

Improved Mechanical Properties and Special Reinforcement Mechanism of Natural Rubber Reinforced by *In Situ* Polymerization of Zinc Dimethacrylate

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ABSTRACT: The peroxide-cured natural rubber (NR) was reinforced by *in situ* polymerization of zinc dimethacrylate (ZDMA). The experimental results showed NR could be greatly reinforced by ZDMA. The tensile strength and the hardness of NR/ZDMA composites increased with the content of ZDMA. The reinforcement mechanism was studied further. Both high crosslinking density provided by ionic crosslinking and strain-induced crystallization improved the mechanical properties. The crosslinking density was determined by an equilibrium swelling method and the crystallization index was measured by Wide-angle X-ray diffraction (WXR). When the amount

of ZDMA was high, the ability of strain-induced crystallization decreased, due to the strong interactions between the rubber phase and the hard poly-ZDMA (PZDMA) nanodispersions. At the moment, the increasing ionic crosslinking density made up for the effect of the drop of the strain-induced crystallization, and played a more important role in the reinforcement. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 920–928, 2010

Key words: natural rubber; zinc dimethacrylate; strain-induced crystallization; ionic crosslinking; reinforcement mechanism

INTRODUCTION

When peroxides are applied to cure elastomers, some coagents are used in the meantime to increase the crosslinking density and form a complex crosslinking network.¹ Metal salts of methacrylic acids, especially zinc dimethacrylate (ZDMA), are the most effective coagents, improving the tear strength, abrasion resistance, and high temperature performance of rubber.^{1–12} During curing process, ZDMA polymerized and reacted with rubber chains to form poly-ZDMA (PZDMA) and rubber-graft-PZDMA (nanophases).^{8,9} The rubbers prepared can be comparable to these filled with conventional fillers, such as carbon black and silica. Especially, they have higher modulus than those conventional reinforced rubbers at low extension.³ Lots of works have been carried out to study the reinforcement mechanism of rubber/ZDMA composites. Lu et al.⁹ studied the

mechanical properties of different rubbers reinforced by ZDMA to illuminate the relation between the mechanical properties and other factors, such as characteristic of the rubber matrix and the kind of ZDMA. Peng et al.^{11,13} suggested that ionic crosslinking had a close relationship with the tensile strength. However, the reinforcement mechanism is still unclear. For the reinforcement of NR, it is accepted that crosslinking and strain-induced crystallization during stretching are the two key factors. The rubber-filler interactions improve the crosslinking, enhancing the mechanical properties of rubber. The induced crystallites can reinforce the material as filler particles or additional crosslinking,^{14,15} bringing out good ultimate tensile property. But one wonders that which plays a more important role in the reinforcement, the strain-induced crystallization, or the crosslinking? This is need of further study, which is the focal point of this article.

In the article, the crosslinking density was determined by an equilibrium swelling method, while the strain-induced crystallization was studied by Wide-angle X-ray diffraction (WXR). The strain amplification effect and nature of strain-induced structures in NR/ZDMA composites were investigated in detail. Onset of strain-induced crystallization occurs much earlier compared with that of the conventional filled rubbers due to the more serious strain

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TABLE I
Formulations of the NR/ZDMA Composites

Ingredient	Amount (phr) ^a	
NR	100	100
DCP	2	2
ZDMA	Variable	–
Carbon black ^b	–	30

^a Parts by weight per hundred parts of rubber.

^b The sample with 30 phr carbon black is prepared for comparison with NR/ZDMA composites.

amplification effect resulting from the special microstructure of NR/ZDMA composites. During deformation, because of the increasing amount of short chains in dense crosslinking regions, the crystallization index rises. However, when the content of ZDMA exceeds 20 phr, it begins to drop, owing to the restriction of rubber chains by the interactions between NR phase and PZDMA nanophases. Under this condition, ionic crosslinking plays a dominant role in the reinforcement.

EXPERIMENTAL

Materials

NR (CSR-10) was supplied by Mengwang Rubber Corporation, China. ZDMA was purchased from Xian Organic Chemical Technology Plant, China. Dicumyl peroxide (DCP) was produced by Chengdu Kelong Chemical Technology Plant, China. Carbon black (N330) with average particle size of 30 nm was purchased from China Rubber Group Carbon Black Research & Design Institute, China.

Preparation of samples

At room temperature NR was plasticated on a laboratory two-roll mill. Then ZDMA/N330 and DCP were added. After mixing, the compound was cured at 155°C in an electrically heated hydraulic press for their optimal cure time (t_{90}) derived from curing curves. The formulation for preparation of rubber composites is shown in Table I.

