

Stress Softening of NR Reinforced by *In Situ* Prepared Zinc Dimethacrylate

Yukun Chen,¹ Chuanhui Xu²

¹School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou 510640, China

²College of Material Science and Engineering, South China University of Technology, Guangzhou 510640, China

Received 7 December 2010; accepted 15 March 2011

DOI 10.1002/app.34584

Published online 8 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The stress softening effect of nature rubber (NR) reinforced by *in situ* prepared zinc dimethacrylate (ZDMA) was studied. Degree of stress softening effect (Ds) in the 4th stress–strain cycle of the NR with 10 phr (parts per hundreds of rubber) ZDMA was only 2.23 (strain = 100%), whereas it reached to 59.98 at 50 phr ZDMA (strain = 200%). The stress softening effects of carbon black filled into NR, and compared with the ZDMA effect, was also studied here. Mooney–Rivlin semiempirical equation was introduced here to analysis the stress–

strain behavior of the NR vulcanize filled with *in situ* prepared ZDMA, and the results showed that the ZDMA/NR system has an obvious Payne effect which is in good agreement with the stress softening effect. Crosslink density analysis indicated a high ionic crosslink density in the NR filled with high content ZDMA, which contributed to the low elastic recovery of the stress softening. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 833–841, 2012

Key words: reinforcement; strain; stress; rubber

INTRODUCTION

A variety of studies on unsaturated carboxylates/ elastomers composites have revealed that most elastomers such as butadiene rubber (BR), styrene butadiene rubber (SBR), ethylene–propylene–diene monomer (EPDM), nitrile-butadiene rubber (NBR), and hydrogenated nitrile-butadiene rubber (HNBR) can be reinforced by adding in metallic salt of methacrylate cured by peroxides.^{1–12} When a peroxide is used as a curing agent, the metal salts of unsaturated carboxylic acids will polymerize during rubber vulcanization, including homopolymerization and graft copolymerization simultaneously, forming ionic crosslinks because of the graft copolymerization.^{1,2} The mechanical properties of the vulcanizates are influenced significantly by the ionic crosslinks.¹³ The metal salts of unsaturated carboxylic acids can be added into rubbers directly or prepared *in situ* in rubbers through the neutralization of metal oxides or hydroxides and acids. The *in situ* prepared zinc dimethacrylate (ZDMA) shows a great reinforcing effect on peroxide-cured rubbers in the absence of any conventional reinforcing fillers.^{10,11,13}

Stress softening is a typical phenomenon observable for many materials during cyclic tension tests.

When a given carbon-black filled elastomer is subjected to a load–unload–reload cycle, the stress accompanying a given stretch is always smaller during reloading than that in the virgin loading path. The stress difference between successive loading cycles has the largest value in the first two cycles and becomes negligible after about 6–10 cycles, depending on the amount of filler and maximum extension. Stress softening is particularly evident for vulcanized rubber, where it is known as Mullins effect.^{14–18} This special phenomenon is associated with the rubber network and filler network. Although slight stress softening does occur in unfilled rubbers as well, its mechanism differs fundamentally from that in filled rubbers. Generally speaking, the reinforcing effect of the filler is more pronounced and the stress softening is more remarkable. Thus, stress softening could be seen as an indirect characterization or reflection on reinforcing effect of the filler.

Up to now, most of the researches about *in situ* prepared ZDMA focused on the mechanical reinforcement on BR, NBR, HNBR, SBR, EPDM, etc. There are few publications concerning detail research about stress softening of nature rubber (NR) reinforced by *in situ* prepared ZDMA. It was verified by many experiment that the reinforcement of *in situ* prepared ZDMA filled in NR and cured with dicumyl peroxide (DCP) was related with an ionic crosslink due to the polymerization and graft polymerization of ZDMA occurred under the

Correspondence to: Y. Chen (cyk@scut.edu.cn).

TABLE I
Raw Materials

Materials	Trade name and characteristics	Source
NR	Thailand Ribbed Smoked Sheet No.3 (RSS-33)	Guangzhou rubber industry research institute (Guangzhou, China)
ZnO	Chemical pure	Tianji Yaohua Chem. Co. (Guangzhou, China)
MAA	Chemical pure	Guangzhou Xingang Chemic factory (Guangzhou, China)
CB	N220, Rubber grade	Guangzhou rubber industry research institute (Guangzhou, China)
DCP	Chemical pure	Sinopharm Chemical Reagent Co. (Shanghai, China)

initiation of DCP.¹³ In this article, stress softening of the NR reinforced by *in situ* prepared ZDMA cured with DCP was investigated, and the crosslink density was analyzed with stress softening, which could help to get a clearer understand of the characteristics of the reinforcement of *in situ* prepared ZDMA.

EXPERIMENTAL

Materials and sample preparation

The raw materials used in the study are shown in Table I. DCP was purified by anhydrous alcohol recrystallization before use. Rubber compounds were prepared in a two-roller mill (x(s)-k160, Shanghai rubber machinery no. 1 factory, China) in accordance with ASTM D3182. Zinc oxide (ZnO) and methacrylate acid (MAA) were added into NR and mixed for several minutes. In some cases, after NR/ZnO/MAA was prepared, carbon black (CB) was added according to the formulation. DCP was added at last when all the fillers have been dispersed well. The compounds were sheeted on the two-roller mill and were press-cured to a 2-mm-thick sheet at 155°C for 20 min.

