Dynamic Mechanical Properties of Particle-Reinforced EPDM Composites

M. S. Sohn,[1] K. S. Kim,[1] S. H. Hong,[1] J. K. Kim[2]

[1]*Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusung-Dong, Yusong-Gu, Taejon 305-701 Korea*
[2]*Department of Polymer Engineering, GyeongSang National University, Gayang-Dong 900, Chinju, GyeongSang Nam-Do 660-701, Korea*

Received 4 November 2001; accepted 5 June 2002

ABSTRACT: The dynamic mechanical property of particle-reinforced ethylene–propylene–diene monomer (EPDM) matrix composites has been studied by using a dynamic mechanical thermal analyzer (DMTA). The individual composite has been reinforced with the various reinforcing particles as follows: silicon carbide particles (SiCps) of 60 μm in average diameter with various volume fractions (i.e., 10–40%); copper (Cu) and aluminum (Al) particles with 20 vol %; and SiCps with 6 and 36 μm in different average diameters with 20 vol % over the total composite volume. It is shown from the experimental results that the dynamic elastic modulus values increase and the composites with 40 vol % SiCps exhibit higher tan δ values through the entire rubbery phase after the glass transition region compared with the composites with lower particle volume percentages. This shows that the composites with 20 vol % Cu particles have the higher dynamic elastic modulus but the lower peak tan δ value than the composites with other particles of 20 vol % do. Scanning electron microscopy results show that the effective particle volume in the composite with Cu particles is higher than the other composites, although the same particle volume fraction of 20% has been used. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1595–1601, 2003

Key words: tan δ; damping property; dynamic elastic modulus; SiCp/EPDM composite; Cu/EPDM composite; Al/EPDM composite

INTRODUCTION

The ethylene–propylene–diene monomer (EPDM) rubber compound is being increasingly demanded in many engineering areas due to its excellent electrical property and oxidation-resistance—e.g., automobile and electrical applications.[1] Since the EPDM has a viscoelastic nature as in other polymeric materials, it has a strong dependence of dynamic mechanical behavior on temperature and frequency.[2] The EPDM compound is often reinforced with the various particles (such as carbon blacks, silica, glass beads, etc.) because of its low stiffness and low tensile strength (i.e., 6.8 and 12.5 MPa, respectively).[3–5] When the particles are incorporated into the matrix material to produce composites, the interaction between particles and matrix (i.e., interface behavior) is an important factor to influence the composite property in addition to the properties of the particle and the matrix material, respectively.[5] Also, continuous break-up and rearrangement of particles take place due to the dynamic loads applied to the composite specimens. All these factors affect the viscosity change and dynamic elastic moduli of the composites.

Although the particles such as carbon black have been used extensively as particle reinforcements,[6] it is not reported that the SiCps have been used with the EPDM matrix composites. It is known that, as the difference between the stiffness values of the particle and the matrix and that between densities are larger, the more significant effect on damping can be obtained owing to the increased scattering effect.[7] (The scattering effect can be indirectly evaluated by measuring the ratio of reflection and transmission wave to the input wave, e.g., by using a pulse/echo method.) The particles, in turn, are expected to contribute to the increase of phase angle (i.e., tan δ) in the rubbery phase of the matrix material beyond the glass transition temperature (T_g).

Once the damping property of polymers is evaluated by measuring dynamic storage and loss modulus values based on the force–frequency principle, it can be a valuable indication for other material properties that can be expressed in energy, e.g., acoustic energy. In fact, polymers are preferably used in noise and vibration damping applications.[8,9] It therefore can be said that the high noise damping and the high acoustic

Correspondence to: M. S. Sohn, on leave during 2001 from Department of Mechanical and Materials Engineering, the University of Western Australia, 35 Stirling Hwy, Crawley 6009, WA, Australia (min@mech.uwa.edu.au).

Contract grant sponsor: Agency for Defense Development, Jinhae, Korea.

Journal of Applied Polymer Science, Vol. 87, 1595–1601 (2003)

attenuation take place in the region where the high tan δ values appear.

