

# Modification of Rubber Powder with Peroxide and Properties of Polypropylene/Rubber Composites

A. M. Shanmugaraj,<sup>1</sup> Jin Kook Kim,<sup>2</sup> Sung Hun Ryu<sup>1</sup>

<sup>1</sup>College of Environment and Applied Chemistry and Industrial Liaison Research Institute, Kyung Hee University, Yongin, Kyunggido, Korea

<sup>2</sup>Department of Polymer Science and Engineering, Gyeongsang National University, Jinju, Korea

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**ABSTRACT:** Waste tire powder was functionalized in the presence of various concentrations of allylamine and benzoyl peroxide. Fourier transform infrared spectroscopy studies confirmed the presence of allylamine on the surface of the rubber powder. The surface energy of the functionalized rubber powder revealed that the introduction of allylamine onto the rubber powder surface increased the surface activity. Improvements in the tensile strength, elongation at break, and storage modulus were observed for polypropylene/modified rubber powder/maleic anhydride grafted

polypropylene, and this was attributed to an improvement in the compatibility due to the chemical interaction between the rubber powder and compatibilizer. Evidence for the reaction between the rubber surface and compatibilizer was observed in Fourier transform infrared studies. This peroxide-initiated monomer-grafting technique is feasible for large-scale processes. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2237–2243, 2007

**Key words:** compatibility; composites; rubber

## INTRODUCTION

The generation of waste tire powder has increased dramatically in the past 2 decades because of the rapid increase in vehicle usage. Many countries have been paying great attention to the comprehensive utilization of discarded tires to achieve the goals of protecting the environment and recycling resources. Waste tire powder poses a lot of environmental, hygiene, aesthetic, and disposal problems. Most waste and scrap tires have been subjected to incineration or landfilling, and only a small percentage of these waste tires have gone into a variety of reuse/recycle options, such as fillers in asphalt road pavement and raw materials for the production of secondary products, including reclaimed rubber, artificial reefs, and breakwaters.<sup>1</sup> Incineration and landfilling produce severe environmental problems such as air pollution and soil contamination.

The reuse or recycling of waste tire powder has become an important social subject, and the recycling of waste rubber powder by means of blending with polymeric materials has become an important topic in recent years. Waste tire powder-filled thermoplastics partially retain the mechanical properties and reprocessability of thermoplastic polymers, with improve-

ments in properties such as the impact resistance. These thermoplastic polymers include polyethylene, polypropylene (PP), polystyrene, and poly(vinyl chloride).<sup>2–4</sup> In general, the addition of waste tire powder to thermoplastics causes considerable deterioration of the mechanical properties because of the poor compatibility/adhesion between the waste tire powder and polymer.<sup>4</sup> The use of a compatibilizer in waste-rubber powder/thermoplastic composites, such as ethylene/acrylic acid copolymer (EAA)/amine-terminated polybutadiene or EAA/epoxidized natural rubber, improves the impact properties moderately.<sup>5,6</sup>

Surface modifications of waste tire powder are widely used to enhance the compatibility with a polymer matrix. Significant work has been done on the modification of waste tire powder and its influence on the properties of thermoplastic composites.<sup>7–9</sup> McInnis et al.<sup>7</sup> modified ground rubber powder by a gas–solid reaction with chlorine containing gas.<sup>7</sup> The influence of various irradiation techniques on the effective reuse of waste rubber has been extensively studied by various researchers.<sup>10–14</sup> Kim et al.<sup>10</sup> reported that acrylamide-grafted tire powder/maleic anhydride grafted polypropylene (MA-PP)/high-density polyethylene composites had improved mechanical properties.<sup>10</sup> The surface functionalization of rubber powder by an electron-beam treatment resulted in an increase in the oxygen concentration on the surface and led to better adhesion of waste-rubber powder to the polymer matrix.<sup>11</sup> Ultraviolet (UV) energy has been extensively applied to modify the surface properties with monomers and photosensi-

Correspondence to: S. H. Ryu (shryu@khu.ac.kr).

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tizers. Lee and Ryu<sup>12</sup> and Yu and Ryu<sup>13</sup> used acrylamide and glycidyl methacrylate as monomers to modify the surface characteristics of vulcanized styrene-butadiene rubber (SBR) with UV. They found that a photografting reaction with a monomer is an efficient way of modifying the surface characteristics of vulcanized SBR, which is one of the major components of tires. Recently, Shanmugaraj et al.<sup>14</sup> reported the surface modification of waste tire powder with UV in the presence of allylamine and revealed that the mechanical properties of the PP/waste-rubber powder composites significantly improved upon the loading of the UV-modified rubber powder. However, UV monomer grafting is not suitable for large-scale processes.

