An Effect of OMMT on the Anti-Reversion in NR/CR Blend System

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ABSTRACT: The influence of dispersed organomodified montmorillonite (OMMT) on curing behaviors of natural rubber (NR)/chloroprene rubber (CR) blend was investigated. The preparing procedure includes premixed rubber individually with its additives and then the two components were blended according to gum weight ratio for NR to CR is 75/25. Sulfur was chosen as the vulcanizing agent, and the research on vulcanization was carried through the rotor-Rheometer at 143°C. Transmission electron microscopy showed the dispersion of OMMT in the rubber blends and detected little OMMT migrated into the NR phase. The scorch time (t_{10}), optimum vulcanizing time (t_{90}), and reversion phenomenon were both measured by the curing curve; meanwhile, the crosslinking densities and mechanical properties were determined through equilibrium swelling-method, magnetic resonance crosslink density spectrometer, and tensile tests. By comparing the test results, an interesting phenomenon was discovered and furthermore was verified that the addition of OMMT can obviously modify the reversion resistance of the binary blend. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 673–679, 2009

Key words: natural rubber; chloroprene rubber; covulcanization; montmorillonite; antireversion

INTRODUCTION

Natural rubber (NR) produced through the bio-synthesis in *Hevea brasiliensis* tree naturally[1] is primarily utilized in the tire industry and shows the best comprehensive property. Especially, the existence of stress-induced crystallization has made this rubber unique among all the elastomers, as far as its mechanical properties are concerned. However, vulcanized NR shows poor weather stability for the existence of many double or unsaturated bonds.[2–3] To improve the ambient stability of NR, researchers have tried to blend NR with chloroprene rubber (CR).[4–5] CR developed by Du Pont in 1931[6] is one of the earliest synthetic rubbers, its vulcanizate brings forth excellent oil resistance, thermal stability, self-extinguish ability, and ozone resistance.[7]

When mentioned the NR/CR blend system, the covulcanization is intractable. There exist two main problems namely, the dispersion of vulcanizing agent and curing reversion. For one side, in covulcanized rubber/rubber blend, dispersion of vulcanizing agent is a complicated one. In general, vulcanizing agent will migrate during mixing or curing. In as much as earlier Gardiner emphasized that migration of curative was related to dispersal during curing, but not to transfer during mixing. Besides, he found that the polarity and unsaturation of an elastomer controlled curative migration.[8–10] For the other side, curing reversion is another significant problem. When polysulfurnic crosslinks are exposed to a temperature–time treatment, it causes decomposition[11–13] and reduction in crosslinking density and, consequently, loss of mechanical properties etc. Furthermore, in a NR/CR blend system, the effect will be pricked up. In the past years, to prevent or reduce reversion, a great effort has been done,[14] among which efficient/semiefficient vulcanization and sulfur donor cure systems were applied. These vulcanizing systems function by generating more mono- and disulfurnic crosslinks while reducing the number of polysulphidic crosslinks in the network. The improvement in reversion resistance is, however, achieved at the expense of losing flex and related strength.

Organized montmorillonite (OMMT) that is a layered silicate can lead to a significant improvement of many properties, such as stiffness, heat resistance, flame retardance, and gas barrier properties with a low loading.[15–17] There are lots of publications reported such aspects, however, few deal with the influence of OMMT on the matrix vulcanization. Here, what causes our interest is the function that adding OMMT to NR/CR binary blend system not only can improve the reinforcement efficiency via betterment of the dispersability[18] but also will affect the vulcanization of the rubber matrix.

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TABLE I
The Formulation Used in the Preparation of Natural Component

	Phr[a]
Natural rubber	100
Stearic acid	2.0
Zinc oxide	5.0
CZ	0.5
D	0.5
Sulfur	2.5

[a] Part per hundred parts of rubber.

The aim of this research is to investigate the function of OMMT in the NR/CR system. And for that, a few tricks were undertaken such as super accelerator tetramethylthiouram disulfide (TMTD) and a little amount of sulfur was brought into CR gumstocks. The addition of sulfur and accelerator can improve the curing rate and reach a high state of cure.[19] And OMMT mixed with the CR to form a masterbatch followed by blending with the other vulcanizing agents. On the basis of the experiment results of curing curves, transmission electron microscopy (TEM), crosslinking density, and affirmatory tensile strength, we get solid evidence that the cure incompatibility and reversion problem of NR/CR covulcanizing system can be well solved by introducing a few loading of OMMT, namely OMMT has the ability of improving reversion resistance of rubber blends.

