

# Compatibility Effect of Reactive Copolymers on Polypropylene/Polyamide 6 Blends from Commingled Plastic Wastes

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**ABSTRACT:** We report the compatibility effect on a recycled polypropylene/nylon (75/25) blend processed with reactive copolymers on the basis of morphological, mechanical, and rheological characteristics. Via a scanning electron microscopy investigation, we found improved surface morphologies with regular and fine domains in a recycled polypropylene/nylon (75/25) blend compatibilized with copolymers containing maleic anhydride as a reactive functional group [styrene-(ethylene/butylene)-styrene-graft-maleic anhydride copolymer and polypropylene-graft-maleic anhydride]. Large increases in both the mechanical and rheological properties with the addition of the styrene-(eth-

ylene/butylene)-styrene-graft-maleic anhydride copolymer could be interpreted with respect to a specific structure at the interface, showing a strong interfacial adhesion between recycled polypropylene and nylon. To confirm the existence of this structure, we used various dynamic rheological parameters: the Cox-Merz rule, storage modulus, and phase angle. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1188–1193, 2006

**Key words:** blends; nylon; poly(propylene) (PP); recycling; rheology

## INTRODUCTION

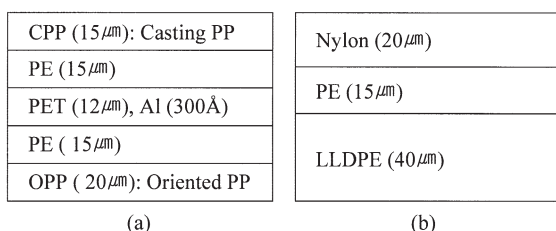
Because synthetic polymers possess many advantages, such as a well-balanced supply, low manufacturing cost, and good processability, they have been used in various applications ranging from cheap domestic appliances to expensive hospital supplies. However, most plastic wastes from synthetic polymers are land-filled or incinerated without recycling, and this causes serious environmental pollution.<sup>1–5</sup> Thus, suitable ways to recycle plastic wastes have been developed to protect the environment and to use scarce resources efficiently. Among developed recycling methods, technology making new products with plastic wastes themselves as raw materials, called material recycling, is widely available because of its high economic value and energy efficiency in comparison with other recycling methods.<sup>3–5</sup> As raw materials for material recycling, mixed polymers dumped in homes, stores, and offices have been so far used less than industrial plastic wastes issued from polymer manufacturing procedures because their heterogeneity makes it difficult to recycle plastic wastes by reducing the mechanical

properties of the final products.<sup>6,7</sup> However, recently the processing of mixed polymers for recycling has been taken into account because a substantial amount of plastic waste is in mixed forms such as polymer blends and composite materials. To recycle these mixed-waste polymers without deteriorated mechanical properties, the compatibility between heterogeneous components must be enhanced by various methods, including both reactive and nonreactive processes. Commonly, compatibility is promoted by the addition of reactive graft or block copolymers, which can enhance adhesion between heterogeneous components by reducing the interfacial tension.<sup>6–10</sup>

In this study, recycled polypropylene/polyamide 6 (PP/nylon) blends were melt-processed with three different types of reactive copolymers: styrene-(ethylene/butylene)-styrene-graft-maleic anhydride copolymer (SEBS-g-MA), polypropylene-graft-maleic anhydride (PP-g-MA), and polypropylene-graft-acrylic acid (PP-g-AA). Various works on the compatibilization of PP/nylon blends have been extensively reported.<sup>11–17</sup> Using the prepared samples, we investigated fractured surface morphologies, mechanical properties, and rheological behaviors in both steady-shear and oscillatory-shear modes, and we compared the compatibility effects of different types of reactive copolymers on the basis of the aforementioned characteristics.

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**Figure 1** Schematic diagram of waste-packaging film layers: (a) recycled PP and (b) recycled nylon.

## EXPERIMENTAL

The resins used in this study were commingled packaging film wastes containing a polypropylene (PP) packaging film system [PP/polyethylene (PE)/aluminum/poly(ethylene terephthalate) (PET)] and a polyamide 6 (nylon) packaging film system [nylon/PE/linear low-density polyethylene (LLDPE)], as presented in Figure 1. To enhance the interfacial adhesion between the blend components, we employed three different types of reactive copolymers, whose types and properties are summarized in Table I. After the materials were dried carefully in vacuo at 80°C for 24 h, recycled PP, recycled nylon, and reactive copolymers were melt-processed with a composition ratio listed in Table II in a corotating twin-screw extruder (length/diameter = 7.5; Prism TSE 16TC, Thermo Electron Co., Woburn, MA). The set temperatures of the extruder were between 180 and 250°C, whereas its screw speed was fixed at 50 rpm. These were compression-molded into disc-type samples in a hot press (HP-200L, Kee-Pae, Seoul, Korea) at 190°C, and this was followed by careful drying in vacuo at 80°C for more than 24 h to minimize the moisture.

