A Study on the Crosslink Network Evolution of Magnesium Dimethacrylate/Natural Rubber Composite

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ABSTRACT: In this article, we study the evolution of networks based on natural rubber (NR) which is reinforced by *in situ* magnesium dimethacrylate (MDMA) during curing at a molecular level. The crosslink density of the compounds cured for different time was evaluated by a dissolution/swell experiment. The curing process was analyzed by using a UR-2030 Rotorless Rheometer. Mechanical properties of the composites cured for different time were also used to evaluate the evolution of the networks. The results reveal that the ionic crosslinks, cooperating with some primary covalent crosslinks and some other physical crosslinks, play an important role in supporting the crosslinked backbone of the composite to bear the external force in the initial curing time. The evolution of crosslinked networks could be divided into three regions in this particular experiment: network forming period dominated by the ionic bonds, fundamental network forming period, and ionic bonds rupture period. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2449–2459, 2012

Key words: curing of polymers; mechanical properties; rubber; vulcanization

INTRODUCTION

Mechanical properties can be changed and improved by the addition of nanoparticles such as carbon black, silica,[1] or clays.[2] These conventional fillers enhancing the mechanical properties of rubbers have been thought to form additional crosslinks resulting from the filler–rubber interactions.[2] For example, filler networks with different level of rigid fillers' aggregates are formed when carbon black particles are dispersed in rubber matrix. Rubber chains locate between the aggregates and are bounded to their active sites through the adsorption effect,[3,4] which results in the additional crosslinks. In recent years, the composites of rubber with metal salts of unsaturated carboxylic acids have attracted researchers' attention because of their excellent mechanical properties in comparison with conventional polymer composites. As a new type of reinforcing agent for rubbers, and with homopolymerization and graft-polymerization taking place in the rubber matrix, metal salts of unsaturated carboxylic acids can be polymerized to form nanodispersion phases acting as nanoparticles and to graft onto rubber chains to enhance the crosslinked network during peroxide curing. The ionic crosslinks are formed by metal salts graft-polymerized onto the rubber chains, whereas the poly-(metal salt) chains separate from the rubber matrix and aggregate into nano-scaled fine particles, forming salt crosslinks.[5–9] As a result, rubbers with metal salts of unsaturated carboxylic acids contain not only conventional covalent crosslinks but also ionic crosslinks and exhibit special crosslink structure and morphology.[5–9] Obviously, the microstructure of rubbers reinforced by metal salts of unsaturated carboxylic acids is complex and differs to that of conventional reinforcing filler. The curing process of metal-salts-of unsaturated-carboxylic-acids/rubber compound is one of important steps relating the essence of rubber network formation and affecting process ability and properties of final products. Lu et al.[10] found that the polymerization of zinc dimethacrylate took place in advance of the crosslinking reaction of rubber, whereas Nie et al.[11] investigated the cure kinetics and the kinetic parameters. However, the evolution of the two networks, namely covalent network and ionic network, is seldom reported. Therefore, it is necessary to study the network evolution of composites during vulcanization at a molecular level.

In this work, we focused on a MDMA/NR system as a metal salts of unsaturated carboxylic acids reinforcing system and analyzed the evolution of networks (contain covalent crosslinks and ionic crosslinks) by using equilibrium swelling and rheometer.

The mechanical properties are also evaluated. The experimental results indicated that an ionic bonds dominated network was formed at the initial time. Moreover, the growing ionic crosslinks, some primary covalent crosslinks, and some physical crosslinks were found to be the main supported backbone of the network in this period. An ionic crosslink rupture period was also observed in this MDMA/NR system.

EXPERIMENTAL AND METHOD

Raw materials and recipes

NR (Malaysia 1#) was provided by Guangzhou rubber industry research institute (China). Methacrylate acid (MAA) purchased from Guangzhou Xin'gang Chemic factory (China) was purified by distillation under nitrogen at reduced pressure. Magnesium oxide (MgO) was purchased from Shanghai TongYa chemical Technology. Co., Ltd (China). Dicumyl peroxide (DCP) purchased from Sinopharm Chemical Reagent Co. Ltd (China) was purified by anhydrous alcohol recrystallization before use.

In this article, NR was reinforced by *in situ* prepared MDMA. Theoretically, 1 mol MgO and 2 mol MAA react to form MDMA and water completely. Equivalent MgO and MAA (MgO/MAA molar ratio 0.5) was used to neutralize in the NR matrix during mixing. A high degree of conversion to MDMA from the *in situ* reaction of MgO and MAA has been verified by many papers.[5,9,12] The compounds containing 100 weight parts of NR, 1.5 phr (parts per 100 parts of rubber) DCP, and 0–40 phr MDMA.

Samples preparation

Rubber compounds were prepared in a two-roller mill. MgO and MAA were added into NR and mixed for several minutes. DCP was added at last. The compound was stored at room temperature for 8 h. The Mooney viscosity (ML(1+ 4) 100°C) of NR after prepared in the two-roller mill was about 53. Isothermal vulcanization was analyzed with a UR-2030 Rotorless Rheometer produced by U-CAN Dynatex Inc. (Taiwan) at 155°C. Samples cured at different set time were taken out and cooled in ice to terminate the cure reaction, then dried and the measurements were carried out as soon as possible.

Crosslink density measurement

The apparent crosslink density was determined by equilibrium swelling experiments. To calculate the crosslink density of rubber, five weighed test pieces of rubber were immersed in toluene at about 23°C for a period of 72 h in sealed dark vials. These meas-ures ensure that swelling equilibrium is reached and that the sample degradation is minimized.[13] Then, the samples were blotted with tissue paper to remove the excess of the solvent and immediately weighed on an analytical balance. Finally, the samples were dried in a vacuum oven for 48 h at 60°C until constant weight. The volume fraction of rubber swollen in the gel, V_r, which was used to represent the crosslink density of the samples, was determined by the following equation.[7,11,12,14–16]

$$v_r = \frac{m_0 \varphi (1 - \alpha) \rho_r^{-1}}{m_0 \varphi (1 - \alpha) \rho_r^{-1} + (m_1 - m_2) \rho_s^{-1}} \quad (1)$$

where m_0 is the mass of the sample before swollen, m_1 and m_2 are the masses of the swelled sample before and after drying, respectively, φ is the mass fraction of NR rubber in the vulcanizates, α is the mass loss of the vulcanizates after swollen, and ρ_r and ρ_s are the rubber and toluene density ($\rho_s = 0.865 g/cm^3$), respectively.

