Improvement of Cutting and Chipping Resistance of Carbon Black-Filled Styrene Butadiene Rubber by Addition of Nanodispersed Clay

Jian-Hua Ma, Yuan-Xia Wang, Li-Qun Zhang, You-Ping Wu

State Key Laboratory of Organic-Inorganic Composites, The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

ABSTRACT: A novel, effective approach to improve the cutting and chipping resistance (CCR) of carbon black (CB)-filled styrene butadiene rubber (SBR) composite was reported in this study. CCR of SBR was dramatically improved more than 30% by addition of 4 phr nanodispersed clay (NC), while not decreasing the stress at 100% and the Shore A hardness of the composite. The curing characteristics, loss tangent (tan δ), and the strength of filler network of the composites were further measured by a Disk Oscillating Rheometer and a rubber processing analyzer, respectively. It was found that the addition of NC led to a slightly lower crosslink density, higher tan δ, and stronger filler network, which contributed to the higher CCR. Therefore, the novel layered NC is more efficient in improving CCR when compared with CB. The results are expected to promote the application of NC in rubber industry. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: clay; nanocomposites; cutting and chipping resistance; styrene butadiene rubber

INTRODUCTION

Cutting and chipping is a major problem in off-the-road (OTR) and heavy-duty (HD) tires, which often contact sharp objects such as rocks, gravel etc. High cutting and chipping resistance (CCR) is even a requirement for OTR and HD tires. Several affecting factors of CCR such as the filler type and amount, elastomer type, and curing system, were investigated in the literatures.[1–5] Reportedly, with increasing the amount of carbon black (CB) in nature rubber (NR) and styrene butadiene rubber (SBR) composites, CCR was first increased rapidly and then reached an optimum, and after that, a further increase in CB loading led to a decrease in CCR due to the overloading of filler.[2] It is reported that introduction of conventional filler silica is beneficial for CCR, 5−15 phr precipitated silica without modified by silane-coupling agent can increase resistance to cutting of CB filled NR.[6]

Clay, different from CB and silica, is of layered structure, and it can be dispersed on a nanometer level in SBR, NR, and carboxylated acrylonitrile-butadiene rubber by latex compounding method (LCM).[7,8] We found that incorporation of 4–5 phr nanodispersed clay (NC) prepared by LCM greatly improved the flex-fatigue life of CB filled SBR[9] and NR composites[10] due to the fact that NC layers had the advantage of crack blunting compared with CB. Similar to flex-fatigue life, CCR is also associated with crack propagation to some extent, and in some cases, CCR and flex-fatigue life are quite independent, exhibiting the similar change trend. The optimum crosslink density for CCR and flex-fatigue life is lower than that for the maximum tensile strength. Lower modulus and higher elongation are thought to be related to the improved CCR and flex-fatigue.[2,3,11] However, up to now there is no report in the literature addressing the effects of NC on the CCR of rubber composites.

In this study, the effects of NC on CCR of the SBR composites filled with CB were investigated, in which 4 phr of NC was adopted, referring to the studies.[9,10] We found that addition of 4 phr NC improved CCR considerably. To understand the underlying mechanism, the curing characteristics, hysteresis (loss tangent), and strength of filler network formed by clay and CB in the composites were measured via disk oscillating rheometer and rubber processing analyzer

TABLE I
The Basic Formulae of CM, RCM, and ACM (phr)

Sample	CM	RCM	ACM
SBR	100	80	80
SBR/clay (100/20) nanocompound	0	24	24
Carbon Black (N234)	50	46	50
Zinc oxide	3	3	3
Stearic acid	2	2	2
Antioxidant 4010NA[a]	2	2	2
Wax	1.5	1.5	1.5
Aromatic oil	10	10	10
MBTS[b]		1.2	1.2
DPG[c]		0.6	0.6
Sulfur		1.5	1.5

[a] N-Isopropyl-N'-phenyl-1,4-phenylenediamine.
[b] 2,2'-Dibenzothiazole disulfide.
[c] N,N'-Diphenylguanidine.