The fractured morphology was investigated with a scanning electron microscope (S-2200, Hitachi, Osaka, Japan) with various magnifications at 15 kV. Samples freeze-fractured in liquid nitrogen were coated with platinum to generate an electric current on the surfaces. In addition, the specimens for mechanical testing were prepared with Baby Plast (Barcelona, Spain) 6/10 under 120 bar at 250°C, and then their mechanical properties were measured with an Instron model 4210 tensile machine and a Radmana ITR-2000 impact strength test machine at a crosshead speed of 10 mm/min according to the standard conditions of ASTM D

**TABLE II**  
Composition of the PP/Nylon Blends

PP/Nylon	Compatibilizer	Content
100/0	None	
75/25	SEBS-g-MA, PP-g-MA, PP-g-AA	5 phr
50/50	None	
25/75	None	
0/100	None	

254 and ASTM D 638, respectively. We also measured the rheological properties of the prepared specimens via a rotational rheometer with a parallel-plate geometry (MCR300, Physica, Germany) 1 mm thick and 25 mm in diameter at 190°C. The shear viscosity and shear stress were obtained in a melt state as a function of the shear rate. In oscillatory-shear mode, we examined the durability for vibration or periodic external stress. The storage modulus ( $G'$ ) and phase angle ( $\delta$ ) were obtained as functions of the frequency within a linear viscoelastic region.

## RESULTS AND DISCUSSION

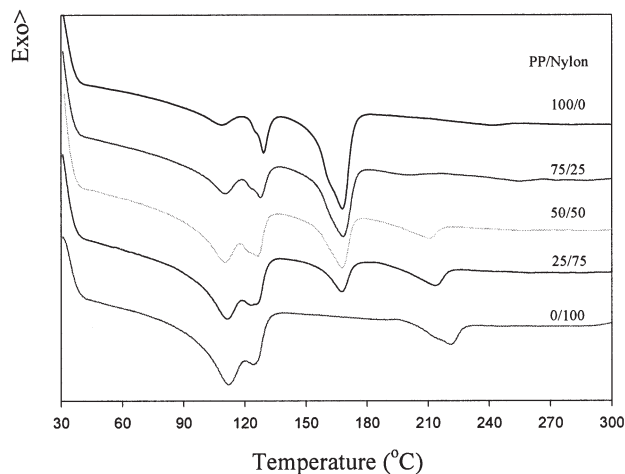
The various compositions of each recycled sample, as given in Figure 1, could also be confirmed from its DSC thermograms shown in Figure 2. The thermogram of recycled PP indicates its composition of low-density polyethylene [LDPE; melting temperature ( $T_m$ ) = 110°C], LLDPE ( $T_m$  = 125°C), PP ( $T_m$  = 165°C), and a tiny amount of PET ( $T_m$  = 250°C). Furthermore, we could also confirm the composition of nylon with LDPE ( $T_m$  = 110°C), LLDPE ( $T_m$  = 165°C), and nylon 6 ( $T_m$  = 225°C). Because of its mixed compositions in the case of nylon, which lowered the average  $T_m$  value of the recycled nylon, the operating temperature of 190°C in this study was good enough to perform.

The fractured surface morphologies of the PP/nylon (75/25) blend compatibilized with various reactive copolymers were investigated to examine their compatibility effect on the PP/nylon (75/25) blend (see Fig. 3). The uncompatibilized PP/nylon (75/25) blend possessed a morphology composed of irregular and coarse particles. By the addition of reactive copolymers, the PP/nylon (75/25) blend was expected to show more regular and finer dispersions of small domains because of the enhancement of the miscibility

**TABLE I**  
Types and Properties of the Compatibilizers

Compatibilizer	Company	Grade	
SEBS-g-MA	Kraton	Kraton FG-1901X	MA (2 wt %)
PP-g-MA	Honam Petrochemical	CM-1120	MI(230) = 50 g/10 min
PP-g-AA	Uniroyal Chemical	Polybond 1001	MI(230) = 40 g/10 min

