Effect of Fillers and Additives on the Properties of SBR Vulcanizates

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ABSTRACT: Methacrylic acid (MAA) and methyl methacrylate (MMA) were used as additives for peroxide-cured styrene–butadiene rubber (SBR) filled with three inorganic fillers with different particle sizes and surface activity, for example, MgO, $Mg(OH)_2$, and $BaSO_4$. The experimental results show that the introduction of MAA can improve the mechanical properties of SBR vulcanizates filled with MgO, $Mg(OH)_2$, or $BaSO_4$. A small amount of MAA leads to significant increases in the modulus, tensile strength, and tear strength. MMA has little effect on the mechanical properties of the SBR vulcanizates. The SEM micrographs show that MAA can improve the interfacial bonding between SBR and the three kinds of fillers. The SBR–filler interaction was studied by Kraus plots. The relationship between the SBR–filler interaction and the mechanical properties was explored. m, a characteristic constant of a filler–SBR matrix, represents the interfacial bonding between fillers and SBR and the accumulated structure of the fillers. At a given ϕ, a high value of m means a strong interaction between SBR and the filler and, therefore, strong mechanical properties. The Payne effect of the SBR vulcanizates was observed, and the vulcanizates have low storage moduli at high strains and high storage moduli at low strains, and the moduli are nonlinear and increase the nonlinearity as the filler content increases. The loss moduli and loss factor reach their maximums at moderate and high strain amplitudes, respectively. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 775–782, 2003

Key words: fillers; rubber; vulcanization; additives

INTRODUCTION

It has been reported that metal salts of unsaturated carboxylic acids are effective reinforcing fillers for dicumyl peroxide (DCP)-cured rubbers.[1–5] The salts can be added into the rubbers directly or be prepared *in situ* in the rubber matrix through the neutralization of metal oxides or hydroxides and acids. For the sake of good mechanical properties, the *in situ* preparation is better than is the direct addition of the metal salt.[6,7] We carried out detailed studies on the *in situ* reinforcement of rubbers such as nitrile–butadiene rubber (NBR), the ethylene–propylene–diene terpolymer (EPDM), and styrene–butadiene rubber (SBR) with metal oxides or hydroxides and unsaturated carboxylic acids[8–10] and found good mechanical properties of the rubber vulcanizates. Based on these studies, methacrylic acid (MAA) can be used as a special additive for rubber vulcanizates filled with metal oxides or hydroxides, such as $Al(OH)_3$, MgO, or $Mg(OH)_2$. During mixing, a metal salt of MAA would be *in situ* prepared in the rubber composites, and the homopolymerization and graft copolymerization of the metal salt of MAA occurred at the same time during the curing of the rubber composites by peroxide.[11] The resulting graft copolymer may play the role of compatilization,[12] thus improving the mechanical properties of the rubber vulcanizates. Therefore, a study on the interaction between the filler and rubber should be meaningful. Based on our previous conclusion that MAA is an effective additive for improving the mechanical properties of DCP-cured SBR vulcanizates with a high loading of $Al(OH)_3$,[13] we carried out a detailed study on the effects of fillers and additives on the mechanical properties of SBR vulcanizates and explored the relationship between the filler–rubber interaction and the mechanical properties of the SBR vulcanizates.

EXPERIMENTAL

Materials and sample preparation

The raw materials used are shown in Table I. the formulations of the rubber compounds are shown in Table II. SBR and the additives were mixed in the mixing chamber of a HAKKE rheometer RC90 at room temperature at a rotor speed of 32 rpm and then pressed into sheets on a two-roll mill. the compound was press-cured for 10 min at 170°C according to the curing curve to obtain specimens for measurement.

Measurements

Tensile and tear tests

Tensile and tear tests were carried out according to the Chinese Standards GB 528-82 and GB 530-81, respec-

TABLE I
Raw Materials

Material	Trade name and characteristics	Manufacturer
SBR	SBR-1500, 23.5% styrene	Qilu Petroleum Co. (China)
MgO	Industrial grade	Jiangsu Kunshang Chemicals Co. (China)
Mg(OH)$_2$	Industrial grade	Neltec Co. (Germany)
BaSO$_4$	Industrial grade	Guangzhou Chemicals Co. (China)
MAA	Chemical pure	Shanghai Wulian Chemicals Co. (China)
MMA	Chemical pure	Shanghai Wulian Chemicals Co. (China)
DCP	Commercial produce	Shanghai Gaoqiao Petroleum Co. (China)

tively, with an Instron 4465 tensile tester at a crosshead speed of 500 mm/min.

Surface morphology

Surface morphology was observed using a Hitachi S-2150 scanning electron microscope (SEM). The specimens were fractured under the cryogenic condition of liquid nitrogen; then, the fractured surface was coated with thin a layer of gold before SEM observation.

V_r, the volume fraction of rubber in swollen gel, was determined by equilibrium swelling. Specimens were swollen in toluene at room temperature for 3 days and then vacuum-dried at 80&Deg;C. V_r was determined by the following equation:

$$V_r = m_0 \, \phi \, (1 - \alpha) \, \rho_r^{-1} / [m_0 \, \phi \, (1 - \alpha) \, \rho_r^{-1} + (m_s - m_d) \, \rho_s^{-1}] \quad (1)$$

where m_0 is the sample mass before swelling; m_s and m_d, the sample masses before and after drying; ϕ, the mass fraction of rubber in the vulcanizate; α, the mass loss of the gum SBR vulcanizate during swelling; and ρ_r and ρ_s, the densities of the rubber and solvent, respectively.