Stress softening

Stress-strain characteristics were carried out by uniaxial tension in accordance with ASTM D412. The stress-strain curves were obtained using dumbbell specimens (6-mm-wide cross section) on a Computerized Tensile Strength Tester (UT-2080) produced by U-CAN Dynatex (Taiwan) with a crosshead speed of 500 mm/min. The specimen was extended to 100% (or 200%) elongation and retraced, then, the operation repeated and stretched again. The fourth operation was performed when the specimen had rested after the first extension for 24 h in the room temperature to ensure full recovery.

Crosslink density

The ASTM D6814 was used as a reference here. The crosslinking density was determined by the equilibrium swelling. After vulcanization, the samples were swollen in toluene at room temperature for 5 days.

The weight of the samples was measured after fully swollen. Then the samples were completely dried under reduced pressure at 80°C for 2 days and reweighed. The volume fraction of rubber swollen in the gel, V_r , which was used to represent the crosslink density of the vulcanizates, was determined by the following equation⁶:

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

where m_0 is the sample mass before swollen, m_1 and m_2 are the swelled sample masses before and after dried, 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 solvent density, respectively. To distinguish ionic crosslinking from covalent crosslinking, the above samples were swollen in a mixture of toluene and chloroacetic acid once again for 5 days to destroy ionic crosslinking, followed by swelling in toluene for 3 days and weighed, then vacuum dried and reweighed. V_{r1} was calculated from eq. (1), which represents the covalent crosslinking density. V_{r2} , which is calculated by subtracting V_{r1} from V_r , was used to represent the ionic crosslinking density.

RESULTS AND DISCUSSION

Stress softening of NR vulcanizate filled with *in situ* prepared ZDMA

Stress softening effect, often discussed in connection with the filler reinforcement, reflecting a kind of viscous loss, can be used to characterize rubber-filler and filler-filler interactions.¹⁴ Theoretically, 1 mol ZnO and 2 mol MAA will react to form ZDMA and water completely. Equivalent ZnO and MAA (ZnO/MAA molar ratio 0.5) was used to neutralize in the NR matrix during mixing. A high degree of conversion to ZDMA from the *in situ* reaction of ZnO and MAA has been verified by many articles,^{10,11} and the neutralization here is assumed to be reacted completely to form ZDMA. Figures 1(a-d) and 2(a-d) show the stress-softening behavior of the NR gum vulcanizate and NR vulcanizates filled with 10 phr, 30 phr and 50 phr *in situ* prepared ZDMA at

