

EFFECT OF NANOCRYSTALLINE CELLULOSE ON THE CURING CHARACTERISTICS AND AGING RESISTANCE PROPERTIES OF CARBON BLACK REINFORCED NATURAL RUBBER*

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Abstract This work focused on the effect of nanocrystalline cellulose (NCC) on the curing characteristics, aging resistance and thermal stability of natural rubber (NR) reinforced with carbon black (CB). Sharing the same fillers loading of 45 parts per hundred rubber (phr), NR/NCC/CB composites with different NCC/CB ratios (*i.e.* 0/45, 5/40, 10/35, 15/30, 20/25 phr) were prepared and analyzed. Resorcinol and hexamethylene tetramine (RH), acting as the modifier in NR/NCC interface, was also discussed for its influence. The result showed that an relatively higher ratio of NCC/CB led to a lower torque, a shorter cure time (T_{90}), a slightly longer scorch time (T_{10}) and a bigger vulcanization rate constant (K). This tendency suggested that the existence of NCC accelerated the vulcanization process. Additionally, modified by RH, NR/NCC/CB compounds exhibited a short T_{10} and a elevated torque. And a moderate RH content would lower the E_a of vulcanization. A 10 phr substitute of CB by NCC can help to improve aging resistance in terms of mechanical properties. In a high temperature aging condition, composites with 10 phr NCC also performed the highest storage modulus (G') among composites tested. A moderate NCC content contributed to the best retention of G' after high temperature aging, so did the incorporation of RH. With the partial replacement of CB by NCC, the temperature of 5% weight-lose had a slight drop and the apparent crosslink density showed a decrease. Thanks to the interaction of RH with both NR and NCC, composites showed an improvement in apparent crosslink density after modified by RH.

Keywords: Nanocrystalline cellulose; Natural rubber; Curing characteristics; Aging resistance; Thermal stability.

INTRODUCTION

Cellulose, as one of the most abundant and renewable resources, shows characteristics of low density, biodegradability, high strength and stiffness. Those features coincide with the expectation to rubber fillers. So, there is a great potential of cellulose serving as the excellent filler. It was reported that the cellulose could not only reinforce the NR latex^[1], but also act as multifunctional additives in the rubber materials^[2–4]. And with a certain preparation process, the filling of cellulose may help to improve one or more aspects of rubber behavior, such as mechanical properties, processibility, degradability and so on^[1–9]. Recent work of this research group have involved in the preparation method and corresponding mechanical properties of NR/NCC composites^[3, 7–13]. It turned out that replacing CB by NCC, especially with the optimal ratio of 10/35 (NCC/CB), not only led to an improved tensile and tear strength of NR/CB composites, but also increased the elongation at break and decreased permanent set. Besides, better flex cracking resistance, lower compression fatigue temperature rising and compression set of NR/NCC/CB composites were observed, compared to those of NR/CB composites. Furthermore, the abrasion resistance of composites containing 5–10 phr NCC wasn't deteriorated,

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even in comparison with that of high abrasion furnace black filled rubber. However, the vulcanization characteristics, especially vulcanization kinetics, of NR/CB composites affected by NCC have rarely been referred, nor have aging resistance based on both mechanical properties and storage modulus. As is known, the vulcanization characteristics are closely related to processing technology and materials' properties. So, it is of great significance to discuss it. In this work, the NR/NCC/CB composites were prepared successfully with RH as a compatibilizer. Then, effects of NCC on the vulcanization characteristics and kinetics were analyzed. What's more, apparent crosslink density was tested to support the analysis. In addition, aging properties, which reflect the behavior of materials, were characterized in terms of mechanical properties and G' , successively. Finally, the effect of NCC on thermal stability of those composites was also reported.

EXPERIMENTAL

Materials and Method

Materials and formulation

Natural rubber latex (61.7 wt%) was supplied by the Eleventh Rubber Factory, Guangzhou. Microcrystalline cellulose (industrial grade) was obtained from the Gaoli Chemicals Company, Guangzhou. Carbon black (N330) was purchased from China Rubber Company, Taiwan. The sulfuric acid (98 wt%) provided by Chemical R&D Center of Guangdong province was of analytical grade. Anhydrous calcium chloride (analytical grade) was the product of Tianjin Fuchen Chemical Company. Adhesive RH (industrial grade) was supplied by Jiangsu Guoli Technology Co., Ltd. Other auxiliary agents were of industrial grade. The basic formulation (phr) is established as follows: NR 100, fillers 45 (NCC/CB: 0/45 5/40 10/35 15/30 20/25), ZnO 5, Stearic acid 2, RH 4, accelerator CZ 1.5, accelerator DM 0.5, antiager 4010NA 1.5, Sulfur 1.5.

Samples preparation

Microcrystalline cellulose was hydrolyzed with H_2SO_4 (64 wt%) at 45 °C for 30 min. Subsequently, the diluted suspension was repeatedly washed with distilled water *via* centrifugation, until the pH reached 6–7. Then, the obtained suspension, which is the water suspension of NCC^[7, 10], was stored at room temperature for spare use.

