Study on the Properties of Ethylene-Vinyl Acetate Rubber Vulcanizate Filled with Superfluous Magnesium Hydroxide/Methacrylic Acid

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ABSTRACT: Ethylene-vinyl acetate rubber (EVM) vulcanizates cured by dicumyl peroxide (DCP) with excellent mechanical properties were obtained by adding superfluous magnesium hydroxides (MH)/methacrylic acid (MAA). Different factors such as the DCP content and MH content were investigated to reveal their effects on the properties of the MH/MAA-filled EVM vulcanizates. The formulation of DCP of 2 phr, MH of 60 phr, and MAA of 5 phr is recommended for the EVM vulcanizates with excellent mechanical properties. The stress relaxation and stress softening behavior of MH/MAA-filled EVM vulcanizates were studied. The stress relaxation and stress softening became faster and more obvious with increasing MH content. The hot air aging resistance of EVM vulcanizates filled with different fillers such as silica and high abrasion furnace were compared, and the MH/MAA-filled EVM vulcanizates had the best aging resistance at 40-phr filler content. The MH/MAA-filled EVM vulcanizates had excellent flame retardancy due to the high MH content. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1813–1819, 2011

Key words: reinforcement; mechanical properties; ethylene-vinyl acetate

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INTRODUCTION

Rubber reinforcement is one of the most important topics in material science since the gum vulcanizates are always soft and weak.[1] Carbon black and silica are the most widely used fillers for rubber reinforcement due to their high reinforcing efficiency.[1–4] In recent years, rubbers reinforced by adding unsaturated carboxylates have attracted more and more researchers' attention.[5–7] The metallic salts of unsaturated carboxylic acid, such as magnesium methacrylate (MDMA)[8] showed a great reinforcing effect on peroxide-cured ethylene-vinyl acetate rubber (EVM) without any traditional reinforcing agent. Unsaturated carboxylates have been widely used in reinforcing polar elastomers such as styrene butadiene rubber (SBR)[9] and nitrile butadiene rubber (NBR).[10] Nonpolar elastomers like ethylene–propylene–diene monomer rubber can also be effectively reinforced by unsaturated carboxylates.[11] Unsaturated carboxylic acid usually can not totally react with the metal oxide or metal hydroxide during the *in situ* preparation of unsaturated carboxylates. It was reported that the neutralization degree of magnesium oxide and methacrylic acid (MAA) was $\sim$ 72.9% when their mol ratio was 0.5.[12] Therefore, the amount of unsaturated carboxylates obtained during processing is usually less than that calculated according to the mol ratio of MAA/metal oxide or metal hydroxide.

EVM known as Levapren, which is the copolymer of ethylene and vinyl acetate (VA), was firstly developed by Lanxess GmbH in Germany. The absence of unsaturated bonds contributes many good properties to EVM such as good heat resistance and excellent weathering, ozone and UV resistance.[13] EVM also has high oil resistance due to the polar VA group. Nevertheless, like most rubbers, EVM usually has poor mechanical properties. The tensile strength of EVM vulcanizates without any reinforcing fillers is only 2–3 MPa, which is too weak to be used. Du[8,14] studied EVM vulcanizates reinforced by the salts of unsaturated carboxylic acid and found that sodium magnesium methacrylate (NaMAA) and MDMA prepared *in situ* had a significant reinforcing effect on EVM vulcanizates; while there is little research focused on reinforcing the EVM by adding inorganic filler such as magnesium hydroxide (MH).

