

Effect of Methacrylic Acid on the Properties of Ethylene–Vinyl Acetate Rubber Vulcanizates Reinforced by Magnesium Hydroxide

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ABSTRACT: Ethylene–vinyl acetate rubber (EVM) vulcanizates with excellent mechanical properties were obtained with magnesium hydroxides (MH) and methacrylic acid (MAA). MAA significantly improved the mechanical properties of the MH-filled EVM vulcanizates. The tensile strength, Shore A hardness, and tensile set modulus of the EVM vulcanizates significantly increased with increasing MAA content. The tensile strength of the MH-filled EVM vulcanizates increased from 12.3 to 18.5 MPa after the addition of 2.5 phr MAA when the MH content was fixed at 60 phr. The gross crosslink density and ionic crosslink density increased with increasing MAA content. The glass-transition temperature and $\tan \delta$ slightly decreased with increasing MAA content. Morphological

study showed that MAA obviously improved the dispersion of the MH particles in the EVM matrix. The thermal stability of the EVM vulcanizates was obviously enhanced after the addition of MAA. Fourier transform infrared analysis indicated that MAA reacted with MH to form magnesium methacrylates, and there was a polymerization of MAA during the curing process in the existence of peroxide. An ionic crosslink bond was thought to be formed on the surface of the MH aggregates; this resulted in a possible structure where MH aggregates were considered as crosslink points. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 279–285, 2011

Key words: morphology; reinforcement; rubber

INTRODUCTION

Magnesium hydroxide (MH) is one of the most widely used inorganic fillers, especially in flame-retardant materials, because of the high-flame retardant efficiency, high decomposition temperature, and low cost of the filled materials.^{1–4} However, the addition of superfluous MH usually leads to a sharp decrease in the mechanical properties of the materials. Many investigations have been carried out on ways to improve the mechanical properties of MH-filled polymers,^{5–7} these studies have mainly included two aspects. The first is the minimization of the particle size,^{7,8} and the other is the surface treatment of the MH particles.^{9,10} Zhang et al.⁷ compared the properties of ethylene–propylene–diene monomer rubber vulcanizates filled with MH with different particle sizes and found that the mechanical properties increased with decreasing MH particle size. Cook and Harper⁹ studied fatty-acid-treated MH and found that the mechanical properties of the

rubber vulcanizates were dependent on both the coating level and the morphology of the MH particles, but the rheological properties were more significantly influenced by the coating level. So far, the surface modification agents are usually silane coupling agents or long-chain fatty acids, such as stearic acid.^{11–13} Little study has focused on MHs treated with unsaturated carboxylic acid, such as methacrylic acid (MAA). On the other hand, the reinforcement of rubbers by the addition or *in situ* preparation of metallic methacrylates, such as magnesium methacrylates (MDMAs),^{14–16} sodium methacrylates,^{17,18} or zinc methacrylates,^{19,20} has attracted the extensive attention of researchers. Yin et al.²¹ reported that a small amount of MAA obviously enhanced the mechanical properties of peroxide-cured styrene–butadiene rubber vulcanizates filled with aluminum hydroxide; this indicated that MAA could also be used as an effective coupling agent.

The ethylene–vinyl acetate rubber (EVM) known as Levapren, which is the copolymer of ethylene and vinyl acetate (VA), was first developed by Lanxess GmbH (Leverkusen, Germany). The absence of unsaturated bonds contributes many good properties to EVM, including good heat resistance and excellent weathering, ozone, and UV resistance.²² The high content of polar VA groups also provides EVM with

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TABLE I
Raw Materials

Material	Characteristics	Producer
EVM	70 wt % VA, $M_{L1+4}^{100^\circ\text{C}} = 60$	Lanxess GmbH (Leverkusen, Germany)
MH	Chemically pure	Shanghai Songkai Chem Co., Ltd. (Shanghai, China)
MAA	Chemically pure	Shanghai Wulian Chem Co., Ltd. (Shanghai, China)
DCP	99.3% pure	Shanghai Gaoqiao Petroleum Co. (Shanghai, China)

good oil-resistance and flame-retardance properties. In this study, we mainly focused on the reinforcement of EVM vulcanizates by adding superfluous MH and a small amount of MAA. The effects of the MAA content on the mechanical properties of the MH-filled EVM vulcanizates were investigated and further related to the morphology. The dynamic mechanical properties and thermal stability of the EVM vulcanizates were also included.

