

# Thermal and Mechanical Properties of Silicon Rubber/*cis*-Polybutadiene Rubber/Ethylene–Propylene–Diene Monomer Blends

Weili Wu,<sup>1,2</sup> Dajun Chen<sup>1</sup>

<sup>1</sup>College of Materials Science and Engineering, Donghua University, 1882 West Yan'an Road, Shanghai, 200051, China

<sup>2</sup>College of Chemistry and Engineering, Qiqihar University, No. 30, Wenhua Street, Qiqihar Heilongjiang, 161006, China

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**ABSTRACT:** Considering the properties of silicon rubber, ethylene–propylene–diene monomer (EPDM), and *cis*-polybutadiene rubber (BR), a blend made by a new method was proposed in this article; this blend had thermal resistance and good mechanical properties. The morphology of the blend was studied by SEM, and it was found that the adhesion between the phases of BR, EPDM, and polysiloxanes (silicon rubber) could be enhanced, and the compatibility and covulcanization were good. The influence of the mass ratio of peroxide and silica on the mechanical properties and thermal resistance of the blend was studied. The results

showed that the mechanical properties and thermal resistance of the blend were improved when silicon rubber/BR/EPDM was 20/30/50, dicumyl peroxide/sulfur was 2.5/2.5, and the amount of silica was 80 phr. The integral properties of rubber blend had more advantages than did the three rubbers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 4462–4467, 2006

**Key words:** polysiloxanes; polybutadiene; blends; mechanical properties; thermal properties

## INTRODUCTION

With the development of automotive industry, more and more excellent properties for automotive braking block material are required.<sup>1</sup> Asbestos and metals are mainly traditional automotive braking blocks. The asbestos braking block has “hotly declining” phenomenon and produces carcinogen during driving. So it is not indicated for long-term usage and endangers health for human beings. The metal’s braking block exhibits some uncomfortable problems for passengers, because its size is too big to decelerate safe.<sup>2,3</sup> The materials not only must be more safe but also must be comfortable during driving. Such materials are lighter, innocuous, wear resistant, and thermal resistant, whose Shore A hardness and elongation at break (toughness) are stronger before and after heat aging. To solve the aforementioned problems, Wu and Feng<sup>4</sup> had investigated the automotive braking block made of BR/HDPE and NBR/PVC blends, whose hardness is good but thermal resistance is lower. Shen et al.<sup>5</sup> had investigated that the automotive braking block was prepared by mold compression at elevated tem-

peratures, using cashew oil phenolic resin as the matrix and needle-like wollastonite and fibrous sepiolite modified with stearic acid as the complex reinforcing agents. Xu et al.<sup>6</sup> found that the airplane brake material was prepared by carbon/carbon composite with different pyrocarbon structure. Sun et al.<sup>7</sup> had studied the beat-braking block reinforced by NACF. Aavin and Somit<sup>8</sup> had reported the abrasion of FRP composite. Lu<sup>9</sup> had investigated the optimization of automotive friction materials. Modi et al.<sup>10</sup> had prepared low-stress abrasive wear behavior of carbon steel. In these investigations, it is mainly reported that raw materials are mostly either a kind of superfiber or more than two mixed fibers. The resource of the supermaterial is lacking, and its price is expensive. In view of aforementioned causes, the application of the material is not ideal, and there are few reports on this aspect till now. Therefore, in this article, the rubbers were used as main automotive braking block material. Their wear resistance steadily builds up, and the service life is prolonged because of their flexibility. The previous works<sup>11–13</sup> revealed that the kind of rubber used is not ideal. Consequently, in this article, BR/EPDM/silicon rubber blend is prepared by combining ethylene–propylene–diene monomer (EPDM),<sup>14–18</sup> silicon rubber,<sup>19,20</sup> and *cis*-polybutadiene rubber (BR).

Silicon rubber exhibits cold resistance and thermal stability, but its mechanical properties is lower comparatively, and the price is expensive. EPDM exhibits

Correspondence to: W.-L. Wu (wuweili2003@163.com).