In this study, rubber powder was treated with an allylamine monomer in the presence of benzoyl peroxide to determine the possibility of using peroxide to functionalize scrapped rubber powder such as waste tire powder. The modified rubber powder was then incorporated into the PP matrix, and its role in the properties of PP/waste rubber powder composites was investigated.

## EXPERIMENTAL

### Materials

Waste rubber powder was obtained from Dong A Tire Co. (Jinju, Korea). The average particle size and size distribution were 300 and 75–800  $\mu\text{m}$ , respectively. Allylamine, used for the surface modification of the rubber powder, was procured from Kanto Chemical Co., Inc. (Tokyo, Japan). Acetone was obtained from Duksan Chemical Co., Ltd. (Seoul, Korea). The polymer was PP (BB110, Samsung Total Chemical Co. Daesan, Korea). Benzoyl peroxide (Aldrich, Yongin, Korea) was used as an initiator, and MA-PP (Polybond 3009, Chemtura Korea, Seoul, Korea) was used as a compatibilizer for the PP/rubber powder composite.

### Sample preparation

Allylamine solutions (0.5, 1.0, 1.25, or 1.5 mol) were prepared by the dissolution of allylamine in 1000 mL of acetone. Rubber powders were soaked in the allylamine solutions for 3 h, and this was followed by 3 h of drying at the ambient temperature; the mixtures were then mixed with benzoyl peroxide dissolved in acetone of various concentrations (0.5, 1.0 and 1.5%) and subjected to stirring at 70°C for 30 min. The rubber powders were designated  $A_{b/c}$ , where suffixes  $b$  and  $c$  represent the allylamine and peroxide concentrations, respectively. PP and MA-PP were melted for 2 min at 200°C, followed by the addition of a calculated amount of the waste-rubber powder to a Brabender plasticorder (Duisburg, Germany) at a speed of

50 rpm, and the mixing was continued for 5 min; 10–80 phr rubber powder on the basis of the weight of PP was mixed with PP, whereas 10–50 wt % MA-PP was added on the basis of the weight of the rubber powder. The PP composite was molded at 200°C for 2 min with a Moore press to prepare tensile sheets 0.15 mm thick.

### Characterization

The unmodified- and modified-rubber powders were characterized with different characterization techniques such as Fourier transform infrared (FTIR) spectroscopy (model 2000, PerkinElmer), thermogravimetric analysis (TGA; model TGA-7, PerkinElmer, Waltham, MA), and surface-energy measurements via the dynamic wicking method.<sup>14</sup> Rubber powder samples were subjected to IR characterization in the range of 4000–400  $\text{cm}^{-1}$ . The spectra were obtained at a resolution of 4.0  $\text{cm}^{-1}$  in the transmission mode. TGA was carried out in the temperature range of 30–700°C at a heating rate of 10°C/min under a nitrogen environment. The rheological properties of the PP/rubber composites were measured with a Rheometrics Stresstech HR mechanical spectrometer (Reologica Instrument AB, Lund, Sweden) in a dynamic mode with a 1% strain at 180°C. FTIR spectra of the PP/rubber composites were taken in the range of 4000–650  $\text{cm}^{-1}$  in the attenuated-total-reflectance mode (model 2000, PerkinElmer) with a zinc selenide crystal. Tensile specimens were punched out from the molded sheets with ASTM Die-C. The test was carried out according to the ASTM D 412-98 method in a Toyo Baldwin universal testing machine (Tokyo, Japan) at a crosshead speed of 50 mm/min at the ambient temperature. The average of three tests was reported, and the results were quite reproducible. Scanning electron microscopy (SEM) studies of tensile-fractured PP/rubber powder composite samples were performed with a Stereoscan 440 (Leica, Cambridge, UK).

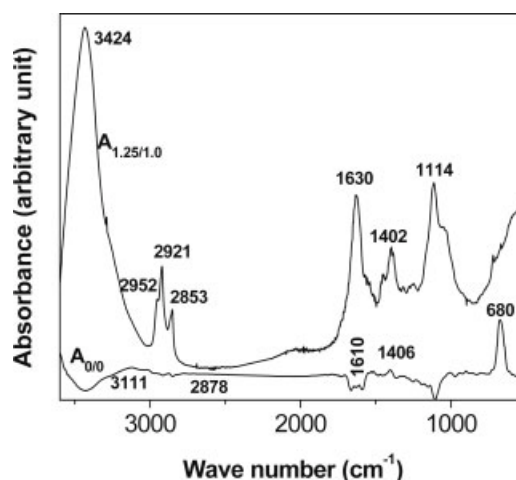


Figure 1 FTIR spectra of  $A_{0/0}$  and  $A_{1.25/1.0}$ .

## RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of the unmodified-rubber powder ( $A_{0/0}$ ) and modified rubber powder ( $A_{1.25/1.0}$ ). The peak at  $3111\text{ cm}^{-1}$  is due to the  $-\text{CH}$  stretching vibration of ring hydrogen present in the styrene group. The peak at  $2876\text{ cm}^{-1}$  corresponds to  $-\text{CH}$  symmetric stretching of the  $>\text{CH}_2$  groups. The small peak observed at  $1610\text{ cm}^{-1}$  and the peaks at  $1318$  and  $680\text{ cm}^{-1}$  are due to  $>\text{C}=\text{C}<$  stretching,

$-\text{C}-\text{C}-$  stretching in the  $-\text{C}-\text{CH}_3$  group, and the ring-deformation vibration of styrene.<sup>1</sup> These peak assignments confirm that the rubber powder used for this study is a blend of natural rubber (NR) and SBR. The new peak at  $3424\text{ cm}^{-1}$  for  $A_{1.25/1.0}$ , corresponding to  $-\text{NH}$  stretching, confirms the presence of allylamine on the rubber powder. The significant improvement in the peak intensity at  $2952$ ,  $2921$ , and  $2853\text{ cm}^{-1}$  indicates the  $-\text{CH}$  asymmetric and symmetric stretching of the  $-\text{CH}_2$  group in the allyl-

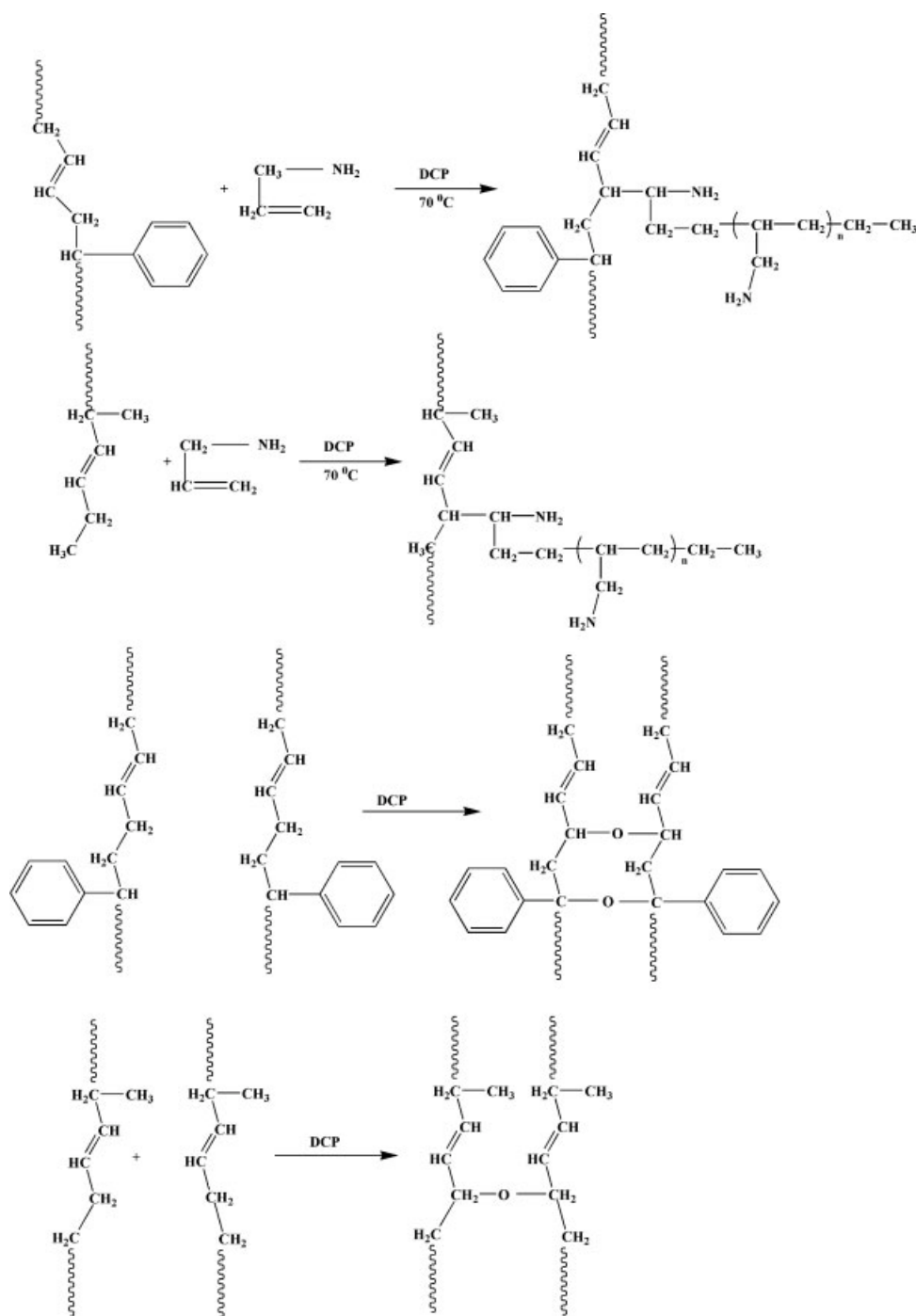
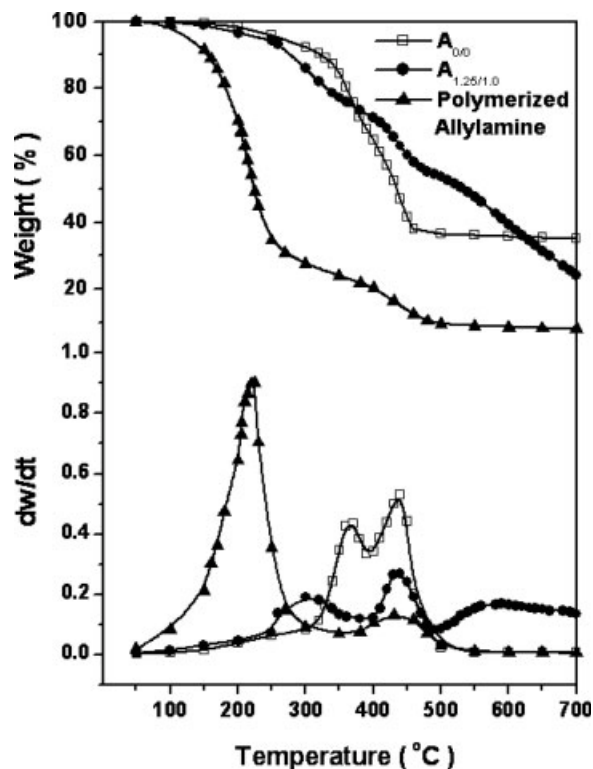


