Polymerization Conversion and Structure of Magnesium Methacrylate in Ethylene–Vinyl Acetate Rubber Vulcanizates

Aihua Du,[1] Zonglin Peng,[2] Yong Zhang,[2] Yinxi Zhang[2]

[1]*Institute of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China*
[2]*Research Institute of Polymer Materials, Shanghai Jiao Tong University, Shanghai 200240, China*

ABSTRACT: Ethylene–vinyl acetate rubber (EVM) filled with magnesium methacrylate (MDMA) was cured with dicumyl peroxide (DCP). The experimental results showed that the mechanical properties of MDMA/EVM vulcanizates were superior to those of high-abrasion furnace carbon black/EVM vulcanizates. The tensile strength of the MDMA/EVM vulcanizate could reach 22.5 MPa and the tear strength was 83.5 kN/m, whereas its elongation at break remained over 300%, even when the MDMA content was 50 phr. FTIR analysis confirmed that polymerization of MDMA occurred under the initiation of DCP, and the polymerization conversion of MDMA decreased with the increase of MDMA content. When the MDMA content increased from 10 to 50 phr, the conversion of MDMA in EVM decreased from 68 to 20%. SEM and TEM observations indicated that 20 μm particles of MDMA powder changed into about 20 nm particles during the curing process, and the finer particles dispersed evenly in the EVM vulcanizates. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2379–2384, 2004

Key words: ethylene–vinyl acetate rubber (EVM); polymerization; reinforcement; structure; curing of polymers

INTRODUCTION

Metal salts of unsaturated carboxylic acids such as magnesium methacrylate (MDMA) and zinc methacrylate (ZDMA) were originally used as coagents for peroxide curing systems.[1,2] They not only increase the crosslinking efficiency in the curing process, but also increase the crosslink density of the vulcanizates. In recent years, the addition of α,β-unsaturated carboxylates to rubber is a new approach to achieve substantial reinforcement. There are many patents and reports about metal salts of unsaturated carboxylic acids to reinforce rubbers. For example, Zeon Chemicals[3] made a high-performance hydrogenated nitrile rubber (HNBR) vulcanizate with tensile strength higher than 55 MPa and elongation at break over 500%. Our previous research on the reinforcement of rubbers such as nitrile rubber (NBR), ethylene–propylene–diene terpolymer (EPDM), styrene–butadiene rubber (SBR), and ethylene–vinyl acetate rubber (EVM) with metal salts of unsaturated carboxylic acids also revealed that the resulting vulcanizates had excellent mechanical properties.[4–7]

When a peroxide was used as a curing agent, the metal salts of unsaturated carboxylic acids polymerized during vulcanization, including homopolymerization and graft copolymerization simultaneously, thus forming ionic crosslinks because of the graft copolymerization.[8–10] The mechanical properties of the vulcanizates are substantially influenced by the ionic crosslinks,[11] so the excellent mechanical properties of the vulcanizates reinforced by metal salts of unsaturated carboxylic acids are related to the reaction of the salts in rubbers during vulcanization. In addition, the structure of the vulcanizate also influences the mechanical properties of the vulcanizates. Saito et al.[12] characterized the structure of HNBR reinforced by ZDMA and found that 20- to 30-nm fine particles exist in the rubber matrix.

In this article, EVM compound filled with MDMA was cured by dicumyl peroxide (DCP). We focused our experiments on the determination of polymerization conversion of MDMA during the curing process of EVM compounds. The objective of this study was to relate the mechanical properties with the structure of EVM vulcanizates.

EXPERIMENTAL

Materials

The raw materials used in this study are shown in Table I.

Correspondence to: A. Du (aihuadu@hotmail.com).