EXPERIMENTAL

Materials and sample preparation

The raw materials used are shown in Table I. Mixtures of EVM and the additives were prepared in a mixing chamber of a Haake rheometer RC 90 (Vreden, Germany) at a rotor speed of 32 rpm and an initial temperature of 40°C. MH was first added to the EVM, and after its dispersion, MAA was added to the chamber; this was followed by the addition of dicumyl peroxide (DCP). The compounding process lasted about 12 min. Then, the compound was sheeted onto the two-roll mill. The compound was press-cured into a 2 mm thick sheet at 170°C for 12 min for measurement.

Measurements

The curing curves at 170°C were recorded in a UR 2030 rheometer, (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 was calculated according to the following equation:

$$\text{Curing rate} = (M_{90} - M_{10}) / (t_{90} - t_{10}) \quad (1)$$

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

The tensile properties were measured with dumbbell specimens (6 mm wide cross sections) according to the Chinese standard GB/T 528-1992. The tear strength was measured on unnotched right-angle specimens according to the Chinese standard GB/T 529-1999. The tests were performed with an Instron series IX 4465 material tester (MA, USA) at a cross-head speed of 500 mm/min. The Shore A hardness was measured with an LX-A durometer (Shanghai, China) according to the Chinese standard GB/T 531-1999. We took the readings 5 s later.

The crosslink density was determined with the equilibrium swelling method. The molded samples were swollen in xylene at 25°C for 96 h to achieve an equilibrium swelling state. The weight of the samples was measured under equilibrium swelling. Then, the samples were dried in a vacuum oven for 72 h at 90°C to remove all of 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:^{14,17,18}

$$V_r = m_0 \varphi (1 - \alpha) \rho_r^{-1} / [m_0 \varphi (1 - \alpha) \rho_r^{-1} + (m_1 - m_2) \rho_s^{-1}] \quad (2)$$

where m_0 is the sample mass before swelling; m_1 and m_2 are the 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 vulcanizates during swelling; ρ_r is the rubber density (1.08 g/cm³ for Levapren 700 XL); and ρ_s is the solvent density (0.88 g/cm³ for xylene). To distinguish ionic crosslinks from covalent crosslinks, the samples were swollen in a mixture of xylene and chloroacetic acid for 5 days to destroy ionic crosslink bonds; this was followed by swelling in xylene for 2 days and then weighing, vacuum-drying, and reweighing. V_{r1} was calculated from eq. (2), which represents the covalent crosslink density. V_{r2} , which we calculated by subtracting V_{r1} from V_r , was used to represent the ionic crosslink density.

The dynamic mechanical properties were measured with a DMTA IV rheometer from Rheometric Scientific (USA) under a tension mode at a frequency of 1 Hz with dynamic strain of 0.01% over a temperature range of -80 to 90°C at a heating rate of 3°C/min. The specimen dimensions were 30 × 4 × 2 mm³.

Thermogravimetric analysis curves of the specimens were recorded on a PerkinElmer 7 series thermal analysis system (MA, USA). The specimens were heated up to 800°C from room temperature at a rate of 20°C/min in a nitrogenous gas atmosphere.

Infrared transmission spectra were obtained with a Paragon 1000 Fourier transform infrared (FTIR) spectrometer from PerkinElmer. The scan range was

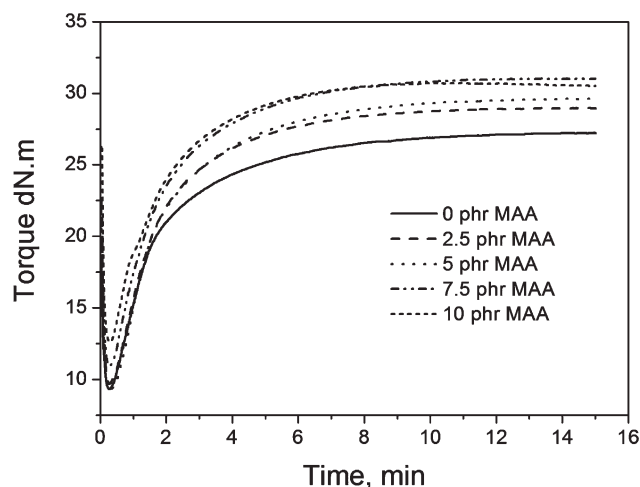


Figure 1 Curing curves of the MH-filled EVM compounds at 170°C with different MAA contents. Formulation: EVM, 100 phr; MH, 60 phr; DCP, 2 phr; and MAA, variable.

