

Mechanical and Dynamic Mechanical Properties of Waste Rubber Powder/HDPE Composite

J. I. KIM,¹ S. H. RYU,¹ Y. W. CHANG²

¹ School of Environment and Applied Chemistry, Kyung Hee University, Yongin, Kyunggi-Do 449-701, South Korea

² Department of Chemical Engineering, Han Yang University, Ansan, Kyunggi-Do, South Korea

Received 24 August 1999; accepted 15 November 1999

ABSTRACT: Mechanical and dynamic mechanical properties of a waste rubber powder-filled high-density polyethylene (HDPE) composite are investigated. Rubber powder is surface-modified with acrylamide (AAM) using ultraviolet. Rubber powder and HDPE are extruded using a single-screw extruder and maleic anhydride-grafted polypropylene is added as a compatibilizer to improve the adhesion between rubber powder and HDPE. The tensile stress and strain of AAM-grafted rubber powder/compatibilizer/HDPE composites always exhibit higher values than those of unmodified rubber powder/HDPE composites. Surface modification of rubber powder is shown to decrease the magnitude of the $\tan \delta$ of the HDPE composite. Higher values of the notched Izod impact strength of a surface-modified rubber-filled composite is observed compared to those of unmodified rubber-filled composite. Experimental results show that acrylamide-grafted rubber powder reacts with maleic anhydride and it results in improved mechanical properties of the HDPE composite. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2595–2602, 2000

Key words: waste rubber powder; HDPE composite; acrylamide; UV photograft

INTRODUCTION

Scrap rubbers, especially scrap tires, cause significant environmental problems. As postconsumer waste, those have few uses; most are landfilled or incinerated. However, these methods are not appropriate to handle waste rubber, because these methods result in other environmental problems such as air pollution or they float to the surface over time. Reutilization technology of waste rubber, especially scrap tire powder, has been widely investigated as an alternative method.

Recently, a surface-modification technique was used for recycling scrap rubber.^{1,2} This approach

consists of modifying the exterior surface of scrap rubber that has been finely ground. Ground waste rubber powders are surface-modified to facilitate combination with other types of polymers.³ McInnis et al. chlorinated waste rubber powders by a gas–solid reaction with chlorine-containing gas.¹ Bagheri et al. used surface-modified waste rubber powders for toughening epoxy polymers.² The redox method and grafting by gamma irradiation were also used to reuse waste rubber.⁴ The technical and commercial feasibility of using modified waste rubber powders as a filler with a polymer has been demonstrated by many applications, such as in roofing material and shoe soles.

In general, photografting is performed by irradiating the light on the polymer to modify the surface properties of a polymer in the presence of a solvent-containing monomer. The energy

Correspondence to: S. H. Ryu.

Journal of Applied Polymer Science, Vol. 77, 2595–2602 (2000)
© 2000 John Wiley & Sons, Inc.

sources commonly used are high-energy electrons, X-rays, UV, and visible light. Monomers, such as glycidyl methacrylate, acrylic acid, and acrylamide, have been used for a photografting reaction. Lee and Ryu⁵ and Yu and Ryu⁶ used acrylamide and glycidyl methacrylate as a monomer to modify the surface characteristics of vulcanized styrene butadiene rubber (SBR) using UV. They found that photografting reaction with a monomer was an efficient way to modify the surface characteristics of vulcanized SBR, which is one of major components of tires.

HDPE is one of the large-consumption polymers and it is difficult to make a polymer blend or a composite due to its nonpolar characteristics. Because the nonpolar characteristics of HDPE often results in poor interfacial adhesion properties with other materials, a third material is used to increase the compatibility between the two components. For example, fillers are surface-treated with coupling agents for a composite and a compatibilizer is added for polymer blends. Coupling agents are used to promote adhesion between organic polymers and inorganic reinforcements and are known to improve the properties of polymeric composite.⁷ Maleic anhydride (MAH)-modified polyolefin is a widely used compatibilizer for polyolefin/polyamide blends^{8,9} and it enhances the compatibility between polyolefin and polyamide through the reaction between the amine groups of polyamide and MAH.

