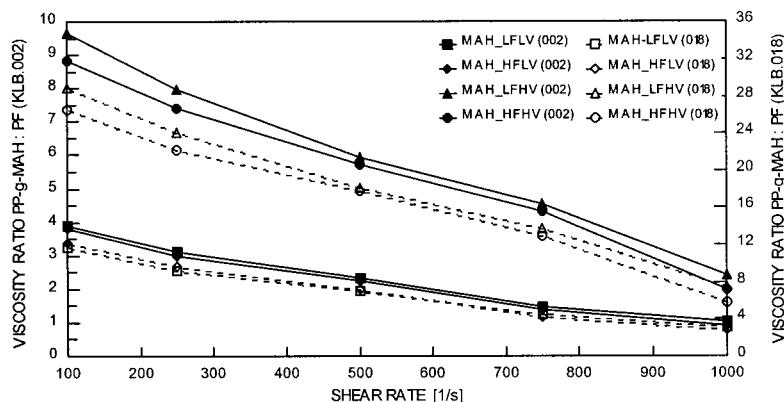
f-PP was fed in barrel 1, and PF resin, in barrel 2, at a total throughput of 3 kg/h. The screw rotation speed was 200 rpm, and the barrel set temperature, 190–195°C, as a flat temperature profile. Average residence time at these conditions was 2.5 min. The extruder was equipped with highly efficient vacuum venting to remove

unreacted species and reaction byproducts. An inert atmosphere was used to reduce polymer degradation. The extrudate was immediately quenched in a water bath and then pelletized. The extruder was equipped with K'tron T20 feeders and a loss-in-weight feeding system for accurate feeding of the raw materials.

### Characterization

The reactants were determined by rheology, chromatography (GPC), spectroscopy (FTIR and NMR), and titration techniques for evaluation of molecular structure and functionality. A systematic characterization of the blends was undertaken by thorough selective extraction followed by sample preparation and spectroscopic analysis. IR analysis was performed on a Perkin-Elmer 1725× FTIR instrument using transillumination, ATR total reflection, or reflection techniques.

The extraction method and solvent were adapted to this specific polymer system, and according to the solubility test of neat polymers, acetone was a selective solvent for the PF polymers. Sufficient extraction time was 48 h on pellets followed by 48 h on film. The film was then repressed for FTIR analysis. Both extracted and nonextracted samples were analyzed. Materials (film) were predried before FTIR analysis at 100°C for 2 h. The films used in this study were sufficiently thin to be within an absorbance range where the Beer-Lambert law is obeyed (<0.6 absorbance units). Polymer films were made using a Pasadena hydraulic press and a distance frame of 0.1 mm.



**Figure 1** Viscosity ratio of PP-*g*-MAH and PF as a function of shear rate. KLB.002 has filled symbols and is plotted on the left axes.

For quantitative analysis of the amount of the reacted PF polymer, data were obtained from the FTIR spectrum of the extracted samples, using the peak height ratio of the C=C peak (ring stretch) at  $1610\text{ cm}^{-1}$  to that for the C—H peak (bend) at  $973\text{ cm}^{-1}$ , and controlled by a corresponding peak height ratio of C=C peak (ring stretch) at  $1641\text{ cm}^{-1}$  to that for the C—H peak (bend) at  $899\text{ cm}^{-1}$ . These ratios were used as a measure for the relative content of PF in the graft copolymer. Calibration for routine FTIR determination of the absolute content of PF was obtained from the corresponding analysis of nonextracted samples. Since PF is a rather high molecular weight species, the content of PF in the samples prior to extraction was assumed to be equal to the feeding content.