(RPA), respectively. The mechanical properties of the composites were also investigated. These investigations are expected to open novel possibilities to improve CCR of rubber composites. It is convinced that the CCR of the rubber composite could be further improved by introducing novel nanoscale layered fillers. This study is also expected to promote the application of NC in rubber industry.

EXPERIMENTAL

Materials

SBR-1502 and SBR-1502 latex were obtained from Jilin Petrochemical Co. (Jilin, China). Clay (Na$^+$ montmorillonite), with a cationic exchange capacity of 93 mequiv·(100 g)$^{-1}$, was purchased from Liufangzi Clay Factory (Jilin, China). CB N234 (primary particle size, 22 nm; BET surface area, 122 m^2/g; DBP value, 125 g/100g CB) was kindly provided by Cabot Chemical Company (Tianjin, China). Other materials are commercially available.

Preparation of SBR/clay nanocompound and SBR/clay/CB nanocomposite

A SBR/clay (100/20) nanocompound was prepared by LCM.[7,8] Clay was dispersed in de-ionized water at a concentration of 2 wt % under vigorous stirring, providing an aqueous suspension of clay. Then, a given amount of SBR latex was added in the aqueous suspension and stirred for 30 min. After that, the suspension was co-coagulated in about 3 wt % hydrochloride acid solution, washed with water until neutral, and then dried in an oven at 60°C for 24 h to obtain the SBR/clay nanocompound.

NC was introduced in SBR via SBR/clay nanocompound, and the basic formulae are listed in Table I. There are totally three samples examined herein, CM, RCM, and ACM. The composite containing 50 phr

CB was named as CM, which was used as a reference. The composite in which 4 phr clay replaced 4 phr CB was named as RCM, while in ACM, additional 4 phr clay was added on the basis of CM and the total amount of filler is 54 phr. According to the formulae above, SBR, SBR/clay nanocompound, CB, and other ingredients were mixed uniformly on a 6-in. two-roll mill at room temperature. At last, the compounds were vulcanized at 150°C for the optimum cure time (t_{90}) in a standard mould to produce SBR/clay/CB nanocomposite.

Characterization

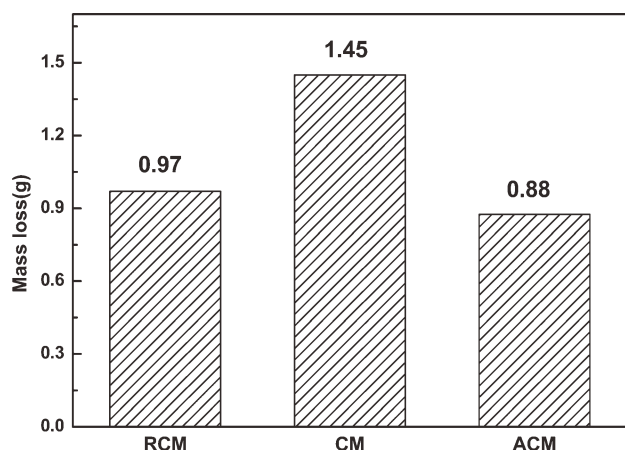#### Cutting and chipping resistance test

The CCR of the composites was performed using a BFGoodrich Cut and Chip Tester (Beijing Wanhui-Yifang Science and Technology Development, China). The test specimen and cutting and chipping tool are shown in Figure 1, and the core wrapped by the compound was vulcanized to obtain the specimen with the internal and the external diameters of 12 mm and 50 mm. For the CCR test, the specimen was rolling at a speed of 720 cpm for 20 min and the frequency of cutting was 2 Hz. CCR for the composite was determined by the average mass loss of the three specimens during cutting and the error is within 3%.