Dynamic mechanical properties

The dynamic mechanical properties were measured using a rheometer of Rheometric Scientific™, Model DMTA IV, under a tension mode by increasing the strain amplitude from 0.007 to 12% (20 points per decade) at a constant temperature of 60^{0}C and a frequency of 1 Hz.

RESULTS AND DISCUSSION

Effect of fillers and additives on the mechanical properties of SBR vulcanizates

The effects of MgO, Mg(OH)$_2$, or BaSO$_4$ and MAA or methyl methacrylate (MMA) on the mechanical properties of the SBR vulcanizates (sample nos. 1–9 in Table II) are shown in Figure 1(i)–(iv). With an increasing MgO or Mg(OH)$_2$ content, the modulus, tensile strength, and tear strength of the SBR vulcanizates increased, and the three properties of the SBR/MgO vulcanizates were higher than those of the SBR/Mg(OH)$_2$ vulcanizates at the same loading of the filler. The elongation at break of the SBR/Mg(OH)$_2$ vulcanizates increased slightly with an increasing Mg(OH)$_2$ content, and the elongation of the SBR/MgO vulcanizates decreased when the MgO content increased to over 100 phr. BaSO$_4$, in the range of 0–150 phr, had little effect on the modulus, tensile strength, and tear strength of the SBR vulcanizates, but led to an increase in the elongation at break.

It was surprising to note that the small amount of 10 phr MAA not only led to a significant improvement of the mechanical properties of the SBR vulcanizate without a filler, but also led to significant increases in the modulus, tensile strength, and tear strength of the SBR vulcanizates filled with MgO, Mg(OH)$_2$, or BaSO$_4$. At a filler content of 25–150 phr, 10 phr MAA increased the modulus and tensile strength of the SBR/MgO and SBR/Mg(OH)$_2$ vulcanizates one- to twofold and the tensile strength of the SBR/BaSO$_4$ vulcanizates two- to threefold. The presence of 10 phr MAA led to a decrease in the elongation at break of the SBR/MgO and SBR/Mg(OH)$_2$ vulcanizates and an increase of the

TABLE II
Formulation of Rubber Compounds (phr)

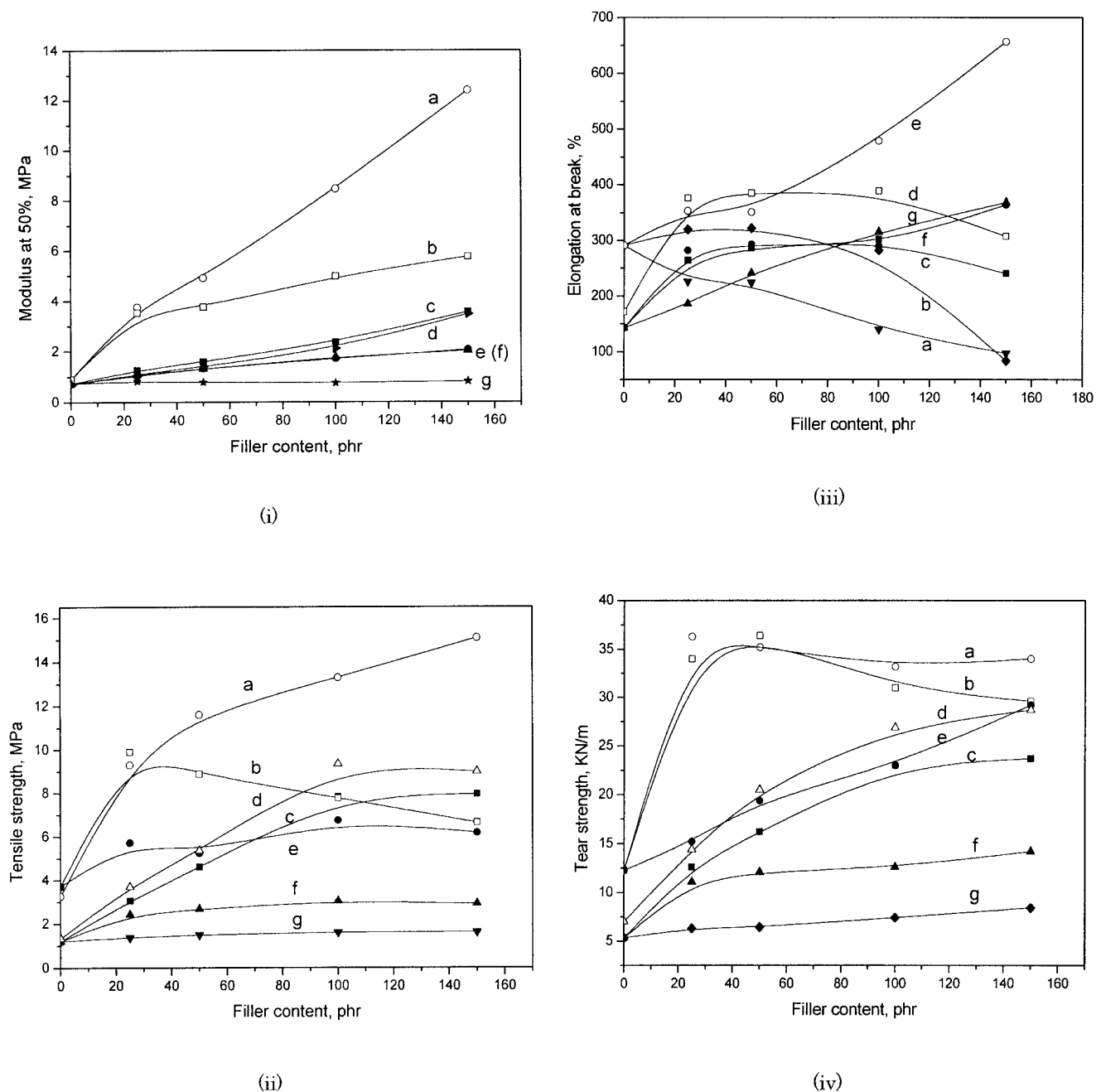| Material	Sample no.								
	1	2	3	4	5	6	7	8	9
SBR	100	100	100	100	100	100	100	100	100
MgO, Mg(OH)$_2$, or BaSO$_4$	0	25	50	100	150	25	50	100	150
MAA or MMA	—	—	—	—	—	10	10	10	10
DCP	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9