In this study, photografting of acrylamide (AAM) onto waste rubber powder was carried out to modify the surface characteristics of the waste rubber powder, and surface-modified waste rubber powders were melt-blended with high-density polyethylene (HDPE) using a single-screw extruder. To increase the compatibility between waste rubber powder and HDPE, MAH-modified polypropylene was added to induce a reaction between MAH and surface-photografted AAM of waste rubber powders and this interfacial reaction is expected to enhance the compatibility between HDPE and waste rubber powders. The aim of this work was to investigate the possibilities of a photografting surface-modification technique for the reutilization of waste rubber powders as a filler in a polymer composite. Mechanical and dynamic mechanical properties of an HDPE/surface-modified rubber powder composite were measured for this purpose.

EXPERIMENTAL

Materials

The rubber powders used were GF-80TM from Rouse Rubber Industries, Inc. (Vicksburg, MS). The average rubber powder size and its distribution were 100 and 20–250 μm , respectively. Its composition was rubber/carbon black/organics/others (53/27/12/8 wt %). AAM was supplied by Junsei (Japan). Benzophenone (BP) was used as a photoinitiator. The monomer and photoinitiator were used as received without any purification. The polymer used was HDPE (Yuzex 8800TM, Yukong) (Seoul, Korea). MAH-grafted polypropylene (PolybondTM 3009, Uniroyal) was used as a compatibilizer for the HDPE/rubber powder composite.

Sample Preparation

Rubber powders were immersed in a 1.25 mol AAM/0.125 mol BP/1000 mL acetone solution for 3 h. After immersion, the powders were dried for 3 h at ambient temperature to remove acetone. The dried powders were placed in a beaker and UV-irradiated for 30 min under high-speed mixing conditions and a nitrogen atmosphere. UV-irradiated rubber powders were washed with acetone and distilled water to remove the ungrafted components as described in our previous work.⁵ A 400-W medium-pressure mercury lamp was used for the photografting reaction. Due to the difficulties of measurement, study of the degree of the AAM graft onto the rubber powders was not carried out. Lee and Ryu, however, reported the efficient photografting reaction of AAM onto a vulcanized styrene–butadiene rubber sheet using UV in their previous work.⁵ Irradiated rubber powders, HDPE, and PolybondTM 3009 were mixed together for 5 min and fed into an extruder. A single-screw extruder (Sin-A, diameter = 20 mm and $L/D = 24$) was used. The barrel temperature profile was 30/210/220/220/220°C and the screw speed was 30 rpm.

Characterization

Stress–strain measurements were performed on a Toyo–Baldwin tensile tester at room temperature at an extension rate of 100 mm/min. The test specimen was a fiber type as extruded and the diameter was measured for each measurement. Compression-molded samples with 3 mm thick-

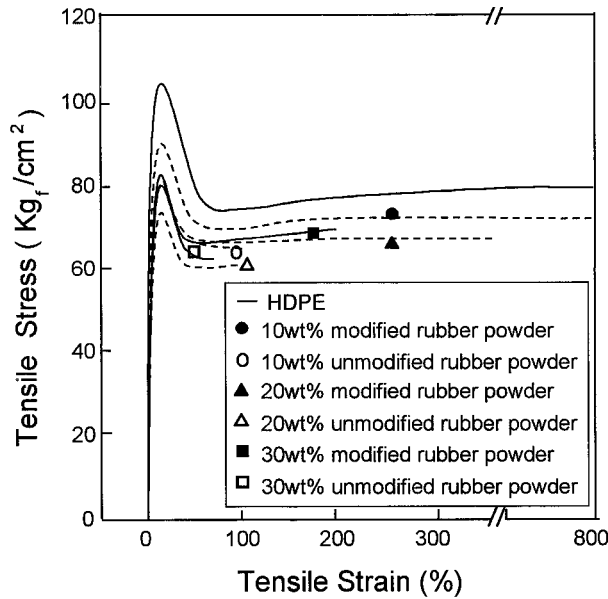


Figure 1 Tensile stress–strain graphs for HDPE and HDPE/rubber composites.