To distinguish ionic crosslinks from covalent crosslinks, the above samples were swollen in a mixture of toluene and chloroacetic acid once again for 120 h to destroy ionic crosslinks, followed by swelling in toluene for 72 h and weighed, then vacuum dried and reweighed. Finally, V_{r1} was calculated from eq. (1), which represents the covalent crosslink density. V_{r2}, which was calculated by subtracting V_{r1} from V_r, was used to represent the ionic crosslink density.[7,11,12,14–16]

Mechanical properties of the vulcanizates

The stress–strain properties were measured with dumbbell specimens (6-mm width in cross section) according to ASTM D412. Tear strength was measured on un-nicked 90° angle test pieces according to ASTM D624. Tensile tests were carried out using a Computerized Tensile Strength Tester (UT-2080) produced by U-CAN Dynatex Inc.(Taiwan) with a crosshead speed of 500 mm/min. Shore A hardness was determined as the conditions given in ASTM-D2240.

RESULTS AND DISCUSSION

Cure characteristics

The torque is considered to be proportional to the concentration of crosslinkings, and the rheometer curve is able to give an indirect information on the rubber reticulation kinetic.[17] Thus, the cure-curve is a general characterization of the structure formation approach of crosslink network. Generally speaking, a significant scorch delay or the induction region can be observed in a sulfur curing system.[18] In this
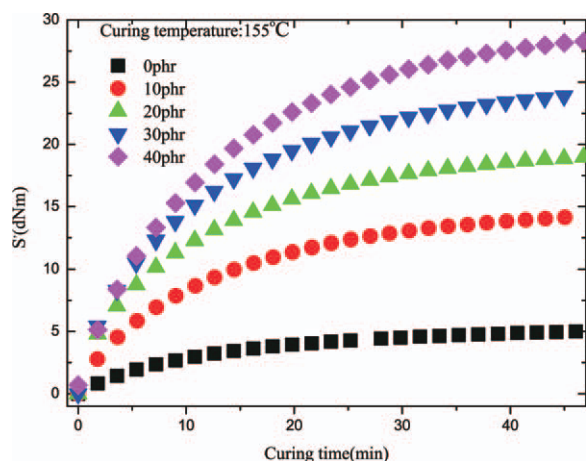
Figure 1 Elastic cure-curve of NR with different amount of MDMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

region, torque keeps at a low plateau, it is usually thought that there is no crosslink formed but polysulfidie pendent groups between rubber and accelerator are formed during this period. However, the fact in a peroxide curing system differs to that. The elastic cure curve (S') of NR and NR/MDMA composites are given in Figure 1. The S' shows an abrupt increase at the beginning, which indicates that the crosslinking takes place and a "crosslinked network" is formed. The "crosslinked network" with double quote here, is different from that in the traditional sense, and, will be discussed in detail later. It was imagined that the crosslinking reaction of rubber occurs concurrently during curing course. However, the further studies reveal that the behavior of compound added MDMA is out of the expectations. The kinetics vulcanization of rubber with peroxide is very complex, and the relative researches have been reported by Milani and Milani.[19,20]
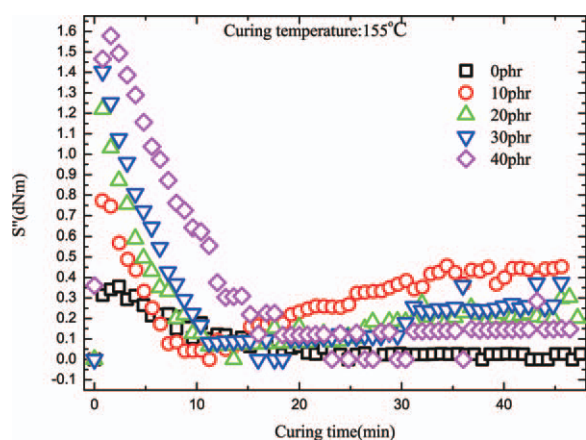
Corresponding to the elastic cure curve, the viscous cure curve (S'') of NR and NR/MDMA compounds versus cure time is shown in Figure 2. In a classical sulfur curing system,[21] the viscous torque increases and reaches a maximum in a certain time. The rise of S'' is due to the formation of polysulfidie pendent groups between rubber and accelerator during the induction step of the cure, which can hinder the rubber chains' mobility. After the peak, the viscous torque declines as the curing process continues until it reaches a plateau at the end of curing. Whereas in the case of compound added MDMA, the S'' illustrates a sharp increase at the initial time, then decreases quickly. The sharp increase is due to the softening of the sample by heat which enhances the mobility of compounds. The quick decreases are attributed to the forming of crosslinks, which make the compounds lost the mobility.

Analysis of crosslink density

To discuss the essential network evolution of composites during vulcanization, it is necessary to understand the crosslinked network structure existing in vulcanizate first. In fact, MDMA polymerized (homo-polymerization and graft-polymerization)[14–16] during vulcanization could result in a complex crosslinked network in a peroxide cured NR/MDMA composite, which contains covalent crosslinks and ionic crosslinks. A classic crosslink density corresponding to the concentration of MDMA is shown in Figure 3. The total crosslink density (V_r) and the ionic crosslink density (V_{r2}) increase with increasing MDMA content, whereas the covalent crosslink density (V_{r1}) decreases. It is reasonable to think that a part of free radicals should have been consumed by the polymerization of MDMA, which leads to the decrease of the covalent crosslink
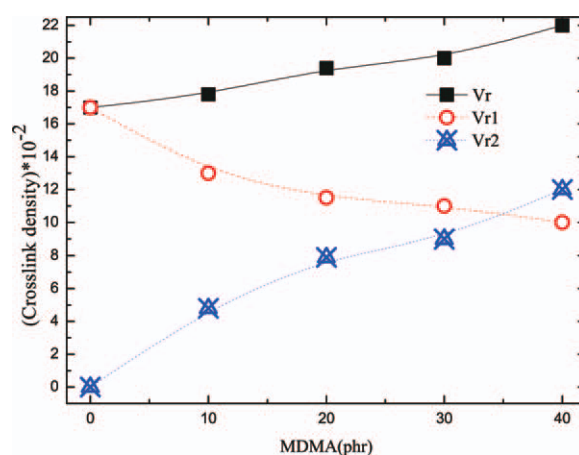

