

# Properties of EVM Vulcanizates Reinforced by *In Situ* Prepared Sodium Methacrylate

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**ABSTRACT:** Ethylene–vinyl acetate copolymer (EVM) vulcanizates with good mechanical properties and high transparency were obtained using sodium methacrylate (NaMAA) as a reinforcing agent. Sodium methacrylate was *in situ* prepared through the neutralization of sodium hydroxide (NaOH) and methacrylic acid (MAA) in an EVM and used to reinforce the EVM cured by dicumyl peroxide (DCP). Different factors such as the DCP content, NaMAA content, and the mol ratio of NaOH/MAA were included to study their effects on the mechanical properties, optical properties, stress-relaxation behavior, and crosslink structure of the EVM vulcanizates. The rheological behavior of the EVM compounds was also investigated and compared with that of the high abrasion furnace carbon black (HAF)/EVM compounds. The experimental results show that with an increase of the NaMAA content the curing rate index ( $C_R$ ) of the EVM compounds is greatly speeded up, while the Mooney viscosities of the compounds remain nearly un-

changed. The mechanical properties and optical properties of the NaMAA-reinforced EVM vulcanizates depend on the NaMAA content and the mol ratio of NaOH/MAA. The formulation of DCP of 3 phr and a NaOH/MAA mol ratio of 1.0 is recommended for the EVM vulcanizate with high mechanical properties. At a given NaOH/MAA mol ratio of 1.0, all the EVM vulcanizates are transparent and the light transmission is over 76% in the NaMAA content range of 10–50 phr. The NaMAA/EVM vulcanizates show faster stress relaxation and more obvious stress-softening effects than those of the HAF/EVM vulcanizates. Crosslink density analysis indicated that the EVM vulcanizates contain both covalent and ionic bonds. The ionic crosslink densities greatly increase with an increasing NaMAA content. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2192–2200, 2003

**Key words:** mechanical properties; reinforcement; transparency

## INTRODUCTION

The addition of unsaturated carboxylates as reactive fillers to rubber is a new trend to achieve substantial reinforcement.<sup>1–3</sup> Metallic salts of unsaturated carboxylic acid, such as zinc methacrylate (ZDMA), show a great reinforcing effect on peroxide-cured elastomers in the absence of any conventional reinforcing agents.<sup>4</sup> The elastomers filled with unsaturated carboxylates have high tensile strength, tear strength, and modulus and, at the same time, retain a high elongation at break. There are two methods for unsaturated carboxylates to reinforce elastomers: One is that a metallic salt of an unsaturated carboxylic acid is added directly into a rubber. The other is that, through the neutralization of a metal oxide or metal hydroxide and methacrylic acid (MAA) or acrylic acid (AA), a metallic salt of unsaturated carboxylic acid is *in situ* prepared in rubber during mixing. The corresponding reports revealed that the reinforcing effect of the latter is better than that of the former.<sup>5</sup> There are many patents and reports about *in situ* preparation of unsat-

urated carboxylate to reinforce rubbers. For example, metallic salts of AA and MAA have also been used for many years to crosslink polybutadiene in forming rubber cores for two-piece golf balls.<sup>6</sup> Also, Zeon Chemicals has made high-performance hydrogenated nitrile rubber (HNBR) with a mixture of zinc oxide and MAA, which has been used in oil fields and to produce automobile parts.<sup>7,8</sup> In addition, Japanese patents<sup>9,10</sup> also reported that styrene–butadiene rubber (SBR) and isoprene rubber (IR) vulcanizates reinforced by *in situ* prepared ZDMA had excellent mechanical properties. We have carried out much work on the research of *in situ* prepared unsaturated carboxylate to reinforce rubbers such as nitrile–butadiene rubber (NBR),<sup>11,12</sup> the ethylene–propylene–diene terpolymer (EPDM),<sup>13</sup> and SBR.<sup>14</sup> The above-mentioned vulcanizates reinforced with *in situ* prepared unsaturated carboxylates had good mechanical properties such as high hardness, tensile strength, and elongation at break.

Up to now, most of the research about *in situ* prepared unsaturated carboxylates focused on divalent metallic salts, such as zinc and magnesium salts of unsaturated carboxylate. To our knowledge, monovalent metallic salts of unsaturated carboxylate have been less studied. The ethylene–vinyl acetate copolymer (EVM) is the copolymer of ethylene and vinyl

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TABLE I  
Raw Materials

| Materials           | Trade name and characteristics                | Source   |
|---------------------|---|--|
| EVM                 | Levaprene VP KA8857, 50 wt % of vinyl acetate | Bayer Co., Ltd. (Leverkusen, Germany)              |
| NaOH                | Chemical pure                                 | Shanghai Songkai Chem. Co., Ltd. (Shanghai, China) |
| MAA                 | Chemical pure                                 | Shanghai Wulian Chem. Co., Ltd. (Shanghai, China)  |
| Carbon black (N330) | Rubber grade                                  | Shanghai Cabot Chem. Co., Ltd. (Shanghai, China)   |
| DCP                 | Purity: 99.3%                                 | Shanghai Gaoqiao Petroleum Co., (Shanghai, China)  |

acetate. The tensile strength of the EVM vulcanizate is very low in the absence of any reinforcing fillers. Our previous work showed that magnesium methacrylate had a good reinforcing effect on the EVM vulcanizate.<sup>15</sup> In this article, through the neutralization of sodium hydroxide (NaOH) and MAA, NaMAA was *in situ* prepared in EVM during mixing and used to reinforce EVM cured by dicumyl peroxide (DCP). The main objective of the study was to consider the basic characteristics of EVM vulcanizate reinforced by sodium methacrylate. Different factors such as the DCP content, NaMAA content, and the mol ratio of NaOH/MAA were included. We focused our work on the measurement of the mechanical properties, stress-strain behavior, optical properties, and crosslink structure of EVM vulcanizates. The rheological behavior of the EVM compound was also investigated and compared with that of the HAF-filled EVM.

