Temperature Dependence of the Mechanical Properties and the Inner Structures of Natural Rubber Reinforced by *In Situ* Polymerization of Zinc Dimethacrylate

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ABSTRACT: In this work, the tensile property of natural rubber (NR) reinforced by zinc dimethacrylate (ZDMA) at various temperatures was studied. The results showed that the strain-induced crystallization of NR chains at larger elongation and the ionic crosslinks are two of the main reasons for the high tensile strengths of the NR/ZDMA composites, and they afforded the apparent tensile strength at different temperature range. Strain–stress curves revealed that the composites could not undergo strain-induced crystallization above 80°C. The results of Rubber Process Analyzer 2000 (RPA2000) confirmed that the effective ionic crosslinks were weakened and destroyed by high temperatures. The crosslink density, determined by an equilibrium swelling method, was used to characterize the structure variation during stretching at different temperatures. At last, the results of thermal gravimetric analysis (TGA) indicated that the ionic crosslinks improved the thermal stability of the NR/ZDMA composites to some extent. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

In recent years, metal salts of methacrylic acids, especially zinc dimethacrylate (ZDMA), have attracted the significant interest of researchers. Many studies[1–15] have revealed that, without any conventional reinforcing filler such as carbon black or silica, peroxide-cured rubbers reinforced by ZDMA obtain high tensile strength, high tear strength and modulus, while still retaining a high elongation at break. It is found that ZDMA polymerize and react with rubber chains to form poly-ZDMA (PZDMA) and rubber-graft-PZDMA during curing process.[9,12,15] The rubber-graft-PZDMA has been suggested to be the main factor to form ionic crosslinks.[12] Because of the strong electrostatic interaction between ion pairs in PZDMA molecules, the PZDMA aggregates are formed which can restrict the mobility of adjacent polymer chains, acting as a kind of crosslinking action—ionic crosslinking.[12] Furthermore, phase separation of PZDMA happens to result in the fine particles with diameter of 20–30 nm which have been observed by many researchers.[10,12,13] As a result, ZDMA-reinforced rubbers contain not only covalent crosslinks but also ionic crosslinks and, exhibit special crosslink structure and morphology. Obviously, the microstructure of rubbers reinforced by ZDMA is complex and differs to that of the rubbers reinforced by conventional fillers. Thus, the mechanical properties of ZDMA-reinforced rubbers have gained considerable attention due to the formed specific structures.

A large number of studies have been carried out to study the excellent mechanical properties of rubber/ZDMA composites. Peng et al.[8] found that ionic crosslinks had a close relationship with the tensile strength. Lu et al.[9–11] studied the mechanical properties of different rubbers reinforced by ZDMA and summarized that not only the ionic crosslinks, but also other factors, such as the characteristic of the elastomer matrix, the type and density of crosslink structures, the feature of reinforcing particles, and their interaction with the elastomer matrix, could affect the mechanical properties. Nie et al.[13] suggested that both high crosslink density provided by ionic crosslinks and strain-

induced crystallization improved the mechanical properties of NR/ZDMA. So far, different mechanisms for reinforcement of rubbers by ZDMA have been put forward based on the experimental results of different rubber/ZDMA systems. Nevertheless, the ionic crosslinks resulted from the rubber-*graft*-PZDMA is an essential or necessary part of those theories.

As known to us, the majority of the reports about ZDMA-reinforced rubbers are carried out at the room temperature, and few publications concern the properties at higher temperatures. Our previous work[16] studied the effects of thermal aging on the mechanical properties of the natural rubber (NR)/ZDMA composites and revealed that the ionic crosslinked network was ruptured after aging at a high temperature and the covalent crosslinked network was mainly to support the mechanical properties of the composite this moment. But how does the NR/ZDMA composite performs in high temperature applications? And how do the ionic crosslinks act at high temperatures? This is need of further study, which is the focal point of this article.

In this work, the NR/ZDMA vulcanizates were stretched at various temperatures, and the crosslink density of the stretched samples was determined by an equilibrium swelling method. The dynamic viscoelasticity at high temperatures was evaluated by Rubber Process Analyzer 2000 (RPA2000). The thermal stability of the NR/ZDMA composites was also evaluated through the weight loss in nitrogen using thermal gravimetric analysis (TGA). We aimed to investigate the performances and action of the ionic crosslinks of the NR reinforced by ZDMA during high temperatures and to explore the application of ZDMA reinforced rubbers in thermal aspect.