Instruments and characterizations

Tensile tests were performed with dumbbell shaped samples according to the Chinese National Standard GB 528–82 on an Instron-5567 material tester. For the Mullins effect, samples were stretched to a predetermined elongation of 200% by cycling three times. For Payne effect, samples were measured at room temperature, at 1 Hz, in the dynamic strain range 0–7500 μm . Besides, Shore A hardness was measured according to the Chinese National Standard GB 531–83.

Crosslinking density was determined on the basis of the equilibrium swelling measurements by application of Flory–Rhener equation.¹⁶

$$-\left[\ln(1 - \Phi_r) + \Phi_r + \chi\Phi_r^2\right] = V_0 n \left[\Phi_r^{1/3} - \frac{\Phi_r}{2}\right] \quad (1)$$

where Φ_r is the volume fraction of polymer in the swollen mass, V_0 is the molar volume of the solvent (106.2 cm^3 for toluene), n is the number of active network chain segments per unit of volume (crosslinking density), χ is the Flory–Huggins polymer–solvent interaction term, which taken as 0.427 + 0.112 Φ_r^2 for crosslinked NR and toluene pair at 25 °C.¹⁷ The value of Φ_r is attained according to the corrected method reported by Valentín¹⁸

$$\Phi_r = \frac{\frac{w_2 - f_{\text{ins}}w_0}{\rho_2}}{\frac{w_2 - f_{\text{ins}}w_0}{\rho_2} + \frac{w_1 - w_2}{\rho_1}} \quad (2)$$

where w_0 represents the weight of the dry sample before the swelling, w_1 and w_2 are the weights of the swollen samples and the deswollen samples, respectively, ρ_1 and ρ_2 are the densities of the solvent and the polymer, f_{ins} is the weight fraction of insoluble components, namely, (insoluble components weight)/(recipe weight) (in our case PZDMA nanophases were taken as a non swellable component due to their strong polarity, so $f_{\text{ins}} = f_{\text{PZDMA}}$). Samples were swollen in toluene for 7 days at 25°C. Subsequently, w_1 was determined after gently wiping off the solvent on the sample surface with filter paper and w_2 was determined after drying at 80°C until constant weight was achieved. In this way, the whole volume fraction of polymer and crosslinking density can be calculated from eqs. (1) and (2). The crosslinking density contains the covalent crosslinking density, the crosslinking density caused by physical adsorption and the ionic crosslinking density. Samples were swollen in toluene/hydrochloric acid/ethanol mixed solvent for 3 days to destroy the ionic crosslinking, and then swollen in toluene for 7 days. Then the residual volume fraction of polymer and the residual crosslinking density (the covalent crosslinking density and the crosslinking density caused by physical adsorption) can be obtained. The ionic crosslinking density can be got by subtracting the residual crosslinking density from the whole crosslinking density.^{10,19}

Transmission electron microscopy (TEM) experiments were carried out on JEM 2010 transmission electron microscope (JEOL Co.) under an acceleration voltage of 200 kV. The specimens for TEM observations were prepared using a Leica ultramicrotome under cryogenic conditions with a diamond knife.

The strain-induced crystallization was tested by WXR D on a Philips diffractometer (Cu K α , 40kV,

TABLE II
Mechanical Properties of the NR/ZDMA Composites

	NR	NR/ZDMA (10phr)	NR/ZDMA (20phr)	NR/ZDMA (30phr)	NR/ZDMA (40phr)
Tensile strength (MPa)	6.55	12.40	17.90	18.99	20.17
Elongation at break (%)	510	306	266	241	230
Hardness	39	49	57	67	79
Initial modulus (MPa)	1.27	2.5	5.03	6.57	8.33

40mA). Samples were firstly stretched at the extension ratio of 3, fixed and then tested. The crystallization index was calculated according to the following equation^{20,21}

$$X_c = A_c / (A_c + A_a) \quad (3)$$

where X_c is the crystallization index, A_c represents the area under the crystal region of the X-ray diffraction patterns, and A_a represents the area under the amorphous region of the patterns.

RESULTS AND DISCUSSION

Improved mechanical properties

The effect of ZDMA content on the mechanical properties of the NR vulcanizates was investigated. As showed in Table II. Tensile strength increases with the content of ZDMA. When the amount of ZDMA is 40 phr, the tensile strength reaches 20.17 MPa, nearly three times of that of the gum vulcanizate, whose tensile strength is about 6.55 MPa. It is indicated that the reinforcing effect of *in situ* polymerization of ZDMA is obvious. Table II also shows the results of hardness with the increment of ZDMA content. Hardness is essentially a measure of modulus.²² So the increasing hardness of the composites reveals the rise of modulus, indicating the great reinforcing effect of ZDMA.