The conversion ratio of the reaction between MAA and metal oxide or metal hydroxide is usually low,[12] and the MAA left may have a strong corrosive effect on the equipments and also play a negative effect during the peroxide curing process. On the other

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TABLE I
Raw Materials

Materials	Grade	Characteristics	Producer
EVM	–	70 wt % VA Content; $ML_{1+4}^{100^\circ C} = 60$	Lanxess GmbH, Germany
MH	Chemical pure	–	Shanghai Songkai Chem.
MAA	Chemical pure	Purity: >98%	Shanghai Wulian Chem.
DCP	Chemical pure	Purity: >99.3%	Shanghai Gaoqiao Petro.
HAF	Rubber grade	Nitrogen surface area: 71–85 cm^2/g	Shanghai Carbot Chem.
Silica	–	Surface density: 130–170 m^2/g	Wuxi Hengheng Silica

HAF, high abrasion furnace black.

hand, it has been reported[9] that the addition of a small amount of MAA could obviously enhance the mechanical properties of peroxide-cured SBR vulcanizates filled with aluminum hydroxide. So it could be available to reinforce EVM with MH and MAA.

In this article, the mechanical properties of MH/MAA-filled EVM vulcanizates were studied, and different factors such as DCP and MH contents were examined. The stress relaxation and stress softening phenomena of MH/MAA-filled EVM vulcanizates were also studied as a function of MH content. The aging resistance of EVM vulcanizates filled with other kinds of fillers such as high abrasion furnace (HAF) and silica was compared. It could be another way to improve the mechanical properties that could be applied in flame retardance cable.

EXPERIMENTAL

The raw materials used are shown in Table I. The mixtures of EVM and the additives were prepared in the mixing chamber of a Germany Haake rheometer RC 90 at a rotor speed of 32 rpm and an initial temperature of 40°C. MH was firstly added to the EVM, and after its dispersion, MAA was added into the chamber, followed by the addition of dicumyl peroxide (DCP). The mixing process lasted about 12 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 12 min for measurement.

Curing characteristics

The curing curves at 170°C were recorded in a UR 2030 Rheometer (U-Can, Taiwan, China). The relative curing degree was represented by the variation between the maximal torque value (M_H) and the minimal torque value (M_L) of the curing curve, and the curing rate (C_R) was calculated according to the following equation:

$$C_R = (M_{90} - M_{10})/(t_{90} - t_{10}) \tag{1}$$

where t_{90} (optimum cure time) is equal to the time for the torque to reach $(M_H - M_L) \times 90\%$ over M_L. t_{10} is equal to the time for the torque to reach $(M_H - M_L) \times 10\%$ over M_L. M_{90} and M_{10} are the torque values at time t_{90} and t_{10}, respectively.

Mechanical properties

The tensile properties were measured with dumbbell specimens (6-mm-wide cross section) according to the ASTM D412-97. Tear strength was measured on unnotched right angle specimens according to the ASTM D624-98, the tests were performed on an Instron series IX 4465 material tester at a crosshead speed of 500 mm/min. Shore A hardness was measured using a LX-A durometer according to ASTM D2240-97, the data was read after the needle point plunged into the specimens for 5 s.

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, and then the operation was repeated twice. The fourth operation was performed when the specimen had rested after the first extension for 24 h in an attempt to ensure full recovery. The stress-softening effect can be expressed as the following:

$$\Delta W_i = \frac{W_1 - W_i}{W_1} \times 100\% \tag{2}$$

where W_1 is the strain energy that is needed in the first stretch, and W_i is the strain energy that is needed in the ith stretch.

Stress relaxation

Dumbbell specimens (6-mm-wide cross section) were used for the stress relaxation. The crosshead speed was 1000 mm/min. The starting time ($t = 0$) was set at the maximum stress σ_0 after the specimen was stretched to the specified elongation (200%), then, stress relaxation for 20 min was measured. The stress ratio σ_R is defined by

$$\sigma_R = (\sigma_t/\sigma_0) \times 100\% \tag{3}$$

where σ_t is the stress at time t ($t_{\max} = 20$ min).