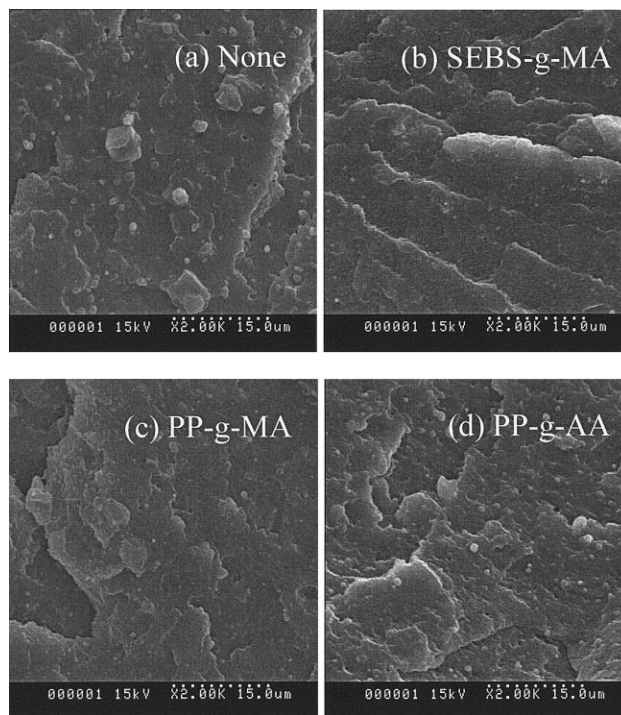
MI, melt index.



**Figure 2** DSC thermograms of recycled PP/nylon blends.

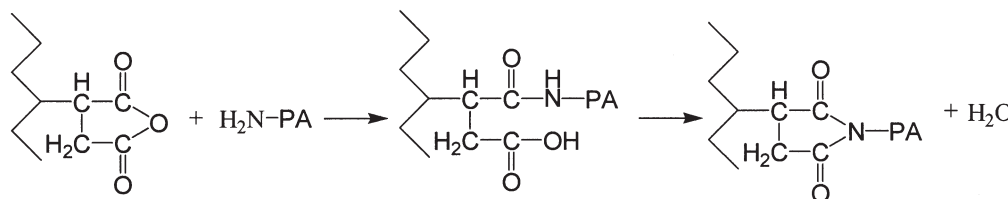
between recycled PP and nylon. However, an apparent compatible outcome seemed to be achieved only in the case of copolymers containing maleic anhydride (MA; SEBS-g-MA and PP-g-MA), showing the efficiency in reducing the domain size and refining the coarsening of the morphology. This was due to the formation of strong interfacial adhesion through the chemical reaction taking place between the MA group and the amine end group of nylon, as shown in Figure 4. When PP-g-AA was added, a regular and fine morphology in comparison with the uncompatibilized PP/nylon (75/25) blend was obtained. However, in comparison with corresponding PP-g-MA, PP-g-AA seemed to be less efficient in reducing the particle size and enhancing the interfacial adhesion between recycled PP and nylon. These morphological characteristics are further discussed on the basis of mechanical and rheological properties later.

Figure 5 presents the measured mechanical properties of PP/nylon (75/25) blends with or without reactive copolymers at room temperature. As expected from the scanning electron microscopy (SEM) analysis, the addition of SEBS-g-MA, grafting MA as a functional group to induce the chemical reaction with the amine end group of nylon, caused a remarkable improvement in the mechanical properties as an indicator of effective compatibilization. Although the tensile strength and elongation at break did not increase

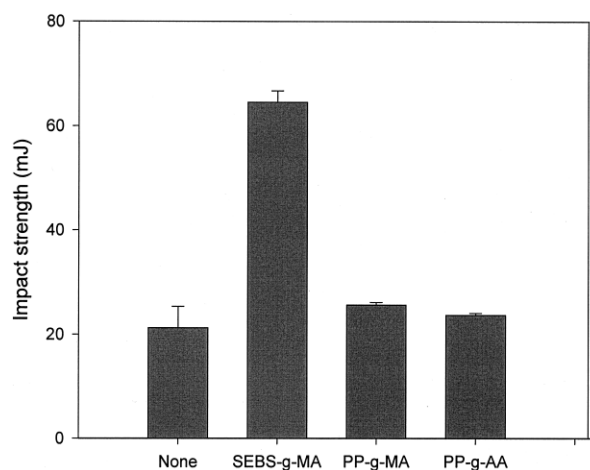


**Figure 3** SEM micrographs of PP/nylon (75/25) blends with or without various compatibilizers (5 phr): (a) none, (b) SEBS-g-MA, (c) PP-g-MA, and (d) PP-g-AA.

