A Study on Mechanical and Thermal Properties of Silicone Rubber/EPDM Damping Materials

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ABSTRACT: Silicone rubber (SR) and ethylene-propylene-diene monomer (EPDM) blends were prepared for damping application. The mechanical and thermal properties of the blends are studied. With the increasing content of EPDM, the tensile strength is decreased but elongation at break is increased. By blending with EPDM, tan δ (at 35 to 200°C) of SR is enhanced. However, thermogravimetric analysis results showed the decrease in thermal stability. Scanning electron microscopy study showed the good filler dispersion of the blends with some large silica particles.
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Key words: silicones; blends; thermal properties; mechanical properties; thermodynamic

INTRODUCTION

High vibration levels often generate excessive noise and leads to cyclic fatigue damage. Polymer damping materials have long been used to reduce vibration levels. The vibration isolation property of polymer materials depends significantly on environmental conditions such as temperature, vibration frequency, preload, dynamic load, etc. The damping usually peaks at or around the glass transition temperature of the material, because the softening of the materials in this region leads a rapid decrease of storage modulus and increase of loss factor. Therefore, considerable attention has been focused on broadening the glass transition regions and improving damping level of the materials.[1–5] However, some materials may be used at the temperature which is far above the glass transition region. So, high temperature damping and heat resistance are necessary for the materials. Silicone rubber (SR) is attractive as high temperature damping materials for steady mechanical and damping properties in a wide temperature range from −50°C to 200°C.[6] However, their damping property is low and modification is necessary. Some techniques like blending,[7,8] copolymerization[9,10] and interpenetrating polymer network[11,12] have been developed. Blending of SR with other polymers possessing for high vibration isolation is a simple method, such as polyacrylates,[7,11] butyl rubber,[13,14] ethylene-propylene-diene monomer (EPDM)[8,15] and so on. Because of the similar solubility parameter and covulcanization by peroxide, EPDM is commonly used to blend with SR,[6] damping capability of the materials has been improved.[8,15] However, in these studies, little attention has been paid on high temperature (100–200°C) damping properties.

In the present work, SR is blended with EPDM to increase the damping value in high temperature region. The mechanical, dynamic–mechanical, and thermal properties of different silicone and EPDM blends are studied.

EXPERIMENTAL

Materials

HRS 0.05 (vinyl group content, 0.05 mmol/g; $M_w = 6.8 \times 10^{-4}$ g/mol), SR was supplied by Hae Ryong Silicone, (Korea). EPDM (grade Vistalon 503 k; ML (1 + 4) at 125°C, 34.0; ethylene content, 55.0%; $M_w = 5.7 \times 10^{-4}$ g/mol) was produced by Kumhopolychem, (Korea). Precipitated silica Z-115GR (BET specific surface area, 112 m^2/g) was obtained from "Rhodia." Isobutyltriethoxysilane (IBS) is commercial material and used as a coupling agent. Peroxide curing agent, HC-8, was also received from Hae Ryong Silicone, which is a gum of 2,5-dimethyl-2, 5-di (*t*-butylperoxy) hexane.

Preparation of samples and the properties of the compounds

The compounds used in this study are shown in Table I. EPDM was cut short and masticated with

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TABLE I
Compound Formulation of Blends and Their Curing Properties

Sample No.	1	2	3	4	5	6
Ingredient (phr)						
SR	100	90	80	70	60	0
EPDM	0	10	20	30	40	100
Silica	40	40	40	40	40	40
IBS	5	5	5	5	5	5
HC-8	3	3	3	3	3	3
Properties						
ML (1 + 4) 100°C	6.1	12.5	19.1	24.7	37.3	39.0
Tc10[1] (min)	1.15	1.15	1.56	1.57	2.06	3.20
Tc90[2] (min)	4.28	5.18	12.15	12.55	14.05	29.11
M_H[3] (dN m)	14.0	10.7	14.6	13.5	13.5	18.0
M_L[4] (dN m)	1.7	2.0	2.6	3.5	3.8	6.7

Tc10[1], scorch time; Tc90[2], optimum cure time; M_H[3], maximum torque; M_L[4], minimum torque.

SR on a two-roll mill for 10 min at 100°C. Then silica and IBS were added and mixed for another 30 min. After that the mixture was compounded with curing agent HC-8 for 5 min and sheet-off. After mixing, the Mooney viscosity [ML(1+4) at 100°C] of the compounds was measured by Mooney viscometer (SMV-200). Measurements of cure degree were conducted at 170°C by using a Moving Die Rheometer model MDR 2000E, from Alpha Technologies, Republic of Korea. Vulcanization was done in hydraulically operated hot press at 170°C and 15 MPa for optimum curing time (Tc90).

