

In Situ Preparation of Zinc Salts of Unsaturated Carboxylic Acids to Reinforce NBR

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Received 21 September 1999; accepted 28 October 1999

ABSTRACT: Through the neutralization reaction of zinc oxide (ZnO) and methacrylic acid (MAA) or acrylic acid (AA), zinc methacrylate (ZMA) or zinc acrylate (ZA) was *in situ* prepared in nitrile rubber (NBR). The mechanical properties and crosslinking structure of the resulting peroxide-cured NBR vulcanizates were studied. The results showed that ZnO/MAA (AA) had a great reinforcing effect for NBR, and their amounts and ratio played important roles in influencing the mechanical properties. Such vulcanizate contains both covalent crosslinks and salt crosslinks, and the change in the tensile strength of the vulcanizate was related to the variation of the salt crosslink density. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2740–2748, 2000

Key words: zinc oxide; methacrylic acid; acrylic acid; *in situ* preparation; reinforcement

INTRODUCTION

Crosslinking polybutadiene with zinc methacrylate (ZMA) results in a very hard rubber with high resilience, and the resulting product has been used for many years in forming rubber cores for two-piece golf balls.¹ Recently, in research conducted by Zeon Chemicals,² it was found that peroxide-cured hydrogenated nitrile rubber (HNBR) containing ZMA has very high tensile strength and excellent abrasion resistance. Similar or even better reinforcing effect can be obtained by substituting ZMA with zinc oxide (ZnO) and methacrylic acid (MAA),³ which were thought to react into ZMA *in situ* in the rubber.

We have reported on the reinforcement of ZMA and magnesium methacrylate (MgMA) for peroxide-cured nitrile rubber (NBR).^{4,5} It was found that, without any conventional reinforcing filler such as carbon black or silica, excellent mechanical properties of the vulcanizates can be ob-

tained. ZMA and MgMA impart high strength and hardness to NBR, while retaining high elongation at break. Similar results were also observed by Costin *et al.*⁶ previously. Their experiments showed that ZMA and zinc acrylate (ZA) increase the hardness and tensile strength of EPDM and NBR, while maintaining rather high elongation at break, but in their work, the amounts of ZMA and ZA were quite low, and carbon black was included in the formulation. The structural analysis in our previous work showed that NBR–ZMA (MgMA) vulcanizates contain not only covalent crosslinks but also salt crosslinks, and the latter have a close relation with the high strength of the vulcanizate. In this article, ZnO and MAA or AA were used to reinforce NBR, the mechanical properties and the crosslink-network structure were investigated, and the *in situ* formation of ZMA and ZA in NBR was also proved.

EXPERIMENTAL

Materials

Raw materials used in this study are shown in Table I.

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Journal of Applied Polymer Science, Vol. 77, 2740–2748 (2000)
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Table I Raw Materials

Material	Tradename & Characteristics	Manufacturer
NBR	JSR N220s, 36–41% of acrylonitrile	Japan Synthetic Rubber Co. Ltd.
ZMA	40 mesh	Xian Organic Chemicals, China
ZnO		Shanghai Jinghua Chemicals Co., China
MAA	chemical pure	Shanghai Wulian Chemicals Co., China
AA	chemical pure	Shanghai Wulian Chemicals Co., China
Dicumyl peroxide (DCP)		Shanghai Gaoqiao Petroleum Co., China

The mixture of NBR and additives was prepared in a HAKKE Rheometer at the rotor speed of 35 rpm and the initial temperature 45°C. ZnO was added first, after the dispersion of ZnO in NBR, MAA, or AA was added, followed by the addition of DCP. The compound was press-cured at 170°C for 10 min, and cut into specimens for measurement.

Measurements

Tensile tests were carried out according to the Chinese National Standard GB 528-82 in an Instron series IX material tester, with grip separation rate of 500 mm/min, using specimens of 2-mm thickness.

Shore A hardness was determined using a hand-held Shore A Durometer according to Chinese National Standard GB 531-83.

The crystal structures of ZnO, ZMA in NBR were studied through a wide-angle X-ray diffraction (WAXD), CuK α line nickel filter.