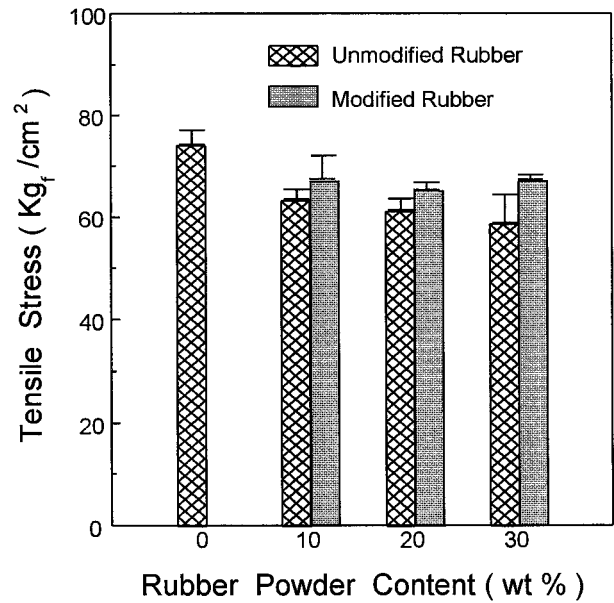


Figure 2 Effect of rubber powder content on the tensile stress for HDPE/rubber powder composites.

ness were used for notched Izod impact strength (Toyoseiki) and Rockwell hardness (Wilson) measurement. More than three different samples were used to obtain the properties and results were quite reproducible.

Dynamic mechanical property measurements on the HDPE/rubber composite were carried out using a DMA 2980 measuring device (DuPont) in the temperature range of -100 to 100°C with a heating rate of 2 K/min . The frequency was 1 Hz and the amplitude was 5 microns .

A scanning electron microscope (Stereoscan 40, Leica Cambridge) was used to examine the surface of the notched Izod impact-fractured specimen. The fractured surface was sputter-coated with gold.

RESULTS AND DISCUSSION

Stress–Strain Behavior

In the case of a more than 30 wt \% rubber content composite, the extrudate surface becomes irregular even for the AAm-grafted rubber-filled composite. Also, it is difficult to operate the extruder in a normal condition due to a die-clogging phenomenon during extrusion. Thus, the rubber content of the composite is limited to 30 wt \% .

Figure 1 shows the typical stress–strain behav-

ior of several specimens. The yield tensile stress decreases with addition of the rubber powder. In general, the AAm-grafted rubber powder-filled HDPE composite shows a higher yield stress than that of the unmodified rubber powder-filled HDPE composite. Figures 2 and 3 show the ten-

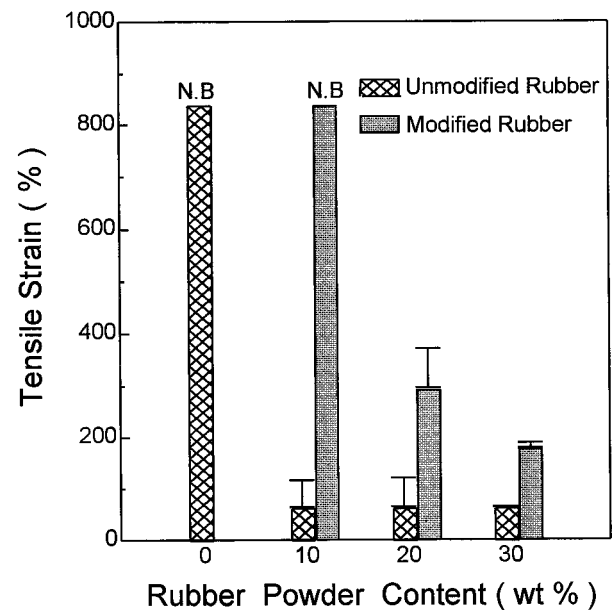


Figure 3 Effect of rubber powder content on the tensile strain for HDPE/rubber powder composites.