EXPERIMENTAL AND METHOD

Raw Materials

NR (Malaysia 1#) was provided by Guangzhou Rubber Industry Research Institute (People's Republic of China). Methacrylic acid (MAA), purchased from Guangzhou Xin'gang Chemical Factory (People's Republic of China), was purified by distillation under nitrogen at reduced pressure. Zinc oxide (ZnO) was purchased from Tianji Yaohua Chem. Co., Ltd (People's Republic of China). Dicumyl peroxide (DCP), purchased from Sinopharm Chemical Reagent Co. Ltd (People's Republic of China), was purified by anhydrous alcohol recrystallization before use.

Samples Preparation[6–8]

Equivalent ZnO and MAA (ZnO/MAA molar ratio 0.5) was used to react in the NR matrix during mixing. The compounds containing 100 weight parts of NR, 1.5 phr (parts per 100 parts of rubber) DCP and 0∼40 phr ZDMA. Rubber compounds were prepared in a two-roller mill. ZnO was added first in NR and mixed for 2 min, then MAA was added slowly while mixing, and the period was 4∼5 min. When MAA was added over, another 5 min mixing was followed, and DCP was added at last. The compound was stored at room temperature for 8 h. After that, the compound was cured at 155°C in an electrically heated hydraulic press for their optimal cure time (t_{90}) derived from curing curves.

Tensile Properties at Different Temperatures

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 width in cross section and 1 mm thick) on an Instron testing machine Mod 5500 R fitted with a heating oven of accuracy to ±1°C at a crosshead speed of 500 mm/min. The test temperature was selected at 25, 30, 40, 60, 80, 100, 120, 150, and 180°C. The test samples were placed in the oven at the target temperature for 15 min to achieve thermal equilibrate before testing.

RPA2000 Test

The strain sweeps were conducted by RPA2000 (Alpha technologies Co., United Kingdom). The cavity house was a biconical test chamber closed by the action of a pneumatic ram operated at a pressure. A slight excess of test material was needed to ensure the cavity house was full. Tests were thus made under pressurized conditions to make sure that porosity did not develop in the samples during the tests. The temperature was kept constant at 155°C first. After the uncured samples were subjected into the cavity house, the curing was started immediately. The curing times were their optimal cure time (t_{90}). After curing, the temperature was reduced or raised to the target temperature. Then conduct strain sweep. Strain sweeps were performed at 0.05°–10°C and the frequency was kept constant at 60 cpm (cycles per minute).

Crosslink Density[6–8,14–16]

The crosslink density was determined by the equilibrium swelling. 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, was determined by the following equation:

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

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 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 crosslinks from covalent crosslinks, the above samples were swollen in a mixture of toluene and chloroacetic acid once again for 5 days to destroy ionic crosslinks, 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 crosslink density. V_{r2}, which is calculated by subtracting V_{r1} from V_r, was used to represent the ionic crosslink density.

Thermal Gravimetric Analysis (TGA)

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 700°C at a constant rise of temperature (20°C/min).

RESULTS AND DISCUSSION

The Influence of the Preheating Period on the Crosslink Structures

Considering the test samples need preheating at the testing temperature for 15 min to achieve thermal equilibrium, the effect of this short heating period on the crosslink structures is investigated. We selected two temperatures, namely 100 and 180°C, to evaluate the influence of the short heating period on the crosslink density. After preheating to achieve thermal equilibrium, the samples were cooled down at room temperature (25°C) and then tested. As shown in Figure 1, the V_r and V_{r2} show a significant increase with increasing ZDMA content, whereas the V_{r1} decreases slightly. The slight decrease in V_{r1} is attributed to the consumption of part of the free radicals by the polymerization of ZDMA during vulcanization.[15] Preheating at 100°C does not destroy the crosslink structures in all the samples. In our previous study,[16] we found that the ionic crosslinks were destroyed severely at 100°C for 12 h. No decrease is observed in the V_{r2} during the preheating which may be due to the very short time. A slight decrease in V_r for the samples preheated at 180°C can be distinguished, which is attributed to the decrease in V_{r2}. However, this short thermal equilibrium period shows almost no influence on the tensile property (not provided in this article), which reveals that the effective reinforcing structures are still maintained.

Evaluation of Tensile Property at Different Temperatures

Polymer physics structure and weak chemical structure are dependent on the temperature. Study on the temperature dependence of the mechanical properties contributes to the understanding of structure of the material. Generally, the motion of rubber chains is enhanced while the weak chemical interaction and physical adsorption between filler–filler, filler–rubber molecular, and rubber molecular–molecular are severely reduced at high temperature, resulting in the dissatisfactory mechanical properties.
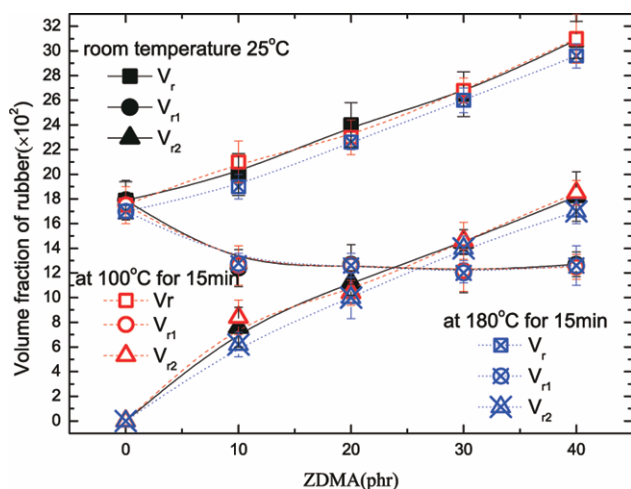