Figure 1 Effect of fillers and modifiers on mechanical properties of SBR vulcanizates: (i) modulus at 50%; (ii) tensile strength; (iii) elongation at break; (iv) tear strength. (a) SBR/MgO/MAA; (b) SBR/Mg(OH)$_2$/MAA; (c) SBR/MgO; (d) SBR/MgO/MMA; (e) SBR/BaSO$_4$/MAA; (f) SBR/Mg(OH)$_2$; (g) SBR/BaSO$_4$. Formulation: SBR, 100; MgO, Mg(OH)$_2$, or BaSO$_4$, 0–150; MAA or MMA, 0 or 10; DCP, 0.9 phr.

elongation of the SBR/BaSO$_4$ vulcanizates. But the small amount of MMA had little effect on the mechanical properties of the SBR/MgO vulcanizates.

Polymer–filler interaction of SBR vulcanizate

The polymer–filler interaction was studied by the swelling of the SBR vulcanizates in toluene. Figure 2 shows the variation of V_{r0}/V_{rf} against $\phi/(1 - \phi)$ according to the Kraus plot[14]:

$$V_{r0}/V_{rf} = 1 - m\phi/(1 - \phi) \qquad (2)$$

where ϕ is the volume fraction of filler in the filled vulcanizate; V_{r0}, the volume fraction of the rubber phase in a swollen gel of gum rubber vulcanizate; and V_{rf}, the volume fraction of the rubber phase in a swollen gel of filled rubber vulcanizates, assuming that the filler does not swell. Both V_{r0} and V_{rf} are determined by eq. (1). m is a characteristic constant of the filler–rubber matrix.
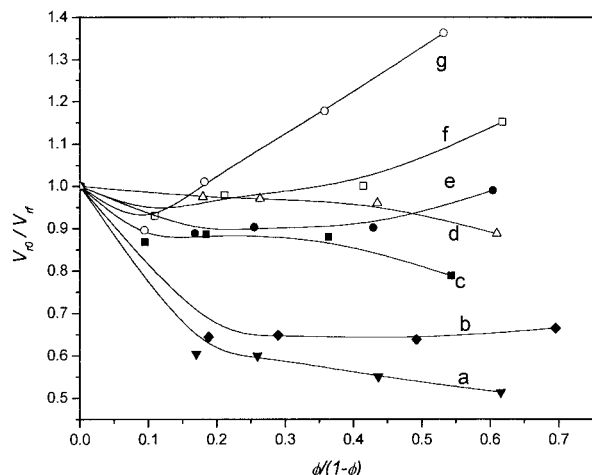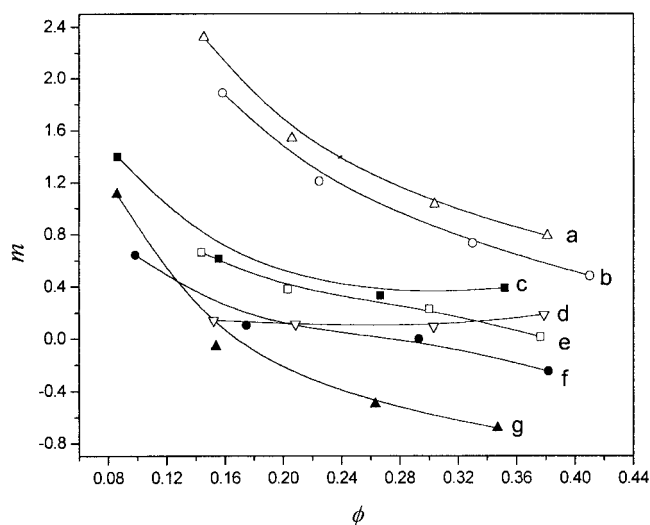
Figure 2 Kraus plots for SBR vulcanizates: (a) SBR/MgO/MAA; (b) SBR/Mg(OH)$_2$/MAA; (c) SBR/MgO; (d) SBR/MgO/MMA; (e) SBR/BaSO$_4$/MAA; (f) SBR/Mg(OH)$_2$; (g) SBR/BaSO$_4$. Formulation: SBR, 100; MgO, Mg(OH)$_2$, or BaSO$_4$, 0–150; MAA or MMA, 0 or 10; DCP, 0.9 phr.
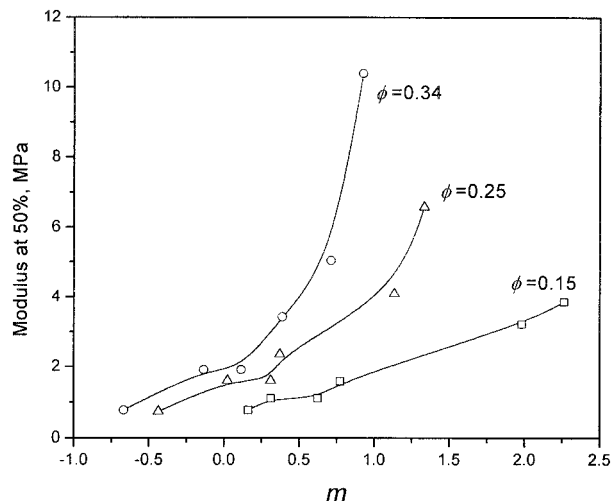

Figure 4 Relationships among modulus at 50%, m, and ϕ. Formulation: SBR, 100; MgO, Mg(OH)$_2$, or BaSO$_4$, 0–150; MAA, 0 or 10; DCP, 0.9 phr.