Figure 2 Viscous cure-curve of NR with different amount of MDMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3 Crosslink density of composites with different amount of MDMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
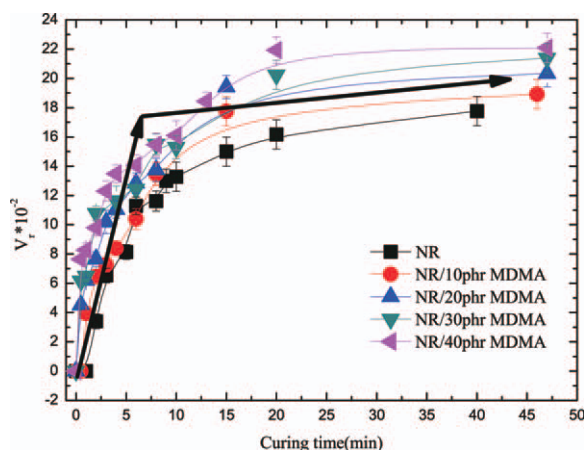
Figure 4 Evolution of the total crosslink density during vulcanization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

density. Many studies about metal salts of unsaturated carboxylic acids reinforcing rubbers have revealed that the ionic crosslinks are supposed to play an important role in the reinforcement of rubber.[16]

The growing of total crosslink

Measurement of crosslink density of the composites with different curing time was carried out to investigate the actual evolution of crosslinked network during curing. The evolution trend of total crosslink densities, covalent crosslink density, and ionic crosslink density are shown in Figures 4–6, respectively. The crosslink density in Figure 4 is referred to the total crosslink density, including covalent crosslink of the NR and ionic crosslink introduced by poly-MDMA and some other physical adsorption crosslinks. Corresponding to the elastic torque of cure-curve, V_r shows a rapid growing at the initial time.
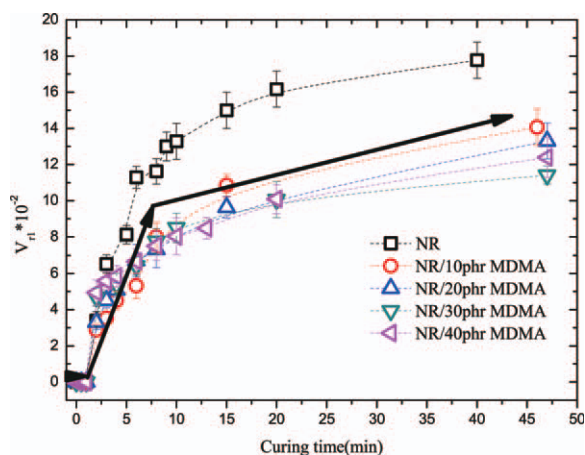
V_r grows quickly in the first 20 min, then, reaches a plateau even the cure process continues until 40 min. The apparent curing rate increases with increasing MDMA content, which can be evaluated form the increasing slope of the V_r curve. This indicates that the vulcanization process of the compounds is promoted by adding MDMA.

The growing of covalent crosslink

The growing of V_{r1} is shown in Figure 5. Differing to V_r, V_{r1} maintains at zero in the initial curing time (about 1 min), whereas V_r increases fast at this monument. V_{r1} maintaining at zero at the beginning means that the covalent network crosslinking between rubber molecules does not take place. In another word, the covalent network backbones of the composites are not formed at this time. In traditional view, only covalent reactions between rubber molecules take place during vulcanization, leading to the formation of rubber crosslinked network and hence the increasing of torque. However, in this particular experiment, the increase of elastic torque suggests that a crosslinked network is formed and yield hindrance to torque. Compared with the curves of V_r, the curves of V_{r1} of the composites with different MDMA content are not far away from each other. This indicates that ionic crosslink has more effects on the apparent properties of the composites. In addition, the V_{r1} of the composites are lower than that of NR, which confirms that the DCP radicals were consumed by the polymerization of MDMA, forming ionic crosslinks.

The growing of ionic crosslink

The growing curves of ionic crosslink densities are shown in Figure 6. The V_{r2} of NR gum shows a line

Figure 5 Evolution of the covalent crosslink density during vulcanization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
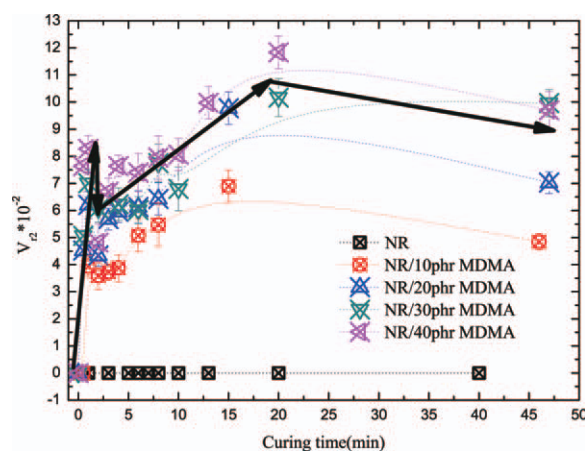

Figure 6 Evolution of the ionic crosslink density during vulcanization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
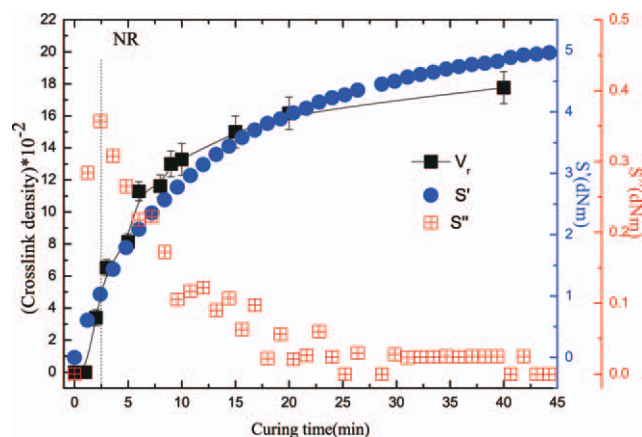
Figure 7 Evolution of crosslinked network of NR during vulcanization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at zero because of no MDMA. Interestingly, the "V_{r2}" exhibits a sharp increasing from zero to a peak point in the first 1 min, then, following a rapid dropping to a certain value. Please be noted that the experimental samples were swollen in a mixture of toluene and chloroacetic acid for 120 h to destroy ionic crosslink. Covalent crosslink density, V_{r1}, was calculated from eq. (1). Ionic crosslink density, V_{r2}, was calculated by subtracting V_{r1} from V_r. The samples at the initial curing period do not dissolved in the toluene but dissolved or dispersed in the mixture of toluene and chloroacetic acid after destroying ionic crosslink; thus, the V_{r1} shown in Figure 5 maintains at zero, whereas V_r increases fast in this period. As a result, the value of "V_{r2}" is the value of "V_r" in this period. The V_{r1} quickly increases with the curing time after 1 min. Therefore, V_{r2} follows a rapid dropping. After that, V_{r2} grows fast.

