

In Situ Preparation of Magnesium Methacrylate to Reinforce NBR

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ABSTRACT: Magnesium methacrylate (MDMA) was *in situ* prepared in nitrile rubber (NBR) by reacting magnesium hydroxide ($\text{Mg}(\text{OH})_2$) with methacrylic acid (MAA) during the mixing step. The formation of MDMA in NBR was proved by the wide-angle X-ray diffraction analysis (WAXD). The mechanical properties, crosslinking structure, and morphology of the resulting peroxide-cured NBR vulcanizates were studied. Results showed that $\text{Mg}(\text{OH})_2$ /MAA mixtures had a great reinforcing effect for NBR, and their amounts and ratio played important roles in influencing the ultimate properties. Both the covalent crosslink density and ionic crosslink density of the vulcanizates were measured. And the nano-composite morphology of such vulcanizates was also observed.
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INTRODUCTION

Metal salts of unsaturated carboxylic acids such as acrylic acid (AA) and methacrylic acid (MAA) have been found to act as effective reinforcing additives for elastomers. Crosslinking polybutadiene with zinc methacrylate (ZMA) results in a very hard rubber with high resilience, which has been used for many years in forming rubber cores for two-piece golf balls.¹ Metal salts of unsaturated carboxylic acids can also be added to EPDM,² SBR,³ NBR,^{2,4,5} and hydrogenated nitrile rubber (HNBR),^{6,7} to give the elastomers higher tensile strength, hardness, modulus, and tear strength. It was found that peroxide-cured HNBR containing ZMA shows tensile strength as high as 50 MPa and excellent abrasion resistance,⁷ and the tensile strength of magnesium methacrylate (MDMA)-reinforced NBR reaches the level of carbon black reinforcement.⁵

Metal salts of unsaturated carboxylic acids-reinforced rubbers exhibit special crosslinking structure and morphology. They contain not only covalent crosslinks but also ionic crosslinks.⁵ They are a kind of nano-composite, and fine particles of diameter 20–30 nm have been observed in elastomer matrix.⁷ It is believed that such structure is originated from the polymerization of metal salts in rubber.^{5,7,8} The polymerization of metal salts, including both homopolymerization and graft copolymerization, occurs during the vulcanization, and the ionic crosslinks are formed because of the graft polymerization of metal salts onto the rubber chains, while the poly-(metal salt) chains separate from the elastomer matrix and aggregate into nano-scaled fine particles.

In placing of directly adding metal salts into rubbers, it is also possible to prepare metal salts *in situ* by reacting metallic oxide or hydroxide with unsaturated carboxylic acids in rubbers.⁹ We have reported on the reinforcement of zinc oxide (ZnO) and MAA or AA on NBR,¹⁰ a similar reinforcing effect was obtained by substituting ZMA with ZnO and MAA. The present article reports

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Table I Raw Materials

Material	Trade Name and Characteristics	Manufacturer
NBR	JSR N220s, 36–41% of acrylonitrile	Japan Synthetic Rubber Co. Ltd.
MDMA	40 mesh	Xian Organic Chemicals, China
Mg(OH) ₂		Shandong Dihuan Superfine Powder Co., China
MAA	Chemical pure	Shanghai Wulian Chemicals Co., China
Dicumyl peroxide (DCP)		Shanghai Gaoqiao Petroleum Co., China

on the reinforcement effect of magnesium hydroxide (Mg(OH)₂) and MAA on NBR. The mechanical properties, crosslinking structure, and morphology of the reinforced NBR vulcanizates were investigated.

EXPERIMENTAL

Materials

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

The mixture of NBR and additives was prepared in a mixing chamber of the HAKKE Rheometer at the rotor speed of 35 rpm and the initial temperature 45°C. Mg(OH)₂ was added first, after the dispersion of Mg(OH)₂ in NBR, MAA 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 Mg(OH)₂, MDMA in NBR were studied through 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 mass fraction of rubber in the vulcanizate, α mass loss of gum NBR vulcanizate during swelling, and ρ_n and ρ_s rubber and solvent density. To distinguish the ionic crosslink density from covalent crosslink density, samples were swollen in propanone/hydrochloric acid mixed solvent for 2 days to destroy the ionic bonds, and then swollen in propanone for 7 days. Vr_1 , which was used to represent the covalent crosslink density, was calculated from eq. (1). And Vr_2 , which is calculated by subtracting Vr_1 from Vr , was used to represent the ionic crosslink density.