Dynamic heat built-up test

The sample for dynamic heat built-up test is a cylinder with diameter of 18 mm and height of 25 mm. The test was done at the initial temperature of 55°C for 25 min according to GB1687-1993 using Goodrich compression fatigue tester (Beijing Wanhui-Yifang Science and Technology Development, China).
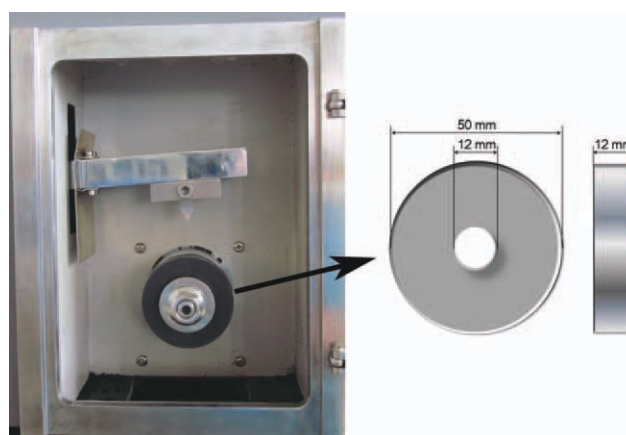
Figure 1 Photograph of the test specimen and cutting and chipping tool. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2 The mass loss of the composites after cutting and chipping.

Figure 3 Surface morphology of the composites after cutting and chipping. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mechanics performance test

The tests for tensile and tear strengths were carried on SANS tensile tester (MTS Systems, China) according to GB/T528-1998 and GB/T529-1999. Dumb-bell shape specimens and right-angle shape specimens were prepared for tensile and tearing tests, respectively. The tensile speed is 500 mm/min.

Transmission electron microscopy (TEM) observation

To investigate the filler dispersion and filler network structure in the rubber matrix, the uncured SBR/clay nanocompound, CM compound, and RCM compound were observed with H-800 TEM (Hitachi, Japan) using an acceleration voltage of 200 kV. The thin sections were cut by microtome under $-100°C$ and collected on the cooper grids.
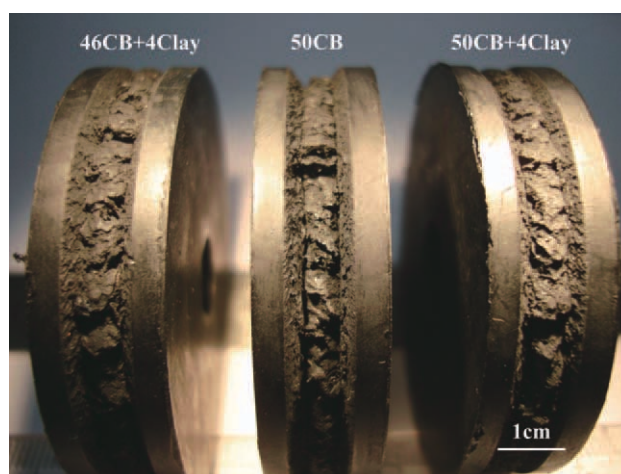
Test of dynamic viscoelastic properties

The dynamic storage modulus G' of the uncured compound was measured with RPA (Alpha Technologies, Akron, OH). Strain sweep from 0.28% to 400% was operated at 100°C, 1 Hz.

The dynamic storage modulus G' and loss tangent (tan δ) of the composite (vulcanlizate) were measured with RPA. Strain sweep from 0.28 to 40% was operated at 60°C, 10 Hz.

RESULTS AND DISCUSSION

Cutting and chipping resistance

The CCR results of the three composites were presented in Figure 2. As shown in Figure 2, the mass losses of RCM and ACM were decreased by 33% and 40%, respectively, compared with that of CM without NC; while a comparison between ACM and

RCM showed that the addition of 4 phr CB had only a slight effect on CCR. These phenomena indicated that layered NC, different from spherical-like CB particles, is beneficial for the improved CCR. The surface morphology of the samples after cutting is presented in Figure 3. The grooves of CM without NC were deeper than those in RCM and ACM, providing a direct evidence for the conclusion that CCR of RCM and ACM was better than CM.

To explore the major factors leading to the improved CCR after addition of 4 phr NC, the microstructure, cure characteristics, mechanical properties, and hysteresis were investigated further, as discussed below.