4400–400 cm^{-1} , and the resolution was 4 cm^{-1} . The MAA sample was prepared by the casting of MAA onto a KBr disc. The sample of the MH-filled EVM compound was pressed into a thin film at room temperature. The film of the gum EVM vulcanizate for testing was prepared by compression molding at 170°C for 12 min.

Scanning electron microscopy (SEM) observations were made with a Hitachi-S-2150 instrument (Japan) at an accelerating voltage of 15 kV. The samples were quenched in liquid nitrogen and then fractured into sections and gold-sputtered onto their rough surface to increase the conductivity. Transmission electron microscopy (TEM) experiments were performed with an H-800-1 (Hitachi, Japan) to observe the dispersion of MH particles in EVM matrix. The samples were shaped as ultrathin films prepared by cryoultramicrotomy.

RESULTS AND DISCUSSION

Curing characteristics

MAA significantly affected the curing properties of the MH-filled EVM vulcanizates (Fig. 1). The final torque of the EVM vulcanizates increased with increasing MAA content. The increase of the final torque was associated with increasing crosslink density; this is discussed later. The curing rate of the EVM vulcanizates gradually increased with increasing MAA content (Fig. 2). MAA is a difunctional compound, and its double bonds could be opened in the existence of peroxides; this enabled MAA to be easily grafted onto the polymer matrix, and meanwhile, its carboxylic groups could react with MH to form ionic crosslink bonds. Therefore, MAA greatly accelerated the curing process of the MH-filled EVM

compounds. Because no curing reversion was observed (see Fig. 1), in the following experiment, the curing time was fixed to 12 min for the EVM compounds to ensure full vulcanization.

Mechanical properties

The mechanical properties of the MH-filled EVM vulcanizates were significantly improved by the addition of MAA (Fig. 3). The tensile strength of the MH-filled EVM vulcanizates increased from 12.3 to 18.5 MPa after the addition of 2.5 phr MAA. With increasing MAA content, the tensile strength rapidly increased when the MAA content was between 0 and 5 phr and slightly increased thereafter. The elongation at break gradually decreased with increasing MAA content. However, even when the MAA content was 10 phr, the elongation at break was still over 300%. The tensile set modulus, tear strength, and Shore A hardness significantly increased with increasing MAA content. Such an effect of the MAA content on the mechanical properties of the MH-filled EVM vulcanizates was probably due to the increasing crosslink density and the interfacial adhesion between the EVM matrix and MH particles. This is discussed further later.

The mechanical properties of the rubber vulcanizates were strongly dependent on the crosslink density. The MAA content significantly affected the relative crosslink density of the MH-filled EVM vulcanizates (Fig. 4). With increasing MAA content, the gross crosslink density of the EVM vulcanizates and the ionic crosslink density obviously increased, whereas the covalent crosslink density changed slightly. The ionic crosslinks were formed by the chemical reaction between MAA and the MH

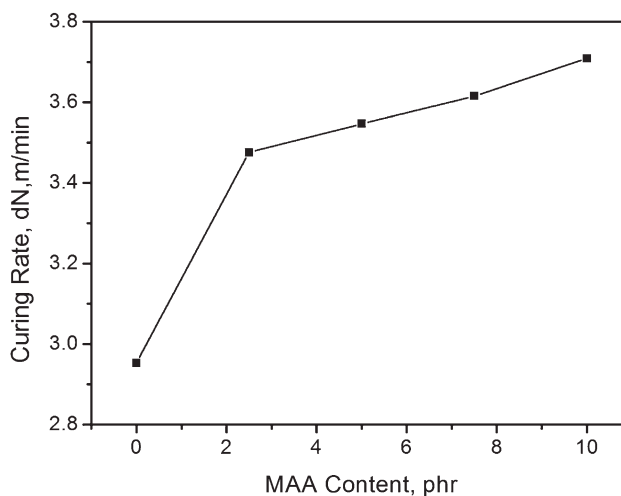


Figure 2 Effect of the MAA content on the curing rates of the MH-filled EVM compounds at 170°C. Formulation: EVM, 100 phr; MH, 60 phr; DCP, 2 phr; and MAA, variable.

