Reinforcement of Peroxide-Cured Styrene–Butadiene Rubber Vulcanizates by Mathacrylic Acid and Magnesium Oxide

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ABSTRACT: Through the neutralization of magnesium oxide (MgO) and methacrylic acid (MAA), magnesium methacrylate [$Mg(MAA)_2$] was *in situ* prepared in styrene–butadiene rubber (SBR) and used to reinforce the SBR vulcanizates cured by dicumyl peroxide (DCP). The experimental results show that the mechanical properties, dynamic mechanical properties, optical properties, and crosslink structure of the $Mg(MAA)_2$-reinforced SBR vulcanizates depend on the DCP content, $Mg(MAA)_2$ content, and the mole ratio of MgO/MAA. The formulation containing DCP 0.6–0.9 phr, $Mg(MAA)_2$ 30–40 phr, and MgO/MAA mole ratio 0.50–0.75 is recommended for good mechanical properties of the SBR vulcanizates. The tensile strength of the SBR vulcanizates is up to 31.4 MPa when the DCP content is 0.6 phr and the $Mg(MAA)_2$ content is 30 phr. The SBR vulcanizates have good aging resistance and limited retention of tensile strength at 100°C. The SBR vulcanizates are semitransparent, and have a good combination of high hardness, high tensile strength, and elongation at break. The T_g values of the SBR vulcanizates depend largely on the DCP content, but depend less on the $Mg(MAA)_2$ content and the MgO/MAA mole ratio. The contents of DCP, $Mg(MAA)_2$, and the MgO/MAA mole ratio have also great effects on the E' values of the vulcanizates. The salt crosslink density is greatly affected by the $Mg(MAA)_2$ content and MgO/MAA mole ratio, but less affected by the DCP content. J Appl Polym Sci 85: 2667–2676, 2002

Key words: high performance polymers; mechanical properties; reinforcement; rubber

INTRODUCTION

Metal salts of unsaturated carboxylic acids have been used as effective reinforcing fillers for dicumyl peroxide (DCP)-cured rubbers.[1–3] In the late 1970s, they were used in forming rubber cores of golf balls, imparting the balls' high hardness while maintaining good resilience.[1,4] Later, research showed that the metal salts of unsaturated carboxylic acids do not only improve the hardness and modulus of rubber vulcanizates, but also reinforce rubbers to different extents.[3,5–9] They can be added into rubbers directly or prepared *in situ* in rubbers through the neutralization of metal oxides or hydroxides and acids. For the sake of good mechanical properties, the *in situ* preparation is better than the direct addition of the metal salt.[10] The Zeon Company in Japan developed a high performance hydrogenated nitrile–butadiene rubber (HNBR) with the trade

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Table I Raw Materials

Material	Tradename and Characteristics	Manufacturer
SBR	SBR-1500, styrene content 23.5%	Qilu Petroleum Co., China
MgO	Industrial grade	Shanghai Jinghua Chemicals Co., China
MAA	CR	Shanghai Wulian Chemicals Co., China
DCP	Industrial grade	Shanghai Gaoqiao Petroleum Co., China

name ZSC, which was reinforced by the *in situ* prepared zinc methacrylate [$Zn(MAA)_2$] from zinc oxide (ZnO) and methacrylic acid (MAA).[10,11]

These studies focused on the reinforcing systems of $Zn(MAA)_2$ and ZnO/MAA, and on the rubbers of HNBR and nitrile–butadiene rubber (NBR). There are few publications concerning SBR reinforcement by metal salts of unsaturated carboxylic acids. It was reported in two Japanese patents that the mixture of ZnO/MAA has a good reinforcing effect on styrene–butadiene rubber (SBR) and high-*cis* polyisoprene rubber (IR).[12,13] It was found in our primary experiment that the mixture of MgO/MAA has a good reinforcing effect on the SBR vulcanizates. In this paper, the reinforcement effect of the MgO/MAA mixture on the SBR vulcanizates was investigated. The effects of compositions on the mechanical and dynamic mechanical properties, optical properties, and crosslink structure of the SBR vulcanizates were also investigated.

EXPERIMENTAL

Materials and Sample Preparation

Raw materials used in this study are listed in Table I.

SBR and additives were mixed in the mixing chamber of a HAKKE Rheometer RC90 at room temperature and a rotor speed of 32 rpm, and then pressed to sheets on a two-roll mill. The compound was then press-cured for 10 min at 170°C, and cut into specimens for measurement.

Measurement

The *tensile test* was carried out according to the Chinese Standards GB 528-82 with an Instron 4465 tensile tester at a crosshead speed of 500 mm/min.

Shore A hardness was measured using a handheld Shore A durometer according to Chinese Standard GB 531-83.

The *dynamic mechanical properties* were measured using a rheometer from Rheometric Scientific model DMTA IV under a tension mode at a frequency of 1 Hz with dynamic strain of 0.012%.

The *optical property* was measured using a hazemeter model M57 produced by Ray Ran Company, UK.

