

# Rheological Behavior of Polypropylene/Novolac Blends

Limei Cui,<sup>1</sup> Zhen Zhou,<sup>1</sup> Yong Zhang,<sup>1</sup> Yinxi Zhang,<sup>1</sup> Xiangfu Zhang,<sup>2</sup> Wen Zhou<sup>2</sup>

<sup>1</sup>Research Institute of Polymer Materials, Shanghai Jiaotong University, Shanghai 200240, China

<sup>2</sup>Shanghai PRET Composites Company, Limited, Shanghai 201700, China

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**ABSTRACT:** The rheological behavior of polypropylene/novolac blends was investigated with special reference to the effects of the blend ratio, compatibilization, and dynamic cure. The polypropylene and all the polypropylene/novolac blends presented evidence of shear-thinning behavior. The novolac, compatibilizer, and dynamic cure had dramatic effects on the rheological behavior of the polypropylene. Various rheological plots, including plots of the viscosity, storage modulus, loss modulus, and loss angle, Han plots, and Cole–Cole plots, were used to ana-

lyze the polypropylene/novolac blends. The results showed that the compatibilization together with the dynamic cure could increase the viscosity and modulus because of the formation of a grafting polymer between the maleic anhydride grafted polypropylene and the curing novolac resin. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 811–816, 2007

**Key words:** compatibility; poly(propylene) (PP); rheology; thermosets

## INTRODUCTION

Dynamic vulcanization is an effective way of preparing thermoplastic vulcanizates.<sup>1–3</sup> This technology has led to a significant number of new thermoplastic elastomer products being commercialized during the mid-to-late 1980s.<sup>4,5</sup> However, there are few publications concerning dynamic vulcanization applied to thermoplastic/thermosetting resin systems.

The well-known novolac-type phenolic resins, which are a major class of thermosetting polymers, are widely used in industry because of their low manufacturing cost, dimensional stability, age resistance, high tensile strength, and chemical reactivity. Therefore, blending novolac resins with other polymers has attracted great industrial interests. Polypropylene (PP) is a commodity polymer used in large quantities in all fields of application. However, it exhibits relatively low modulus and stiffness in comparison with engineering plastics.

Previous studies carried out in our laboratories applied dynamic vulcanization to prepare PP/novolac blends and focused on the determination of the mechanical properties, crystallization kinetics, and thermal stability of these materials.<sup>6,7</sup> The blends were prepared in the mixing chamber of a Haake rheometer through the dynamic curing of a novolac resin in molten PP. As the novolac resin and PP were immiscible, maleic anhydride grafted polypropylene (MA-g-PP) was used as a compatibilizer. The experi-

mental results showed that dynamically cured PP/MA-g-PP/novolac blends had better mechanical properties and thermal stability than uncured PP/novolac blends, uncured PP/MA-g-PP/novolac blends, and dynamically cured PP/novolac blends. The dynamic cure of novolac led to an improvement in the modulus and stiffness of the PP/novolac blends. The compatibilization and dynamic cure further led to obvious increases in the mechanical properties. Moreover, for dynamically cured PP/MA-g-PP/novolac blends, the tensile strength, flexural modulus, and flexural strength increased significantly with increasing novolac content, whereas the elongation at break dramatically decreased. This study is a part of a series of investigations, and the main goal is to evaluate the processability and flow properties of PP/novolac blends because the rheological parameters are very sensitive to structural changes in the polymer under the processing fields. The effects of the composition, compatibilizer, and dynamic cure on the rheological properties of blends were investigated. Moreover, various rheological plots were used to analyze the PP/novolac blends.

## EXPERIMENTAL

### Materials

PP (F401) was produced by Liaoning Panjin Petrochemical Co., Ltd. (Panjin City, Liaoning Province, China), with a melt flow index of 2.3 g/10 min (230°C, 2.16 kg). The novolac resin was purchased from Qinan Adhesive Materials Factory (Shanghai, China). MA-g-PP with a maleic anhydride (MAH) content of 1% (w/w) was prepared by Shanghai

Correspondence to: Y. Zhang (yxzhang@sjtu.edu.cn).

Sunny New Technology Development Co., Ltd. (Shanghai, China). The curing agent, hexamethylenetetramine (HMTA), was produced by Shanghai Chemical Agent Co. (Shanghai, China).