NR/NCC compounds were prepared by reinforcing NR with various contents of NCC ranging from 0 to 20 phr. The NR latex and NCC aqueous suspension were first mixed, followed by vigorously stirring *via* mechanical agitation for over 15 min. After that, the mixed solution was spread as thin as possible on a large tray and sprayed with 10% $CaCl_2$ solution to coagulate. Wash the coagulated complex with clean water for 8 h, so as to remove the useless components. Lastly, the ensuring complex was dried in a ventilated oven at 70 °C for 8 h.

Based on the basic formulation above, mixing of the dried NR/NCC compounds and other additives (including CB) was carried out in a two-roll mill (XK-160, Shanghai Rubber Machinery NO.1 Factory, China) in accordance with ASTM D3182. Those compounds were then compression molded into vulcanizates at 143 °C using a hot press for various cure time, T_{90} .

Testing

The curing behavior of NR/NCC/CB compounds was determined at five different temperatures around 143 °C with a UR-2030 rheometer to obtain the curing curve and corresponding parameter.

The apparent crosslink density was measured by equilibrium swelling experiments. First, samples of vulcanizates were totally immersed in a glass vessel containing hexane at room temperature. The vessel was kept in the dark to avoid oxidation. After the samples swelled enough, the qualities (m_b) were weighed. Then, the apparent crosslinking density (V_r) of samples could be calculated by:

$$V_r = \frac{1}{1 + \left(\frac{m_a}{m_b} - 1\right) \cdot \frac{\rho_r}{\alpha \rho_s}}$$

where ρ_r is the relative density of rubber, ρ_s is the density of solvent, α is the mass fraction of rubber in samples, m_a is the original quality of sample.

The mechanical properties were measured with dumbbell and un-nicked 90° angle specimens according to GB/T528-1998, GB/T529-1999, respectively, using U- CAN UT-2060 tester. The crosshead speed during test was 500 mm/min. Shore A hardness was characterized based on GB/T531-1999.

Hot air aging test was carried out in a laboratory-type oven (U-CAN UA-2071B) at 70 °C for 72 h, according to GB/T3512-2001. The oven possessed a sensitivity of ± 1 °C. After aging, the samples were taken out of the oven and tested for mechanical properties.

High temperature aging was conducted *via* RPA2000 at 165 °C for 30 min. The storage modulus (G') was tested at a fixed strain of 7% and frequency of 1 Hz during aging. Strain sweep before and after aging was performed from 0.28%–100%, at 60 °C and 1 Hz.

Thermal gravimetric analysis (TGA) was performed on TGA Q5000. About 10 mg of vulcanizate samples was heated in nitrogen atmosphere to 600 °C at a temperature rising rate of 10 K/min.

RESULTS AND DISCUSSION

Curing Characteristics

Figure 1 and Table 1 show the effect of partial replacement of CB by NCC on the curing curve and parameters. As was exhibited, the maximum torque (M_H) decreased with increasing loading ratio of NCC/CB. This observation was attributed to the reduction of crosslink density, which would be shown later in crosslink density results. And it probably implied a slightly worse compatibility of NR/NCC, compared to NR/CB. Although a small change happened in minimum torque (M_L), it was clear that M_L touched the bottom as the ratio of NCC/CB is 15/30. Explanation could be that too many contents of CB or overdose of NCC both deteriorated the dispersion of fillers and resulted in the aggregation of filler, thus affecting the M_L . 5 phr substitute was not enough to break the CB network; instead, the NCC with high stiffness slightly increased M_L . As was known, a relatively low M_L suggested good flow ability. So it could be concluded that a moderate NCC/CB ratio led to a better processibility. T_{90} experienced an obvious reduction, while NCC content increased. The reduction

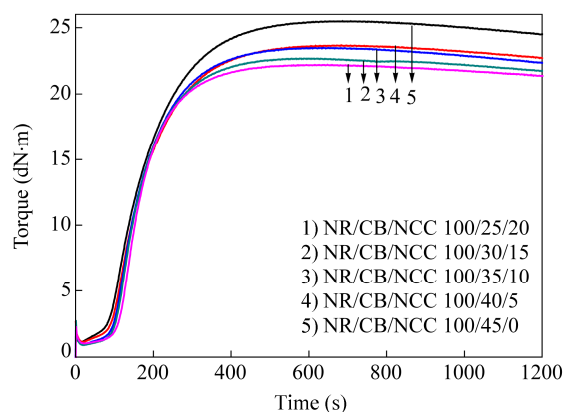


Fig. 1 Curing curves of NR/NCC/CB compounds (143 °C)

Table 1. Vulcanization characteristics of NR/NCC/CB compounds (143 °C)

NR/NCC/CB (phr)	T_{10} (s)	T_{90} (s)	M_L (dN·m)	M_H (dN·m)	ΔM (dN·m)
100/0/45	95	341	1.12	25.49	24.37
100/5/40	101	331	1.15	23.66	22.51
100/10/35	105	314	0.98	23.48	22.50
100/15/30	107	299	0.90	22.68	21.78
100/20/25	115	290	1.02	22.20	21.18

indicated that NCC accelerated the process of vulcanization. Whereas, T_{10} wasn't so subject to the NCC/CB ratio: only a slight delay occurred on T_{10} . The delayed T_{10} may be good for the process of processibility in some degree.