The *crosslink density* was determined by equilibrium swelling. Samples were swollen in toluene at room temperature for 3 days, and then vacuum dried. Vr, the volume fraction of rubber in swollen gel, representing the whole crosslink density of the vulcanizates, was determined by the following equation:

$$Vr = m_0 \cdot \phi \cdot (1-\alpha) \cdot \rho_n^{-1} / [m_0 \cdot \phi \cdot (1-\alpha) \cdot \rho_n^{-1} + (m_s - m_d) \cdot \rho_s^{-1}] \quad (1)$$

where m_0 is the sample mass before swelling, m_s and m_d are sample masses before and after drying, ϕ is the mass fraction of rubber in the vulcanizate, α is the mass loss of the gum SBR vulcanizate during swelling, and ρ_n and ρ_s are the densities of the rubber and solvent, respectively. The vulcanizates contain both salt crosslinks and covalent crosslinks, so it is significant to distinguish the salt crosslink density from the covalent one. To determine the covalent crosslink density Vr_1, samples were swollen in toluene/dichloroacetic acid solution with the concentration of 0.7686 mol/L for 5 days to destroy the salt bonds, and then swollen in toluene for 3 days. Vr_1 was also calculated from eq. (1). Vr_2, calculated by subtracting Vr_1 from Vr, was used to represent the salt crosslink density.

The *neutralization degree* of MgO and MAA in the compound was determined by titration. A certain quantity of the compound with the MAA content X_1 was dissolved in toluene and then filtrated, the MAA in the filtrate was neutralized by a certain volume of KOH/ethanol solution with the concentration of 0.1172 mol/L, and the residual KOH was titrated by hydrochloric acid/etha-

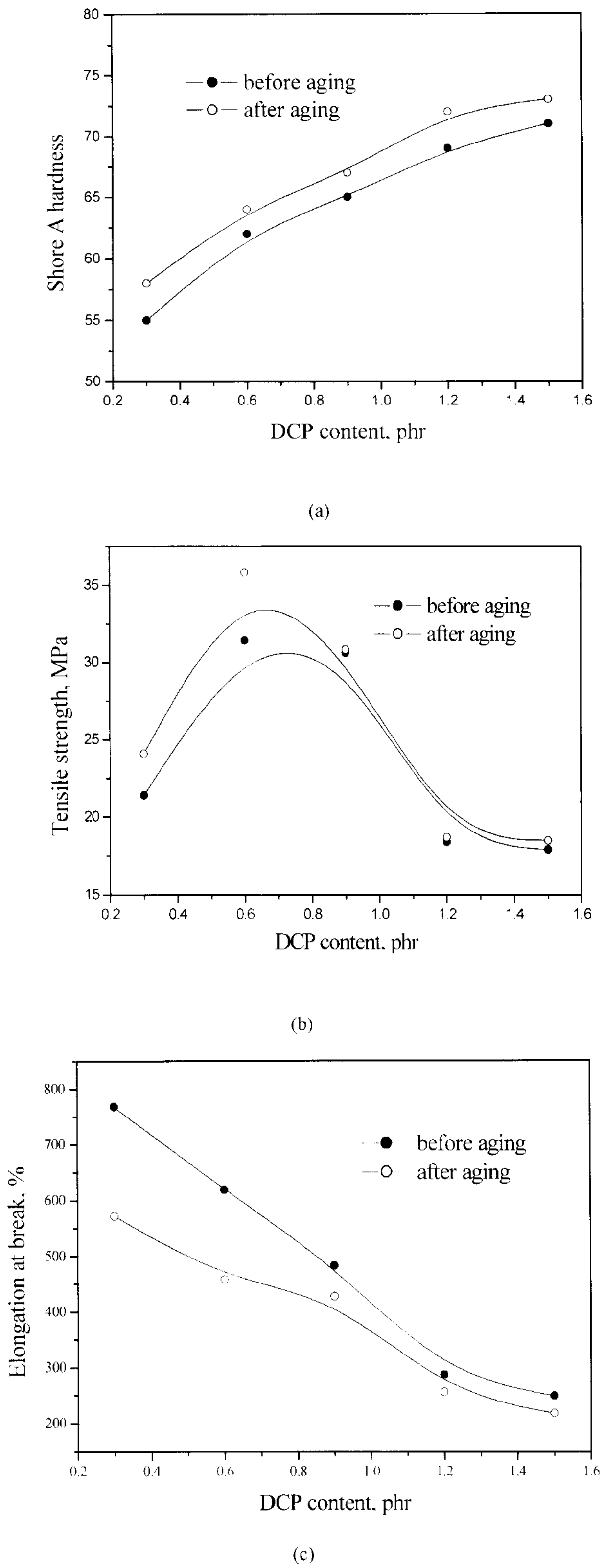


Figure 1 Effect of DCP content on mechanical properties before and after aging. (a) Shore A hardness; (b) tensile strength; (c) elongation at break. Formulation: SBR 100, MgO/MAA 6.2/26.6 phr, DCP variable.

nol solution with the concentration of 0.1083 mol/L. X_2, the content of the residual MAA in the compound was calculated according to neutralization formulas. X_2/X_1 was used to represent the neutralization degree of MgO and MAA.