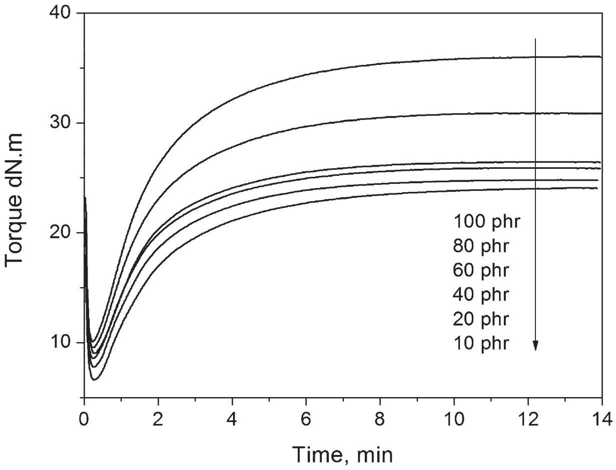

Figure 1 Curing curves of MH/MAA-filled EVM compounds at 170°C with different MH content. Formulation: EVM 100; MAA 5; DCP 2; MH variable.

Aging resistance

Aging resistance was determined according to the ASTM D573-99. The EVM vulcanizates were aged in an oven for 120 h at 100°C. The mechanical properties were tested every 24 h according to the ASTM D412-97.

Determination of crosslink density

The crosslink density was determined using an equilibrium swelling method. Molded samples (size about 2 cm ×2 cm ×2 mm) were swollen in xylene at 25°C for 96 h to achieve a swelling equilibrium. The weight of the samples was measured under a swelling equilibrium. Then, the samples were dried in a vacuum oven for 72 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:

$$V_r = m_0 \cdot \varphi \cdot (1-\alpha) \cdot \rho_r^{-1} / [m_0 \cdot \varphi \cdot (1-\alpha) \cdot \rho_r^{-1} + (m_1 - m_2) \cdot \rho_s^{-1}] \quad (4)$$

where m_0 is the sample mass before swelling; m_1 and m_2 are sample masses before and after drying, respectively; φ is the mass fraction of rubber in the vulcanizate; α is the mass loss of the gum EVM vulcanizate during swelling; ρ_r is the rubber density (ρ_r = 1.08 g/cm^3); and ρ_s is the solvent density (xylene, ρ_s = 0.88 g/cm^3). To distinguish ionic crosslink from covalent crosslink, samples were swollen in the mixture of xylene and chloroacetic acid for 5 days to destroy ionic crosslink bonds, followed by swelling in xylene for 2 days and then weighed, vacuum dried, and reweighed. V_{r1} was calculated from eq. (4), 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.

TABLE II
ΔW of EVM Vulcanizates with Different MH Content in Stress Softening Test

MH content (phr)	Curing rate (dN m/min)	$M_h - M_l$ (dN m)	OCT (T_{90}) (min : s)
10	2.87	17.52	5 : 29
20	3.28	17.10	4 : 43
40	3.34	17.32	4 : 42
60	3.44	17.41	4 : 42
80	4.03	21.35	4 : 48
100	4.70	25.96	4 : 58

Formulation: EVM 100; MAA 5; DCP 2; MH variable.

RESULTS AND DISCUSSIONS

Curing characteristics

The curing curves of EVM vulcanizates containing different MH content are shown in Figure 1. The final torque increases with increasing MH content at a constant MAA content. The increase of the final torque is mainly attributed to two reasons. First, MH is a kind of rigid inorganic filler and increasing its content can definitely lead to an obvious increase of the final torque. Secondly, the increase of the final torque is also attributed to the increase of crosslink density of EVM vulcanizates with increasing MH content, which will be discussed later. The crosslink degree and the curing rate of EVM vulcanizates gradually increase with increasing MH content (Table II). Since no curing reversion is observed in Figure 1, in the following experiment, the curing time was fixed to 12 min for EVM compounds to ensure full vulcanization.