Without doubt, the great reinforcing effect has close relations with the special structure of NR/ZDMA composites. To reveal features of the networks under extension further, stress-strain curves were transformed according to the Mooney-Rivlin equation,²³ as shown in Figure 1

$$\sigma^* = \sigma / (\alpha - \alpha^{-2}) = 2C_1 + 2C_2\alpha^{-1} \quad (4)$$

where σ denotes the nominal stress, σ^* is the reduced stress, α is the extension ratio, and $2C_1$ and $2C_2$ are constants independent of α .

Onset of crystallization and serious strain amplification effect

An unfilled elastomer that cannot undergo strain-induced crystallization exhibits an almost constant

value of the reduced stress at increasing deformations. When compounded with reinforcing fillers, the elastomer displays upturns in the modulus attributed to the limited chain extensibility of short chains bridging neighboring filler particles. However, the unfilled NR also displays an abrupt increase in the reduced stress at large deformations (Fig. 1), due to strain-induced crystallization, which occurs during stretching because of the very uniform microstructure of rubber chains.^{14,24} When filled with fillers, rubber exhibits upturn at smaller deformations. In fact, short chains connecting neighboring filler particles can crystallize when they are extended at the limited chain extensibility. Trabelsi et al.²⁵ and Rault et al.²⁶ discovered that the strain at the onset of crystallization of NR filled with carbon black was smaller than pure NR, owing to the strain amplification effect.^{23,27,28} When rubbers are reinforced by ZDMA, some phenomenon can be found in Figure 1. Firstly, The reduced stress of NR filled with ZDMA decreases in small deformation during stretching, attributed to Payne effect.^{29,30} This phenomenon will be investigated later. Secondly, the onset extension ratio of upturn (α'') decreases with the increment of ZDMA content. In the meantime, the reduction extent of α'' is much larger than NR filled with carbon black.²⁷ The values of α'' are listed

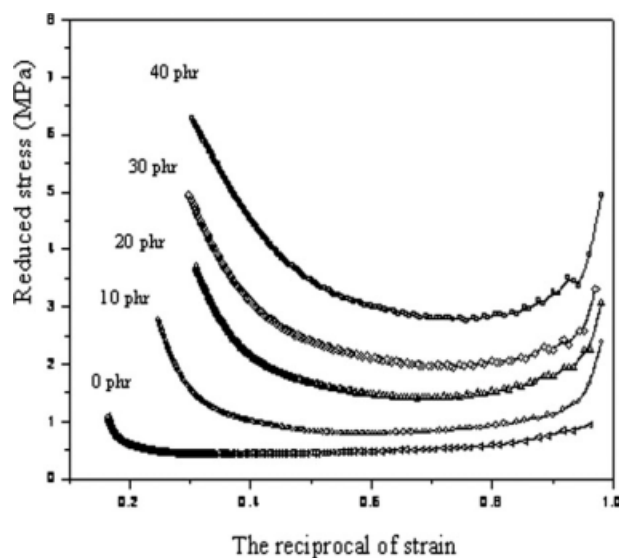


Figure 1 Mooney-Rivlin plots for NR/ZDMA composites.

TABLE III
Onset Extension Ratio of Upturn for Unfilled and Filled NR Samples

Sample	Volume fraction of filler		Onset extension ratio of upturn		
	φ	φ_e	α''	$\alpha_e''(\varphi)$	$\alpha_e''(\varphi_e)$
NR	–	–	3.33	3.33	3.33
NR/10phr ZDMA	0.0498	0.1399	1.80	2.26	2.70
NR/20phr ZDMA	0.0954	0.3767	1.50	1.92	2.80
NR/30phr ZDMA	0.1417	0.5226	1.40	1.84	3.10
NR/40phr ZDMA	0.1994	0.5979	1.36	1.87	3.31
NR/40phr Carbon black ^a	–	–	2.8	–	–
NR/60phr Carbon black ^a	–	–	2.7	–	–

^a The data were got from the literature 27.

in Table III. It is also found that the tensile stress at 100% and 200% elongation of NR/ZDMA composites is bigger than that of rubbers filled with carbon black, as shown in Table IV. The upturn of the reduced stress is attributed to the onset of crystallization for NR.^{14,24} Therefore, the strain-induced crystallization of NR/ZDMA composites occurs earlier. For filled rubbers, strain amplification effect happens. The effective extension ratio of the rubber portion is larger than the macroscopic extension ratio, due to the presence of hard filler particles, changing the stress field, increasing the local strain of the rubber chains and leading to local heterogeneities.²⁵ The expression of strain amplification is given as follows^{28,31,32}

$$\alpha_e = \frac{\alpha - \varphi^{1/3}}{1 - \varphi^{1/3}} \quad (5)$$

where α_e is the effective extension ratio, φ is the volume fraction of filler. The density of PZDMA attained by pycnometer method is 1.5376 g cm⁻³.