The curing curves can be used for the study of vulcanization kinetics, for vulcanization process determines the torque variety and the degree is nearly in proportion to the torque value. Thus, the rate (V) of vulcanization is commonly expressed by velocity of torque's variation^[14]:

$$V = -d(M_H - M_t)/dt = K(M_H - M_t)^n \quad (1)$$

where M_t is the torque value at curing time t , K is reaction rate constant, n is the reaction order.

The process of vulcanization can be segmented into three periods, the "induction, curing and overcure periods^[15]". It emerged that the vulcanization during the curing period tended to obey one order reaction, namely $n = 1$ ^[14]. In such a condition, Eq. (1) can be written as:

$$\ln(M_H - M_t) = B - Kt \quad (2)$$

where B is the constant of integration. According to Eq. (2), $-\ln(M_H - M_t)$ can be viewed as a function of time t . Therefore, the values of K , which presented as the slope of lines, were calculated through linear fitting of the experimental data.

The curing curves of NR/NCC/CB composites at 5 different temperatures for 20 min were tested. All of the samples with different NCC/CB ratios shared the similar tendency as was shown in Fig. 2. Among all the samples tested, it was revealed that samples suffered from undercure at 137 °C, since additional but slower torque improvement happened in the end stage of curing; when the temperature was 140 °C and 143 °C, a plat curve appeared in the end stage, which implied the network matured by equilibrium; as the temperature exceeded 145 °C, an overcuring reversion reaction was easily observed in the end stage^[16]. Other obvious phenomenon was that the curing period advanced as temperature went up, reflected by the early torque rising period. Based on the curing curves and data in Fig. 2, the value of K had been calculated and displayed in Table 2. For various samples tested, there was an obvious increase in K 's value as the temperature improved. Besides, the higher the ratio of NCC/CB was, the larger the value of K turned. This trend also supported the accelerating effect of NCC on vulcanization.

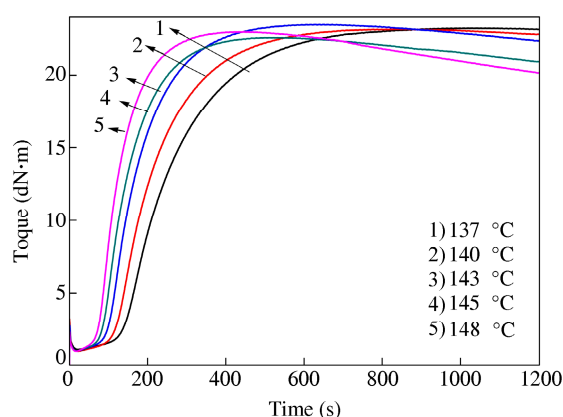


Fig. 2 Curing curves of NR/NCC/CB compounds at different temperatures

Table 2. The value of K at different temperatures for various samples tested

NR/NCC/CB (phr)	137 °C	140 °C	143 °C	145 °C	148 °C
100/0/45	0.0057	0.0071	0.0096	0.0112	0.0140
100/5/40	0.0060	0.0076	0.0099	0.0123	0.0150
100/10/35	0.0068	0.0081	0.0108	0.0135	0.0160
100/15/30	0.0069	0.0088	0.0116	0.0132	0.0180
100/20/25	0.0080	0.0101	0.0122	0.0143	0.0178

Arrhenius equation^[17] is commonly adopted to analyze the curing reaction and express the relationship between K and temperature (T):

$$d\ln K/dT = E_a/RT^2$$

This differential equation is also equivalent to:

$$\ln K = -E_a/RT + \ln A \quad (3)$$

where E_a is the activation energy, R is the universal gas constant, and A is the preexponential factor. A plot of $\ln K$ versus $1/T$ should form a straight line, which gives the slope ($-E_a/R$) and intercept ($\ln A$).

According to the data in Table 2, a plot of $\ln K-1/T$ is shown in Fig. 3. The set of kinetic parameters, derived from Fig. 3, were reported in Table 3. It appeared that the E_a varied slightly around 120 kJ/mol, when 0 to 15 phr NCC replaced CB. However, the obvious decline of E_a occurred while 20 phr CB was substituted by NCC. Thus, conclusion could be made that the replacement by NCC facilitated the curing reaction.