Mechanical properties

The DCP content significantly affects the mechanical properties of MH/MAA-filled EVM vulcanizates (Table III). The tensile strength, 100 and 300%

TABLE III
Effect of DCP Content on the Mechanical Properties of MH/MAA-Filled EVM Vulcanizates

Mechanical properties	DCP content (phr)					
	0.5	1	1.5	2	3	4
Tensile strength (MPa)	9.46	15.81	18.61	21.6	21.8	22.4
Elongation at break (%)	520	370	329	306	231	217
Tear strength (kN/m)	49.7	51.8	47.2	45.9	44.5	42.3
Modulus at 100% (MPa)	4.08	6.61	8.14	9.03	11.82	12.5
Modulus at 300% (MPa)	8.04	15.9	18.15	20.33	–	–

Formulation: EVM 100; MH 100; MAA 5; DCP variable.

modulus of EVM vulcanizates increase gradually with increasing DCP content while the tear strength go through the maximum value at the DCP content of 1 phr. When the DCP content is 2 phr, the tensile strength is over 20 MPa while the elongation at break is still over 300%. Considering the general mechanical properties of EVM vulcanizates, 2 phr of DCP was chosen in the following study. The mass ratio of MH/MAA is 20 and the mol ratio is ~ 29.7.

The mechanical properties of EVM vulcanizates with different MH content are shown in Figure 2. With increasing MH content, the tensile strength of EVM vulcanizates sharply increases when the MH content is below 60 phr and slightly decreases thereafter. Even when the MH content is as high as 100 phr, the tensile strength of EVM vulcanizates is still over 20 MPa, indicating that superfluous MH has a great reinforcing efficiency on EVM gum vulcanizates. The tear strength, Shore A hardness, 100, and 300% modulus gradually increase with increasing MH content. The mechanical properties of filler reinforced rubber are highly dependent on the compatibility between filler and polymer matrix. The compatibility between polymer matrix and fillers is usually associated with the polarity of polymer matrix.[15] Zhang[15] reported that the dispersion of MH in rubber matrix had a close relationship with the polarity of polymer matrix. EVM is a kind of polar rubber and has similar polarity with MH particles, which enables MH a good dispersion in EVM matrix. However, the addition of excess MH will cause a serious aggregation of MH particles in EVM vulcanizates, and therefore the tensile strength slightly decreases at the MH content over 60 phr. Furthermore, MAA can be grafted to the EVM chain and meanwhile react with MH particles to increase the interfacial adhesion between MH and EVM, which contributes to the excellent mechanical properties of MH/MAA-filled EVM vulcanizates.

The elongation at break has the maximum value of 400% at the MH content of 60 phr and decreases sharply thereafter. Even when the MH content is as high as 100 phr, the elongation at break of EVM vulcanizates is still over 300%. Generally, the addition of fillers may cause an obvious decrease of elongation at break because fillers can not be stretched like rubber. In fact, it is impossible to make the filler particles uniformly disperse in the rubber matrix and the particles are always prone to aggregate. These aggregates can also be stretched in the existence of an external force. Furthermore, there is a slippage between the aggregates and rubber matrix. Therefore, the elongation at break increases with increasing MH content in the beginning. Excess MH fillers will cause a bad dispersion, leading to a total desquamation of fillers from rubber chains, and thus the elongation at break decreases. Zhang[16] studied the mechanical properties of MH-filled NBR vulcanizates and reported the same phenomenon.