When φ was used to calculate the effective onset extension ratio of upturn ($\alpha_e''(\varphi)$) of the filled rubbers, it was found that the results obtained were much smaller than α'' of the unfilled rubber, as shown in Table III. Compared to the conventional fillers, such as carbon black and silica, the nanodispersed PZDMA phase has higher specific surface area, making it have more chance to interact with rubber phase. As shown in Figure 2, in which the domain size of PZDMA nanophases (dark phase) is about 10–20 nm. In addition, much ionic crosslinking (Fig. 3) exists. The ionic crosslinking is caused by the ion multiplets consisting in PZDMA.^{19,33} They are strong rubber-PZDMA interactions in essence. And many grafted PZDMA molecules exist in the interface of NR phase and ungrafted PZDMA phase, largely improving the interactions between NR and PZDMA, revealed in our other study.¹⁹ So the strain amplification effect is more serious and φ used can not exactly reveal the intensive influence of PZDMA

nanophases on local deformation of the rubber phase. Then the volume fraction of PZDMA in eq. (5) must be modified by the effective volume fraction of filler (φ_e).

Table II shows the initial modulus (E_i) of the filled rubbers is obviously larger than that of the pure rubber. The values of E_i were determined from the slope of the stress vs. strain curves in the vicinity of $\sigma = \alpha = 0$. Generally speaking, the increase in stiffness is attributed to the hydrodynamic effect causing by the presence of rigid particles and the improvement of the crosslinking density coming from the polymer–filler interactions.^{28,31}

The Guth and Gold equation is usually used to describe the filler reinforcement quantitatively^{34,35}

$$E = E_0(1 + 2.5\varphi + 14.1\varphi^2) \quad (6)$$

where E and E_0 are the modulus of the filled rubbers and the rubber matrix, respectively. The modulus used in the article is the initial modulus.

Equation (6) was used to calculate φ_e , at which φ was replaced by φ_e . The results are also shown in Table III. Subsequently, φ_e replaces φ in eq. (5), and the effective onset extension ratio of upturn modified ($\alpha_e''(\varphi_e)$) was obtained finally (Table III). The values of $\alpha_e''(\varphi_e)$ are closer to α'' of the unfilled rubber, and the deviation of $\alpha_e''(\varphi_e)$ calculated can be due to the experiment error for the samples used in this article.

TABLE IV
Tensile Stress at 100 and 200% Elongation

Sample	Tensile stress at 100% elongation (MPa)	Tensile stress at 200% elongation (MPa)
NR	0.67	1.09
NR/ZDMA (10phr)	1.55	3.84
NR/ZDMA (20phr)	2.94	9.12
NR/ZDMA (30phr)	4.42	13.0
NR/ZDMA (40phr)	6.01	16.27
NR/N330 (40phr)	1.40	4.42

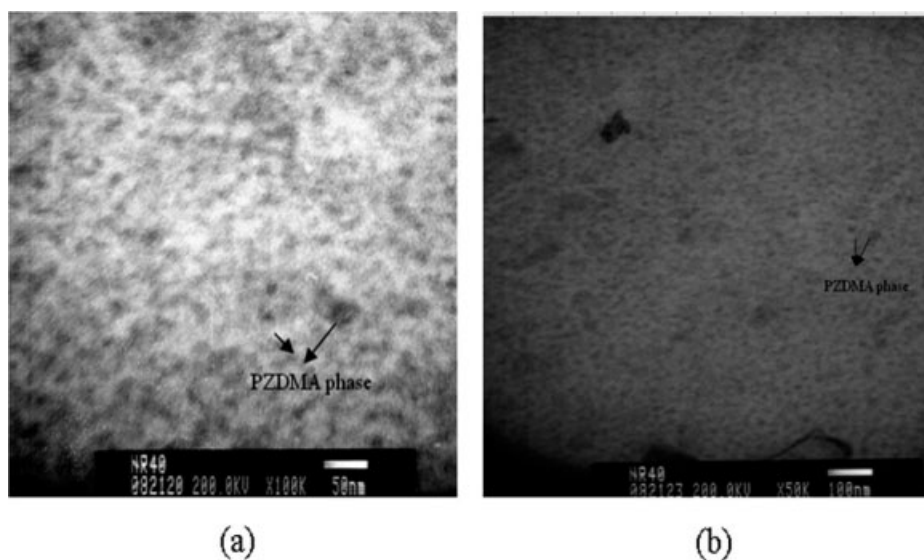


Figure 2 TEM of rubbers filled with 40 phr ZDMA (a) 50 nm and (b) 100 nm.

