

Thermal Aging on Mechanical Properties and Crosslinked Network of Natural Rubber/Zinc Dimethacrylate Composites

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ABSTRACT: This article dealt with the relationship between mechanical properties and crosslinked networks of natural rubber (NR) reinforced by zinc dimethacrylate (ZDMA) after thermal aging. After thermal aging at the present experimental conditions, the covalent crosslink density showed a decrease all the time, whereas the ionic crosslink density was stable at 80°C but decreased at a higher temperature. The decrease in the total crosslink density after aging indicates the degradation of the cross-

linked network. However, an experimental phenomenon observed was that the tensile strength and tear strength increased in a certain degree after aging at 80°C or at a 100°C for a short time. In addition, the thermal stability of the NR/ZDMA composite was evaluated by thermal gravimetric analysis. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2240–2249, 2012

Key words: mechanical properties; crosslinking; aging; rubber

INTRODUCTION

Metal salts of unsaturated carboxylic acids such as zinc dimethacrylate (ZDMA) have been found to act as effective reinforcing additives for rubbers. Their dramatic reinforcement has attracted the significant interest of researchers. Metal salts of unsaturated carboxylic acids can be added into rubbers directly or prepared *in situ* through the neutralization of metal oxides and acids.^{1,2} Many kinds of rubbers could be reinforced by metal salts of methacrylic acids such as NR, butadiene rubber, ethylene–propylene–diene monomer, nitrile-butadiene rubber, and poly (a-octylene-co-ethylene) elastomer.^{3–11}

As new type of effective reinforcing additives, many studies about them have been reported, such as the mechanical properties, the course of the polymerization, the morphology, the mechanism for the reinforcement, the crosslinked structure, and so on. Rubbers reinforced with this kind of reinforcing agents have high tensile strength, tear strength, and modulus, while still keep a high elongation at break.⁸ When peroxide was used as a curing agent, the metal salts of unsaturated carboxylic acids will be polymerized during rubber vulcanization no matter in homo-polymerization or graft-polymerization simultaneously. The ionic bond crosslinkings were formed due to the

graft-polymerization of metal salts onto the rubber chains, while the poly-(metal salt) chains separate from the rubber matrix and aggregate into nano-scaled fine particles, forming salt crosslinkings.^{6,12–16} The fine particles with diameters of 20–30 nm were found to disperse in rubber matrix.¹⁴ This structure originated from the polymerization of metal salts in rubber is the reason of the reinforcement.^{13,16}

However, there are still many aspects need to be studied to complete this new type of effective reinforcing additives system. For example, the aging properties of the composites and thermal stability are seldom reported. In this work, we aimed to investigate the mechanical properties and cross-linked structure of NR reinforced by *in situ* prepared ZDMA after aging without any rubber antioxidant and the thermal stability of the resulting peroxide-cured vulcanizates, and to explore the application of *in situ* prepared metal salts of unsaturated carboxylic acid reinforcing rubbers in thermal aspect.

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. Zinc oxide (ZnO) was purchased from Tianji Yaohua Chem.

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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 ZDMA. Theoretically, 1 mol ZnO and 2 mol MAA 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.^{9,11} The compounds containing 100 weight parts of NR, 1.5 phr (parts per 100 parts of rubber) DCP and 0–80 phr ZDMA. Rubber compounds were prepared in a two-roller mill (x(s)-k160, Shanghai rubber machinery no. 1 factory, China) in accordance with ASTM D3182. ZnO and MAA were added into NR and mixed for several minutes. DCP was added at last. The compounds were sheeted on the two-roller mill and were pressured to a 2-mm-thick sheet at 155°C.

Thermal aging

Thermal aging studies were carried out in a laboratory-type oven (Electro-mag with sensitivity of $\pm 1^\circ\text{C}$) according to ASTM D573. The samples were kept at 80, 100, and 120°C for 24 h, respectively. Another thermal aging study was that the samples were exposed to 100°C for different periods of time up to 96 h. After aging, the samples were taken out of the oven and tested for mechanical properties.

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 cross-head speed of 500 mm/min. Shore A hardness was determined as the conditions given in ASTM-D2240.

Crosslink density

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 (one vial for each sample). These measurements ensure that swelling equilibrium is reached, and the sample degradation is minimized by protecting it from the environment light.¹⁷ 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:

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

where m_0 is the sample mass before swelling, m_1 and m_2 are the swelled sample masses 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 swelling, and ρ_r and ρ_s are the rubber and toluene density ($\rho_s = 0.865 \text{ g/cm}^3$), respectively.

To distinguish ionic crosslinkings from covalent crosslinkings, the above samples were swollen in a mixture of toluene and chloroacetic acid once again for 120 h to destroy ionic crosslink, 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 is calculated by subtracting V_{r1} from V_r , was used to represent the ionic crosslink density.¹⁶

Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) was performed on TGA Q5000 (TA Instrument, America). About 10 mg of sample cut as small pieces was heated in an Al_2O_3 crucible in nitrogen atmosphere from ambient temperature to 580°C at a constant rise of temperature (20°C/min).

RESULTS AND DISCUSSION

The relation of tensile stress and crosslink density

Figure 1 presents the mechanical properties of NR/ZDMA vulcanizates cured by DCP. The *in situ* formed ZDMA shows a remarkable reinforcement for NR. The tensile strength at break depending on ZDMA content shows a maximum value of 27 MPa, whereas NR gum gives 9 MPa. The tear strength and hardness increase gradually with increasing ZDMA content from 17 KN m^{-1} and 32 of NR gum to 53 KN m^{-1} and 69 at 40 phr ZDMA, respectively. Although the elongation at break decreases rapidly, it is still over 390%, even the ZDMA content is as much as 40 phr.