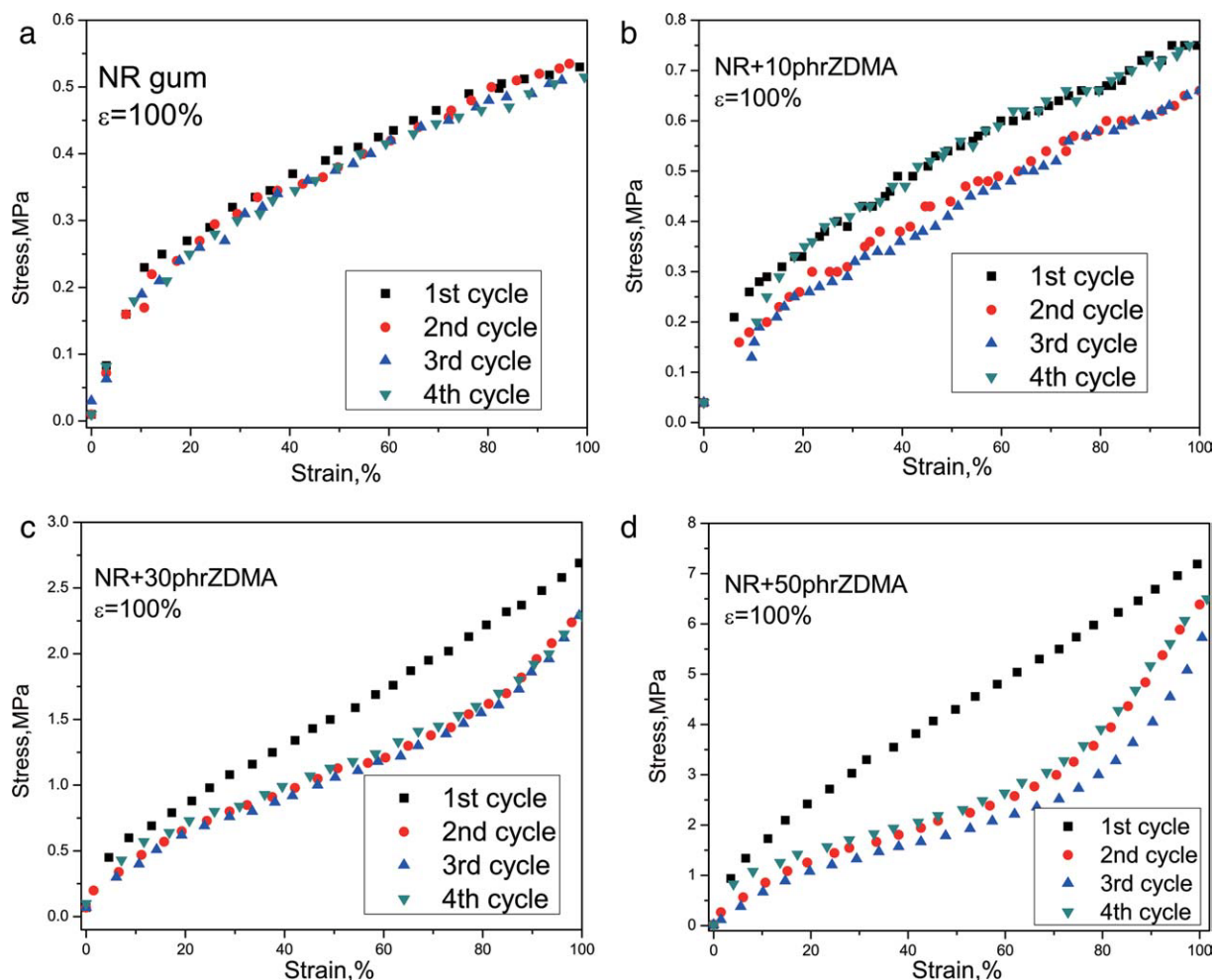


Figure 1 Stress–strain curves at 100% strain of the ZDMA-reinforced NR. (a) Pure NR; (b) *in situ* ZDMA 10 phr; (c) *in situ* ZDMA 30 phr; (d) *in situ* ZDMA 50 phr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

100% strain and 200% strain, respectively. As shown in Figures 1 and 2, the stress softening degree of NR gum [Figs. 1(a) and 2(a)] is lower than that of filled vulcanizates [Figs. 1(b–d) and 2(b–d)], and the stress increases with increasing the content of ZDMA at a fixed strain. The stress increases greatly at a high content of ZDMA (50 phr) and a higher strain (200%) which could be seen as a great reinforcement of the NR filled with *in situ* prepared ZDMA. A similar behavior of the stress–strain characteristics at both 100% strain and 200% strain can be found that the second tension stress decreased for NR/ZDMA samples as compared with the first tension stress and the third tension stress is lower than the second one. But the fourth tension–stress curve (of the sample after the first extension for 24 h in the room temperature) shows an interesting behavior that it positions nearby the second one both at 100% strain and 200% strain with different ZDMA contents, except the one at 100% strain with 10 phr ZDMA. As shown in Figure 1(b), the fourth tension–stress curve

is recovered close to the first tension stress curve. This interesting phenomenon will be discussed later.

To illustrate more intuitively the difference of stress softening with different amount of *in situ* prepared ZDMA, the degree of stress softening effect (D_s) can be expressed as following^{12,19}:

$$D_s = \frac{w_1(\varepsilon) - w_i(\varepsilon)}{w_1(\varepsilon)} \times 100, \quad (2)$$

where W_1 is the strain energy needed in the first stretch and W_i is the strain energy needed in the no. i stretch. The variations of the D_s of the NR vulcanizates reinforced with different amount of ZDMA during stress softening at 100% strain and 200% strain are shown in Table II. The degree of stress softening at high strain is higher than that at low strain with the same content of ZDMA. The D_s of NR gum is only 3.45 at the third stretch which shows a slight stress softening. The D_s of filled samples has a recover after 24 h in the room temperature. There are several