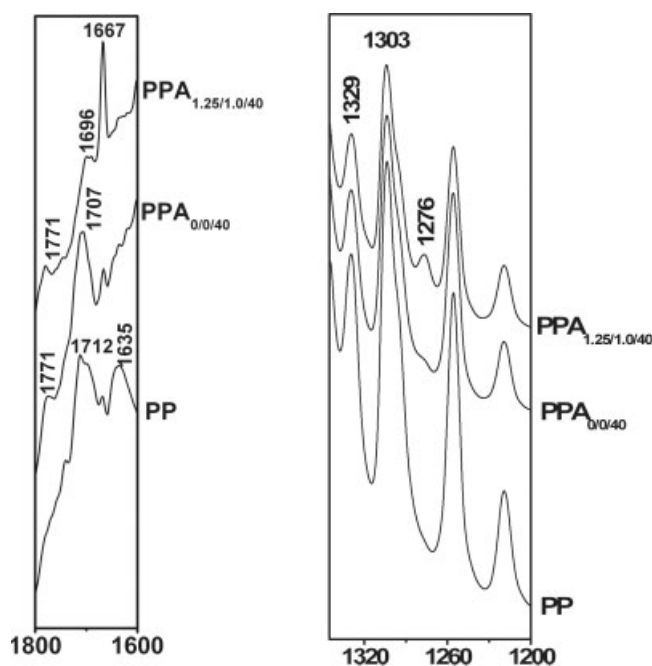
Figure 2 Proposed reaction mechanism for allylamine onto a rubber surface.

amine present on the surface of the rubber powder. The increase in the peak intensity at  $1630\text{ cm}^{-1}$  corresponds to the in-plane deformation of the  $-\text{NH}_2$  group, and the  $>\text{C}=\text{C}<$  stretching of unreacted allylamine corroborates the presence of allylamine on the surface of the rubber powder. The peak at  $1402\text{ cm}^{-1}$ , which corresponds to the bending vibration of the  $-\text{CH}_2$  group, further supports this fact. An increase in the peak intensity at  $1114\text{ cm}^{-1}$  corresponds to  $-\text{COC}-$  stretching existing in the surface of the rubber powder. The absence of a peak at  $680\text{ cm}^{-1}$  in the allylamine-g-rubber powder indicates the coating of allylamine on the surface of the rubber powder. Figure 2 shows the probable mechanism of interaction between the allylamine and rubber powders on the basis of FTIR results. The same reaction scheme can be expected in the NR phase of the waste-tire powder.