### Sample preparation

Before the blending, PP, MA-g-PP, and the novolac resin were dried at 70°C under a vacuum for about 12 h. Dynamically cured PP/novolac blends were prepared in the mixing chamber of a Haake RC90 rheometer at 190°C and 50 rpm. MA-g-PP and PP were first mixed for 2 min, and then the novolac-type phenolic resin was added. 2 min later; the curing agent, HMTA, was added under continuous mixing. The total mixing time was 10 min. The compound was taken out and compression-molded at 190°C for 20 min and then was cold-pressed to produce samples for testing.

### Rheological measurements

Dynamic and steady-state shear measurements were performed with a rotational rheometer (Gemini 200HR, Bohlin Co., UK) equipped with a parallel-plate geometry and 25-mm-diameter plates at 190°C. The dynamic measurements were performed in the frequency range from 0.1 to 100 rad/s, whereas the steady-state shear measurements were carried out in the shear rate range from 0.1 to 10 s<sup>-1</sup>.

The storage modulus ( $G'$ ), loss modulus ( $G''$ ), complex viscosity ( $\eta^*$ ), and loss tangent ( $\tan \delta$ ; i.e., the ratio of the viscous force to the elastic force) were measured in the frequency sweep experiments.  $\eta'$  is the real part of  $\eta^*$ , and  $\eta''$  is the imaginary part of  $\eta^*$ .  $\eta'$  and  $\eta''$  were calculated according to the following equations:

$$\eta'' = G''/\omega \quad (1)$$

$$\eta' = G'/\omega \quad (2)$$

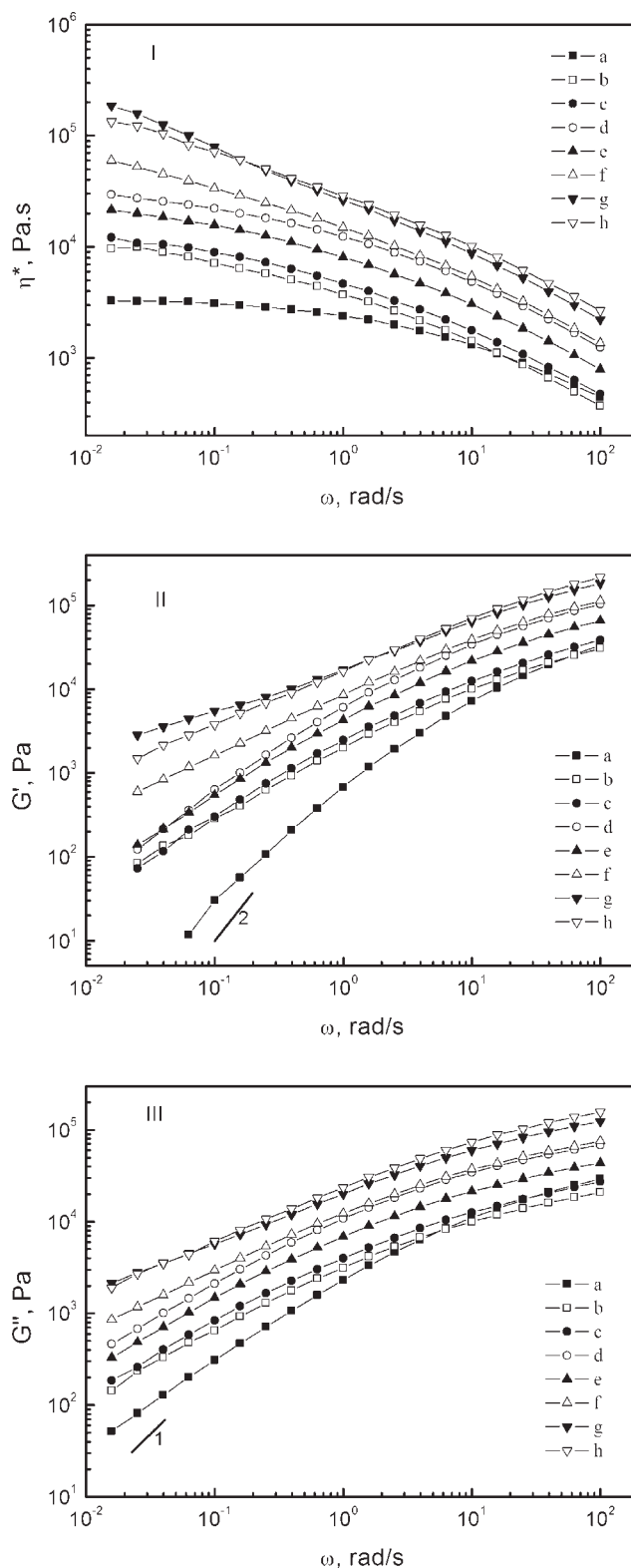
where  $\omega$  is the angular frequency.