Cure characteristics

The curing characteristics of the composites are presented in Figure 4 and Table II. We observed that the minimum torques (M_L) of RCM and ACM are
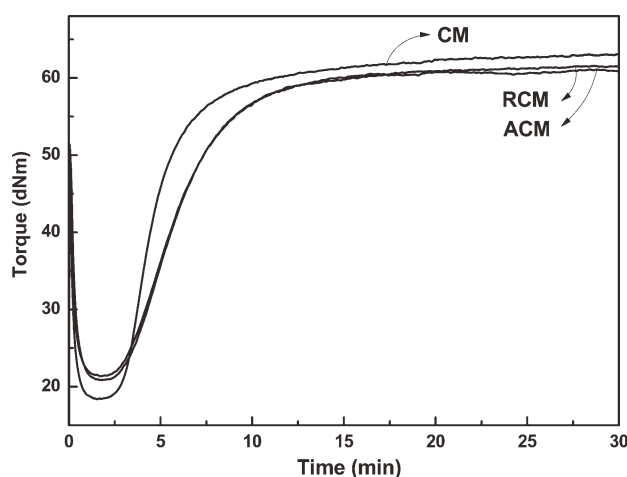
Figure 4 The vulcanization curves of the composites.

TABLE II
Curing Characteristics of the Composites

Sample	RCM	CM	ACM
t_{90} (min)	10.5	9.2	10.4
M_L (dNm)	20.8	18.4	21.4
M_H (dNm)	61.6	63.1	61.1
ΔM (dNm)	40.8	44.7	39.7

slightly higher than that of CM without NC, and the differences between the minimum and maximum torques (ΔM) of RCM and ACM are lower than that of CM, indicating that NC increased the viscosity of the compound and decreased the crosslink density of the composite. The increased viscosity results from the layered structure, higher aspect ratio than that of CB [see Fig. 6(c)]. The decreased crosslink density may be attributed to the reason that clay can absorb the accelerating agents.[12,13] In addition, it can be seen that the curing curves of RCM and ACM are almost the same, reflecting that CB has little influence on curing.

Mechanical properties

The mechanical properties of the composites are shown in Table III. As shown in Table III, the tensile strength, tear strength, and stress at 100% of RCM and ACM are slightly higher compared with CM. Since the D-value is within 10%, the 300% modulus of RCM, CM, and ACM can be thought to be almost at the same level. Compared with CM, incorporation of 4 phr NC resulted in an evident increase in Shore A hardness and elongation at break of RCM and ACM, while addition of CB had little influence on hardness and elongation. It is again indicated that the role of NC is greatly different from that of CB, which is in good agreement with CCR and curing results. CCR of composites highly depended on the deformation ability under the impact of cutting tool, and a high elongation at break thus led to a high CCR.[2] Also in our investigated systems, we obtained the similar results. Of particular interest is that the elongation at break increased greatly by the addition of NC for RCM and ACM, while the stresses at 100% of RCM and ACM are a little higher than that