This phenomenon can also be proved by thermodynamic process. The crystallization of NR chains happens in a supercooled state.^{36,37} Namely, the melting temperature (T_m) increases during deformation. When T_m exceeds the ambient temperature, the onset of the crystallization takes place. This can be analyzed by the following equation³⁷

$$\frac{1}{T_{m,s}} = \frac{1}{T_{m,0}} - \frac{\Delta S_d}{\Delta H} \quad (7)$$

where $T_{m,s}$ is the melting temperature in the stretched state, $T_{m,0}$ is the melting temperature in the unstretched state, ΔH is the melting enthalpy, and ΔS_d is the difference of the entropy between the stretched and the unstretched states. So the onset of the crystallization is determined by ΔS_d , which is as a function of strain. For the NR/ZDMA composites, due to the effective extension ratio of the rubber portion larger than the macroscopic extension ratio, the values of ΔS_d at the same strain in NR/ZDMA composites are larger than those in the pure rubber. This means the supercooled state will be reached earlier by the composites during deformation. So the onset of crystallization happens in advance.

Because of much ionic crosslinking existing in the NR/ZDMA composites and the strain-induced crystallization appearing much earlier, the modulus at low extension is much larger than NR filled with carbon black, as shown in Table IV.

Reinforcement mechanism

In the filler reinforcement mechanism, two primary effects should be taken into account: crosslinking containing both chemical crosslinking and physical

crosslinking, and strain-induced crystallization during stretching. So both crosslinking and strain-induced crystallization should be investigated. Lu et al.⁹ suggested that the strain-induced crystallization should be the main reason for the high strength, but Yuan et al.¹³ thought the presence of ionic crosslinking might be the mechanism of the reinforcement. As shown in Figure 4, at the same extension ratio (3), the WXR patterns of NR reinforced by ZDMA show two diffraction peaks at $2\theta = 14.14^\circ$ and 20.65° , due to the emergence of strain-induced crystallization (PZDMA is in glass state under room temperature³⁸). Figure 5 displays the variation of the crystallization index for different amount of ZDMA. It can be found that the crystallization index firstly increases. When the content of ZDMA reaches 20 phr,

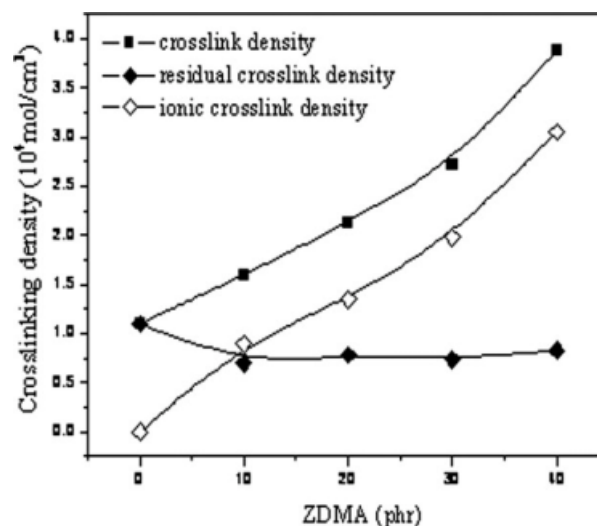


Figure 3 Three kinds of crosslinking density as a function of the loading amount of ZDMA.

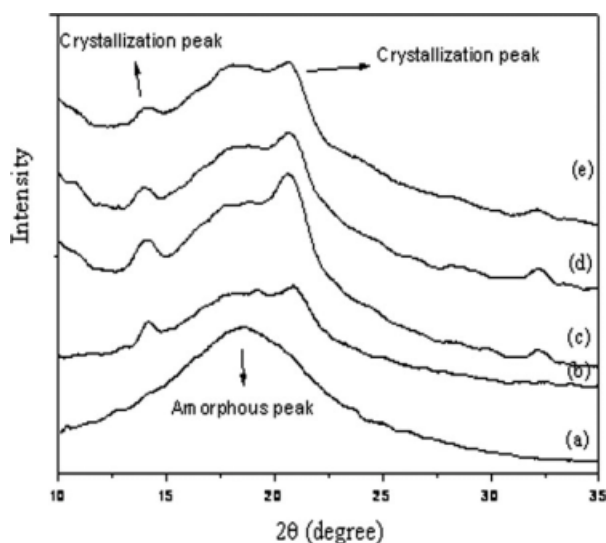


Figure 4 XRD patterns of NR/ZDMA composites with different content of ZDMA at the extension ratio of 3: (a) pure rubber; (b) 10 phr ZDMA; (c) 20 phr ZDMA; (d) 30 phr ZDMA; (e) 40 phr ZDMA.