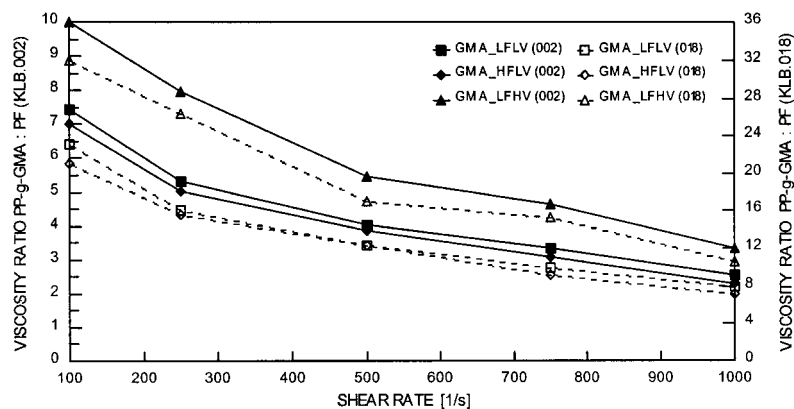
$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectroscopy for characterization of the synthesized PF resins were conducted on a Bruker 500 MHz instrument. The

samples were analyzed using a Bohlin CSM rheometer equipped with 25-mm parallel plates and 1-mm gap setting. The rheometer was modified to reduce polymer degradation during analysis by applying a nitrogen gas blanket outside the analysis cell.

## RESULTS AND DISCUSSION

### Viscosities of Component Polymers

The melt viscosity ratios as a function of shear rate for PP-*g*-MAH and PF and for PP-*g*-GMA and PF are shown in Figures 1 and 2, respectively. Since the measuring temperature was the same as the extrusion temperature,  $190^\circ\text{C}$ , the measured viscosity ratios indicate the ratio that dominated under the processing conditions. Typical shear rates during reactive extrusion were  $10^2$ –



**Figure 2** Viscosity ratio of PP-*g*-GMA and PF as a function of shear rate. KLB.002 has filled symbols and is plotted on the left axes.

$10^3 \text{ s}^{-1}$ .<sup>23</sup> In Figure 1, the viscosity ratios between PP-g-MAH grades toward the high molecular PF, KLB.002, are plotted on the left axis and, similarly, toward a low molecular weight PF on the right. The effect of shear on the viscosity ratio was much more noticeable for the high-viscosity PP-g-MAH ratios than for the low-viscosity grades. Similar, but less pronounced, effects were also observed for the PP-g-GMA grades in Figure 2. Due to difficulties of the determination of exact processing shear rates, a shear rate of  $500 \text{ s}^{-1}$  was selected for further consideration of the results. This value was assumed to best describe the average shear rate for a TSE equipped with various conveying, neutral kneading blocks, and gear-mixing elements.

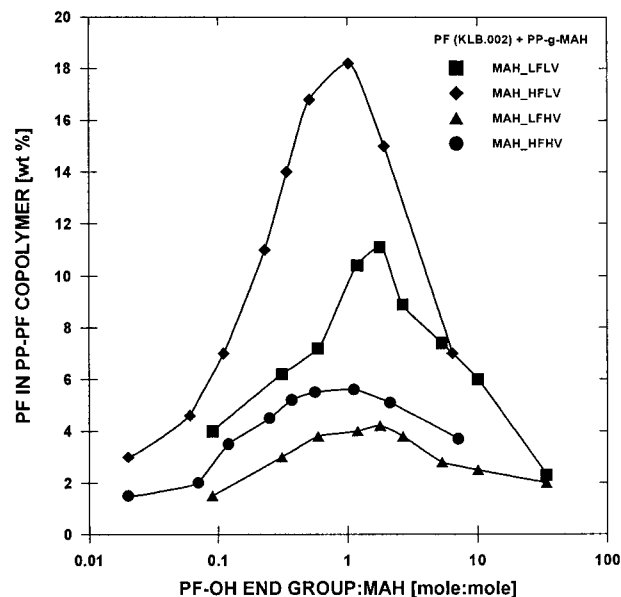
### Synthesis of PP-PF Graft Copolymers

PP-PF graft copolymers were synthesized by reaction in the molten stage using a TSE.