Crosslink density was determined by equilibrium swelling. Samples were swollen in propanone at room temperature for 7 days, and then vacuum dried. Assuming the mass loss of the rubber during swelling is the same for all the samples, the volume fraction of rubber in swollen gel Vr , which was used to represent the crosslink density of the vulcanizate, was determined by the following equation:

$$Vr = m_0 \cdot \phi \cdot (1 - \alpha) \cdot \rho_n^{-1} / [m_0 \cdot \phi \cdot (1 - \alpha) \cdot \rho_n^{-1} + (m_s - m_d) \cdot \rho_s^{-1}] \quad (1)$$

where m_0 is the sample mass before swelling, m_s and m_d are sample masses before and after drying, ϕ the mass fraction of rubber in the vulcanizate, α the mass loss of the gum NBR vulcanizate during swelling, and ρ_n and ρ_s the rubber and solvent density. As mentioned previously, vulcanizates contain both salt crosslinks and covalent

crosslinks, so it is significant to distinguish the salt crosslink density from covalent crosslink density. To determine covalent crosslink density, samples were swollen in propanone/hydrochloric acid mixed solvent for 2 days to destroy the salt bonds, and then swollen in propanone for 7 days. Vr_1 was calculated from eq. (1). Vr_2 , which is calculated by subtracting Vr_1 from Vr , was used to represent the salt crosslink density.

RESULTS AND DISCUSSION

In Situ Formation of Zinc Salts of Unsaturated Carboxylic Acids

To prove the *in situ* formation of zinc salts of unsaturated carboxylic acids, the X-ray diffraction scans of the following samples (see Table II) were measured. As can be seen in Figure 1(a) and (b), Samples 1 and 2 show typical crystalline patterns, which belong to ZnO and ZMA crystals, respectively. The characteristic peaks of ZnO crystal appear at approximately $2\theta = 36^\circ, 32^\circ, 56^\circ, 63^\circ,$ and 68° , while the characteristic peaks of ZMA appear at about $2\theta = 9.8^\circ, 10.9^\circ,$ and 7.3° . Figure 1(c) is the WAXD pattern of unvulcanized NBR–ZnO–MAA compound of Sample 3, in which the mol ratio of ZnO to MAA was 0.5. It shows almost the same pattern as that of Sample 2, and the characteristic peaks of ZnO cannot clearly be observed. This result implies that ZnO and MAA indeed reacted into ZMA in NBR during the mixing step. Figure 1(d) and (e) are WAXD patterns of Samples 4 and 5. For the ZnO/MAA-reinforced NBR vulcanizate, no crystalline pattern is observed because of the polymerization of ZMA during curing step, which will be discussed later. ZMA-reinforced NBR vulcanizate shows a weak ZMA crystalline pattern, which means that there was little residual ZMA in the vulcanizate.

Table II The Samples for WAXD

Sample No.	1	2	3	4	5
NBR	100	100	100	100	100
ZMA		30.0			30.0
ZnO	10.5		10.5	10.5	
MAA			22.0	22.0	
DCP			1.0	1.0	1.0
Vulcanization (170°C × 10 min)	No	No	No	Yes	Yes

Mechanical Properties

The effect of the ratio of ZnO to MAA on the mechanical properties was first investigated. The research of Zeon Chemicals showed that, in HNBR, better reinforcement was obtained when ZnO was in excess, and the optimal mol ratio of ZnO to MAA is about 0.6.³ Figure 2 shows the comparison between the tensile properties of vulcanizates in which the mol ratios of ZnO to MAA are 0.5 (equivalent) and 0.8 (ZnO excess), respectively. Suppose ZnO and MAA would totally react into ZMA for any ratio; the amount of ZMA that could be obtained was used to represent the content of ZnO/MAA used. As can be seen, the tensile strength of vulcanizates are quite similar for both cases, but the elongations at break have a big difference. When ZnO and MAA are equivalent, the elongation at break remains almost unchanged as the amount of ZnO/MAA increases, while for the case of ZnO in excess, with the increase of the content of ZnO/MAA the elongation decreases markedly. The comparison can also be made for different mol ratios of ZnO and MAA, which could produce the same amount of ZMA (25 phr) on the grounds of the above hypothesis, and the results are shown in Table III. As the ratio of ZnO to MAA increases, the 100% modulus increases and the elongation decreases, while the tensile strength has little variation. Based on the data above, it is evident that the ratio of ZnO to MAA has little effect on the tensile strength of the vulcanizate, but the excess of ZnO will decrease the elongation at break. It should be noted that similar reinforcement can also be obtained for the case of MAA in excess, but MAA is rather volatile and not very soluble in the rubber, which may lead to some processing difficulties, so the excess of MAA is better avoided.