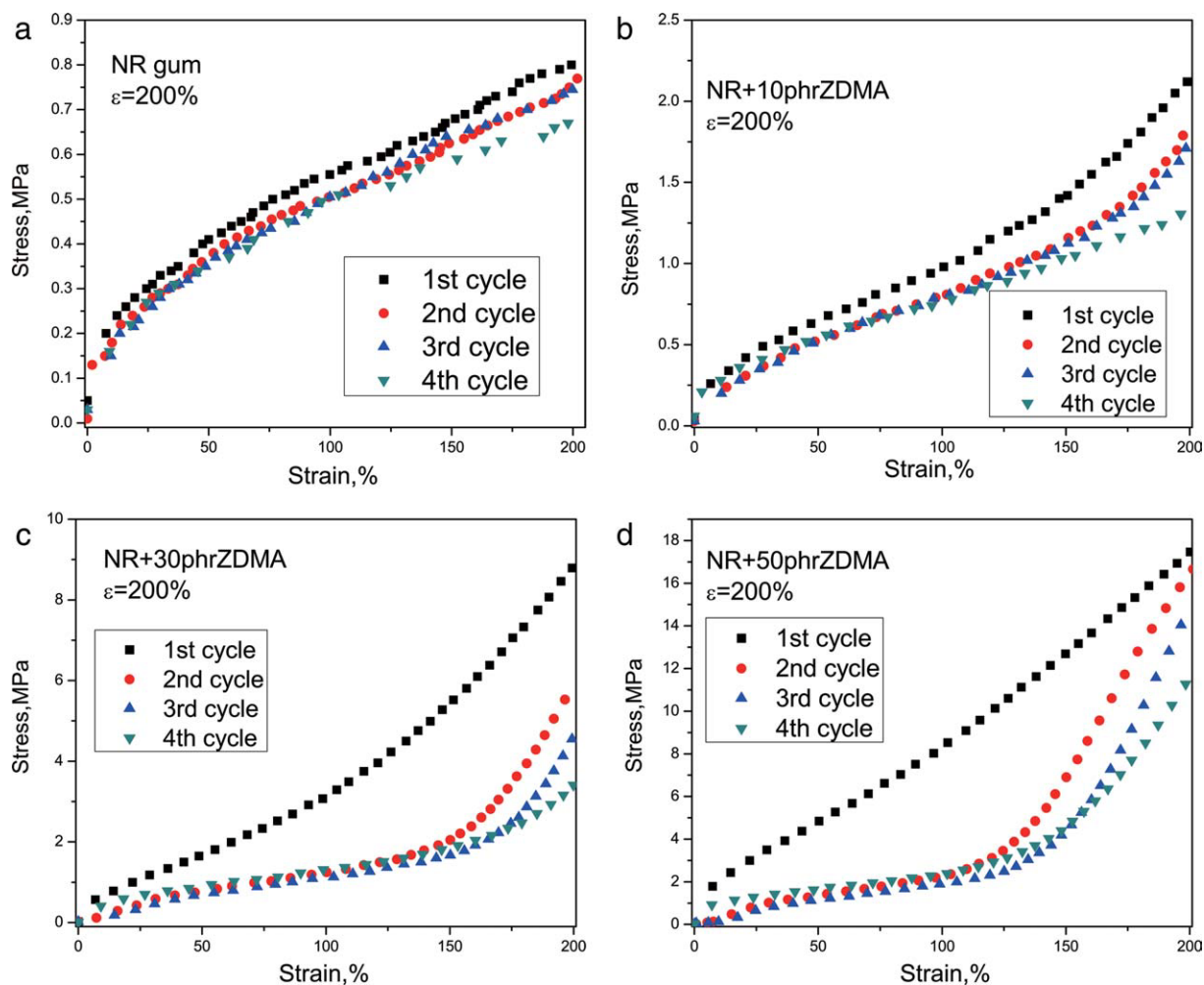


Figure 2 Stress–strain curves at 200% strain of the ZDMA-reinforced NR. (a) Pure NR; (b) *in situ* ZDMA 10 phr; (c) *in situ* ZDMA 30 phr; (d) *in situ* ZDMA 50 phr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interesting data shown in Table II: 21.43 and 2.23 (NR + 10 phrZ, 100% strain), 62.21 and 61.29 (NR + 30 phrZ, 200% strain), 61.55 and 59.98 (NR + 50 phrZ, 200% strain). These different stress softening behaviors could be related to the filler–filler and filler–rubber micro-interactions. When the composite was stretched, there were some sources of damage including debonding and recreation of crosslinks, slippage and chain breakage. All these micro-interac-

tions contributed to the specific reinforcing mechanism: homopolymerization and graft polymerization of ZDMA during vulcanizing. DCP initiated the homopolymerization and graft polymerization of ZDMA, thus the filler in NR vulcanizate was poly-ZDMA, and the resulting graft copolymer might play the role of compatibilization of poly-ZDMA and NR and enhanced interaction between poly-ZDMA and NR molecular to form the salt bonds.¹³

TABLE II
Degree of Stress-Softening (D_s) of NR Vulcanizate with Different Content of ZDMA at 100% and 200% strain

	D_s (strain = 100%)		D_s (strain = 200%)	
	3rd cycle	After 24 h	3rd cycle	After 24 h
NR	3.45	5.28	9.86	13.23
NR + 10 phr ZDMA	21.43	2.23	21.58	25.12
NR + 30 phr ZDMA	27.18	25.71	62.21	61.29
NR + 50 phr ZDMA	51.02	43.11	61.55	59.98

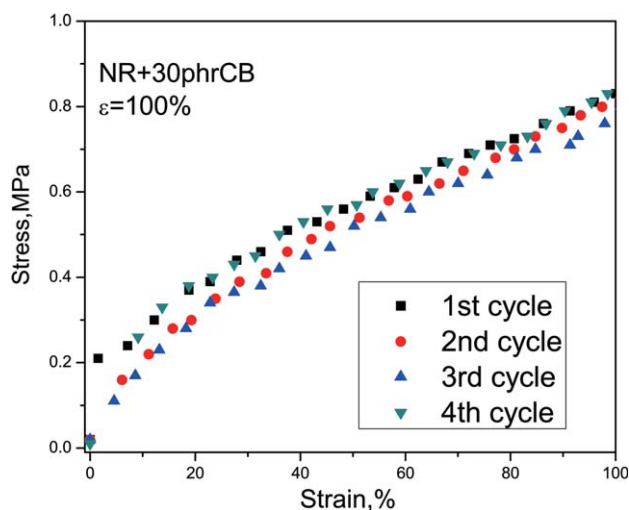


Figure 3 Stress–strain curves of CB reinforced NR at 100% strain. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Stress softening of NR vulcanizate filled with CB at a fixed content

With different fillers, the network could be formed in different ways which would respond differently to stress softening. To get a more clear understanding of the stress softening of NR reinforced with *in situ* prepared ZDMA, CB was also used to fill into the NR, and compared the reinforcing effects of CB with that of ZDMA. The content of filler was fixed at 30 phr. The stress-softening curves of NR/CB at 100% strain and 200% strain are shown in Figures 3 and 4, respectively. The D_s of vulcanizates is listed in Table III. Comparing the tension stress curves for different fillers at 30 phr, it can be seen that the reinforcing effect is ZDMA > CB. Corresponding, Table

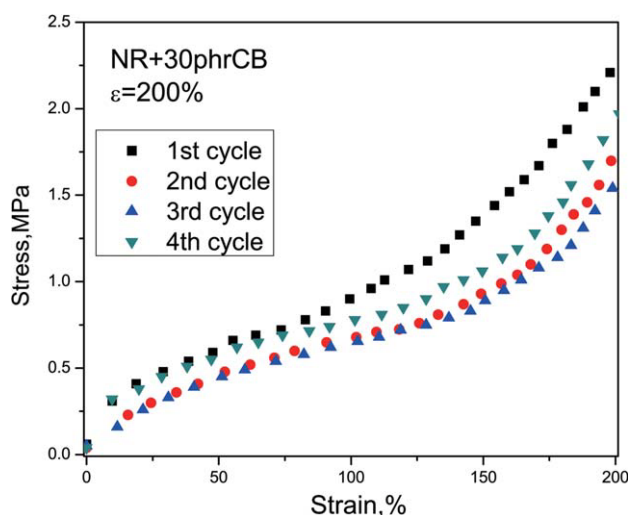


Figure 4 Stress–strain curves of CB reinforced NR at 200% strain. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Degree of Stress-Softening (D_s) of CB Reinforced NR at 100% strain and 200% strain