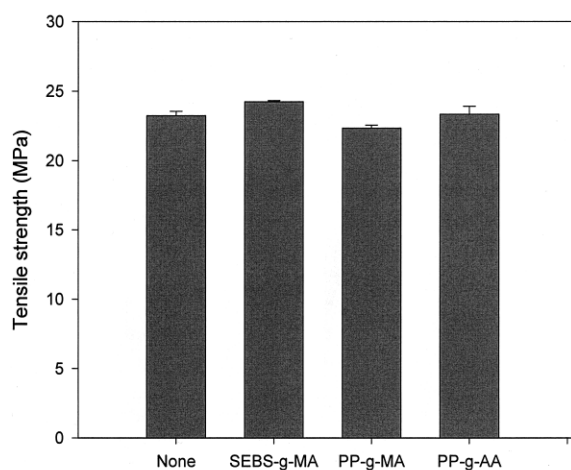
remarkably, a large increase in the impact strength above nearly 200% was observed in comparison with the uncompatibilized PP/nylon (75/25) blend system. However, in contrast to the results of SEM analysis, PP-g-MA did not show a significant compatibility effect. It can be explained that the graft chains that formed at the interface between recycled PP and nylon by the chemical reaction were not strong enough to hold under external input such as tensile force, which caused interfacial breakage.<sup>18</sup> In addition, the already present compatibilizers in the recycled samples might have affected the morphology even though it could be negligible. On the other hand, the mechanical properties of the PP/nylon (75/25) blend compatibilized with PP-g-AA were higher than those of the uncompatibilized PP/nylon (75/25) blend by about 10–20%. This small increase can be explained in conjunction with the somewhat rough morphological characteristics observed via SEM.



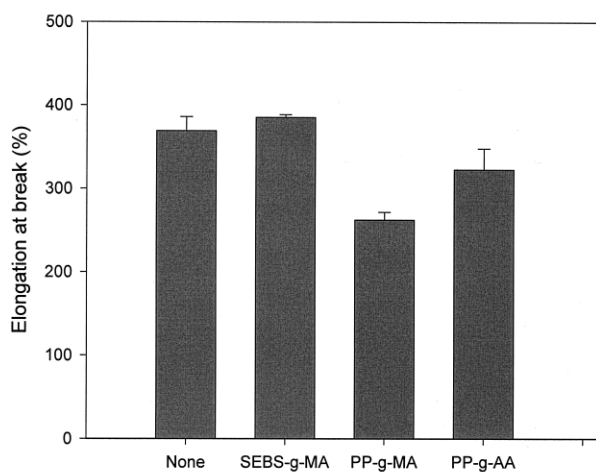
**Figure 4** Reaction between the MA groups and the amine end groups of nylon.



(a)

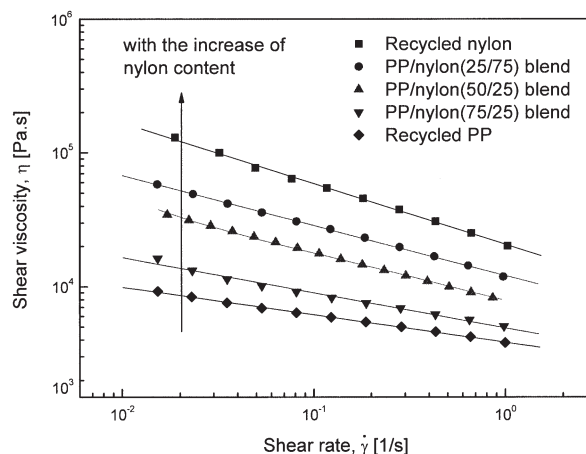


(b)

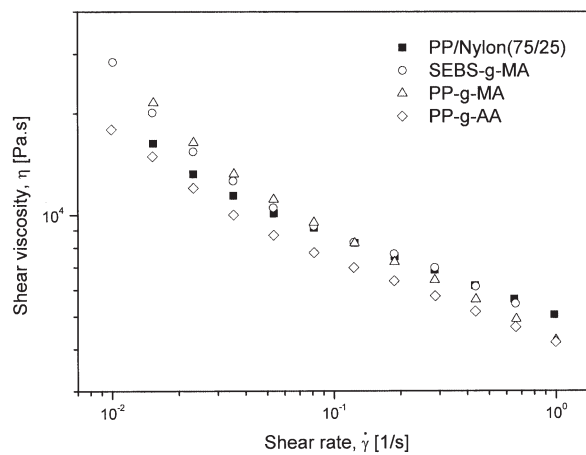


(c)

**Figure 5** Mechanical properties of PP/nylon (75/25) blends with or without various compatibilizers (5 phr): (a) notched Izod impact strength, (b) tensile strength, and (c) elongation at break.