the crystallization index reaches the maximum and begins to decrease. The maximal crystallization index at the extension ratio of 3 is 25.99%, which is bigger than that of the rubbers filled with the conventional filler at the same extension ratio.³⁹ Considering that the crystallization onset of NR filled with more ZDMA is earlier than that of NR filled with less ZDMA, and when the content of ZDMA exceeds 20 phr, the crystallization index at the same extension ratio drops, it can be deduced that the utmost crystallization index in NR filled with 30 phr and 40 phr ZDMA is smaller than that of NR filled with 20 phr ZDMA. Thus, the optimal content of ZDMA for strain-induced crystallization is around 20 phr.

Figure 3 shows the ionic crosslinking density increases with the content of ZDMA. From Table II it can be found the tensile strength increases fast until the content of ZDMA reaches 20 phr, and then it increases slowly, and nearly levels off. Based on our study aforementioned, the reasons are as follows: At the low content of ZDMA (10 and 20 phr), both the crystallization index and the ionic crosslinking density increase fast, so the reinforcing effect is obvious. At the high content of ZDMA (30 and 40 phr), the crystallization index begins to drop, while the ionic crosslinking density still keeps increasing. The increment of the ionic crosslinking density makes up for the effect of the drop of the strain-induced crystallization.

Therefore, the reinforcement mechanism is perspicuous. At the low content of ZDMA, both the strain-induced crystallization and the crosslinking largely influence the ultimate mechanical properties, whereas crosslinking, compared to the strain-

induced crystallization, plays a more important role in the reinforcement at the high content of ZDMA.

Strain-induced crystallization

The reason why crystallization index drops at high content of ZDMA may be attributed to the change of structure during deformation. The crosslinking points in the pure NR distribute inhomogeneously.^{40,41} In other words, the network in the pure NR is composed of chains with a wide distribution of chain lengths between the crosslinking points, and in the meantime the crosslinking density of the pure NR is low. So the proportion of long chains is much higher, as shown in the schematic diagram of the strain-induced crystallization structure reported by Toki et al.⁴⁰ During stretching, only the short chains between the densely packed crosslinking points can be oriented and form crystallites, whereas the long chains remain in the random coil state. As stretching continues, the short chains would break. When the breakage develops to a limit, the rubber simple would rupture. This means long chains remain in the unoriented amorphous state during deformation, resulting in low crystallization index. The schematic models of strain-induced crystallization of the NR/ZDMA composites are illustrated in Figure 6. When NR is filled with 10 and 20 phr ZDMA, the crosslinking density increases, attributed to the appearance and increment of ionic crosslinking, as revealed in Figure 3. Then the proportion of short chains increases. Furthermore, the special strain amplification effect also makes for the orientation. So more rubber chains can participate in crystallization and the crystallization index rises. As shown in Figure 5.

However, due to the strong rubber-PZDMA, and PZDMA-PZDMA interactions, when the content of

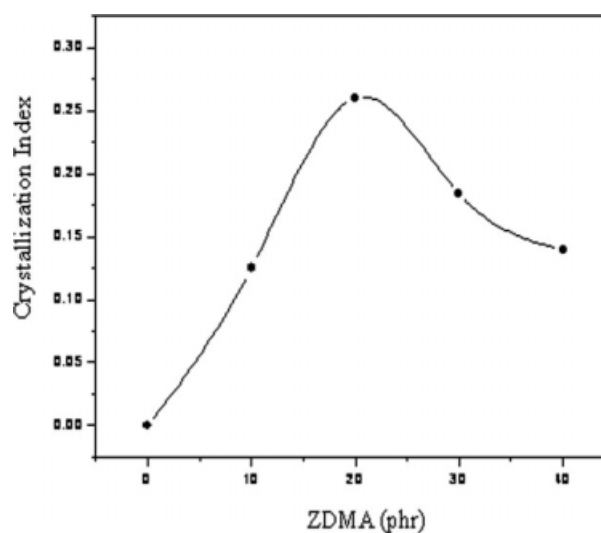


Figure 5 Crystallization index at the extension ratio of 3.