Mechanical properties

The mechanical properties of samples were determined according to ASTM D 412–07 by a universal testing machine, Tensometer 2000 (Republic of Korea). The tensile strength, elongation at break and modulus were measured by using a 500 mm/min cross-head speed. The dumb bell-shaped specimens (The initial length of the specimens was 20 mm) were punched out from vulcanized sheet by using ASTM Die C. Five specimens were measured for each blend at same elongation rate. The hardness measurements were carried out using a Durometer (DPX-1000, USA) following the ASTM D2240 standard. Heat resistance of the samples was characterized following ASTM D573 method. Vulcanized specimens were exposed to air at 100°C for 48 hrs, after that their physical properties were measured for aging property.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) is a method that measures the stiffness (shear, tensile, flexile modulus) and mechanical damping [internal friction or dissipation (loss) factor tan δ] as a function of temperature or as a function of impressed frequency. The dynamic mechanical properties of the samples were determined using a DMA Q800 (TA Instrument) in strain mode. Rectangular film specimens were used for this study. Samples were heated from 45 to 200°C at a heating rate 10°C/min in air atmosphere at a frequency of 15 Hz.

Scanning electron microscopy (SEM) studies

Scanning electron microscopy (SEM) micrographs were taken from the tensile fractured samples by a Philips XL 30S scanning electron microscope (Philips, Netherlands). The fracture surfaces were gold-coated before SEM and observed.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an instrument simply measures weight change vs. temperature. For TGA measurement, specimens were cut from the samples as small pieces (5–10 mg). The specimen is heated from 40 to 600°C at a constant rise of temperature (10°C/min) in nitrogen atmosphere. The equipment (Model TGAQ50) manufactured by TA Instrument was used to test the samples.

RESULTS AND DISCUSSION

Mooney viscosity and curing properties

The Mooney viscosity and curing properties of the blends are shown in Table I. With the increase of EPDM content in blends, the Mooney viscosity is increased because that EPDM has higher mooney viscosity than that of SR. It also shows an improvement of scorch time (Tc10) and optimum cure time (Tc90) by increasing EPDM content in blends, which is due to the lower cure rate of EPDM compared to

TABLE II
Mechanical Properties of the Blends

Sample No.	1	2	3	4	5	6
Tensile strength (MPa)	4.0	4.5	3.9	3.5	2.7	2.6
Elongation at break (%)	956	906	1124	1178	1237	–
Modulus 100% (MPa)	0.5	0.5	0.5	0.5	0.5	–
Modulus 200% (MPa)	0.7	0.8	0.6	0.7	0.7	–
Modulus 300% (MPa)	0.9	1.1	0.8	0.8	0.8	–
Hardness	35	37	37	39	40	47

that of SR. The torque differences (M_H-M_L) of blends are lower than that of EPDM and SR, which can be explained that the large cure rate difference between SR and EPDM, affects the formation of chemical cross-links.

Mechanical properties

The mechanical properties of samples are presented in Table II, Figures 1 and 2. It indicates that sample 2 (SR/EPDM, 90/10) possess the highest tensile strength and modulus, and lowest elongation among all the samples. For SR/EPDM blends, with increase in EPDM content in the blends, the tensile strength decrease as well as the elongation at break increase, but modulus has little difference. Furthermore, the sample 6 (EPDM) is not broken in the measuring range of instrument because of the inadequate crosslink. EPDM and SR have the highest and lowest hardness respectively, and which of blends is little difference. After aging, the tensile strength and elongation of samples all decrease to some extent, and the changes of elongation are more significant.

Dynamic mechanical analysis

The damping properties of the samples are investigated by means of DMA testing. The technique gives information about storage modulus and loss modulus that are related to storage and dissipation of energy, respectively. The ratio of loss modulus to storage modulus is referred to as internal damping or the loss tangent (tan δ). The temperature range has been chosen in this study is from 30 to 200°C, which is above the glass transition temperature (T_g) of SR and EPDM, because that the working temperature of the damping material is far above its T_g value. The dynamic mechanical spectra (tan δ as a function of temperature and at 140°C) for samples are shown in Figures 3 and 4, respectively. It shows that tan δ of neat SR and its blends have little dependence on temperature. However tan δ values of EPDM increase with the increase in temperature, which may be explained that EPDM has low crosslink and the movement of molecules at higher temperature results in more viscous for the material. In the inspecting temperature ranging, EPDM has the highest tan δ and SR has the lowest one. Samples 2 and 3 have the