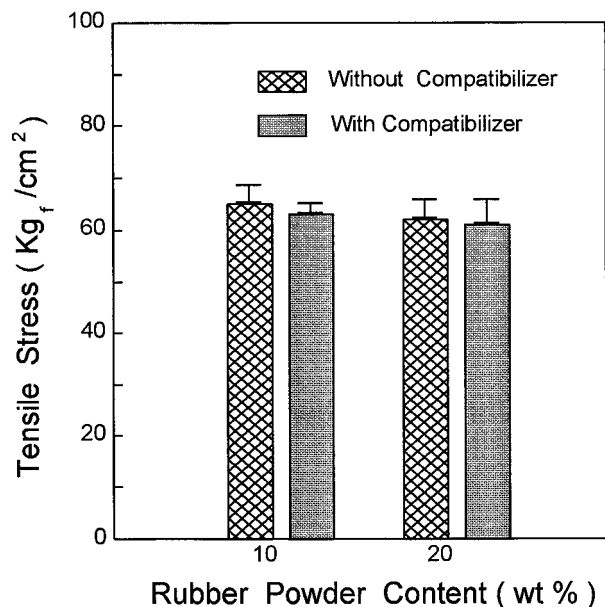


Figure 4 Effect of compatibilizer on the tensile strain for the unmodified rubber powder/HDPE composite.

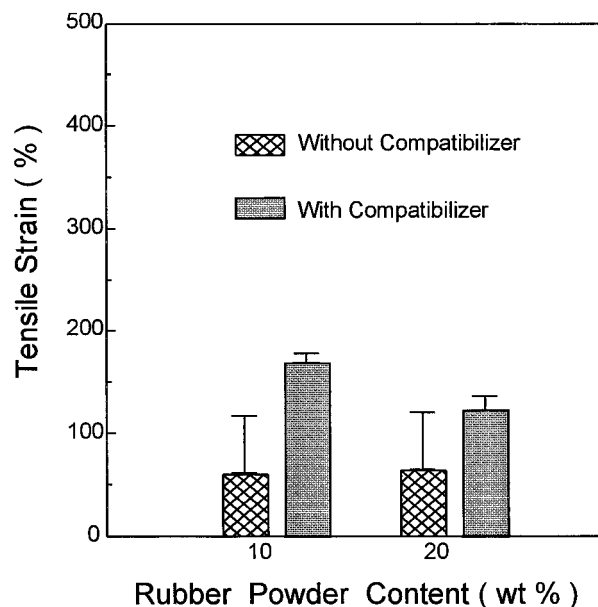


Figure 5 Effect of compatibilizer on the tensile strain for the unmodified rubber powder/HDPE composite.

sile stress and tensile strain at break of the HDPE composite filled with AAm-grafted or unmodified rubber powders. The tensile strain is measured up to 830% due to the limit of the tensile tester. For the AAm-grafted rubber powder-filled system, 50 wt % commercial MAH-grafted polypropylene (Polybond™ 3009) based on the amount of rubber powder was added. The tensile strain and stress decrease with increasing rubber content for both the AAm-grafted and the unmodified rubber powder-filled composites. However, the magnitude of the tensile strain and stress is significantly different depending on the modification of the rubber powder. HDPE composites filled with AAm-grafted rubber powder always show a higher tensile stress and strain than that of the unmodified rubber powder-filled composite within experimental rubber content range. It was observed that the AAm grafting effect is more significant for tensile strain. For the unmodified rubber powder-filled composite, a significant decrease of the tensile strain is observed even with the addition of 10 wt % rubber powder, while the AAm-grafted rubber powder-filled composite shows no break for a 10 wt % rubber powder content and 300–400% even for a 20 wt % content. Different tensile strain behavior between two composites can be attributed to the difference of bonding between the rubber powders and HDPE.