## RESULTS AND DISCUSSION

### Dynamic rheological behavior

Generally, in the case of homopolymers, the flow behavior depends on the flow geometry and processing conditions. In the case of polymer blends, the flow behavior becomes more complex and is influenced by additional factors such as the miscibility of the system, the morphology, the interfacial adhesion, and the interfacial thickness.<sup>8</sup>

Figure 1 shows double logarithmic plots of  $\eta^*$ ,  $G'$ , and  $G''$  as functions of  $\omega$  for PP and different systems



**Figure 1** (I)  $\eta^*$ , (II)  $G'$ , and (III)  $G''$  versus  $\omega$  for PP and PP/novolac blends at 190°C: (a) PP, (b) 70/30 PP/novolac, (c) 60/10/30 PP/MA-g-PP/novolac, (d) 70/30/3 PP/novolac/HMTA, (e) 80/10/10/1 PP/MA-g-PP/novolac/HMTA, (f) 70/10/20/2 PP/MA-g-PP/novolac/HMTA, (g) 60/10/30/3 PP/MA-g-PP/novolac/HMTA, and (h) 40/10/50/5 PP/MA-g-PP/novolac/HMTA.

of PP/novolac blends at 190°C. It is apparent that the novolac, compatibilizer, and dynamic cure have dramatic effects on the rheological behavior of the blends.

As shown in Figure 1(I), all curves present evidence of shear-thinning behavior with increasing frequencies, indicating the pseudoplastic nature of the blends. The addition of novolac to PP evidently increases  $\eta^*$ , especially at low frequencies, and this can be attributed to the formation of a two-phase structure. The existence of interfacial interactions between PP and novolac leads to the increase in the viscosity of the blend, although the viscosity of the novolac resin is very low compared with that of the neat PP. Moreover, the addition of MA-g-PP to the PP/novolac blend slightly increases  $\eta^*$  in comparison with that of the PP/novolac blend because the dipolar interaction between the MAH group of MA-g-PP and the novolac resin causes a reduction in the interfacial tension.

The effect of the dynamic cure is pronounced at all frequencies. The dynamically cured PP/novolac blend exhibits a higher viscosity in the whole frequency range than the uncured samples. As the dynamic cure proceeds, the crosslinked novolac resin increases the molecular weight of the blends, and this makes it difficult for the material to flow and hence increase the viscosity of the blend. It behaves like thermoplastic elastomer vulcanizate/PP blends.<sup>9,10</sup>

Furthermore, it is clear from Figure 1(I) that the compatibilization and dynamic cure can further increase  $\eta^*$  over the entire frequency range.  $\eta^*$  of dynamically cured PP/MA-g-PP/novolac blends increases with increasing novolac content. A suitably selected compatibilizer will be located at the interface between the two phases, leading to a reduction in the interfacial tension and an enhancement in the interfacial adhesion.<sup>8</sup> In a previous report, on the basis of an extraction test, PP was absolutely extracted (68.2 wt %) and was totally soluble in xylene from a dynamic cure of a PP/novolac (70/30) blend. However, in the case of a dynamic cure of an MA-g-PP/novolac (70/30) blend, 56.5 wt % of MA-g-PP was extracted, and this indicates that the compatibilizer (MA-g-PP) can react with the curing agent (HMTA).<sup>7</sup> Moreover, the curing leads to a crosslinking novolac network with a stable nitrogen-containing structure. Consequently, the compatibilizer molecules chemically graft to the novolac phase during curing. The graft copolymers *in situ* preferentially reside at the interface, and this increases the interfacial layer thickness; this leads to effective stress transfer between the dispersed phase and the continuous phase and an increase in the interfacial adhesion. This contributes to the reduction in the interlayer slip and therefore to an increase in the viscosity.<sup>8</sup>