EXPERIMENT

Materials

CSR-10 (Chinese Standard Natural Rubber-10) and chloroprene (CR-2442, Changshou) were used in this study as received. And both rubbers were supplied by Sichuan Rubber Factory. The OMMT (DK3), stated by the manufacturer to possess surface area 750 m^2/g and aspect ratio 200, is from Fen hong Clay Factory (Zhejiang, China). The accelerators used were N-Cyclohexyl-2-benzothiazyl sulfonamide (CZ) and Diphenyl guanidine (DPG) for NR while TMTD and CZ for CR. N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenedianine (Antioxidant 4020) was chosen as the antioxidant. Other compounding ingredients such as zinc oxide, stearic acid, magnesium oxide, and sulfur of commercial grades were used without further purification.

Mixing and sample preparation

A typical recipe used in the study is shown in Tables I and II. NR and CR was individually blended with its own additives. And the mixing procedure was in reference to ASTM D 3184 by using a two-roll mill and two components were blend according to gum weight ratio for NR to CR is 75/25. The rubber compound was compression molded into test specimens at 143°C according to the respective optimum vulcanizing times determined by the Rheometer R 100E. Dumb-bell samples were cut from a 2 mm thick molded sheet and prepared for the test of mechanical properties.

Characterization of the rubber compound

Measurement of curing curves

The sheeted rubber compound was conditioned at room temperature for 24 h before curing test using a Rheometer R 100E. The Rheometer gave outputs of curing curves and related values such as scorch time t_{10} (time required to achieve 10 Mooney units above the minimum viscosity), t_{90} (time required to achieve 90 Mooney units above the minimum viscosity), and related torsions.

Dispersion of OMMT in the binary rubber blend

To detect the dispersion or migration of OMMT in the rubber blends, the technique of TEM was used. TEM measurements were carried out with a JEOL JEM-1010 transmission electron microscope applying an acceleration voltage of 100 keV. The specimens were prepared using an Ultra cut R (Leica) ultra microtome. Thin sections of about 100 nm thicknesses were cut with a diamond knife at approximately −100°C.

Mechanical properties

Measurements of tensile mechanical properties were carried out in a computerized tensile tester (Reger 3010) as per ASTM D 412-80. Affirmatory elongation strength at 100, 200, and 300% were determined. And Shore A hardness measurements were carried out in LX-A dial gauge hard meter as ASTM D2240. All tests were conducted in five-fold at room temperature (25°C) and the results were averaged.

TABLE II
The Formulation Used in the Preparation of CR Component

	Phr
Chloroprene rubber	100
Stearic acid	1.5
Zinc oxide	5.0
Magnesium oxide	4.0
CZ	1.0
TMTD	0.5
Sulfur	0.5
DK3	variance

Measurement of crosslinking density, sol fraction, and swelling index

The determination of the crosslinking density was performed by magnetic resonance crosslink density experiment[20] or equilibrium swelling method.[21] The magnetic resonance crosslink density experiments have been performed on an IIC XLDS-15 polymer/rubber crosslink density analyzer and NMR spectrometer. This spectrometer operates at a proton resonance frequency of 15 MHz. The length of the 90°pulse was 3 µs. A VTU-130 temperature controller was used for temperature regulation. The temperature gradient and stability were better than 1°C. In this work, the samples were conditioned in glass tubes probe head and the sample size was 5 mm or smaller and preheated at 90°C for 5 min. Two different measurement methods, that is, AP saturation recovery was used to record the decay of the longitudinal magnetization (T_1 decay) and a Hahn-Echo pulse sequence was applied to record the decay of the transverse magnetization (T_2 decay). And the crosslinking density (XLD) was measured after the analysis of the data as follows:

$$M(t) = A_0 + A_1 \exp[-t/T_2 - (qM_2t^2)/2] + A_2 \exp(-t/T_2)$$

where $M(t)$ is transversal magnetization decay (s^{-2}), t is decay times (ms), qM_2 is the residual dipolar moment ($\sim 10^{-4}/s^2$), T_2 is the spin–spin relaxation time ($\sim$ ms), A_1 and A_2 are amplitude factors, and A_0 is the fitting factor (no physical meaning). The data was acquired with the spectrometer controlling software IICNMR and processed by fully automatic data acquisition software IIC-Analysis after setting the sample as blend of NR and CR. And for each sample, threefold test was repeated and the results averaged were offered.