RESULTS AND DISCUSSION

Effect of DCP Content on the Properties of SBR Vulcanizates

$Mg(MAA)_2$ can be added in SBR directly for reinforcement, but the tensile strength of the DCP-cured SBR vulcanizates is always less than 20 MPa.[14] To get the combination of high hardness, high tensile strength and elongation at break, the method of *in situ* formation of $Mg(MAA)_2$ through the neutralization of a MgO/MAA mixture in SBR was chosen. In the formulation, MgO and MAA were designed to react in the MgO/MAA mole ratio of 0.5 and to give $Mg(MAA)_2$ content of 30 phr. As shown in Figure 1, the effect of DCP content on the mechanical properties of MgO/MAA-reinforced SBR vulcanizates before aging is significant. With increasing DCP content, the hardness of the SBR vulcanizates increased while the elongation at break decreased. It is surprising to note that the tensile strength reached maximum value of 31.4 MPa when the DCP content is 0.6 phr. The DCP content in the range of 0.6–0.9 phr is recommended for a good combination of all the mechanical properties under investigation.

The MgO/MAA-reinforced SBR vulcanizates were aged in an oven for 24 h at 100°C. The effect of DCP content on the aging resistance of the vulcanizates is also shown in Figure 1. After aging, the hardness increased slightly; the elongation at break decreased with retention of 74–89% values in the range. The tensile strength increased slightly at low DCP content, and remained almost the same as that before aging when DCP content is more than 0.9 phr. These results show that the SBR vulcanizates have good aging resistance.

The effect of DCP content on the tensile properties of MgO/MAA-reinforced SBR vulcanizates at 100°C is shown in Table II. The high temperature of 100°C leads to sharp decrease in tensile strength and elongation at break, and the retention values were in the range 20–34 and 46–61%, respectively, when compared to the tensile properties at room temperature. This implies that the tensile properties of the vulcanizates at high temperature are to be improved.

Table II Effect of DCP Content on Tensile Properties at 100°C[a]

	DCP Content (phr)				
Properties	0.3	0.6	0.9	1.2	1.5
Tensile strength (MPa)	5.30	8.05	6.27	6.35	5.39
Elongation at break (%)	474	368	225	170	122

[a] Formulation: SBR 100, MgO/MAA 6.2/26.6 phr, DCP variable.

When a strain is imposed periodically with a sinusoidal alternation at a frequency on the rubber specimens that possess viscoelastic behavior, the stress will also alternate sinusoidally but will be out of phase, i.e., the stress lagging the applied stress. Thus, the dynamic losses are usually associated with hysteresis and some mechanisms of molecular or structural motion in rubber materials. The damping characteristics are extensively measured as "the tangent of the phase angle (tanδ)." If a rubber vulcanizate is used for tires, high tanδ of the vulcanizate at temperature 0–30°C is favorable to the wet skid resistance of the tires, and low tanδ at temperature 30–70°C is favorable to the reduced rolling resistance. The tanδ values at 0 and 60°C, and T_g of the SBR vulcanizates are listed in Table III. The effect of DCP content on the storage modulus (E') and tanδ of the SBR vulcanizates is shown in Figure 2. As can be seen, at a certain temperature, with increasing DCP content from 0.3 to 1.5 phr, the E' values increased as was observed in the case of the modulus at 100% [see Fig. 1(a)]. The T_g values increased significantly from −45.8 to −39.1°C, which should be explained by the increase of the covalent crosslink density. The tanδ values decreased slightly at temperatures over 0° C, especially at high DCP content of 1.5 phr.

The crosslink structure of the MgO/MAA-reinforced SBR vulcanizates was measured by equilibrium swelling. The values of Vr (representing the whole crosslink density), Vr_1 (representing the covalent crosslink density), and Vr_2 (representing the salt crosslink density) were influenced by the DCP content as shown in Figure 3. The whole crosslink density and covalent

Table III Effect of DCP Content on T_g and Tan δ at 0 and 60°C

	Property		
DCP Content (phr)	T_g (°C)	Tan δ at 0°C	Tan δ at 60°C
0.3	−45.8	0.162	0.151
0.9	−42.5	0.125	0.089
1.5	−39.1	0.101	0.059

[a] Formulation: the same as in Table II.