Figure 1. Effect of preheating period on the crosslink density. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
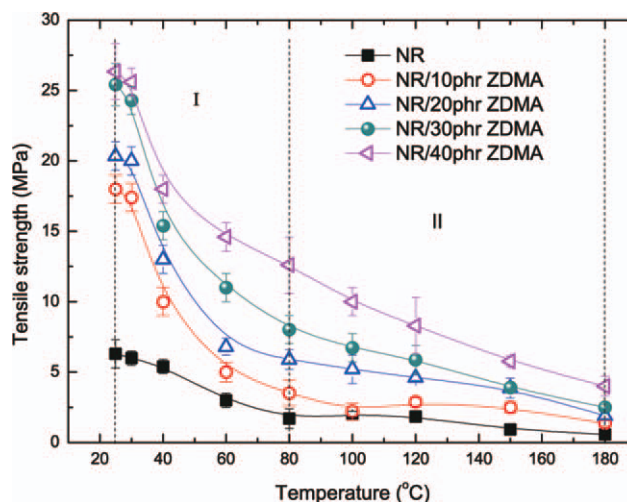

Figure 2. Tensile strengths at various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The changes of tensile strength, elongation at break and permanent set upon different temperatures are presented in Figures 2–4, respectively. Figure 2 shows a decrease in tensile strength with temperature for all the samples. The dropping course for tensile strength can be divided into two stages grossly. At the first stage, the tensile strength shows a slight decrease around room temperature within 5°C. And then, ranging from 30 to 80°C, the strength has a dramatic drop. Please note that the tensile strength of the neat NR is decreased from 6 to 2 MPa in this temperature range, whereas it just decreases slightly above 80°C. It is well known that the considerable tensile strength of neat NR is due to the strain-induced crystallization.[17,18] Thus, this temperature range may be the range where melting of microcrystalline structures[11] occurs in NR. For this reason, the sudden fall in strength of the NR/ZDMA composites mainly attributed to the loss of microcrystalline structures.[11] At the second stage, with increasing of temperature, the tensile strengths of neat NR and NR with lower content of ZDMA decrease at relatively small rate to that at the first stage. However, NR with 40 phr ZDMA still shows a large decrease in tensile strength. The reduction in the strength at the second stage is likely related to the destruction of reinforcing structures formed through *in situ* polymerization of ZDMA.[11] The high temperatures weaken the electrostatic interaction between ion pairs while enhance the motion of rubber chains, which make the "restricted" adjacent polymer chains easy to break free from the ion clusters during stretching. For this reason, the decrease in strength of the NR/ZDMA composites is regarded as the instability and broken of the effective ionic crosslinks. Although tensile strength of all the NR/ZDMA composites is decreasing with increasing temperature, the high temperature tensile strength is improved apparently with high ZDMA loading level (Table I). This suggests the possibility of ZDMA to improve the high temperature performances of rubbers.[16]

As shown in Figure 3, the elongations at break maintain at a high level below 100°C, but reduce severely when the temperature exceeds 120°C. Stretching to break generally is associated
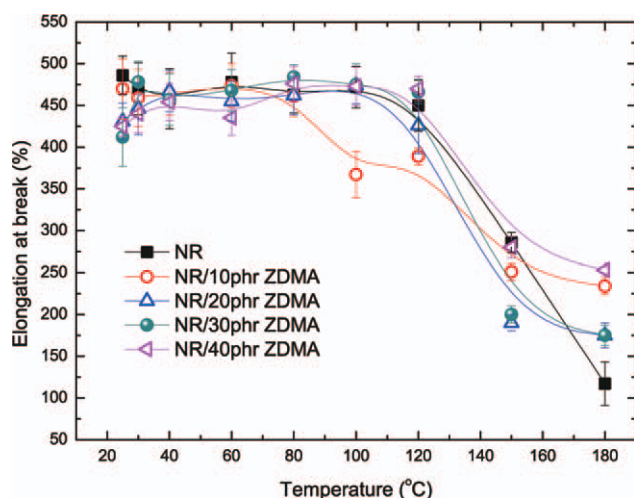
Figure 3. Elongations at break at various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]
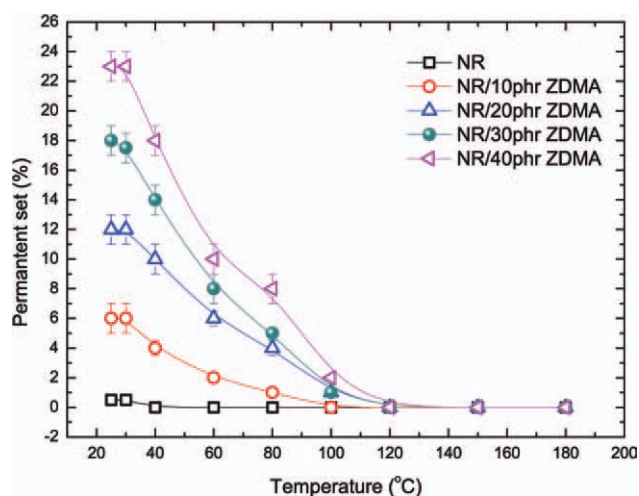