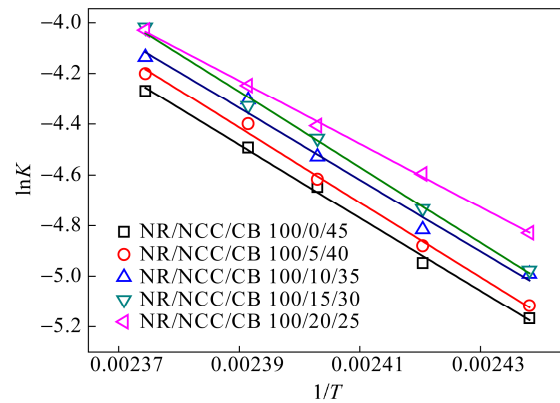


Fig. 3 Relation of $\ln K$ and $1/T$

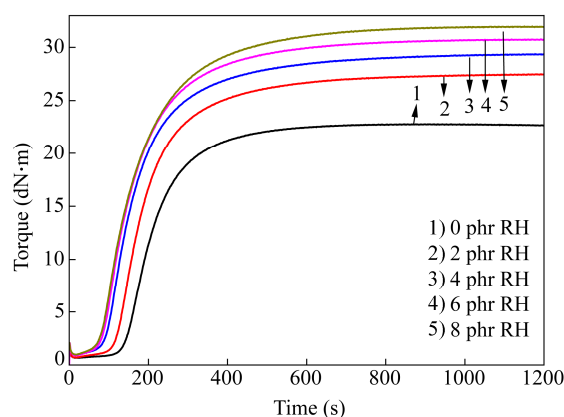
Table 3. E_a of vulcanization for NR/NCC/CB composites

NR/NCC/CB (phr)	100/0/45	100/5/40	100/10/35	100/15/30	100/20/25
E_a (kJ/mol)	119.9	122.7	117.6	123.7	103.5

At a high temperature, RH, the compatibilizer of composites discussed, would release radicals such as phenols, methyl and amine. In the process of vulcanization, those released radicals joined the crosslinking reaction^[18] and brought about better interaction between NR and NCC, thus improving the behavior of this composites. The curing curves and characteristics of NR/NCC/CB compounds with different RH contents are shown in Fig. 4 and Table 4. It seemed that advanced M_L and reduced T_{10} of NR/NCC/CB compounds were achieved with increasing RH content. This phenomenon could be explained that the mentioned radicals were released in the early stage, even before compounds performed their best flow ability, resulting in an advanced start of crosslinking reaction and increased M_L . Allowing for the safety of processibility, too many RH content would not be accepted. In addition, M_H markedly improved as RH was added, probably because that the participation of RH in vulcanization led to the increase of crosslink density, which could be supported by the apparent crosslink density result later. As was known, the M_H was commonly related with the stretching stress at 300%, so it could be deduced RH not only compensated the slight decline caused by NCC, but further improved the stretching stress of NR/NCC/CB composites, which were proved by study of mechanical properties^[8]. When RH content was more than 6 phr, M_H tended to be relatively less subjected to the fluctuation of RH content. Additionally, T_{90} varied irregularly from 258 s to 276 s.

Table 4. Vulcanization characteristics of compounds (143 °C)

NR/NCC/CB/RH (phr)	T_{10} (s)	T_{90} (s)	M_L (dN·m)	M_H (dN·m)	ΔM (dN·m)
100/10/35/0	148	358	0.67	22.80	22.13
100/10/35/2	125	375	0.70	27.49	26.79
100/10/35/4	101	368	1.16	29.38	28.22
100/10/35/6	92	358	0.90	30.77	29.87
100/10/35/8	89	376	0.98	31.97	30.99

**Fig. 4** Curing curves of NR/NCC/CB compounds (143 °C)

Samples, containing 0, 2, 4, 6, 8 phr RH respectively, were tested for curing curves at 5 different temperatures. And all of the samples exhibited a similar trend as was shown in Fig. 5. It could be seen that the curing curves at 158 °C reflected an obvious tendency of overcure with a gradually declined torque after M_H was achieved. At 143 °C and 148 °C, the curing curves depicted a stable torque around M_H in a relatively long period, which was the optimal choice of vulcanization condition. As for the curves at 138 °C, an undercure state was easily observed. According to the curves in Fig. 5, rate constant (K) of vulcanization was calculated and exhibited in Table 5. It revealed that the value of K was elevated as the temperature went up. Besides, at a relatively low temperature (*i.e.* 138 °C), the value of K seemed to decrease as RH content increased, while in relatively high temperatures (*i.e.* 158 °C), larger K appeared as more RH was incorporated. Reasons could be that the rate of radicals-release tended to slow down at low temperatures, thus resulting in a long period with crosslink reaction existed; the more RH the composites contained, the longer time the radicals-release took, so K decreased as RH content went up. However, at high temperatures, this process was finished quickly; hence the facilitating effect of RH tended to show out with a rising value of K as RH content improved.

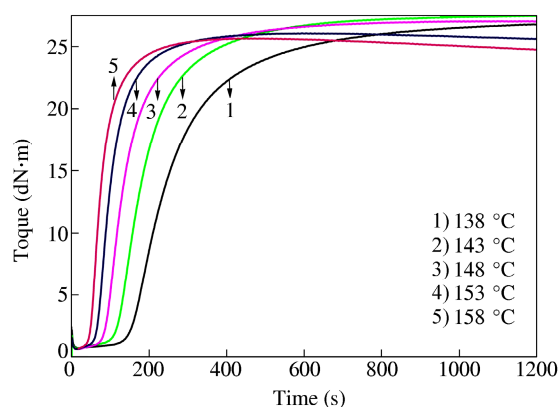
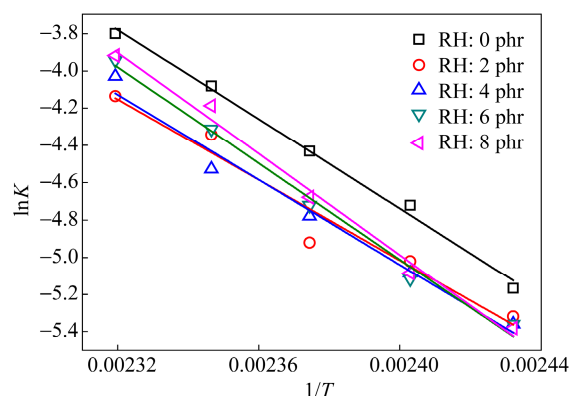
**Fig. 5** Curing curves of NR/NCC/CB compounds at different temperatures