In this particular composite, such significant mechanical properties are related to the complex crosslinked network due to poly-ZDMA. The *in situ* free radical polymerization of ZDMA monomers

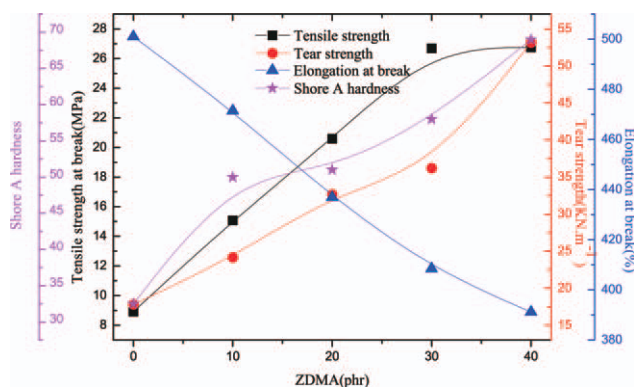


Figure 1 Effect of ZDMA amount on the mechanical properties of NR/ZDMA vulcanizates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

diffused in the NR matrix during compounding took place in the peroxide curing process, and the formed poly-ZDMA aggregated to form nanodispersion.^{5,6} In this process, the ZDMA grafted to NR molecule in presence of free radical because of the unsaturated bond. As a result, a more complex network (contain ionic crosslink and covalent crosslink) formed, which enhanced the mechanical properties of the vulcanizate.¹⁶

The crosslink density of the vulcanizate with different amount of ZDMA is given in Figure 2. The total crosslink density (V_r) and the ionic crosslink density (V_{r2}) increase with increasing ZDMA content, whereas the covalent crosslink density (V_{r1}) shows a slightly decrease. Perhaps, a more developed ionic crosslink network is formed at 40 phr ZDMA result in good mechanical properties. Thus, comparing the mechanical properties and crosslink density, it is easy to find out the ionic crosslink network plays an important effect on the reinforcement of the composite.

Evaluation of mechanical properties aging at different temperatures for 24 h

The changes of tensile strength, elongation at break, tear strength, and hardness upon different aging temperatures are shown in Figure 3. The mechanical properties of vulcanizates show severe drops after aging at 120°C for 24 h; this indicates that the NR/ZDMA vulcanizates own a bad aging resistance at such a high temperature.

An experimental phenomenon can be observed is that some properties such as tensile strength and tear strength show an increase for 10–30 phr ZDMA but decrease at a higher ZDMA content (40 phr) after aging at 80°C for 24 h, see Figure 3(a,c). The increase of tensile strength after aging investigated from our experiment is similar to the report by Yin et al.¹⁸; they found out that tensile strength increased

for low content of magnesium methacrylate but decreased at higher contents. Other properties such as elongation at break and hardness show a good retention of the original properties. These results reveal that NR/ZDMA vulcanizates have a good aging resistance at 80°C.

In the case of aging at 100°C for 24 h, the aging resistance is between that at 80°C and 120°C. As shown in Figure 3, the mechanical properties of NR gum reveal the poor aging resistance in terms of decreasing the original properties after aging at 100°C. After adding ZDMA, the NR/ZDMA composites obtain a considerable aging resistance except the NR/40 phr ZDMA. This conclusion can be supported from tensile strength of 10 phr and 20 phr ZDMA [Fig. 3(a)], elongation at break [Fig. 3(b)], tear strength of 10–30 phr ZDMA [Fig. 3(c)], and hardness [Fig. 3(d)]. However, the mechanical properties of 40 phr ZDMA worsen after aging at different temperatures. The retention values of mechanical properties upon different aging temperatures are also given in Tables I–IV.

Evaluation of crosslinked network aging at different temperatures

The mechanical properties of the vulcanizates have been shown a significant variation after aging. The higher aging temperature results in worse mechanical properties. As mentioned before, the crosslinked structure of the NR/ZDMA composite is complex and differs to that of NR reinforced by conventional filler. The crosslinkings contain not only the covalent crosslinking but also the ionic crosslinking. What is happened about the crosslinked structure after aging? Is the crosslinked network enhanced after aging due to the increase of some mechanical

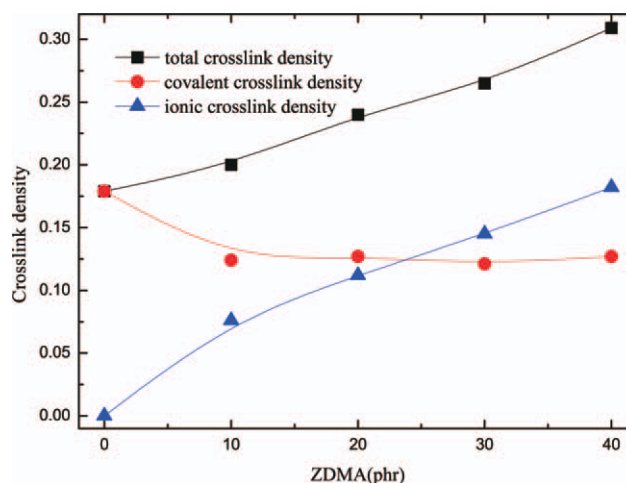


Figure 2 Effect of ZDMA content on crosslink density of NR/ZDMA vulcanizates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