And the equilibrium swelling-method was undertaken as described by Jain et al.[21] In this part, the swell ratio, sol fraction (Q), swelling index (S_i), and crosslinking intensity (V_c) were acquired.

RESULTS AND DISCUSSION

Curing curves, OMMT dispersion

A typical NR/CR blend was prepared and the curing curve measurement was carried through the rotor-Rheometer at 143°C. The variation of curing curves of NR, CR and CR/NR gums is shown in Figure 1. It is dominant that NR gum shows a wide plateau, whereas the CR/NR and CR exhibits degressive and ascending trend, respectively. By controlling the vulcanizing system, the coordinate curing rate (both t_{90} are about 12.5 min) was acquired as shown in Figure 1. For the curing curve
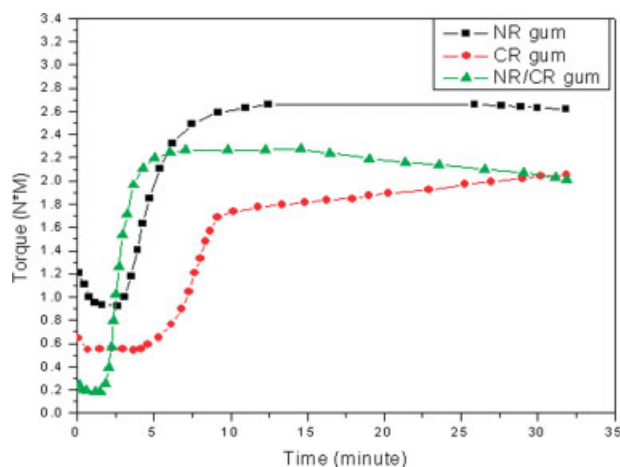

Figure 1 Curing curves of NR, CR and NR/CR gums. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of NR/CR binary blend, it can be found that the reversion is dominant. In general, reversion of rubber is roughly attributed to the decomposition of the main chain and also the rearrangement of the polysulfurnic bonds which turn into mono- or disulfurnic bonds. However, here we conclude the reversion mainly results from the thermal degradation. Because the thermal degradation of rubber will give birth to active free radicals or ionic molecules, which may accelerate the degradation of the main chain of macromolecules.[22,23] Although for the sulfur cured NR/CR system shows high unsaturated degree, the reversion phenomenon is much more likely to occur when induced by some vulcanizing by-products. And CR that comprises *tert*-butyl chlorine (by-products of polymerization) will release hydrochloride during cure.[24] Perara et al. have found that the hydrogen chloride liberated from CR causes structural changes in epoxidized natural rubber (ENR) which lead to the formation of furanized ENR in CR/ENR blend.[25] And acids are fairly effective in rendering rubber more easily oxidized.[26] Thus, the curing course of CR would impair that of NR and result in reversion. And hydrochloride, at the situation, will diffuse easily into NR and then promote and boost degradation of NR. Consequently, leading to the decrease of crosslinking density (which will be mentioned in the following parts) and curing reversion occurs.

Taking into account of the diffusion of hydrochloride, here we added OMMT into CR of the rubber blend. And first of all, we determined the dispersion and migration of OMMT in the rubber blend and then the influence of OMMT on the vulcanization of NR and CR. Figure 2 shows TEM micrographs taken from the NR/CR/OMMT nanocomposites. The dispersion of the organoclay is far less homogeneous in
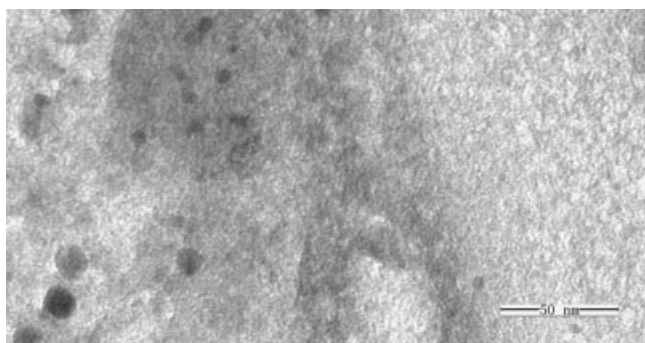
Figure 2 TEM micrograph of the NR/CR/OMMT composite filled with 5 wt % OMMT.