## EXPERIMENTAL

### Materials and sample preparation

The raw materials used in the study are shown in Table I. The mixtures of EVM and the additives (Bayer Co. Ltd., Leverkusen, Germany) were prepared in the mixing chamber of a Haake rheometer at a rotor speed of 32 rpm and the initial temperature of 45°C. NaOH was first added to the EVM. After its dispersion, MAA was added into the chamber, followed by the addition of DCP. The compounding process lasted about 10 min. Then, the compound was sheeted on the two-roller mill. The compound was press-cured to a 2-mm-thick sheet at 170°C for 10 min for measurement.

### Rheological behavior

Mooney viscosities ( $ML_{1+4}$  at 100°C) of the EVM compounds were determined on an automation Mooney viscometer (Mooney MV 2000 from Alpha Technologies, USA) according to ASTM Standard D 1646-81. Cure characteristics were measured over a 25-min period at 170°C using a moving-die rheometer (UCAN

2030 from Taiwan) according to ISO 3417. The curing rate index ( $C_R$ ) was used to represent the curing rate of the compound, which was determined according to ISO Standard 3417:

$$C_R = 100 / (t_{90} - t_{s2}) \quad (1)$$

where  $t_{90}$  is the optimum curing time and  $t_{s2}$  is the scorch time.

### Mechanical properties

#### Tensile and tear tests

The tensile properties were measured with dumbbell specimens (6-mm-wide cross section) according to the Chinese Standard GB528-82. Tear strength was measured on unnotched 90°-angle test specimens according to the Chinese Standard GB530-81. The tests were performed with an Instron series IX 4465 material tester at a crosshead speed of 500 mm/min.

#### Shore A hardness

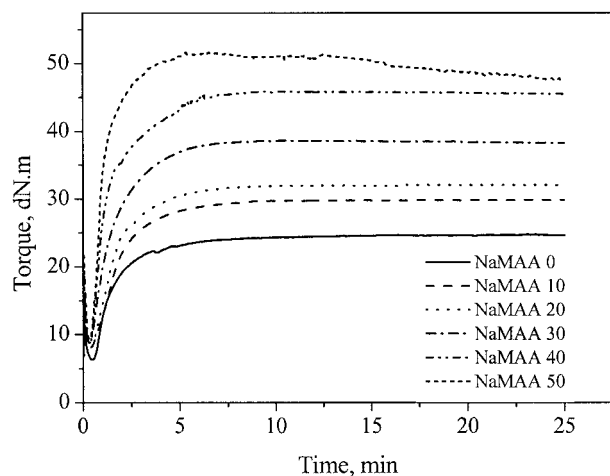
Shore A hardness was determined using a hand-held Shore A durometer according to Chinese Standard GB531-83.

#### Stress softening

Stress-strain curves were obtained using dumbbell specimens (6-mm-wide cross section) on an Instron series IX 4465 material tester at a crosshead speed of 500 mm/min. A specimen was extended to 200% elongation and retraced, then the operation repeated and stretched again. The fourth operation was performed when the specimen had rested after the first extension for 24 h in an attempt to ensure full recovery.

#### Stress relaxation

Dumbbell specimens (6-mm-wide cross section) were used for the stress relaxation. The rate of grip separa-



**Figure 1** Curing curves of EVM compounds at 170°C with different NaMAA content. Formulation: EVM 100; DCP 3.0; NaMAA variable.

tion was 1000 mm/min. The starting time ( $t = 0$ ) was set at the maximum stress  $\sigma_0$  after the specimen was stretched to the specified elongation (200%); then, stress relaxation for 10 min was measured. The stress ratio  $\sigma_R$  is defined by

$$\sigma_R = (\sigma_t / \sigma_0) \times 100 \quad (2)$$

where  $\sigma_t$  means stress at time  $t$  ( $t = 10$  min).

### Measurement of optical properties

The light transmission and haze of EVM vulcanizates were measured with a 1-mm sheet on a Spherical Hazemeter (Model 57 from Diffusion System Ltd., U.K.).

### Determination of the crosslink density

The crosslink density was determined by equilibrium swelling. Molded samples were swollen in xylene at 25°C for 72 h to achieve the equilibrium swelling condition. The weight of the samples was measured under swollen conditions. Then, the samples were dried in a vacuum oven for 36 h at 90°C to remove all the solvent and reweighed. The volume fraction of the rubber in the swollen gel,  $V_r$ , which was used to represent the relative crosslink density of the vulcanizate, was determined by the following equation<sup>12</sup>:

$$V_r = \frac{m_0 \phi (1 - \alpha) / \rho_r}{m_0 \phi (1 - \alpha) / \rho_r + (m_1 - m_2) / \rho_s} \quad (3)$$

where  $m_0$  is the sample mass before swelling;  $m_1$  and  $m_2$ , sample masses before and after drying, respectively;  $\phi$ , the mass fraction of rubber in the vulcanizate;  $\alpha$ , the mass loss of the gum EVM vulcanizate

during swelling; and  $\rho_r$  and  $\rho_s$ , the rubber and solvent density, respectively.

