Reinforcement of EPDM by *In Situ* Prepared Zinc Dimethacrylate

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ABSTRACT: The mechanical properties and crosslink density of peroxide-cured ethylene-propylene-diene rubber (EPDM) reinforced with zinc dimethacrylate (ZDMA) were studied. ZDMA was *in situ* prepared in EPDM matrix through the neutralization reaction of zinc oxide (ZnO) and methacrylate acid (MAA). The effect of ZnO/MAA amount and molar ratio of ZnO/MAA on the properties of the EPDM vulcanizate were investigated in detail. The experimental results showed that EPDM can be greatly reinforced by ZDMA. The excess amount of ZnO considerably increases the tensile strength of the EPDM vulcanizate to reach as high as 37 MPa, whereas its elongation at break keeps over 350%. The process of *in situ* formation of ZDMA in the EPDM compound was verified by WAXD. Such vulcanizate contains both covalent crosslinks and ionic crosslinks. Crosslink density was determined by an equilibrium swelling method. Dependence of crosslink density on the amount and molar ratio of ZnO/MAA was studied and the extraordinary high tensile strength of the EPDM/ZDMA vulcanizate was related to ionic crosslink density. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1339–1345, 2002; DOI 10.1002/app.10112

Key words: zinc dimethacrylate; ethylene-propylene-diene rubber; *in situ* preparation; reinforcement; crosslink density

INTRODUCTION

In general, synthetic rubbers must be reinforced before their use as products. The conventional reinforcing agents are carbon black or silica that can enhance the mechanical and abrasion properties of cured rubber. Finding new methods to reinforce rubber is still an attractive subject in the field of rubber processing for the sake of new or special properties of rubber products.

Metal salts of unsaturated carboxylic acids are originally used as coagents for peroxide curing. They not only increase the crosslinking efficiency of the vulcanization process, but also increase the crosslink density as well.[1,2] In recent years, it was found that higher loading of zinc dimethacrylate (ZDMA) in peroxide-cured hydrogenated nitrile rubber (HNBR) results in a rubber with very high tensile strength and excellent abrasion resistance.[3] Metal salts of methacrylic acids were also used for curing natural rubber (NR) or nitrile rubber (NBR), which exhibit high modulus at low strain and good extensibility.[4] Chemical analysis on HNBR/ZDMA vulcanizates showed that *in situ* polymerization of ZDMA took place during the curing process, including both homopolymerization and graft copolymerization. Thus, such vulcanizates contain not only covalent crosslinks but also ionic ones.[5] In our previous publications, magnesium dimethacrylate and zinc dimethacrylate have effective reinforcing effects on NBR and

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Table I List of the Materials Used

Materials	Properties	Source
EPDM: EP35	43 wt % propylene; termonomer ENB, iodine number 26; ML(1+4) at 100°C, 83	Japan Synthetic Rubber Co. Ltd.
EPDM: EP98	Low propylene content; extender oil 75 phr; termonomer ENB, iodine number 15; ML(1+4) at 120°C, 66	Japan Synthetic Rubber Co. Ltd.
EPDM: Mitsui 4045	30 wt % propylene; termonomer ENB; iodine number 24; ML(1+4) at 100°C, 42	Mitsui Chemical Co. Ltd., Japan
EPDM: Keltan 4703	48 wt % ethylene; 9 wt % termonomer ENB; ML(1+4) at 125°C, 65	DSM Idemitsu Co. Ltd., Japan
EPDM: Keltan 4802	52 wt % ethylene; 4.5 wt % termonomer ENB: ML(1+4) at 125°C, 77	DSM Idemitsu Co. Ltd., Japan
Zinc oxide (ZnO)	Rubber grade, spec. grav. 5.6	Shanghai Jinghua Chemicals Co., China
Methacrylic acid (MAA)	Chemically pure	Shanghai Wulian Chemicals Co., China
Dicumyl peroxide (DCP)	Chemically pure	Shanghai Gaoqiao Petroleum Co., China
Zinc dimethacrylate (ZDMA)	Grey powder, 40 mesh	Xian Organic Chemicals, China

a conclusion was drawn that the tensile strength of the vulcanizate is related to the salt crosslink density.[6,7]