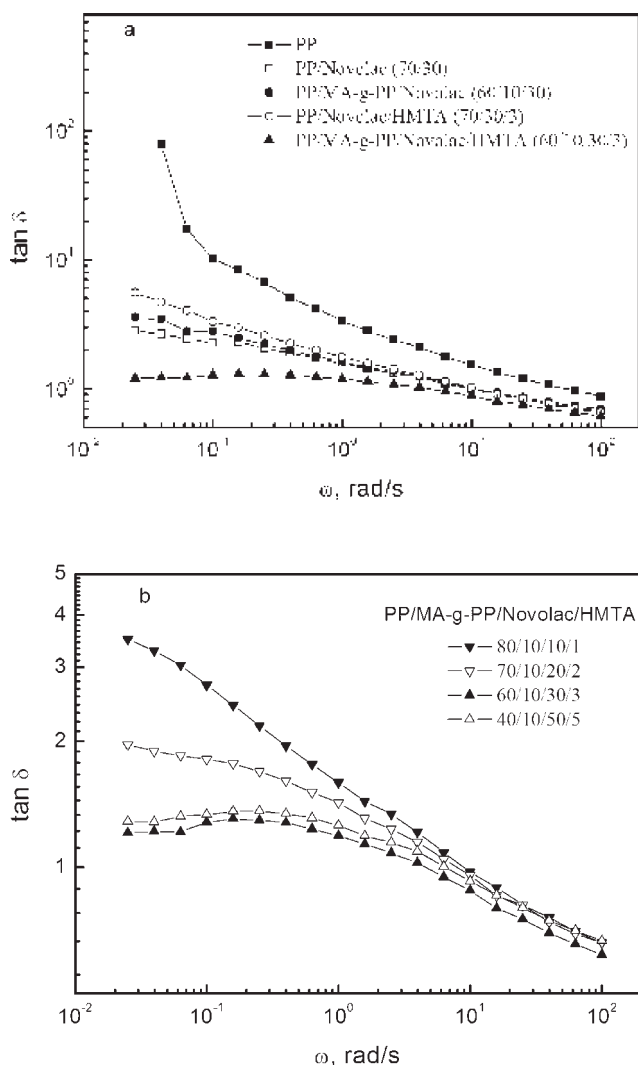
Such an increase in the viscosity upon the compatibilization of immiscible polymer blends has been

reported by several researches.<sup>11–13</sup> Asthane and Jayaraman<sup>14</sup> found that an interfacial reaction resulted in a reduction in the particle size of the dispersed phase and in the interfacial tension between PP and polyamide 6 (PA6). The interfacial tension decreased with an increasing extent of the interfacial reaction. In comparison with the nonreactive blends, there was an additional relaxation mechanism occurring in the reactive blends leading to enhanced  $G'$ .<sup>15</sup>

The increase in the viscosity is caused by a similar increase in  $G'$  and  $G''$ . As can be seen in Figure 1(II,III), the compatibilized PP/MA-g-PP/novolac blend show higher  $G'$  and  $G''$  values than the uncompatibilized blend and neat PP. Moreover, the compatibilizer MA-g-PP and curing can further enhance the values over the entire range of frequencies. In the terminal zone, in which only the longest relaxation time contributes to the viscoelastic behavior,  $G'$  and  $G''$  of linear polymers follow the well-known frequency dependence,<sup>16</sup> that is,  $G' \sim \omega^2$  and  $G'' \sim \omega^1$ . The neat PP exhibits the typical terminal behavior ( $G' \sim \omega^{1.95}$  and  $G'' \sim \omega^{0.91}$ ), which indicates that it is linear polymer. However, the terminal slopes of  $G'$  and  $G''$  dramatically decrease for all PP/novolac blends. The nonterminal behavior of the blends suggests that the relaxation time of the blends is prolonged and there is a longer relaxation process. Moreover, it shows that the addition of novolac, MA-g-PP, or cured novolac not only causes the restriction of PP chain relaxation but also influences the short-range dynamics or local motion of the PP chains in the blends. It has been reported that the enhanced elasticity and prolonged relaxation time at low frequencies for immiscible polymer blends are related to the phase-separated morphology of the blend.<sup>17</sup> Poor compatibility induces a strong local interaction that has a long relaxation time.<sup>18</sup>

Although a number of dynamic rheological parameters can give useful information for the interpretation of viscoelastic properties, the  $\tan \delta$  value obtained from a rotational rheometer is a very sensitive and effective value for expressing the contribution of a specific structure to viscoelastic behavior.<sup>19,20</sup>

Figure 2 presents  $\tan \delta$  as a function of the oscillation frequency. Perfectly viscous fluids have  $\tan \delta = \infty$ , whereas elastic solids have  $\tan \delta = 0$ .<sup>21</sup> Usually,  $\tan \delta$  of a polymer blend without a specific structure decreases monotonically with the frequency. As shown in Figure 2(a), the rheological behavior of neat PP is typical of polymer melts, showing a negative slope in  $\tan \delta$  over the entire tested frequency range. Dynamic curing and the addition of novolac and MA-g-PP drastically change the PP rheology. Moreover, all PP/novolac blends are much more elastic than the PP materials at low frequencies, especially the dynamically cured PP/MA-g-PP/novolac blend. The difference in the elasticity becomes smaller with increasing frequency.