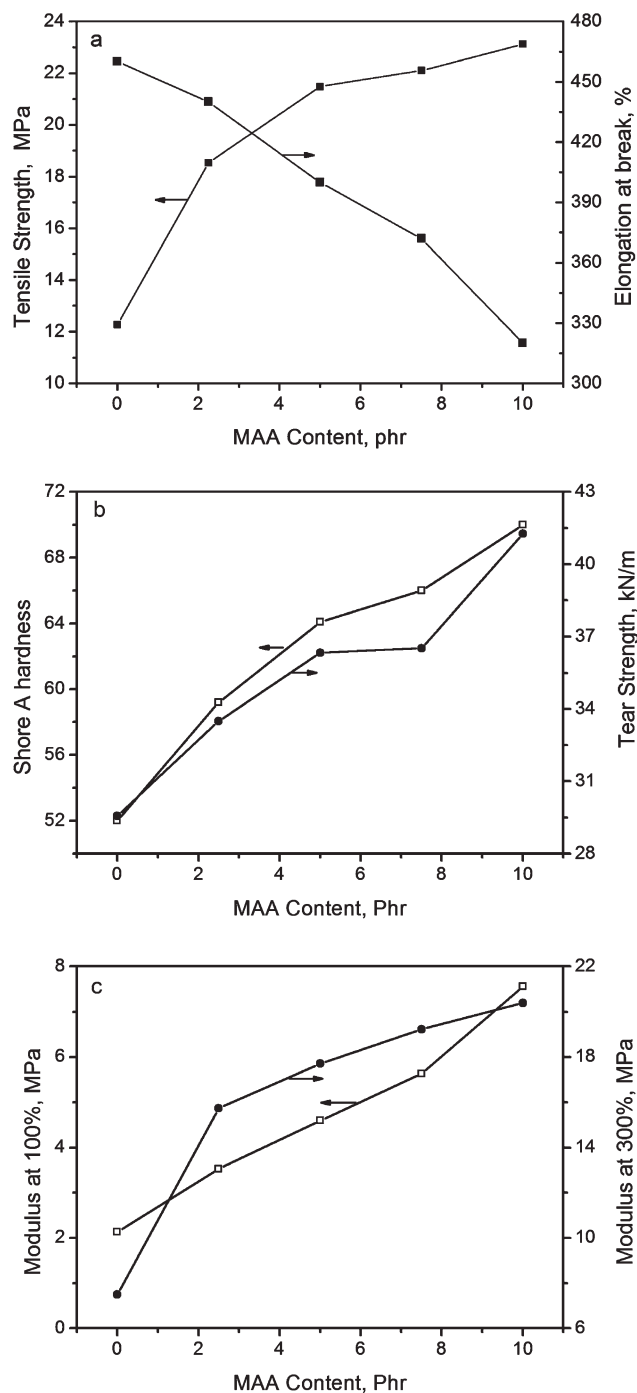


Figure 3 Effect of the MAA content on the mechanical properties of the EVM vulcanizates. (a) tensile strength and elongation at break, (b) tear strength and Shore A hardness, and (c) modulus at 100 and 300%.

particles. The increasing MAA content certainly favored such a chemical reaction, and therefore, the ionic crosslink density increased with increasing MAA content. The DCP content remained the same, and thus, the covalent crosslink density seldom changed. Although the ionic crosslink density increased with increasing MAA content, the covalent crosslink density remained the main part of the

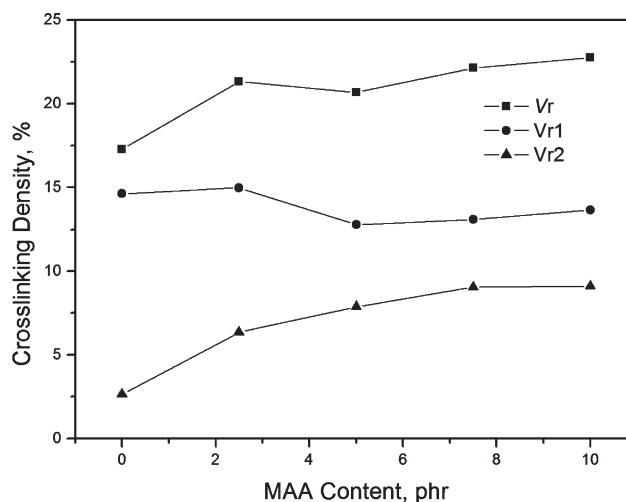


Figure 4 Effect of the MAA content on the crosslink density of the MH-filled EVM vulcanizates. Formulation: EVM, 100 phr; MH, 60 phr; DCP, 2 phr; and MAA, variable.