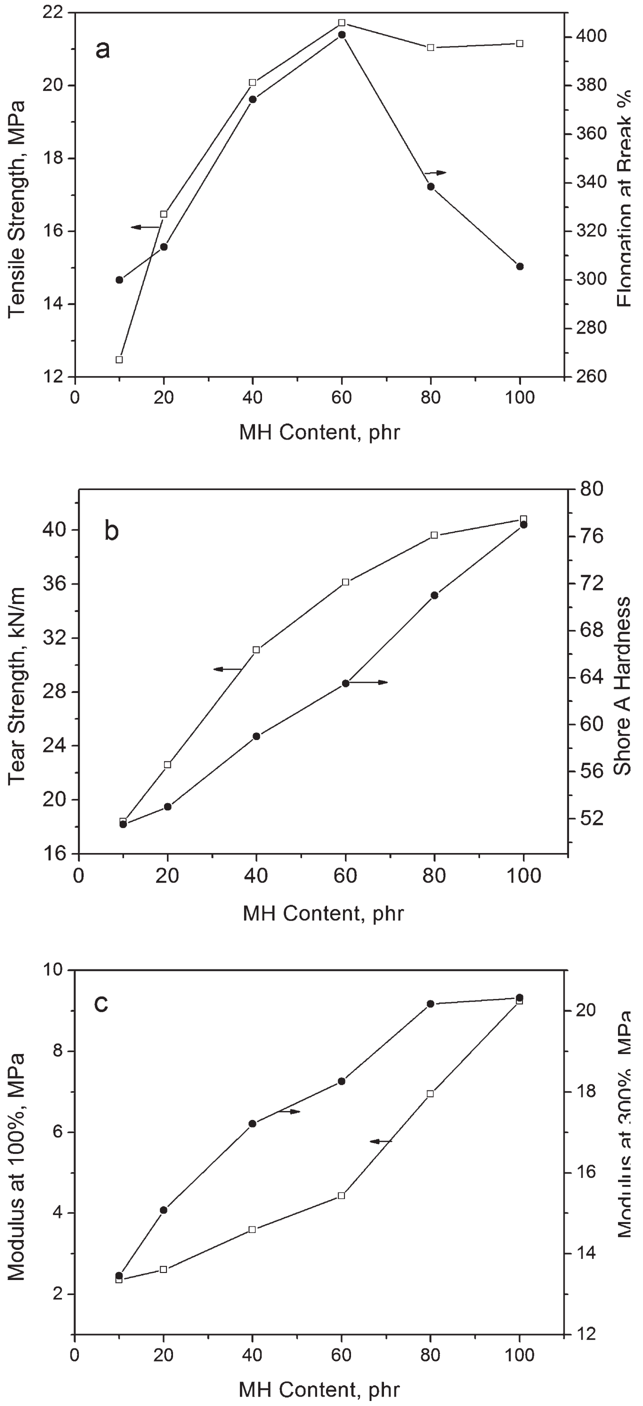

Figure 2 Effect of MH content on the mechanical properties of MH/MAA-filled EVM vulcanizates. Formulation: EVM 100; MAA 5; DCP 2; MH variable.

Stress softening effect

The stress softening effect, also indicated as Mullins effect,[17] is an important stress–strain behavior of rubber vulcanizates. The MH content significantly

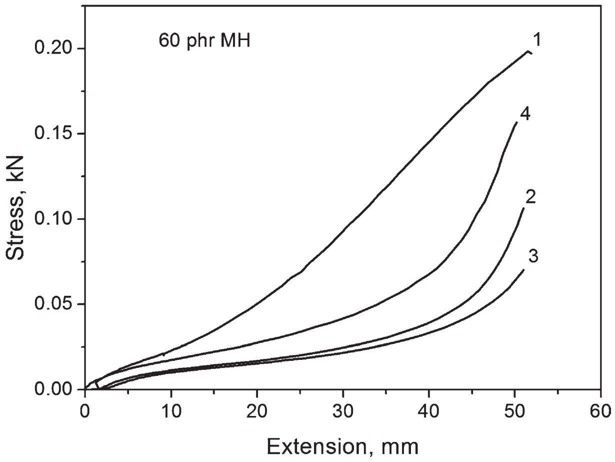

Figure 3 Stress softening curves of MH/MAA-filled EVM vulcanizates with different MH content. Formulation: EVM 100, MAA 5, DCP 2, MH 60.

affects the stress softening behavior of EVM vulcanizates (Fig. 3). The variation of the strain energy is listed in Table IV. The stress softening of MH/MAA-filled EVM vulcanizates is derived mainly from the breakage of the MH aggregates and the chain slippage of the attached polymer segments along the surface. The degree of stress softening of EVM vulcanizates increases with increasing MH content. After resting for a period, EVM vulcanizates gain part of its elastic recovery due to the thermal motion of the molecule, so that ΔW of the fourth stretch decreases. Du[14] studied the stress softening behavior of NaMAA-filled EVM vulcanizates and found the NaMAA-filled EVM vulcanizates could not get an elastic recovery or merely got a limited elastic recovery in the fourth stretch after resting for a period. Herein the observed stress softening behavior of MH/MAA-filled EVM vulcanizates is totally different from that of NaMAA-filled EVM vulcanizates, indicating MAA here acts as a coupling agent rather than carboxylic acid to form MDMA.