In theory, the plot of V_{r0}/V_{rf} against $\phi/(1 - \phi)$ is a beeline for two presuppositions[15]: First, the filler is firmly bonded to the rubber matrix with an adhesion strong enough to withstand desorption by the best solvents investigated. Second, the crosslink yield is, in general, not strongly influenced by the filler. In reality, the two presuppositions are not always achieved, so the linear relation according to the Kraus plot is not obeyed. The deviating degree of the slope to the $V_{r0}/V_{rf} = 1$ horizontal line can be related to the polymer–filler interaction: The more the plot deviates the horizontal line downward ($m > 0$), the greater the polymer–filler interaction and the better the mechanical

properties.[16] But, sometimes, the plot deviates the horizontal line upward ($m < 0$) for the poor polymer–filler interaction.[14,17] Therefore, m can be used to reflect the filler–polymer interaction, and a high value of m means a strong interaction.

A plot of V_{r0}/V_{rf} against $\phi/(1 - \phi)$ of the SBR vulcanizates is shown in Figure 2. As can be seen, the Kraus plots deviate from the horizontal line in different degrees and in different directions, indicating the different polymer–filler interactions. Related to the mechanical properties discussed above, the Kraus plots correspond to them well. The interaction of the polymer–filler of the SBR/MgO/MAA vulcanizate is the strongest, followed by the interaction in the SBR/Mg(OH)$_2$/MAA and SBR/MgO vulcanizates in turn,
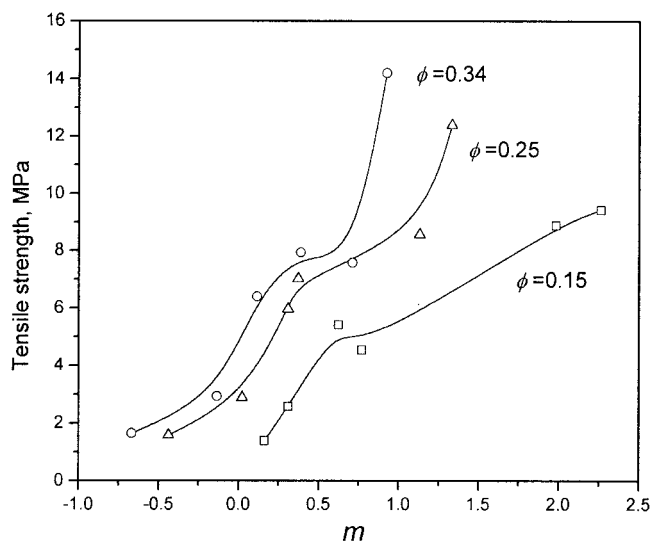

Figure 3 $m - \phi$ plots for SBR vulcanizates: (a) SBR/MgO/MAA; (b) SBR/Mg(OH)$_2$/MAA; (c) SBR/MgO; (d) SBR/MgO/MMA; (e) SBR/BaSO$_4$/MAA; (f) SBR/Mg(OH)$_2$; (g) SBR/BaSO$_4$. Formulation: SBR, 100; MgO, Mg(OH)$_2$, or BaSO$_4$, 0–150; MAA or MMA, 0 or 10; DCP, 0.9 phr.