For the 0.5 mol ratio of ZnO and MAA (AA), the relationships between ZnO/MAA (AA) contents and the mechanical properties of the vulcanizates are shown in Figure 3(a), (b), and (c). As can be

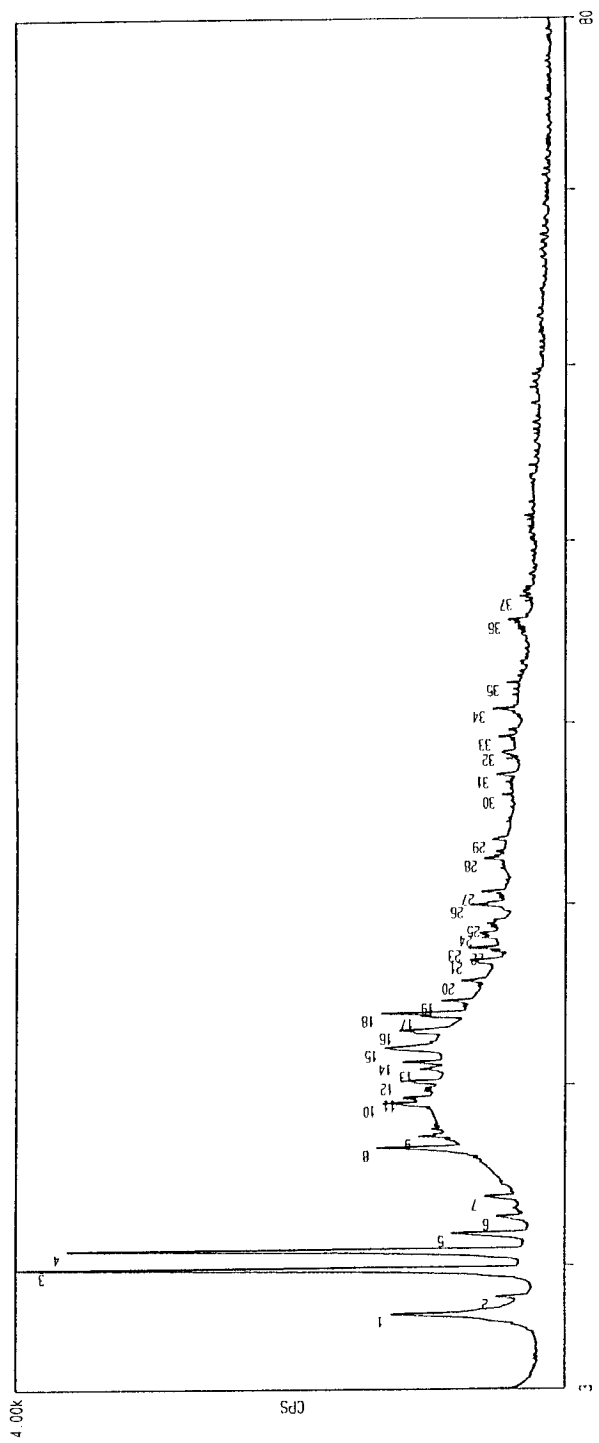
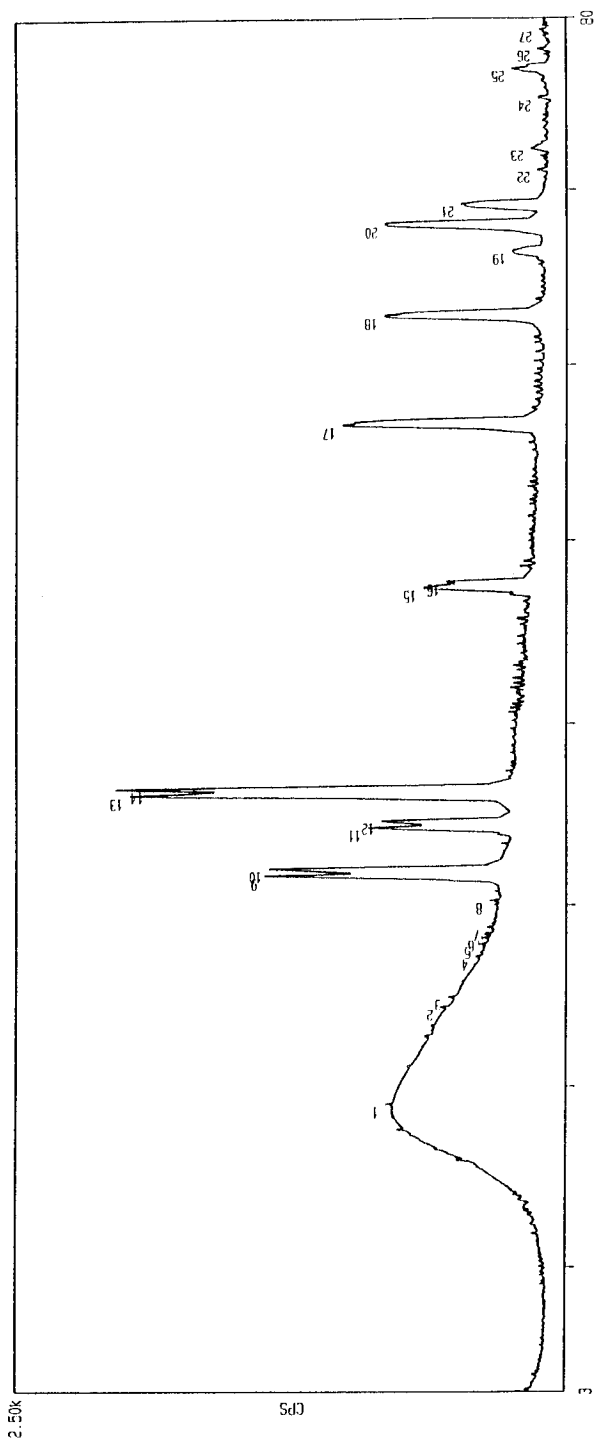
seen, with increasing content of ZnO/MAA (AA), the tensile strength, 100% modulus, and hardness of the vulcanizates increase dramatically. The maximum tensile strength is about 30 MPa, indicating the maximum reinforcing coefficient of ZnO/MAA (AA) for NBR is up to 10. It should be noted that there is no conventional reinforcing filler such as carbon black in the formulations. Compared with the method of directly adding ZMA into NBR,⁴ the *in situ* preparation method has achieved similar reinforcing effect.