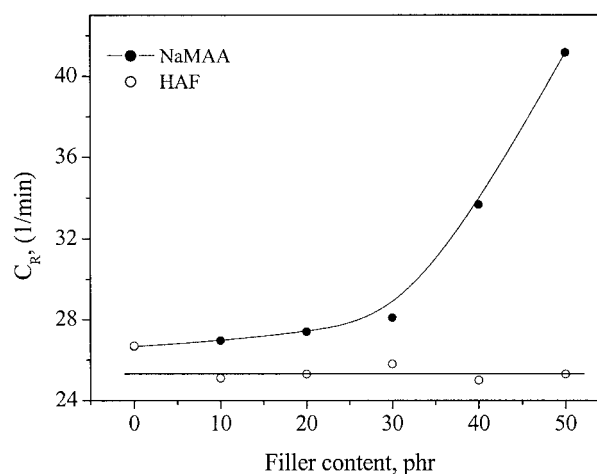
To distinguish an ionic crosslink from a covalent crosslink, samples were swollen in the mixture of xylene and chloroacetic acid for 5 days to destroy ionic crosslinks, followed by swelling in xylene for 2 days and then weighed, vacuum-dried, and reweighed.  $V_{r1}$  was calculated from eq. (2), which represents the covalent crosslink density.  $V_{r2}$ , which was calculated by subtracting  $V_{r1}$  from  $V_r$ , was used to represent the ionic crosslink density.

## RESULTS AND DISCUSSION

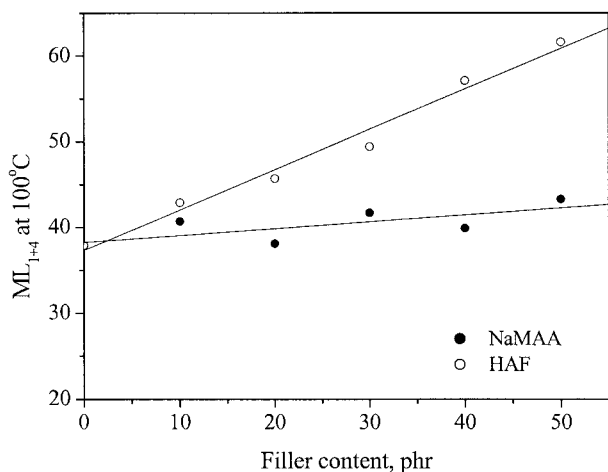
### Rheological analysis

The curing curves of EVM/NaMAA/DCP (100/variable/3.0) compounds are shown in Figure 1. It can be seen that NaMAA can accelerate the curing process. According to the literature,<sup>4</sup> a salt of unsaturated carboxylic acid not only acts as a filler, but also acts as a crosslinking coagent that is highly reactive in the presence of free radicals and readily reacts to form crosslinks with elastomers. It should follow the same mechanism as that of conventional coagents such as multifunctional esters of MAA. So, we believe that a similar mechanism occurs in the NaMAA-filled EVM compound to that of the multifunctional esters. With increase of the NaMAA content in the EVM compound, the scorch time ( $t_{s2}$ ) and optimum curing time ( $t_{90}$ ) were shortened. As calculated from Figure 1,  $t_{90}$  decreased from 4.5 min for EVM gum to 2.9 min for the EVM filled with 50 phr NaMAA. Since there was no curing reversion for the EVM compound, the actual curing time of 10 min was used for all the EVM compounds to ensure full vulcanization.

Figure 2 shows the effects of NaMAA and HAF on



**Figure 2** Effect of filler content on the curing rates of EVM compounds. Formulation: EVM 100; DCP 3.0; filler: NaMAA and HAF.



**Figure 3** Mooney viscosities of EVM compounds filled with different fillers. Formulation: EVM 100; DCP 3.0; filler: NaMAA and HAF.

the curing rates of EVM compounds. The curing rate index ( $C_R$ ) represents the curing rate of EVM compounds in Figure 2. Seen from Figure 2, the curing rates of the EVM compounds are greatly improved with increase of the NaMAA content. At the same time, the curing rates of HAF-reinforced EVM compounds remain nearly unchanged.

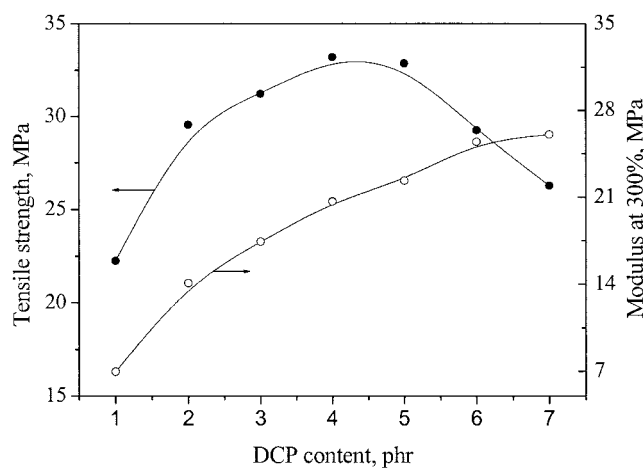
Figure 3 shows the Mooney viscosities of EVM compounds filled with different fillers. Mooney viscosities increase gradually with increase in the carbon black content, but the amount of NaMAA almost had no influence on the Mooney viscosities of the EVM compounds. It is considered that bound rubber is formed because of the strong interaction between EVM and HAF during processing. Bound rubber is one of the major factors in reinforcement. While NaMAA formed during mixing, it cannot react with EVM under compounding conditions and does not influence the Mooney viscosity.