gross crosslink density. The increase of the gross crosslink density corresponded to the increases in the Shore A hardness and tensile set modulus of the MH-filled EVM vulcanizates.

Dynamic mechanical properties

The effect of the MAA content on the dynamic mechanical properties is shown in Figure 5. The glass-transition temperature (T_g) of the MH-filled EVM vulcanizates slightly shifted toward low temperature after the addition of MAA. The phenomenon observed here was in contrast with the convention that the T_g of rubber usually increases with increasing crosslinking density. Such inconsistency was

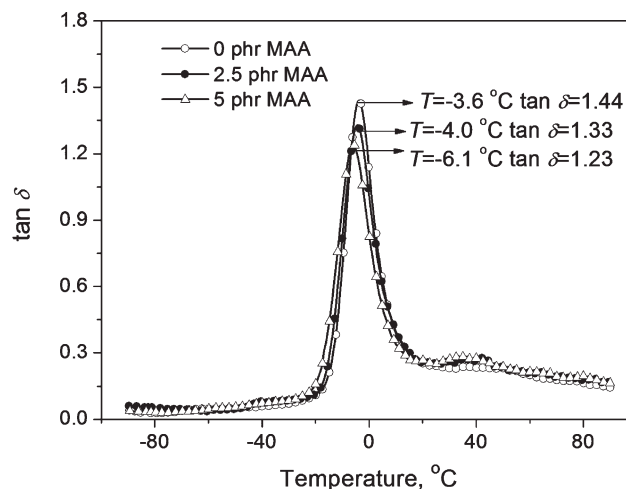


Figure 5 Effect of the MAA content on the dynamic mechanical properties of the MH-filled EVM vulcanizates. Formulation: EVM, 100 phr; MH, 60 phr; DCP, 2 phr; and MAA, variable (T = temperature).

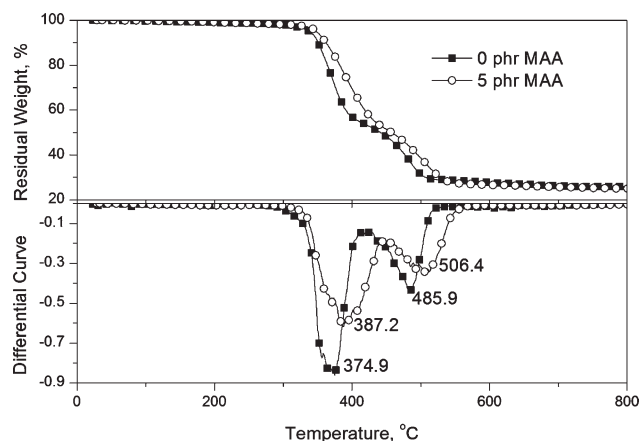


Figure 6 Effect of MAA on the thermal stability of the MH-filled EVM vulcanizates. Formulation: EVM, 100 phr; MH, 60 phr; DCP, 2 phr; and MAA, variable.

probably due to the graft reaction between MAA and the EVM polymer chain in the presence of peroxide. The graft of small-molecule MAA to EVM could have lengthened the distances between the polymer chains, increased the mobility of the EVM polymer chain, and thus, decreased the T_g of EVM rubber. Du et al.¹⁴ studied the dynamic mechanical properties of EVM vulcanizates reinforced by MDMA and also reported that the T_g of the EVM vulcanizates decreased with increasing MDMA content because of the graft reaction between MDMA and the EVM main chain. The observed phenomenon indicated that compared with the crosslink degree, the graft was the main factor determining the T_g of the MH-filled EVM vulcanizates. This was evidence to prove that MAA was grafted onto the polymer chains in the existence of peroxides. The decrease in $\tan \delta$ indicated that the level of damping was greater; this is usually associated with an increasing filler–matrix interaction.⁶ Here, $\tan \delta$ of the MH-filled EVM vulcanizates also slightly decreased after the addition of MAA. Therefore, the results demonstrate that MAA strengthened the interactions between the MH particles and EVM matrix.