Figure 4. Permanent sets after stretching at various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with structure rupture. The sudden fall in elongation at 150 and 180°C is attributed to the changes in internal structures of the samples, which will be discussed later.

The permanent set refers to the residual extension remaining after a material sample is stretched and released. As shown in Figure 4, the neat NR shows a good recovery which is due to the relaxation of rubber chains. The residual extension of NR/ZDMA composite increases significantly with ZDMA loading level, which is due to the increase of the ionic crosslinks. The slippage of ionic bonds is a normal behavior under the effect of stress.[14] At room temperature, the covalent crosslink network of NR is deformed and lots of ionic bonds are easy to slip during stretching but reconstruct rapidly. New ionic bonds or ion cluster, reconstructed rapidly at current position, will restrict the relaxation of NR molecular. Above 100°C, all the test samples show no permanent set. This is good representation of the weakened electrostatic interaction between ion pairs at high temperatures. In another word, the effective ionic crosslinks are destroyed by stretching at high temperature.

The Effect of Stretching at Different Temperatures on the Crosslink Structures

The crosslink density is decreased significantly at the failure elongation, which indicates that damage of the structures

occurred during stretching. As shown in Figure 5, the V_r value at break (V_{r-b}) of the neat NR is close to the unstretched one whereas the V_{r-b} values of the NR/ZDMA composites are lower than that of the unstretched one. This implies that stretching at room temperature does not damage the networks of the neat NR, while the reverse fact is true for the NR/ZDMA composites.

The V_{r-b} values of the NR/ZDMA composites maintain at a relative high level below 60°C but at a lower level in the range from 80 to 120°C, except the NR/10 phr ZDMA. The V_{r-b} values in the range from 30 to 60°C are close to that at 25°C, which may be considered as an indirect support for that the sudden fall in tensile strength of the NR/ZDMA composites is related to the microcrystalline structures more than the crosslink structure. However, the V_{r1-b} (Figure 6) shows a slight decrease in this temperature range, which indicates that more of the covalent crosslink network is ruptured during stretching at a higher temperature in this range. In the range from 80 to 120°C, V_{r1-b} also maintains at a relative low level.

As shown in Figure 7, the V_{r2-b} values seem more stable compared to the V_{r1-b}. A slight drop at about 100°C can be distinguished. This reveals that the high temperatures weaken the ionic crosslinks and worsen the tensile strength. However, it can be seen that the tensile strength decreasing with temperature for

Table I. Retentions of the Tensile Strength at Various Temperatures

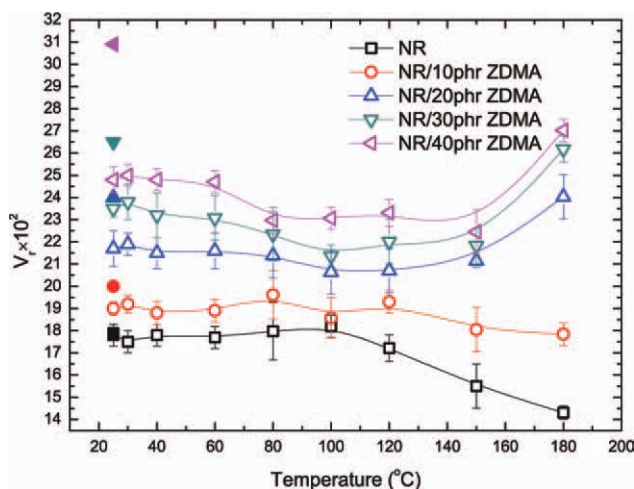| ZDMA content (phr)	Retentions of the tensile strength (%)							
	30°C	40°C	60°C	80°C	100°C	120°C	150°C	180°C
0	95	86	48	27	28	24	13	9
10	94	56	28	19	12	16	13	8
20	98	64	33	29	26	23	19	9
30	93	62	44	32	26	24	16	10
40	96	70	58	50	39	32	22	15