Attempts have been made to examine the compatibility of pure EPDM rubber compound and SiCp/EPDM composite materials for the application of acoustic sensor backing materials from the viewpoint of the dynamic mechanical property.[10] The backing material is located between the SONAR arrays equipped in the head part of underwater weapon system. The acoustic property of the backing material must be satisfied with remarkably high acoustic attenuation at a given frequency range. In the selection of a promising candidate material for the backing material, several significant factors must be carefully considered, e.g., T_g, tan δ, Young's modulus, and density. The T_g is especially a very important parameter because polymer chains show a significant mobility, and thus damping property (e.g., tan δ and loss modulus values) can be maximal near at T_g. This implies that the highest absorption of either mechanical or acoustic energy is attained. In order to acquire the maximal damping effect from the material, it is well known that Young's modulus and density of the matrix material must be low because highly dense material transmits the sound wave with high velocity—that is, being of low damping property.[7]

This paper focuses on the effects of particle volume fractions, particle size, and different particle types on dynamic mechanical properties of particle-reinforced EPDM composites using a dynamic mechanical thermal analyzer (DMTA). Also, microstructures of the fracture surface of the composites were observed by using a scanning electron microscope (SEM) to examine the morphology of the particles and the interaction between the particles and the EPDM matrix material.

MATERIALS AND EXPERIMENTAL PROCEDURES

The matrix material used in this study was EPDM (DuPont NDR 3720P). A curing agent for the EPDM rubber compound was dicumyl peroxide (DCP). Three different sizes of SiC particles as reinforcement materials were used—i.e., 6, 36, and 60 μm in average diameter; also, aluminum particles of 43 μm and copper particles of about 200 μm were used to examine the effects of particle size and particle type, for comparison purposes. The Al particles were selected because their density value was similar to that of the SiCp and the Cu particles were selected because their impedance value was similar to that of the SiCp. Table I lists the values of Young's modulus, density, and impedance for the materials used in this investigation and details of the EPDM rubber compound.

TABLE I
Material Information of EPDM and Particles Used in This Study

Materials	Young's modulus (GPa)	Density (kg/m^3)	Impedance (Mrayl)
EPDM[a]	0.007	0.86	0.09
SiCp	400	3.13	37.0
Copper	130	8.9	42.7
Aluminum	71	2.7	17.3

[a] EPDM used in this study has a ethylene/propylene ratio of 69/30.5 containing 0.5% diene ENB (5-ethylidiene-2 norbornene).

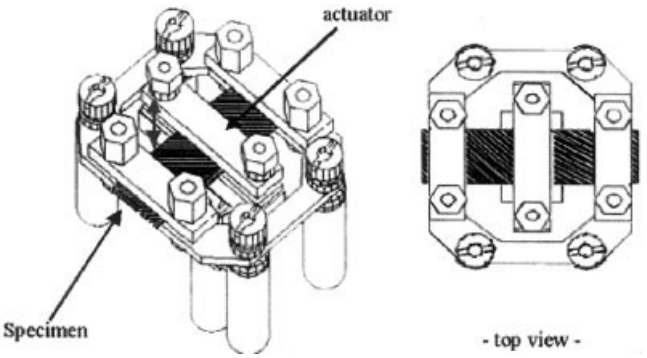

Figure 1 Geometry of DMTA test setup.

In order to incorporate particles and DCP into the EPDM rubber compound, a Banbury internal mixer and a two-roll mill machine were employed. The processing temperature for Banbury internal mixer was 130°C and the rotor speed was about 20 rpm. The EDPM rubber compounds in "as-received" pellet forms were put into the mixing chamber and softened by the heat for about 1 min. Particles, then, were filled within the EPDM matrix material. And then, 5 wt % of DCP was added to invoke crosslinking process of the EPDM polymer chains during mixing. Rubber composite material produced by using the Banbury internal mixer cannot be conveniently used for the molding process because of their irregular shape. Therefore, a two-roll mill was used to modify the shape of the mixed EPDM into the form of sheet with the thickness of about 10 mm. The temperature and speed of the rolls were about 110°C and 15 rpm, respectively. The size of the final specimens for DMTA (Mark IV, Rheometric Scientific) was $30 \times 12.7 \times 3.1$ (± 0.1) mm^3. The error of the specimen thickness values comes from the different amount of the incorporated particles.