#### Effect of Component Ratios for PP-g-MAH

The PF contents in the formed PP-PF graft copolymers (PP-g-PF) were determined using selective extraction, to remove unreacted PF followed by FTIR. The efficiency of the extraction was checked by a control sample based on unmodified PP and 10 wt % PF. The extraction method removed all PF resin, as determined by FTIR. In Figure 3, the PF content (in wt %) is plotted as a function of calculated starting mol ratio of the PF end-group to MAH for a high-viscosity PF grade. Four PP-g-MAH grades with different molecular weights and contents of the functionality were studied. All trials were conducted at exactly the same conditions to be able to isolate the effect of the polymer system variables, even if the esterification reaction had not reached an equilibrium stage. However, earlier results showed that the reaction is close to equilibrium after 2.5 min of reaction time.<sup>24</sup>

From the figure, it can be seen that the favored ratio of PF end-groups to MAH was close to 1 for obtaining the highest PF content in the final copolymer. Lower or higher ratios resulted in lower efficiency for all four PP-g-MAH grades. The figure also indicates the effect of functionality density and viscosity ratio for such a reaction between end-hydroxyl groups and MAH f-PP. The optimum PP-g-MAH grade resulted in about 18 wt % PF in the copolymer and was characterized by low viscosity and high functionality, MAH\_H-

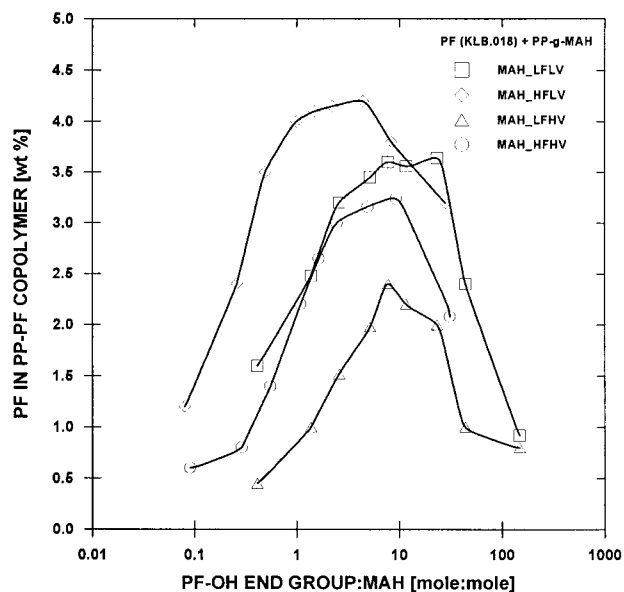


**Figure 3** PF content (wt %) in PP-PF graft copolymer from the reaction of PP-g-MAH and PF grade, KLB.002.

FLV. The low viscosity in this case gave close to an ideal viscosity ratio within the range of extrusion shear rates, giving excellent dispersive and distributive mixing of the two polymers. The high MAH concentration means that the reaction can take place in a less “diluted” system, with higher density of reactive sites and, therefore, higher probability of reaction. The resulting graft copolymer in this case was also assumed to be a more efficient compatibilizer for specific polymers due to the high concentration of PF molecules onto the PP backbone.

The second best combination was obtained from the low functionality and viscosity grade, MAH\_LFLV. An upper content of about 11 wt % PF was achieved in this case at a 1 : 1 functional group ratio. The high-viscosity grades, MAH\_LFHV and MAH\_HFHV, were much less efficient compared to the two first PP-g-MAH grades. Curves for these grades were also much broader over a broader range of functional group ratios.