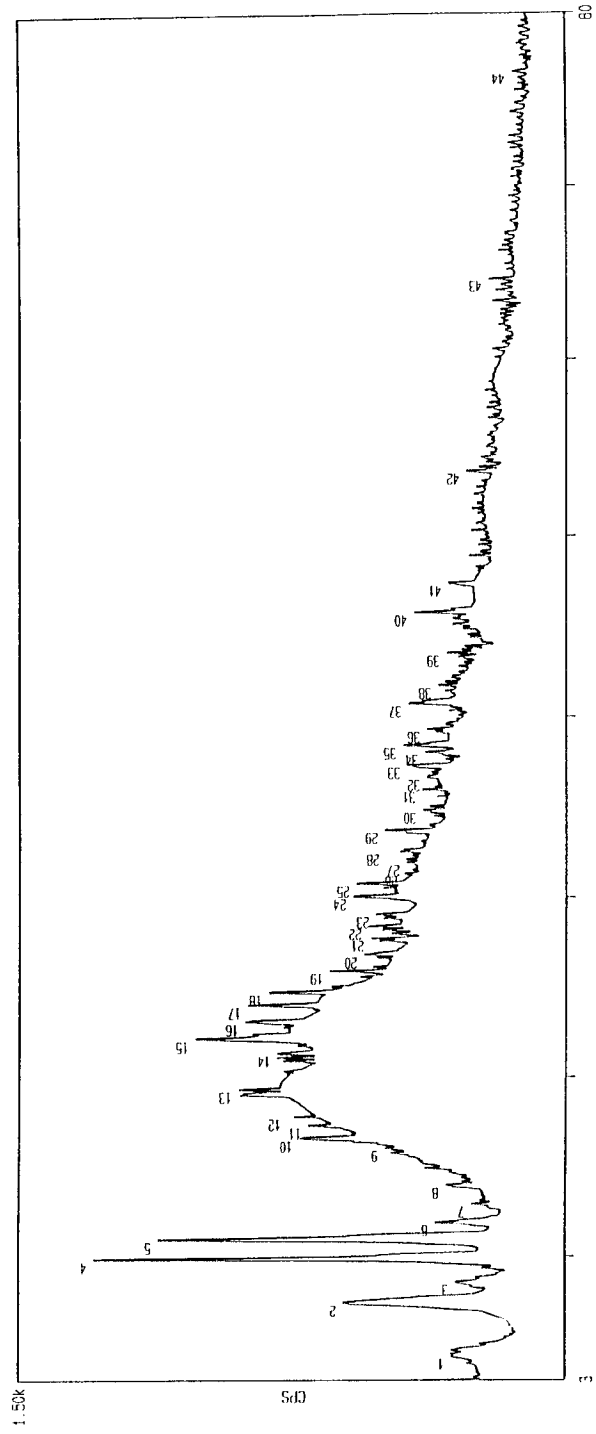
The data in Figure 3 also show that ZnO/MAA and ZnO/AA have similar tensile strength; however, ZnO/AA gives higher 100% modulus and hardness values while much lower elongation at break than ZnO/MAA. As the amount of ZnO/AA increases, the values of elongation at break of vulcanizates decrease rapidly to 100–200%, while ZnO/MAA gives the vulcanizate a very slow decrease of elongation at break.