Small-angle X-ray scattering (SAXS) measurements were performed at a D/max-1200 SAXS Facility using Cu K α radiation with $\lambda = 1.54 \text{ \AA}$ and pinhole collimation of the incident beam, scanning scope 0.07° to 0.9°, speed of scanning 0.1°/min. All data were corrected for empty cell scattering and electronic background. For the resolution of the diffusion scattering spectrum, the method of successive tangents of minimum slope was applied.¹¹

RESULTS AND DISCUSSION

In Situ Formation of MDMA by Mg(OH)₂ and MAA

To prove the *in situ* formation of MDMA by Mg(OH)₂ and MAA, the X-ray diffraction scans of the following samples (see Table II) were measured. As can be seen in Figure 1(a) and (b), Sample 1

Table II The Samples for WAXD

Sample No.	1	2	3
NBR	100	100	100
MDMA		30.0	
Mg(OH) ₂	9		9
MAA			27
DCP			1.0
Vulcanization (170°C × 10 min)	No	No	No

and Sample 2 show typical crystalline patterns, which belong to Mg(OH)₂ and MDMA crystals, respectively. The characteristic peaks of Mg(OH)₂ crystal appear at approximately $2\theta = 18.5^\circ$, 37.9° , and 50.8° , while the characteristic peaks of MDMA appear at about $2\theta = 8.2$, and 9.1° . Figure 1(c) is the WAXD pattern of the unvulcanized NBR/Mg(OH)₂/MAA compound of Sample 3, in which the mol ratio of Mg(OH)₂ to MAA is 0.5. It shows almost the same pattern as that of Sample 2, and the characteristic peaks of Mg(OH)₂ cannot be clearly observed. This result implies that Mg(OH)₂ and MAA have indeed reacted into MDMA in NBR during the mixing step.

Mechanical Properties

Previous studies^{9,10} showed that the mechanical properties of the vulcanizates are greatly influenced by the ratio of metal oxide or hydroxide to unsaturated carboxylic acids. So the effect of the ratio of Mg(OH)₂ to MAA on the mechanical

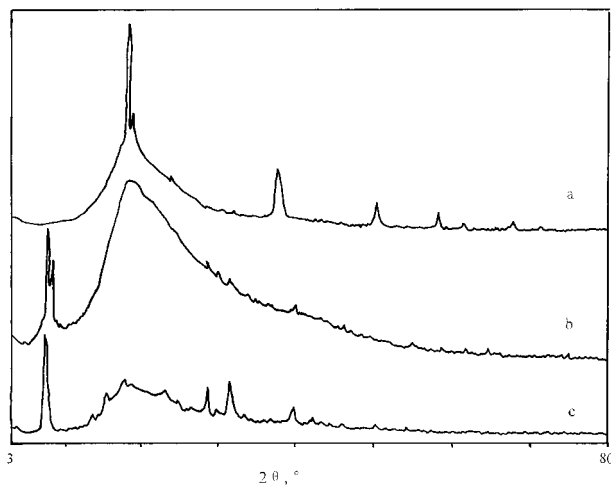


Figure 1 WAXD patterns of (a) sample 1, (b) sample 2, (c) sample 3.

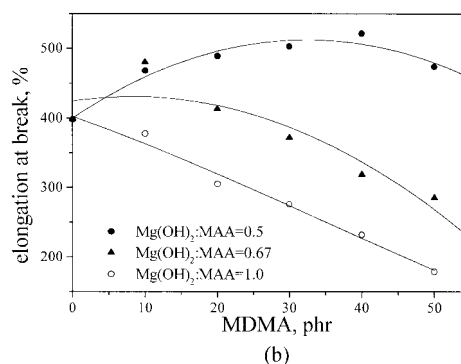
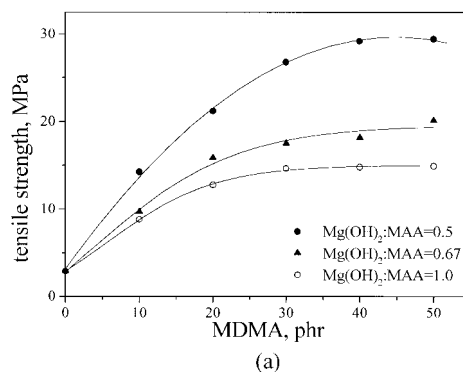


Figure 2 Effect of the mol ratio of Mg(OH)₂ to MAA on (a) the tensile strength, (b) elongation at break NBR 100, DCP 1.0, Mg(OH)₂/MAA variable, 170°C × 10 min.