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TABLE I  
Fundamental Recipe of the Ingredients (Part by Mass, g)

Rubber	100
Silica	30
DCP	3
Sulfur	2.5
ZnO	2.5
SA	1
Accelerant M	1
Antioxidant D	1

heat-aging resistance, chemical resistance, impact strength and mechanical properties, and dielectric property. Its shortcoming is slowly cured speed, blending hard, poor in internal viscous and mutual viscous. BR has the best elasticity of all rubbers, good flexibility, and abrasion resistance, but its stress-strength and tear-strength are lower, and its processability is difficult. We hope a kind of blending be prepared, which not only surmounts aforementioned rubber shortcoming, but also take its advantages.<sup>21–25</sup>

To the best of our knowledge, there is no report on BR/EPDM/silicon rubber blend. In this work, the blend was prepared by adding a crosslinking agent BR. After adding curing agents and silica, their effects on the mechanical and thermal properties of the samples were investigated. A BR/EPDM/silicon rubber blend with ideal formulation was prepared. The morphology of blend was analyzed by means of scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

BR (grade-BR-9000) is from Jinzhou Petrochemical (China). EPDM (grade-EPDM-23080 P) is from Jilin chemical industrial Inc. (China). Silicon rubber (methyl ethylene silicon rubber; ethylene content, 0.09 wt %;  $M_n$ ,  $5.8 \times 10^6$ ) is supplied by DC Chejue organic silicon aggregation group (China). Dicumyl peroxide (DCP) (analytical grade) and benzoperoxide (BPO) (analytical grade) are supplied by Shanghai chemical reagents company of Chinese medicine group (China). The other agents are all common commercially available materials and were used as purchased (China).

### Preparation of samples

The raw rubbers, such as silicon rubber, BR, and EPDM, were first masticated on an XK-160 two-roll mill for 10 min, in which the roll temperature was 45–55°C, and the distance between the two rolls was about 0.5 mm. After that, the mixed rubber was prepared by adding various ingredients shown in Table I, and the order of process was as follows: Silicon rubber/BR/EPDM or Silicon rubber/EPDM (raw rubbers

masticated) → ZnO, stearic acid, antioxidant D → DCP (or BPO) → silica → sulfur, accelerant M, adjusted up into 50–60°C, and the distance between the two rolls was kept at 4.0 mm for 30 min. Then the mixer was vulcanized at 160°C for 30 min under 10 MPa (optimum curing condition) in a compression mold. At last, the vulcanizates were cut out into dumbbell-shaped testing specimens.

### Characterization

First, the vulcanizate sample was fractured in liquid nitrogen, and then the fractured surface was sprayed with gold, and after that, the fracture morphologies of the blending samples were observed by SEM (model JSM-5200 JEOL Co.) The IR spectrum of the blends was recorded at a resolution of  $4000 \text{ cm}^{-1}$  on an IR-7685 Fourier transform infrared (FTIR) spectrometer (Shanghai analyzer plant). Tensile tests were performed on dumbbell-shaped specimens according to ISO 37–1994. Shore A hardness was measured on 6-mm-thick specimens according to ISO 48–1994. The samples were tested, and the average of the values was taken. Heat aging of the samples was performed for 24 h at 250°C by a 401-B air aging oven (Jiangsu Test Mechanical Ltd.) according to ISO 188–1998.

## RESULTS AND DISCUSSION

### Effect of silicon rubber/EPDM mass ratio on blend properties

The mechanical properties of silicon rubber are lower, but those of EPDM are stronger. Both possess high elasticity and are nonpolar and backbone-saturated rubbers. Since there are a few vinyl groups in silicon rubber, and EPDM is combined with a few third monomers, whose unsaturated double bonds play a crosslinking role in blending rubbers. Thus we thought it a good idea that the blend should have the advantages of both rubbers, showing not only the thermal resistance of silicon rubber but also the mechanical properties of EPDM.<sup>26,27</sup> The effects of silicon rubber (SiR)/EPDM mass ratio on blending properties are reported in Table II.

As seen in Table II, as the amount of silicon rubber decreases and EPDM increases in the recipe, the tensile strength of the blending rubber decreases gradually, and Shore A hardness increases. The reason is that silicon rubber at room temperature is uncrystallized, the cohesion is comparatively low, and the macromolecules flow easily. On one hand, the higher the silicon rubber content in the recipe, the softer the mixed rubber, the lower the Shore A hardness, and the larger the elongation at break. All of the aforementioned properties will make that so the blend is not able to form, for example Sample 1 (silicon rubber/

TABLE II  
Effect of SiR/EPDM Mass Ratio on Blend Properties

	Samples			
	1	2	3	4
SiR (phr)	50	40	35	30
EPDM (phr)	50	60	65	70
Tensile strength (MPa)	—	2.5	2.3	2.3
Hardness (Shore A)	—	53	55	57
Elongation at break (%)	—	37.8	15.1	6.9
Change before and after aging (200°C × 24 h)				
Hardness (Shore A)	—	6	7	7
Elongation at break (%)	—	8	10	14

EPDM = 50/50). On the other hand, the content of EPDM increases or silicon rubber decreases, Shore A hardness does not improve obviously, for example Sample 4. The reason can be thought that the cohesion of EPDM macromolecules is lower. EPDM and silicon rubber are scarcely compatible, and the blend shows lower mechanical properties. So silicon rubber/EPDM cannot make use of main material.