HDPE is a well-known typical nonpolar material. So, the interaction between HDPE and unmodified rubber powders is not expected and it results in poor bonding between the rubber powder and HDPE. A significant drop in tensile

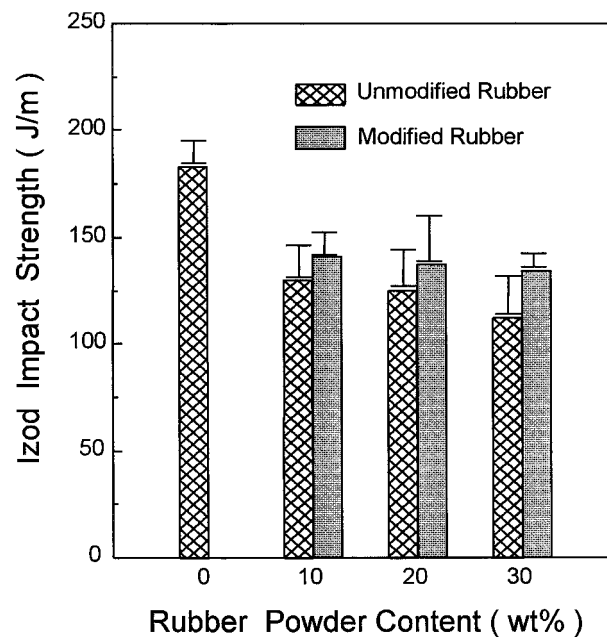


Figure 6 Notched Izod impact strength of HDPE/rubber powder composites as a function of rubber content.

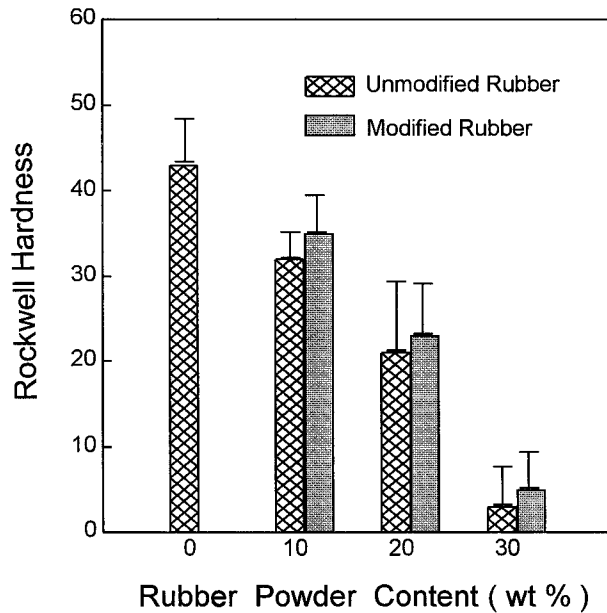


Figure 7 Rockwell hardness of HDPE/rubber powder composites as a function of rubber content.

strength and strain of the unmodified filler-reinforced polymers was already observed by many investigators.^{10,11} In general, mineral fillers were treated with a coupling agent to improve the bonding between the polymer matrix and the filler and compatibilizers were added to enhance the compatibility between the matrixes for polymer blends. A compatibilizer can be either nonreactive or reactive with the matrix. It has been known that the amine group is very reactive with MAH and this reaction system has been widely used to increase the compatibility for various polymer blend systems, especially for polyolefin/polyamide blends. Thus, the reaction between the amine group of the AAm of the AAm-grafted rubber powder and the MAH of the compatibilizer can occur during extrusion and this interfacial reaction is expected to increase the compatibility between HDPE and the rubber powders.

To investigate the effect of surface modification of rubber powder on the tensile strength and strain, a 50 wt % compatibilizer based on the amount of the rubber powder was melt-blended with the HDPE/unmodified rubber powder. As shown in Figures 4 and 5, the tensile strain increases to 100%, while the tensile strength rather slightly decreases by the addition of the compatibilizer. The result shows that the addition of the compatibilizer affects the tensile properties, espe-

cially the tensile strain, even for the unmodified rubber powder-filled composite. However, the magnitude of the increase of the tensile strain in the unmodified rubber/HDPE/compatibilizer composite is much lower than that of the AAm-grafted rubber/HDPE/compatibilizer composite. This remarkable difference can be attributed to the existence of the reaction between the compatibilizer and rubber powders. It is observed that the AAm-grafted rubber/HDPE composite without the compatibilizer shows similar tensile properties to those of the unmodified rubber powder/HDPE composite. This also supports that the improvement of the tensile properties of the AAm-