**Figure 2** (a)  $\tan \delta$  versus  $\omega$  plots for PP and different PP/novolac blends and (b)  $\tan \delta/\omega$  plots for PP/MA-g-PP/novolac/HMTA blends at 190°C.

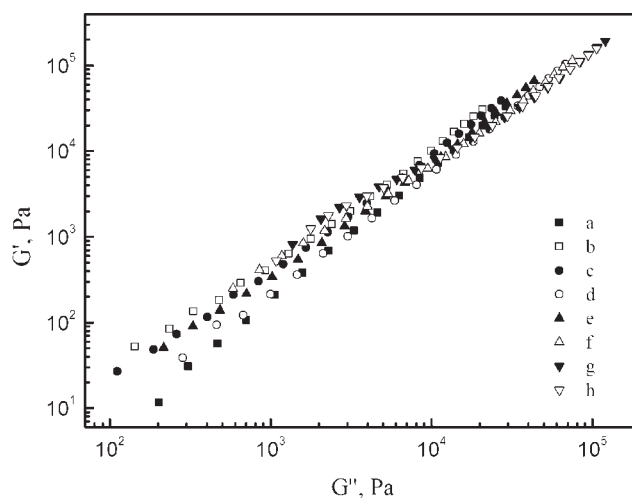
Figure 2(b) shows  $\tan \delta$  versus  $\omega$  plots for dynamically cured PP/MA-g-PP/novolac blends at 190°C. The elasticity of dynamically cured PP/MA-g-PP/novolac blends increases with increasing novolac content. When the novolac content in the blends is above 30 wt %, a significant variation of  $\tan \delta$  is found in a low-frequency range. The slope of  $\tan \delta/\omega$  plots in the low-frequency zone is positive. With an increase in the frequency, the slope first reaches a plateau (zero slope) and then becomes negative. These changes indicate the rheological transition from melt-like behavior to solidlike behavior. It is evident that gelation starts at a novolac concentration of 30 wt %. A polymeric gel can be defined as a three-dimensional network in which polymer chains are bound by physical or chemical crosslinks. Fu et al.<sup>22</sup> reported that at the gel point,  $\tan \delta$  is frequency-independent, so the critical gel manifests itself by the appearance of a zero-slope plateau in the  $\tan \delta$  curve. The slopes in

the  $\tan \delta$  curves are negative for the melts and positive for the solids (gels) beyond the gel point.

The gelation of blends may occur for the following reasons. First, there is strong interfacial adhesion due to a specific structure that forms at the interface through the chemical reaction that takes place between the MA group and the curing agent HMTA. This hinders the chain mobility, causing the blends to behave in a solidlike way. Second, the high content of crosslinked novolac leads to solidlike behavior. Hong et al.<sup>23</sup> reported that the addition of the compatibilizer maleic anhydride-grafted styrene-ethylene-butylene-styrene block copolymer (MA-g-SEBS) to PP/PA6 led to a decrease in  $\tan \delta$  with an inflection point at a low frequency because of a specific structure that formed at the interface and showed strong interfacial adhesion.

The rheological data can be analyzed in a Han plot<sup>24</sup> ( $\log G' - \log G''$ ) and a Cole-Cole plot<sup>25</sup> ( $\eta'' - \eta'$ ). The Han plot has been used to investigate the miscibility of polymer blends.<sup>26,27</sup> If a blend is miscible, the same slope is observed between the blend compositions and the pure component; otherwise, it is considered to be an immiscible or phase-separated blend. The extent of the spread of the two curves in the  $\log G'/\log G''$  plots for a given polymer pair will depend on the extent of miscibility, polydispersity, and plateau moduli of the constituents.<sup>19</sup> As shown in Figure 3, PP and all PP/novolac blends exhibit different slopes. The large difference in the slopes of the  $G'/G''$  plot indicates poor miscibility.