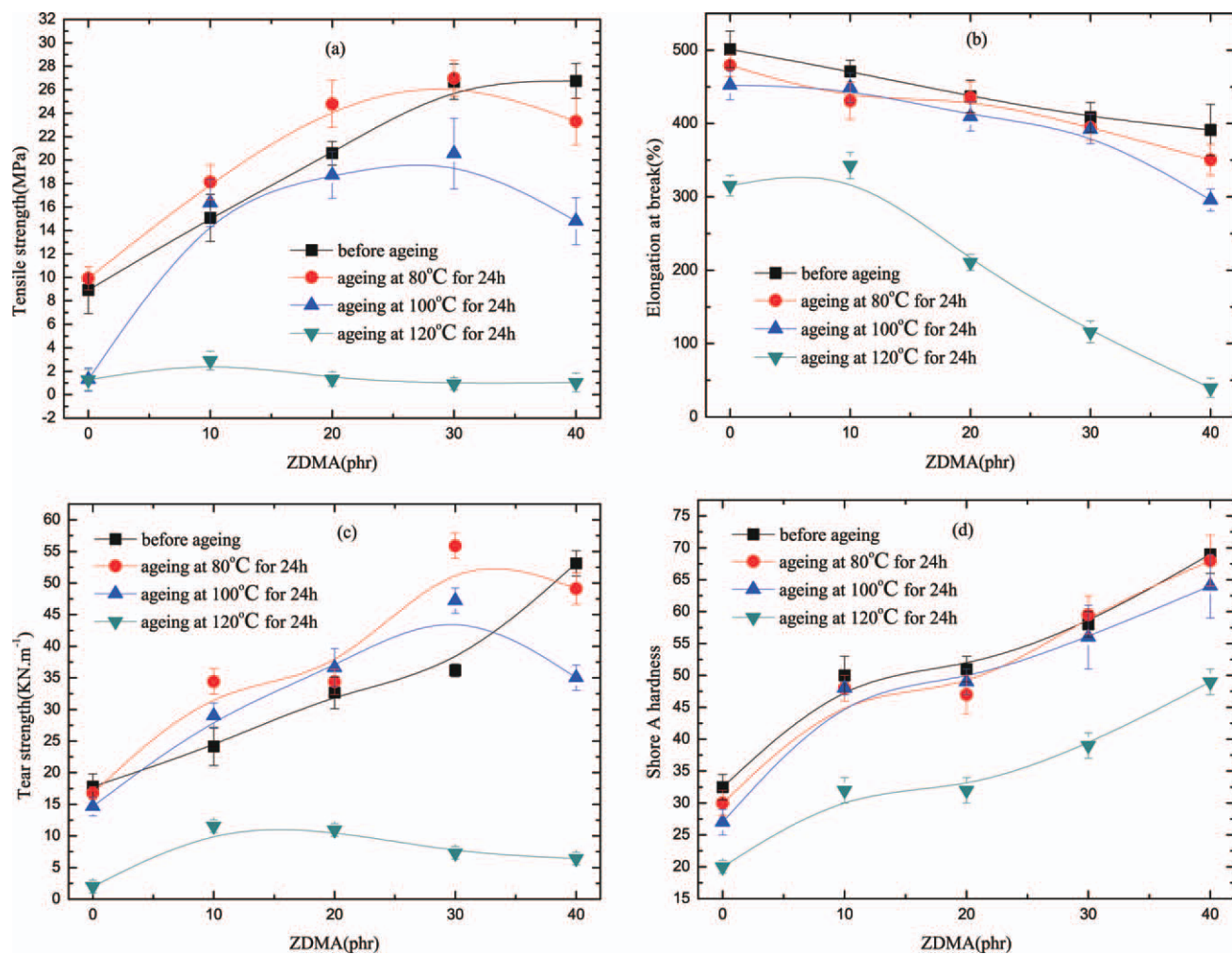


Figure 3 Changes of mechanical properties upon aging temperatures: (a) tensile strength, (b) elongation at break, (c) tear strength, and (d) shore A hardness. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

properties? Therefore, it is necessary to investigate the changes of crosslinkings after aging.

The changes of total crosslink density, covalent crosslink density, and ionic crosslink density are shown in Figure 4, Figure 5, and Figure 6, respectively. The crosslink density of the vulcanizates aging at 120°C is not given in the figures as the samples

with high ZDMA content were partly dissolved in toluene (the solution was not transparent). This means that a severe rupture of inside crosslinked network has been taken place after aging at 120°C. Generally speaking, the transition metals can give rise to the degradation of rubber at a high temperature without any rubber antioxidant.^{19–21}

TABLE I
Retention of Tensile Strength Upon Different Aging Temperatures for 24 h

ZDMA content (phr)	Retention of tensile strength (%)		
	Aging at 80°C	Aging at 100°C	Aging at 120°C
0	111	15	14
10	120	107	19
20	121	91	6
30	101	99	4
40	87	56	5

TABLE II
Retention of Elongation at Break Upon Different Aging Temperatures for 24 h

ZDMA content (phr)	Retention of elongation at break (%)		
	Aging at 80°C	Aging at 100°C	Aging at 120°C
0	96	90	63
10	90	95	76
20	100	93	49
30	97	96	28
40	90	75	10

TABLE III
Retention of Tear Strength Upon Different Aging Temperatures for 24 h

ZDMA content (phr)	Retention of tear strength (%)		
	Aging at 80°C	Aging at 100°C	Aging at 120°C
0	94	82	12
10	141	120	46
20	106	112	34
30	152	130	19
40	92	66	11

Trace of copper would for instance causes a severe degradation at 120°C. Thus, the poor thermal stability at 120°C might be caused by impurities of other transition metals which was introduced by ZnO. The heavy metal contents of ZnO used in this experiment are list in Table V.