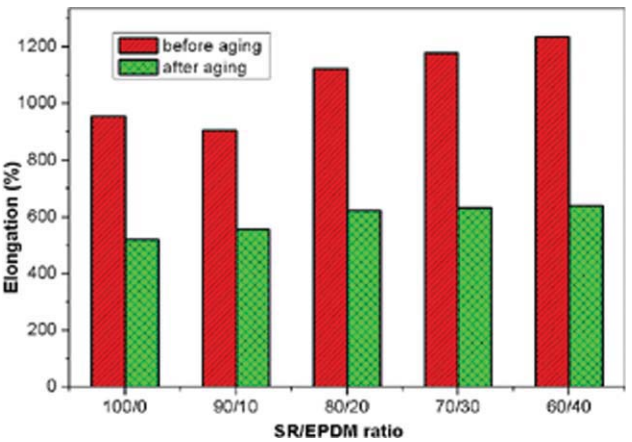

Figure 2 Elongation at break of prepared samples, before and after aging. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

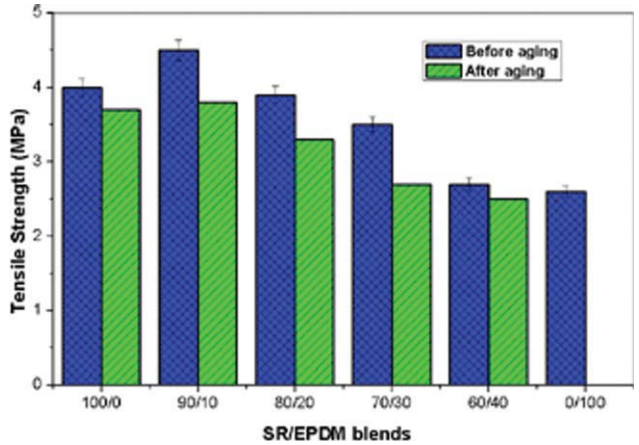

Figure 1 Tensile strength of prepared samples, before and after aging. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

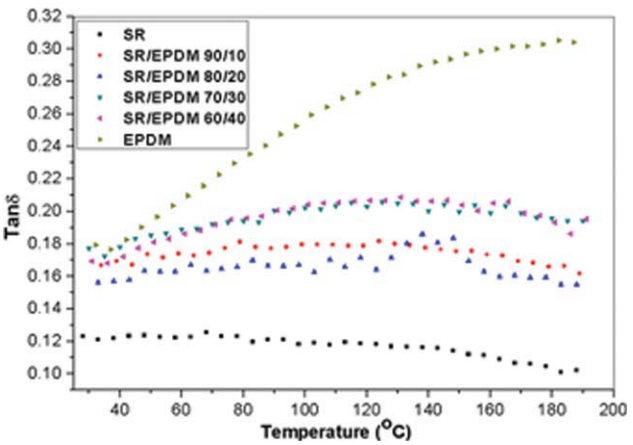

Figure 3 Tan δ for different prepared samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

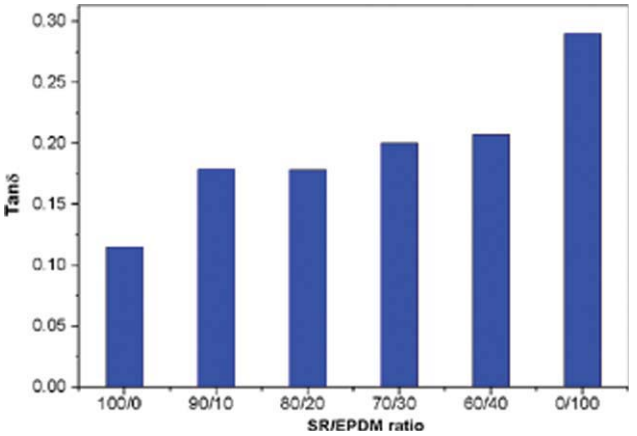

Figure 4 Tan δ at 140°C for the samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

close tan δ, in addition, sample 4 and 5 also show the similar results, but the latter is higher than the former. It indicates that with the increase of EPDM content, the values of tan δ increase.