Stress relaxation

The stress relaxation of crosslinked rubbers is one of the most important mechanical characteristics. It includes physical relaxation and chemical relaxation.

TABLE IV
ΔW of EVM Vulcanizates with Different MH Content in Stress Softening Test

MH content (phr)	ΔW_2	ΔW_3	ΔW_4
40	54.6%	60.6%	38.4%
60	68.4%	74.1%	49.1%
80	70.2%	76.1%	51.6%
100	74.0%	77.9%	53.0%

Formulation: EVM 100; MAA 5; DCP 2; MH variable.

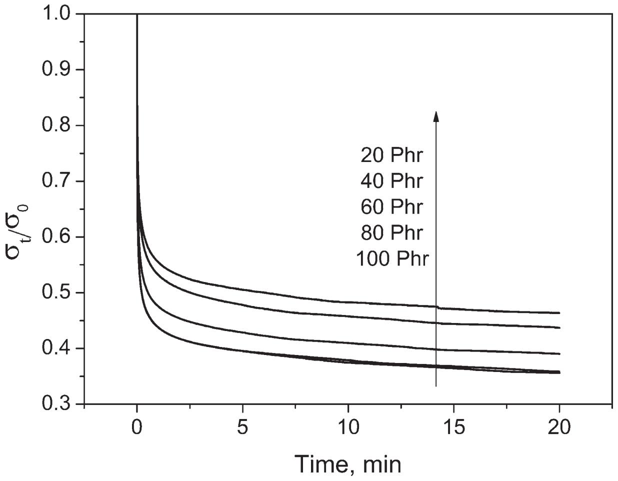

Figure 4 Stress relaxation curves of EVM vulcanizates with different MH content. Formulation: EVM 100, MAA 5, DCP 2, MH variable.

The former is due to the rearrangement of molecular chains while the latter is due to the rupture of polymer chain and/or crosslink bond and the formation of new crosslink bond. In this work, the stress relaxation of EVM vulcanizates with different MH content was investigated to identify the relationship between MH content and stress relaxation rate. Figure 4 shows the effect of MH content on the stress relaxation ratio σ_t at the elongation of 200%. EVM vulcanizates with higher MH content have much faster stress relaxation as well as lower stress ratio. Such change becomes less obvious when MH content is high. Figure 5 describes stress-time relationship at the beginning of stress relaxation. The axis is scaled in logarithm coordinate to make the phenomenon clear. Clearly, EVM vulcanizates with higher MH content have faster stress relaxation. Generally, rubbers are considered as stress holders

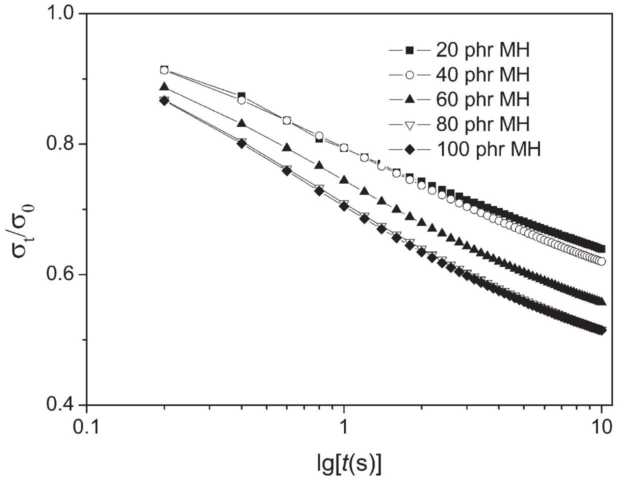

Figure 5 Stress relaxations of EVM vulcanizates with different MH content. Formulation: EVM 100, MAA 5, DCP 2, MH variable.