Many studies of the unsaturated salts reinforcing rubbers focused on polar rubbers, typically HNBR[3,8,9] and NBR.[7] However, few publications concern the properties of ethylene-propylene-diene rubber (EPDM) reinforced with *in situ* generated salts except several patents that mentioned ZDMA powder filled ethylene-propylene rubber (EPR) or EPDM.[10,11] In this work, we aim to investigate the mechanical properties of EPDM reinforced by *in situ* prepared ZDMA and the crosslink structure of the resulting peroxide-cured EPDM vulcanizates and to explore the application of *in situ* generated salts of unsaturated carboxylic acid as reinforcing agents in nonpolar elastomers.

EXPERIMENTAL

Materials

Details of the materials used are given in Table I.

EPDM and all the additives were mixed in the mixing chamber of a Hakke Rheometer RC 90 at 60°C at a rotor speed of 32 rpm. First, EPDM was allowed to plasticate for 3 min. Then, ZnO was added and mixed for 4 min, followed by the addition of methacrylic acid, and mixed for another 5 min. Finally, DCP was added and mixed for 2 min. After mixing, the compound was sheeted out in a two-roll mill, press-cured to a 2-mm-thickness sheet at 170°C for 15 min, and cut into specimens for measurements.

For ZDMA powder directly filled EPDM compound, ZDMA was mixed into EPDM on a 6-in. two-roll mill at room temperature, followed by addition of DCP. Vulcanization condition was the same as *in situ* prepared ZDMA samples. All the samples were based on JSR EP35 for measurements except for those specified.

Measurements

The stress–strain properties were measured with dumbbell specimens (6-mm width in cross section) according to Chinese National Standard GB528-82. Tear strength was measured on unnicked 90° angle test pieces according to Chinese National Standard GB530-81. The tests were performed on an Instron series IX 4465 material tester at a crosshead speed of 500 mm/min. Shore A hardness was determined as Chinese National Standard GB531-83.

The wide-angle X-ray diffraction (WAXD) studies of the samples were performed with a Rigaku X-ray diffractometer (type D/maxIIIA) by using nickel-filtered CuK_{α} radiation. Accelerating volt-

Table II The Samples for WAXD

Sample No.	1	2	3
EPDM	100	100	100
ZnO	13.8	13.8	13.8
MAA	—	29.3	29.3
DCP	—	—	1.0
Vulcanization (170°C × 15 min)	No	No	Yes

age and electric current were 35 kV and 25 mA, respectively. Samples for WAXD measurement were listed in Table II.

Determination of the Crosslink Density

The crosslink density was determined by equilibrium swelling. Samples were swollen in toluene at room temperature for 72 h and then removed from the solvent and the surface toluene was quickly blotted off with tissue paper. The samples were immediately weighed on an analytical balance to the tolerance of 1 mg and then dried in a vacuum oven for 36 h at 80°C to remove all the solvent and reweighed. The volume fraction of EPDM in the swollen gel, V_r, was calculated by the following equation:

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

where m_0 is the sample mass before swelling, m_1 and m_2 are sample masses before and after drying, ϕ is the mass fraction of rubber in the vulcanizate, α is the mass loss of the gum EPDM vulcanizate during swelling, and ρ_r and ρ_s are the rubber and solvent density, respectively.