TABLE III
The Mechanical Properties of the Composites

| Sample	RCM	CM	ACM
Stress at 100% (MPa)	2.2	2.0	2.5
Stress at 300% (MPa)	9.1	10.1	10.5
Tensile strength (MPa)	20.3	19.4	21.7
Tear strength (kN m^{-1})	60.9	58.6	61.3
Elongation at break (%)	553	473	556
Permanent set (%)	12	8	12
Shore A hardness (°)	73	70	74
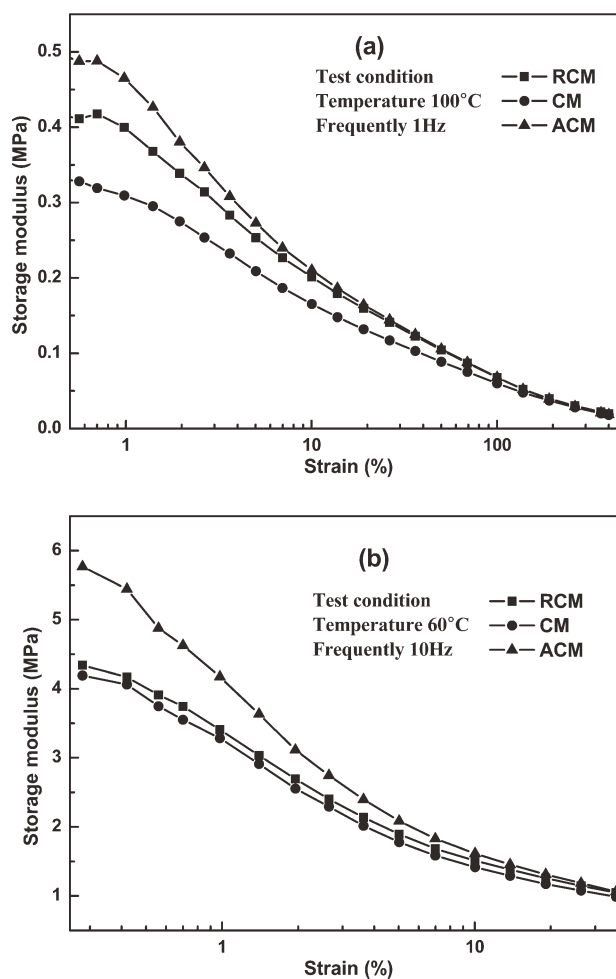
Figure 5 Curves of the storage modulus vs. strain of the compounds (a) and the storage modulus vs. strain of the composites (b).

of CM. Such results cannot be achieved just by reducing the crosslink density.

Payne effect and filler network

The amplitude-dependence of the dynamic storage modulus (G') of the compounds is referred to as Payne effect, which is closely related to filler network.[14] To investigate the effect of 4 phr NC on the filler network, the strain sweep of the three compounds is shown in Figure 5(a). Figure 5(a) shows that the order of the initial modulus for the three compounds is ACM > RCM > CM, which should be attributed to the stronger ability of the layered clay to form a stronger filler network than CB particles,[9] in consistent with the results of curing curve—the increased viscosity of ACM and RCM compared with CM. After curing, the difference between the curves of RCM and CM is reduced [Fig. 5(b)], most likely resulting from the decreased crosslink density of RCM compared with CM mentioned
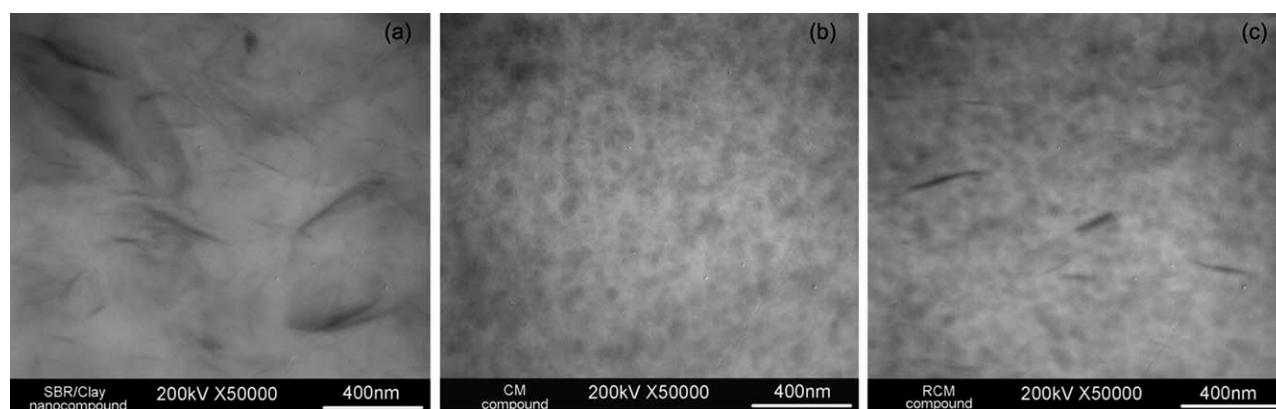
Figure 6 TEM micrographs of the SBR/clay nanocompound, CM compound, and RCM compound.
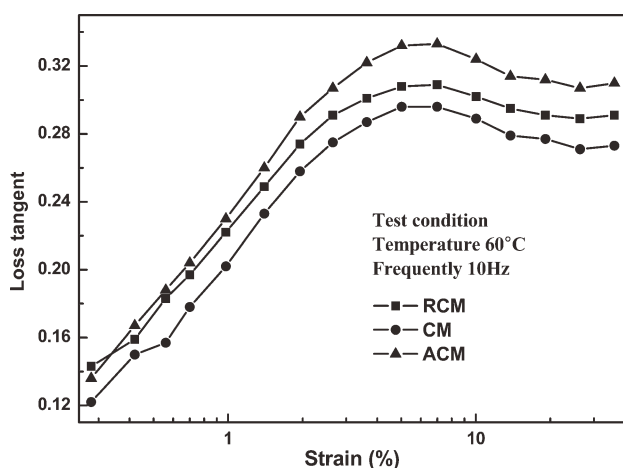
above. Owing to the largest amount of filler in ACM, the modulus of ACM is still the highest among the three composites.