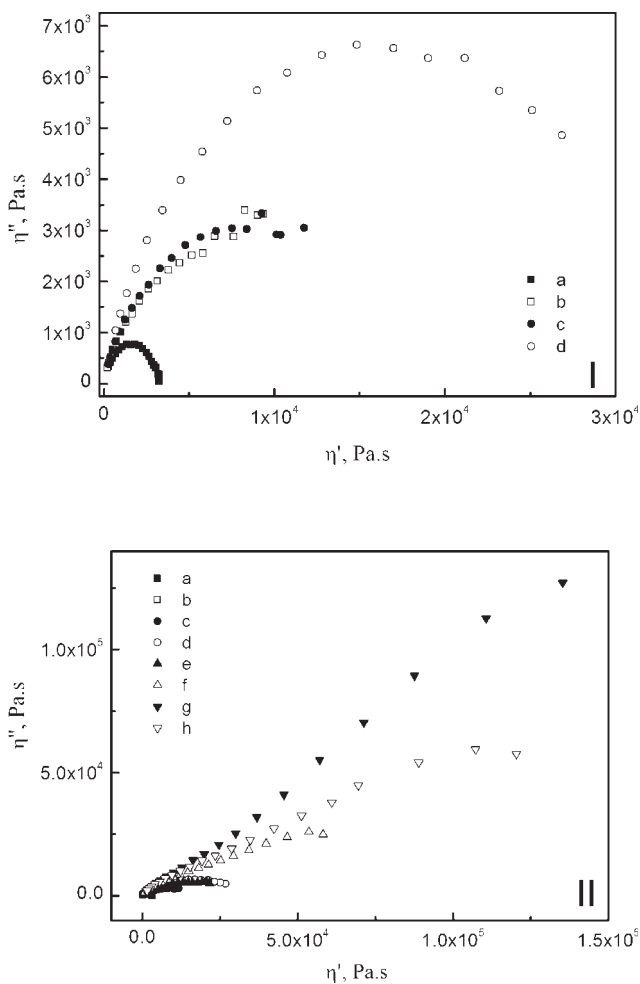
It is also well known that a Cole-Cole plot can be used to analyze the miscibility of polymer blends. A smooth, semicircular shape of the plotted curves sug-



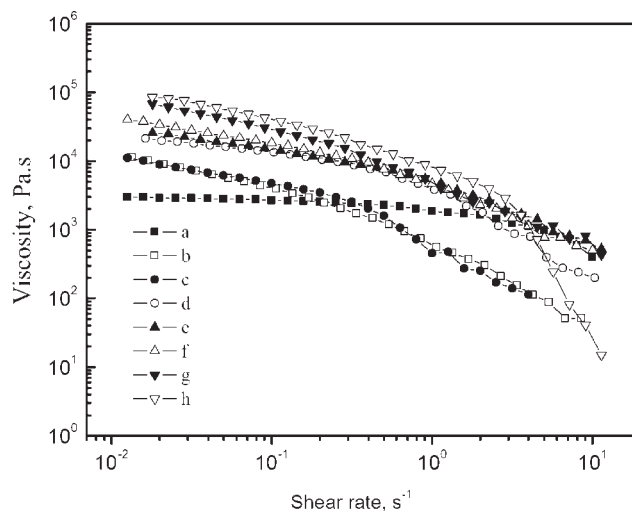
**Figure 3** Han plot of the PP and PP/novolac blends: (a) PP, (b) 70/30 PP/novolac, (c) 60/10/30 PP/MA-g-PP/novolac, (d) 70/30/3 PP/novolac/HMTA, (e) 80/10/10/1 PP/MA-g-PP/novolac/HMTA, (f) 70/10/20/2 PP/MA-g-PP/novolac/HMTA, (g) 60/10/30/3 PP/MA-g-PP/novolac/HMTA, and (h) 40/10/50/5 PP/MA-g-PP/novolac/HMTA.



gests good compatibility, that is, phase homogeneity in the melt, and any deviation from this shape shows nonhomogeneous dispersion and phase segregation due to immiscibility.<sup>20</sup> As can be seen in Figure 4, the differences of these samples are very clear. For the plain PP and dynamically cured PP/novolac blend, the Cole–Cole plots are close to a semicircle. Especially for the dynamically cured PP/novolac blend, the plot has a bigger diameter than that of PP. It appears that the dynamically cured PP/novolac blend is compatible or at least finely dispersed. The effect of the dynamically cured novolac resin on the rheological behavior of the blends is complex and needs further investigation. The dynamically cured novolac resin is similar to a filler, which can change the rheological and viscoelastic behavior of a polymer by introducing filler–matrix interactive forces or a restriction of polymer chain movement by filler particles.