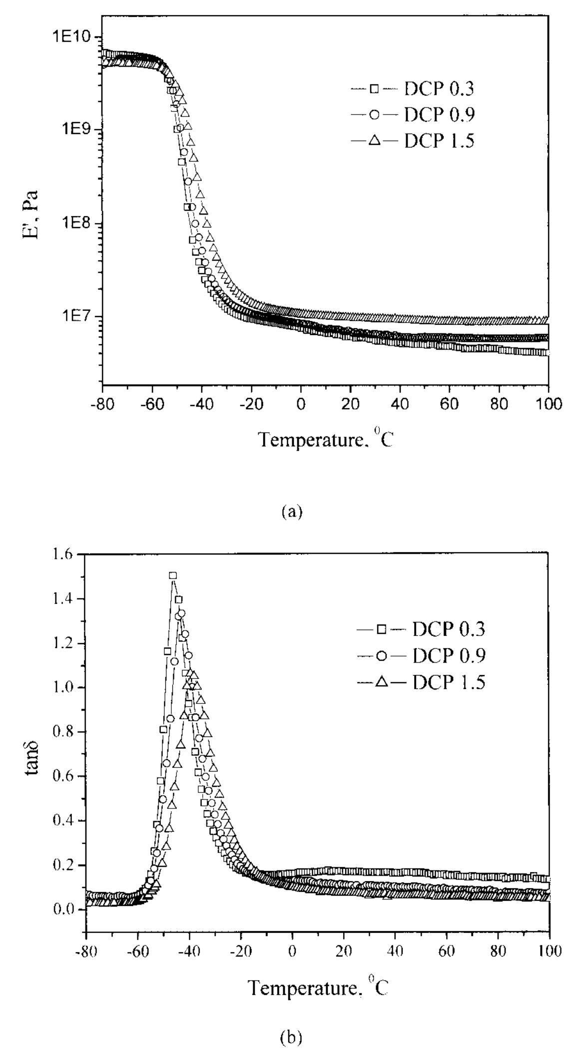


Figure 2 Effect of DCP content on dynamic mechanical properties. (a) E'; (b) tanδ. Formulation: the same as in Figure 1.

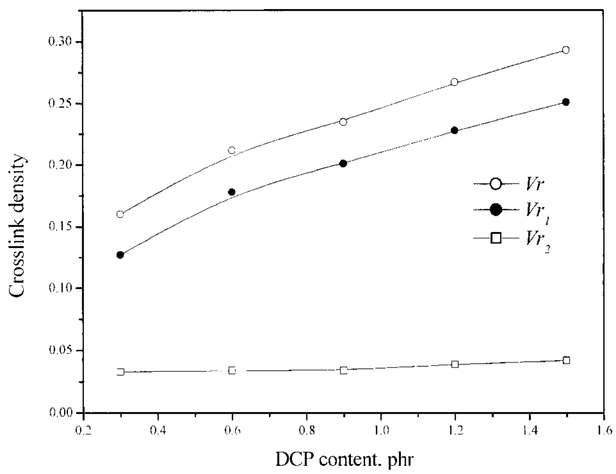


Figure 3 Effect of DCP content on crosslink densities. Formulation: the same as in Figure 1.

crosslink density increased with increasing DCP content. However, the DCP content has little effect on the salt crosslink density.

The MgO/MAA-reinforced SBR vulcanizates are semitransparent. The effect of DCP content on the light transmission and haze of the vulcanizates is shown in Table IV. The values of light transmission of all the SBR vulcanizates are about 23%, and independent of DCP content. However, the haze decreased with increasing DCP content. This implies that high DCP content favors high transparency of the SBR vulcanizates.

Effect of $Mg(MAA)_2$ Content on the Properties of SBR Vulcanizates

In the basic formulation, MgO and MAA was designed to react totally in the mole ratio of 0.5 and the productivity of $Mg(MAA)_2$ was in the range of 0–50 phr, and the DCP content was 0.9 phr. The effect of $Mg(MAA)_2$ content on the mechanical properties of the MgO/MAA-reinforced SBR vulcanizates is significant as shown in Figure 4.

Table IV Effect of DCP Content on Optical Properties[a]

	DCP Content (phr)				
Properties	0.3	0.6	0.9	1.2	1.5
Transmission (%)	23.8	23.3	22.2	23.5	22.6
Haze (%)	62.5	58.9	50.4	46.1	46.6

[a] Formulation: the same as in Table II.