Thermogravimetric analysis

TGA spectra, derivative thermogravimetry (DTG) curves and some thermal degradation value are shown in Figures 5, 6 and Table III, respectively. Figure 5 (TGA) and Figure 6 (DTG) show that neat SR and EPDM have an one stage weight loss at 420–580°C and 350–480°C, respectively. However the SR/EPDM blends display two distinct stages of degradation at 360–490°C and 490–580°C. Each stage of degradation on the TG curves is reflected in one maximum peak on the DTG curves. The temperature of maximum peak (T_{max}) in each stage of degradation corresponds to the degradation temperature of the maximum rate at this stage, as listed in Table III. It can be seen from Figures 5 and 6 that all the samples

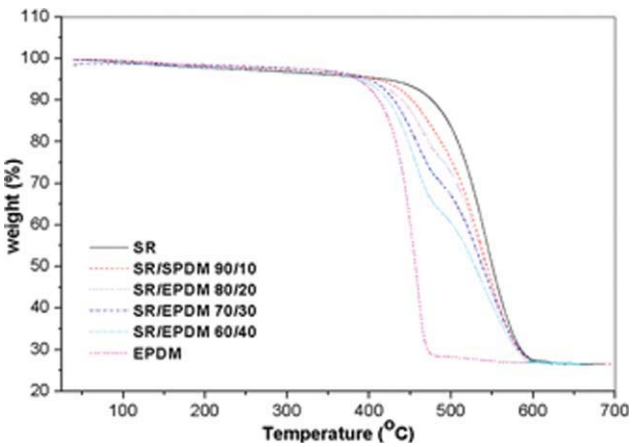

Figure 5 TGA curves of prepared blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

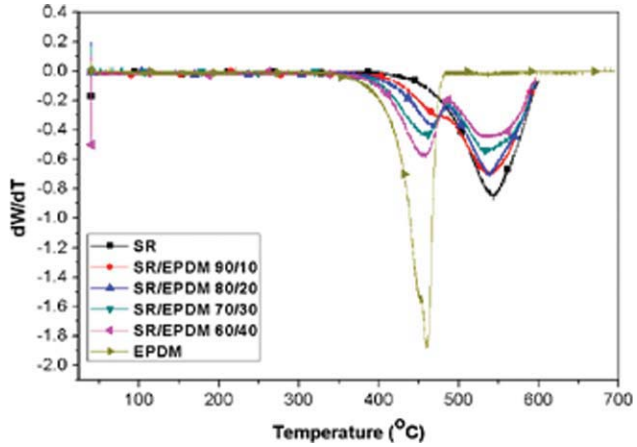

Figure 6 DTG curves of blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

have no significant weight change (about 3%) below 300°C, which means that all samples provide same stability up to 300°C. TGA and DTG curves also indicates that sample 1(SR) has the highest thermal stability and sample 6(EPDM) has the lowest one. Furthermore, with the increase of EPDM content in the blends (samples 2–5), the thermal stability decreases. The values of residue weight of samples at 450, 500, 550°C (Table III) also illustrate the same trend.

SEM studies

The tensile fracture samples are scanned after gold coating, and are represented in Figure 7. The micrographs of the samples are characterized by a smooth, rubbery failure (which is a smooth failure in the case of rubber samples without the formation of necking) where the fillers are clearly seen; the appearance is associated with a low tensile strength.[16] Figure 7(a,b) show that EPDM (deep dark points) is scattered as a dispersed phase into continuous SR phase and the size of EPDM phase becomes smaller with increase its content in the matrix. With more increase of EPDM content [Fig. 7(c,d)], it shows a continuous structure and the blend becomes two-phase continuous structure. Furthermore, some large silica particles (about 1–2 μm) can be seen in the graph, which indicates the dispersion of silica is not very good.

TABLE III
Characteristic Value of Thermal Degradation

Sample No.	1	2	3	4	5	6
T_{max1} (°C)	544	480	476	467	458	460
T_{max2} (°C)	–	537	536	535	533	–
Residues at 450 (%)	93.5	90.5	87.6	83.2	78.7	60.3
Residues at 500 (%)	83.5	75.6	72.4	66.96	60.4	28.19
Residues at 550 (%)	50.55	45.7	44.5	43.8	40.9	27.24