TABLE I
Raw Materials

Material	Property	Source
Ethylene–vinyl acetate rubber (EVM)	Levaprene VP KA8857, 50 wt % of vinyl acetate	Bayer AG (Leverkusen, Germany)
Magnesium Methacrylate (MDMA)	Industrial grade	Xi'an Organic Chemicals (Xi'an, China)
Dicumyl peroxide (DCP)	Purity: 99.3%	Shanghai Gaoqiao Petroleum Co. (Shanghai, China)
High-abrasion furnace carbon black (HAF N330)	Industrial grade	Shanghai Carbot Chem. Co., Ltd. (Shanghai, China)
Rhenogran P-50	Industrial grade	Qingdao Rhein Chemie Co. (Qingdao, China)

Compounding and sample preparation

Mixtures of EVM and additives were prepared in the mixing chamber of a Haake rheometer (Bersdorff, Germany) at 50°C and a rotor speed of 32 rpm. All the samples were based on 100 parts by weight of EVM, and the filler loading varied from 10 to 70 phr. MDMA was first added to EVM and mixed for 4 min. After its dispersion DCP was added to the chamber and mixed for another 2 min. The whole compounding process lasted about 8 min. The compounds were then sheeted out on the two-roller mill. The compounds were press-cured to a 2-mm-thick sheet at 170°C for 10 min.

Measurement of mechanical properties

Tensile properties were measured with dumbbell-shape specimens (6 mm wide in cross section) according to ASTM D412. Tear strength was tested according to ASTM D624 using the unnotched 90° angle test piece. Both tensile and tear tests were performed on an Instron series IX 4465 material tester (Canton, MA) at a crosshead speed of 500 mm/min. Shore A hardness was determined using a handheld Shore A Durometer according to ASTM D2240. All tests were carried out at 23°C.

FTIR analysis

Infrared transmission spectra were obtained using an FTIR spectrometer (model Paragon 1000; Perkin Elmer Cetus Instruments, Norwalk, CT). The scanning range was from 4400 to 400 cm^{-1} with a resolution of 4 cm^{-1}. The EVM sample was prepared by directly casting its xylene solution onto a KBr disc, then heating under a heat lamp for about 10 min to drive off the xylene solvent. The MDMA powder sample was prepared by milling MDMA with KBr and compressed to a KBr disc for testing. The sample of MDMA-filled EVM compound was pressed to obtain a thin film at room temperature. The film was cured by compression molding at 170°C for 10 min for further testing. The

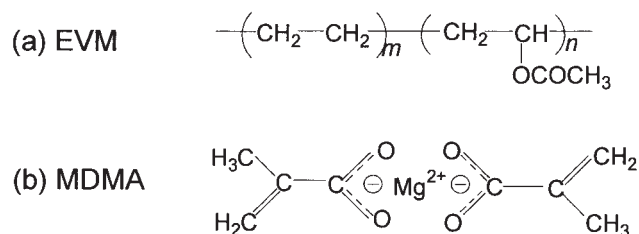chemical structure of EVM and MDMA for FTIR analysis are shown in Scheme 1.

Morphology observation

MDMA powder was coated with a thin gold layer and examined by Hitachi S-2150 scanning electron microscope (SEM; Hitachi, Osaka, Japan). The ultrathin films of samples for transmission electron microscope (TEM) testing were cut by microtome at about -100°C, then stained with OsO_4 and examined by a JEM-1230 TEM instrument (JEOL, Tokyo, Japan) with an accelerating voltage of 120 kV.

RESULTS AND DISCUSSION

Mechanical properties

Figure 1 shows the effects of MDMA and high-abrasion furnace carbon black (HAF) on the mechanical properties of EVM vulcanizates. The tensile strength increases with increasing amount of MDMA, and there is a maximum for the tensile strength when the MDMA content is 20 phr. The tensile strength is over 20 MPa in all cases as the MDMA content increases from 20 to 50 phr. The tensile strength of MDMA/EVM vulcanizates approaches that of HAF/EVM vulcanizates. With increasing content of fillers, the modulus and tear strength of the vulcanizates increase significantly. The tear strength of the vulcanize in-

Scheme 1 Chemical structure of EVM and MDMA for FTIR analysis.