The elastically active network chain density, υ_e, which was used to represent crosslink density, was then calculated by the well-known Flory–Rehner equation[12]:

$$\upsilon_e = -\frac{\ln(1-V_r) + V_r + \chi V_r^2}{V_s(V_r^{1/3} - V_r/2)} \quad (2)$$

where V_r is the volume fraction of the polymer in the vulcanizate swollen to equilibrium and V_s is the solvent molar volume (106.5 cm^3/mol for toluene). χ is the EPDM–toluene interaction parameter and is taken as 0.49,[13] because the presence of coagent in EPDM peroxide vulcanizates did not significantly influence the value of the χ parameter.[14]

As mentioned above, the vulcanizates contain both covalent and ionic crosslinks. To distinguish ionic crosslinks from covalent crosslinks, samples were swollen again in the mixture of toluene and chloroacetic acid (95 : 5 by volume)[15] for 120 h to destroy ionic crosslinks, swollen in toluene for 72 h and weighed, and then vacuum dried and reweighed. V_{r1} calculated by eq. (1) represents the extent of swelling after destroying ionic crosslinks. υ_{e1} calculated by eq. (2) represents the covalent crosslink density. υ_{e2} calculated by subtracting υ_{e1} from υ_e represents ionic crosslink density.

RESULTS AND DISCUSSION

Mechanical Properties

The effect of the ZnO/MAA amount on the mechanical properties of EPDM vulcanizates was first investigated in detail. Theoretically, 1 mol ZnO and 2 mol MAA will react to form ZDMA and water completely. Equivalent ZnO and MAA (ZnO/MAA molar ratio 0.5) was used to neutralize in the EPDM matrix during mixing. We estimated that ZnO and MAA *in situ* react to form zinc dimethacrylate at a high degree of conversion, which will be proven by WAXD later. The amount of ZDMA that could be obtained was used to represent the content of ZnO/MAA used. Moreover, mechanical properties of ZDMA powder-filled EPDM vulcanizate were also investigated for comparison. Figure 1(a) shows the tensile properties of peroxide-cured EPDM containing ZDMA at different amounts. The tensile strength depends on ZDMA content and shows a maximum at about 60 phr of ZDMA, and the maximum tensile strength is about 20 MPa, indicating the maximum reinforcing coefficient of ZDMA for EPDM is about 10. Elongation at break shows a gentle peak at 40 phr ZDMA. High loading of ZDMA means high-volume fraction of ZDMA, leading to a decrease in tensile strength. Nagata[8] also observed the same effect in HNBR/ZDMA vulcanizate. *In situ* prepared ZDMA has a better reinforcement effect than directly filled ZDMA on EPDM vulcanizates, especially at low ZDMA content.

As shown in Figure 1(b), tear strength of the vulcanizates increases rapidly and reaches a plateau with increasing ZDMA content. Hardness is proportional to the content of ZDMA. The method of *in situ* prepared ZDMA and directly filled