	D_s (strain = 100%)		D_s (strain = 200%)	
	3rd cycle	After 24 h	3rd cycle	After 24 h
NR + 30 phr CB	14.20	0.43	32.47	14.48

III shows that the D_s of the sample is also ZDMA > CB. In the situation of CB, the D_s of the fourth stretch at 100% strain is very low which shows a good elastic recovery of stress softening, and the D_s is higher at 200% strain as compared with 100% strain. On the contrary, D_s of the fourth stretch in the situation of ZDMA shows a bad elastic recovery. Obviously, the stress softening mechanism of ZDMA differs from that of CB.

In the situation of CB as fillers, a set of NR chains sat between two aggregates and bounded to their active sites through the adsorption effect. These NR chains generally represent a part of longer NR chains. In the course of deformation, the NR chains began to slide on or be debonded from the aggregates' surface. This debonding started with the shortest chain and gradually involved longer and longer chains. The strength of monomer bonds within NR chains was far higher than that of NR–filler bonds. Thus, even at larger strains NR chains did not break but rather slid from their bonding sites on the aggregate surface.¹⁵ During consequent unloading, the debonded chains reattached back to the aggregates surface to rebuild the initial network. Thus, the stress softening could be described as the rubber–filler debonding or the destruction of the filler–rubber network on certain level. The physical adsorption of NR chains on CB aggregates was dynamic and could be rebuilt after a long time of relaxation or upon heat treatment. Therefore, after 24 h in the room temperature, the tension stress recovered to near the first tension stress, and the D_s was very low.

In the situation of ZDMA as fillers, as mentioned before, the peroxides initiated the polymerization of ZDMA (both homopolymerization and graft polymerization).^{6–13} As a result, there were three types of ZDMA components in the vulcanizate: homopolymer of poly-ZDMA, grafted poly-ZDMA, and residual monomeric ZDMA. Thus, the vulcanizates contained both covalent crosslink and ionic crosslink and the slippage of ionic bonds was a normal behavior under the effect of stress. When a sample was stretched, the covalent crosslink network and ionic crosslink network deformed, and some debonded like in the situations of CB, but lots of ionic bonds slipped and broke, specifically at a high content of

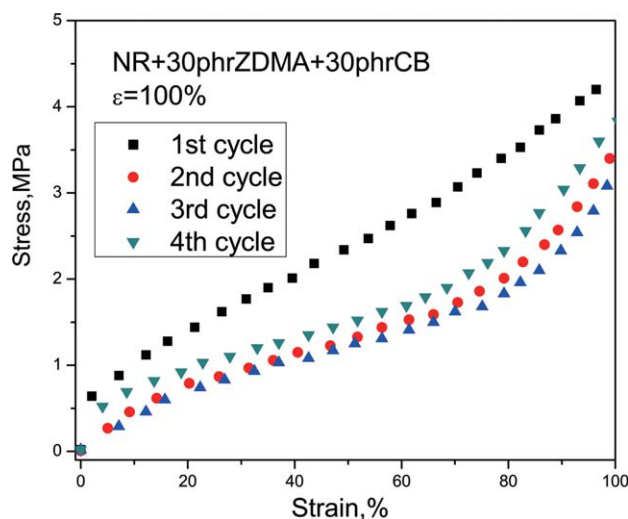


Figure 5 Stress–strain curves at 100% strain of ZDMA/CB reinforced NR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ZDMA. At the same time, a new ionic crosslink might form rapidly. Once the stress was relieved, the slippage of ionic bonds ceased, thus the elastic recovery was very low, and the D_s of the forth was very close to that of the third.¹²

In situ prepared ZDMA cooperated with CB

Stress softening of *in situ* prepared ZDMA cooperated with CB as reinforcing filler filled in NR vulcanizate was also investigated, with a fixed filler content of 30 phr. The stress–strain curves are shown in Figure 5 (100% strain) and Figure 6 (200% strain). D_s of the vulcanizates shown in Table IV indicates a clear contrast. Compared Table IV with Table III, the D_s of cooperated fillers in the 3rd cycle show a greatly enhancement but elastic recovery of the forth stretch is weaker than the situation using BC singly.

In the situation of ZDMA/CB as fillers, there were two stress softening mechanisms: (1) thermal motion of molecule, adsorption and desorption^{15,19}(CB) and (2) exchange reaction of ionic bonds (ZDMA). Both the two mechanisms functioned at the same time during the load–unload–reload cycle. Unfortunately, they maybe affect each other. During the resting period in the room temperature after the third extension for the CB sample, the distance which was stretched between aggregates decreased again due to thermal motion of molecule, and the NR segments which detached from CB aggregates adsorbed again to the active sites of the aggregates. However, for ZDMA, new ionic bonds had formed a new ionic crosslink network which prevented the recovery. The dispersed CB also handicapped the formation of new ionic crosslink network. As a result, the curve of the forth stretch was in

between the first and second stretch curves, D_s of the forth stretch showed a recovery in a certain degree but maintained more softening.