Thermogravimetric analysis

MAA affected the thermal stability of the MH-filled EVM vulcanizates significantly (Fig. 6). The addition of 5 phr MAA obviously enhanced the thermal stability of the MH-filled EVM vulcanizates. The decomposition of EVM included two steps: the first was the decomposition of the side groups [temperature at the maximum rate of weight loss (T_{max}) = 360°C], and the second was the decomposition of the polyethylene main chain (T_{max} = 450°C). The decomposition of MH (T_{max} = 380°C) was located between these two steps and could not be distinguished clearly.

Therefore, there were still two peaks instead of three in the differential curves of the MH-filled EVM vulcanizates. Both these peaks had a significantly shift toward high temperature after the addition of 5 phr MAA, whereas the residual weight at 800°C showed little change. The improvement in the thermal stability of the MH-filled EVM vulcanizates was probably due to the more uniform dispersion of MH particles in the EVM matrix and also to the increasing filler–matrix interactions between MH and EVM after the addition of MAA; these enabled the MH particles to act more effectively as a protective shield to prevent heat and gas diffusion.

FTIR analysis

Figure 7 shows the FTIR spectra of the EVM, MAA, and EVM/MH/MAA compounds and vulcanizates. Figure 7(a) shows the spectrum of the pure EVM gum with characteristic absorption peaks at 1460 and 1374 cm^{-1} , generated from C–H deformation vibration of the methyl group. The characteristic peaks at 1736 and 1235 cm^{-1} were attributed to the stretching vibrations of C=O and C–O. Figure 7(b) shows the spectrum of MAA. MAA exists as a dimer because of the strong hydrogen bonds between the MAA molecules. The MAA dimer had characteristic absorption bands at 1698 and 1634 cm^{-1} , which were attributed to C=O and C=C stretching vibrations, respectively.

Figure 7(c,d) shows the spectra of the EVM compound and vulcanizates, respectively. When EVM was mixed with MH and MAA, the characteristic peaks of all of the components in the compound did not change. Compared with the spectrum of the

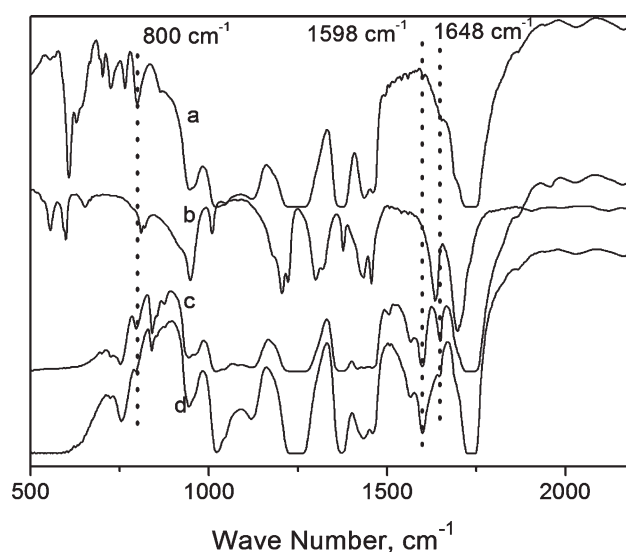


Figure 7 FTIR spectra of the (a) EVM, (b) MAA, (c) 100/60/5/2 EVM/MH/MAA/DCP compound, and (d) 100/60/5/2 EVM/MH/MAA/DCP vulcanizates.