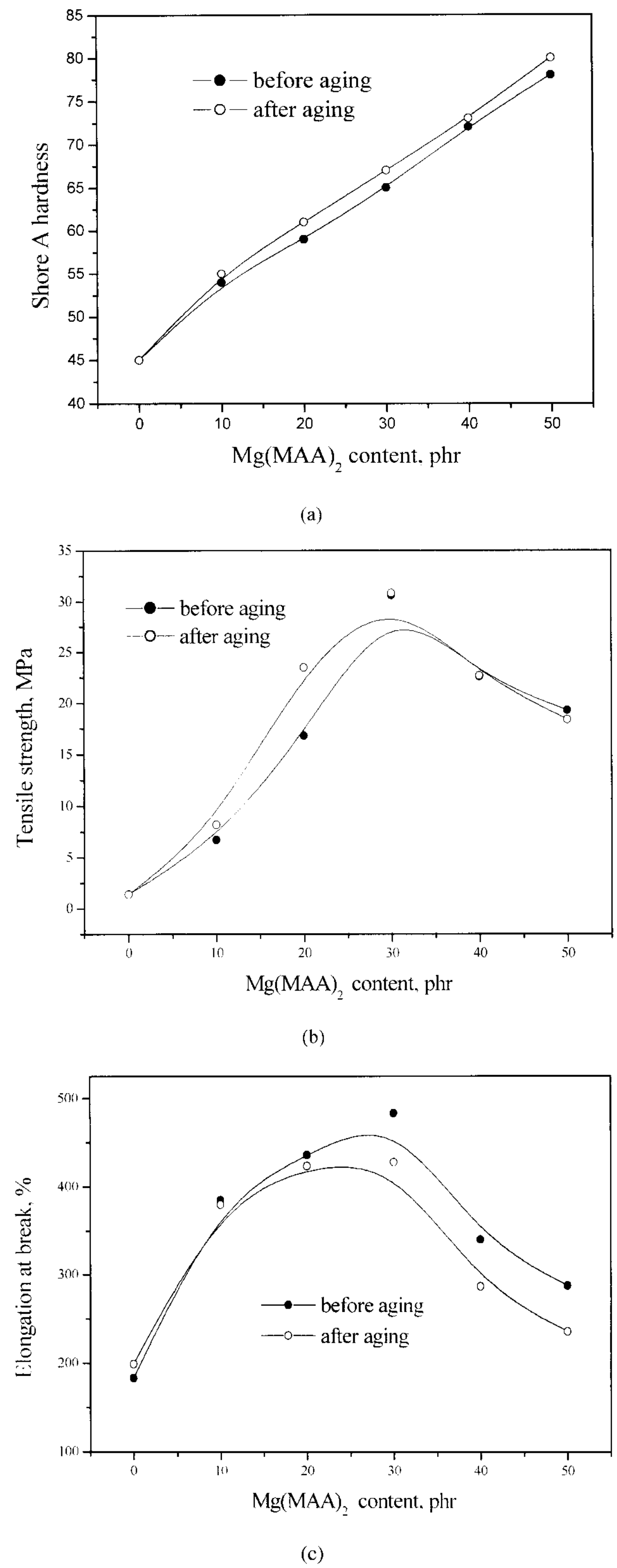


Figure 4 Effect of $Mg(MAA)_2$ content on mechanical properties before and after aging. (a) Shore A hardness; (b) tensile strength; (c) elongation at break. Formulation: SBR 100, DCP 0.9 phr, $Mg(MAA)_2$ (calculated based on MgO/MAA content) variable.

Table V Effect of $Mg(MAA)_2$ Content on Tensile Properties at 100°C[a]

Properties	Mg(MAA)₂ Content (phr)					
	0	10	20	30	40	50
Tensile strength (MPa)	0.79	1.91	4.12	6.27	7.02	6.65
Elongation at break (%)	57.4	162	235	225	189	143

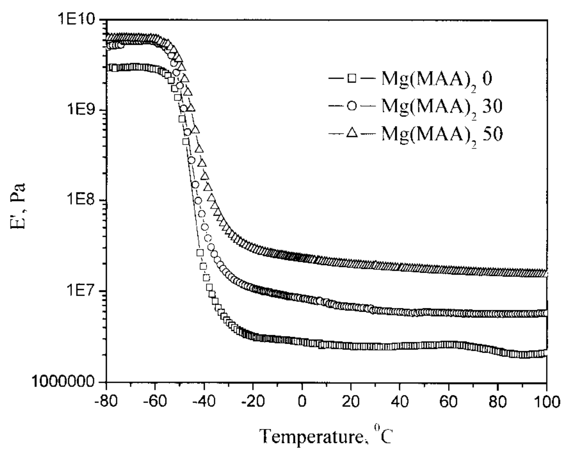
[a] Formulation: SBR 100, DCP 0.9 phr, $Mg(MAA)_2$ (calculated based on MgO/MAA content) variable.

With increasing $Mg(MAA)_2$ content, the hardness increased; the tensile strength and elongation at break reached their maximum values of 30.6 MPa and 483%, respectively, at the $Mg(MAA)_2$ content of 30 phr. The $Mg(MAA)_2$ content of 30–40 phr is recommended for a good combination of all the mechanical properties.

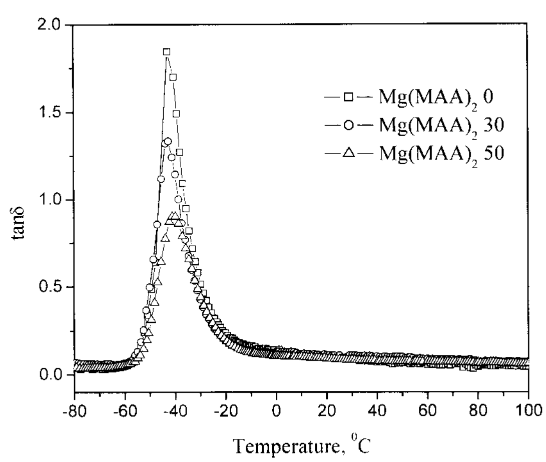
The MgO/MAA-reinforced SBR vulcanizates were aged in an oven for 24 h at 100°C. The effect of $Mg(MAA)_2$ content on the aging resistance of the vulcanizates is shown in Figure 4. After aging, the hardness increased slightly; the elongation at break decreased with retention values in the range 81–98%; the tensile strength increased for $Mg(MAA)_2$ content of 0–30 phr, but decreased at higher $Mg(MAA)_2$ contents. These results also indicate that the SBR vulcanizates have good aging resistance.

The effect of $Mg(MAA)_2$ content on the tensile properties of the MgO/MAA-reinforced SBR vulcanizates at 100°C is shown in Table V. The high temperature of 100°C leads to sharp decrease in the tensile strength and elongation at break, and their retention values were 20–34% and 42–55%, respectively, when compared to the tensile properties at room temperature.