All the sample aging at 80°C and 100°C swollen in the toluene were an integral gel and the solution were transparent, which means the 80°C and 100°C aging do not affect the equilibrium swelling experiment. As shown in Figure 4, the total crosslink density after aging at 80°C displaces a slight decrease which is mainly attributed to the decrease of covalent crosslink density shown in Figure 5, whereas the aging at 80°C has little influence on the ionic crosslink density (Fig. 6). However, after aging at 100°C, both the covalent crosslink density and ionic crosslink density exhibit severe drops result in the decrease of total crosslink density. The covalent crosslinked network degraded even aging at 80°C, and the drops of covalent crosslink density increases with increasing ZDMA content (see Fig. 5). However, it can be observed that the ionic bonds are stable at 80°C. When the aging temperature up to 100°C, the ionic bonds are destroyed result in the rupture of ionic crosslinked network. From the above results, a conclusion can be obtained is that the whole crosslinked network of the vulcanizates degraded after aging even though the ionic crosslinked network is relative stable at lower temperature. Note tensile strength showing some increases after 80°C aging [Fig. 3(a)] and tear strength

TABLE IV
Retention of Shore A Hardness Upon Different Aging Temperatures for 24 h

ZDMA content (phr)	Retention of shore A hardness (%)		
	Aging at 80°C	Aging at 100°C	Aging at 120°C
32.5	93	84	67
50	96	96	64
51	92	96	63
58	101	96	67
69	99	93	71

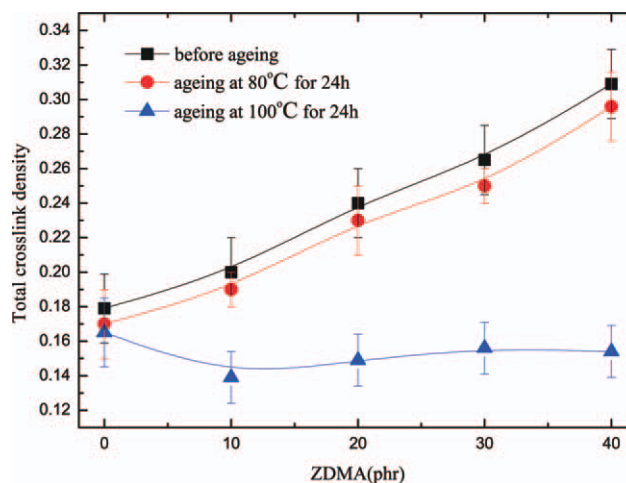


Figure 4 Change of total crosslink density upon aging temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increases even after 80°C and 100°C aging [Fig. 3(c)]; these results cannot be interpreted by the crosslink density analysis as the crosslink densities do not show any increase but decrease. The enhancement of tensile strength and tear strength after aging is not only related to the crosslink density but also related to some other factors. This peculiar behavior will be discussed later.

The weight loss of the samples after thermal aging

The weight loss of the samples after aging was also tested and the results are shown in Figure 7. Obviously, the weight of the samples decreases after aging. For aging at 80°C and 100°C, the weight of the samples decreases with increasing ZDMA concentration. On the contrary, the weight of the samples with ZDMA maintains at a relative stable

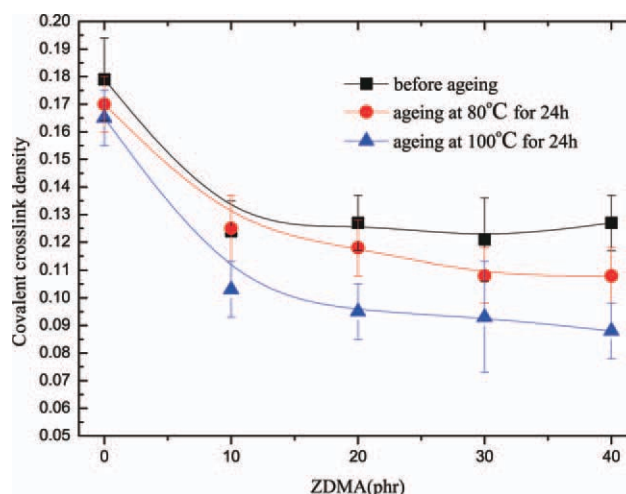


Figure 5 Change of covalent crosslink density upon aging temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

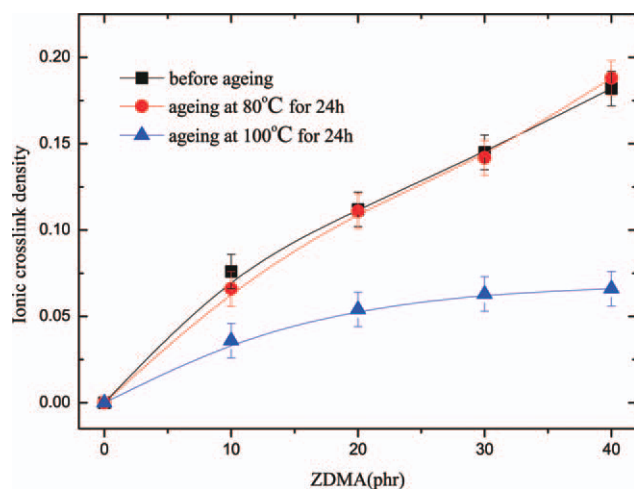


Figure 6 Change of ionic crosslink density upon aging temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

extent after aging at 120°C. These results may be related to the evaporation of water at high temperature and the complex chemical reactions occurred during aging.

It is reasonable to understand that adding ZDMA not only enhance the mechanical properties of NR but also raise the overall polarity of the composites. As a result, the polarity leads to absorbing moisture into the composite. Thus, the more ZDMA was added into NR, the higher polarity was obtained, and more moisture was absorbed. After aging at 80°C and 100°C, the weight loss is mainly attributed to the evaporation of water. In the situation of aging at 120°C, the ionic bonds are unstable. Degradation occurs which can be supported by the decrease of covalent crosslink density. Oxidation is one of the chemical reactions in degradation at such a high temperature.¹⁹ The absorbing oxygen in the air makes up for a deficiency of evaporation of water. As a result, the weight of the samples with ZDMA can be maintained at a relative stable extent.