### Mechanical properties

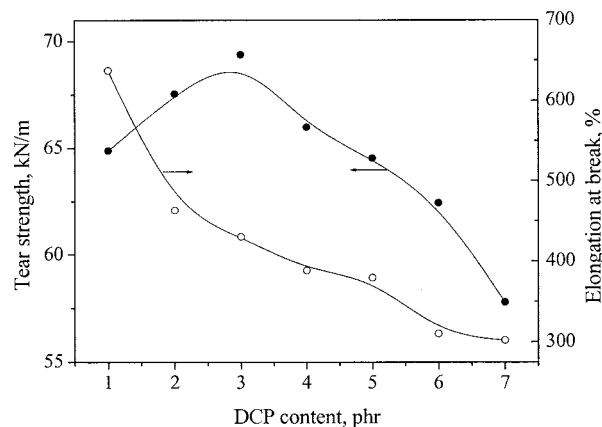
The effect of the DCP content on the mechanical properties of EVM vulcanizates is shown in Figure 4. The mol ratio of NaOH/MAA is 1.0 (equivalent) for all the formulations in Figure 4. The amount of NaMAA represents the theoretical value obtained from the neutralization of NaOH and MAA. As can be seen from Figure 4, the modulus at 300% of the EVM vulcanizates increased gradually with an increasing DCP content, while the elongation at break decreased rapidly. However, even when the DCP content was as high as 7 phr, the elongation at break of the vulcanizate was still over 300%. The tensile strength of the EVM vulcanizate was over 30 MPa when the DCP content was 3–5 phr. The tear strength was as high as 69.4 kN/m with a DCP content of 3 phr. Considering

the mechanical properties of the EVM/NaMAA vulcanizates, 3 phr of DCP was chosen as the base for the following study.

The mol ratio of metal oxide or metal hydroxide to MAA influences the mechanical properties of vulcanizates. The research of Zeon Chemicals showed that, in highly saturated nitrile elastomers (HNBR), the best reinforcement was obtained when ZnO was in excess and the optimum mol ratio of ZnO to MAA was about 0.75.<sup>3</sup> Our previous research showed that in magnesium methacrylate-reinforced SBR vulcanizate the optimum mol ratio of MgO to MAA was 0.5–0.75.<sup>14</sup> The effect of the mol ratios of NaOH to MAA at various levels (0.5–2.0) on the mechanical properties of the EVM vulcanizate was studied. Based on 30 phr of NaMAA prepared from neutralization, the mol ratio of NaOH/MAA varied from 0.5 to 2.0 (the corresponding weight ratio varied from 11.1/47.8 to 22.2/23.9), and the results are listed in Table II. As the mol



(a)



(b)

**Figure 4** Effect of DCP content on the mechanical properties of EVM vulcanizates. Formulation: EVM 100; NaMAA 30; DCP variable.

**TABLE II**  
Effect of NaOH/MAA Mol Ratios on Mechanical Properties of EVM Vulcanizates

| Property                | NaOH/MAA mol ratio              |                     |                    |                     |                    |                    |
|-------------------------|---------------------------------|---------------------|--------------------|---------------------|--------------------|--------------------|
|                         | 0.5<br>(11.1/47.8) <sup>a</sup> | 0.75<br>(11.1/31.9) | 1.0<br>(11.1/23.9) | 1.25<br>(13.9/23.9) | 1.5<br>(16.7/23.9) | 2.0<br>(22.2/23.9) |
| Hardness (Shore A)      | 75                              | 80                  | 81                 | 81                  | 82                 | 83                 |
| Modulus at 300% (MPa)   | 9.96                            | 8.92                | 18.19              | 12.98               | 11.45              | 9.14               |
| Tensile strength (MPa)  | 21.73                           | 22.86               | 33.32              | 26.69               | 18.35              | 9.30               |
| Elongation at break (%) | 534                             | 566                 | 414                | 477                 | 514                | 379                |
| Tension set (%)         | 38                              | 52                  | 48                 | 48                  | 77                 | 102                |
| Tear strength (kN/m)    | 65.60                           | 65.59               | 67.13              | 64.13               | 70.85              | 72.95              |

<sup>a</sup> Data in parentheses represent the exact amount of NaOH and MAA corresponding to the mol ratio.

ratio of NaOH to MAA increases, the hardness increases at a slower rate and the tension set increases greatly. The tensile strength and 300% modulus vary with the same trend and exhibit a maximum when NaOH and MAA are equivalent in mol mass, whereas for the case of NaOH in excess the tensile strength decreases dramatically with increase of the mol ratio. The mol ratio of NaOH to MAA has little effect on the tear strength of vulcanizates, but the excess of NaOH increases the tear strength slightly. For general consideration of the mechanical properties of EVM vulcanizates, the optimum mol ratio of NaOH to MAA is 1.0 (equivalent).

When NaOH and MAA are equivalent, the effect of the NaMAA (NaOH/MAA) content on the mechanical properties of the EVM vulcanizate is as shown in Figure 5. It may be noted that both the 300% modulus and hardness increase greatly with an increasing amount of NaMAA. The tensile strength increases rapidly between a 10 and 30 phr NaMAA content and at a slower rate thereafter. The tensile strength of the EVM vulcanizate with a 50 phr NaMAA content reaches as high as 34.8 MPa. The tear strength increases monotonically, and the tear strength of the vulcanizate increases by 200% when the NaMAA content increases from 10 to 50 phr [Fig. 5(a)]. The modulus at 300% and the hardness of the vulcanizate almost linearly increase with increase of the NaMAA content [Fig. 5(b)]. The elongation at break almost has no variation between a 10 and 30 phr NaMAA content and decreased rapidly thereafter, but it was still over 350% even when the NaMAA content is 50 phr. The tension set increases obviously with an increasing NaMAA content [Fig. 5(c)]. It appears that *in situ* prepared NaMAA is effective for the reinforcement of EVM and can maintain high elongation at break while increasing the modulus and tensile strength of the EVM vulcanizate.