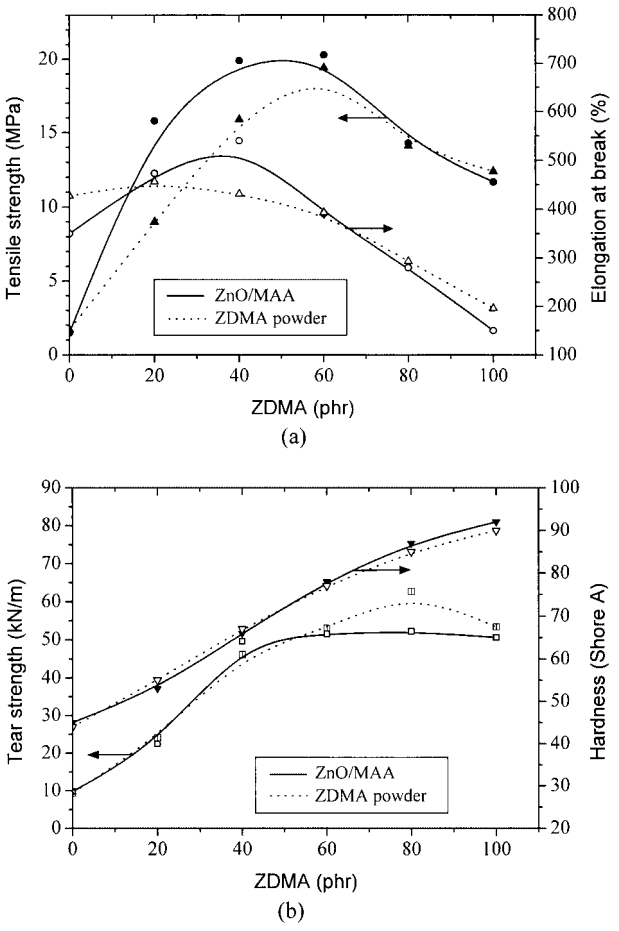

Figure 1. Mechanical properties of EPDM/ZDMA vulcanizates containing various amounts of *in situ* prepared ZDMA (ZnO/MAA molar ratio 0.5) or ZDMA powder. Formulation: EPDM 100; DCP 1; ZDMA variable.

ZDMA show almost the same effect on the tear strength and hardness of EPDM vulcanizates.

The vulcanizates have high elongation at break (over 350%) when ZDMA content is less than 60 phr. It is a characteristic property of metal salts of unsaturated carboxylic acids that they impart high hardness and strength, while retaining high elongation.[3]

Effect of ZnO/MAA Molar Ratio

The effect of the molar ratio of ZnO to MAA upon the mechanical properties is shown in Figure 2. The molar ratio of ZnO/MAA ranges from 0.4 to 1.0. ZnO was added to the compound by two different methods during mixing. One was to add ZnO into EPDM by one step, which was followed by the addition of MAA, even though the amount of ZnO was in excess. The other was to add equivalent ZnO/MAA to mix and neutralize in EPDM at first, followed by the addition of the excess amount of ZnO. As can be seen in Figure 2, the tensile strength increased greatly as the amount of ZnO increased for both cases, whereas higher tensile strength of vulcanizates was obtained through the second method that ZnO was added by two steps. Elongation at break, hardness, and tear strength had slight differences for the two methods. Hardness and tear strength increased significantly as ZnO content increased. Elongation at break decreased rapidly when the molar ratio of ZnO/MAA was over 0.8. In a word, the excess amount of ZnO is favorable for high performance of EPDM vulcanizate. The best mechanical properties of EPDM/ZDMA vulcanizate were obtained when the molar ratio of ZnO/MAA was from 0.65 to 0.8 and ZnO was added by the two-step method. Tensile strength and tear strength