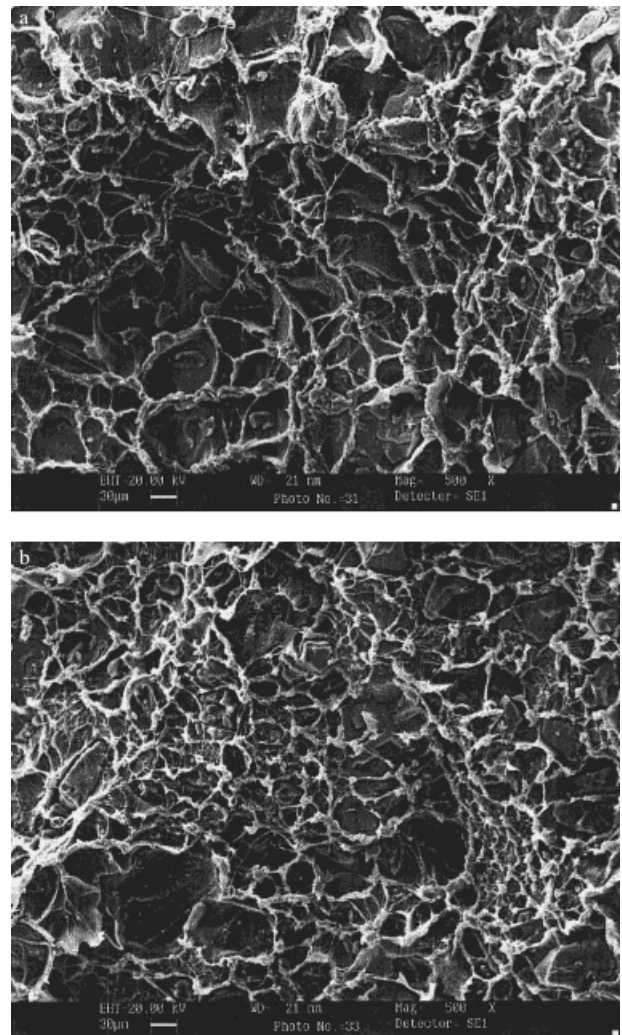


Figure 8 Electron micrographs of fractured surface of (a) HDPE/20 wt % surface-modified rubber/compatibilizer and (b) HDPE/20 wt % unmodified rubber powder composite.