### Stress-softening effect

A phenomenon often discussed in connection with filler reinforcement is stress softening.<sup>16</sup> The stress-

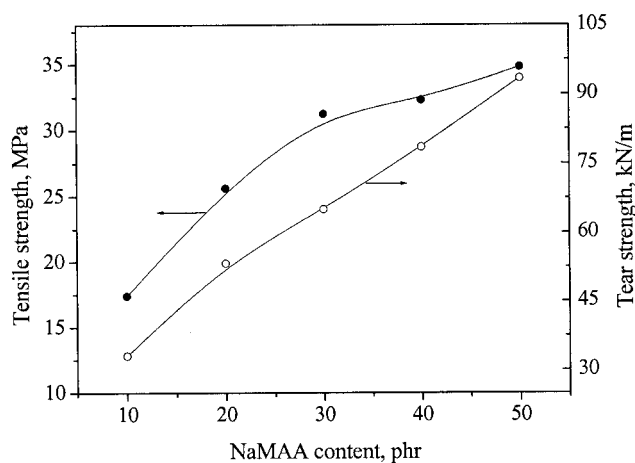
softening effects of EVM vulcanizates reinforced with HAF and NaMAA are shown in Figure 6(a,b), respectively. The stress-softening effect can be expressed as the following:

$$\Delta W = \frac{W_1 - W_i}{W_1} \times 100\% \quad (4)$$

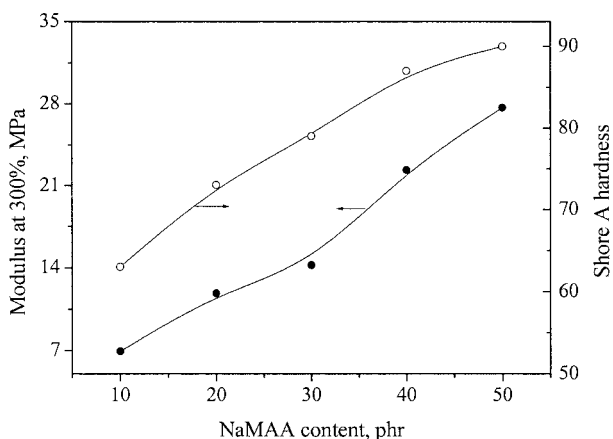
where  $W_1$  is the strain energy that is needed in the first stretch, and  $W_i$  the strain energy that is needed in the no.  $i$  stretch. The variations of the strain energy of the EVM compound reinforced with different fillers during stress softening are shown in Table III. The degree of stress softening of the EVM vulcanizates reinforced with NaMAA was greater than that of HAF; furthermore, the EVM vulcanizates filled with HAF had greater elastic recovery than that of the NaMAA/EVM vulcanizates after resting 24 h. The difference is attributed to the different nature of stress softening. The stress softening of the HAF-filled EVM vulcanizate is derived mainly from the breakage of aggregates of HAF particles and the chain slippage of the attached polymer segments along the surface. Instead of a chain breaking or detaching from the surface, the point of attachment is visualized as slipping along a chain and/or surface in such a way as to lengthen the distance between the absorbed segments.<sup>16</sup> After resting for a period, the HAF-filled vulcanizate gained part of its elastic recovery due to the thermal motion of the molecule, so that  $\Delta W$  of the fourth stretch decreased. According to the literature,<sup>17</sup> the slippage of ionic bonds is normal behavior under the effect of stress. So, the stress softening of the EVM vulcanizate filled with NaMAA is attributed to the exchange reaction of ionic bonds under the effect of stress. The slippage of ionic bonds for the vulcanizate is ascribed to the breaking of ionic bonds under stress and at the same time forming new crosslinkage. Once the stress is relieved, the ionic bonds cease to slip, so the elastic recovery is very low.

### Stress relaxation

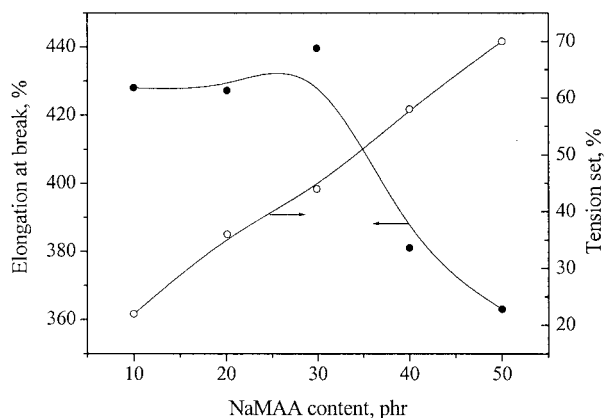
Figure 7 shows the effects of fillers on the stress-relaxation ratio  $\sigma_R$  at a fixed stretch ratio of  $\lambda = 3$



(a)



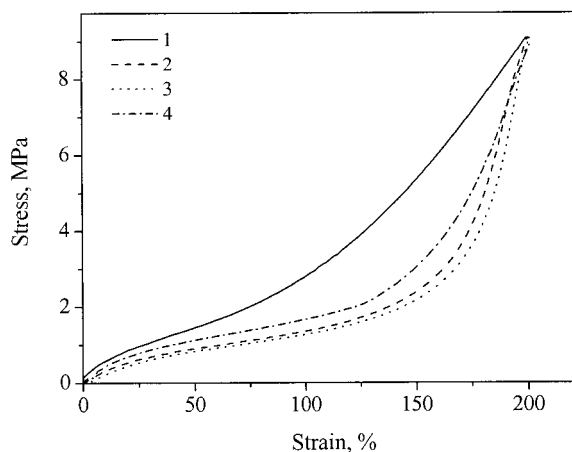
(b)