TEM observation

The TEM micrographs are shown in Figure 6. In Figures 6(a,c), the dark lines are the intersections of the clay layers. In SBR/clay compound, the dispersion of clay is on the nanometer level. In RCM, the dispersion of clay is still kept almost the same as that in SBR/clay compound. At the clay loading of 4 phr, the number of dispersed clay layers is not high enough to form the clay network. By comparing Figure b and c, it seems that addition of clay did not change the dispersion of CB. In RCM, clay layers, together with CB, formed filler network, stronger than that of individual CB network.

Hysteresis and heat build-up

The loss tangent (tan δ) of the composites is presented in Figure 7. Compared with CM, the tan δ of

RCM and ACM are higher in the investigated strain range, indicating that the addition of clay increased hysteresis of RCM and ACM at the same strains. The increased hysteresis should be attributed to the stronger filler network formed by layered clay and CB together than the individual CB network. When compared the composites with the same level of the stresses at 100% and 300%, the higher hysteresis leads to a higher heat built-up.[15,16] In our investigated three composites, their stresses at 100% and 300% can be regarded as the same level, and the temperatures rising of the composites are shown in Figure 8. The order of heat build-up is ACM > RCM > CM, consistent with that of hysteresis as discussed above, which is in agreement with the results in the literature.[16] It is found that the surface temperature of the sample rose rapidly during the cutting and chipping process.[17] Higher heat bulit-up indicates that more energy during cutting and chipping process is changed into heat, and correspondingly less energy is used to demage the rubber molecule chains. Thus, the composite with a higher hysteresis and a higher heat build-up should perform a better CCR, as shown in our study.

Figure 7 Curves of the loss tangent vs. strain of the composites.
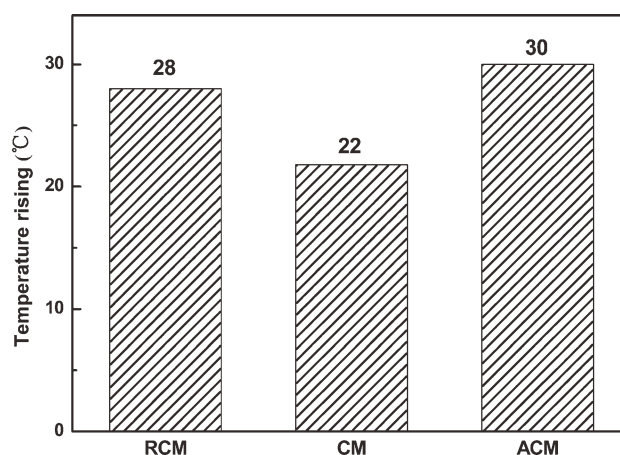
Figure 8 The heat built-up measurement of the composites.