The Crosslinking Structure

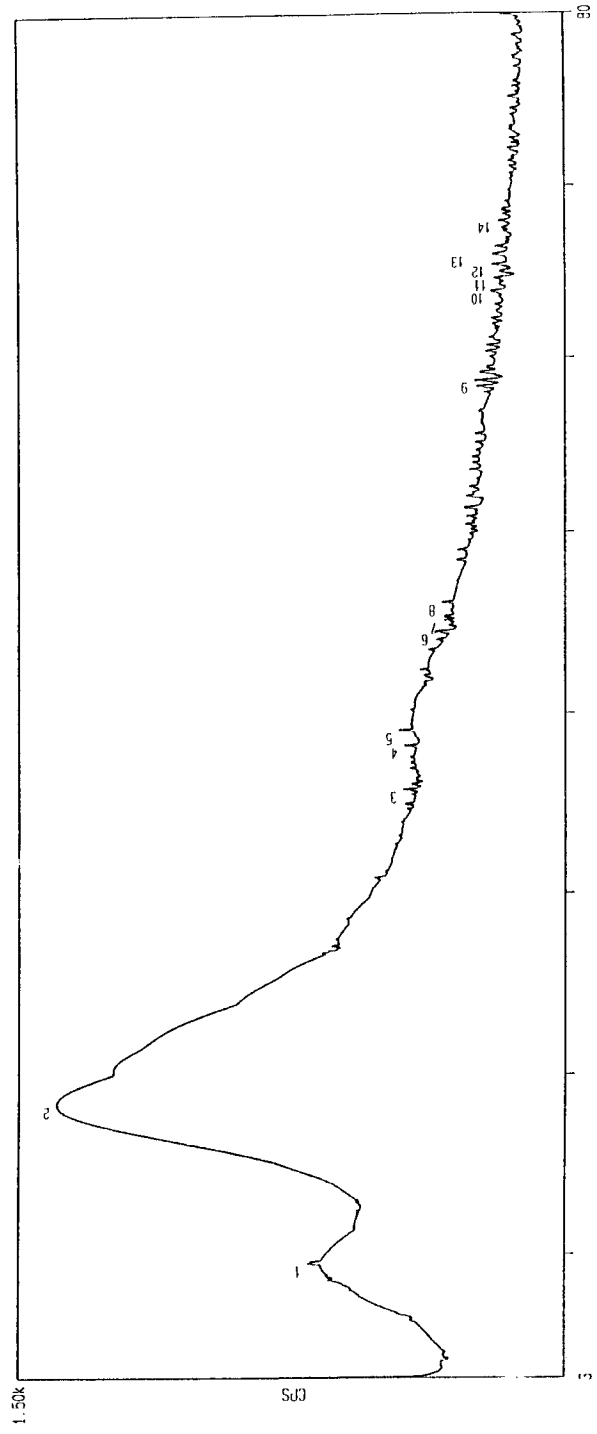
It is well recognized that, because of the existence of peroxide during the vulcanization step, the *in situ* polymerization of the metal salt of unsaturated carboxylic acid, including both homopolymerization and graft-polymerization, occurs at the same time that the curing reaction of rubber takes place.^{2,7,8} Our chemical analysis data⁹ showed that there are three types of MgMA components in the NBR/MgMA vulcanizate: homopolymer of poly-MgMA, grafted poly-MgMA, and residual monomeric MgMA. Similarly, in Nagata et al.'s work, the existence of homopolymer of poly-ZMA, and grafted poly-ZMA in the vulcanizate of HNBR/ZMA was also observed.⁸ Moreover, the poly-ZMA generated in rubber can aggregate into 20–30-nm fine particles in the vulcanizate, acting as rigid fillers.²

It is well known that vulcanizates containing salt crosslinks have good mechanical properties





(c)



(d)