Figure 4 Curing curves of CR gum and CR loaded with 10 wt % OMMT. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the blend system where most parts stay in the CR phase, that is, dark regions lie in the left part of the clear-cut between rubber phases shown in the TEM micrograph.

The curing curves of NR, CR gum-stocks, and hybrids (DK3 10 wt %) are shown in Figures 3 and 4, respectively. By comparing the curing curves of rubber component with and without OMMT, as foursquare line and dotted line indicated, it can be found that blending with OMMT will extend the vulcanization flatness of NR just as shown in Figure 3; and after blending in OMMT, the slope of the curing curve of CR after t_{90} is much bigger, shown in Figure 4, which indicates that curing rate is accelerated. So it is clear that filling OMMT will prevent either NR or CR from reversion. This is the basal step to further study the influence of OMMT on the cure of NR/CR binary blend.

As shown in Figure 5, by introducing just a low loading of OMMT (5 wt %), an improved vulcaniz-
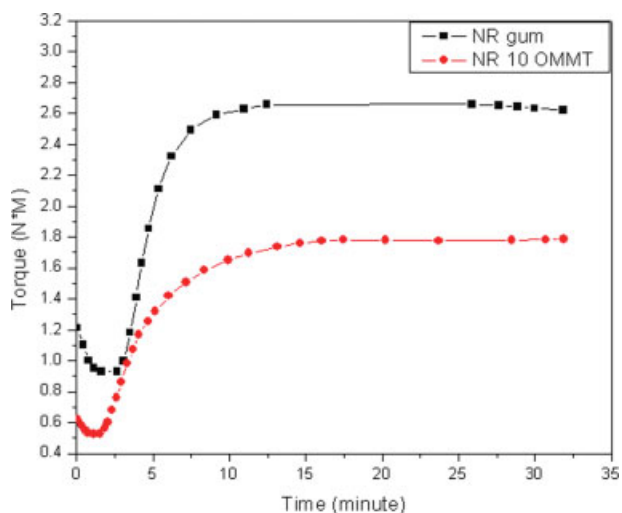
ing property of NR/CR blend was gained. Here, OMMT shows absorption and barrier and decreases the chance of hydrochloride diffuses into NR phase. Thus, OMMT plays an important role in the antireversion of NR/CR blend.

Mechanical properties

The mechanical characteristics such as Affirmatory tensile strength and hardness of rubber blend containing OMMT or not are shown in Figures 6 and 7. According to the statistical theory of rubber elasticity,[27] when the primary molecule weight of the rubber is high, the force (f) necessary to maintain a

Figure 3 Curing curves of NR gum and NR loaded with 10 wt % OMMT. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
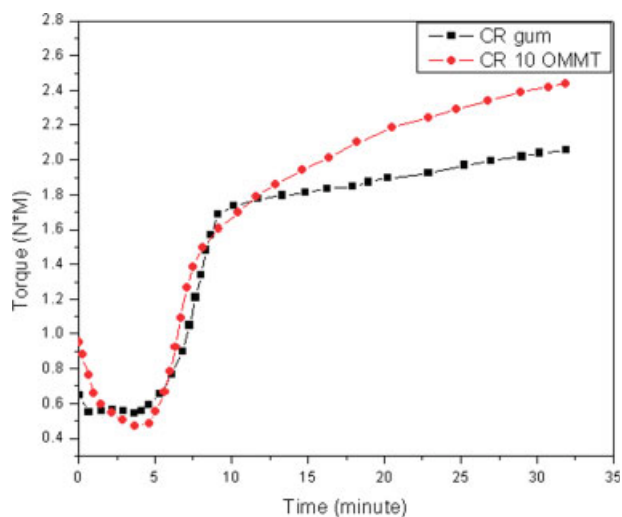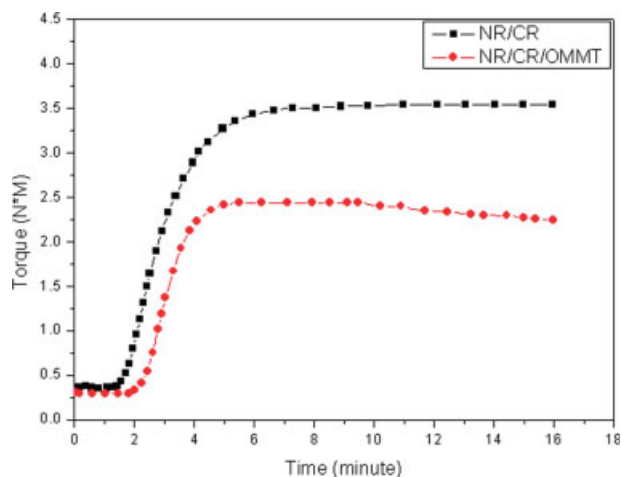