The surface energies of  $A_{0/0}$  and  $A_{1.25/1.0}$  are compared to determine the change in the surface features with the modification. The contact angle between the water and rubber powder surface is calculated by the measurement of the equilibrium time with the Washburn equation.<sup>15,16</sup> The dispersive component, polar component, and total surface energy of the unmodified- and modified-rubber powders are determined with the Goodrich-Girifalco equation.<sup>10</sup> Upon subjection to allylamine modification, the dispersive compo-



**Figure 3** TGA and differential thermogravimetry graphs of PA,  $A_{0/0}$ , and  $A_{1.25/1.0}$ .



**Figure 4** FTIR spectra of PP,  $PA_{0/0}$ , and  $PA_{1.25/1.0}$ .

nent of the rubber powder decreases from  $0.74$  to  $0.2\text{ mJ/m}^2$ , whereas the polar component increases from  $22.9$  to  $29.5\text{ mJ/m}^2$ . The total surface energy of the modified rubber powders is higher than that of the unmodified rubber powders, indicating their high surface activity in comparison with the unmodified-rubber powders.

Figure 3 shows TGA and its differential thermograms for  $A_{0/0}$  and  $A_{1.25/1.0}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . For comparison, TGA of polymerized allylamine (PA) is also included in Figure 3. In  $A_{0/0}$ , the onset degradation of the first component begins at  $297^\circ\text{C}$  with the maximum peak at  $380^\circ\text{C}$ , followed by the degradation of the second component starting at  $410^\circ\text{C}$  with the maximum peak at  $462^\circ\text{C}$ ; this indicates that the rubber powder is a blend of NR and SBR.<sup>3</sup> An earlier report on the thermal degradation of components of tires reported the presence of two major degradation peaks at  $375$  and  $440^\circ\text{C}$  that corresponded to the NR and SBR phases.<sup>17</sup> In this study, waste-tire powder exhibits a degradation peak in a similar range, confirming the fact that it is a blend of an NR and SBR system. However, the onset of degradation of the NR and SBR components shifts to lower temperatures in the case of  $A_{1.25/1.0}$ , with the starting degradation temperatures at  $200$  (for the NR phase) and  $400^\circ\text{C}$  (for the SBR phase). Also, the maximum peak of the first degradation step (NR phase) occurs at  $300^\circ\text{C}$  in  $A_{1.25/1.0}$ . The shift of the peak degradation temperature of functionalized rubber to a lower temperature can be attributed to the presence of unreacted peroxide that initiates the reaction at a low temperature.

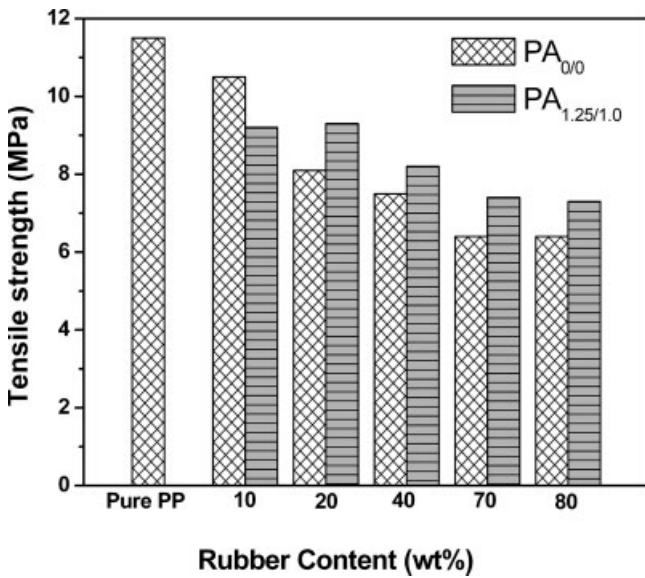


Figure 5 Tensile strength of PP composites with various concentrations of rubber powder.

The FTIR spectra of the PP/rubber powder/MA-PP composite in the specific regions are included in Figure 4. Rubber powder (40 phr) and 50 wt % MA-PP were added on the basis of the PP and rubber powder, respectively. A close examination of the peaks in the region of 1800–1600 cm<sup>-1</sup> shows that the peak at 1712 cm<sup>-1</sup> for pure PP may be due to the >C=O group that forms on the surface because of surface oxidation. For the composite of PP and unmodified-rubber powder (PA<sub>0/0</sub>) with 40 phr rubber powder, the peak at 1772 cm<sup>-1</sup> may indicate the >C=O group due to the anhydride group present in the maleic anhydride group of MA-PP. An increase in the peak intensity at 1772 cm<sup>-1</sup> can be attributed to