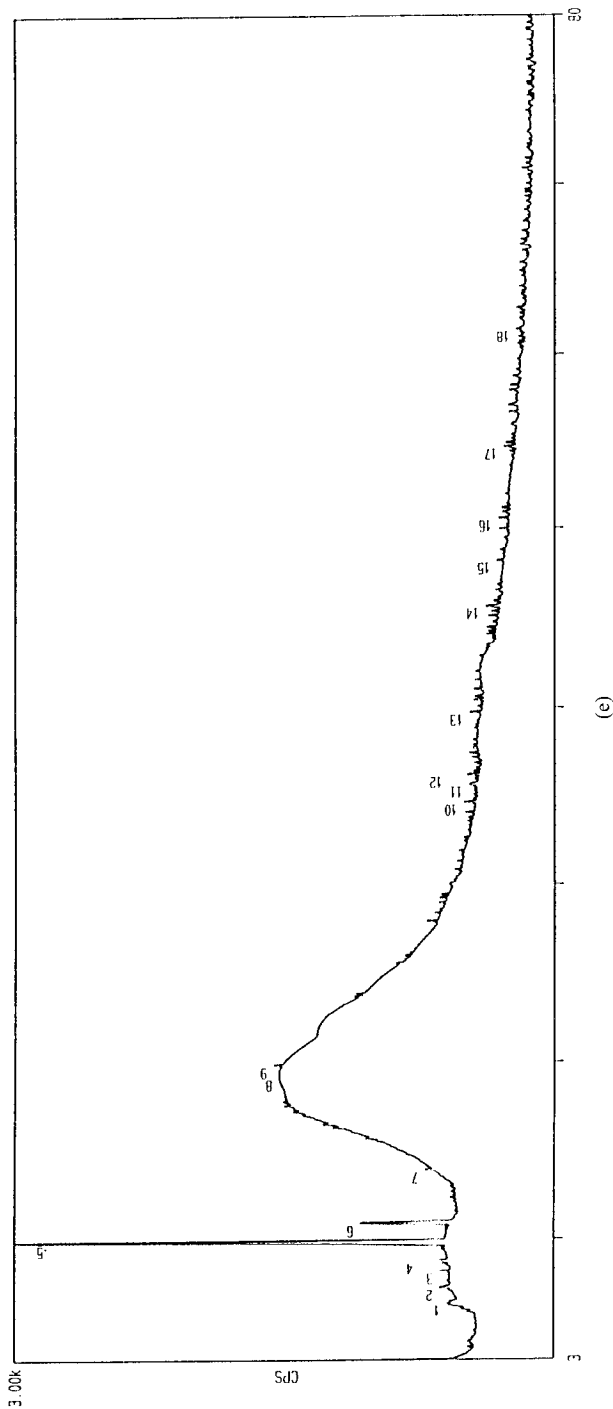


Figure 1 WAXD patterns of (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4, (e) sample 5.

without any reinforcing filler, and the reinforcing effect of salt linkages predominantly stems from energy dissipation.¹⁰⁻¹² Neutralizing carboxylated rubber with metal oxide is the most common way to form salt crosslinks, and the correspond-

ing rubber is called an ionic elastomer or ionomer, which has been extensively reported.¹² In this study, salt crosslinks were also obtained because of the graft copolymerization of poly-ZMA (ZA) onto NBR. Such vulcanizates differ from common ionic elastomers in that they contain not only salt crosslinks but also covalent crosslinks. In addition, the term "ionomer" generally means a polymer containing less than 10 mol % salt groups, but in vulcanizates obtained in this work the salt groups are much greater.

Crosslinking-network structure of the vulcanizate was measured by equilibrium swelling. The values of V_r (representing the whole crosslink density of the vulcanizate), V_{r_1} (representing covalent crosslink density of the vulcanizate), and V_{r_2} (representing salt crosslink density of the vulcanizate) were calculated according to eq. (1). Because neither poly-ZMA (ZA) nor poly-MAA (AA) is soluble in propanone, none of them was

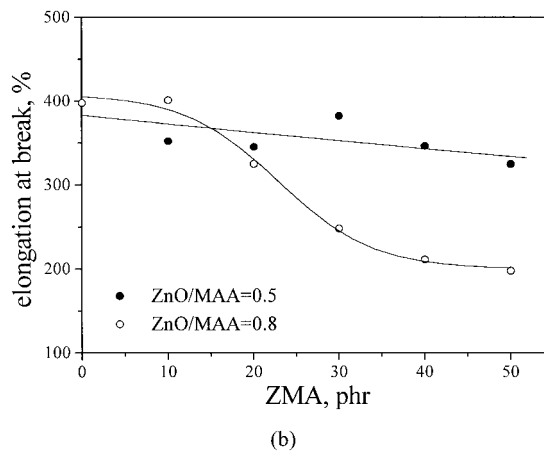
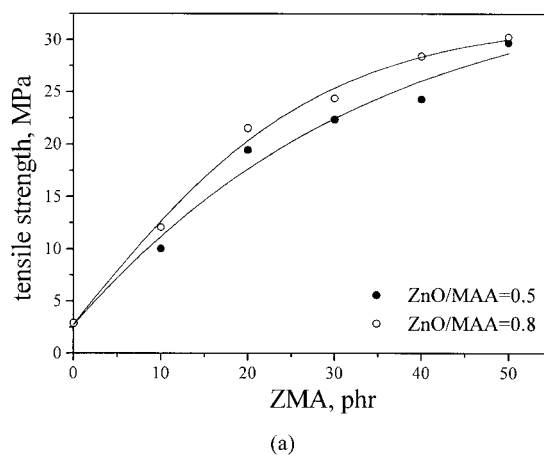


Figure 2 Effect of the mol ratio of ZnO to MAA on (a) the tensile strength, (b) elongation at break. NBR 100, DCP 1.0, ZnO/MAA variable, 170°C × 10 min.