#### Effect of BR content on the blend properties

Based on said the aforementioned properties, BR is chosen, with which silicon rubber and EPDM are able to dissolve by adding crosslinking agent, to improve the mechanical properties of the blend.<sup>28</sup> Effects of SR/BR/EPDM mass ratio on blend properties are shown in Table III

As shown in Table III, when the mass ratios change, Shore A hardness and tensile strength exhibit a little change, and there is no rule followed, but the mechanical properties get obvious improvement. When the mass ratio of silicon rubber/BR/EPDM is 20/30/50, the samples have highest elongation at break and tensile strength, and the mechanical properties do not change obviously after air-oven aging, especially elongation at break. It can be seen that silicon rubber/BR/

TABLE III  
Effect of SiR/BR/EPDM Mass Ratio on Blend Properties

	Samples				
	5	6	7	8	9
BR (phr)	20	25	30	30	40
EPDM (phr)	40	50	50	40	40
SiR (phr)	40	25	20	30	20
Tensile strength (MPa)	7.9	7.9	8.4	8.1	8.3
Hardness (Shore A)	78	76	65	73	81
Elongation at break (%)	11.0	12.6	55.7	18.5	11.9
Change before and after aging (200°C × 24 h)					
Hardness (Shore A)	3	4	3	5	4
Elongation at break (%)	4.8	4.5	2.8	4.3	2.8

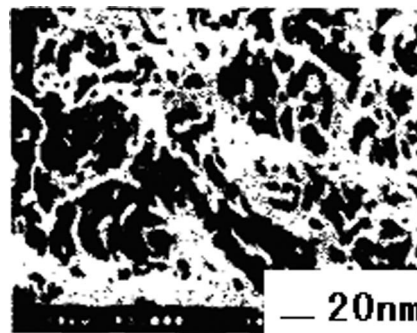
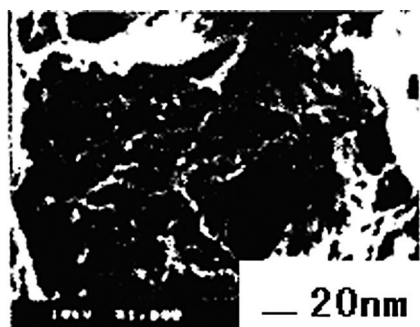


Figure 1 SEM photos of tensile fracture of SiR/BR/EPDM SiR/BR/EPDM = 20/30/50.

EPDM blends exhibit better tensile strength and thermal stability than do silicon rubber/EPDM from Tables II and III, and so the optimal mass ratio is 20/30/50. The reason is that the backbones of silicon rubber and EPDM are saturated, whose compatibility between them is difficult. The unsaturated BR has two kinds of actions, first it fixed a part of silicon rubber and a little EPDM into cube network structure (and cured BR is shown as Fig. 1), thereby the blend comes into three direction network. The results are in the improvement of the mechanical properties and thermal stability. Second, BR plays a role of a crosslinking agent. Adding BR is the same as increasing linking agent in blend system, the double bonds of BR combine by curing agent, with a few double bonds on EPDM and silicon rubber surfaces, forming chemical crosslinking cube network, leading to improving the compatibility of EPDM and silicon rubber, reducing the contact of oneself and the molecule chain breaking down, decreasing the stress concentrate as well as heat expansibility, so that the mechanical and heat ageing properties of BR/EPDM/silicon rubber are both improved.

SEM photograph of tensile fracture of SiR/BR/EPDM blend is shown in Figure 1. BR penetrates between EPDM and silicon rubber to crosslinking network (light areas), the interfacial areas between EPDM and silicon rubber are not as obvious as the areas of Figure 2 (SEM photograph of tensile fracture of SiR/EPDM blend). It suggests that BR, which locates at the interface between silicon rubber and EPDM, has the propensity to penetrate into these two phases and formed the shared networks after *in situ* polymerization during the curing process. The macromolecules interpenetration took place at the phase boundaries, and the interfacial combination was promoted. As shown that the compatibility of silicon rubber/EPDM by adding BR (SiR/BR/EPDM) is better than silicon rubber/EPDM (Fig. 2).