Figure 5 Curing curves of rubber blend with and without OMMT. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
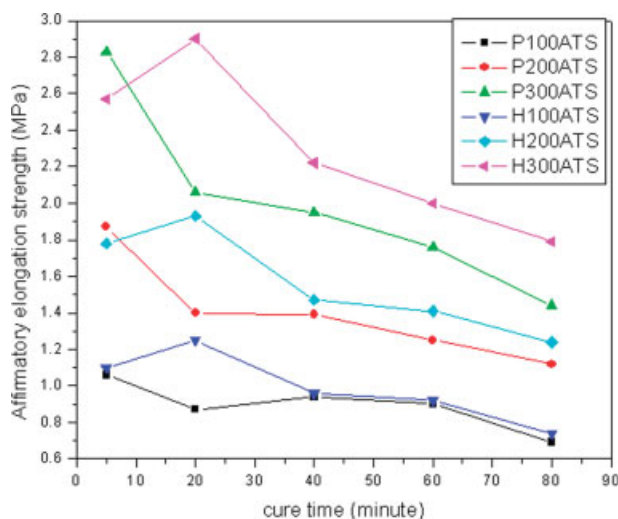
Figure 6 Affirmatory elongation strength versus cure time (P NR/CR blend, H 10 wt % OMMT loaded NR/CR blend). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sample of vulcanized rubber at an elongation ratio, α, during simple extension, is

$$f = \frac{\rho R T}{M_c} A_0 \left(\alpha - \frac{1}{\alpha^2} \right)$$

where ρ is the density of the nonswollen rubber, A_0 is the cross-sectional area of the undeformed sample, α is the ratio of the length of the elongated specimen to its original length, M_c the average molar weight of polymer between crosslinks, R the gas constant, and T absolute temperature. Obviously the hardness and affirmatory tensile strength are closely related to the crosslinking density. As shown in Figures 6 and 7, with increasing cure time, the OMMT filled rub-
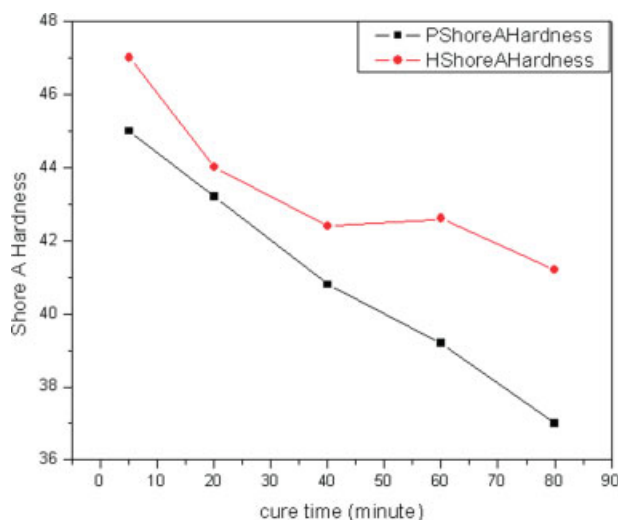

Figure 7 Shore A Hardness versus cure time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ber system shows a higher affirmatory elongation strength and Shore A Hardness than that of pure ones, which indicates that the NR/CR/OMMT sample has higher crosslinking density maintenance (which will be mentioned in the following parts) and better thermal stability. This coincides with the curing curves.