RESULTS AND DISCUSSION

The effect of particle volume fractions on E' and E''

A DMTA was used to evaluate dynamic elastic (both storage and loss) moduli of the particle-reinforced EPDM matrix composite materials. Figure 1 shows the schematic of DMTA experimental setup (supplied from the user's manual) based on the dual cantilever

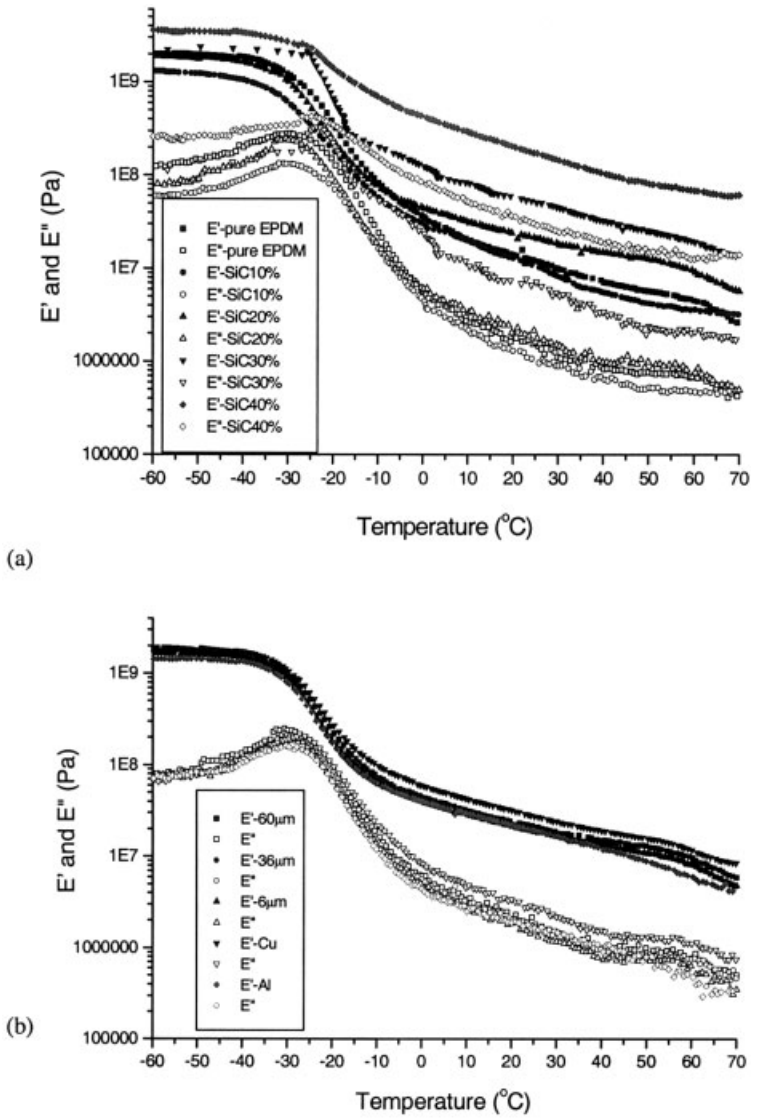

Figure 2 Temperature dependency of E' and E'' vs temperature on (a) SiCp volume fraction and (b) different particle size and different particle type.

bending geometry. The frequency was selected as 1 Hz and the strain used was 0.01%. When the dynamic mechanical testing machines [e.g., DMTA or Advanced Rheometric Expansion System (ARES)] are used, such small strain values should be used to minimize the sinusoidal effect.

Figure 2(a) shows the plots of dynamic storage elastic moduli, E' (closed symbols), and dynamic loss moduli, E'' (open symbols), against temperature in the range from -60 to 70°C for the composites with various particle volume fractions (0, 10, 20, 30, and 40%), and Figure 2(b) exhibits those of the composites with different particle sizes (60, 36, and 6 μm) and different particle types (SiCp, Al, and Cu), respectively. It is shown from Figure 2(a) that dynamic elastic modulus values (both storage and loss) in the glassy region has not increased with the increasing SiCp volume fractions up to 20 vol %. However, the composite with 40 vol % shows remarkably higher E' and E'' values. And, all the composites showed higher E' and E'' values in the order of 40 to 0 vol % SiCp/EPDM composites in the rubbery region.