The evolution trends of networks

The evolution trends of V_r, V_{r1}, and V_{r2} are also marked in Figure 4, Figure 5, and Figure 6, respectively, represented by black arrows. The V_{r1} maintains at zero for about 1 min, and after that increase rapidly in the following 15 min, then the increasing trend smooth down. From Figure 6, four main regimes can be seen from the evolution trends of V_{r2}: (1) an abrupt increasing; (2) sharp dropping; (3) soft growing; and (4) decreasing. The slow increase of V_{r1} cooperated with the decrease of V_{r2} results in a plateau of V_r at the curing time exceed 20 min. The decrease of V_{r2} is due to the instability of ionic bonds at high temperature for a long time. This implies that the NR/MDMA composite curing at a relative lower temperature may have better mechanical properties. A further and detailed investigation of the relation between mechanical properties and

crosslinked network structure and curing temperature will be discussed in a future article.

Evolution of network structure of the composites

In a MDMA-reinforcing NR composite system, the chemical crosslinks contain covalent crosslink and ionic crosslink; thus, a further discussion of the evolution trend of crosslink density and compared with the cure-curve is necessary. In this particular experiment, the evolution of crosslinked network can be divided into three regions.

Ionic crosslink network dominating period

The first curing process region can be defined at curing time from 0 to 1 min. As it can be seen from Figure 7, the "scorch time" of NR gum is very short. S' drops a little in the first 1 min then increases immediately. The S'' reaches its maximum at about 2.5 min, then decreases with the going of the curing time, and then reaches its bottom at about 20 min. The growing of V_r is consistent with the increasing of S', which means that there is no covalent-crosslinked network formed in the first 1 min. The dropping of S' at initial time is just because of the softening of NR heated by the moving die of rheometer. After that, the DCP initiates the covalent crosslinking vulcanization of NR.

As shown in Figures 8–11, the "scorch times" of the compounds added with MDMA disappears. V_r, S', and S'' increase rapidly even at initial. The growing of V_{r1} of the compounds is similar to that of the NR gum, which means that the covalent crosslinking backbones of the composites are not formed in this period. However, the "V_{r2}" shows a "peak" in this period, which indicates that ionic crosslinking is initiated by DCP in this time. As mentioned before, the

Figure 8 Evolution of crosslinked network of the composite with 10 phr MDMA during vulcanization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
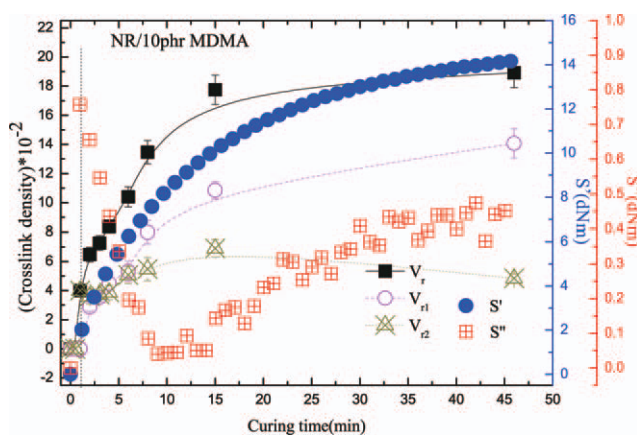
Figure 9 Evolution of crosslinked network of the composite with 20 phr MDMA during vulcanization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
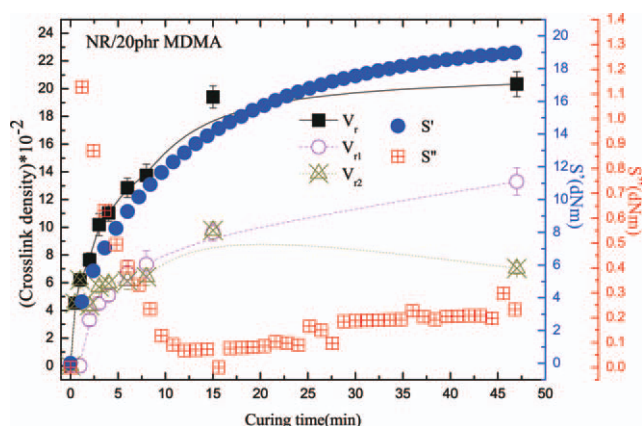
value of "V_{r2}" is the value of "V_r" in this period, and V_{r2} drops to a certain value after the peak. Theoretically, the polymerization of MDMA is initiated by DCP radicals, and the ionic crosslink density increases with the curing time. A "peak" should not appear during initial curing time. However, the samples in this curing period do not dissolved in the toluene but dissolved or dispersed in the mixture of toluene and chloroacetic acid after destroying ionic crosslinks, which suggests that the ionic crosslinks play an important role in supporting the crosslinking backbone of the composite during this period. Noted the peak of "V_{r2}" and the dropping afterwards, a conclusion can be obtained that the "V_{r2}" contains not only the really ionic crosslinks but also some primary covalent crosslinks and some other physical crosslinks which may contribute to the "V_{r2}" in this period.[22]