**Figure 4** Cole–Cole plots of the PP and PP/novolac blends: (a) PP, (b) 70/30 PP/novolac, (c) 60/10/30 PP/MA-g-PP/novolac, (d) 70/30/3 PP/novolac/HMTA, (e) 80/10/10/1 PP/MA-g-PP/novolac/HMTA, (f) 70/10/20/2 PP/MA-g-PP/novolac/HMTA, (g) 60/10/30/3 PP/MA-g-PP/novolac/HMTA, and (h) 40/10/50/5 PP/MA-g-PP/novolac/HMTA.



**Figure 5** Shear viscosity versus the shear rate for PP and PP/novolac blends at 190°C: (a) PP, (b) 70/30 PP/novolac, (c) 60/10/30 PP/MA-g-PP/novolac, (d) 70/30/3 PP/novolac/HMTA, (e) 80/10/10/1 PP/MA-g-PP/novolac/HMTA, (f) 70/10/20/2 PP/MA-g-PP/novolac/HMTA, (g) 60/10/30/3 PP/MA-g-PP/novolac/HMTA, and (h) 40/10/50/5 PP/MA-g-PP/novolac/HMTA.

Joshi et al.<sup>20</sup> reported that a high-density polyethylene/octamethyl polyhedral oligomeric silsesquioxane blend with 1, 2, or 5 wt % polyhedral oligomeric silsesquioxane presented a semicircular shape. However, other PP/novolac blends show an upward inflection, which may be indicative of poor compatibility or yield behavior. Moreover, the Cole–Cole plots of the dynamically cured PP/MA-g-PP/novolac blends are higher than those of the other PP/novolac blends and show more evident deviation at a high viscosity with increasing novolac content, indicating a longer relaxation time. These blends are quite different from one another, possibly because of the different sizes of the dispersed particles and the different interphase effects.

### Steady shear tests

Melt viscosity results as a function of the shear rate at 190°C are shown in Figure 5 for PP and PP/novolac blends. The viscosity of the studied materials decreases with an increasing shear rate, and this indicates the pseudoplastic nature of the blends. This is because the randomly oriented and entangled polymer chains become oriented and disentangled upon the application of the shear rate, lowering the melt viscosity.

It has also been observed that PP presents a lower viscosity than PP/novolac blends at low shear rates. Moreover, the dynamic cure and the compatibilizer can further increase the value of the blends. This fact is more pronounced at low shear regions than at high

shear regions. With increasing novolac content, the viscosity of dynamically cured PP/MA-g-PP/novolac blends increases. The trend of the results is similar to that of dynamic tests. The differences in the melt viscosity can also be explained by the intermolecular interactions and interfacial adhesion and composition.<sup>28</sup>

### CONCLUSIONS

The rheological behavior of PP/novolac blends has been investigated. PP and all PP/novolac blends present evidence of shear-thinning behavior with increasing frequencies, and this indicates the pseudoplastic nature of the blends. Novolac, the compatibilizer MA-g-PP, and the dynamic cure have dramatic effects on the rheological behavior of the blends.

The addition of MA-g-PP to the PP/novolac blend slightly increases  $\eta^*$  because of the dipolar interaction between the MAH group of MA-g-PP and the novolac resin. The dynamically cured PP/novolac blend exhibits higher  $\eta^*$  than the uncured blends. Furthermore, the compatibilizer and dynamic cure can further increase the viscosity over the entire frequency range. This increase is due to an enhancement in the interfacial interaction between the two polymers, which is associated with the grafting reaction between MA-g-PP and the curing novolac resin.

The rheological properties of PP/novolac blends, such as higher  $G'$  at a low frequency, deviating from the  $G'-G''^2$  scaling of a linear polymer in a Han plot and the upward inflection in a Cole-Cole plot, can be related to the different relaxation mechanism versus that of linear PP. At the same time, the PP/novolac blends have poor compatibility. With an increase in the novolac content of dynamically cured PP/MA-g-PP/novolac blends, the chain mobility is hindered, and the viscosity increases. Above 30 wt % novolac, the blends exhibit solidlike (gelation) behavior at a low frequency.

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