FTIR spectra of silicon rubber/BR/EPDM and silicon rubber/EPDM blends are shown in Figure 3. The spectrum of silicon rubber/BR/EPDM not only re-



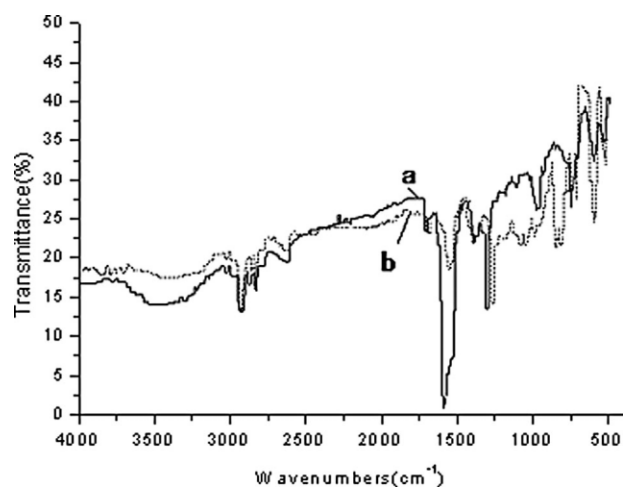
**Figure 2** SEM photos of tensile fracture of SiR/EPDM SiR/EPDM = 40/60.

mains the characteristic band of silicon rubber/EPDM of  $\text{CH}_2$  at  $2920\text{ cm}^{-1}$ ,  $\text{C}=\text{C}$  at  $1630\text{ cm}^{-1}$ ,  $\text{CH}_3$  at  $1430\text{ cm}^{-1}$ , and  $\text{Si}-\text{O}$  at  $1131\text{ cm}^{-1}$ , but also emerges the characteristic peaks of  $\text{C}=\text{O}$  at  $1730\text{ cm}^{-1}$  and  $\text{C}-\text{O}-\text{C}$  at  $1020\text{ cm}^{-1}$ , which demonstrates that the crosslinking agent BR has combined on the surfaces of silicon rubber and EPDM.

#### Effect of silica content on blend properties

The reinforcing fillers are indispensable in rubber industry.<sup>29</sup> As shown in Table III, the hardness of silicon rubber/BR/EPDM blends is lower. According to silicon rubber structure, silica is selected as the reinforcing filler.<sup>30</sup> The effects of silica content on blend properties are shown in Table IV.

It is shown that, with increasing silica loading, the hardness of blends increases, the tensile strength does not vary obviously, the elongation at break and the changes of the ageing properties are less and less. It suggests that the thermal stability is increased by adding silica when the amount of silica is less than 80 phr. This is because the rubbers and silica crosslink to form



**Figure 3** FTIR spectrum of silicon rubber/BR/EPDM (a) and silicon rubber/EPDM (b).

**TABLE IV**  
Effect of Silica Content on Blend Properties

	Samples					
	10	11	12	13	14	15
Silica (phr)	40	50	60	70	80	85
Tensile strength (MPa)	8.2	8.1	8.2	8.2	8.3	—
Hardness (Shore A)	75	79	86	87	90	—
Elongation at break (%)	48.1	25.0	32.3	31.1	22.1	—
Change before and after aging ( $200^\circ\text{C} \times 24\text{ h}$ )						
Hardness (Shore A)	5	5	4	3	1	—
Elongation at break (%)	4.0	5.0	3.9	3.8	2.7	—

SiR/BR/EPDM = 20/30/50.

a cube network structure, and the silica plays a reinforcing role. However, the amount of the silica may not be excessive, when more than 80 phr silica was used in blend system, the rubber matrix content is a little and not enough to envelop all scrap silica filler to form effective interface layer. With increasing free spaces of the filler, the interaction of the filler increases, the weak interaction and bonding between the filler and the rubber matrix results in the interface deterioration and the descending of the mechanical and thermal aging properties. It is the reason why Sample 15 (silica content is 85 phr) cannot prepare sample, and there is no testing results. At last, the best content of the silica is 80 phr.

#### Effect of curing agents on blend properties

Curing agents play the crosslinking role in BR/EPDM/silicon blend. Since the backbones of EPDM and silicon rubber are saturated, there are a few third unsaturated monomers (the content is 1–2 wt %) in EPDM structure, and unsaturated extent is very low, the action of the sulfur is little on the saturated rubber.<sup>31</sup> DCP and BPO are often used as the curing agents in the rubber industry, but the best curing agent used for unsaturated BR is sulfur. The effects of curing agents on blend properties are shown in Table V.