Theoretically, only crosslinking between rubber molecules is enough to form an insoluble gel. In a classic sulfur-curing rubber system, the crosslinking
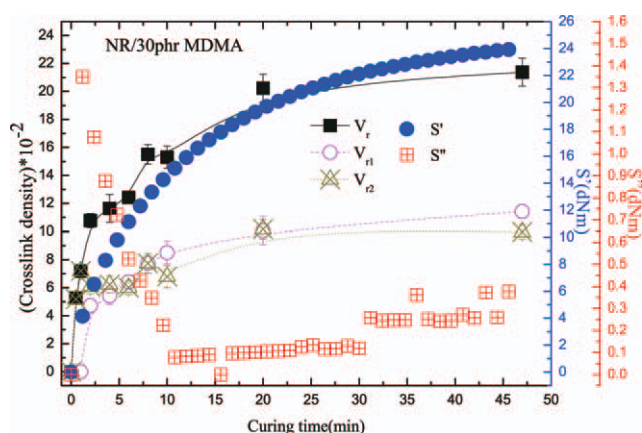

Figure 10 Evolution of crosslinked network of the composite with 30 phr MDMA during vulcanization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 11 Evolution of crosslinked network of the composite with 40 phr MDMA during vulcanization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
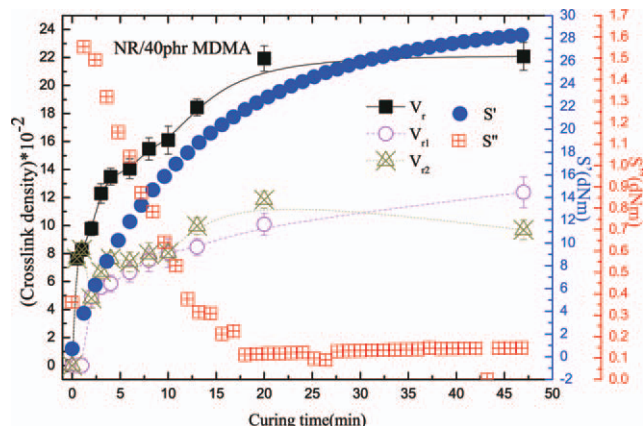
reaction takes place only in a small scale at the scorch period to form a primary network.[18] The formed network is not strong enough to bear the force exerted by the moving die, and there is relative sliding between rubber molecules under force and the network contributes little to the macroscopic mechanical properties. However, in NR/MDMA/DCP system, the increasing of S' indicates that the formed network is strong enough to bear the force exerted by the moving die in this period. This result also supports the suggestion that ionic crosslinks contribute to the remarkable reinforcement of MDMA. All the crosslinkings existing in this period cooperate to enhance the torque and make the composites in this period insoluble in toluene.

To give an intuitive observation of the ionic crosslinked network dominating period, the sample of composite with 40 phr MDMA cured for 1 min was immersed in toluene for 72 h, then, immersed in the mixture of toluene and chloroacetic acid once again for 72 h. The photographs of dissolution/swell experiment are shown in Figure 12. The sample swollen in the toluene was an integral gel, and both the swollen sample and the solution were transparent, which indicates that the formation of network can only swell but cannot be dissolved in toluene. However, after the same sample being transferred to the mixture of toluene and chloroacetic acid to cut off the ionic crosslinks, it dissolved in the mixture solvents forming microgel and the whole solution was in a muddle. All these experiments indicate that the continuous fundamental covalent network was not formed during this period, and the ionic crosslink network dominated in this period. The sample with 40 phr MDMA cured for 15 min did not dissolve in the mixture of toluene and chloroacetic acid, as shown in Figure 13. In this case, the sample lost its transparence, while the whole solution was
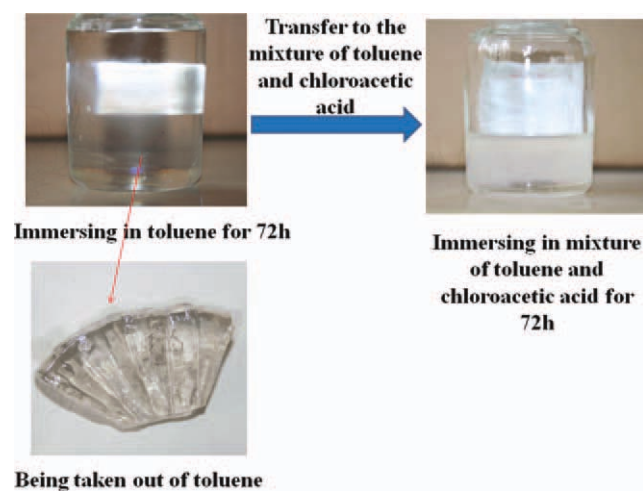
Figure 12 Illustration of dissolution/swell experiment using the sample with 40 phr MDMA curing for 1 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

transparent. This demonstrates that the covalent crosslinked network has been formed to support the integrity of the swollen sample after the ionic crosslinkings being cut off.

Fundamental network forming period

With going the curing time, the S', V_r, V_{r1}, and V_{r2} all show an apparent increase. In this period, the covalent crosslinking of rubber molecules and the polymerization of MDMA occur simultaneously. The whole network grows larger and larger, which raises the modulus and mechanical properties of the composite, and so does the torque of cure-curve. More drop in S'' means going far away the viscose nature and denotes a higher elasticity. It is reasona-

Figure 13 Photograph of the sample with 40 phr MDMA curing for 15 min swell in the mixture of toluene and chloroacetic acid once again for 72 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Percent Change of Parameters Related to Network Structure of the Composite with 10 phr MDMA During Vulcanization

Curing time (min)	$\Delta V_{rt}/\Delta V_r$ (%)	$\Delta V_{r1t}/\Delta V_{r1}$ (%)	$\Delta V_{r2t}/\Delta V_{r2}$ (%)	$\Delta S'_t/\Delta S'$ (%)
0.5	0	–	–	7
1	18	–	54	12
2	34	20	51	21
3	38	25	53	28
4	44	32	55	34
6	54	38	72	44
8	71	57	78	52
15	93	77	98	71

ΔV_{rt} is the total crosslink density change at cure time t ($V_{rt} - V_{r\min}$), ΔV_r is the total crosslink density ($V_{r\max} - V_{r\min}$); ΔV_{r1t} is the covalent crosslink density change at cure time t ($V_{r1t} - V_{r1\min}$), ΔV_{r1} is the total crosslink density ($V_{r1\max} - V_{r1\min}$); ΔV_{r2t} is the ionic crosslink density change at cure time t ($V_{r2t} - V_{r2\min}$), ΔV_{r2} is the ionic crosslink density ($V_{r2\max} - V_{r2\min}$); $\Delta S'_t$ is torque change at cure time t ($S'_t - S'_{\min}$); $\Delta S'$ is total torque ($S'_{\max} - S'_{\min}$).

ble considering that the developing of two different crosslinked networks prevents the mobility of rubber molecules, which resulting in the decrease of S''. The formation of covalent crosslinking backbone is completed in this period, as seen from Figure 13. The network evolution of composite during vulcanization can also be reflected from the parameters related to network structure shown in Tables I–IV.