(a)

(c)

(b)

(d)
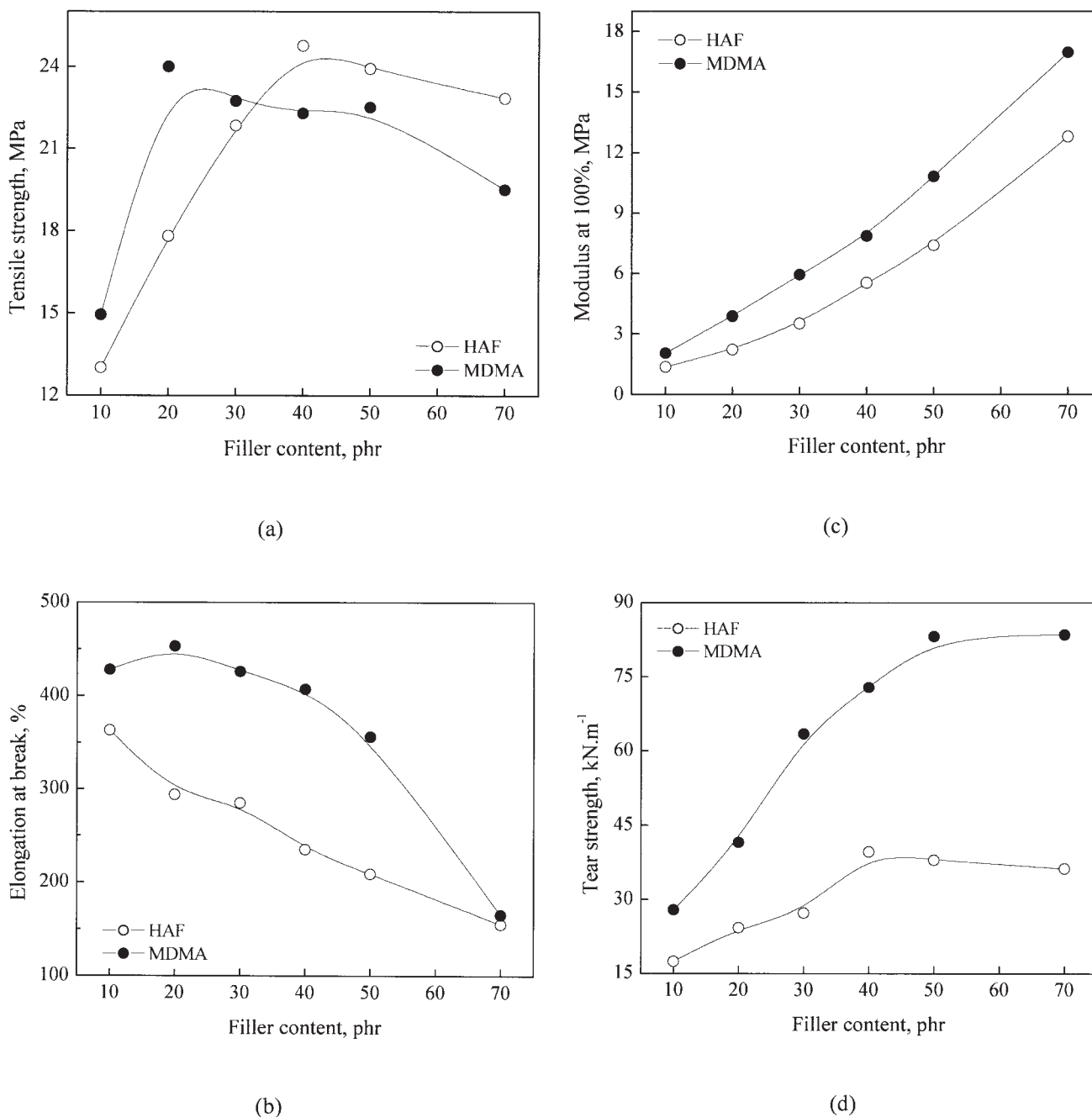
Figure 1 Effect of filler contents on the mechanical properties of EVM vulcanizates. Formulation: EVM 100; DCP 4; filler variable: (a) tensile strength, (b) elongation at break, (c) modulus at 100%, (d) tear strength.

creases by about 200% when the MDMA content increases from 10 to 70 phr. The elongation at break scarcely changes when the MDMA content is in the range of 10 to 30 phr, and decreases gradually thereafter (although it is still over 350% even when the MDMA content is 50 phr), whereas the elongation at break of HAF/EVM vulcanizates substantially decreases with increasing HAF content, and it is below 300% when the HAF content is 20 phr. It is obvious that the EVM vulcanizates reinforced by the two fillers have good mechanical properties. Compared with

HAF, MDMA is more effective for the reinforcement of EVM. It appears to be a unique ability of MDMA to maintain high elongation at break while increasing the modulus and tensile strength of the vulcanizates.