The crosslink density analysis has given a fact that both covalent crosslink density and ionic crosslink density do not increase after aging. Therefore, a possible explanation is that the absorbing water worsens the tensile strength and tear strength of the samples. A fact must be point out is that the vulcanizates have been store for about a week at room temperature before this particular experiment. After aging at

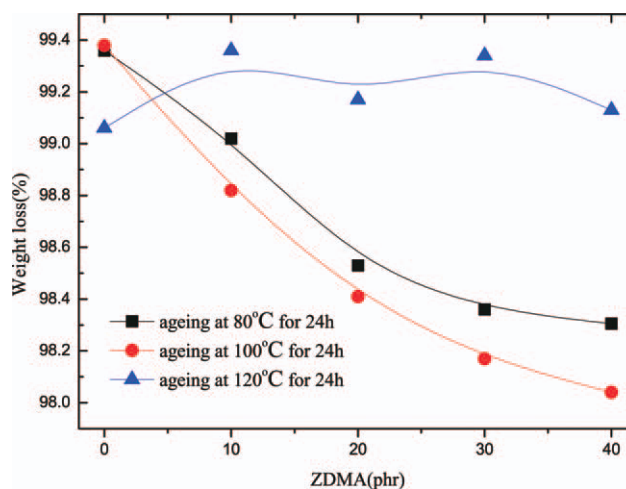


Figure 7 Weight loss of the NR/ZDMA vulcanizates after aging. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a relative low temperature, the absorbing water evaporated. In addition, the crosslinked network was not seriously degraded. Thus, the tensile strength and tear strength of the samples show an increase after aging. However, a significant degradation having occurred after aging at a higher temperature results in the poor mechanical properties.

The stress–strain characteristics analysis

As shown in Figure 8, aging at 120°C leads to a severe decrease of stress and strain at break. The stress–strain curves aging at 120°C reveal that the vulcanizate have lost the rubber characteristic after aging at such a high temperature due to the rupture of crosslinked networks. The stress–strain curve

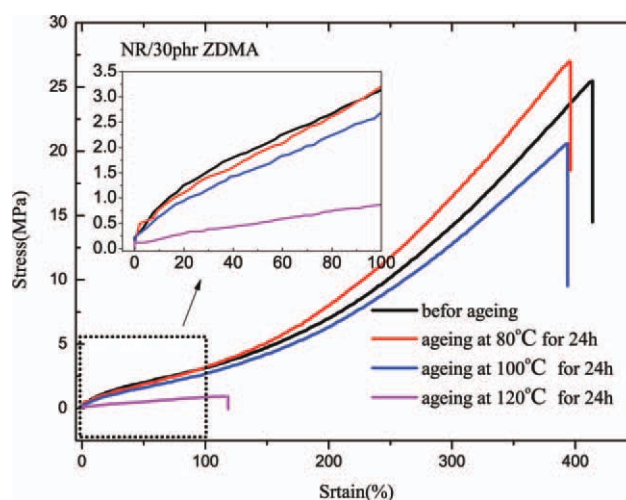


Figure 8 The stress–strain curves of the NR/30 phr ZDMA composite aging at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE V
The Heavy Metal Contents of Zinc Oxide^a

Description	Zinc oxide	Metal (zn)	PbO (Pb)	CuO (Cu)	MnO (Mn)
Parameter (%)	99	0.01	0.15	0.001	0.001

^a The data were obtained from the manufacturer.

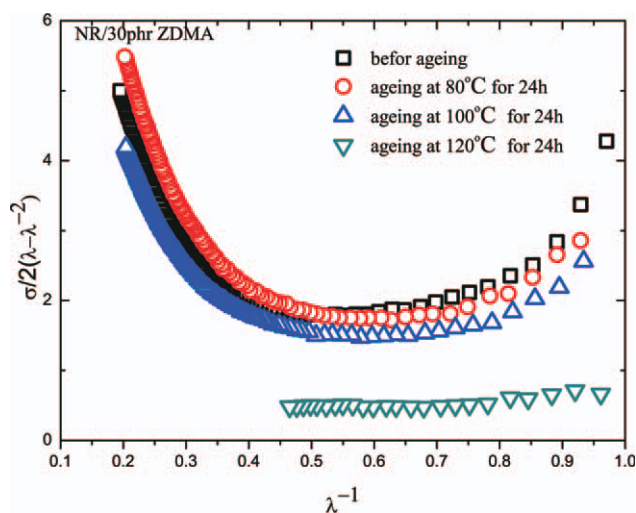


Figure 9 Mooney-Rivlin plots of the NR/30 phr ZDMA composite aging at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

aging at 80°C is close to the unaging curve at a low strain (100%) then exceed it at higher strain. This indicates that the crosslinked networks do not degraded and tensile properties is proved after aging at 80°C. When a filled rubber is stretched, crosslinked network will be deformed. The phenomenological Mooney-Rivlin^{22,23} theory provides a semiempirical equation:

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

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

The relationship of Mooney-Rivlin curves is shown in Figure 9. $\sigma/2(\lambda - 1/\lambda^2)$ decreases with increasing the strain at first and then increases at a higher strain. The decreasing of $\sigma/2(\lambda - 1/\lambda^2)$ at low strain is more significant for the unaging curve. For small strain (λ^{-1} is 0.7–1), the reduction of $\sigma/2(\lambda - 1/\lambda^2)$ is due to Payne effect. For filled rubber,^{24,25} there is always a difference in the surface energy between filler and rubber, so that even for a system in which the filler is 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. The reduction of $\sigma/2(\lambda - 1/\lambda^2)$ of the unaging curve is the most significant, while the curve aging at 120°C shows no Payne effect. For large strain ($1/\lambda$ is 0.5–0.2), increasing of $\sigma/2(\lambda - 1/\lambda^2)$ is due to that the end-to-end distance of the chains tends

to its inextensibility limit. The upturning tendency of the curve aging at 80°C exceed the unaging curve which means there is a strong restriction of the NR molecular chains.