Figure 5 Relationships among tensile strength, m, and ϕ. Formulation: SBR, 100; MgO, Mg(OH)$_2$, or BaSO$_4$, 0–150; MAA, 0 or 10; DCP, 0.9 phr.
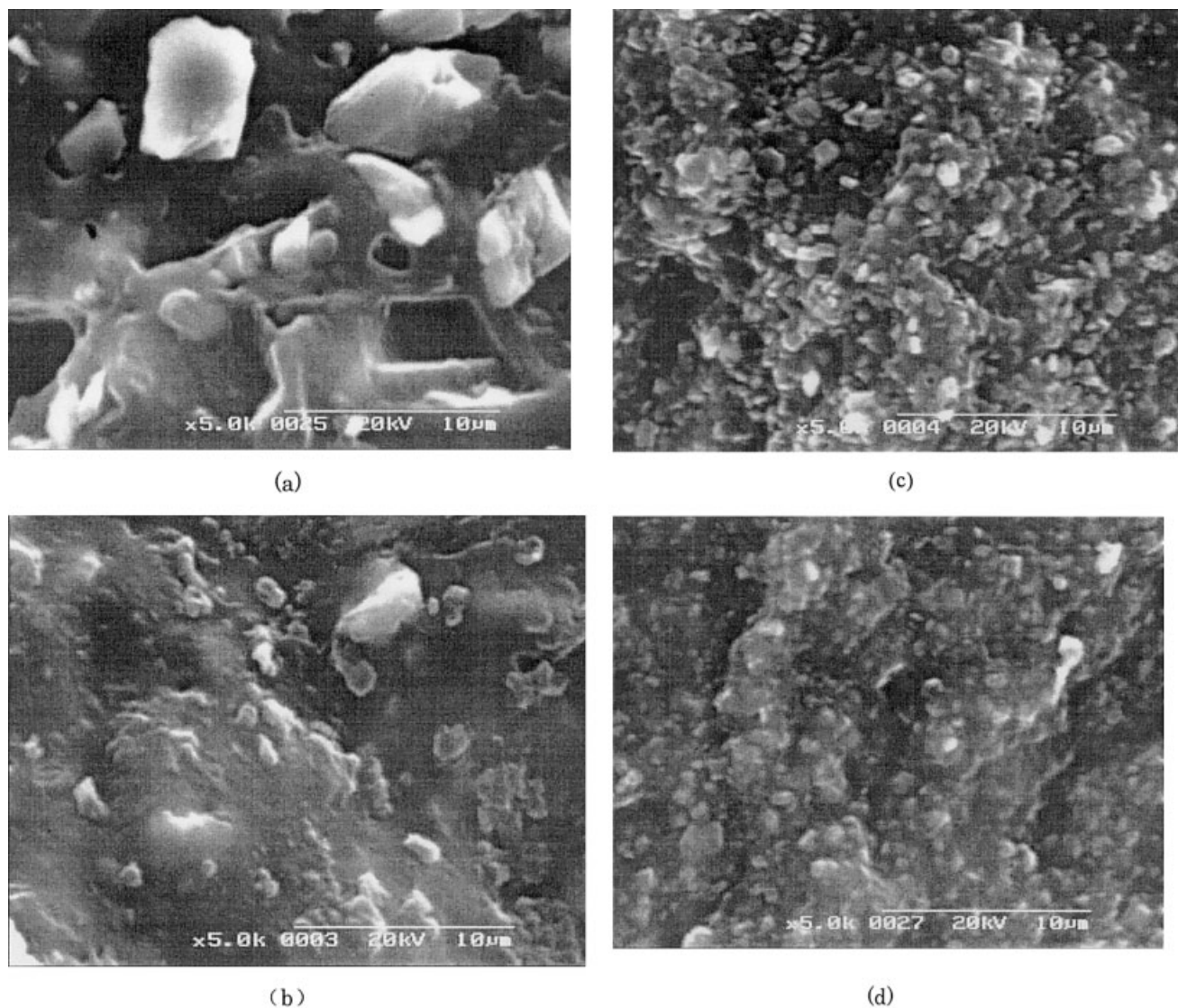
Figure 6 Morphology of fracture surface of SBR vulcanizates with 150 phr fillers: (a) SBR/BaSO$_4$; (b) SBR/BaSO$_4$/MAA; (c) SBR/Mg(OH)$_2$; (d) SBR/Mg(OH)$_2$/MAA; (e) SBR/MgO; (f) SBR/MgO/MAA; (g) SBR/MgO/MMA.

and the interaction in the SBR/BaSO$_4$ and SBR/Mg(OH)$_2$ vulcanizates are the poor. The mechanical properties of the SBR/MgO/MAA vulcanizate is the best, followed by the SBR/Mg(OH)$_2$/MAA and SBR/MgO vulcanizates in turn, and the SBR/BaSO$_4$ and SBR/Mg(OH)$_2$ vulcanizates have poor mechanical properties.

A plot of m against ϕ in the SBR vulcanizates is shown in Figure 3. As can be seen, m decreased with an increasing ϕ for all the SBR vulcanizates except the SBR/MgO/MMA vulcanizate. A basic explanation for this phenomenon is that the fillers should have accumulated at the interface and, consequently, some portion of the fillers would not be available in the rubber matrix for resisting solvent penetration. This causes a lower V_{rf} than expected, resulting in an increase in the ratio of V_{r0}/V_{rf} and a decrease in m according to eq. (2). As for the SBR/MgO/MMA vulcanizate, the MgO particles should have dispersed evenly in SBR and no

accumulation would be found [see Fig. 6(g)], so the increase of ϕ has little effect on m. From Figure 3, another conclusion may be drawn, that at the same ϕ, the m values for different SBR vulcanizates are different, that is, the filler–SBR interactions are different. The m values decrease from the SBR/MgO/MAA vulcanizate to SBR/Mg(OH)$_2$/MAA, SBR/MgO, SBR/BaSO$_4$/MAA, SBR/Mg(OH)$_2$, and SBR/BaSO$_4$ vulcanizates in turn, which is nearly in the same sequence with that drawn from Figure 2.