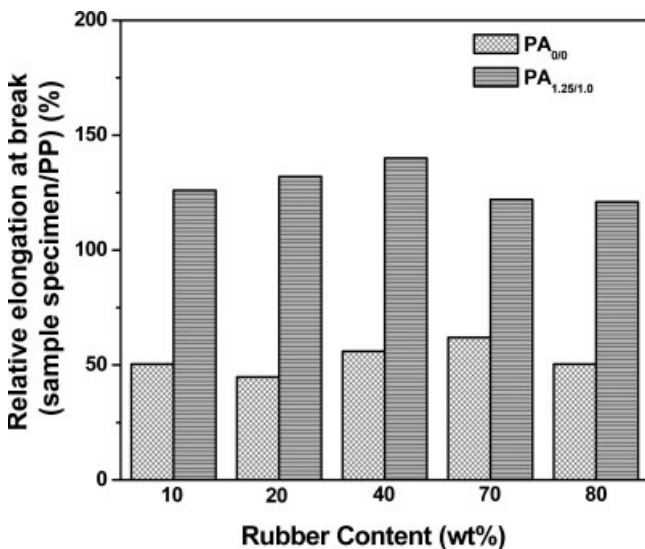


Figure 6 Elongation at break of PP composites with various concentrations of rubber powder.

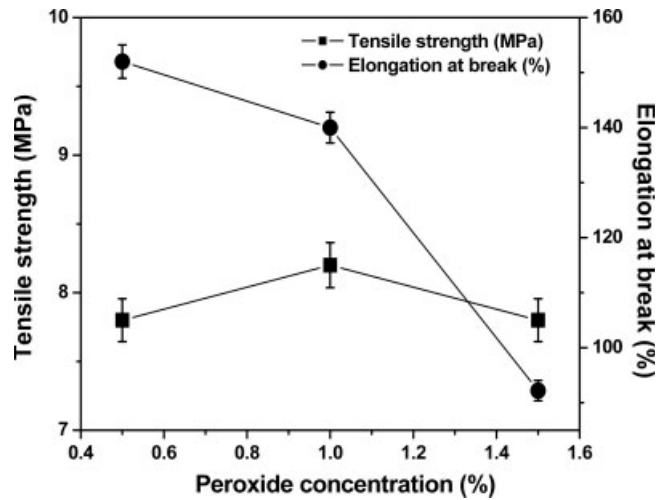


Figure 7 Effect of the peroxide concentration on the mechanical properties of PP composites.

the —C=O stretching of the —CON group that forms because of the chemical interaction between the allylamine-g-rubber powder and MA-PP. This is further confirmed by the appearance of the new peak at 1667 cm<sup>-1</sup> for the PP/functionalized-rubber powder/MA-PP composite (PA<sub>1.25/1.0</sub>) with 40 phr rubber powder, which is due to the —C=O stretching present in the amide. This is further supported by the peak at 1276 cm<sup>-1</sup>, which is due to the —C—N stretching between the blends.

The tensile strength and relative elongation at break of PP/rubber blends with various rubber-powder concentrations are shown in Figures 5 and 6. The relative elongation at break is calculated as the ratio of that of the PP composite to that of pure PP. In this study, rubber powders A<sub>0/0</sub> and A<sub>1.25/1.0</sub> were used, and 50 wt % MA-PP was added on the basis of the rubber powder. The tensile strength of pure PP is 11.5

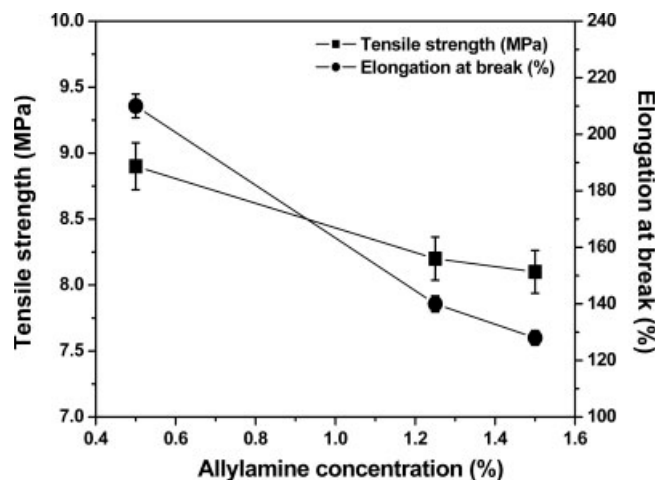


Figure 8 Effect of the allylamine concentration on the mechanical properties of PP composites.