Figure 5. Total crosslink density of the composites stretched at various temperatures. (Solid represents unstretched; hollow represents stretched to failure). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. Ionic crosslink density of the composites stretched at various temperatures. (Solid represents unstretched; hollow represents stretched to failure). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the NR/ZDMA composites is basically a gradual change (Figure 2). This feature is obviously different from the sudden strength dropping at the specific temperature observed in the typical ionic polymer or metallic oxide crosslinked carboxyl rubber.[11,19,20] Hence, it may be deduced that the ionic crosslinks are not the unique reinforcing structure for NR/ZDMA composites.[11]

Above 120°C, the NR/ZDMA composites show an apparent increase in crosslink density whereas the neat NR and NR/10 phr ZDMA show a notable decrease at such high temperatures. The increase in crosslink density is an abnormal phenomenon, which is not the actual value. It is obvious that some chemical reaction occurs during stretching at such high temperatures. Note that the crosslink density of the samples preheated at
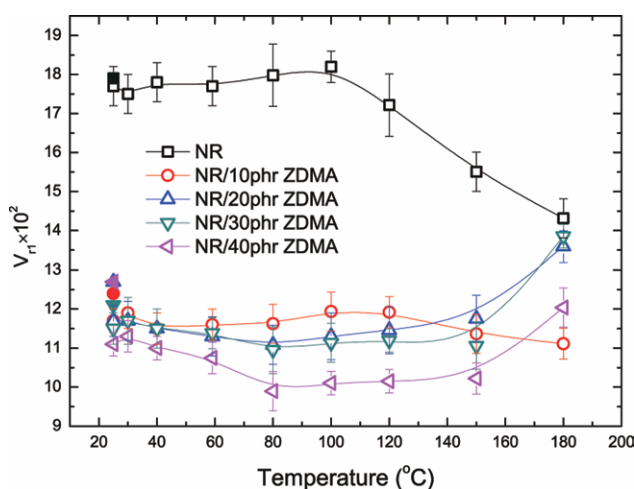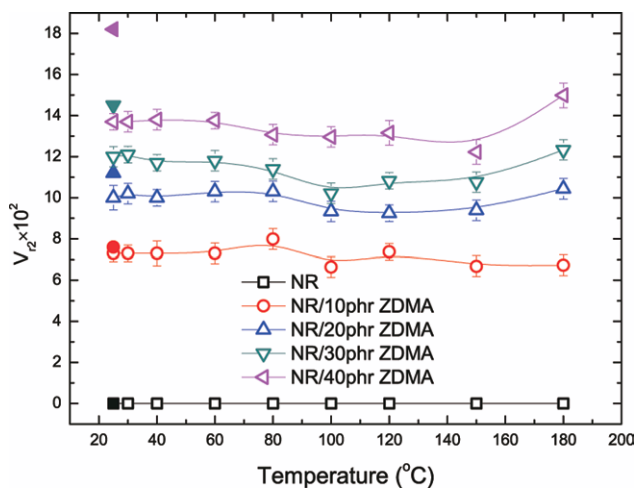
180°C shows almost no significant changes (Figure 1); thus, a conclusion may be deduced that stretching at high temperature will be easier to induce the chemical reactions, for instance, the possible thermal aging.[16] Here, we provide the photographs of the samples with 40 phr ZDMA being aged at 80, 100, 120, and 150°C for 24 h. As shown in Figure 8, the color of the sample turns to yellow after a higher temperature aging, indicating the oxidation. As a result of exposure to 150°C for 24 h, the samples lost their rubber characteristic to be hard and brittle. As evidenced by the photographs of the aged samples, high temperatures indeed cause the samples to become hard after aging. This is consistent with the observed increase of crosslink density at 180°C (Figure 5). Thus, stretching at high temperatures leads to the increase of crosslink density may be attributed to the thermally and mechanically induced aging in this particular experiment. The thermally and mechanically induced aging effect may be the same reason for the drop in elongation at break (Figure 3).