Figure 4 shows curves of the modulus at 50% versus m at a given ϕ of 0.15, 0.25, or 0.34 for different filler-filled SBR vulcanizates with or without MAA, and Figure 5 shows curves of the tensile strength versus m at a given ϕ of 0.15, 0.25, or 0.34. As can be seen, the modulus at 50% and the tensile strength of different SBR vulcanizates increase with increasing ϕ at a given m and increase with an increasing of m at a given ϕ. So, it can be concluded that m, representing
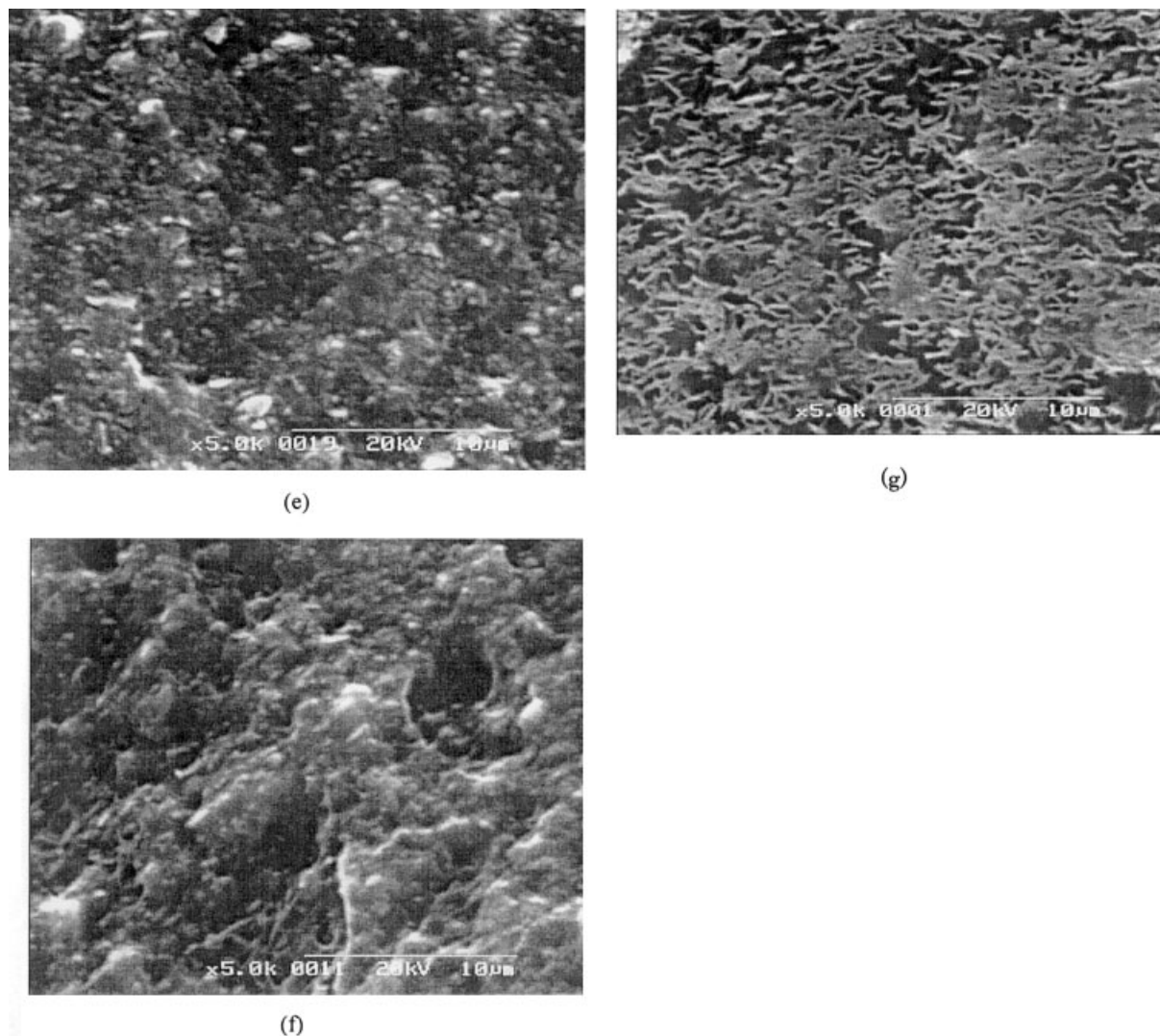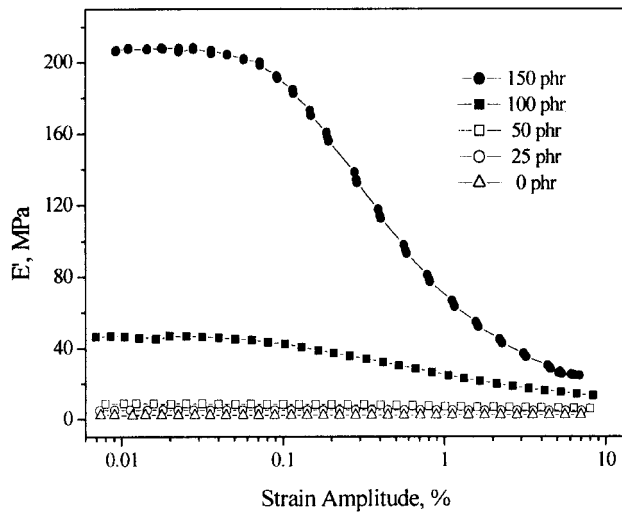
(e)

(g)

(f)

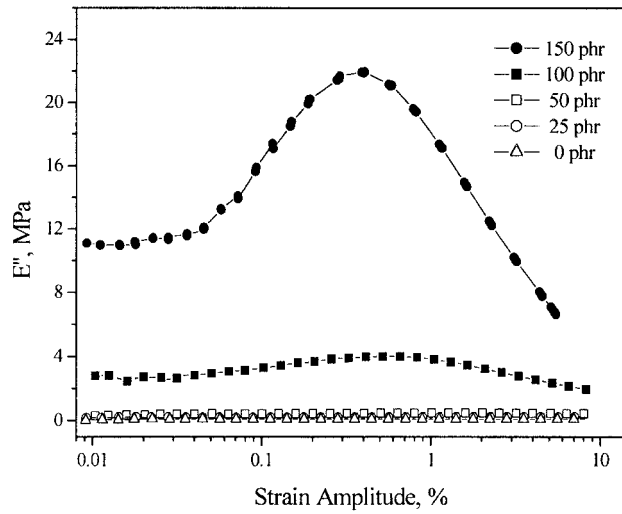**Figure 6** (*Continued from the previous page*)