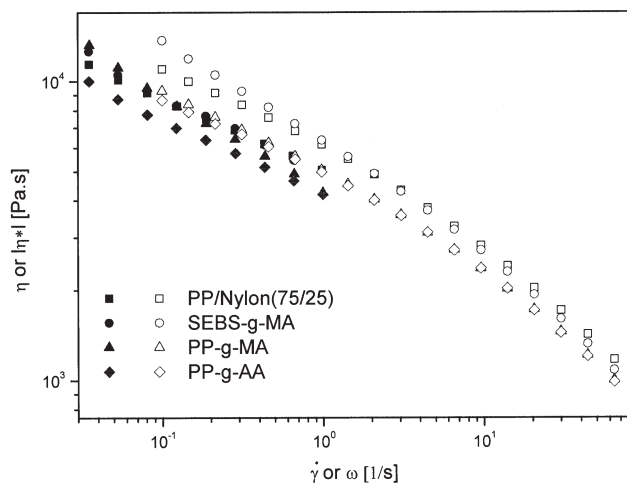
(a)



(b)

**Figure 6**  $\eta$  for (a) PP, nylon, and its blend and (b) PP/nylon (75/25) blends with or without various compatibilizers (5 phr).

The steady-shear viscosities of the pure components and its blend are shown in Figure 6(a). In the shear rate range explored, both the steady-shear viscosity ( $\eta$ ) and the degree of shear thinning for the PP/nylon blends were more enhanced with the nylon content. These rheological parameters, which represent the flow behavior of polymer blends at a fixed temperature, can be used to optimize their processing conditions.<sup>19,20</sup> On the other hand, the addition of a copolymer containing MA (SEBS-g-MA or PP-g-MA) made the blend more resistant to flow, as presented in Figure 6(b) for PP/nylon (75/25), and this suggested strong interfacial adhesion at the interface through the chemical reaction taking place between the MA group and the amine end group of nylon.<sup>7,9</sup> However, the PP/nylon (75/25) blend compatibilized with PP-g-MA exhibited lower  $\eta$  than the uncompatibilized PP/nylon (75/25) blend in a high shear rate region. This means that the graft chains that formed at the interface



**Figure 7**  $\eta$  and  $\eta^*$  of PP/nylon (75/25) blends with or without various compatibilizers (5 phr).

between recycled PP and nylon by the chemical reaction broke easily under a high shear force as anticipated from the mechanical test.

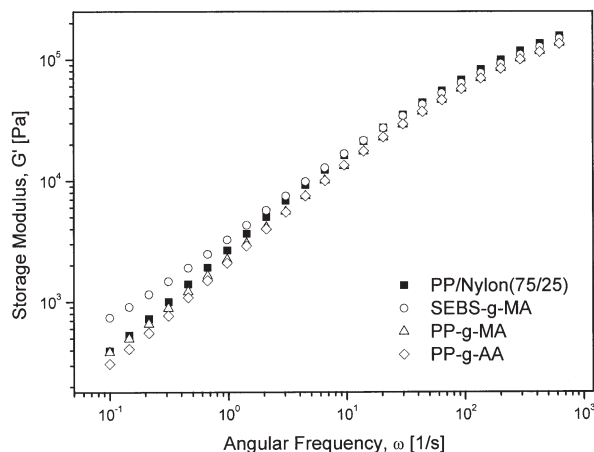
On the basis of these results, we concluded that the overall compatibility effect mainly originated from not the surface morphology but the degree of interfacial adhesion. Thus, to confirm clearly the existence of a specific structure (graft chains) at the interface showing a strong interfacial adhesion,<sup>7,21</sup> various rheological properties are further discussed in this study.