Table III Effect of the Ratio of ZnO to MAA on the Tensile Properties

ZnO/MAA Ratio	0.25	0.33	0.5	0.75	1.0	1.5
Tensile strength, MPa	18.8	19.4	18.2	17.8	16.2	18.9
Elongation at break, %	491	465	365	321	310	304
100% modulus, MPa	3.45	3.63	4.04	5.73	6.64	6.93

Formulation: NBR 100, DCP 1.0, ZMA 25. 170°C × 10 min.

considered as a component of rubber in the calculation above. The results are shown in Figure 4. As can be seen, with the increase of the content of ZnO/MAA and ZnO/AA, the whole crosslink density of the vulcanizates increase, and ZnO/AA gives a higher Vr value. When ZnO/MAA is used, the covalent crosslink density decreases slowly as the ZnO/MAA content increases, but for ZnO/AA, because of the addition of ZnO/AA, the covalent crosslink density has a limited increase. For both

ZnO/MAA and ZnO/AA, the salt crosslink density increases with the increase of the content of ZnO/MAA (AA), and their Vr_2 values have little difference.

It can be concluded that the addition of ZnO/MAA (AA) generates salt crosslinks in NBR, the salt crosslink density increases with the increase of ZnO/MAA (AA) content, and the increase of the whole crosslink density of the vulcanizate mainly arise from the increase of the salt crosslink den-

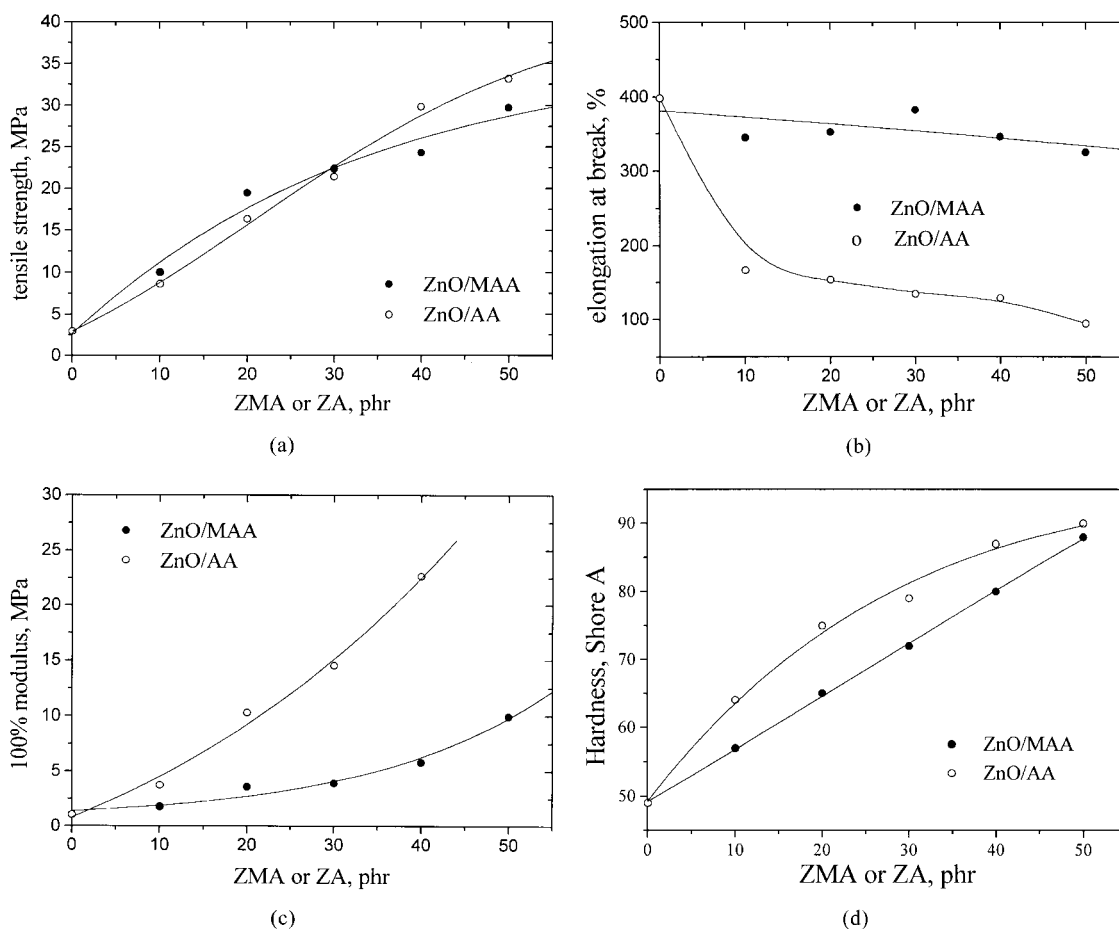


Figure 3 The content of ZnO/MAA and ZnO/AA vs. (a) the tensile strength, (b) elongation at break, (c) 100% modulus, (d) hardness. NBR 100, DCP 1.0, ZnO : MAA = 0.5, 170°C × 10 min.