As shown in Figure 2(b), the composites reinforced by SiCps of 60, 36, and 6 μm in different sizes and different particles (SiCp of 60 μm, Cu and Al) with 20 vol % show little difference for the dynamic elastic moduli. The composite reinforced with Cu particles, however, shows higher values of dynamic elastic modulus than those of the other composites. This is attributed to the increase of the effective volume of the particles for the composite with Cu particles, which may be due to extensive EPDM rubber segments adhered to the surface of Cu particles. Details will be explained based on the supports from observation of the microstructures of particle-filled EPDM matrix in the following section.

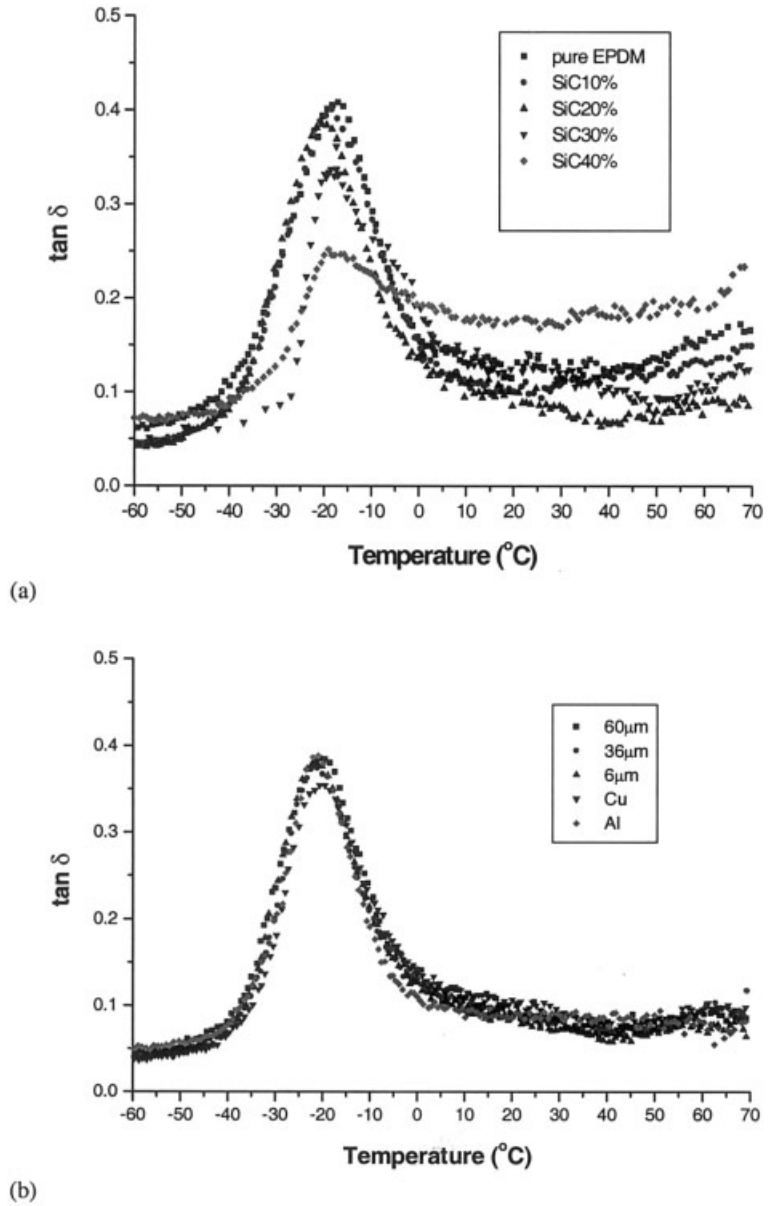

Figure 3 Temperature dependency of tan δ vs temperature on (a) SiCp volume fraction and (b) different particle size and different particle type.