FTIR analysis

Figure 2 shows the FTIR spectra of EVM, MDMA, and their compound and vulcanizate. Curve (a) in Figure 2 is the spectrum of pure EVM gum with characteristic
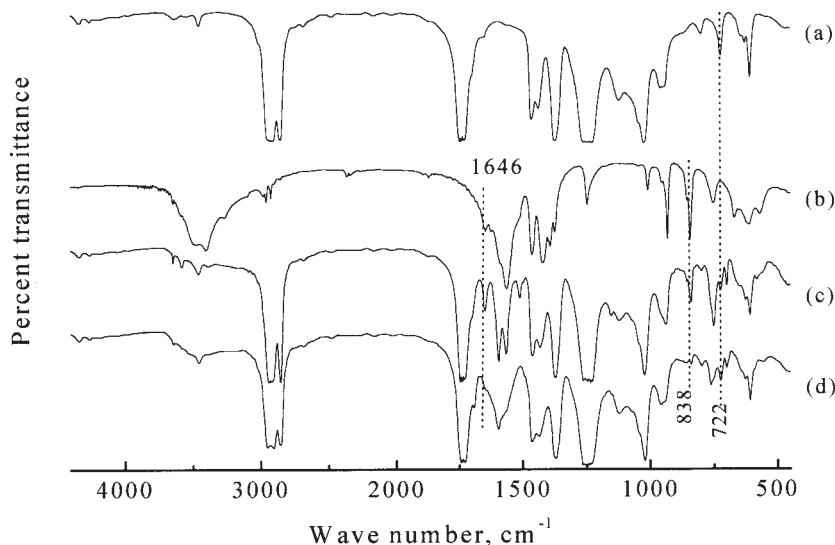
Figure 2 Transmission FTIR spectra of (a) EVM; (b) MDMA; (c) EVM/MDMA/DCP (100/10/4) compound; (d) EVM/MDMA/DCP vulcanizate.

absorbing peaks at 2925, 2865, 1465, and 1380 cm^{-1} generated from C—H stretching and deformation vibration of the methyl group. The characteristic peaks at 1740 and 1240 cm^{-1} are attributed to the stretching vibrations of C=O and C—O. The peak at 722 cm^{-1} is ascribed to the bending vibration of the methylene group. Curve (b) in Figure 2 is the spectrum of MDMA powder. The carboxylic anion has two strongly coupled carbon to oxygen bonds, which give rise to the separately asymmetric and symmetric stretching vibrations. The strong asymmetric stretching band is from 1610 to 1560 cm^{-1}. The weak and broad peaks at 1440 to 1360 cm^{-1} are attributed to the symmetric band.[13] The band at 838 cm^{-1} is ascribed to C—H out-of-plane bending vibration from =CH$_2$. Curves (c) and (d) in Figure 2 are the spectra of the EVM compound and vulcanizate, respectively. When the EVM is mixed with MDMA, the characteristic peaks of all the components in the compound do not change. Compared with the spectrum of the EVM compound, the spectrum of the vulcanizate has a significant change in the peak at 1646 cm^{-1}: the characteristic absorption band of C=C at 1646 cm^{-1} disappears completely. The relative intensity of =CH$_2$ absorption at 838 cm^{-1} obviously becomes weak, indicating that the carbon–carbon double bonds have reacted to a great extent in the process of vulcanization. So the polymerization of MDMA can be confirmed from the spectra shown in curve (d) of Figure 2.