Discussion of tensile deformation of *in situ* ZDMA reinforced NR

Many researchers have studied the stress softening behavior of filled rubber and agree that the stress softening behavior was related to the interaction of filler and rubber molecules.^{15–22} When a filler rubber is stretched, crosslink network will deforms, and the elongation of the rubber molecular chains between filler particles will be restricted by the interaction of filler and rubber molecules. During consequent unloading process, the distance between aggregates again decreases. During the stretching, this force is enhanced greatly as the end-to-end distance of the chains tends to its inextensibility limit. The strength of monomer bonds within polymer chains is far higher than that of polymer–filler bonds. Thus, even at large strains the polymer chains do not break but rather slide from their bonding sites on the aggregate surface and then “desorption” occurs. The above analysis can be conducted by phenomenological Mooney–Rivlin²² theory which provides a semi-empirical equation:

$$\frac{\sigma}{\lambda - 1/\lambda^2} = 2C_1 + 2C_2\lambda^{-1}, \quad (3)$$

λ is the principal stretch ratios, σ is the stress, and C_1 and C_2 are constants.

As shown in Figure 7, relationship of $\sigma/2(\lambda - 1/\lambda^2)$ and λ^{-1} is different between NR and ZDMA-filled NR with high filler content. $\sigma/2(\lambda - 1/\lambda^2)$ of

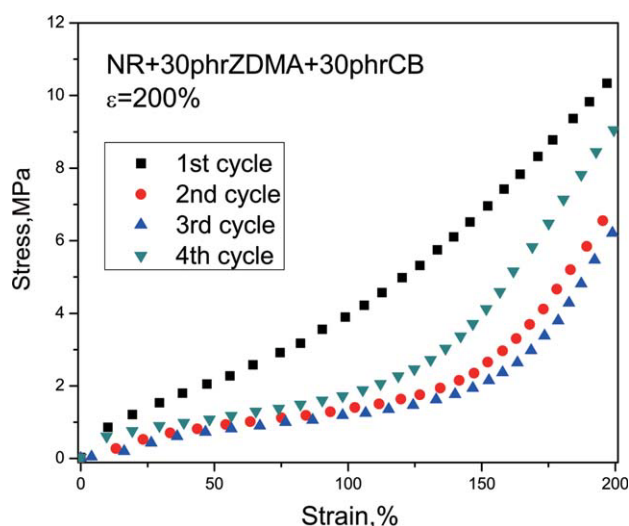


Figure 6 Stress–strain curves at 200% strain of ZDMA/CB reinforced NR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
Degree of Stress-Softening (Ds) of ZDMA/CB Reinforced NR at 100% strain and 200% strain

	Ds (strain = 100%)		Ds (strain = 200%)	
	3rd cycle	After 24 h	3rd cycle	After 24 h
NR + 30 phr ZDMA + 30 phr CB	44.51	31.88	61.10	35.97

vulcanizates increases with the increasing of ZDMA content. $\sigma/2(\lambda - 1/\lambda^2)$ of vulcanizates filled with 30 phr or 50 phr *in situ* prepared ZDMA decreases with increasing the stretch ratios at first and then increases at a high stretch ratios. The decreasing of $\sigma/2(\lambda - 1/\lambda^2)$ at low stretch ratios is more obviously at a high content of ZDMA (50 phr). Many researchers proposed that this interesting behavior reflects two additional effects²⁴: (1) for low strain (λ^{-1} is 0.7–0.9), the reduction of $\sigma/2(\lambda - 1/\lambda^2)$ was due to Payne effect. For filled rubber, there was always a difference in the surface energy between filler and rubber, so that even for a system in which the filler was well uniformly dispersed in rubber matrix, the aggregates would inexorably tend to flocculate during storage and vulcanization of the compound forming a filler network. Exerted a strain, the initial network of filled rubber would deform. The breakdown of the filler network by increasing strain would cause the decrease of modulus. $\sigma/2(\lambda - 1/\lambda^2)$ of vulcanizate filled with 30 phr or 50 phr *in situ* prepared ZDMA decreased at the low stretch ratios showed a obvious Payne effect, whereas that of 10 phr ZDMA was much similar to the neat NR which was a line showing no Payne effect, corresponding to the Ds (2.23).

(2) For high strain (λ^{-1} is 0.5–0.3), increasing of $\sigma/2(\lambda - 1/\lambda^2)$ was due to that the end-to-end distance of the chains tends to its inextensibility limit. The upturning tendency of the curve increased with increasing content of ZDMA which meant there was a strong restriction of the NR molecular chains by filler particles at a high content of ZDMA. Thus, a strong interaction between filler and rubber showed a good reinforcement of high content ZDMA. When the vulcanizate was stretched to a certain strain, more rubber chains were getting to inextensibility limit because more short rubber molecular chains were restricted between fillers, then, a high stress softening behavior occurred.