Effect of particle size on tan δ

Figures 3(a) and 3(b) show the temperature dependency of tan δ for the composites employed in this study. As exhibited in Figure 3(a), the peak tan δ values of the composites decrease with the increasing SiCp volume fraction, i.e., from 0.41 to 0.25. It should be noted, however, that the width of tan δ curve for the composite with 40 vol % is remarkably wider, and the tan δ values are much higher in the temperature region after the peak tan δ (i.e., in the rubbery phase) than those of the other composites. It is noted that the scatters of data exhibited in this figure may be due to the change of specimen rigidity and the expansion of the specimen volume with the increase of temperature, i.e., from glassy to rubbery state. The specimens may respond more or less unstably to the applied dynamic strain during the test. Since the elastomeric materials are always practically used in the rubbery phase, one needs to draw more attention to the performance and behavior of the material in the temperature range after T_g. Since it is known that the tan δ is closely related to the acoustic and damping property, the composite with 40 vol % SiCps can be used beneficially as a better damping material than the other composites and the pure EPDM. Figure 3(b) shows that the peak tan δ for the composite with 20 vol % Cu particles is slightly lower than that of the other composites used

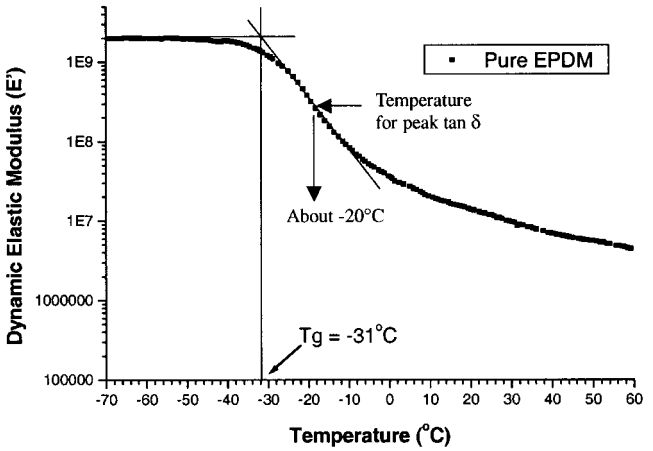

Figure 4 Determination of T_g by using DMTA.

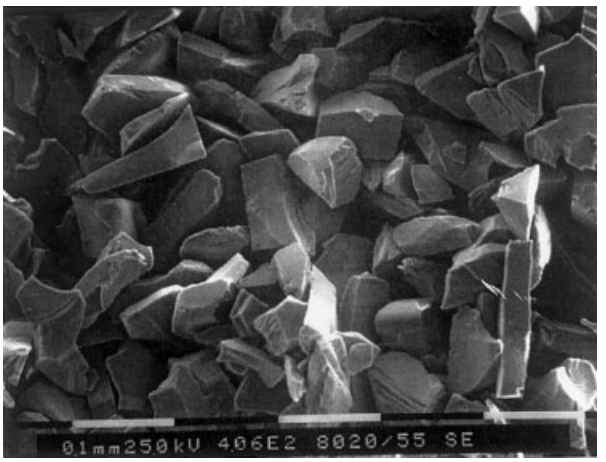

Figure 5 SiCps of 60 μm in average size.

in this study even though all the curves appear very similar. Also, the widths of the tan δ curves for all the composites are about same. Overall, the composite with 20 vol % Cu particles does not show any increase in damping property.

T_g evaluation by using DMTA

Glass transition temperature (T_g) is a significant factor in investigating the relationship between the mechanical, thermal, and acoustic property of polymeric materials because it is closely related with tan δ and acoustic attenuation. When the T_g is known, it is possible to predict the temperature of the peak tan δ by analyzing a DMTA curve of E' vs temperature. It should be noted that the peak tan δ does not necessarily occur at T_g.[12] The temperature at peak tan δ can be found at the point of equal position of the descending curve of E', as indicated in Figure 4.

It is disputable in selecting an appropriate method to determine T_g (refs. 11–13) because different T_gs can be obtained often by using different instruments. In the current investigation, T_g value of pure EPDM rubber has been evaluated by using DMTA at 1 Hz. The heating rate has been selected as 5°C/min. The result shown in Figure 4 indicates that T_g is −31°C. The reported T_g measured by DSC is about −40°C, and it can be said that the difference (i.e., 9°C) is reasonably close to each other (within 10°C) according to the study done by Sircar et al.[13] They have carried out a comprehensive study on glass transition of elastomers using various thermal analysis methods. It is concluded from their study that T_g shows higher value in the order DSC → thermomechanical analyzer (TMA) → DMTA. They also note that the zero heating rate DSC T_g (extrapolated from different heating rate values) agrees with the DMA loss peaks in the range of 10^{-4} to 10^{-3} Hz.