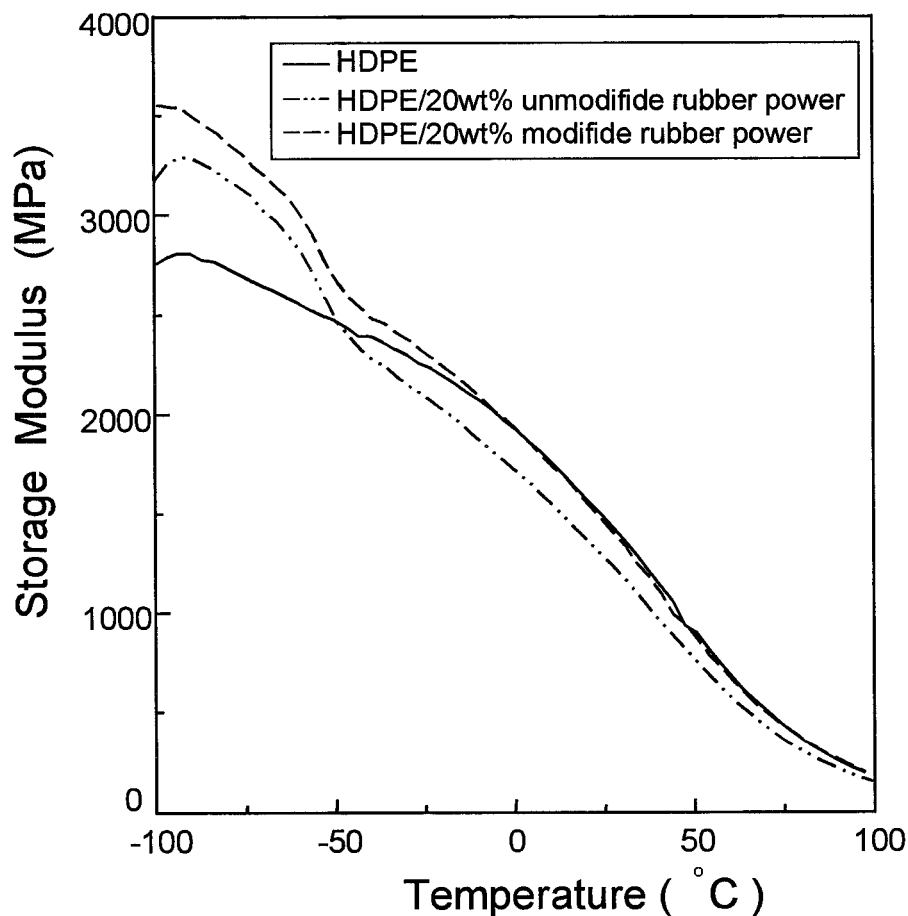


Figure 9 Variation of storage modulus of HDPE and HDPE/rubber powder composites as a function of temperature.

grafted rubber/HDPE/compatibilizer composite is related to the interfacial reaction between the AAm-grafted rubber powder and the compatibilizer.

Figure 6 shows the notched Izod impact strength as a function of the rubber powder content. It decreases with an increasing rubber powder content for both composites. The impact strength of the AAm-grafted powder-filled composite shows higher values than those of the unmodified powder-filled system and this is also attributed to the bonding effect between rubber powders and the compatibilizer. The AAm-grafted powder-filled composite also shows higher Rockwell hardness within the experimental range (Fig. 7).

Electron Microscopy

Figure 8(a,b) shows scanning electron micrographs for the 20 wt % unmodified rubber/HDPE

and 20 wt % modified rubber/HDPE/compatibilizer composites, respectively. It is observed that many rubber powders still remain on the fractured surface of the modified rubber powder-filled composite, while few rubber powders are found in the unmodified rubber powder-filled composite. The fractured surface morphology difference of the two samples is dependent on the existence of an interfacial reaction between the AAm of the modified rubber powder and the MAH of the compatibilizer and it agrees with the trends of the mechanical properties as discussed above.

Dynamic Mechanical Property

To understand the effect of surface modification on the properties of the composite, one must examine the interphase characteristics and it can be well described by dynamic mechanical analysis. The variation of the storage modulus as a function of the temperature of HDPE and the 20 wt %

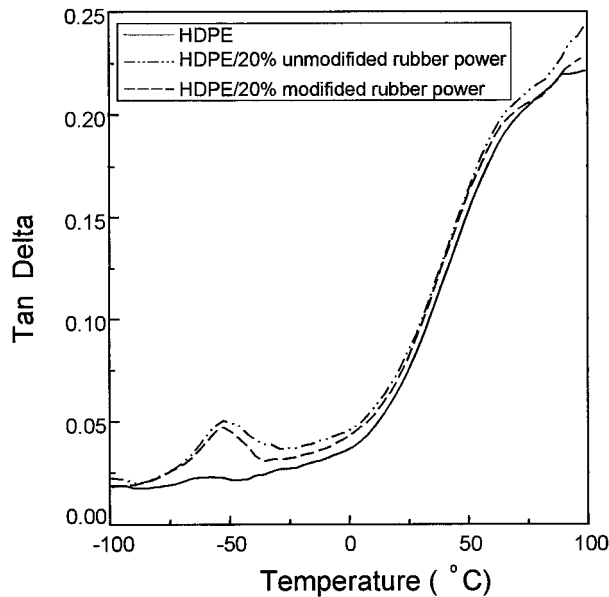


Figure 10 Temperature dependence of the $\tan \delta$ of HDPE and the HDPE/rubber powder composites.

rubber powder-filled composites is shown in Figure 9. With the addition of rubber powders, the storage modulus at low temperature is increased and, also, the surface-modified rubber powder-filled composite shows higher values of the storage modulus than those of an unmodified rubber powder-filled composite. The increase in the storage modulus of the surface-modified rubber powder composite can be attributed to increase of the interfacial interaction between the AAm of the surface-modified rubber powder and the MAH of the compatibilizer via interfacial reaction. Similar behavior was reported in compatibilized polymer blends.^{12,13}

Figure 10 presents typical loss tangent data from dynamic mechanical experiments for HDPE and the 20 wt % rubber powder-filled composites. In this figure, the damping factor, $\tan \delta$, is plotted as a function of temperature at 1 Hz. The $\tan \delta$ peak is not observed for HDPE, while the rubber powder-filled composites show the $\tan \delta$ peak at -55°C , which indicates the glass transition temperature of the rubber powder. It is observed that the surface-modified rubber powder-filled composite shows lower values of $\tan \delta$ than those of the unmodified rubber powder-filled composite.