Evaluation of mechanical properties and crosslinked network aging at 100°C for different time

For aging at 100°C, the mechanical properties aging for different time are also investigated and shown in Figure 10. The tensile strength [Fig. 10(a)] and tear strength [Fig. 10(c)] show an increase at some ZDMA content for a short aging time, then, decrease as the extend aging time. As shown in Figure 10(c), the tear strength of 10–30 phr ZDMA exhibits a considerable increase when the aging time does not exceed 24 h. However, the tear strength of 40 phr ZDMA decreases all the time. The similar trend can be found in tensile strength. The hardness [Fig. 10(d)] and the elongation at break [Fig. 10(b)] are decreased with increasing aging time for all the samples. In general, all the mechanical properties show a decreasing trend with increasing aging time, nevertheless, the mechanical properties after aging are higher than the NR gum which indicate the NR/ZDMA vulcanizates have a better aging resistance compare NR gum.

The temperature of 100°C leads to sharp decrease in ionic crosslink density (Fig. 13) of the NR/ZDMA composites result in the sharp decrease of total crosslink density (Fig. 11). Moreover, the sharp decrease occurs even at a short aging time (e.g., 12 h). This implies that the ionic crosslinked network at 100°C is ruptured. The ionic bonds show a poor aging resistance at high temperature. By comparing the ionic crosslink density, the covalent crosslink density (Fig. 12) seems relative stable at this aging temperature as the amplitude of decrease is not significant. However, the tensile strength and tear strength of some samples are increased after aging for 12 h as show in Figure 10. These experimental results are similar to that of aging at 80°C (Fig. 3) for 24 h. Once again, the absorbing moisture can be used here to interpret the “increase” of the tensile strength and tear strength. Age at 100°C for a short time, the absorbing water evaporated, and the oxidation did not develop to degrade the whole covalent crosslinked network to support the mechanical properties. The ionic crosslinked network has been ruptured at this time lead to the decrease of hardness and elongation. However, the author must point out that there must be some other essential reasons for this peculiar experimental phenomenon which need be further studied. For instance, the NR chain network evolves and stress-induced crystallization occur at large deformations.²⁶ After aging, the

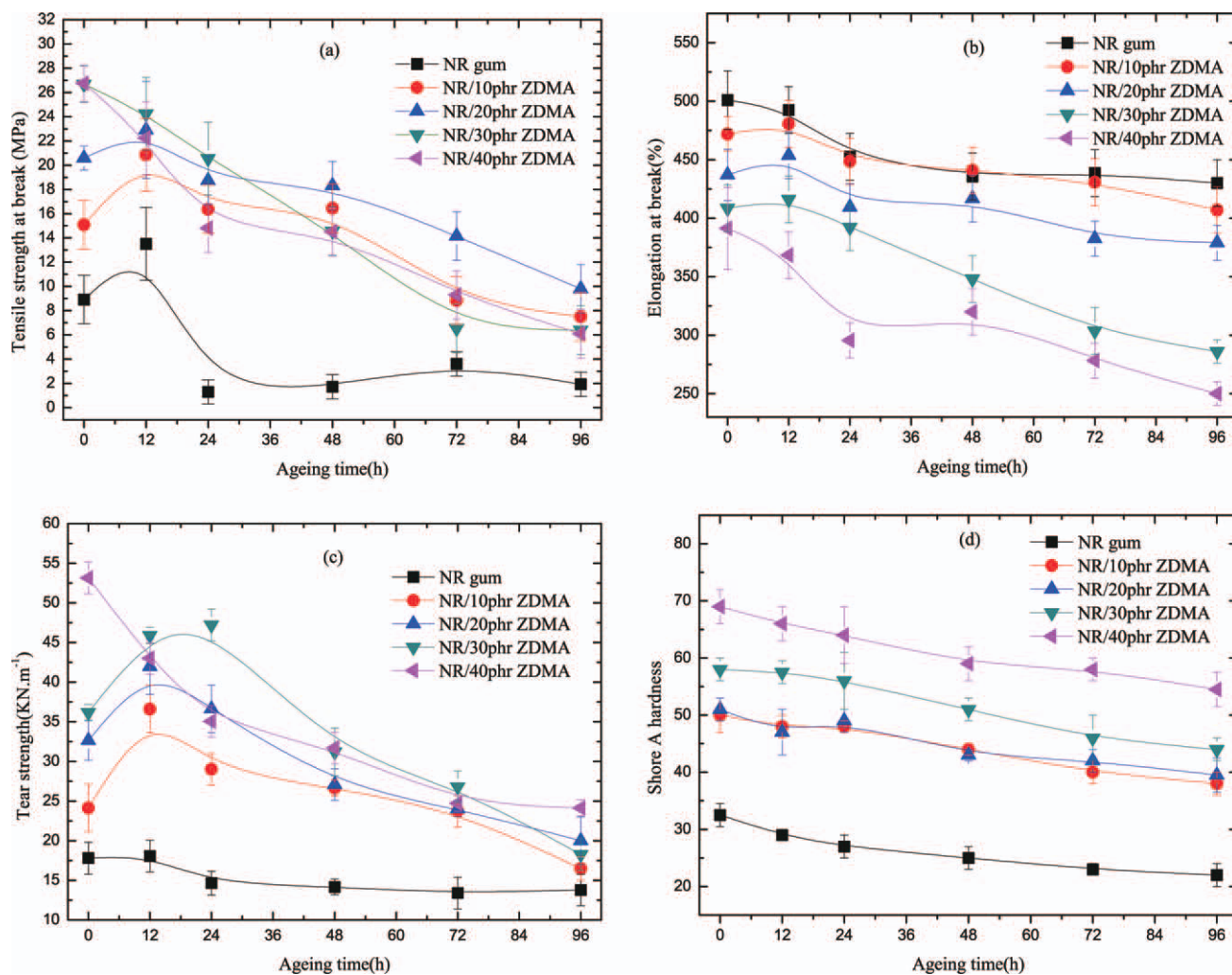


Figure 10 Change of mechanical properties upon aging time at 100°C: (a) tensile strength, (b) elongation at break, (c) tear strength, and (d) shore A hardness. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