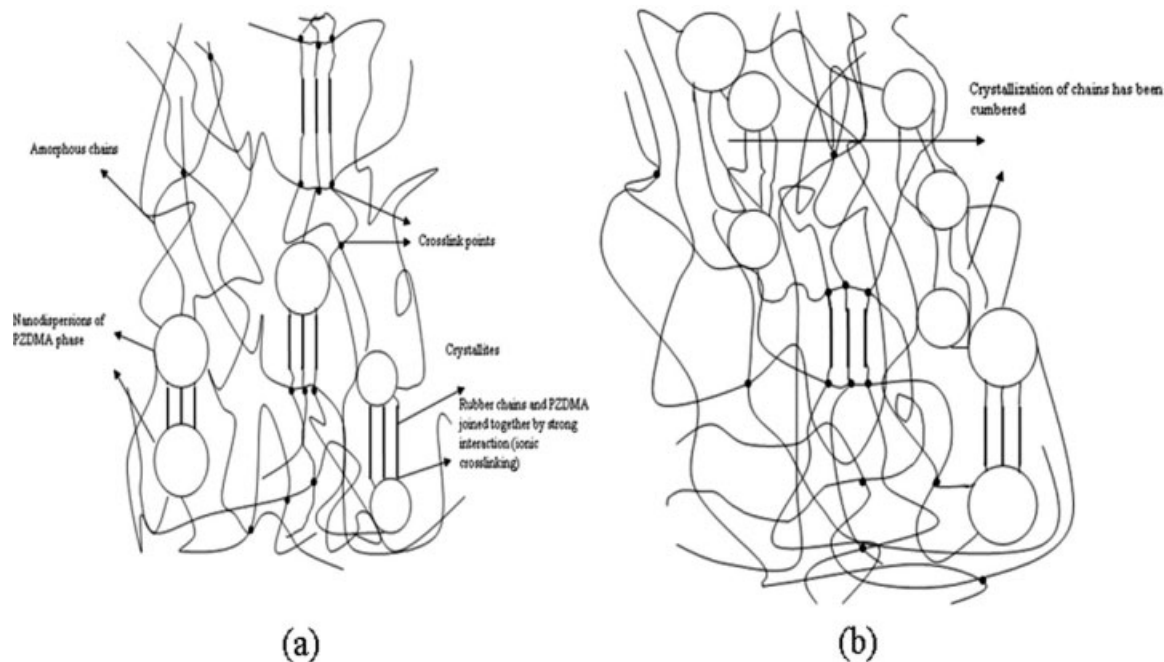


Figure 6 Schematic diagram of strain-induced structure in stretched NR filled with (a) optimal content of ZDMA, (b) high content of ZDMA.

the hard PZDMA nanophases reaches a limit, the PZDMA nanophases distributing in the rubber may begin to hinder the rubber chain orientation in the extension direction, so the ability of strain-induced crystallization of rubber chains drops. This phenomenon can be revealed by the Payne effect and the Mullins effect,^{42,43} revealing the intensity of the filler–filler and rubber–filler interactions, respectively.^{27,44–46} Figure 7 reveals the Payne effect of NR filled with different content of ZDMA. The amplitude of the Payne effect rises, as the amount of ZDMA increases, illuminating the presence of strong

interactions between PZDMA nanophases. Therefore, at high content of ZDMA, network of PZDMA phases may form and restrain the orientation of rubber chains. Figure 8 shows the influence of ZDMA content on the Mullins effect. To quantitatively illuminate the Mullins effect of the rubbers filled with different content of ZDMA, the Mullins hysteresis,²⁸ defined as the area between the first and the second extension, was calculated to reveal the magnitude of the Mullins effect. The results are revealed in Figure 9. Before the amount of ZDMA reaches 20 phr (the effective volume fraction of PZDMA is

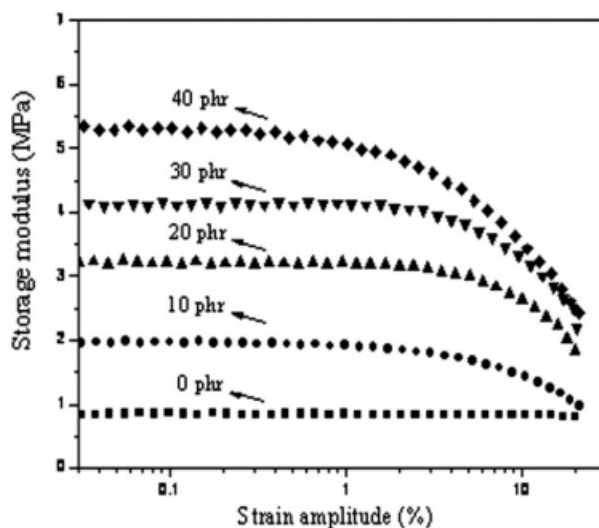


Figure 7 Storage modulus as a function of strain amplitude.