sity. Figure 5 shows that there is a relationship between the salt crosslink density and the tensile strength, i.e., the tensile strength increases almost linearly with the increase of the salt crosslink density, which implies that they are very closely related. Our study on MgMA-reinforced NBR showed that, after swelling the vulcanizates in the propanone/HCl mixed solvent to destroy the salt crosslinks, the tensile strength values of vulcanizates decreased markedly to the level of gum NBR vulcanizates.⁵

In addition, the vulcanizates that contain ZnO/MAA and ZnO/AA have about the same level of salt crosslink density, and the higher whole crosslink density for ZnO/AA is obtained from its higher covalent crosslink density. This difference in crosslinking structure is probably the reason why the vulcanizates containing ZnO/AA have higher 100% modulus and hardness, while having a lower elongation at break than those containing

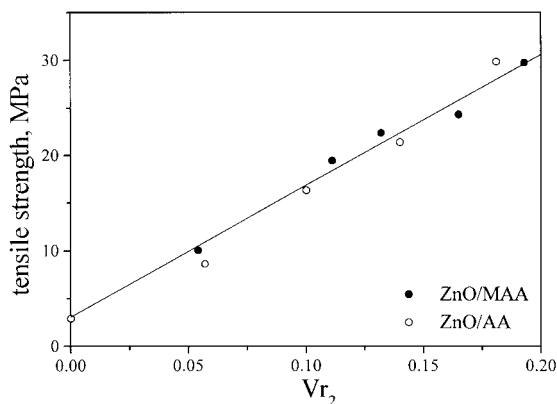


Figure 5 The relationship between the tensile strength and salt crosslink density.

ZnO/MAA. But why the covalent crosslinks increase for ZnO/AA, while decreasing for ZnO/MAA, should be related to the different radical activity of ZMA and ZA, needs further investigation.

CONCLUSIONS

1. WAXD analysis proved that ZnO and MAA indeed react into ZMA *in situ* in NBR during the mixing step.
2. *In situ* preparation of ZMA can achieve a similar excellent reinforcing effect on NBR as the direct addition of ZMA into the rubber.
3. The kind of unsaturated carboxylic acids greatly affects the mechanical properties, as well as the crosslinking structure of the vulcanizate. ZnO/AA shows greater reinforcing effect than ZnO/MAA, but leads to lower elongation at break. This may be attributed to the higher covalent crosslink density and whole crosslink density for ZnO/AA compared with ZnO/MAA.
4. The addition of ZnO/MAA (AA) into NBR produces a great amount of salt crosslinks in vulcanizates, and increases the whole crosslink density. The salt crosslinks generated in vulcanizate has a close relationship with the reinforcement of NBR.

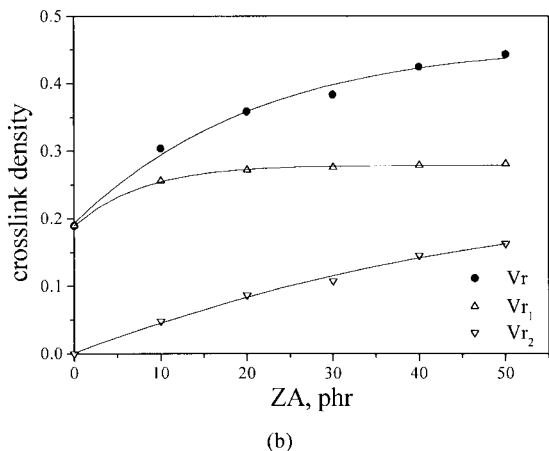
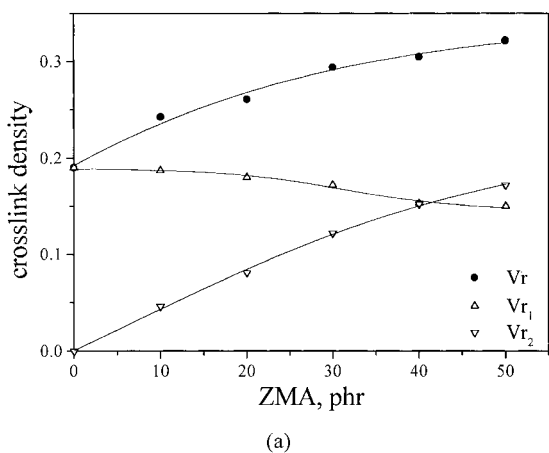


Figure 4 The crosslink density of (a) NBR-ZnO/MAA vulcanizates, (b) NBR-ZnO/AA vulcanizates. NBR 100, DCP 1.0, ZnO : MAA (AA) = 0.5, 170°C × 10 min.

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