Crosslinking density, sol fraction, and swelling index

To further demonstrate the anticuring reversion action of MMT, the crosslinking density was gotten by the way prescribed earlier. NMR spectroscopy has been used in the past to study of the crosslinked elastomers. It was shown by Smith et al.[28] that the method provides a variety of structural detail, that is, structural voids, compression-, and reaction-induced gradients of chain segment mobility of elastomers of different crosslinking densities. And during the work of C. Fülber et al.,[29] the vulcanization as a function of time was presented. Here we applied the XLDS-15 NMR spectrometer to study the reversion of our object rubber blend. The magnetic resonance crosslink density spectrometer is a modified solid magnetic resonance instrument which can give the crosslinking information by determining T_1 and T_2 which then translated into the XLD information, or present the crosslinking information directly by crosslink density measurement. And all the results gotten by spectrometer were analyzed directly by XLDS-15 polymer/rubber crosslink density analyzer. At last, we got the test results in the form of longitudinal magnetization (T_1 decay), transverse magnetization (T_2 decay), and crosslinking density (XLD), which was shown in Table III. As the precise evidence, the magnetic resonance crosslink density spectrometer results exhibit in Figure 8(a): It

TABLE III
Longitudinal Magnetization (T1 decay), Transverse Magnetization (T2 decay), and the Crosslinking Density (XLD) of Rubber Blend

	T_1 (ms)	T_2 (ms)	XLD[a] (mol/cm^3)	M_c[b] (kg/mol)
P5	62.74	2.11	1.466×10^{-4}	6.48
H5	66.86	2.19	1.803×10^{-4}	5.27
P20	61.71	3.19	1.239×10^{-4}	7.67
H20	61.28	2.44	1.375×10^{-4}	6.91
P40	62.26	2.62	1.142×10^{-4}	8.32
H40	63.88	2.29	1.328×10^{-4}	7.15
P60	59.11	3.32	1.107×10^{-4}	8.58
H60	64.94	2.58	1.128×10^{-4}	8.42
P80	63.40	3.07	0.989×10^{-4}	9.60
H80	58.40	3.30	1.098×10^{-4}	8.65

[a] Crosslinking density by magnetic resonance crosslink density spectrometer.
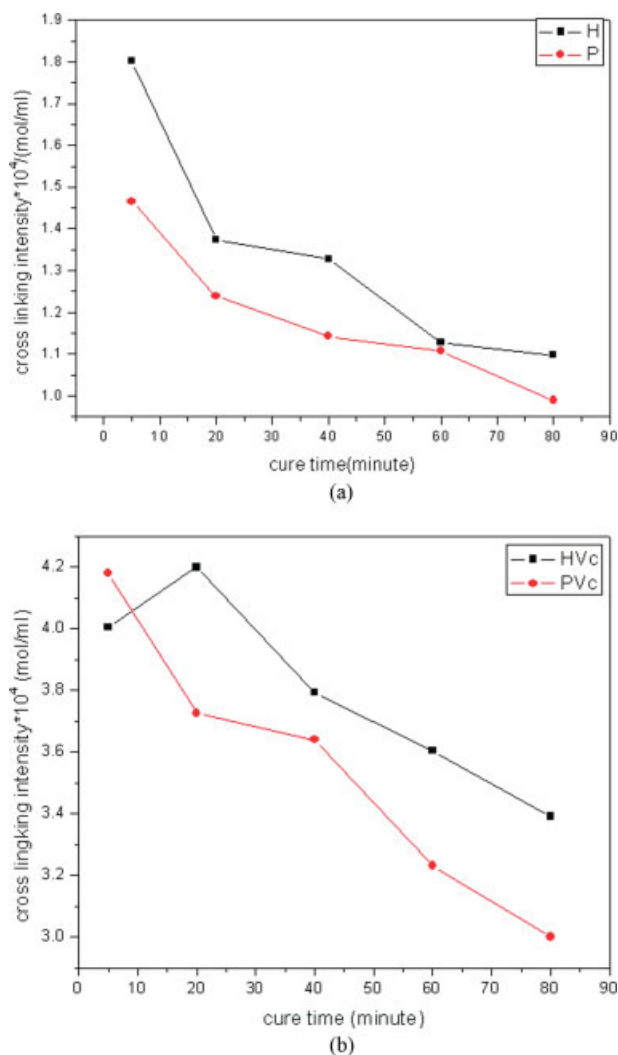[b] The average molecule weight of rubber between crosslinks.