properties was first investigated. Provided that Mg(OH)₂ and MAA would totally react into MDMA for any given Mg(OH)₂/MAA ratio, the amount of MDMA that could be obtained was used to represent the content of Mg(OH)₂/MAA used. Figure 2 shows the comparison between the tensile properties of vulcanizates in which the mol ratios of Mg(OH)₂ to MAA are 0.5 (equivalent), 0.67 (Mg(OH)₂ excess) and 1.0 (Mg(OH)₂ excess), respectively. As can be seen, with the increase of the ratio of Mg(OH)₂ to MAA, both the tensile strength and the elongation at break decrease markedly. When Mg(OH)₂ and MAA are equivalent, the elongation at break has a slight increase as the amount of Mg(OH)₂/MAA increases; while for the case of Mg(OH)₂ in excess, with the increase of the content of Mg(OH)₂/MAA the elongation decreases dramatically. In a word, the excess of Mg(OH)₂ will decrease both the tensile strength and the elongation at break, and the best tensile properties are obtained when Mg(OH)₂ and MAA are equivalent.

For the 0.5 mol ratio of Mg(OH)₂ and MAA, the relationships between Mg(OH)₂/MAA contents

Table III Mechanical Properties of Mg(OH)₂/MAA Reinforced NBR Vulcanizates

NBR, phr	100					
DCP, phr	1.0					
Mg(OH) ₂ , phr	0	3	6	9	12	15
MAA, phr	0	9	18	27	36	45
MDMA obtained, phr	0	10	20	30	40	50
170°C × 10 min						
Hardness, Shore A	49	56	60	64	68	73
Tensile strength, MPa	2.91	14.28	21.22	26.82	29.21	29.46
100% modulus, MPa	1.05	1.45	1.96	2.26	2.83	3.48
300% modulus, MPa	2.57	4.30	6.96	8.75	10.62	13.79
Elongation at break, %	398	468	489	503	522	474

and the mechanical properties of the vulcanizates are shown in Figure 2 and Table III. As can be seen, with increasing the content of Mg(OH)₂/MAA, the tensile strength, modulus, and hardness of the vulcanizates increase dramatically. The maximum tensile strength is about 30 MPa, indicating the maximum reinforcing coefficient of Mg(OH)₂/MAA 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 MDMA into NBR,⁵ the *in situ* preparation method has achieved similar reinforcing effect.

The Crosslinking Structure

As mentioned above, metal salts of unsaturated carboxylic acids reinforced vulcanizates contain both covalent crosslinks and ionic crosslinks. In this work, the crosslinking 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 ionic crosslink density of the vulcanizate) were calculated according to eq. (1). Because neither poly-MDMA nor poly-MAA is soluble in propanone, none of them was considered as a component of rubber in the calculation above.

The results are shown in Figure 3. As can be seen, when the content of MDMA is 10 phr, the whole crosslink density of vulcanizate becomes slightly lower than that of gum NBR vulcanizate, but with the further increase of the content of Mg(OH)₂/MAA, the whole crosslink density increase, and becomes higher than that of gum NBR vulcanizate. The values of the covalent crosslink density drops markedly on the addition of Mg(OH)₂/

MAA, but the change in Mg(OH)₂/MAA content has little effect on the covalent crosslink density, while the ionic crosslink density increases greatly as the content of Mg(OH)₂/MAA increases.

It can be concluded that the addition of Mg(OH)₂/MAA into NBR generates ionic crosslinks in vulcanizates, and the ionic crosslink density increases with the increase of Mg(OH)₂/MAA content. As mentioned above, such ionic crosslinks arise from the graft polymerization of MDMA onto the elastomer. Also, because of the polymerization of MDMA, some of the peroxide radicals should have been consumed, which thus decreases the covalent crosslink density. When the content of Mg(OH)₂/MAA was less than 10 phr, the amount of ionic crosslinks generated might have not compensated for the loss the covalent crosslinks, so the whole crosslink density decreases and is lower than that of gum NBR vulcanizate. With the further increase of the content of Mg(OH)₂/MAA and the further increase of the ionic crosslinks, the whole crosslinks increase and become higher than that of gum NBR vulcanizate.

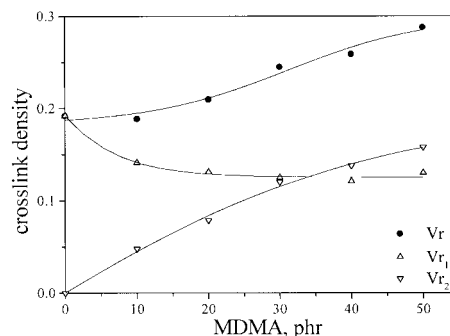


Figure 3 The crosslink density of Mg(OH)₂/MAA reinforced NBR NBR 100, DCP 1.0, Mg(OH)₂ : MAA = 0.5, 170°C × 10 min.