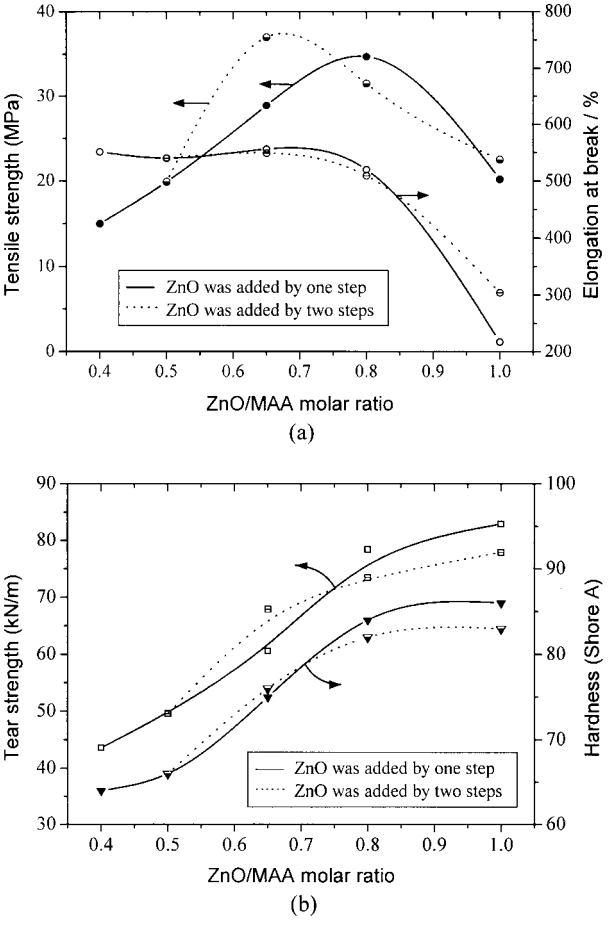

Figure 2. Effect of the molar ratio of ZnO to MAA and mixing step of ZnO on mechanical properties of EPDM/ZDMA vulcanizates. Formulation: EPDM 100; DCP 1; ZDMA (*in situ* prepared) 40.

reach as high as 37 MPa and 70 kN/m, respectively. Comparing the maximum tensile strength of 20 MPa of equivalent ZnO/MAA-reinforced EPDM vulcanizate, an excess amount of ZnO almost brings a double increase of tensile strength. It is proven that *in situ* preparation of ZDMA in EPDM matrix is an effective reinforcement method for EPDM, whereas the properties of EPDM conventionally reinforced with carbon black cannot reach such high values.

In Klingender's research of HNBR, better reinforcement was obtained when ZnO was in excess and the optimal weight ratio of ZnO to MAA was 0.75 (molar ratio is 0.8) to achieve a moderate increase in tensile strength.[16] In our previous research, the molar ratio of ZnO to MAA has a slight effect on the tensile strength of NBR.[7] In contrast, the excess amount of ZnO has considerable effect on tensile strength of EPDM vulcanizate.

The effect of *in situ* prepared ZDMA on reinforcement of several types of EPDM was also investigated. As shown in Figure 3, EPDM vulcanizates without any reinforcing agent show very low tensile strength. Even though different types of EPDM have different ethylene/propylene/diene ratios, all of them can be greatly reinforced by *in situ* prepared ZDMA. Especially, an excess amount of ZnO, which was mixed by two steps, brings a further increase in the tensile strength of EPDM/ZDMA vulcanizates.

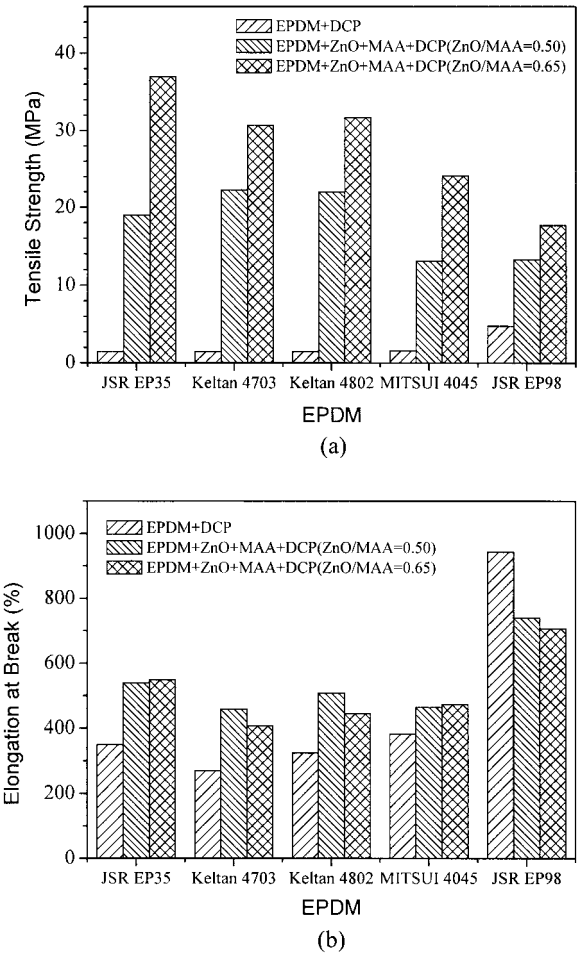

Figure 3. Mechanical properties of several types of EPDM reinforced with *in situ* prepared ZDMA. Formulation: EPDM 100; ZDMA 40; DCP 1.0.