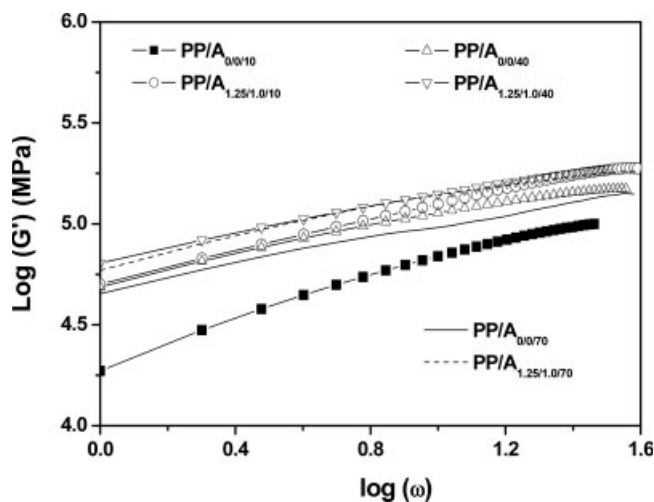


Figure 9 Storage modulus ( $G'$ ) of PP composites.

MPa, and it decreases with increasing rubber powder content. However, the  $PA_{1.25/1.0}$  composite shows a slightly higher value than  $PA_{0/0}$ . The modified-rubber powder improves the elongation behavior of the PP composite significantly. The relative elongation at break of  $PA_{1.25/1.0}$  is twice that of  $PA_{0/0}$ . This can be attributed to the interaction between the amine of the modified rubber and the maleic anhydride of MA-PP. The possible chemical interaction between the allylamine modified rubber powder and the maleic anhydride of MA-PP forms a coating over the surface of the rubber powder, leading to the compatibilization and dispersion of the waste-rubber powder in the PP matrix, and thereby improves the properties of the composite.

Modified rubbers with various peroxide concentrations ( $A_{1.25/0.5}$ ,  $A_{1.25/1.0}$ , and  $A_{1.25/1.5}$ ) were used to determine the effect of peroxide on the mechanical

properties of PP composites with 40 phr rubber powder on the basis of PP. Figure 7 shows the variation of the tensile strength and elongation at break of the PP composites. The tensile strength shows more or less similar values, regardless of the peroxide concentration within the experimental range, whereas the elongation at break decreases with increasing peroxide concentration. From the results, it is clear that even at low peroxide concentrations, the allylamine grafted onto the rubber surface forms a uniform coat that is responsible for the high tensile strength and elongation at break of the PP composites. The significant decrease in the elongation at break with increasing peroxide concentration is probably due to the degradation of PP, which is due to the migration of free peroxide to the plastic phase.

Figure 8 shows the tensile properties of PP composites with various allylamine concentrations used to modify the rubber powder at a 1.0 wt % peroxide concentration ( $A_{0.5/1.0}$ ,  $A_{1.0/1.0}$ , and  $A_{1.5/1.0}$ ). Rubber powder (40 phr on the basis of PP) was added. The tensile strength and elongation at break decrease with increasing allylamine concentration. At lower allylamine concentrations, it forms a thin coating over the surface, which can chemically interact with MA-PP. At a high allylamine concentration, however, the thickness of the allylamine coating over the surface will be great, and this may result in chain slippage during extension and thereby reduce the tensile strength and elongation at break.

The variation of the storage modulus as a function of frequency is shown in Figure 9. PP composites with 10, 40, or 70 wt % rubber powder ( $A_{1.5/1.0}$ ) were used. The composites of PP and modified rubber powder exhibit higher storage moduli than the composite of PP and unmodified rubber powder over the range of frequencies studied at all weight percen-