T1-T4

Ionic crosslink rupture period

When the curing time exceeds about 20 min, the V_{r2} displays a decrease, whereas the V_{r1} increases all the

TABLE II
Percent Change of Parameters Related to Network Structure of the Composite with 20 phr MDMA During Vulcanization

Curing time (min)	$\Delta V_{rt}/\Delta V_r$ (%)	$\Delta V_{r1t}/\Delta V_{r1}$ (%)	$\Delta V_{r2t}/\Delta V_{r2}$ (%)	$\Delta S'_t/\Delta S'$ (%)
0.5	22	–	45	10
1	30	–	62	17
2	37	25	43	26
3	50	34	56	33
4	54	39	59	39
6	63	51	61	48
8	67	56	64	55
15	95	75	97	75

ΔV_{rt} is the total crosslink density change at cure time t ($V_{rt} - V_{r\min}$), ΔV_r is the total crosslink density ($V_{r\max} - V_{r\min}$); ΔV_{r1t} is the covalent crosslink density change at cure time t ($V_{r1t} - V_{r1\min}$), ΔV_{r1} is the total crosslink density ($V_{r1\max} - V_{r1\min}$); ΔV_{r2t} is the ionic crosslink density change at cure time t ($V_{r2t} - V_{r2\min}$), ΔV_{r2} is the ionic crosslink density ($V_{r2\max} - V_{r2\min}$); $\Delta S'_t$ is torque change at cure time t ($S'_t - S'_{\min}$); $\Delta S'$ is total torque ($S'_{\max} - S'_{\min}$).

TABLE III
Percent Change of Parameters Related to Network Structure of the Composite with 30 phr MDMA During Vulcanization

Curing time (min)	$\Delta V_{rt}/\Delta V_r$ (%)	$\Delta V_{r1t}/\Delta V_{r1}$ (%)	$\Delta V_{r2t}/\Delta V_{r2}$ (%)	$\Delta S'_t/\Delta S'$ (%)
0.5	28	–	58	9
1	30	–	61	15
2	50	42	55	25
4	54	49	59	37
6	58	58	57	46
8	72	70	73	54
10	71	77	64	61
20	95	90	96	82

ΔV_{rt} is the total crosslink density change at cure time t ($V_{rt} - V_{rmin}$), ΔV_r is the total crosslink density ($V_{rmax} - V_{rmin}$); ΔV_{r1t} is the covalent crosslink density change at cure time t ($V_{r1t} - V_{r1min}$), ΔV_{r1} is the total crosslink density ($V_{r1max} - V_{r1min}$); ΔV_{r2t} is the ionic crosslink density change at cure time t ($V_{r2t} - V_{r2min}$), ΔV_{r2} is the ionic crosslink density ($V_{r2max} - V_{r2min}$); $\Delta S'_t$ is torque change at cure time t ($S'_t - S'_{min}$); $\Delta S'$ is total torque ($S'_{max} - S'_{min}$).

time. This demonstrates that the ionic bond is unstable at such a high temperature for a long time. The ionic crosslink is influenced by temperature and time. In this period, the ionic crosslink begins to rupture, whereas the covalent crosslinked network continents to develop.

Mechanical properties analysis

Certainly, the ionic crosslinking induced by polymerization of MDMA makes the crosslinked network more complex and stronger. To further illustrate the evolution of networks, we use a common method: testing mechanical properties. We select two critical points of time, namely 1 min and 15 min, as experimental curing time. Figure 14 depicts the mechanical properties of NR reinforced by MDMA as a function of the amount of MDMA. In Figure 14(a), it can be seen that the tensile strengths of MDMA/NR composites possess the similar trend of variation with the amount of MDMA increasing: the strength increases gradually until reaching a maximal value at 30 phr MDMA, then comes down. Figure 14(b) shows that the elongation at break of MDMA/NR composites cured for 15 min decreases with increasing of MDMA loading, especially a sharp drop appears at 40 phr MDMA, whereas the elongation at break of MDMA/NR composites cured for 1 min increases to reach a maximal value at 20 phr MDMA, then comes down. Figure 14(c) and Figure 14(d) display the similar increase trend of MDMA/NR composites for tear strength and hardness, respectively.

It is easy to find out that the mechanical properties of the composite cured for 15 min are much

higher than that cured for 1 min. In addition, the mechanical properties are enhanced with increasing of MDMA loading, probably because of a more developed crosslinked network of the MDMA/NR composites being formed at a higher loading of MDMA.[11] The previous analysis of crosslink density has revealed that the ionic crosslink density increases with increasing MDMA content, whereas the covalent crosslink density decreases. Therefore, it might be taken for granted that the developed ionic crosslinked network formed at higher content of MDMA is to play an important role to support the remarkable mechanical properties.[23] However, the drop of tensile strength at 40 phr MDMA, which may be related to the NR chain network evolves and stress-induced crystallization occur at large deformations, need to be further studied. Moreover, it should be noticed that the composites cured for 1 min also exhibit considerable mechanical properties. For instance, the tear strength can reach to 25 KN m^{-1} at 40 phr MDMA. The mechanical properties are related to the crosslinked network in a certain extent. As discussed before, the covalent crosslink backbones of the composites are not formed in this period and a "peak" of V_{r2} appears. Once again, it is reasonable to suggest that the ionic crosslinked network cooperates with some primary covalent crosslinkings and some other physical crosslinkings to constitute the backbones of the composites and to embody the apparent considerable mechanical properties in this period.