Figure 8 Crosslinking density of rubber blends with (H) or without (P) OMMT versus cure time (a) magnetic resonance crosslink density spectrometer (b) swelling method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

can be seen that the crosslinking density of the NR/CR/OMMT sample, goes down from 1.803×10^{-4} to 1.098×10^{-4} mol/cm^3 with the variation of cure time from 5 to 80 min, whereas in NR/CR sample the corresponding numbers change from 1.466×10^{-4} to 0.989×10^{-4} mol/cm^3. And the average molar weight of rubber between crosslinks (M_c) shows a contrary trend, namely a less XLD value corresponds to a bigger M_c value.

In as much as the swelling experiment, five pieces were tested for each sample and the mean values were shown in Table IV and Figure 8(b). As shown in Figure 8(b), the V_c, that is, the crosslinking density decreases for rubber containing OMMT or not as the curing time increases, which implies that the crosslinking density in both systems decreased for the occurrence of curing reversion. Figure 8(b) shows the same trend as Figure 8(a), but some dif-

ferences in the crosslinking density values. Thus the phenomenon of curing reversion in the OMMT filled system is eased apparently than the system not containing OMMT. According to the statistical theory, vulcanized rubber may therefore be regarded as a number of flexible molecules whose flow is prevented only by occasional crosslinks along their molecular chain. Naturally, the low density of crosslinks decides that the vast majority of the segments making up the long-chain molecule are free to move by virtue of kinetic energy. And crosslinking density can be used to detect the degree of curing reversion, which is closely related to mechanical properties of the rubber. So by determining the crosslinking density, it has proved that the ability of antireversion of the rubber blend is enhanced by adding with OMMT. This is in accordance with both the curing curves and the mechanical characteristic results. Combined with results of NMR spectroscopy, it is natural that NR/CR/OMMT blend shows higher crosslinks retention than the corresponding NR/CR sample.

The unique result mentioned above may be attributed to the special properties of OMMT.[17] The compatibility between MMT and rubber is improved after modifying MMT with cationic surfactant such as hexadecyl trimethyl ammonium chloride. Reasonably, CR shows high polarity and can form a compact joint with OMMT,[5] and this will manifestly restrict the flow of CR molecule and lead to the ascending of torque as shown in Figure 4. And most important, the dispersed OMMT will offer CR with superior barrier properties against gas and hydrochloride transmission.[18] Whereas NR is just nonpolarity, so most parts of OMMT will stay in CR phase after blending and vulcanization as shown in

TABLE IV
Crosslinking Density, Sol Fraction, and Swelling Index of Rubber Blend

	Q^a	S_i^b	V_c^c (mol/mL)
P5	2.80	280	4.18×10^{-4}
H5	2.92	292	4.01×10^{-4}
P20	3.07	307	3.73×10^{-4}
H20	2.75	275	4.20×10^{-4}
P40	3.09	309	3.64×10^{-4}
H40	3.04	304	3.79×10^{-4}
P60	3.40	340	3.23×10^{-4}
H60	3.13	313	3.60×10^{-4}
P80	3.68	368	3.00×10^{-4}
H80	3.32	332	3.39×10^{-4}

[a] Sol fraction.
[b] Swelling index.
[c] Crosslinking density by equilibrium swelling method. H NR/CR with 10 wt % OMMT added in CR and cured for 5, 20, 40, 60, 80 min, respectively; P NR/CR blend without OMMT and cured for 5, 20, 40, 60, 80 min, respectively.
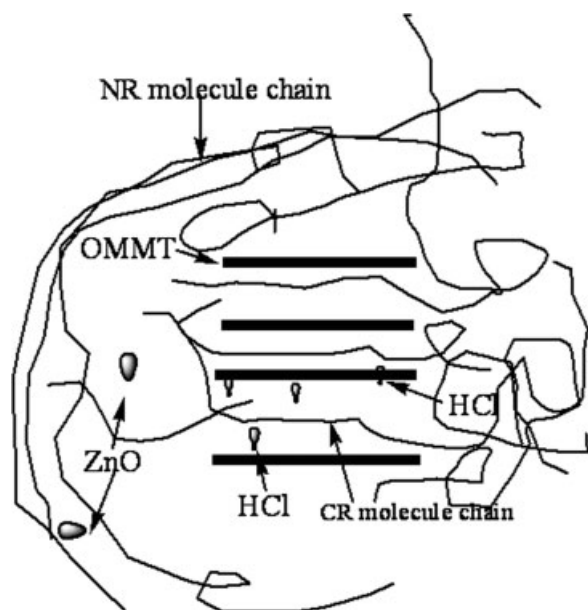
and mechanical properties further demonstrated this finding with improved mechanical properties. Our further study on this subject is on the road.