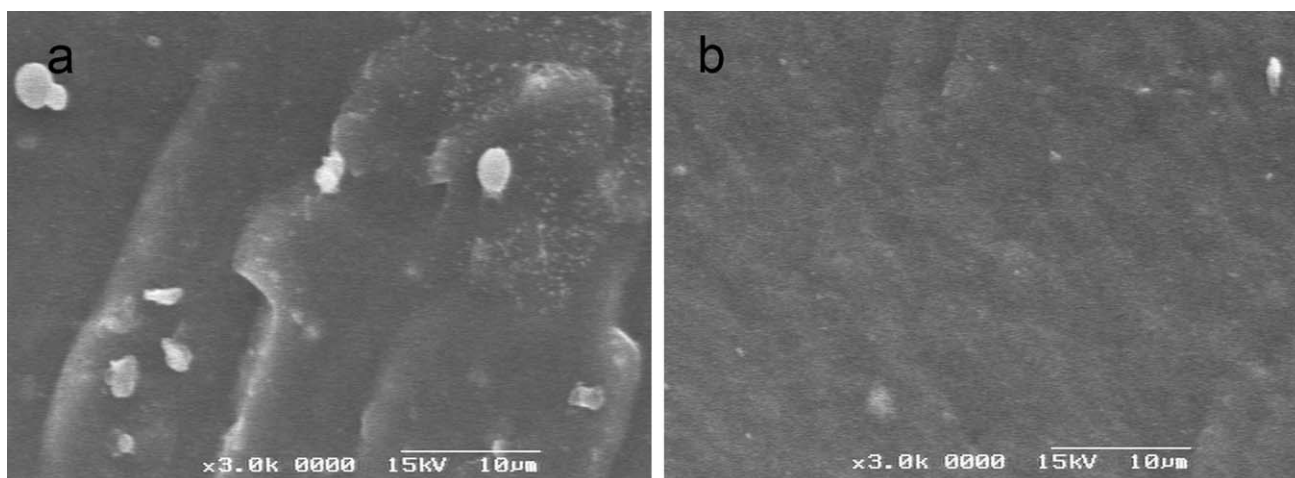


Figure 8 SEM graphs of the MH-filled EVM vulcanizates (a) without and (b) with MAA. Formulation: EVM, 100 phr; MH, 60 phr; DCP, 2 phr; and MAA, variable.

EVM compound, the spectrum of the EVM vulcanizates showed a significant change in the peak at 1648 cm^{-1} ; this resulted from the vibration of $\text{C}=\text{C}$ in unsaturated carboxylates. The characteristic absorption band of $\text{C}=\text{C}$ at 1648 cm^{-1} disappeared completely in the EVM vulcanizates; this indicated that the double bonds ($\text{C}=\text{C}$) reacted to a great extent during the vulcanization process to form homopolymers and graft polymers. Carboxylic anions had two strongly coupled $\text{C}=\text{O}$ bonds, The peak at 1598 cm^{-1} in Figure 7(c,d), which is the characteristic absorption peak of salts of carboxylic acid, was ascribed to the $-\text{COO}^-$ symmetric stretching vibration; this demonstrated that MAA reacted with MH to form MDMA. Also, because of the formation of MDMA in the EVM compound and vulcanizates, the $\text{C}=\text{C}$ peak shifted a little from 1634 to 1648 cm^{-1} in comparison with the FTIR spectra of MAA.

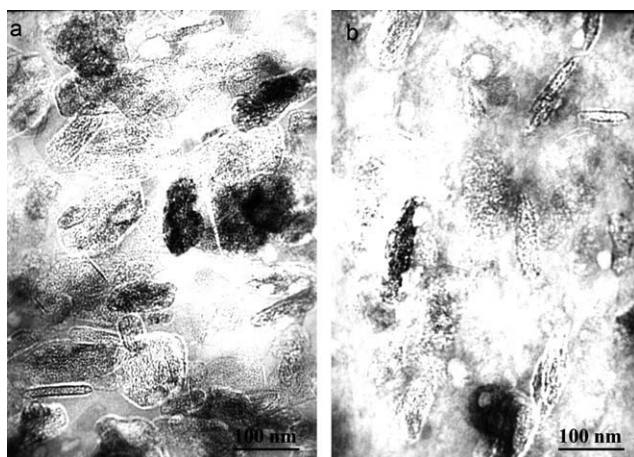


Figure 9 TEM graphs of the MH-filled EVM vulcanizates (a) without and (b) with MAA. Formulation: EVM, 100 phr; MH, 60 phr; DCP, 2 phr; and MAA, variable.