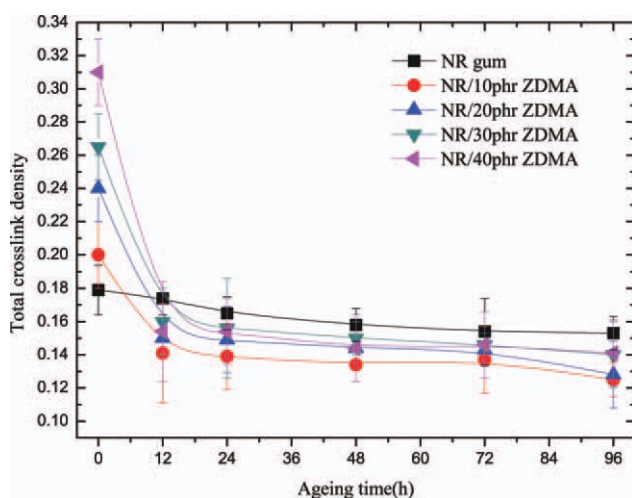


Figure 11 Change of total crosslink density upon aging time at 100°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

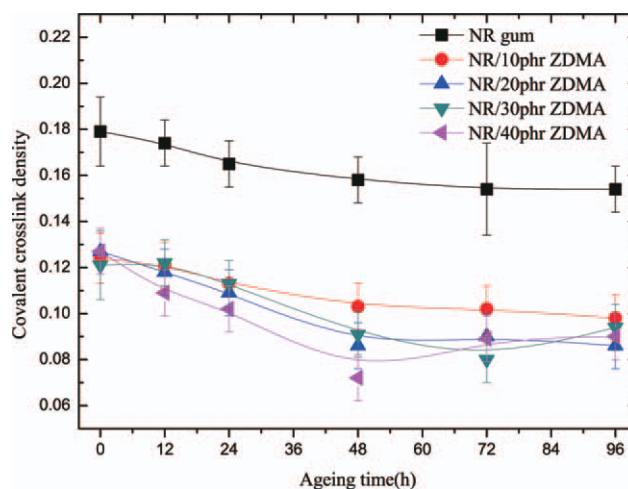


Figure 12 Change of covalent crosslink density upon aging time at 100°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

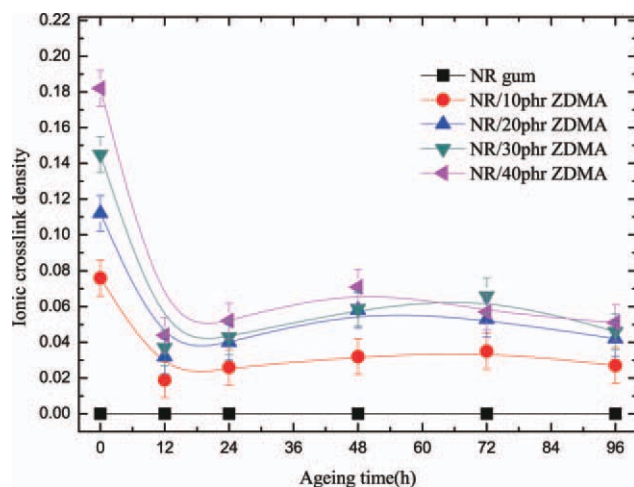


Figure 13 Change of ionic crosslink density upon aging time at 100°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decrease of crosslinkings may be favorable to stress-induced crystallization result in the enhancement of tensile strength and tear strength.

Evaluation of thermal stability of NR/ZDMA vulcanizate

The thermal stability of the vulcanizates was evaluated through the weight loss in nitrogen using TGA. Only a single degradation step for NR is observed in the thermal degradation under nitrogen, as shown in Figure 14, but two degradation steps are observed for the NR/ZDMA composites. In this case, the DTG curves are more convincing than the TGA curves. Corresponding to the TGA curves, the DTG curves for the composite samples are characterized by two degradation peaks, but only one maximum for NR sample, which indicates the existence

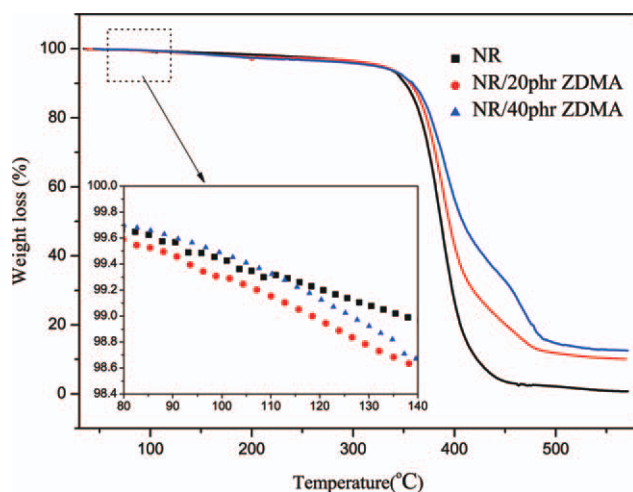


Figure 14 TGA curves for NR and NR/ZDMA obtained in nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

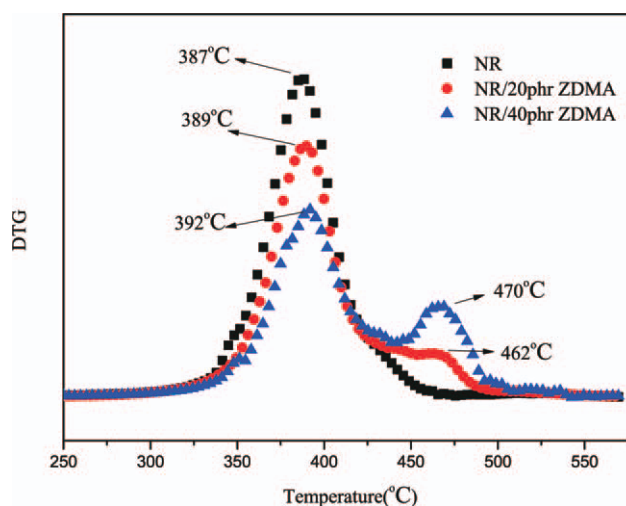


Figure 15 DTG curves for NR and NR/ZDMA obtained in nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of different degradation. As shown in Figure 15, the first degradation peak is attributed to the degradation of NR matrix and second degradation peak is attributed to the degradation of Poly-ZDMA.