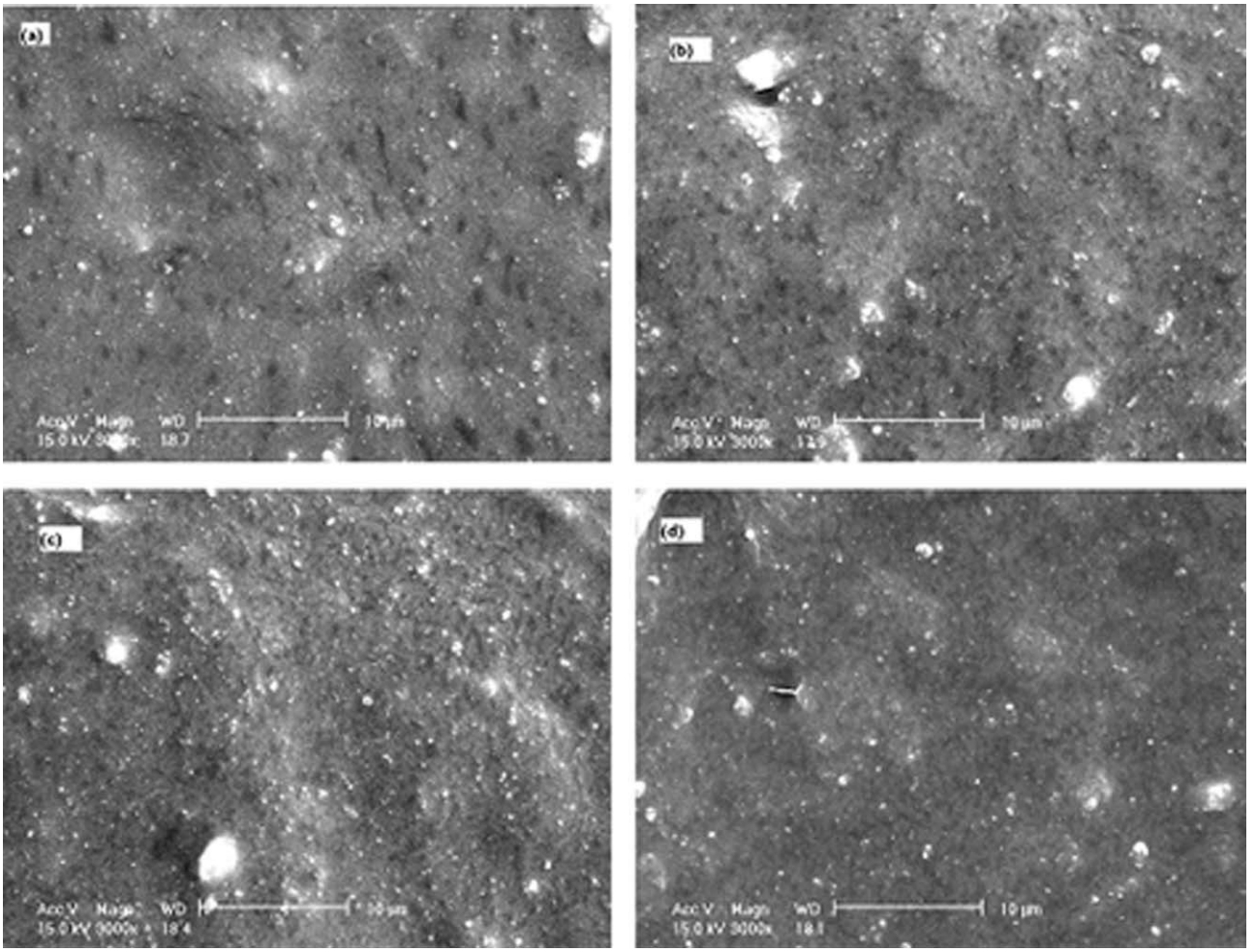

Figure 7 SEM pictographs of blends, (a) SR/EPDM 90/10, (b) SR/EPDM 80/20, (c) SR/EPDM 70/30, and (d) SR/EPDM 60/40.

Integrating the results of DMA and SEM datas, it illustrates that sample 2 and 3 have the similar tan δ because they all show the dispersion phase of EPDM, and sample 4 and 5 have continuous structure of EPDM, which also results in close tan δ.

CONCLUSIONS

The mechanical and thermal properties of SR, EPDM, and different blends of them are investigated. The Mooney viscosity, scorch time (Tc10) and optimum cure time (Tc90) of SR has been improved by EPDM content. With the increase of EPDM content in blends, the tensile strength decreases and elongation at the break increases. DMA result indicates that obtained tan δ (30–200°C) of SR blends is enhanced by blending with EPDM. But TGA shows that the thermal stability deteriorates by EPDM.

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