Microstructures of particle-reinforced EPDM matrix

The information attained from the micrographs of fracture surfaces shown in this section is used to provide the scientific supports for the morphology and the particle distribution of incorporated particles, the interfacial area between the particles and the EPDM matrix, and the adhered rubber segments to the surface of particles within the scope of bound rubber concept.[14]

Figure 5 shows "as-received" SiCps of 60 μm in size. The average aspect ratio of the particle is about 1.8. Particularly, some long particles are found as shown in the micrograph. After freezing the EPDM composite samples in the liquid nitrogen long enough, fracture surfaces of the particle/EPDM matrix composites have been manually produced. Figure 6 exhibits a micrograph on the overall fracture surface of the 40 vol % SiCp/EPDM composite. It is observed that the SiCps are evenly distributed and the particles appear to be well adhered to the matrix.

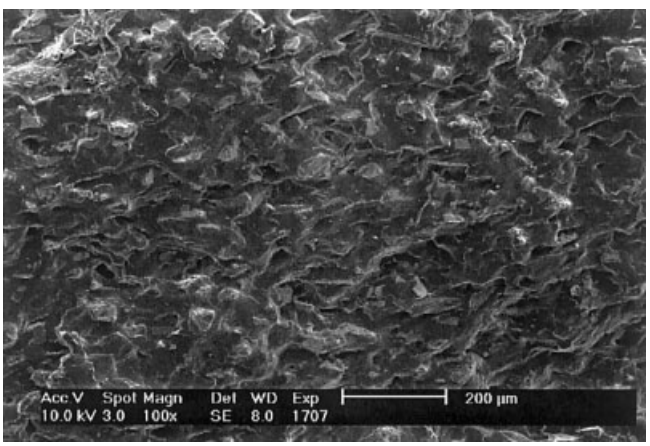

Figure 6 SiCp distribution in 40 vol % SiC/EPDM composite.

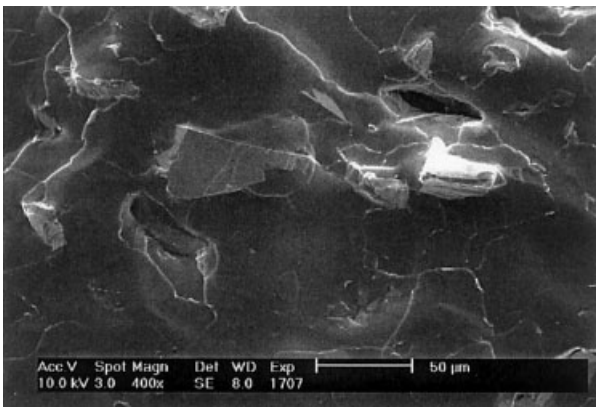

Figure 7 EPDM composites reinforced with 20 vol % SiCp.

Figures 7 and 8 display the fracture surfaces of 60 μm SiCp/EPDM with volume fraction of 20% and with that of 40%, respectively. A particle pull-out is shown in the upper right-hand side of the micrograph as shown in Figure 7. In the other locations, the micrograph shows reasonably strong bond between the SiCp and the EPDM matrix. Comparing with the microstructure exhibited in Figure 7, it is shown in Figure 8 that the distance between the particles is much closer due to the higher volume percentage of the particles. The thickness value of the entrapped rubber between the two particles shown in the upper middle of the micrograph seems to be about 2 $\sim$ 5 μm. The rubber segments entrapped among the particles become less mobile in the transition region from glassy to rubbery phase because the free volume that offers the space for polymer chain mobility does not increase as expected due to the polymer chains anchored to rigid particle surfaces. The free volume change is in close association with the damping property of polymeric materials, i.e., the tan δ values decrease when the free volume change becomes smaller. And therefore, the peak tan δ values decrease with the increase of particle volume fraction as shown in Figure 3(a). It