Table 5. The value of K at different temperatures for various samples tested

NR/NCC/CB/RH (phr)	138 °C	143 °C	148 °C	153 °C	158 °C
100/10/35/0	0.0057	0.0089	0.0119	0.0169	0.0224
100/10/35/2	0.0049	0.0066	0.0073	0.0130	0.0160
100/10/35/4	0.0047	0.0062	0.0084	0.0108	0.0178
100/10/35/6	0.0047	0.0060	0.0089	0.0134	0.0194
100/10/35/8	0.0046	0.0062	0.0093	0.0152	0.0199

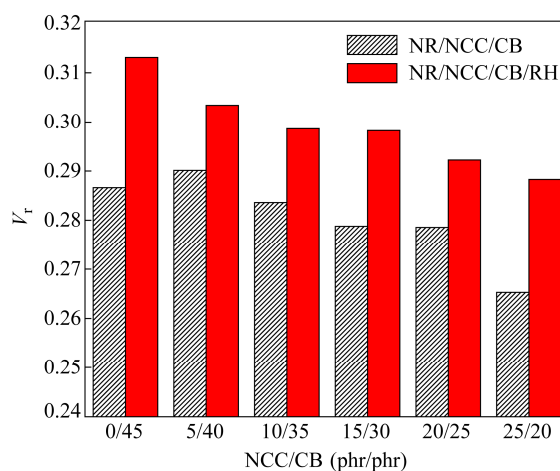
According to the data of Table 5, a plot of $\ln K$ versus $1/T$ is shown in Fig. 6. The set of kinetic parameters, derived from Fig. 6, are reported in Table 6. It appeared that small amounts of RH would help to lower the E_a , indicating the promotion to vulcanization. However, when RH content was beyond 4 phr, E_a would improve as more RH existed. It was probably a result of side-reaction, which would compete with crosslinking reaction.

**Fig. 6** Relation of $\ln K$ and $1/T$ **Table 6.** E_a of vulcanization for various samples tested

NCC/CB/RH (phr)	10/35/0	10/35/2	10/35/4	10/35/6	10/35/8
E_a (kJ/mol)	99.5	89.6	94.7	107.2	112.7

Apparent Crosslinking Density

Relation of V_r and NCC/CB ratio is exhibited in Fig. 7. It revealed that a 5 phr substitute of NCC for CB led to a slight increase in V_r . Then, larger NCC/CB ratio caused a gradual decline of V_r . It was probably because that the presence of NCC would break the network of CB; that is to say, NCC reduced the crosslink level of filler network^[8]; however, 5 phr NCC was not enough to break it and its high stiffness led to a slight increase. Besides,

**Fig. 7** V_r of NR/NCC/CB and NR/NCC/CB/RH composites

the incorporating of RH resulted in markedly elevating of V_r . It could be explained by two point: on the one hand, adhesive RH enhanced the crosslinking density of rubber network, on the other hand, RH improved the interaction between rubber matrix and NCC filler by hydrogen bonding interaction with NCC, thus notably elevating the value of V_r . This was also the mechanism of RH acting as the compatibilizer (Fig. 8).

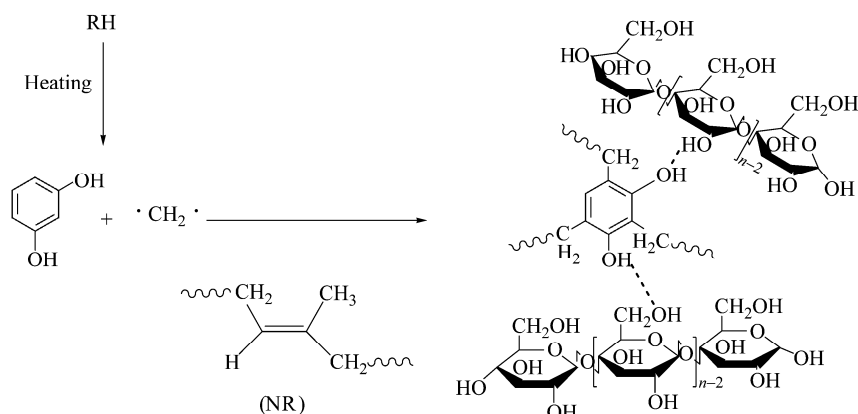


Fig. 8 A possible mechanism of RH acting as a compatibilizer

Aging Resistance Properties

It is known that the rubber materials tend to aging under the interaction of oxygen and heat, and finally lead to scrapping. Therefore, the aging resistance is one of the necessary parts to assess the behavior of rubber materials. In this work, the aging process was conducted both by hot air aging using an oven and high temperature aging simulated with RPA2000. The latter was wholly supervised for the variation of samples during aging. Aging resistance properties were evaluated according to the mechanical properties and storage modulus (G'), respectively.