Similar curves for the low-viscosity PF grade coded KLB.018 are shown in Figure 4. For all four PP-g-MAH grades, the viscosity ratios at the processing conditions are 4 or higher (Fig. 1), giving far from ideal conditions for mixing. The overall PF content in the resulting PP-PF graft copolymer was much lower in this system. It is also interesting to note that the maximum PF content was not obtained at a 1 : 1 functional group ratio



**Figure 4** PF content (wt %) in PP-PF graft copolymer from the reaction of PP-g-MAH and PF grade, KLB.018.

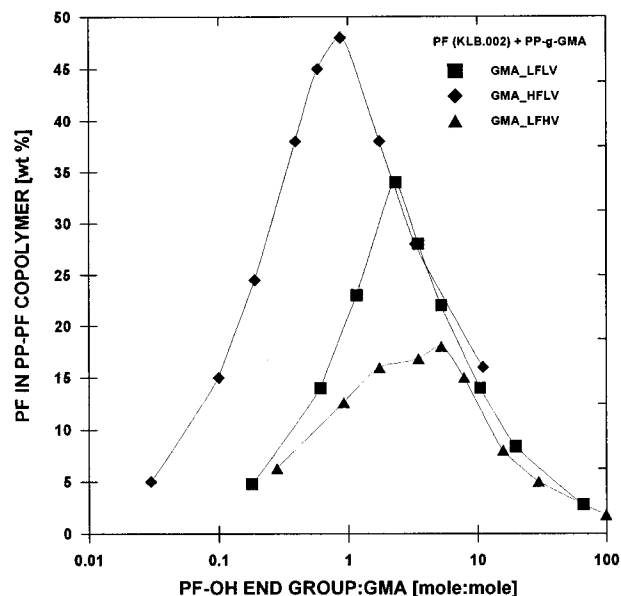
any longer, but between 5 : 1 and 10 : 1 (PF-OH end-group : MAH). The reason for this might be that some of the PF was never in contact with the f-PP due to the great difference in viscosities. Some of the PF may have functioned as a lubricant and was located at the polymer/extruder barrel interphase. This is verified by earlier experiments conducted in a Brabender mixer, where considerable difficulty of mixing these PP-g-MAH grades with the KLB.018 was observed.

Again, the low-viscosity and high-functionality grade, MAH\_HFLV, was the most efficient system, giving a PF content of 4.2 wt %. But, the PF levels for the other PP-g-MAH grades are not very different. With the least efficient grade, MAH\_LFHV, a PF content of about 2.5 wt % was obtained.

#### Effect of Component Ratios for PP-g-GMA

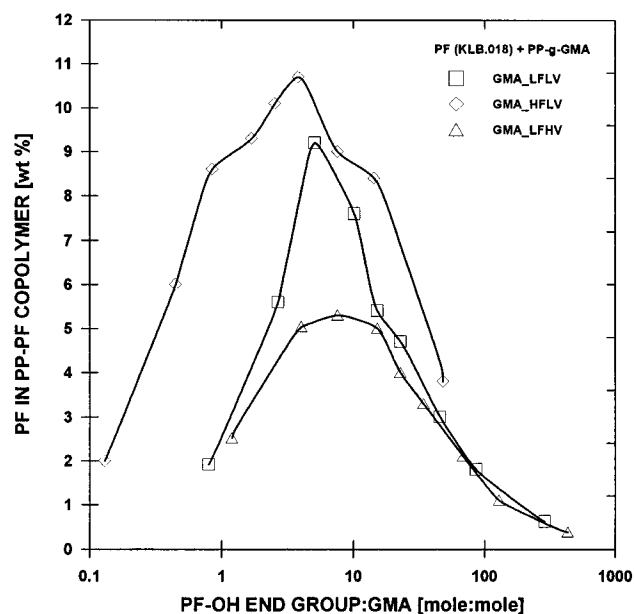
In Figures 5 and 6, similar curves are shown for GMA f-PP (PP-g-GMA). In these reactions, no base catalyst was added and the reactions were assumed to follow the first proposed mechanism for epoxides in this article. All experiments were conducted at the same conditions, which were equal to that for PP-g-MAH.

The three curves in Figure 5 show the reaction between PP-g-GMA and the high-viscosity PF, KLB.002. The curves indicate that the PF content was much higher in this case than that for MAH.