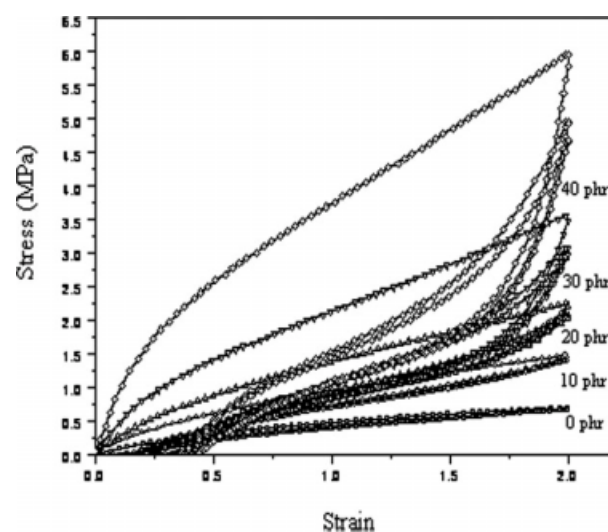


Figure 8 Influence of the loading of ZDMA on the Mullins effect.

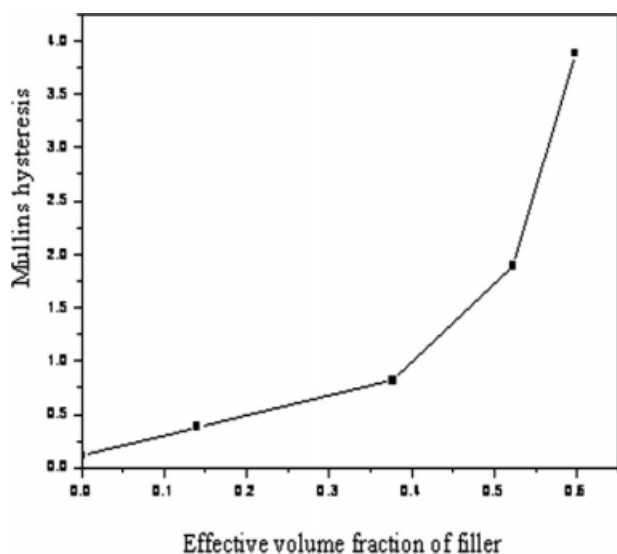


Figure 9 Influence of the effective volume fraction of PZDMA on the Mullins hysteresis.

0.3767), the Mullins hysteresis increases slowly. At the high content (the effective volume fraction is bigger than 0.3767), the Mullins hysteresis rises fast. This means the interactions between the PZDMA phase and the rubber phase begin to play a more important role in the reinforcement, and the orientation of the rubber chains during stretching is restricted more seriously. So the ability of the strain-induced crystallization is reduced. In fact, under the action of external force during deformation, the amorphous chains will orient, but parts of them can not achieve the orientation degree required by crystallization. In other words, ΔS_d of those chains is too small for them to reach the supercooled state. Thus, it can be deduced that the fraction of oriented amorphous chains may be higher owing to the much ionic crosslinking in contrast to the conventional filled NR. This deduction will be validated in the future. On the other hand, the increasing effective crosslinking density can produce higher nucleation, leading to higher crystallization index.⁴⁷ But as the crosslinking density increases, the proportion of rubber chains restricted by the PZDMA nanophases rises to a limit, at which the total content of rubber chains, which can take part in crystallization begins to drop. Therefore, the crystallization index begins to decrease. Nevertheless, more works detailed and quantitative on the crystallization property and the relationship between it and the structure of the composites are still needed, which are in the scope of our future study.

CONCLUSIONS

The addition of ZDMA largely improves the mechanical properties of NR. The onset extension ratio of upturn in Mooney-Rivlin plots appears in

advance due to the strain amplification effect, meaning the onset of strain-induced crystallization of the filled rubbers is earlier. Because of the specific structure of the composites and the nano-reinforcing effect of the PZDMA nanophases, the volume fraction of filler is modified by φ_e , obtained by the Guth and Gold equation. The values of $\alpha_e^u(\varphi_e)$ are close to α^u of the unfilled rubber. However, the rubber filled with 20 phr ZDMA has the maximal crystallization index at the extension ratio of 3. The ability of strain-induced crystallization of rubber at high content of ZDMA (more than 20 phr) decreases. Because the orientation of rubber chains during stretching is restricted more seriously. This phenomenon can be revealed by the Mullins effect and the Payne effect. The Mullins hysteresis increases much faster after the content of ZDMA exceeds 20 phr. The ionic crosslinking plays a more important role in the ultimate mechanical properties at the high content of ZDMA.

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