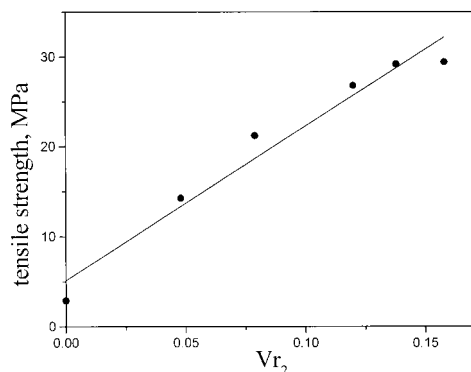


Figure 4 The relationship of the tensile strength and ionic crosslink density.

Figure 4 shows that there is a the 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 much closely related.

The Morphology

SAXS scattering diagrams are drawn in Figure 5, and marked diffused scattering within the range $2\theta = 0.07^\circ$ to 0.4° can be observed, which indicates that small discrete particles exist as disperse phases in the vulcanizates. And the relative intensity of the X-ray scattering rises with the increase of the content of $\text{Mg}(\text{OH})_2/\text{MAA}$, indicating that this scattering was caused by the addition of $\text{Mg}(\text{OH})_2/\text{MAA}$.

The results of SAXS calculations are reported in Table IV, indicating that there is a random distribution of fine particles of about 20 nm in diameter in the vulcanizates.

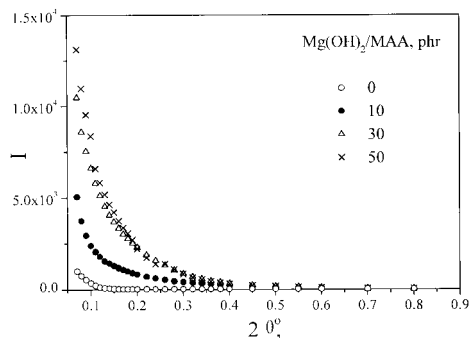


Figure 5 SAXS curves of $\text{Mg}(\text{OH})_2/\text{MAA}$ reinforced NBR.

Table IV Resolution of SAXS Diagrams of $\text{Mg}(\text{OH})_2/\text{MAA}$ Reinforced NBR

$\text{Mg}(\text{OH})_2/\text{MAA}$, phr	10	30	50
Radii 1, Å	70	61	65
Bulk percent, %	77.7	50.74	49.55
Radii 2, Å	147	149	147
Bulk percent, %	18.67	45.49	48.24
Radii 3, Å	339	340	338
Bulk percent, %	3.63	3.77	2.21
Mean radii, Å	94	112	111
Mean diameter, nm	18.8	22.4	22.2

The data above show that $\text{Mg}(\text{OH})_2/\text{MAA}$ reinforced NBR vulcanizate is a kind of nano-composite. Such nano-composite morphology has also been observed by Nagata⁷ through transmission electronic microscopy in ZMA/HNBR vulcanizates. It is believed that the fine particles are aggregates of segments of poly-metal salt chains.

Such particles are linked to the elastomer network by chemical bonds, which come into existence as a result of the graft copolymerization, and act as both high functionality crosslinks and active reinforcing fillers. This is thought of as the mechanism of the reinforcement of the metal salts of unsaturated carboxylic acids.

The above data show that for a given vulcanizate containing 10 phr $\text{Mg}(\text{OH})_2/\text{MAA}$, its whole crosslink density is lower than that of gum NBR vulcanizate, while its hardness and modulus are higher than those of gum NBR vulcanizate. It may also be explained by the nano-composite morphology of the vulcanizate. It is the existence of fine particles that gives the vulcanizate great hardness and modulus when its crosslink density is still low.

CONCLUSIONS

1. WAXD analysis proved that $\text{Mg}(\text{OH})_2$ and MAA could react into MDMA *in situ* in NBR during the mixing step.
2. *In situ* preparation of MDMA can achieve a similar excellent reinforcing effect on NBR as the direct addition of MDMA into the rubber. The ratio of $\text{Mg}(\text{OH})_2$ to MAA plays an important role in influencing the ultimate mechanical properties of the vulcanizates.
3. The addition of $\text{Mg}(\text{OH})_2/\text{MAA}$ into NBR produces great amount of ionic crosslinks

in NBR vulcanizates. The ionic crosslinks generated in vulcanizate have a close relationship with the reinforcement.

4. Mg (OH)₂/MAA reinforced NBR vulcanizate is a kind of nano-composite; there is a random distribution of fine particles of about 20 nm in diameter in the vulcanizates.

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