Analysis on the Stress–Strain Curves

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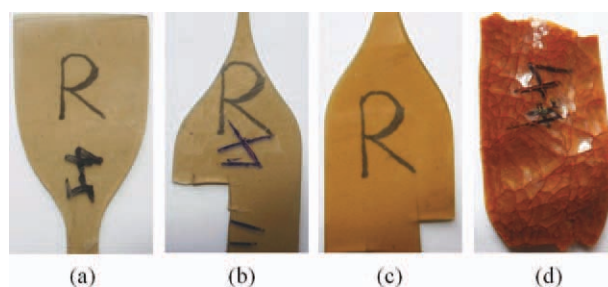

Figure 6. Covalent crosslink density of the composites stretched at various temperatures. (Solid represents unstretched; hollow represents stretched to failure). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. Photograph of the NR/40 phr ZDMA composite after thermal aging for 24 h at different temperatures: (a) 80°C, (b) 100°C, (c) 120°C, and (d) 150°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
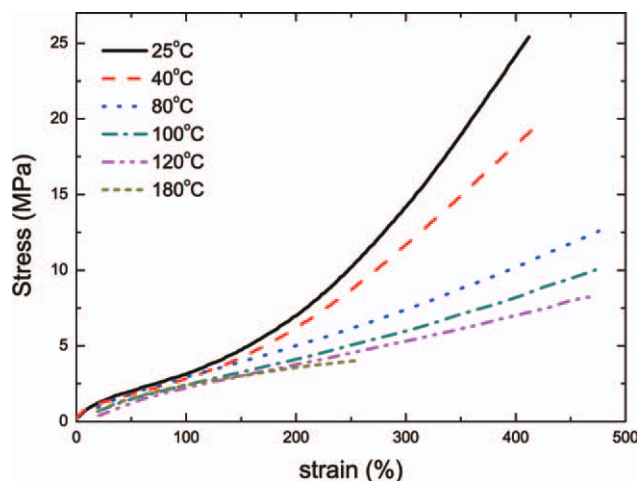
Figure 9. Strain–stress curves of NR reinforced by ZDMA (40 phr) at various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

effect of temperature on the inner structure of the composite during stretching. Figure 9 compares the stress–strain behavior of the NR/40 phr ZDMA composite at various temperatures. At 25°C, the stress increases rapidly when the strain exceeds 200%, which is due to the ionic crosslinks and tensile-induced crystallization.[13] At 40°C, the stress–strain curve is below the one at 25°C, but still exhibits considerable tensile property. An apparent upturning at large strain also can be observed, revealing that the strain-induced crystallization also occurs at 40°C. When the temperature reaches 80°C, the ultimate stress is only half of that at 25°C. All the stress–strain curves ($\geq$80°C) are almost linear, showing no signs of strain-induced crystallization. In our previous study,[16] we found that the ionic crosslinks were relatively stable at 80°C. Thus, the crosslink structure is mainly to afford the tensile stress at this temperature. Nie et al.[13] found out that the ionic crosslinks played a more important role in the ultimate mechanical properties at the high content of ZDMA. Considering that high temperature tensile strength and ionic crosslink density are increased apparently with ZDMA loading (see Figure 1), we also believe that the ionic crosslinks play an important role in the ultimate tensile strength when the temperature is above 80°C. As for 180°C, the poor stress–strain behavior is due to the damage of the inner structure by thermally and mechanically induced aging.

Analysis on the Viscoelastic Behaviors at Different Temperatures

The viscoelastic behaviors at different temperatures are also investigated. As shown in Figure 10(a), no remarkable "Payne effect"[21,22] can be observed for neat NR. The higher temperature results in higher storage modulus (G'). During testing of NR at high temperatures, the possible chemically induced stress relaxation may occur due to chain scission and cleavage of crosslinks, which contribute to decrease of storage modulus. Please note that the G' of neat NR at 180°C decreases faster than that at lower temperatures. This is obviously due to the chemically induced stress relaxation. Loss modulus (G'') is related to the energy dissipated during the deformation that it is generally