The mechanism of CCR improved by addition of NC

When the tire tread strikes a sharp object with enough force, cutting and chipping occurs in the course of the impact process. In this experiment, the sharp object is a metal blade, which impacted the sample repeatedly with a fixed energy. During the cutting and chipping process, the damage and fracture of the sample can be divided into two stages. In the first stage, no debris was cut off from the surface of the composite, because the impact loading energy was absorbed by the composite via deformation. With a cyclic cutting, micro-crack occurring on the surface induced an observable damage and then the second stage began. In the second stage, with the micro-crack propagated further by the repeated impact, the debris was detached from the composites.[18,19] The addition of NC greatly increases the deformation ability (higher elongation) and the hysteresis, which are closely related to the ability to transform the cutting energy into heat energy, and thus prevents the composite from being ruptured from cutting. At the same time, 4 phr NC improve the tear strength and thus the composites exhibit higher ability of inhibiting crack propagation. The combination of high deformation ability, hysteresis and preventing crack propagation, contributes largely to the increase in CCR of the composites with NC.

CONCLUSION

CCR of CB-filled SBR was improved more than 30% via an addition of 4 phr NC. NC and CB formed stronger filler network than that of CB alone and increased the hysteresis of the composite. The addition of NC greatly increased the elongation at break and hardness of the composites, while not decreasing the stress at 100%. These results are of great importance to develop new approaches to improving CCR of rubber composites and promote the practical applications of NC in tires and other rubber products, such as transportation belts used in mining industry.

References

1. Maya, S.; Mark, R. G. J Elastom Plast 2003, 35, 73.
2. Beatty, J. R.; Miksch, B. J. Rubber Chem Technol. 1982, 55, 1531.
3. Schwarz, D. L.; Askea, D. W. Rubber World 2003, 228, 28.
4. Gent, A. N.; Lai, S. M.; Nah, C.; Wang, C. Rubber Chem Technol 1994, 67, 610.
5. Manas, D.; Stanek, M.; Manas, M.; Pata, V.; Javorik, J. Kaut Gummi Kunst 2009, 62, 240.
6. Okel, T. A.; Waddell, W. H. Rubber Chem Technol 1994, 67, 217.
7. Wu, Y. P.; Zhang, L. Q.; Wang, Y. Q.; Liang Y.; Yu, D. S. J Appl Polym Sci 2001, 82, 2842.
8. Wu, Y. P.; Wang, Y. Q; Zhang, H. F.Wang, Y. Z.; Yu, D. S.; Zhang, L. Q. Compos Sci Technol 2005, 65, 1195.
9. Wu, Y. P.; Zhao, W.; Zhang, L. Q. Macromol Mater Eng 2006, 291, 944.
10. He, S. J.; Wang, Y. Q.; Wu, Y. P.; Wu, X. H.; Lu, Y. L.; Zhang, L. Q. Plast Rubber Compos 2010, 39, 33.
11. Dick, J. S. How to Improve Rubber Compounds: 1500 Experimental Ideas for Problem Solving; Hanser Gardner Publications, Inc.: Ohio, 2004; Chapter 3, p 160.
12. Sugata, C.; Saptarshi, K.; Saikat, D.; Rabindra, M.; Samar, B.; Mangala, J.; Suresh, C. A. J Appl Polym Sci 2010, 116, 1660.
13. Sun, Y. H.; Luo, Y. F.; Jia, D. M. J Appl Polym Sci 2008, 107, 2786.
14. Payne, A. R. J Appl Polym Sci 1962, 6, 57.
15. Wang, M. J. Kaut Gummi Kunstst 2007, 60, 438.
16. Wang, L.; Zhao, S. H.; Li, A.; Zhang, X. Y. Polymer 2010, 51, 2084.
17. Nah, C. W.; Jo, B. W.; Kaang, S. Y. Appl Polym Sci 1998, 68, 1537.
18. Persson, B.N.; Albohr, O.; Heinrich, G.; Ueba, H. J Phys Condens Mater 2005, 17, 1071.
19. Felhös, D.; Karger-Kocsis. J. Recent Adv Elastomer Nanocompos, 2011, 9, 343.