Samples 16 and 23 do not form blends, and it is thought that Sample 16 uses only sulfur to cure BR, and silicon rubber and EPDM are not cured, and so the blend cannot be formed. But Sample 23 uses only BPO to cure little EPDM, in similar manner, and the blend is not formed. Therefore, there are no testing results for Samples 16 and 23. It can be seen from Tables IV and V that the mechanical properties of the vulcanizates with added peroxides and sulfur are better than those of the vulcanizates, with only peroxide or sulfur, and sulfur/DCP is obviously better than sulfur/BPO. This is because that BPO can adequately cure a little EPDM in blending system, but not cure much silicon rubber. On the basis of two kinds of

TABLE V  
Effect of Curing Agents on Blend Properties

	Samples							
	16	17	18	19	20	21	22	23
Sulfur (phr)	5.0	3.0	2.5	2.0	0	2.5	2.5	0
DCP (phr)	0	2.5	2.5	2.5	5.0	0	0	0
BPO (phr)	0	0	0	0	0	2.5	3.0	5.0
Tensile strength (MPa)	—	8.3	8.5	8.2	7.5	8.1	7.9	—
Hardness (Shore A)	—	91	92	90	52	92	93	—
Elongation at break (%)	—	21.5	23.4	20.7	11.2	15.8	17.7	—
Change before and after aging (200°C × 24 h)								
Hardness (Shore A)	—	3	1	3	5	4	2	—
Elongation at break (%)	—	2.8	2.7	3.0	7.9	3.0	4.4	—

Silica 80 phr, SiR/BR/EPDM = 20/30/50.

materials' compatibility principle, the construction and polarity of DCP and silicon rubber are more similar when compared with BPO,<sup>32-34</sup> thus the compatibility of DCP with silicon rubber is better than that of PBO, and DCP curing agents can also cure EPDM. So sulfur/DCP is the best curing agent suitable for silicon rubber/BR/EPDM blend, and the mechanical properties of the blend with added sulfur/DCP are better. In Table V, the properties of Sample 18 are the best when the mass ratio of sulfur/DCP is 2.5/2.5.

As mentioned earlier, the optimal recipe of the blending rubber is determined, which is (silicon rubber + BR + EPDM): silica: DCP : sulfur : ZnO : SA : accelerant M : antioxidant D = (20 + 30 + 50) : 80 : 2.5 : 2.5 : 2.5 : 1.0 : 1.0 : 1.0.

#### Comparison of the properties of blend and three rubbers

Comparison of the properties of three rubbers and blend under the optimal recipe are shown in Table VI. It can be seen from Table VI that silicon rubber could not form vulcanizates, and there is no testing results. The integrate properties of the blend are better than

those of pure rubbers except that elongation at break is little lower.

#### CONCLUSIONS

1. The compatibility of silicon rubber/EPDM with added BR (silicon rubber/BR/EPDM) is better than that of silicon rubber/EPDM, and BR plays a crosslinking agent role in blending system. The heat aging properties of silicon rubber/BR/EPDM are better than those of silicon rubber/EPDM or pure rubbers.
2. With the increase in the reinforcing filler (silica) loading, Shore A hardness of blends improves gradually, the changes of the tensile strength are not obvious, the elongation at break and the changes of heat aging properties are less and less, and the thermal stability of the blend is increased. The maximum content filled silica is 80 phr.
3. The mechanical properties of the vulcanizates with added peroxides and sulfur are better than those of the vulcanizates with only peroxide or sulfur. And sulfur/DCP is obviously better than sulfur/BPO. The mechanical properties of the vulcanizates and the thermal stability are the best when the mass ratio of sulfur/DCP is 2.5/2.5.
4. The change of Shore A hardness and elongation at break of silicon rubber/BR/EPDM blend is low after heat aging under optimal recipe condition, and it suggest that the thermal stabilities are stronger.

TABLE VI  
Comparison of the Properties of Blend and Three Rubbers

	Samples			
	Blend	BR	SiR	EPDM
Tensile strength (MPa)	8.5	1.9	—	1.7
Hardness (Shore A)	92	74	—	86
Elongation at break (%)	23.4	39.5	—	21.1
Change before and after aging (200°C × 24 h)				
Elongation at break (%)	2.7	49.5	—	3.9
Hardness (Shore A)	1	6	—	9

BR sulfur (5 phr); SiR and EPDM DCP (5 phr).

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