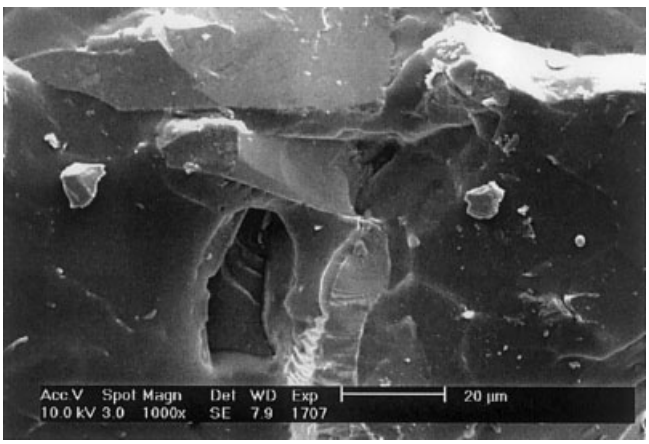

Figure 8 EPDM composites reinforced 40 vol % SiCp.

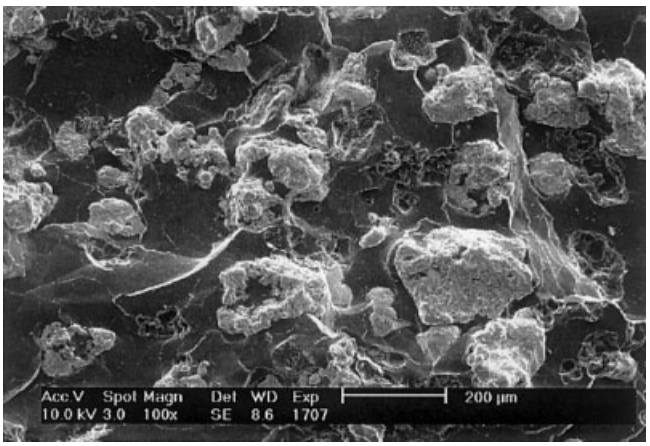

Figure 9 Cu particles incorporated in EPDM matrix.

does not necessarily mean that the material having the higher peak tan δ values has higher overall damping property. It is because the width of the tan δ curve is inversely proportional to the height (the peak tan δ value).[15] Therefore, both height and width of tan δ curves should be carefully examined to evaluate the damping property of the materials. It is noted that the explanation made above does not attempt to correlate the failure properties to the dynamic property of the composites employed in this investigation.

The fracture surfaces of Cu/EPDM composite with volume fraction of 20% are displayed in Figures 9 and 10. Figure 9 shows the distributed Cu particles in the EPDM matrix. As shown in the micrograph, the size of the particles is in the range from 20 to 250 μm—that is, a quite large distribution in size. As in the SiCp/EPDM composite, the adhesion between Cu particles and EPDM matrix seems to be quite strong. Figure 10 shows a couple of the major morphological features including rubber segments entrapped among the particles and on the particle surface and Cu particle clus-

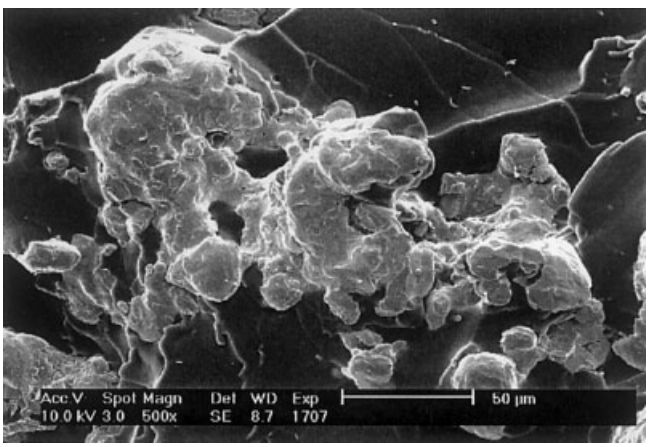

Figure 10 EPDM composites with 20 vol % Cu particles: Cu clusters and rubber segments adhered to the particle surfaces.

ter. The entrapped rubber segments limit the mobility of the polymer chains as aforementioned. In the composite with Cu particles, it is notable that small rubber segments are filled in the pores on particle surfaces and strongly adhered. It promisingly increases the amount of the rubber adhered to the particle surfaces and, as a result, leads to the increase of the effective particle volume.