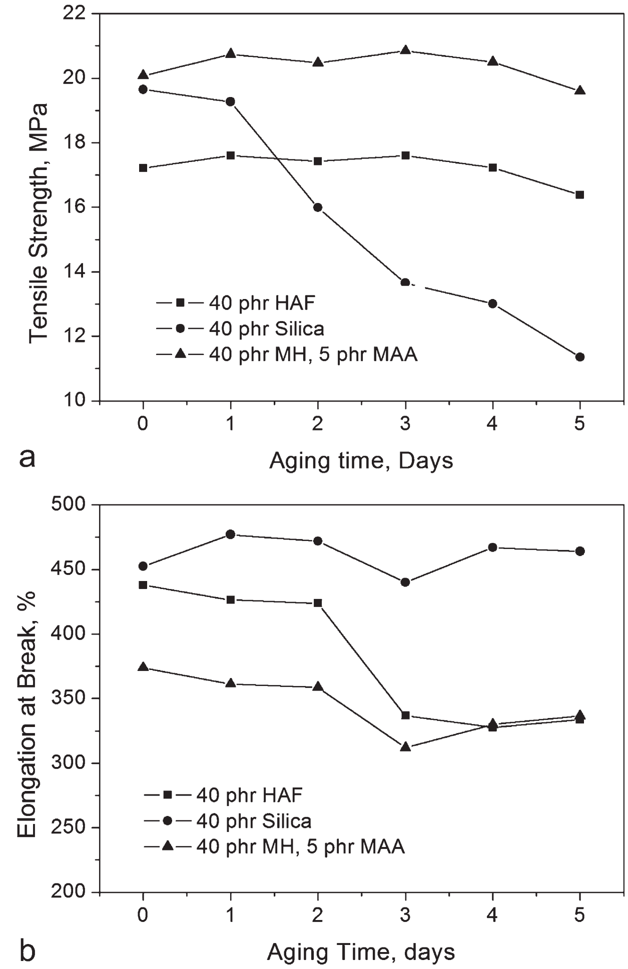

Figure 6 Effect of aging time on the mechanical properties of EVM vulcanizates. Formulation: EVM 100; DCP 2; Filler variable.

while the addition of filler can cause a decrease of the volume fraction of rubber. Therefore the stress relaxation rate usually increases with increasing filler content.

Aging resistance

The properties of rubber materials may have significant change as a result of aging, and materials will fail to meet the requirements.[18] Therefore, the aging resistance is also an important property for rubber materials. The aging resistance of vulcanizates is dependent on many factors such as the chemical nature of polymer, compound formulation, and the environmental conditions. The hot air aging properties of EVM vulcanizates filled with MH, silica or HAF were investigated (Fig. 6). Both MH/MAA-filled EVM vulcanizates and HAF-filled EVM vulcanizates have good aging resistance. The tensile strength has no significant changes over 5 days aging. However, the former has relatively higher tensile strength than the latter. The tensile strength of silica-filled EVM vulcanizates is as high as that of MH/MAA-filled EVM vulcanizates, but significantly decreases with increasing aging time. The elongation at break of MH or HAF-filled EVM vulcanizates slightly decreases but all the materials have high elongation (over 300%) after 5-day aging.

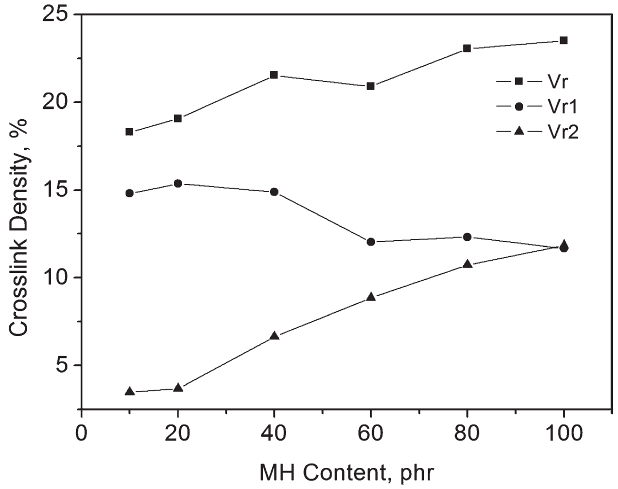

Figure 7 Effect of MH content on the crosslink density of EVM vulcanizates. Formulation: EVM 100, MAA 5, DCP 2, MH variable.