Morphology

MAA significantly influenced the morphology of the MH-filled EVM vulcanizates (Fig. 8). It was evident that MAA obviously improved the dispersion of MH particles in the EVM matrix. The MH particles were prone to aggregating in the EVM matrix and forming aggregates with diameters of $2\text{--}3\text{ }\mu\text{m}$. After the addition of MAA, large-scale aggregates could hardly be seen, and the MH particles had a much better dispersion. The polymer–filler interfaces became less obvious after the addition of MAA. The same phenomenon was also observed in TEM graphs (Fig. 9). The hexagon of the MH crystal was quite obvious when no MAA was added. After the addition of MAA, the interfaces between MH and EVM became hazy. The improvement of the dispersion of MH provided evidence for increased interfacial adhesion between the MH particles and EVM matrix; this adhesion was responsible for the improved mechanical properties of the EVM vulcanizates.

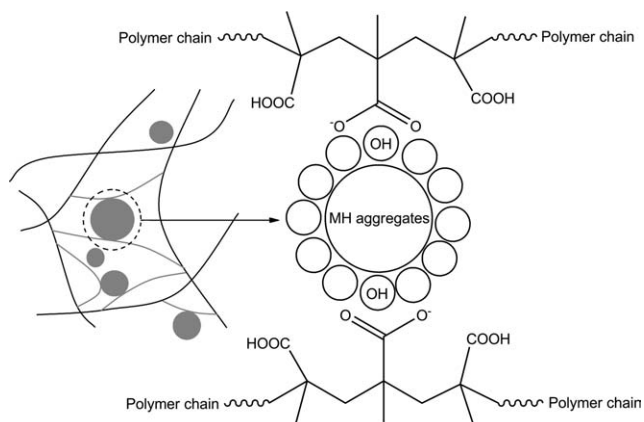


Figure 10 Possible mechanism of the MAA-reinforcing MH-filled EVM vulcanizates.

Possible mechanism

MAA is a difunctional compound and can greatly promote the crosslink process of EVM composites. It was reported that²³ metallic methacrylates underwent *in situ* polymerization during the process of vulcanization, including homopolymerization and graft copolymerization. MAA also has double bonds, and therefore, several reactions took place during the compounding and curing process: polymerization, grafting to EVM, and neutralization with MH. Ionomers might be formed if MAA is grafted to EVM, and meanwhile, it reacts with MH particles. In this study, the molar ratio of MH to MAA was 17.8 (mass ratio, 60/5); this indicated that the MAA dosage was far from enough to convert all of the MH into MDMA, but EVM vulcanizates with excellent mechanical properties were still obtained. Because the fillers were always prone to aggregating in the polymer matrix, we supposed that it was these aggregates that located between the two carboxylic groups instead of metallic ions such as Mg^{2+} . The MH aggregates could be bonded on the rubber crosslink network when two or three grafted MAA molecules reacted with the same MH aggregates by the formation of ionic bonds; this resulted in the possible structure where MH aggregates were considered to be ionic crosslink points (Fig. 10). Similar phenomenon were also found in ethylene-propylene–diene monomer rubber vulcanizates filled with calcium carbonate that were coated *in situ* with MAA.²⁴ Ionomers were formed when the reacted MAA was grafted to the EVM chains in the presence of peroxide. Therefore, EVM vulcanizates with excellent mechanical properties could still be obtained even when a little MAA was used.

CONCLUSIONS

The mechanical properties of EVM vulcanizates filled with MH were significantly affected by MAA. The tensile strength increased significantly with increasing MAA content. The formulation of 100 phr EVM, 60 phr MH, 5 phr MAA, and 2 phr DCP was responsible for the excellent mechanical properties of the EVM vulcanizates. The tensile strength reached over 20 MPa, whereas the elongation at break was approximately 400%. MAA greatly enhanced the thermal stability of the MH-filled EVM vulcanizates. Both the gross crosslink density and the ionic crosslink density increased with increasing MAA content, whereas the covalent crosslink density changed slightly. FTIR analysis indicated the formulation of carboxylates and the polymerization

of MAA or MDMA in the curing process. The microscope analysis showed that MAA greatly improved the dispersion of MH in the EVM matrix. Although the crosslink density increased, T_g shifted slightly toward low temperature with increasing MAA content because of the graft reaction. The intensity of $\tan \delta$ decreased after the addition of MAA; this demonstrated an increasing filler–matrix interaction; this was the main factor for the reinforcing effect of MAA on the MH-filled EVM vulcanizates. Ionic crosslink bonds were thought to be formed on the surface of the MH aggregates; this resulted in the possible structure where MH aggregates were considered to be crosslink points.

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