The effect of $Mg(MAA)_2$ content on the E' and tanδ of the SBR vulcanizates is shown in Figure 5. The values of T_g and tanδ at 0 and 60°C are listed in Table VI. At a certain temperature, with increasing $Mg(MAA)_2$ content, the E' values increased markedly as observed in the case of the modulus at 100% [see Fig. (4a)]. The T_g values increased slightly, which may be attributed to the slight increase of covalent crosslink density; the tanδ values beyond the glass transition tempera-



(a)



(b)

Figure 5 Effect of $Mg(MAA)_2$ content on dynamic mechanical properties. (a) E'; (b) tanδ. Formulation: the same as in Figure 4.

Table VI Effect of $Mg(MAA)_2$ Content on T_g and Tan δ at 0 and 60°C[a]

Mg(MAA)₂ Content (phr)	Property		
	T_g (°C)	Tan δ at 0°C	Tan δ at 60°C
0	−42.8	0.129	0.064
30	−42.5	0.125	0.089
50	−41.0	0.109	0.075

[a] Formulation: the same as in Table V.

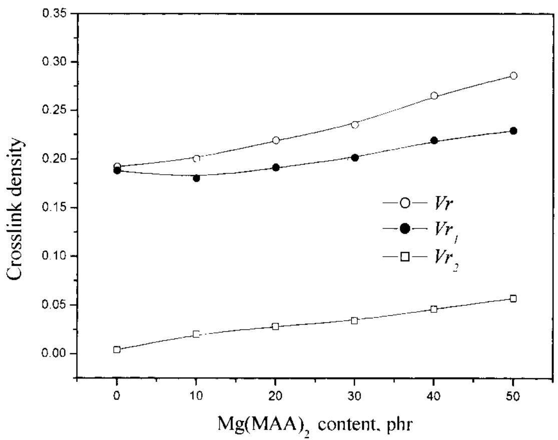


Figure 6 Effect of $Mg(MAA)_2$ content on crosslink densities. Formulation: the same as in Figure 4.

ture zone of the SBR vulcanizates have slight variations.

The effect of $Mg(MAA)_2$ content on the crosslink density of the MgO/MAA-reinforced SBR vulcanizates is shown in Figure 6. With increasing $Mg(MAA)_2$ content, the whole crosslink density, covalent crosslink density, and salt crosslink density all increased to different extents, although the salt crosslink density was much less than the covalent crosslink density.

The effect of $Mg(MAA)_2$ content on the light transmission and haze of the MgO/MAA-reinforced SBR vulcanizates is shown in Table VII.. The SBR vulcanizate without MgO/MAA is light-brown in color and its light transmission is only 15.5%, but the light transmission of the SBR vulcanizates containing MgO/MAA increased to 20–25%. The haze increased with increasing $Mg(MAA)_2$ content. This indicates that the high loading of $Mg(MAA)_2$ is unfavorable to the transparency of the vulcanizates.

Effect of MgO/MAA Mole Ratio on the Properties of SBR Vulcanizates

To achieve content level of 30 phr $Mg(MAA)_2$, MgO and MAA were designed to react at the mole

Table VII Effect of $Mg(MAA)_2$ Content on Optical Properties[a]

	Mg(MAA)$_2$ Content (phr)					
Properties	0	10	20	30	40	50
Transmission	15.5	20.2	21.0	22.2	25.0	22.1
Haze	—	—	43.5	50.4	69.7	88.7

[a] Formulation: the same as in Table V.