Stretching to 100% strain and 200% strain at different cycles of a NR filled with a high content of 50 phr of *in situ* prepared ZDMA was also dealt with Mooney–Rivlin semiempirical equation as shown in Figure 8. The reduction of $\sigma/2(\lambda - 1/\lambda^2)$ of the first stretch at 200% strain is the most significant, whereas the fourth stretch at 200% strain shows a weak Payne effect and the third stretch at 200% strain shows no Payne effect. This means that the third stretch had reached the stable stretch and the filler network of the sample rested for 24 h had recovered a little. High content of ZDMA provided

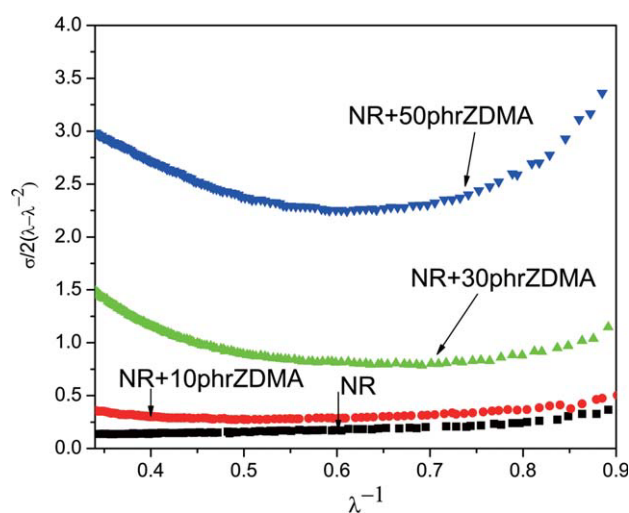


Figure 7 Relationship of $\sigma/2(\lambda - 1/\lambda^2)$ and λ^{-1} at different content of *in situ* ZDMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

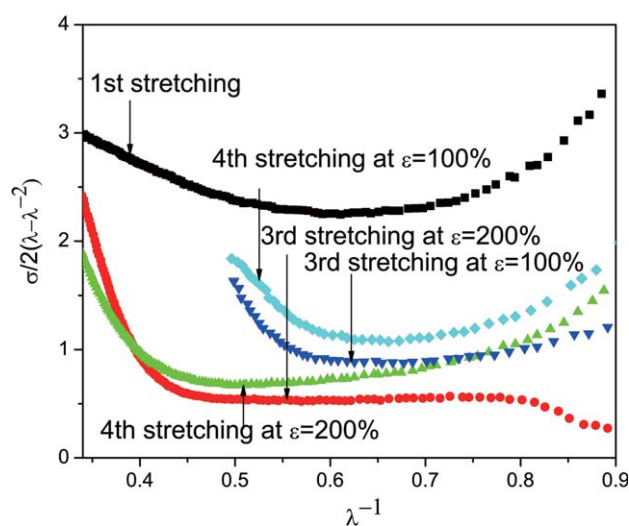


Figure 8 Relationship of $\sigma/2(\lambda - 1/\lambda^2)$ and λ^{-1} at 50 phr *in situ* ZDMA of various degree and deformation of tensile. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

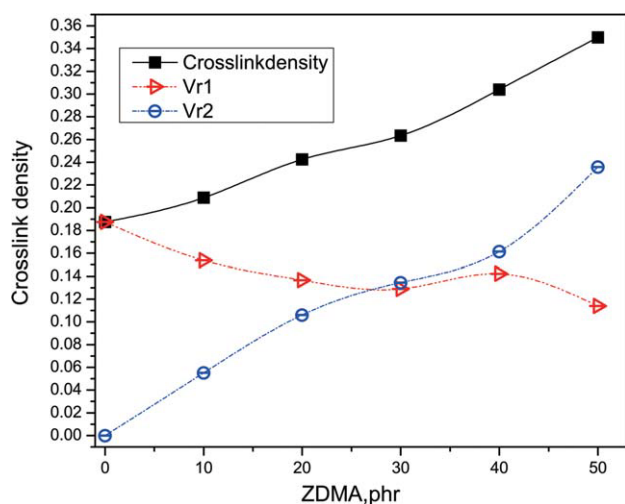


Figure 9 Effect of *in situ* ZDMA content on crosslink density of vulcanizates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

more ionic bonds and more developed ionic network. When the sample was stress to a high strain, more ionic crosslinks were broken and new ionic crosslinks formed which prevent the recovery of initial filler network. So, Payne effect of forth stretch was low, and D_s was high.

However, as Figure 8 shows, the destruction of filler network at 100% strain was slighter as compared with that at higher strain. Low strain may have less influence on the ionic crosslink network, thus the Payne effect of the forth stretch have a better recovery, and the D_s showed a lower value.

Crosslink density analysis of NR vulcanizate filled with *in situ* prepared ZDMA

Figure 9 shows the crosslink density of the vulcanizate with different amount of ZDMA. It can be seen that the total crosslink density (V_r) and the ionic crosslink density (V_{r1}) increased with increasing ZDMA content. On the contrary, the covalent crosslink density (V_{r2}) decreased. Figure 10 gives a clearer illustration of the relationship between the ionic crosslink density, V_{r1} , and the covalent crosslink density, V_{r2} . With increasing ZDMA content, V_{r2}/V_r increased, whereas V_{r1}/V_r reduced. V_{r2}/V_r is lower than V_{r1}/V_r at a low ZDMA content. However, the reverse occurs at a high ZDMA content with a crossover point of around 30 phr in this particular system.

As mentioned before, the forth tension stress was recovered very close to the first tension stress and the D_s was only 2.23 at 100% strain with a content of 10 phr ZDMA and 59.98 at 200% strain with content of 50 phr ZDMA. Combined the stress softening analysis, the V_{r2} is only 0.06 at 10 phr ZDMA,

whereas it reaches to a high value of 0.23 at 50 phr ZDMA, and, the V_r at 10 phr ZDMA (0.21) is very close to the pure rubber, whereas it reaches nearly 0.35 at 50 phr ZDMA. As the sample of 10 phr ZDMA was stretched at a low strain (100%), there were very few ionic bonds to form ionic crosslink network because of the very little content of filler, thus the stress-strain behavior was like as the gum rubber. When the content of ZDMA was increased to 50 phr, the ionic crosslink was dominant in the vulcanizate and the total crosslink density was also high. Then, a more developed ionic crosslink network was formed. As the sample of 50 phr ZDMA was stretched at a higher strain (200%), more ionic bonds were broken and at the same time new ionic bonds were formed. As a result, a new ionic crosslink network was developed which was able to adapt to the new stress. Thus, the D_s of the forth stretch was maintained at a high value closed to the third one.