**Figure 5** PF content (wt %) in PP-PF graft copolymer from the reaction of PP-g-GMA and PF grade, KLB.002.

As also observed for PP-g-MAH/KLB.002, the maximum PF was at around a 1 : 1 functional group ratio. However, the trend was not as consistent for all three PP-g-GMA cases as for PP-g-MAH. The main reason for that is most probably



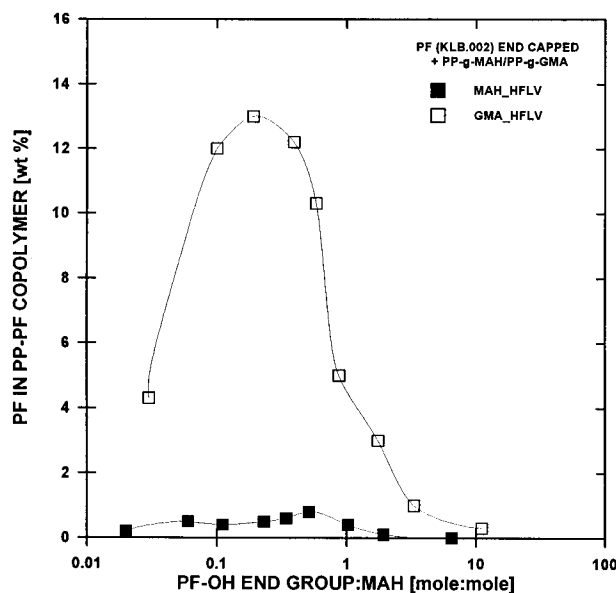
**Figure 6** PF content (wt %) in PP-PF graft copolymer from the reaction of PP-g-GMA and PF grade, KLB.018.

that the PP-*g*-GMA is generally higher in viscosity than is PP-*g*-MAH, giving viscosity ratios not as ideal for proper mixing. The most efficient case, the high-functionality and low-viscosity grade, GMA\_HFLV, resulted in PF contents of almost 48 wt % PF. This high conversion observed for the GMA monomer could be explained by the generally higher reactivity of GMA compared to MAH. MAH will normally react only with the PF end hydroxylic groups; the GMA molecule may also react with the phenolic—OH groups. This will significantly increase the probability of reaction and, thereby, the PF content. For GMA, the probability of crosslinking will also increase due to the PF multisite reactivity. This crosslinking phenomenon was also reported earlier.<sup>24</sup> This means that the observed levels of the PF content are not only gained by reaction with PF end groups, but, to some extent, also by phenolic —OH reactions.

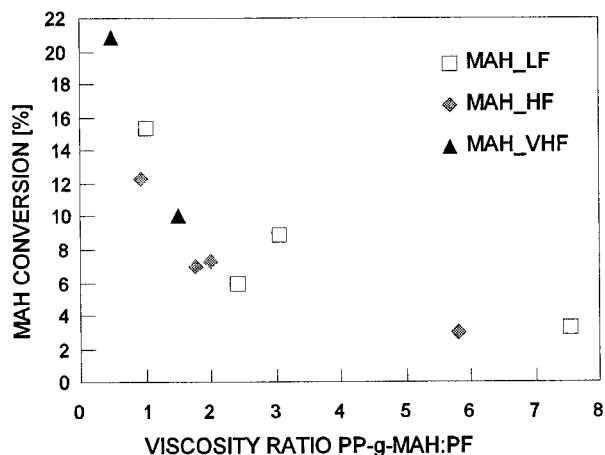
In Figure 6, the reactions of PP-*g*-GMAs with the low-viscosity PF, KLB.018, are shown. The level of PF content was again higher than for the similar case for MAH in Figure 4, but still much less than for the high-viscosity KLB.002 in Figure 5. As for the curves in Figure 4, these curves were also relatively broader than in the optimum viscosity case.

#### Effect of End-group Functionality

Two experiments were run with high-functionality and low-viscosity PP-*g*-MAH and PP-*g*-GMA



**Figure 7** PF content (wt %) in PP-PF graft copolymer from melt mixing of f-PP with acetyl chloride end-capped PF (KLB.002).