MDMA polymerization conversion in EVM vulcanizates

According to Figure 2, the absorption band at 722 cm^{-1} is attributed to the bending vibration of the

methylene group in EVM. MDMA has an absorption band at 838 cm^{-1} attributed to the vibration of C—H on the C=C bond. The position of the two bands is not disturbed by other bands of the EVM compound and vulcanizate. The two bands can be used for quantitative analysis. When the MDMA content in EVM compounds increases, the intensity of the absorption band at 838 cm^{-1} increases, whereas the position of the band does not change. Saito et al.[8–10] investigated the polymerization behavior of ZDMA in the HNBR/ZDMA compound during the curing process and found that ZDMA underwent homopolymerization and graft copolymerization, and thus it is considered that a similar reaction also occurred on MDMA during the curing process of EVM compound by DCP. After the polymerization, the intensities of the absorption bands related to the C=C bonds decrease. The inten-
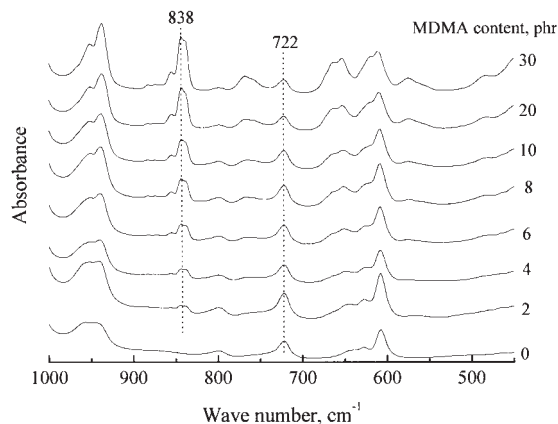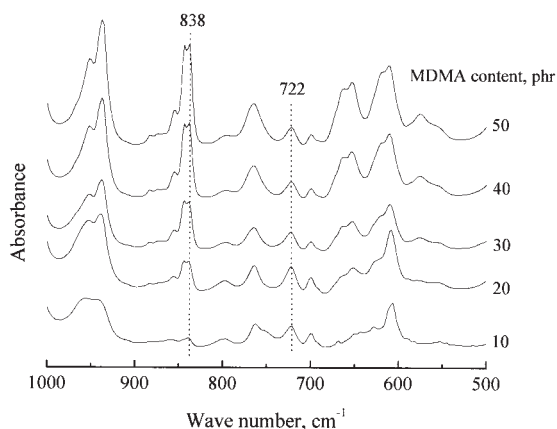

Figure 3 FTIR of EVM compounds with different MDMA contents. Formulation: EVM/MDMA = 100/variable.
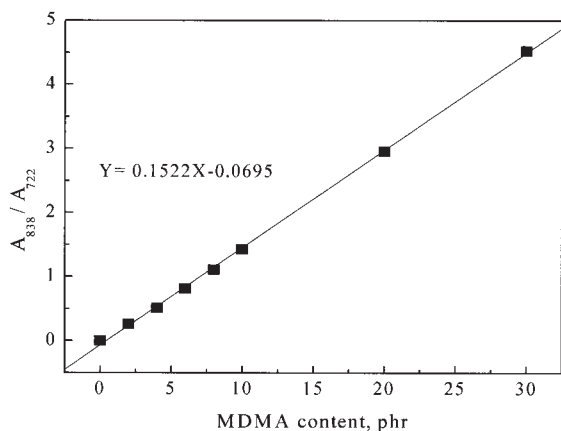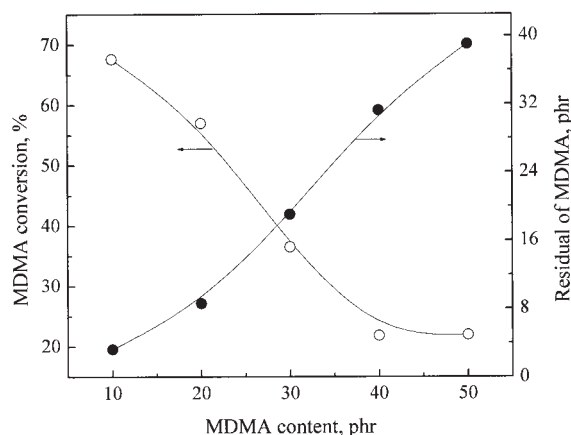
Figure 4 Calibration curve of the absorbance ratio at 838 to 722 cm^{-1} versus MDMA content in the EVM compound. Formulation: EVM/MDMA = 100/variable.