The tensile and tear strengths before and after aging are exhibited in Fig. 9. Results showed that the strength wasn't deteriorated, after aging at 70 °C for 3 d. It was possibly because of the post cure effect. Namely, at the temperature of 70 °C for 3 d, crosslinking reaction triumphed the chain breakage reaction. Furthermore, sample with 15 phr NCC performed the highest and most obvious increase in tensile strength among 5 different samples. And the tear strength reached a peak, while NCC/CB ratio is 10/30. The variation of all the mechanical properties tested is shown in Table 7. It revealed that both elongation at break and permanent set decreased after aging. Nevertheless, RH helped to minimize the decrease. Additionally, stress at 300% and hardness enhanced after aging. With incorporation of RH, the tear strength of aging samples decreased, while the tensile strength enhanced. There results indicated a relatively good aging resistance of NR/NCC/CB composites at 70 °C. Overall, however, the sample with ratio of 10/35/5 (NCC/CB/RH) performed the best aging resistance in terms of mechanical properties. Therefore, conclusion could be made that NCC replacing CB was helpful to aging resistance of CB reinforced NR.

Table 7. Change rate of various mechanical properties before and after aging

NCC/CB/RH (phr)	0/45/0	5/40/0	10/35/0	15/30/0	20/25/0	25/20/0	0/45/5	5/40/5	10/35/5	15/30/5	20/25/5	25/20/5
Stress at 300% (%)	+17	+23	+28	+34	+31	+28	+13	+18	+15	+15	+13	+18
Tensile strength (%)	+4	+1	+2	+7	+6	+1	+3	+3	+8	+4	-3	+4
Tear strength (%)	+15	+10	+16	+1	+14	-4	-2	-7	-3	-10	-11	-1
Elongation at break (%)	-5	-7	-10	-9	-7	-9	-4	-7	-3	-2	-6	-4
Permanent set (%)	-37	-19	-13	-18	-18	-26	-12	-4	-9	-14	-16	-14
Hardness	+2	+2	+5	+3	+5	+7	+5	+2	+7	+7	+3	+7

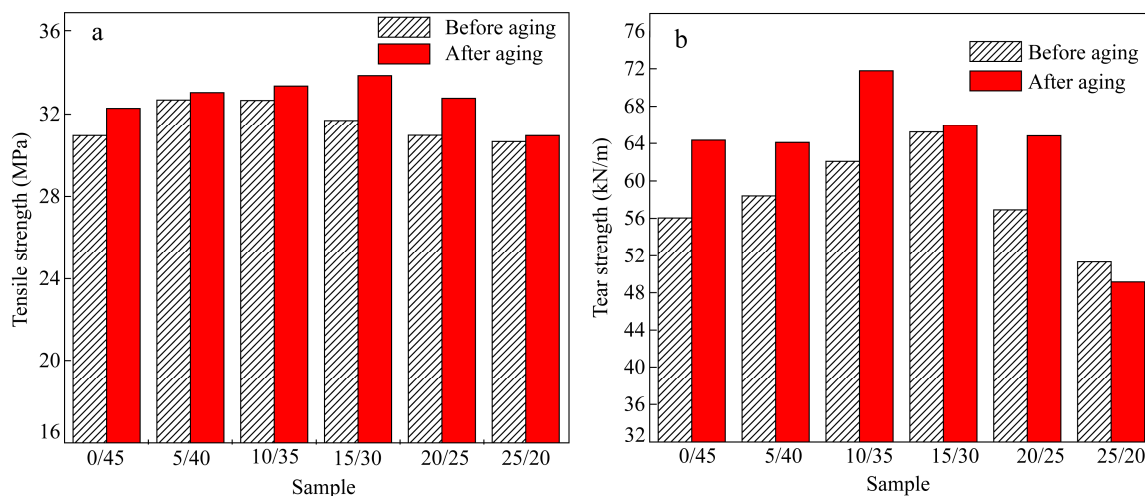


Fig. 9 Tensile strength and tear strength before and after aging of NR/NCC/CB composites