X-ray Analysis

To prove the *in situ* formation of zinc dimethacrylate in EPDM, the WAXD scans of the samples (see Table II) were measured. As can be seen in Figure 4, sample 1 shows a typical crystalline pattern of ZnO crystal with characteristic peaks at $2\theta = 36.1°$, 31.5°, 56.4°, 62.6°, and 67.7°. After neutralizing ZnO with equivalent methacrylic acid (MAA) in EPDM matrix, Sample 2 shows characteristic peaks at $2\theta = 10.7°$, 9.6°, and 11.6°, which are attributed to ZDMA crystal,[7,8] and the peaks of ZnO almost disappeared. The result implies that ZnO and MAA indeed reacted to form ZDMA in EPDM during the mixing step. Sample 3 is a peroxide-cured EPDM/ZnO/MAA vulcanizate. WAXD measurement shows that no crystalline pattern is observed. It indicates the most of the ZDMA monomer polymerized or grafted to EPDM during the curing step. The results coincide with those of the WAXD analyses of the *in situ* formation of ZDMA in NBR as reported in our early publication,[7] indicating that the *in situ* formation of ZDMA is not affected by the polarity of the elastomer.

Crosslink Structure

Competitive reactions of peroxide-initiated crosslinking of polymer and polymerization of zinc salts may simultaneously proceed during vulcanization of the compound.[15] It was recognized that there are three types of ZDMA components in HNBR/ZDMA vulcanizate: homopolymer of poly-ZDMA, grafted poly-ZDMA, and residual monomeric ZDMA.[8] Thus, the vulcanizates contain both covalent crosslinks and ionic crosslinks. In addition, the term ionomer generally means a polymer containing less than 10 mol % salt groups, but for vulcanizates obtained in our work, the content of salt groups is very high. The crosslinking structure of

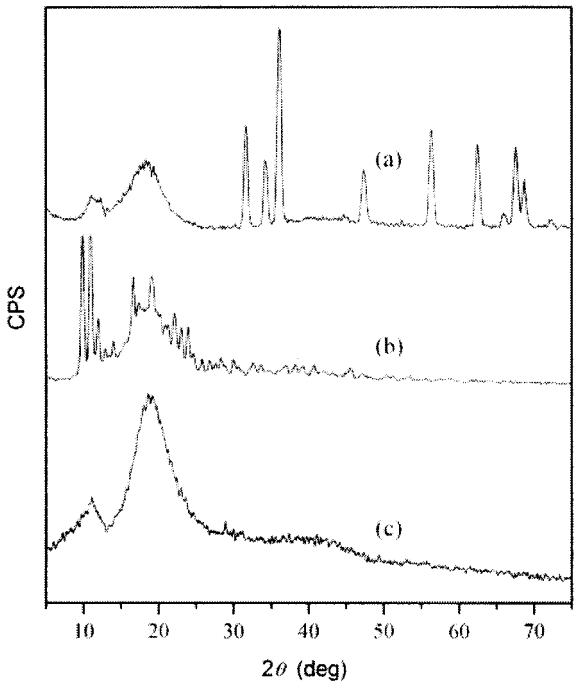

Figure 4. WAXD patterns of (a) sample 1, (b) sample 2, (c) sample 3.

the vulcanizate was measured by equilibrium swelling in toluene. The volume fraction of polymer in the swollen gel was measured twice, before and after treating with toluene–chloroacetic acid mixture. Poly-ZDMA was not considered as a component of rubber in the calculation because poly-ZDMA is insoluble in toluene. Then, the gross crosslink density and covalent crosslink density was calculated by the Flory–Rehner equation.