Morphology observation

SEM micrographs of the fractured surface of the vulcanizates filled with 150 phr filler are shown in Figure 6. As shown in Figure 6(a,ce), the $BaSO_4$, $Mg(OH)_2$, and MgO particles can be observed clearly for the SBR vulcanizates without MAA, especially the $BaSO_4$ particles. This indicates the poor adhesion between fillers and the SBR matrix and that the fracture partially took place on the surface of the particles. Figure 6(b,d,f) shows the fracture surfaces of the highly filled SBR vulcanizates containing MAA, in which the particles cannot be observed easily and the fracture surfaces become blurrier, especially for the SBR/$BaSO_4$/MAA vulcanizate, and the $BaSO_4$ particles are bound in the
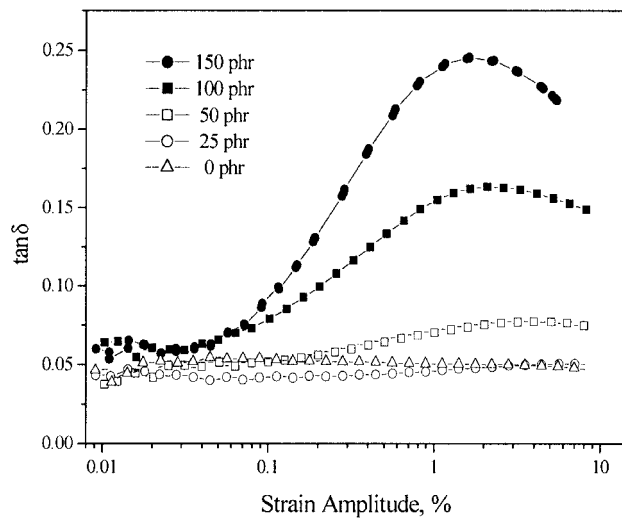
vulcanizate. This indicates that the interaction between the fillers and the SBR matrix has been improved by the presence of MAA. For SBR/MgO/ MAA and SBR/$Mg(OH)_2$/MAA vulcanizates, MAA can react with MgO or $Mg(OH)_2$ to form $Mg(MAA)_2$ during mixing, and the homopolymerization and graft copolymerization of $Mg(MAA)_2$ can occur at the same time during curing of the SBR composites by peroxide.[11] The resulting graft copolymer may play the role of compatilization.[12] For the SBR/$BaSO_4$/MAA vulcanizate, MAA cannot react with $BaSO_4$ as the $BaSO_4$ is an inert filler, and the reason for the adhesion improvement between $BaSO_4$ and the SBR matrix should be accounted for by that MAA grafts to the SBR molecule make the crosslink density and polarity of the vulcanizate increase and increase the molecular interaction. For the SBR/MgO/MMA vulcanizate, the MgO particles can still be observed clearly, implying that MMA has not improved the interaction between MgO and SBR.
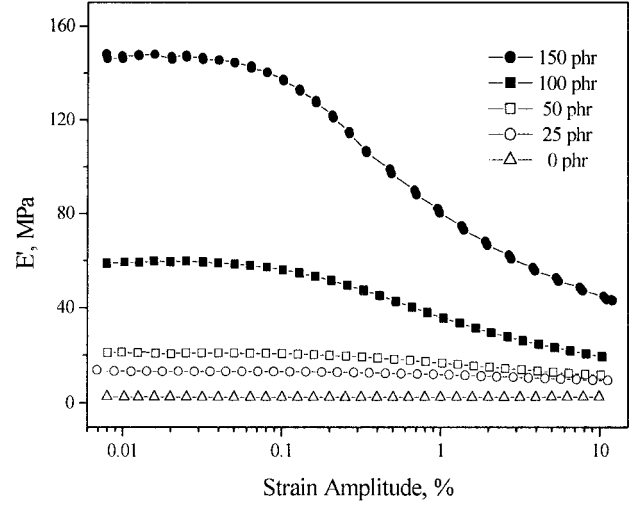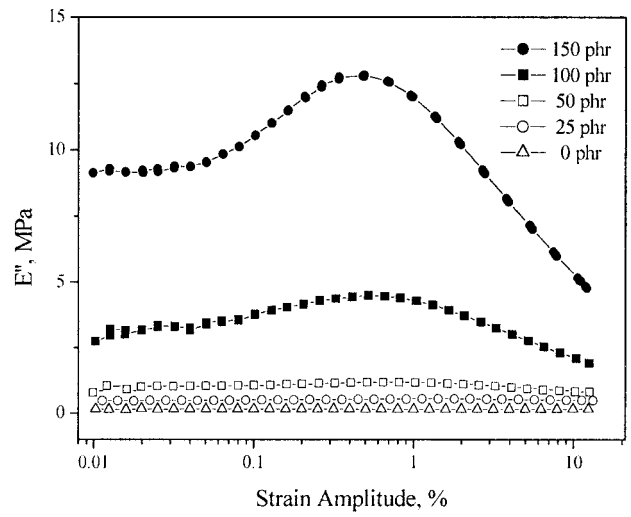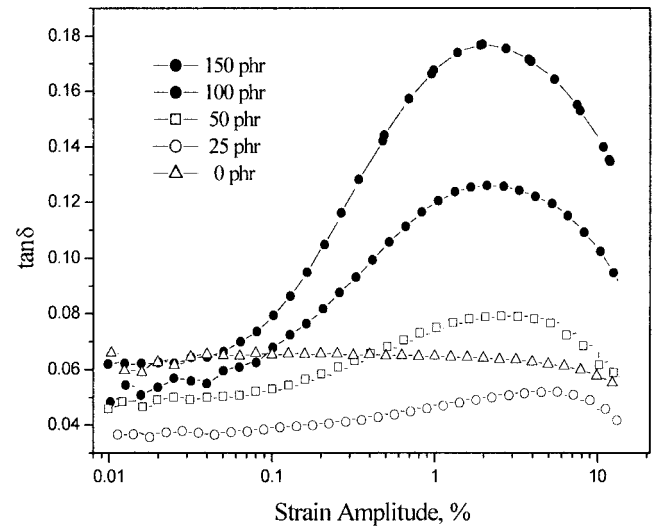
(e)

(g)

(f)

Figure 6 (*Continued from the previous page*)

the surface adhesion of the filler–SBR and the accumulated structure of the fillers, is well related to the modulus at 50% and tensile strengths of the SBR vulcanizates filled with various fillers.