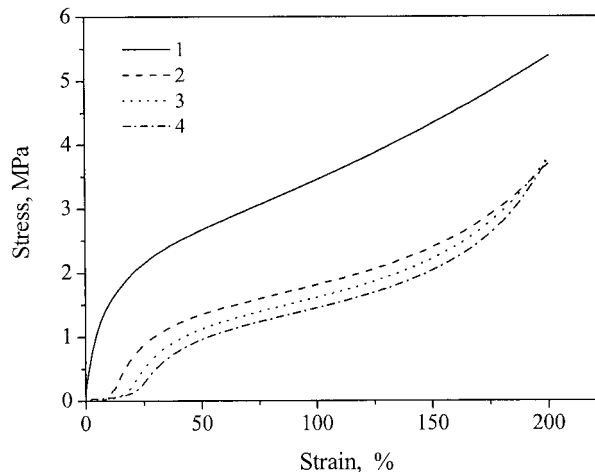
(c)

Figure 5 Effect of NaMAA content on the mechanical properties of EVM vulcanizates. Formulation: EVM 100; DCP 3.0; NaMAA variable.

(200% elongation). The stress ratio of EVM/NaMAA is less than that of EVM/HAF. This is also due to the slippage of ionic bonds. The breaking of a strained



(a)



(b)

Figure 6 Stress-softening curves of different filler-reinforced EVM vulcanizates. Formulation: (a) EVM 100; DCP 3.0; HAF 30 (b) EVM 100; DCP 3.0; NaMAA 30.

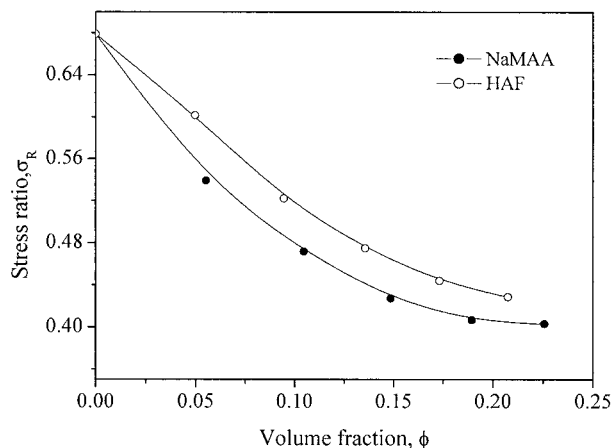
ionic bond and reforming of an unstrained ionic link led to higher relaxation and, therefore, a high permanent set.<sup>18</sup>

Optical property

The effect of NaOH/MAA mol ratios on the light transmission and haze of the EVM vulcanizates is shown in Table IV. The EVM vulcanizate reinforced

TABLE III  
ΔW of EVM Vulcanizates Filled with NaMAA and HAF During Stress Softening

|                     | EVM vulcanizate filled with NaMAA | EVM vulcanizate filled with HAF |
|---------------------|-----------------------------------|---------------------------------|
| ΔW <sub>2</sub> (%) | 46.34                             | 42.02                           |
| ΔW <sub>3</sub> (%) | 51.61                             | 47.42                           |
| ΔW <sub>4</sub> (%) | 56.17                             | 31.41                           |



**Figure 7** Effects of fillers on stress-relaxation ratios. Formulation: EVM 100; DCP 3.0; filler: NaMAA and HAF.

by *in situ* prepared NaMAA has high transparency, especially at a low mol ratio of NaOH to MAA. When the mol ratio was between 0.5 and 1.25, all the EVM vulcanizates were transparent and the light transmission remained over 72%. With increase of the NaOH content, the EVM vulcanizate changed from transparent to opaque. With increase of the mol ratio of NaOH and MAA, the haze of the vulcanizate also increased.

Table V shows the effect of the NaMAA content on the light transmission of the EVM vulcanizates. With increase of the NaMAA content, the haze of the vulcanizates gradually increased and the light transmission slightly decreased. Even if the NaMAA content was 50 phr, the EVM vulcanizate still had high transparency and the light transmission was 76.3%. After the addition of MAA to EVM/NaOH, the compound changed from transparent to white, whereas after vulcanization it turned transparent. Figure 8 compares the optical properties of the EVM compound and the vulcanizate. Saito et al.<sup>19–21</sup> investigated the polymeric behavior of ZDMA in the HNBR/ZDMA compound during the curing process and found that ZDMA underwent homopolymerization and graft polymerization. Their study showed that 20–30-nm poly(ZDMA) particles were produced as the vulcanization proceeded. The chemical reaction of MDMA in SBR dur-

**TABLE IV**  
Effect of NaOH/MAA Mol Ratios on Optical Properties of EVM Vulcanizates

| NaOH/MAA (mol ratio) | Light transmission (%) | Haze <sub>2</sub> (%) |
|----------------------|------------------------|-----------------------|
| 0.5                  | 72.1                   | 18.7                  |
| 0.75                 | 78.1                   | 10.2                  |
| 1.0                  | 78.2                   | 17.5                  |
| 1.25                 | 72.6                   | 26.5                  |
| 1.5                  | 46.6                   | 22.2                  |
| 2.0                  | Opaque                 |                       |