The effect of NCC content on G' of cured samples during aging at a high temperature of 165 °C is shown in Fig. 10. It revealed that G' of all samples increased in the early 2 min, then decreased in the following aging process. That tendency indicated an early aging period while crosslink reaction predominated (post cure effect) and a mainly aging period as chain rupture prevailed. It could be seen sample containing 10 phr NCC showed the highest growth of G' in the early period, which happened to agree with the optimal aging resistance of sample with 10 phr NCC replacing CB. Thus, it could be deduced the aged samples with improved mechanical properties may reach the aging degree corresponding to this early period. Furthermore, according to the change of G' in the beginning and end of aging (the 2nd picture of Fig. 10), sample with 10 phr NCC content also exhibited minimum decrease, which further supported the best aging resistance of this sample. The G' curves also told samples with NCC performed higher G' than those without it. The G' values for composites of different NCC/CB/RH ratios decrease in a sequence of 10/35/4, 15/30/4, 20/25/4, 5/40/4 and 0/45/4, successively. Another obvious phenomenon was that sample containing RH (0/45/4) performed higher G' and larger decrease in G' than original sample (0/45/0). Since RH joined the crosslinking reaction, crosslink density of composites improved. Consequently, the plastic flow of molecular chain was obstructed in same degree, which would result in a high G' . Besides, the partly breakage of crosslink bond built by RH contributed to the extra decrease in G' . Nevertheless, the 10 phr substitute of CB by NCC not only compensated this decrease caused by RH, but led to a relatively high retention of G' after aging, as was shown in the 2nd picture of Fig. 10.

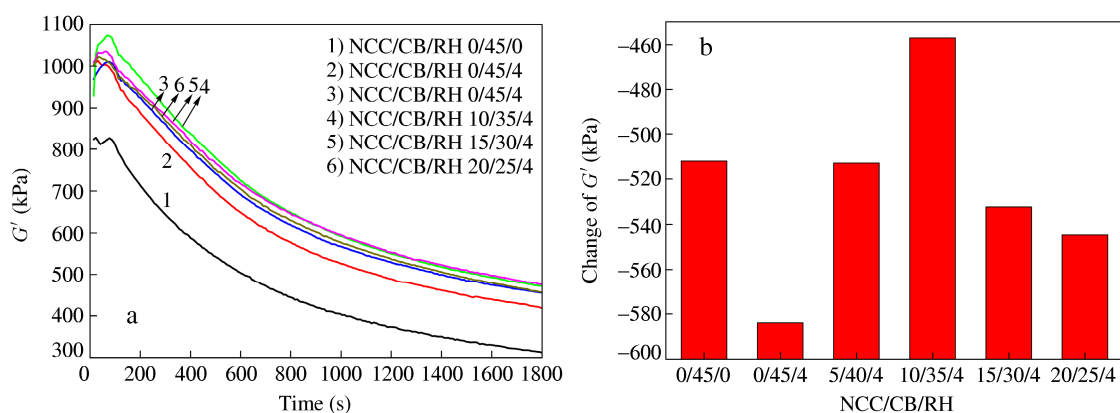


Fig. 10 The effect of NCC on G' of cured samples during aging and the differential value of G'

The G' of cured samples at strain scanning condition before and after aging at 165 °C is shown in Fig. 11. It revealed that G' at small strain (G'_S), G' at large strain (G'_L) and $G'_S - G'_L$ ($\Delta G'$) decreased after aging. Thus, it could be known that high temperature aging treatment not only caused the degradation of polymer, but also partly broke the unstable network. Additionally, the G' curves, especially G'_L of different samples tended to coincide after aging, except for those of original sample. Reasons could be that weak bond existing in network structure was broken after aging, while the remaining strong bond is similar among various NR/NCC/CB/RH composites tested. However, the network of original sample didn't strengthen by RH, and for other samples the crosslink points built by RH were not wholly destroyed. Consequently, the G' value of original sample was lower than that of other samples both before and after aging, so was the retention of G' (Table 8). According to the retention percentage of G' after aging shown in Table 8, sample with 10 phr NCC exhibited the highest retention of G' , indicating a good ability of network resistant to high temperature aging.

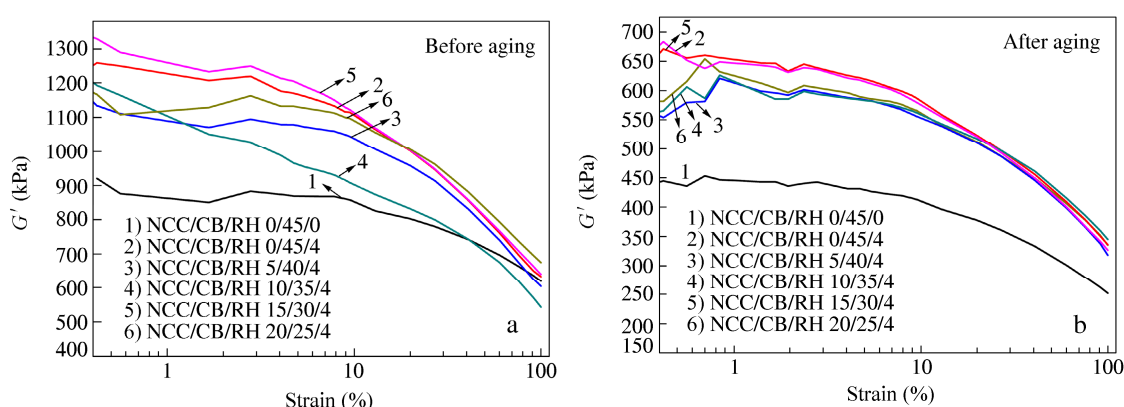


Fig. 11 G' -strain curves of cured samples before and after aging

Table 8. The retention percentage of G' after aging (%)