Leblanc[14] categorized the matrix rubber in the vicinity of the particles into tightly bound rubber, loosely bound rubber, extractable rubber, and connecting filament. It is interesting to note that the tightly bound rubber is the remaining segments on the surface of particles even after extraction of the rubber from the material system, and is significantly involved in the particular morphology in uncured filled rubber compound. From this viewpoint, in the Cu/EPDM composites used in this study, the amount of tightly bound rubber is increased because of the rough surface characteristics of the particle and a good adhesion between Cu and EPDM. And thus a higher constraining effect for the mobility of the bound rubber segments on the particle surfaces in Cu/EPDM composites is obtained than in composites with other reinforcement particles.

CONCLUDING REMARKS

In this investigation, the dynamic mechanical properties of the particle-reinforced EPDM matrix composites have been evaluated by using a DMTA. The following concluding remarks have been made from the current investigation:

- The tan δ values of the composite with 40 vol% SiCps were higher in the rubbery phase up to a temperature of 70°C than the composites with lower SiCp volume percentages, i.e., 10, 20, and 30 vol %, although the peak tan δ value was lower. Also, the peak tan δ value of the composite with 20 vol % Cu particles was lower than that of the composites with other particles of 20 vol % because more rubber segments were adhered on the rough Cu particle surfaces.
- From the obtained DMTA results on the dynamic storage modulus, T_g has been determined for the EPDM rubber compound, i.e., −31°C.
- The amount of polymer rubber segments entrapped among the particles increased with the increase of the particle volume fraction. As a result, the mobility of the polymer chains was restricted in the transition area from glassy to rubbery state. This supports the fact for the decrease of the peak tan δ values of the composites when the particle volume fraction increased and the Cu particles with rough surface characteristics are used.
- It was found by observing microstructures using a scanning electron microscope that the adhesion between particles (i.e., SiCp, Cu, and Al) and EPDM matrix appeared to be quite strong.

The Korea Science & Engineering Foundation (KOSEF) is gratefully acknowledged by the first author (MSS) for providing an APEC postdoctoral fellowship during 2001. The authors wish to thank the Agency for Defense Development (ADD), Jinhae, Korea, for the continuous financial support for this project.

References

1. Kim, J. K.; Kim, I. J Appl Polym Sci 2001, 79, 2251.
2. Murayama, T. Dynamic Mechanical Analysis of Polymeric Material; Elsevier: New York, 1978.
3. Eggers, H.; Schummer, P. Rub Chem Tech 1996, 69(2), 253.
4. Gwaily, S. E.; Abedl-Aziz, M. M.; Madani, M. Polym Test 1998, 17, 265.
5. Wang, M.-W. Rub Chem Tech 1997, 71(3), 520.
6. Medalia, A. I. Rub Chem Tech 1978, 51, 437.
7. Kim, K. S.; Jung, H. K.; Hong, S. H. Proc Third Asian-Australasian Conference on Composite Materials: (ACCM-2), Kyonju, Korea, August 18–20, 2000, 1239.
8. Hartman, G. Acoustic Properties: Encyclopedia of Polymer Science and Engineering; Wiley & Sons: New York, 1984.
9. Trask, C. A.; Thomas, D. A.; Hickey, E. C.; Sperling, L. H. J Appl Polym Sci 1975, 19, 1731.
10. Sohn, M. S.; Kim, K. S.; Hong, S. H.; Kim, J. K. Proc Korea-Japan Joint Symposium on Composite Materials, Seoul, Korea, October 18, 2001, 91.
11. Standard Test Method for Glass Transition Temperatures by Differential Scanning Calorimetry or Differential Thermal Analysis, ASTM Designation: E1356–91.
12. Standard Test Method for Assignment of the Glass Transition Temperature by Dynamic Mechanical Analysis, ASTM Designation: E1640–94.
13. Sircar, A. K.; Galaska, M. L.; Rodrigues, S.; Chartoff, R. P. Rub Chem Tech 1999, 72(3), 513.
14. Leblanc, J. L. J Appl Polym Sci 2000, 78, 1541.
15. Hartman, B.; Lee, G. F.; Fedderly, J. J. J Acoust Soc Am 1997, 101(4), 2008.