CONCLUSIONS

1. NR vulcanizate reinforced by *in situ* prepared ZDMA as filler has pronounced stress softening which shows the good reinforcement of ZDMA.
2. The softening mechanism in the system with ZDMA filler is different from that with CB filler. The stress softening of NR filled with ZDMA is attributed to the exchange reaction of ionic bonds under the effect of stress. The slippage of ionic bonds for vulcanizate is ascribed to the breaking of ionic bonds under stress and

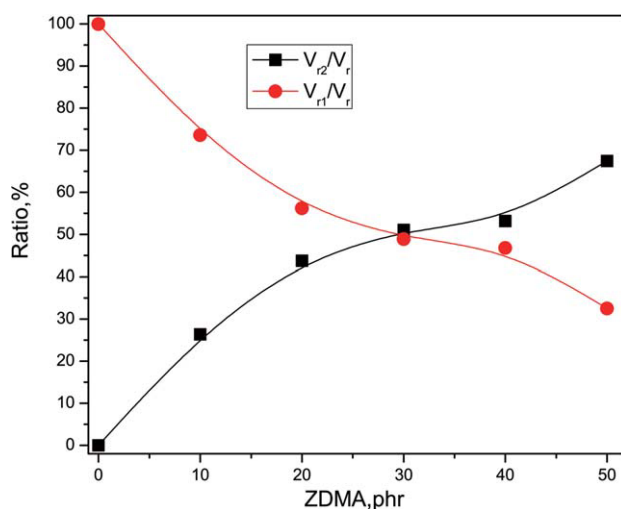


Figure 10 Effect of *in situ* ZDMA content on ratio of crosslink densities of vulcanizates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

forming new ionic crosslink during consequent unloading.

- From the crosslink density analysis and Mooney–Rivlin analysis, the higher content of ZDMA filled, the higher ionic density induced, thus a network with more developed ionic crosslink formed, resulting in a more pronounced Payne effect and a more obvious stress softening effect.

References

- Nomura, A.; Takano, J.; Toyoda, A.; Saito, T. *Jpn Rubber Soc* 1993, 66, 830.
- Saito, Y.; Nishimura, K.; Asada, M.; Toyoda, A. *J Jpn Rubber Soc* 1994, 67, 867.
- Horiuchi, K.; Hamada, A. *Eur. Pat.* 0,582,487 (1994).
- Granatowicz, D. S.; Morris, M. T.; Pilkington, M. V.; Tompkin, G. R. *Eur. Pat.* 0,864,607 (1998).
- Yamamoto, K.; Ikeda, K.; Koshiba, J. *Eur. Pat.* 0,589,701 (1994).
- Gao, G. X.; Zhang, Z. C.; Zheng, Y. S.; Jin, Z. H. *J Appl Polym Sci* 2009, 113, 3901.
- Yin, D.; Zhang, Y.; Zhang, Y.; Peng, Z.; Fan, Y.; Sun, K. *J Appl Polym Sci* 2002, 85, 2667.
- Yin, D.; Zhang, Y.; Peng, Z.; Zhang, Y. *Eur Polym Mater* 2003, 39, 99.
- Lu, Y. L.; Liu, L.; Yang, C.; Tian, M.; Zhang, L. Q. *Eur Polym Mater* 2005, 41, 577.
- Peng, Z.; Liang, X.; Zhang, Y.; Zhang, Y. *J Appl Polym Sci* 2002, 84, 1339.
- Lu, Y. L.; Liu, L.; Shen, D. Y.; Yang, C.; Zhang, L. Q. *Soc Chem Ind* 2004, 53, 802.
- Du, A.; Peng, Z.; Zhang, Y.; Zhang, Y. *J Appl Polym Sci* 2003, 89, 2192.
- Nie, Y. J.; Huang, G. S.; Qu, L. L.; Zhang, P.; Weng, G. S.; Wu, J. R. *J Appl Polym Sci* 2010, 115, 99.
- Bueche, F. *J Appl Polym Sci* 1960, 10, 107.
- Roosbeh, D.; Mikhail, I. *Int J Solids Struct* 2009, 46, 2967.
- Guo, Z.; Sluys, L. J. *Eur J Mech A/Solid* 2006, 25, 877.
- Yoshihide, F. *J Appl Polym Sci* 2005, 95, 60.
- Dorfmann, A. *AMS* 2003, 165, 117.
- Mullins, L. *Rubber Chem Technol* 1969, 42, 339.
- Schlegel, R.; Wilkin, D.; Duan, Y.; Weidisch, R.; Heinrich, G.; Uhrig, D.; Mays, J. W.; Iatrou, H.; Hadjichristidis, N. *Polymer* 2009, 50, 6297.
- Mooney, M. *J Appl Phys* 1940, 11, 582.
- Rivlin, R. S. *Philos Trans R Soc Lond Ser A* 1948, 241, 379.
- Mullins, L.; Tobin, N. R. *J Appl Polym Sci* 1965, 9, 2993.
- Julie, D.; Bruno, F.; Pierre, G. *Eur Polym Mater* 2009, 45, 601.