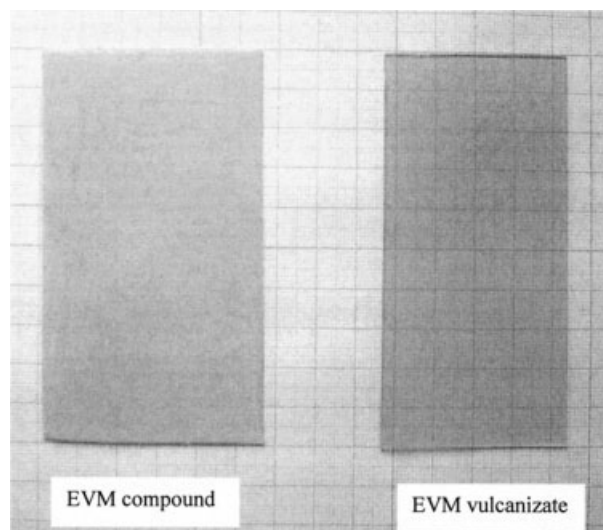
**TABLE V**  
Effect of NaMAA Content on Optical Properties of EVM Vulcanizates

| NaOH/MAA (phr) | Light transmission (%) | Haze (%) |
|----------------|------------------------|----------|
| 10             | 80.7                   | 15.3     |
| 20             | 79.1                   | 16.9     |
| 30             | 78.2                   | 17.5     |
| 40             | 77.8                   | 18.3     |
| 50             | 76.3                   | 22.2     |

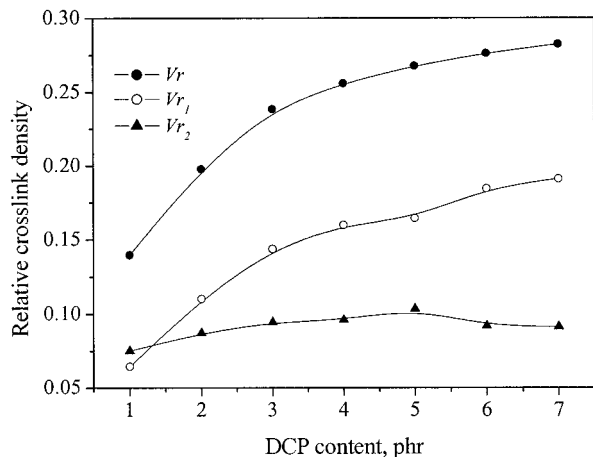
ing vulcanization was reported in our early publication.<sup>22</sup> So, it is supposed that *in situ* prepared NaMAA undergoes a chemical reaction in the peroxide-cured EVM vulcanizate. In the process of vulcanization, NaMAA partly dissolves in EVM at first, then polymerizes under the initiation of DCP and forms poly(sodium methacrylate) (P-NaMAA), which is distributed in the EVM matrix as nanoparticles. So, the EVM vulcanizate has a high transparency.

#### Crosslink density

It is well known that DCP can initiate the crosslink of rubber in the peroxide curing system at the same time that it initiates the polymerization of the metallic methacrylate, including both homopolymerization and graft polymerization.<sup>20</sup> To investigate the effect of NaMAA on the crosslink structure of the peroxide-cured EVM vulcanizate, it is necessary to measure the crosslink densities of ionic and covalent bonds. In the monovalent metallic salt-reinforced vulcanizates, the ionic crosslink bonds result from the electrostatic forces between the bound ions on the polymer chain.<sup>23</sup> The relative crosslink densities were determined by



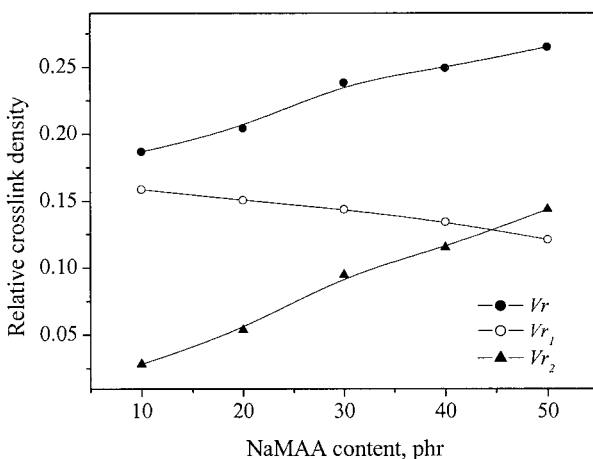
**Figure 8** Comparison of optical properties between EVM compound and vulcanizate. Formulation: EVM 100; DCP 3.0; NaMAA 50.



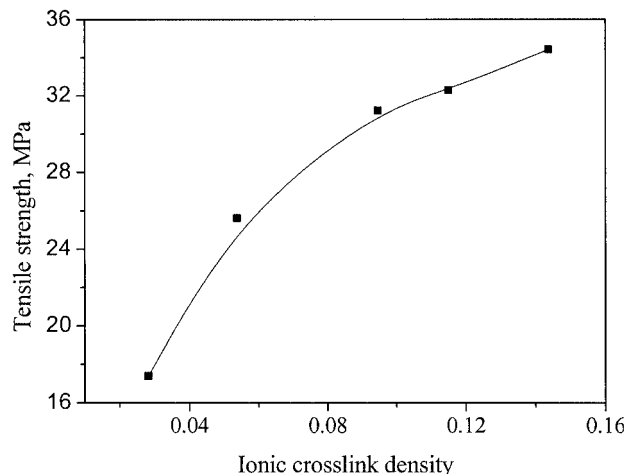
**Figure 9** Effects of DCP content on the relative crosslink density of EVM vulcanizates. Formulation: EVM 100; NaMAA 30; DCP variable.

the equilibrium swelling method. The values of  $V_r$  (representing the gross crosslink density of the original vulcanizates) and  $V_{r_1}$  (representing the covalent crosslink density of the vulcanizates treated with acid) were calculated according to eq. (3).  $V_{r_2}$  (representing the ionic crosslink density of the vulcanizates) was calculated by subtracting the covalent crosslink density from the gross crosslink density.