**Figure 8** Conversion of MAH as a function of viscosity ratio of PP-*g*-MAH and PF.

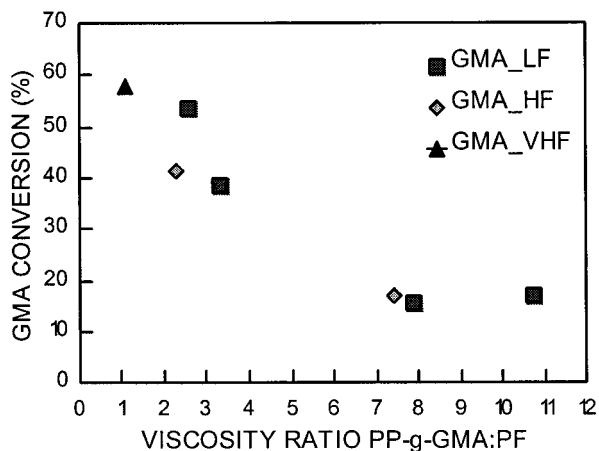
and an end-capped PF polymer to identify the reaction mechanism. The end-capped polymer was similar to KLB.002, except for the end-capping during the last synthesis step with acetyl chloride ( $\text{CH}_3\text{COCl}$ ). This compound is considered reactive only with the primary hydroxyls at the PF end, leaving the phenolic—OH unmodified.<sup>25</sup> This end-cap functionality is assumed nonreactive with MAH and GMA.

The two curves in Figure 7 clearly show that reaction with the GMA functionality was still pronounced with the end-capped PF, whereas for MAH, almost no reactivity was observed. This again verifies that the GMA will react with the phenolic hydroxyl groups to form a PP-PF graft copolymer, giving validation to the “crosslink theory.”

#### Effect of Viscosity Ratios

So far, the PF content (wt %) has been presented as a function of functional group ratio for PP-*g*-X with various functionality and viscosities. Another very important parameter to consider is conversion of the functionalized groups of the PP functionality. It is important that this f-PP conversion is as high as possible to utilize the introduced functionality.

In Figure 8 is shown the conversion of MAH in various PP-*g*-MAH grades having three levels of functionality; low (LF), high (HF), and very high functionality (VHF). The figure shows that maximum conversion of MAH was obtained with viscosity ratios of about 1. At the best conditions, 21% conversion was achieved. The figure also



**Figure 9** Conversion of GMA as a function of viscosity ratio of PP-g-GMA and PF.

shows that the MAH conversion was more or less independent of the functionality density.

A similar plot is shown for PP-g-GMA in Figure 9. Figure 9 also shows that maximum conversion of GMA was obtained with viscosity ratios of about 1. At these conditions, almost 60% conversion of GMA was obtained. Again, the independence of the density of functional groups was observed.

## CONCLUSIONS

PP-PF graft copolymers from thermoplastic PF resins and f-PP were synthesized by reactive extrusion. The content of PF in the graft copolymer was determined by reaction variables such as type and density of functionality on PP, molecular weight of PF, and viscosity ratio of f-PP and PF. The results showed that the viscosity ratio is of primary importance for such reactive processing. Also, type and concentration of the functional groups were important variables. The GMA functionality resulted in higher conversions than did PP-g-MAH within the available reactions times.

This work was part of a Ph.D. thesis and could not have been performed without the help of a number of people at Borealis AS and The Norwegian Institute of Science and Technology, Department of Machine Design and Materials Technology. This work was financed by the Norwegian Research Council (NFR) and Borealis AS, Bamble.

## NOMENCLATURE

PP polypropylene  
PF phenol formaldehyde resin

f-PP functionalized PP  
MAH maleic anhydride  
GMA glycidyl methacrylate  
PP-g-MAH MAH-grafted PP  
PP-g-GMA GMA-grafted PP  
FTIR Fourier-transform IR spectroscopy

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