Crosslink density

The crosslink density of EVM vulcanizates is highly dependent on the MH content (Fig. 7). At a given MAA content, with increasing MH content, the gross crosslink density of EVM vulcanizates and the ionic crosslink density obviously increase, while the covalent crosslink density slightly decrease. The increase of the ionic crosslink density with increasing MH content should be interpreted as follows. MAA can

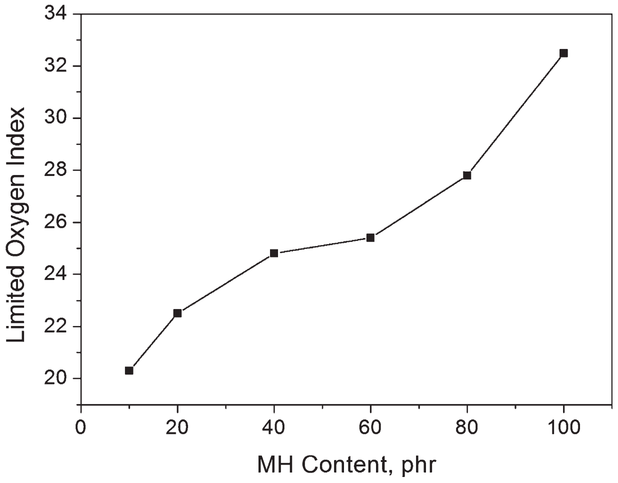

Figure 8 The LOI of EVM materials with different MH content. Formulation: EVM 100, MAA 5, DCP 2, MH variable.

be easily grafted to the EVM matrix in the existence of peroxides and can also react with MH to form ionic crosslink bond. However, as we mentioned before, MAA can not totally react with MH, increasing MH content can favor such neutralization reaction, which enables the EVM vulcanizates to form a more complete crosslink network.

Flame retardancy

One of the most important applications of MH is to improve the flame retardancy of polymers due to its endothermic dehydrolyzation at high temperature.[19,20] The MH content has significant effect on the limited oxygen index (LOI) of EVM vulcanizates (Fig. 8). The LOI of EVM vulcanizates gradually increases with increasing MH content. The LOI is over 21 when 20 phr MH is added, and the material can be used as flame retardance material. When MH content is 100 phr, the LOI of EVM vulcanizates is over 30, and the materials can be regarded as self-extinguishing materials with excellent flame retardancy.

CONCLUSION

The DCP and MH contents have significant effects on the mechanical properties of EVM vulcanizates filled with MH and MAA. The formulation of EVM 100 phr, MH 60 phr, MAA 5 phr, and DCP 2 phr was responsible for the excellent mechanical properties of EVM vulcanizates. The tensile strength was over 20 MPa while the elongation at break was $\sim$ 400%. The MH/MAA-filled EVM vulcanizates had better hot air aging resistance than those filled with HAF or silica. The addition of MH accelerated the stress-relaxation process of EVM vulcanizates and the stress ratio σ_t decreased with increasing MH content. The EVM vulcanizates with higher MH content showed more obvious stress softening behavior. The MH/MAA-filled EVM vulcanizates were able to get an elastic recovery after resting for a period, which is totally different from the metal methacrylates filled EVM vulcanizates. MH increased the gross crosslink density and the ionic crosslink density while slightly decreased the covalent crosslink density. The MH/MAA-filled EVM vulcanizates showed excellent flame retardancy due to the high MH content. EVM vulcanizates with excellent flame retardency, mechanical properties, and aging resistance were successfully prepared by adding superfluous MH in the existence of a little MAA.

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