NCC/CB/RH (phr)	0/45/0	0/45/4	5/40/4	10/35/4	15/30/4	20/25/4
G'_S	48.3	53.5	55.0	57.0	51.5	54.5
G'_L	40.6	51.6	57.1	58.6	52.5	49.7

Thermal Gravimetric Analysis

Thermal gravimetric (TG) test can reflect the thermal stability of materials. The TG curves and characteristics of composites are shown in Fig. 12 and Table 9, respectively. It could be seen that the NR/NCC/CB composites and NR/NCC/CB/RH composites had similar curves, so they would be discussed altogether. Various TG curves corresponding to different NCC/CB ratios seemed to share the similar tendency. While, due to the good stability of CB, there was obvious difference of the residue weight. The higher the NCC/CB ratio was, the lower the residue weight turned. Additionally, the maximum rate of weight-loss improved as NCC content increased. The temperature when maximum rate of weight-loss appeared didn't move obviously. Partially replacing CB by NCC, the composites tended to loss 5 wt% at a lower temperature but still beyond 295 °C and 289 °C respectively for NR/NCC/CB composites and NR/NCC/CB/RH composites. All those analysis above indicated that the thermal stability of composites had a slight decline with CB partial replaced by NCC.

Table 9. TGA and DTG data of NR/NCC/CB and NR/NCC/CB/RH composites

NR/NCC/CB/RH	Temperature of 5% weight loss (°C)	NR/NCC/CB/RH	Temperature of 5% weight loss (°C)
100/0/45/0	317.1	100/0/45/5	307.8
100/5/40/0	302.7	100/5/40/5	298.1
100/10/35/0	295.7	100/10/35/5	298.7
100/15/30/0	307.1	100/15/30/5	290.1
100/20/25/0	296.4	100/20/25/5	289.1

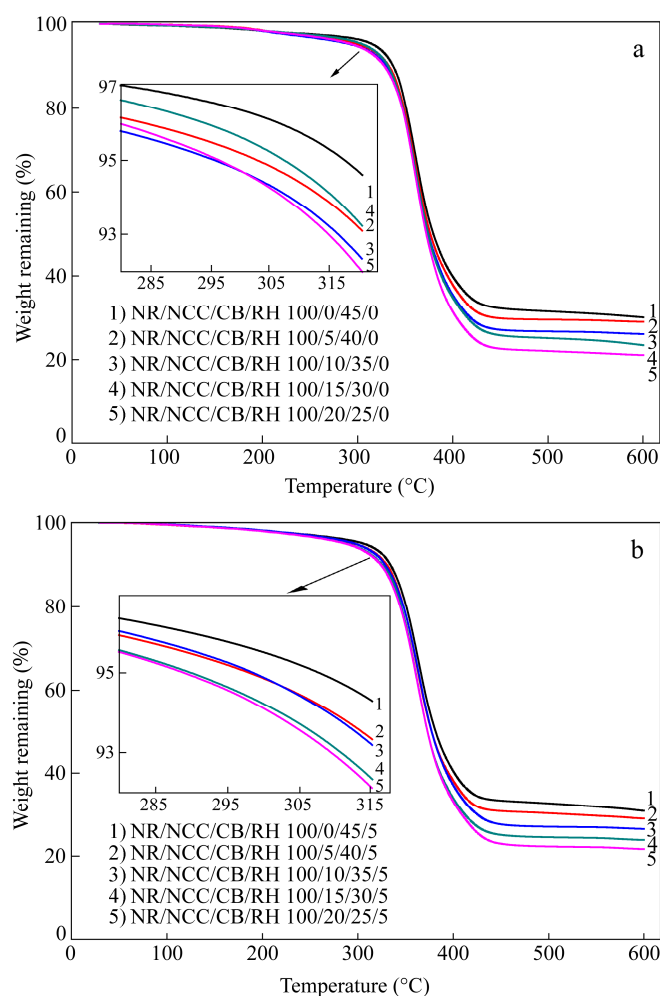


Fig. 12 TGA curves of NR/NCC/CB and NR/NCC/CB/RH composites

CONCLUSIONS

1. The filling of NCC resulted in a decrease in M_H , due to the reduction of crosslink density. Thanks to the good dispersion of fillers, a moderate NCC/CB ratio (15 phr) helps to lower M_L slightly, suggesting better processibility. The T_{90} turned short but T_{10} didn't change obviously as NCC content increased. More NCC content and higher temperature both contributed to a rise in vulcanization rate constant implying facilitating function of NCC to vulcanization.

2. Since RH joined and facilitated reaction of vulcanization, the existence of RH led to an elevated torque, short T_{10} and T_{90} . A moderate content (below 5 phr) of RH decreased the value of E_a for vulcanization.

3. The apparent crosslink density decreased as NCC/CB ratio increased. Whereas, the incorporation of RH improved crosslink density, markedly.

4. Partial replacement of CB by NCC didn't deteriorate the aging resistance of the composites. Composites containing 10 phr NCC, modified by RH, performed the best mechanical properties relatively. And, samples with NCC, especially with 10 phr NCC, show higher G' and retention of G' than those without it at a high temperature.

5. The substitute of CB by NCC had a slightly side effect on the thermal stability.

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