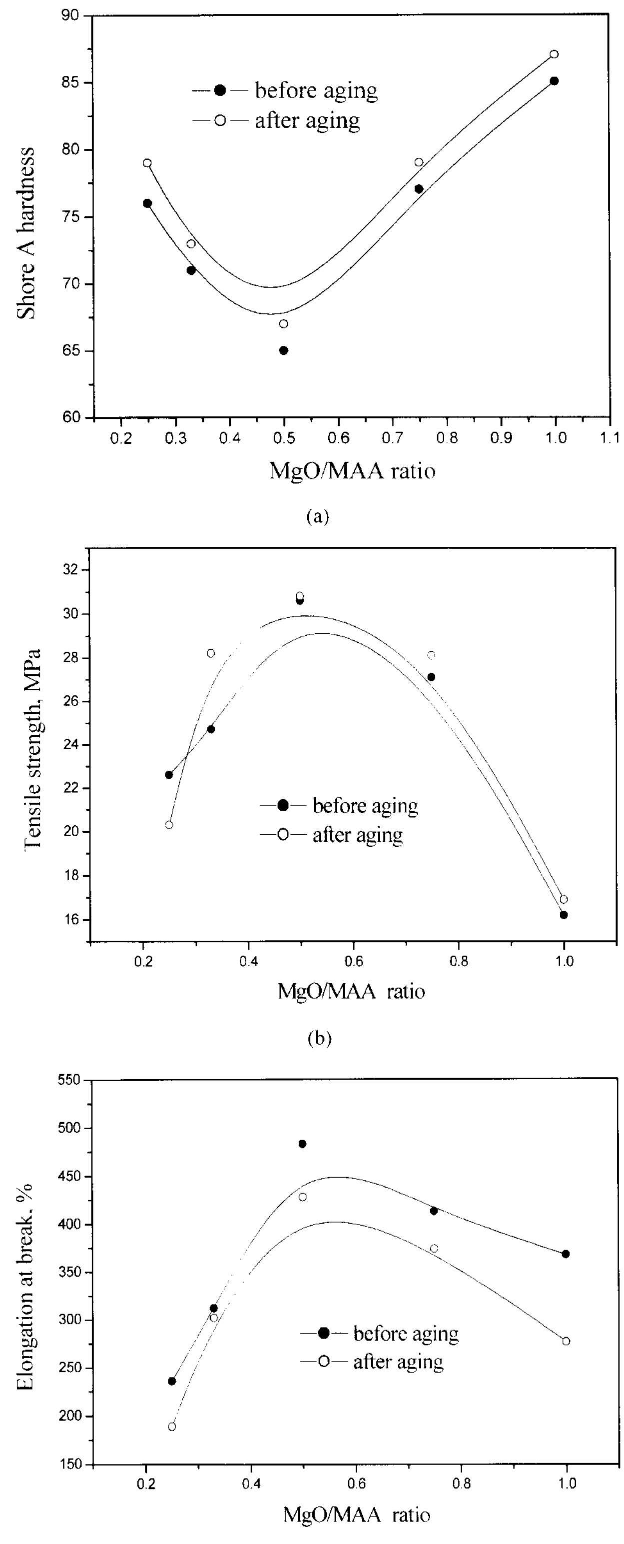


Figure 7 Effect of MgO/MAA mole ratio on mechanical properties before and after aging. (a) Shore A hardness; (b) tensile strength; (c) elongation at break. Formulation: SBR 100, DCP 0.9 phr, MgO/MAA mole ratio variable.

Table VIII Effect of MgO/MAA Mole Ratio on Tensile Properties at 100°C[a]

	MgO/MAA Mole Ratio				
Properties	0.25	0.33	0.50	0.75	1.00
Tensile strength (MPa)	7.18	8.13	6.27	7.93	8.90
Elongation at break (%)	154	219	225	185	151

[a] Formulation: SBR 100, DCP 0.9 phr, MgO/MAA mole ratio variable.

ratio of 0.25–1.0, corresponding to mass ratio in the range of 6.19/53.2–12.4/26.6. The significant effect of MgO/MAA mole ratio on the MgO/MAA-reinforced SBR vulcanizates before aging is shown in Figure 7. The hardness reached its minimum value at MgO/MAA mole ratio of 0.50, where on the contrary the tensile strength and elongation at break reached their maximum values. The MgO/MAA ratio of 0.50–0.75 is recommended for a good combination of all the mechanical properties.

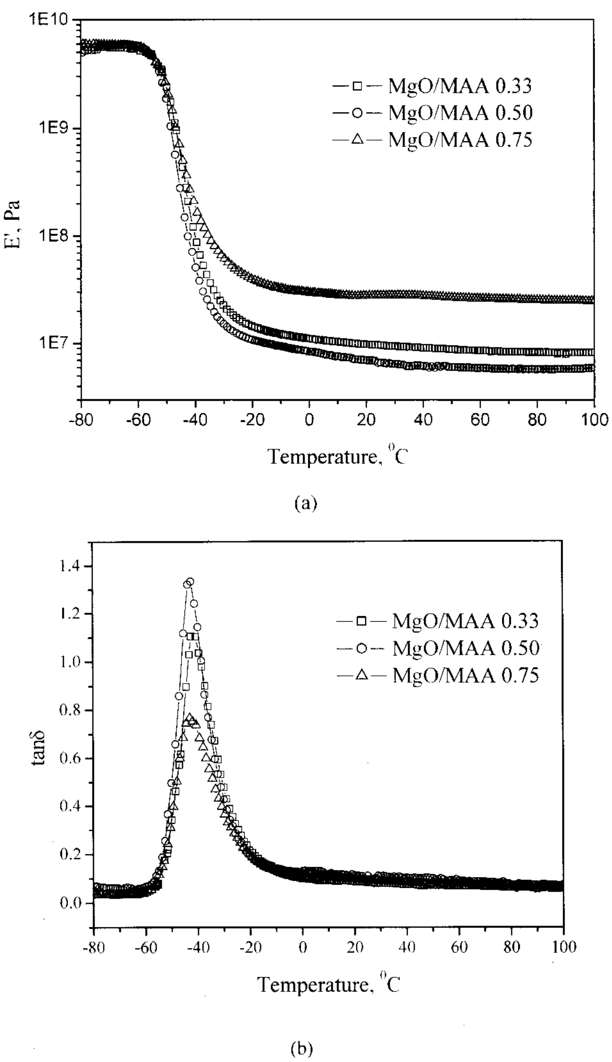


Figure 8 Effect of MgO/MAA mole ratio on dynamic mechanical properties. (a) E'; (b) tanδ. Formulation: the same as in Figure 7.

The MgO/MAA-reinforced SBR vulcanizates were aged in an oven for 24 h at 100°C. The effect of MgO/MAA ratio on the aging resistance of the vulcanizates is shown in Figure 7. After aging, the hardness increased slightly; the elongation at break decreased with retention values in the range 75–96%; the tensile strength increased slightly at MgO/MAA mole ratio of 0.33–1.0. These results also show that the SBR vulcanizates have good aging resistance.