Figure 7 compares  $\eta$  and the complex viscosity ( $\eta^*$ ) via the empirical Cox–Merz relationship<sup>22,23</sup> as given in eq. (1). Providing a homogeneous internal structure, a polymer melt should exhibit the same energy-dissipation mechanism in both steady-shear and oscillatory-shear modes. Cox and Merz found that  $\eta^* [\eta^* = G^*/(i\omega)$ , where  $\omega$  is the angular frequency, and  $G^*$  is the complex modulus] was roughly equal to the viscosity obtained at  $\dot{\gamma} = \omega$ , where  $\dot{\gamma}$  is the shear rate. However, despite the homogeneous surface morphology, as observed from the SEM photographs, a comparison showed the most distinct discrepancy with the addition of SEBS-g-MA. This indicated that a specific structure that formed at the interface between recycled PP and nylon did not break under a high shear force and disturb the homogeneous energy dissipation in the PP/nylon blend:

$$\eta(\dot{\gamma})|_{\dot{\gamma}=\omega} = |\eta^*(\omega)| = \sqrt{\eta'^2(\omega) + \eta''^2(\omega)} \quad (1)$$

where  $\eta'$  is the dynamic viscosity and  $\eta''$  is an elastic part of complex viscosity.

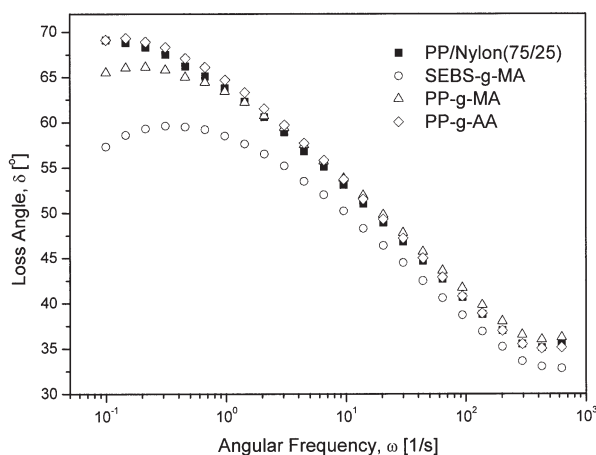
In an oscillatory test mode, we also could get  $G'$  as a function of  $\omega$ . In comparison with the uncompatibilized PP/nylon (75/25) blend, the addition of SEBS-g-MA induced a remarkable increase in  $G'$  at a low frequency, whereas the addition of other copolymers



**Figure 8**  $G'$  of PP/nylon (75/25) blends with or without various compatibilizers (5 phr).

showed no significant change (Fig. 8). In the case of the PP/nylon (75/25) blend compatibilized with SEBS-g-MA, the curve had two steep portions separated by a plateau region of a smaller slope. The high-frequency steep portion was due to the viscoelasticity of the polymer blend itself, and the low-frequency steep portion was due to the interfacial contribution.<sup>24</sup> Thus, we can conclude that this increase in  $G'$  at a low frequency is indicative of strong adhesion between recycled PP and nylon, showing the formation of a specific structure at the interface.

Although a number of dynamic rheological parameters can give useful information for the interpretation of viscoelastic properties, the  $\delta$  value obtained from a rotational rheometer is a very sensitive and effective value for expressing the contribution of a specific structure in viscoelastic behavior.<sup>25–27</sup> Figure 9 exhibits the evolution of  $\delta$  as a function of frequency. Usually,  $\delta$  of a polymer blend without a specific structure



**Figure 9**  $\delta$  of PP/nylon (75/25) blends with or without various compatibilizers (5 phr).

decreases monotonically with frequency as in a PP/nylon (75/25) blend. However, a significant variation of  $\delta$  was found in a low-frequency range with the addition of SEBS-*g*-MA. This could be explained as follows: because of a specific structure that formed at the interface through the chemical reaction that took place between the MA group and the amine end group of nylon, the PP/nylon blend was more solid-like, showing a decrease in  $\delta$  with an inflection point at a low frequency.

### CONCLUSIONS

We investigated the compatibility effect on a recycled PP/nylon (75/25) blend processed with reactive copolymers on the basis of morphological, mechanical, and rheological characteristics. Via SEM investigation, we found improved surface morphologies with regular and fine domains in recycled PP/nylon (75/25) blends compatibilized with copolymers containing MA as a reactive functional group (SEBS-*g*-MA and PP-*g*-MA). Such morphological characteristics were further analyzed with the results of mechanical and rheological tests. However, in contrast to our expectation, a tremendous increase in both the mechanical and rheological properties was obtained only with the addition of SEBS-*g*-MA. This can be interpreted with respect to a specific structure at the interface, showing a strong interfacial adhesion between recycled PP and nylon. To confirm the existence of this structure, we used various dynamic rheological parameters: the Cox–Merz rule,  $G'$ , and  $\delta$ .

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