associated with the internal friction of molecular chains. At large strain amplitudes, the abrupt increase in the G'' at 180°C [Figure 10(b)] represents the havoc on NR crosslink network which is consistent with the decrease of G'. As shown in Figure 11(a), the NR/30 phr ZDMA exhibits remarkable "Payne effect", this is due to the PZDMA.[14] A noticeable decrease in G' at the very small strain amplitudes can be seen, which is due to the rupture of PZDMA network and the holding instantaneous structure by the developed ionic crosslinks which is not favorable to rebuild the PZDMA network.[14] When the temperature exceeds 100°C, this peculiar phenomenon disappears because the high temperature weakens the ionic crosslinks[16] (see Figure 7). The influences of temperatures on the ionic crosslinks can also be investigated from the G''. As shown in Figure 11(b), the small loss peak at about 2~3° strain amplitude is attributed to the energy dissipated involving ionic crosslinks slippage and rubber covalent crosslinks deformation.[14] Above 100°C, this loss peak disappears because of the weakened ionic crosslinks. Furthermore, the NR/30 phr ZDMA shows an abrupt increase in G'' at 120, 150, and 180°C, this may be the evidence of
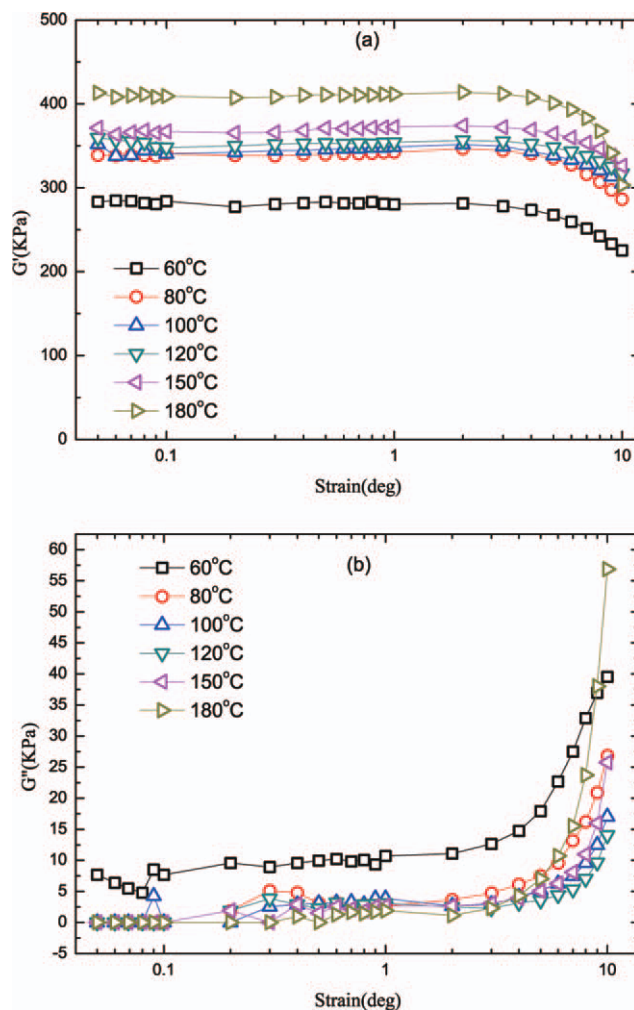

Figure 10. Strain sweep on the neat NR: (a) G'; (b) G''. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
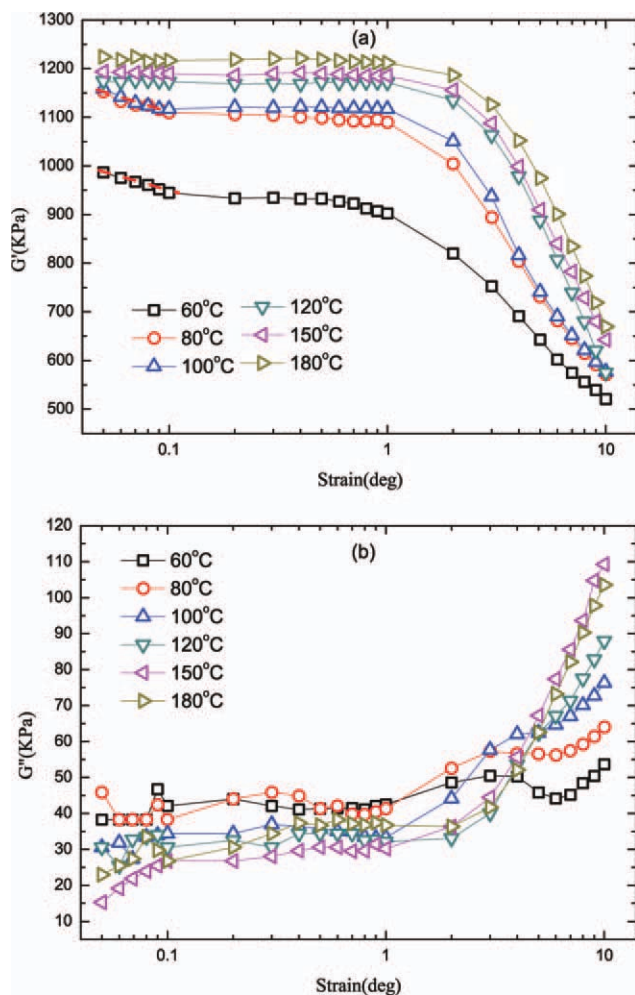
Figure 11. Strain sweep on the NR/30 phr ZDMA composite: (a) G'; (b) G''. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chemically induced stress relaxation. However, it is difficult to clearly differentiate physical filler–filler interactions and chemically induced effects which contribute to the decrease of G' at large strains. As shown in Figure 11(a), the NR/30 phr ZDMA does not show a significant drop in storage modulus at 120, 150, and 180°C, comparing that at other temperatures.