Figure 9 shows the effects of the DCP content on the relative crosslink densities of the EVM vulcanizates. In the case of a given NaMAA content, with an increasing DCP content, the gross crosslink density of EVM vulcanizates increase and the covalent crosslink densities also obviously increase, while the ionic crosslink density is little changed. Figure 10 shows the effect of the NaMAA content on the relative crosslink density of the EVM vulcanizates. At a given peroxide content, both the gross crosslink density and ionic crosslink



**Figure 10** Effects of NaMAA content on the relative crosslink density of EVM vulcanizates. Formulation: EVM 100; DCP 3.0; NaMAA variable.



**Figure 11** Crosslink density versus tensile strength of EVM/NaMAA vulcanizates. Formulation: EVM 100; DCP 3.0; NaMAA variable.

density increase with an increasing NaMAA content, while the covalent crosslink density shows a slight decrease. It is reasonable to suppose that the higher NaMAA concentration is favorable to the formation of grafted NaMAA onto the backbone of EVM and leads to more ionic crosslinks.

Figure 11 shows the relationship between the tensile strength and the ionic crosslink density. The tensile strength of the EVM vulcanizate depends on the ionic crosslink density. It is believed that the existence of ionic bonds means a good ability to slip along the hydrocarbon chains and a recovery, which prevents the formation of a local stress concentration and leads to a higher tensile strength.

**CONCLUSIONS**

EVM vulcanizates reinforced by *in situ* prepared sodium methacrylate has good mechanical properties and a high transparency. A formulation of a DCP content of 3.0 phr, NaMAA content of 30 phr, and a NaOH/MAA mol ratio of 1.0 imparts good mechanical properties to the EVM vulcanizate. The tensile strength of the EVM vulcanizate was 29.5 MPa and the tear strength was 65kN/m. At the same time, the EVM vulcanizate retains a high elongation at break of over 400%. When the mol ratios of NaOH/MAA are 0.5–1.25, the EVM vulcanizates are transparent. At a given mol ratio of NaOH/MAA of 1.0, all the EVM vulcanizates have a light transmission over 76% in the NaMAA content range of 10–50 phr. The NaMAA-reinforced EVM vulcanizate has a more obvious stress-softening effect and faster stress relaxation than those of the HAF-reinforced EVM vulcanizates. Crosslink density analysis revealed that the ionic crosslink densities of the EVM vulcanizates greatly increase with an increasing NaMAA content. Com-



pared with the HAF/EVM compounds, the Mooney viscosities of the HAF/EVM compounds remain nearly unchanged, but the curing rates increase significantly with an increasing filler content.

## References

1. Molitor, R. P. U.S. Patent 4 726 590, 1988.
2. James, A.; Lentz, P.; Joseph, H.; Moricun; Rochester. U.S. Patent 4 314 006, 1982.
3. Klingender, R. C.; Oyama, M.; Saito, Y. *Rubber World* 1990, 202(3), 26.
4. Costin, R.; Nagel, W.; Ekwall, R. *Rubber Chem Technol* 1991, 64, 152.
5. Saito, Y.; Fujino, A.; Ikeda, A. Presented at the SAE International Congress & Exposition, Detroit, MI, 1989; no. 890259.
6. Martin, F. S.; Melvin, T.; Pieroni, J. K. U.S. Patent 4 266 772, 1981.
7. Nagata, N. *Polyfile* 1991, 28(8), 53.
8. Saito, Y. *Nippon Gomu Kyokaishi* 1989, 62(5), 29.
9. Sugimoto, T.; Nakahara, A. *Jpn. Patent JP 7 165 993*, 1995.
10. Tanaka, K. Suzuki, F. *Jpn. Patent JP 6 287 358*, 1994.
11. Yuan, X.; Peng, Z.; Zhang, Y.; Zhang, Y. *Polym Polym Compos* 1999, 7, 431.
12. Yuan, X.; Peng, Z.; Zhang, Y.; Zhang, Y. *J Appl Polym Sci* 2000, 77, 2740.
13. Peng, Z.; Zhang, Y.; Zhang, Y. *Polym Polym Compos* 2001, 9, 275.
14. Yin, D.; Zhang, Y.; Zhang, Y.; Peng, Z. *China Synth Rubber Ind* 2002, 25(22), 104.
15. Du, A.; Peng, Z.; Zhang, Y.; Zhang, Y. *Polym Test* 2002, 21, 889.
16. Mullins, L. *Rubber Chem Technol* 1969, 42, 339.
17. Holliday, L. *Ionic Polymer*; Applied Science: London, 1975; p 54.
18. Holliday, L. *Ionic Polymer*; Applied Science: London, 1975; p 190.
19. Nomura, A.; Takano, J.; Toyoda, A.; Saito, Y. *Nippon Gomu Kyokaishi* 1993, 66, 830.
20. Nagata, N., Sato, T., Saito, Y. *J Appl Polym Sci* 1994, 53, 103.
21. Saito, T.; Nomura, A.; Sato, T. *Nippon Gomu Kyokaishi* 1994, 67, 867.
22. Yin, D.; Zhang, Y.; Peng, Z.; Zhang, Y. *Eur Polym J*, in press.
23. Holliday, L. *Ionic Polymer*; Applied Science: London, 1975, p 37.