The strain–stress curve reflecting the whole tensile course of the rubber composite is extremely helpful for understanding the reinforcing mechanism of the

TABLE IV
Percent Change of Parameters Related to Network Structure of the Composite with 40 phr MDMA During Vulcanization

Curing time (min)	$\Delta V_{rt}/\Delta V_r$ (%)	$\Delta V_{r1t}/\Delta V_{r1}$ (%)	$\Delta V_{r2t}/\Delta V_{r2}$ (%)	$\Delta S'_t/\Delta S'$ (%)
0.5	34	–	63	7
1	37	–	68	12
2	44	48	35	20
3	55	47	55	26
4	61	49	63	32
6	63	55	62	42
8	70	62	66	51
10	72	66	67	58
13	83	71	83	67
20	99	84	98	82

ΔV_{rt} is the total crosslink density change at cure time t ($V_{rt} - V_{rmin}$), ΔV_r is the total crosslink density ($V_{rmax} - V_{rmin}$); ΔV_{r1t} is the covalent crosslink density change at cure time t ($V_{r1t} - V_{r1min}$), ΔV_{r1} is the total crosslink density ($V_{r1max} - V_{r1min}$); ΔV_{r2t} is the ionic crosslink density change at cure time t ($V_{r2t} - V_{r2min}$), ΔV_{r2} is the ionic crosslink density ($V_{r2max} - V_{r2min}$); $\Delta S'_t$ is torque change at cure time t ($S'_t - S'_{min}$); $\Delta S'$ is total torque ($S'_{max} - S'_{min}$).
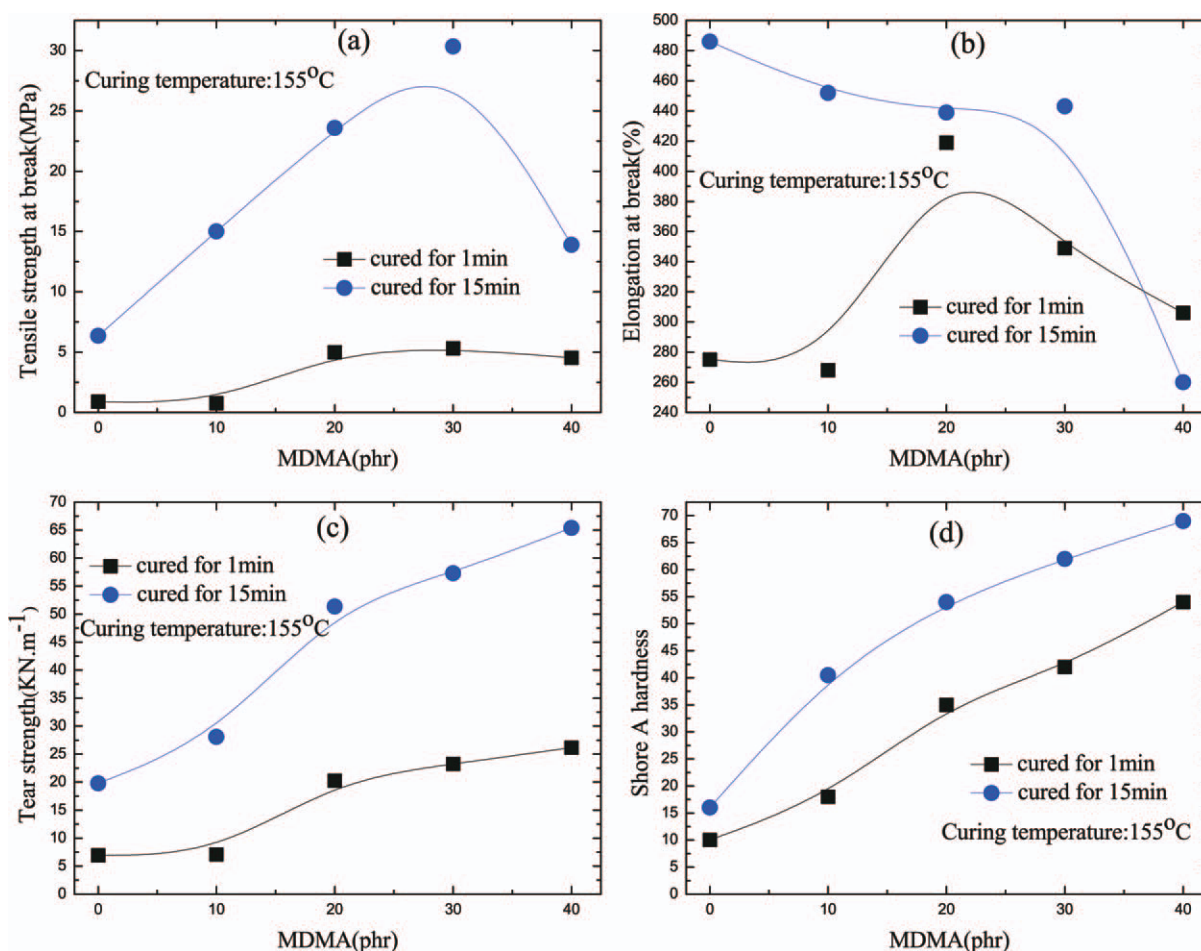
Figure 14 Mechanical properties of the composites curing for 1 min and 15 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composite.[24] In this article, we also recur to the strain–stress curve to evaluate the evolution of networks. Figure 15 compares the strain–stress behavior of composites with various MDMA/NR content cured for 1 min [Fig. 15(a)] and 15 min [Fig. 15(b)]. As shown in Figure 15(a), the composite with 10 phr MDMA displays a very low stress value even until the destruction of the specimen, which indicates no developed network formed. The ionic crosslink density shown in Figure 8 demonstrates that ionic crosslinking has taken place in 1 min. Thus, it is reasonable to suggest that the ionic bands formed in the composite with 10 phr MDMA could not be able to form a developed network to support the high stretch force. When the content of MDMA exceed 20 phr (containing 20 phr), the stress obtains a remarkable enhancement. Observing the curves in Figure 15(a), the stress values increase rapidly in the early stage of the strain development. This is a good support for the forming of ionic crosslinked network. As the curing time goes to 15 min, both the ionic crosslinked network and covalent crosslinked network have been devel-

oped, exhibiting an excellent tensile property, as shown in Figure 15(b).