Figure 6 Residual MDMA and polymerization conversion MDMA in the EVM vulcanizates. Formulation: EVM/MDMA/DCP = 100/variable/4.

sity of the band at 838 cm^{-1}, attributed to the vibration of C—H on the C=C bond, decreased; thus the polymerization conversion of MDMA in EVM vulcanizate can be determined by using the absorption ratio of 838 and 722 cm^{-1} (A_{838}/A_{722}). A_{838} and A_{722} are the height of the characteristic absorption bands at 838 and 722 cm^{-1}, respectively.

The FTIR spectra of the EVM compounds with different MDMA content are shown in Figure 3. Because there is no DCP in EVM compounds and the films for FTIR testing were compression-molded at room temperature, polymerization of MDMA did not occur during the preparation process of the films. As seen from Figure 3, the intensity of the absorption band at 838 cm^{-1} increases significantly with increasing MDMA content. The calibration curve of A_{838}/A_{722} ratio versus the MDMA content was obtained from the data in Figure 3 and is shown in Figure 4. The A_{838}/A_{722} ratio increased in proportion to the MDMA content.

The EVM compounds filled with different MDMA content were compression-molded at 170°C for 10 min. The FTIR spectra of EVM vulcanizates filled with 10–50 phr MDMA are shown in Figure 5. The A_{838}/A_{722} ratios were calculated based on the FTIR spectra of Figure 5, and the contents of residual MDMA were calculated from the calibration curve shown in Figure 4. Then the polymerization conversions of MDMA were obtained. The residual MDMA content and the MDMA conversion versus MDMA content in EVM are shown in Figure 6. With increasing MDMA content, the polymerization conversion of MDMA decreased and the residual MDMA content increased. When the MDMA content was 10 phr, the polymerization conversion was 68%; when the MDMA content reached 50 phr, the conversion of MDMA was about 20%.

Morphology observation

The SEM micrograph of MDMA powder is shown in Figure 7. As seen from Figure 7, the shape of MDMA

Figure 5 FTIR spectra of EVM vulcanizates with different MDMA contents. Formulation: EVM/MDMA/DCP = 100/variable/4, vulcanized at 170°C for 10 min.
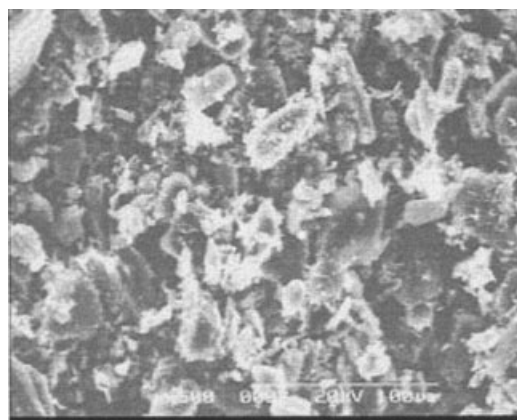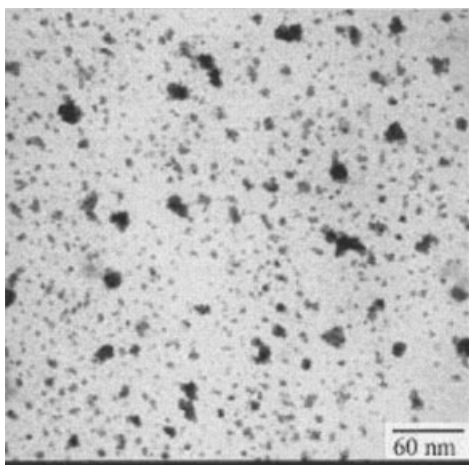

Figure 7 SEM micrograph of MDMA powder.