Morphology observation

SEM micrographs of the fractured surface of the vulcanizates filled with 150 phr filler are shown in Figure 6. As shown in Figure 6(a,ce), the $BaSO_4$, $Mg(OH)_2$, and MgO particles can be observed clearly for the SBR vulcanizates without MAA, especially the $BaSO_4$ particles. This indicates the poor adhesion between fillers and the SBR matrix and that the fracture partially took place on the surface of the particles. Figure 6(b,d,f) shows the fracture surfaces of the highly filled SBR vulcanizates containing MAA, in which the particles cannot be observed easily and the fracture surfaces become blurrier, especially for the SBR/$BaSO_4$/MAA vulcanizate, and the $BaSO_4$ particles are bound in the

vulcanizate. This indicates that the interaction between the fillers and the SBR matrix has been improved by the presence of MAA. For SBR/MgO/ MAA and SBR/$Mg(OH)_2$/MAA vulcanizates, MAA can react with MgO or $Mg(OH)_2$ to form $Mg(MAA)_2$ during mixing, and the homopolymerization and graft copolymerization of $Mg(MAA)_2$ can occur at the same time during curing of the SBR composites by peroxide.[11] The resulting graft copolymer may play the role of compatilization.[12] For the SBR/$BaSO_4$/MAA vulcanizate, MAA cannot react with $BaSO_4$ as the $BaSO_4$ is an inert filler, and the reason for the adhesion improvement between $BaSO_4$ and the SBR matrix should be accounted for by that MAA grafts to the SBR molecule make the crosslink density and polarity of the vulcanizate increase and increase the molecular interaction. For the SBR/MgO/MMA vulcanizate, the MgO particles can still be observed clearly, implying that MMA has not improved the interaction between MgO and SBR.

(a)

(b)

(c)

Figure 7 Dynamic mechanical properties of the SBR/MgO vulcanizates with different MgO content: (a) E'; (b) E''; (c) tan δ. Formulation: SBR, 100; MgO, 0–150; DCP, 0.9 phr.

(a)

(b)

(c)

Figure 8 Dynamic mechanical properties of the SBR/MgO/MAA vulcanizates with different MgO content: (a) E'; (b) E''; (c) tan δ. Formulation: SBR, 100; MAA, 10; MgO, 0–150; DCP, 0.9 phr.

Dynamic mechanical properties

The dynamic mechanical properties of the SBR/MgO and SBR/MgO/MAA vulcanizates are shown in Figure 7(a–c) and Figure 8(a–c), respectively. In both cases, the Payne effect[18–20] is observed. The storage moduli E' are constant at a very low strain and decrease with an increasing strain amplitude from about 0.1 to 10%. This trend is especially clear for the SBR vulcanizates with a high loading of MgO, and for the SBR vulcanizates without MgO, the E'''s are constant at the whole strain amplitude. On the other hand, E' increases nonlinearity with an increasing MgO content. In contrast to E' of the MgO-filled SBR vulcanizates which decrease monotonously, the loss modulus E'' and loss factor tan δ increase and pass through their maximums with an increasing strain amplitude, and the tan δ maximum appears at a higher strain amplitude than that of E''. E'' and tan δ also increase with an increasing MgO content.

The Payne effect is related to the filler network formed in the SBR matrix[21]; E' is related mainly to the filler network which is reduced during dynamic strain; E'' is related to the breakdown and reformation of these structures; and tan δ is the ratio between the portion capable of being broken down and reconstituted and those remaining unchanged during dynamic strain. At a strain amplitude small enough that the filler network is unable to be broken, the strain dependence of E' and E'' of the SBR vulcanizates would be eliminated. With an increasing strain amplitude to a moderate one, the breakdown of the filler network increases to make E' decrease and the reformation of this structure diminishes more rapidly than does its disruption, so a maximum appears for E''. At a strain amplitude high enough that the filler network is destroyed to such an extent that it cannot be reconstructed in the time scale of dynamic strain, the effects of the filler network on the E' and E'' will disappear.

CONCLUSIONS

MAA is an effective additive for improving the mechanical properties of the DCP-cured SBR vulcanizates with a high loading of MgO, Mg(OH)$_2$, or BaSO$_4$. A small amount of MAA can improve the interfacial bonding between the fillers and SBR, thus leading to significant increases in the modulus, tensile strength, and tear strength of the SBR vulcanizates. MMA has little effect on the mechanical properties of the SBR vulcanizates.

m represents the interfacial bonding between the fillers and SBR and the accumulated structure of the fillers. At a given ϕ, a high value of m means a strong interaction between the filler and SBR and, therefore, strong mechanical properties.

The SBR vulcanizates follow the Payne effect in having low storage moduli at high strains and high storage moduli at low strains, and the moduli are nonlinear and increase the nonlinearity as the filler content increases. The loss moduli and loss factor reach their maximums at a moderate and high strain amplitudes, respectively.

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