Thermal Stability

The thermal stability of the NR/30 phr ZDMA was also evaluated. As shown in Figure 12(a), only a single degradation step for NR is observed in the thermal degradation under nitrogen, whereas two degradation steps are observed for the NR/ZDMA composites. Corresponding to the TG curves, the DTG curves [Figure 12(b)] for the composite samples are characterized by two degradation peaks, but only one maximum for NR sample, which indicates the existence of different degradation. For the NR/30 phr ZDMA composite, the first degradation peak is attributed to the degradation of NR matrix and second degradation peak is attributed to the degradation of PZDMA.[16] In addition, the weight drop of NR/30 phr ZDMA composite is highlighted compared to NR. It can be found from the DTG curve

in Figure 12(b) that the temperature of maximum thermal decomposition in composites is improved. The neat NR is decomposed completely before 460°C whereas the complete decomposition can only occur with temperature above 490°C for composites. The improved thermal stability of the NR/ ZDMA composite further facilitates the applications of this type of composites in thermal fields.

To evaluate the effect of ionic crosslinks on the thermal stability, the sample of NR/30 phr ZDMA was swollen in the mixture of toluene and chloroacetic acid for 5 days to destroy ionic crosslinks, then extracted by acetone for 24 h. As shown in Figure 12(a), the negligible residual weight verifies that all the ionic crosslinks have been cut off, and the Zn^{2+} have been replaced by H^{+}, which have been removed via acetone extraction. As shown in Figure 12(b), the second degradation peak is attributed to the degradation of polymerized methacrylic acid (Poly-MMA) resulted from the swollen treatment. The resulting thermal stability shows a little decrease. The complete decomposition temperature is reduced to 475°C. The two maximum rate decomposition temperatures (T_{max}) are 2 and 33°C lower than
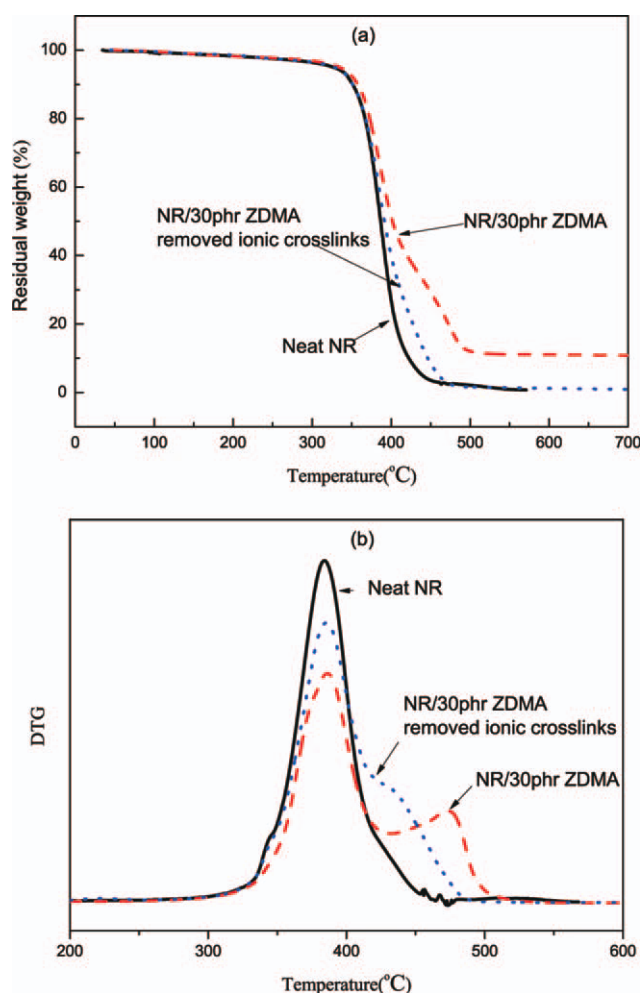

Figure 12. TG (a) and DTG (b) curves for NR and NR/ZDMA (30 phr) in nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that of the untreated sample, respectively. Nevertheless, based on Figure 12, the ionic crosslinks seem to make the composite more stable compared to neat NR at high temperatures.

CONCLUSIONS

The strain-induced crystallization of chains at large elongation and the ionic crosslinks are the two main reasons for the good tensile strength of NR/ZDMA composites at room temperature. The higher temperature resulted in the poorer tensile strength. Below 80°C, the worsening of tensile strength is mainly attributed to the melting of microcrystalline structures; above 100°C, the decreasing of tensile strength is mainly attributed to the weakening of the effective ionic crosslinks. At higher temperature, e.g. above 150°C, stretching leads to thermally and mechanically induced aging which further worsen the tensile property of the NR/ZDMA composites. Nevertheless, tensile strength of the NR/ZDMA composites at high temperature is improved by ZDMA, and, the ionic crosslinks also improve the thermal stability of the NR/ZDMA composites.

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