Figure 5 shows the crosslink density of EPDM

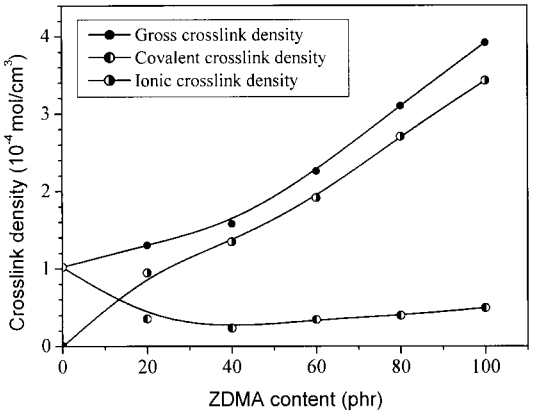

Figure 5. Effect of ZDMA content on crosslink density of EPDM/ZDMA vulcanizates. Formulation: EPDM 100; DCP 1; ZDMA (*in situ* prepared) variable.

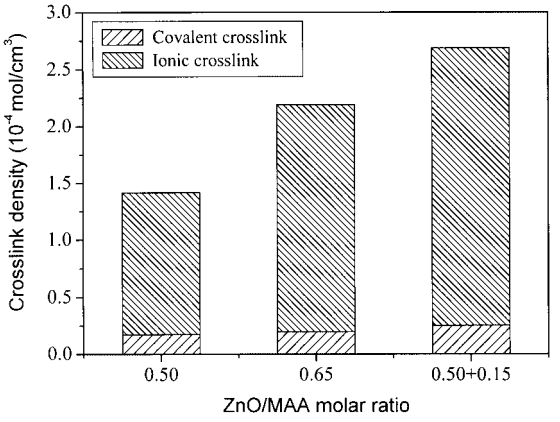

Figure 6. Dependence of the molar ratio of ZnO to MAA and mixing step of ZnO on crosslink density. Formulation: EPDM 100; DCP 1; ZDMA 40.

vulcanizate with different amounts of ZDMA. The gross crosslink density and ionic crosslink density increased greatly with increasing ZDMA content. The covalent crosslink density became lower than that of gum EPDM vulcanizate when the content of ZDMA was 20 phr, but the further increase of the content of ZDMA had little influence on the covalent crosslink density. It can be concluded that the addition of ZDMA into EPDM generates ionic crosslinks in the vulcanizates that arise from the graft polymerization of ZDMA onto the EPDM. Also, because of the polymerization of ZDMA, some free radicals should have been consumed, which leads to the decrease of the covalent crosslink density.

The effect of the ZnO/MAA molar ratio on crosslink structure was illustrated in Figure 6. An excess amount of ZnO led to an increase in the ionic crosslink density to a great extent, whereas the covalent crosslink density in the vulcanizate had little increase. The mechanism of ZnO improved ionic crosslink density needs further investigation and our preliminary study showed that an excess amount of ZnO reacted in the EPDM/ZDMA compound. As mentioned before, an excess amount of ZnO compared to MAA greatly increased the tensile strength of the vulcanizate. It can be concluded that ionic crosslink structure has a close relationship with the tensile strength. High density of ionic crosslinks is favorable for high performance of the vulcanizate.

CONCLUSION

In situ prepared ZDMA by ZnO and methacrylic acid in EPDM compound has a great reinforce-

ment effect on peroxide-cured EPDM. The molar ratio of ZnO to MAA has remarkable influence on the mechanical properties of the EPDM vulcanizates. The best performance can be achieved in the conditions that the ZnO/MAA molar ratio is from 0.65 to 0.8 and ZnO is mixed by two steps. WAXD analysis proved that ZnO and MAA indeed reacted to form ZDMA in EPDM *in situ* during the mixing step. Crosslink structure analysis shows the gross crosslink density was mainly increased by ionic crosslinks, which play an important role in the contribution of ZDMA to the high tensile strength of the EPDM/ZDMA vulcanizate.

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