The superior thermal stability of the composite samples over that of NR sample is immediately apparent, as shown in Figure 15. The thermal stability of the composite samples increases with increase the content of ZDMA. This indicates that the ZDMA improves the thermal stability of NR, which is consisted with the mechanical properties after thermal aging. In the first zone, the decrease of weight can be attributed to desorption of water. In addition, the weight drop of NR/ZDMA composites is highlighted compared to NR. It can be found from the DTG curve in Figure 15 that the temperature of maximum thermal decomposition in composites is higher than that of pure NR. Pure NR is decomposed completely before 460°C, whereas the complete decomposition can only occur with temperature above 490°C for composites. This indicates that the thermal stability of NR/ZDMA composites is superior to that of the pure NR. It further demonstrates that the ZDMA improves the thermal stability of NR to a certain extent, which facilitates the applications of the resulting composites in many fields.

CONCLUSIONS

The ZDMA not only enhanced the mechanical properties of NR significantly but also improved the aging resistance in a certain degree. The higher aging temperature resulted in worse mechanical properties. The ionic bond is relative stable at 80°C but very unstable at a higher temperature (e.g., 100°C). After aging at a higher temperature, the

ionic crosslinked network was ruptured. The poor thermal stability at 120°C might be caused by impurities of other transition metals which was introduced by ZnO. The absorbed moisture due to the polarity introduced by adding ZDMA could affect the mechanical properties of the composite such as tensile strength and tear strength. In addition, the ZDMA improved the thermal stability of the NR/ZDMA composite to some extent.

References

1. Yin, D. H.; Zhang, Y.; Peng, Z. L.; Zhang, Y. X. *Eur Polym Mater* 2003, 39, 99.
2. Yuan, X. H.; Peng, Z. L.; Zhang, Y.; Zhang, Y. X. *J Appl Polym Sci* 2000, 77, 2740.
3. Sato, K. *Rubber Chem Technol* 1983, 56, 943.
4. Ikeda, T.; Yamada, B. *Polym Int* 1999, 48, 367.
5. Medalia, A. I.; Alesi, A. L.; Mead, J. L. *Rubber Chem Technol* 1992, 65, 154.
6. Saito, Y.; Nishimura, K.; Asada, M.; Toyoda, A. *J Jpn Rubber Soc* 1994, 67, 867.
7. Lu, Y. L.; Liu, L.; Yang, C.; Tian, M.; Zhang, L. Q. *Eur Polym Mater* 2005, 41, 577.
8. Lu, Y. L.; Liu, L.; Tian, M.; Geng, H. P.; Zhang, L. Q. *Eur Polym Mater* 2005, 41, 589.
9. Peng, Z. L.; Liang, X.; Zhang, Y. X.; Zhang, Y. *J Appl Polym Sci* 2002, 84, 1339.
10. Rossi, E. F.; Martelli, A. F. *Eur Polym Mater* 1972, 8, 351.
11. Lu, Y. L.; Liu, L.; Shen, D. Y.; Yang, C.; Zhang, L. Q. *Polym Int* 2004, 53, 802.
12. Nomura, A.; Takano, J.; Toyoda, A.; Saito, T. *J Jpn Rubber Soc* 1993, 66, 830.
13. Yuan, X. H.; Peng, Z. L.; Zhang, Y.; Zhang, X. *Polym Polym Comp* 1999, 7, 431.
14. Nagata, N.; Sato, T.; Fujii, T.; Saito, Y. *J Appl Polym Sci* 1994, 53, 103.
15. Dontsov, A.; Candia, F. D.; Amelino, L. *J Appl Polym Sci* 1972, 16, 505.
16. Nie, Y. J.; Huang, G. S.; Qu, L. L.; Zhang, P.; Weng, G. S.; Wu, J. R. *J Appl Polym Sci* 2010, 115, 99.
17. Valentin, J. L.; Carretero-González, J.; Mora-Barrantes, I.; Chassé, W.; Saalwächter, K. *Macromolecules* 2008, 41, 4717.
18. Yin, D. H.; Zhang, Y.; Zhang, Y. X.; Peng, Z. L.; Fan, Y. Z.; Sun, K. *J Appl Polym Sci* 2002, 85, 2667.
19. Osawa, Z. *Polym Degrad Stab* 1988, 20, 203.
20. Sato, S.; Honda, Y.; Kuwahara, M.; Watanabe, T. *Biomacromolecules* 2003, 4, 321.
21. Hovorka, S. W.; Schöneich, C. *J Pharm Sci* 2001, 90, 253.
22. Mooney, M. *J Appl Phys* 1940, 11, 582.
23. Rivlin, R. S. *Philos Trans R Soc London Ser A* 1948, 241, 379.
24. Mullins, L.; Tobin, N. R. *J Appl Polym Sci* 1965, 9, 2993.
25. Julie, D.; Bruno, F.; Pierre, G. *Eur Polym Mater* 2009, 45, 601.
26. Le Cam, J.-B.; Toussaint, E. *Macromolecules* 2008, 41, 7579.