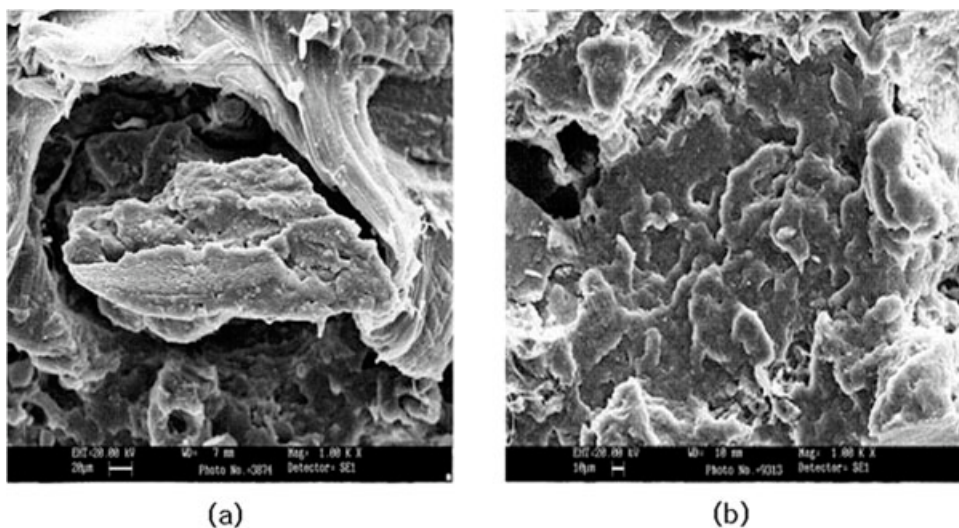


Figure 10 SEM photographs of tensile-fractured surfaces of (a)  $PA_{0/0}$  and (b)  $PA_{1.25/1.0}$ .

tages. The increase in the storage modulus of the surface modified rubber composites can be attributed to the increase in the interfacial interaction between allylamine of the rubber surface and maleic anhydride of MA-PP. Similar behavior has been reported for compatibilized polymer systems.<sup>18,19</sup> SEM photographs of the fracture surfaces of PA<sub>0/0</sub> and PA<sub>1.25/1.0</sub> with 40 phr rubber powder are shown in Figure 10(a,b), respectively, and they provide more evidence about the interactions in PA<sub>1.25/1.0</sub>.

### CONCLUSIONS

The surface of waste rubber powder can be functionalized with allylamine in the presence of benzoyl peroxide, and then the functionalized powder can be blended with PP. FTIR results show that allylamine can be successfully grafted onto a rubber powder surface. The functionalization of the powder surface has also been confirmed by the increasing polar surface energy. The tensile strength and elongation at break of the PP/modified rubber powder/compatibilizer composite are higher than those of the PP/pristine rubber powder/compatibilizer composite. The elongation at break decreases with increasing peroxide concentration, whereas a similar tensile strength can be observed. The tensile strength and elongation at break decrease with increasing allylamine concentration. The storage modulus of the PP/modified rubber powder/compatibilizer composite is higher than that of the PP/pristine rubber powder/compatibilizer composite, and this can be attributed to the reaction between allylamine on the powder surface and maleic

anhydride in the compatibilizer. This has been confirmed by the FTIR study.

### References

1. Wu, J. U.; Vallabhapuram, R. *Hazardous Waste Management Handbook*; PTR Prentice Hall: Upper Saddle River, NJ, 1994.
2. Bhattacharya, S. N.; Sbarski, I. *Plast Rubber Compos Process Appl* 1998, 27, 317.
3. Tipanna, M.; Kale, D. D. *Rubber Chem Technol* 1997, 70, 815.
4. Phadke, A. A.; De, S. K. *Polym Eng Sci* 1986, 26, 1079.
5. Pramanik, P. K.; Baker, W. E. *Plast Rubber Compos Process Appl* 1995, 24, 229.
6. Duhaime, J. R. M.; Baker, W. E. *Plast Rubber Compos Process Appl* 1991, 15, 87.
7. McInnis, E. L.; Bauman, B. D.; Williams, A. U.S. Pat. 5,506,283 (1996).
8. Bagheri, R.; Williams, A.; Pearson, R. A. *Polym Eng Sci* 1997, 37, 245.
9. Bauman, B. D. *Rubber World* 1995, 5, 30.
10. Kim, J. I.; Ryu, S. H.; Chang, Y. W. *J Appl Polym Sci* 2000, 77, 2595.
11. Rajalingam, P.; Sharpe, J.; Baker, J. E. *Rubber Chem Technol* 1993, 66, 664.
12. Lee, K. I.; Ryu, S. H. *Elastomer* 1998, 33, 363.
13. Yu, J. J.; Ryu, S. H. *J Appl Polym Sci* 1999, 73, 1733.
14. Shanmugharaj, A. M.; Kim, J. K.; Ryu, S. H. *Polym Test* 2005, 24, 739.
15. Inagaki, K.; Tasaka, S.; Abe, H. *J Appl Polym Sci* 1992, 46, 595.
16. Vanoss, C. J.; Giese, R. F.; Li, Z.; Murphy, K.; Norris, J.; Chaudhury, M. K.; Good, J. J. *J Adhes Sci Technol* 1992, 6, 413.
17. Williams, P. T.; Besler, S. *Fuel* 1995, 9, 1277.
18. Fowkes, M. In *Treatise on Adhesion and Adhesives*; Patrick, R. L., Ed.; Marcel Dekker: New York, 1967.
19. George, S.; Neelakantan, N. R.; Varughese, K. T.; Thomas, S. *J Polym Sci Part B: Polym Phys* 1997, 35, 2309.