The nonlinear behavior is evident from the Mooney-Rivlin curve shown in Figure 16, where the reduced $\sigma/2(\lambda - 1/\lambda^2)$ is plotted against the inverse of λ^{-1}. It is observed that the samples cured for 15 min are highly nonlinear systems, whereas the samples cured for 1 min are more linear. Composites with higher MDMA show nonlinear behavior at smaller λ when compared with the composite with low MDMA (10 phr), and this nonlinear behavior increases with increase in MDMA. For small strain (λ^{-1} is 0.8–1), the reduction of $\sigma/2(\lambda - 1/\lambda^2)$ is due to Payne effect.[25–27] $\sigma/2(\lambda - 1/\lambda^2)$ of vulcanizate filled with 20–40 phr MDMA at the low stretch ratios shows an apparent nonlinear behavior, whereas that of 10 phr MDMA shows a weak nonlinear behavior. The nano-poly-MDMA has been verified in many papers by using TEM and SEM.[5,10–12,28] Thus, the higher concentration of MDMA leads to a higher nonlinear behavior. Here, the observed nonlinear behavior of the samples cured for 1 min supports the polymerization of MDMA, which provide the ionic

crosslinks. This also have mentioned in the introduction.[5–9] For large strain (λ^{-1} is 0.4–0.2), increasing of $\sigma/2(\lambda - 1/\lambda^2)$ is due to that the end-to-end distance of the chains tends to its inextensible limit due to the crosslinked network. Curing for 1 min, $\sigma/2(\lambda - 1/\lambda^2)$ showing a line at large λ is a good support of the unformed fundamental covalent crosslinked network (of course some primary covalent crosslinking points may be formed).

CONCLUSIONS

In the first 1 min, the polymerization of MDMA takes place rapidly to develop the ionic crosslinkings, whereas the covalent crosslink backbones of the composites is not formed in this time. The ionic crosslinks, cooperating with some primary covalent crosslinks and some other physical crosslinks, plays an important role in supporting the crosslinked backbone of the composite to bear the external force in this period. Immediately after the first 1 min, it is
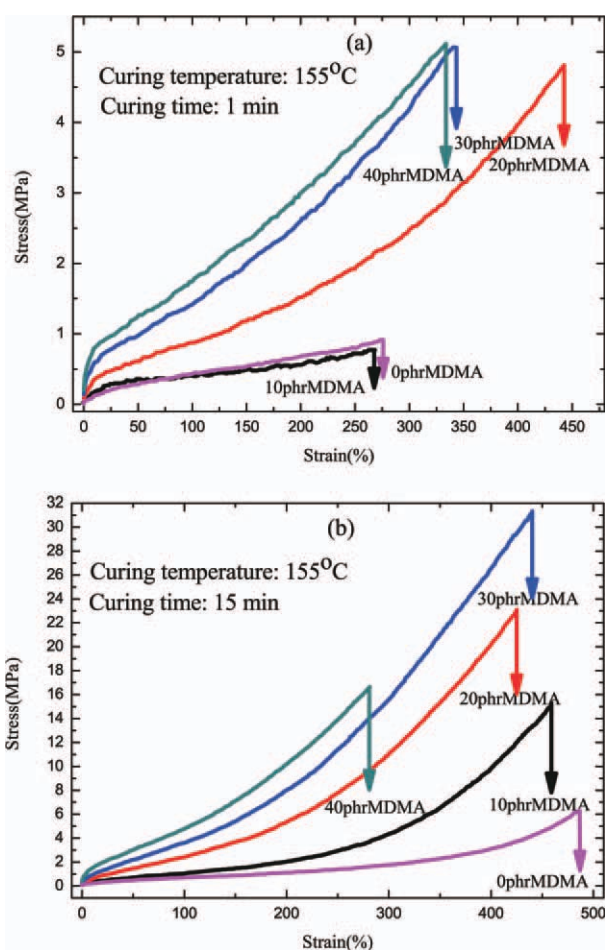

Figure 15 The stress–strain curves of the composite: (a) curing for 1 min and (b) curing for 15 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
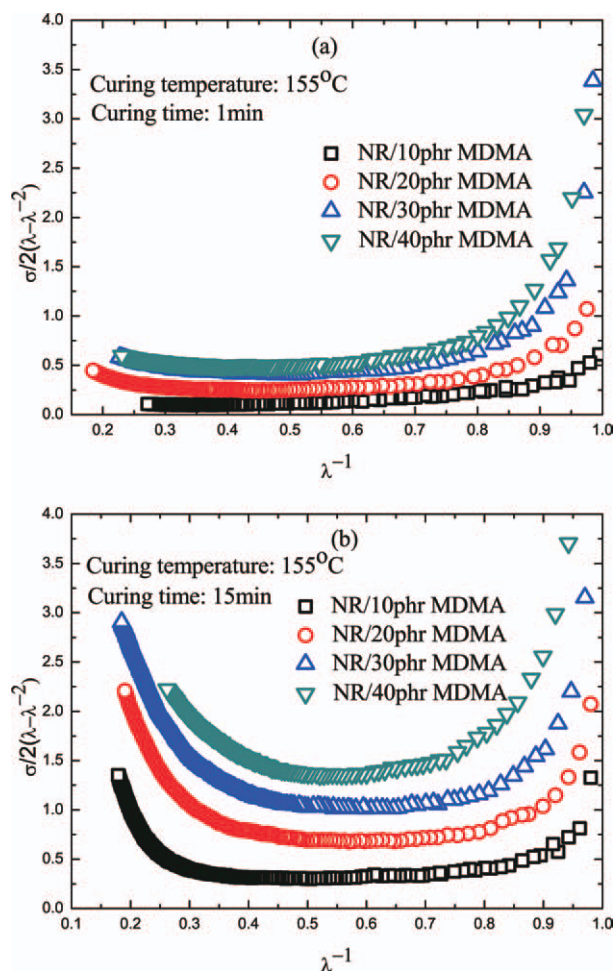
Figure 16 Mooney-Rivlin plot: (a) curing for 1 min and (b) curing for 15 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a fundamental network forming period. In this period, the covalent crosslink and ionic crosslink are both developed quickly, and the vulcanization is mature and a significantly enhanced mechanical property is obtained from the composite. When the curing time exceeds 20 min, the ionic crosslink rupture period appears due to the instability of ionic bond at high temperature. The ionic crosslinks bestow the excellent mechanical properties of the MDMA/NR composites.

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