The effect of MgO/MAA mole ratio on the tensile properties of MgO/MAA-reinforced SBR vulcanizates at 100°C is shown in Table VIII. The high temperature of 100°C lead to marked drop in tensile strength and elongation at break, and their retention values were in the range 20–54% and 41–70%, respectively, when compared to the tensile properties at room temperature.

The effect of MgO/MAA mole ratio on the E' and tanδ values of the SBR vulcanizates with increasing temperature is shown in Figure 8. The T_g and tanδ values at 0 and 60°C are listed in Table IX. At the MgO/MAA mole ratio of 0.50, the SBR vulcanizates have the lowest E' values. The overloading of MgO or MAA leads to an increase

Table IX Effect of MgO/MAA Mole Ratio on T_g and Tan δ at 0 and 60°C[a]

MgO/MAA Mole Ratio	Property		
	T_g (°C)	Tan δ at 0°C	Tan δ at 60°C
0.33	−41.7	0.121	0.078
0.50	−42.5	0.125	0.089
0.75	−43.0	0.101	0.070

[a] Formulation: the same as in Table VIII.

in E' as observed in the case of the modulus at 100% [see Fig. 8(a)]. With increasing MgO/MAA mole ratio, the T_g values decreased, which can be attributed to the decrease of the covalent crosslink density. At a certain temperature, the tanδ values beyond the glass transition temperature zone is independent of the MgO/MAA mole ratio.

The effect of MgO/MAA mole ratio on the crosslink density of the MgO/MAA-reinforced SBR vulcanizates is shown in Figure 9. With increasing the MgO/MAA mole ratio, the covalent crosslink density decreases linearly; the whole crosslink density and salt crosslink density reached their minimum values at the MgO/MAA mole ratio of 0.50 and increased significantly after that.

The MgO/MAA mole ratio has a significant effect on the light transmission and haze of the SBR vulcanizates as shown in Table X. The vulcanizates are semitransparent at the MgO/MAA mole ratio of 0.25–0.50, and the transmission is about 22%. But they became opaque when MgO is overloaded, that is, the MgO/MAA mole ratio is more than 0.50.

Neutralization Degree of MgO and MAA

The neutralization degree of MgO and MAA was determined by measuring the residual MgO in the SBR compound by titration. For the SBR compounds with the MgO/MAA mole ratio of 0.50 and 1.0, the neutralization degree of MgO and MAA was 72.9% for the former and 87.5% for the latter. This implies that the neutralization mainly occurs in the compounding process but cannot reach 100%, and some free MAA molecules remain unreacted even when MgO is highly loaded.

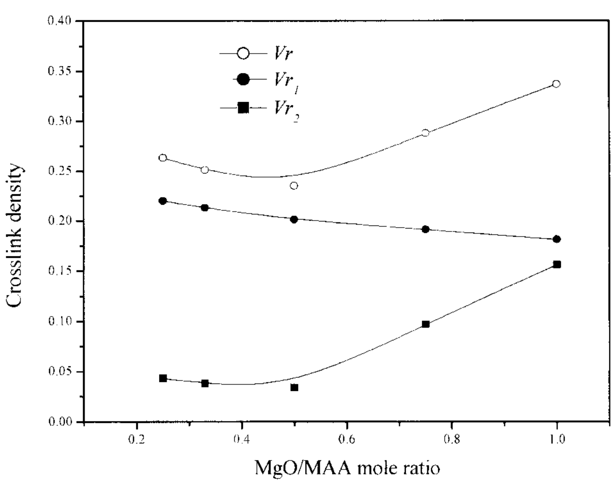


Figure 9 Effect of MgO/MAA mole ratio on crosslink densities. Formulation: the same as in Figure 7.

Table X Effect of MgO/MAA Mole Ratio on Optical Properties[a]

	MgO/MAA Mole Ratio				
Properties	0.25	0.33	0.50	0.75	1.00
Transmission	24.4	24.3	22.2	8.4	2.8
Haze	39.7	39.1	50.4	/	/

[a] Formulation: the same as in Table VIII.

CONCLUSIONS

The DCP content, $Mg(MAA)_2$ content, and MgO/MAA mole ratio have significant effects on the mechanical properties of MgO/MAA-reinforced SBR vulcanizates; their optimum contents are 0.6–0.9 phr for DCP, 30–40 phr for $Mg(MAA)_2$, and 0.50–0.75 for MgO/MAA ratio. The tensile strength of the vulcanizates reached 31.4 MPa when the DCP and $Mg(MAA)_2$ content are 0.6 and 30 phr, respectively. The vulcanizates have good thermal aging resistance and limited retention of tensile properties at 100°C.

The salt crosslink density of the vulcanizates are affected clearly by the $Mg(MAA)_2$ content and MgO/MAA mole ratio, but is independent of the DCP content. The T_g values are influenced by the covalent crosslink density of the vulcanizates, and depend largely on the DCP content, but it has little dependence on the $Mg(MAA)_2$ content and the MgO/MAA mole ratio. The DCP content, Mg-$(MAA)_2$ content, and the MgO/MAA mole ratio also have great effects on the E' of the vulcanizates.

The vulcanizates are semitransparent, and have a good combination of high hardness, high tensile strength, and elongation at break.

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