Figure 8 TEM micrograph of MDMA-reinforced EVM vulcanizate. Formulation: EVM 100; MDMA 30; DCP 4.0.

particle is irregular and the dimension is uneven. The average size of particles is about 20 μm.

Figure 8 is the TEM microphotograph of MDMA-reinforced EVM vulcanizate. The sample was stained with OsO_4. According to the principles of TEM image formation, it is known that the dark areas are the Mg-rich regions, and the bright areas are the rubber phase. As seen from Figure 8, there are many nanometer-scale particles dispersed in the rubber matrix and the average size of the particles is about 20 nm. The size of dispersed particles in EVM vulcanizate is much smaller than that of MDMA powder.

How did the micrometer particles of MDMA powder change into nanometer particles in the EVM vulcanizate? As well known, the melting point of MDMA is very high ($\sim$ 266°C)[14]; it does not melt under the curing condition (170°C) of EVM compound. It still exists as a solid in the EVM vulcanizate. Although the MDMA powder turned into finer particles under the action of the shear force during compounding, the pure shear action could not make MDMA powder turn into nanometer particles in the EVM vulcanizate. According to FTIR analysis, the polymerization of MDMA leads to the formation of finer particles in EVM vulcanizate. As mentioned above, an abundance of unreacted MDMA monomer still exists in the EVM

vulcanizate with increasing MDMA content, so it is considered that the nanometer particles dispersed in the vulcanizate were composed of unreacted MDMA powder and poly-MDMA.

CONCLUSIONS

MDMA has a good reinforcing effect on the EVM vulcanizate. Compared with HAF-reinforced EVM vulcanizate, the EVM vulcanizate reinforced with MDMA has high modulus, elongation at break, and tensile strength. The good mechanical properties are attributed to the reaction of MDMA in EVM during vulcanization by DCP. The particles in the EVM vulcanizate are nanometer scale and disperse evenly in the EVM vulcanizate. FTIR analysis confirmed the polymerization of MDMA in EVM vulcanizates during the curing process, and the polymerization conversions of MDMA powder decrease with increasing MDMA content in EVM vulcanizates.

References

1. The B. F. Goodrich Company, Br. Pat. 1091818, 1967.
2. Baitsch, J. R.; Lebanon, N. J. U.S. Pat. 3,438,933, 1969.
3. Klingender, R. C.; Oyama, M.; Saito, Y. Rubber World 1990, 202, 26.
4. Yuan, X. H.; Peng, Z. L.; Zhang, Y.; Zhang, Y. X. Polym Polym Compos 1999, 7, 431.
5. Peng, Z. L.; Yin, D. H.; Zhang, Y.; Zhang, Y. X. Kautsch Gummi Kunstst 2002, 55, 94.
6. Yin, D. H.; Zhang, Y.; Peng, Z. L.; Zhang, Y. X. J Appl Polym Sci 2002, 85, 2667.
7. Du, A. H.; Peng, Z. L.; Zhang, Y.; Zhang, Y. X. Polym Test 2002, 21, 889.
8. Nomura, A.; Takano, J.; Toyoda, A.; Saito, Y. Nippon Gomu Kyokaishi 1993, 66, 830.
9. Saito, Y.; Nishimura, K.; Asada, M.; Toyoda, A. Nippon Gomu Kyokaishi 1994, 67, 867.
10. Sato, T.; Fujino, A.; Hayashi, S.; Oyama, M. Rubber Chem Technol 2002, 75, 943.
11. Yuan, X. H.; Peng, Z. L.; Zhang, Y.; Zhang, Y. X. J Appl Polym Sci 2000, 77, 2740.
12. Nagata, N.; Sato, K.; Fujii, T.; Saito, Y. J Appl Polym Sci 1994, 53, 103.
13. Jing, X. Y.; Chen, S. D.; Me, E. Y. Manual of FTIR Application; Tianjin Technology Press: Tianjin, China, 1992; p. 92.
14. Peng, Z. L. Ph.D. Dissertation, Shanghai Jiao Tong University, 2001.