Powder-polymer friction, where there is essentially no adhesion at the interface and excess damping in the polymer near the interface because of induced thermal stresses or changes in

polymer conformation, results in a high value of $\tan \delta$,¹⁴ indicating that if there were good interactions between the rubber powders and the polymer and if the powders were well dispersed in the polymer matrix, there should be a decrease in the damping factor. Thus, the results of dynamic mechanical analysis also give a clue that rubber powder-polymer interactions exist for a surface-modified rubber system and, at the same time, it probably enhances the uniform dispersion of the rubber powders.

From the results of dynamic mechanical analysis, SEM, and mechanical property measurements, it can be concluded that AAm-grafted rubber powder induces an interfacial reaction with a reactive compatibilizer and it results in improved mechanical properties of an HDPE/rubber powder composite.

CONCLUSIONS

Photografting surface modification of rubber powder was investigated for its use as a filler for HDPE. UV was used for photografting and the monomer and photoinitiator used were AAm and BP, respectively. Surface-modified rubber powders were extruded with HDPE using a single-screw extruder. MAH-grafted polypropylene was used as a reactive compatibilizer to induce a reaction with the AAm of the modified rubber powder. Tensile and impact properties were decreased with addition of rubber powders irrespective of the surface modification of the rubber powder. However, it was observed that the AAm-grafted rubber powder/HDPE/compatibilizer composite shows better mechanical properties compared to the HDPE/unmodified rubber powder composite. Especially, the effect of surface modification is significant for the tensile strain property. These are attributed to the improved compatibility between the AAm-grafted rubber powder and HDPE through an interfacial reaction by the compatibilizer. Dynamic mechanical analysis also showed improved rubber-polymer interface behavior for the surface-modified rubber powder/HDPE/compatibilizer composite. Experimental results showed that photografting of AAm onto rubber powder using UV is a simple and efficient recycling method of waste rubber powder which can be used as a filler with polymeric materials without loss of physical properties.

REFERENCES

1. McInnis, E. L.; Bauman, B. D.; Williams, A. U.S. Patent 5 506 283, 1996.
2. Bagheri, R.; Williams, M. A.; Pearson, R. A. *Polym Eng Sci* 1997, 37, 245.
3. Bauman, B. D. *Rubb World* 1995, May, 30.
4. Adam, G.; Sebenik, A.; Osredkar, U.; Veksli, Z.; Ranogajec, F. *Rubb Chem Tech* 1990, 63, 660.
5. Lee, K. I.; Ryu, S. H. *Elastomer* 1998, 33, 363.
6. Yu, J. J.; Ryu, S. H. *J Appl Polym Sci* 1999, 73, 1733.
7. Plueddemann, E. *Silane Coupling Agents*; Plenum: New York, 1982.
8. Ide, F.; Hasagawa, A. *J Appl Polym Sci* 1974, 18, 963.
9. Borggreve, R. J. M.; Gaymans, R. J. *Polymer* 1989, 30, 71.
10. Boria, M. S.; Chaffey, C. E. *Polym Eng Sci* 1977, 17, 715.
11. Okunu, K.; Woodhams, R. T. *Polym Eng Sci* 1975, 15, 308.
12. George, S.; Neelakantan, N. R.; Varughese, K. T.; Thomas, S. *J Polym Sci Part B Polym Phys* 1997, 35, 2309.
13. Holsti-Miettinen, R. M.; Seppala, J. V.; Ikkala, O. T.; Reima, I. T. *Polym Eng Sci* 1994, 34, 395.
14. Nielsen, I. E. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, 1974.