Figure 9 Schematic figure of barrier and adsorption effect of OMMT.

Figure 2. Consequently, for the NR/CR binary blend, blending OMMT into CR conform a barrier through structures of multiple layers of MMT.[16,30,31] And the latter restricts the migration of hydrochloride towards NR by postponing the path for the gas or small molecules to past, which is illustrated in Figure 9.

CONCLUSIONS

In this work, effect of OMMT on the antireversion in NR/CR blend system has been investigated. From the solid evidences on the curing reversion of NR/CR blend, the following conclusion is obtained: loading with OMMT will abate cure reversion to NR/CR binary blend which corresponds to higher crosslinks retention during reversion. The main mechanism can be concluded that the adding of OMMT will restrict the migration of hydrochloride (by-products of the vulcanization of CR) towards NR by postponing the path for the gas or small molecules to pass. Besides, the determination of crosslinking density

References

1. Kawahara, S. J Appl Polym Sci 2000, 78, 1510.
2. Mullins, L. Phys Technol 1984, 15, 177.
3. Treloar, L. R. G. Rep Prog Phys 1973, 36, 755.
4. Aimura, Y.; Wada, N. Polym Test 2006, 25, 166.
5. Choi, S. S. J Appl Polym Sci 2002, 83, 2609.
6. Coleman, M. L. Chloroprene Polymers, Encyclopedia of Polymer Science and Engineering, Vol. 3; Wiley: New York, 1985.
7. Barlow, F. W. Elastomers: Polybutadiene and Chloroprene, Rubber Compounding Principles, Materials and Techniques, 2nd ed.; Marcel Dekker: New York, 1993.
8. Gardiner, J. B. Rubber Chem Technol 1970, 43, 370.
9. Gardiner, J. B. Rubber Chem Technol 1968, 41, 1312.
10. Gardiner, J. B. Rubber Chem Technol 1969, 42, 1058.
11. Bateman, L.; Moore, C. G.; Porter, M.; Saville, B. The Chemistry and Physics of Rubber like Substances, Part III; Bateman, L., Ed.; McLaren: London, 1963; Chapter 15.
12. Kuan, T. H. Rubber world 1985, 194, 20.
13. Coran, A. Y. Science and Technology of Rubber; Irich, F. R., Ed.; Academic Press: New York, 1978, Chapter 7.
14. Skinner, T. D.; Watson, A. A. Rubber Age 1967, 99, 76.
15. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Karauchi, T.; Kamigaito, O. J Mater Res 1993, 6, 1185.
16. Frounchi, M.; Dadbin, S. J Membr Sci 2006, 282, 142.
17. Wagner, M. P. Rubber Chem Technol 1976, 49, 703.
18. Michael, A.; Philippe, D. Mater Sci Eng 2000, 28, 1.
19. Hofman, W. Vulcanization and Vulcanizing Agents; Palmerton Press: New York, 1967.
20. Zhang, P.; Shi, X. Y.; Zhao, S. G. J Appl Polym Sci 2008, 107, 1911.
21. Jain, S. R.; Sekkar, V.; Krishnamurthy, V. N. J Appl Polym Sci 1993, 48, 1515.
22. Owen, E. Degradation and Stabilization of PVC; Elsevier Applied Science Press: London and New York, 1984.
23. Morrison, N. J.; Porter, M. Rubber Chem Technol 1984, 57, 63.
24. Pongdhorn, S.; Chakrit, S.; Uthai, T.; Kannika, H. J Eur Polym 2007, 43, 185.
25. Perera, M. C. S.; Elex, J. A.; Bradbury, J. H. J Polym Sci Part A: Polym Chem 1988, 26, 637.
26. Naunton, W. J. S. Applied science of rubber; Edward Arnold Press: London, 1961; Chapter 2.
27. Flory, P. J Chem Rev 1944, 35, 51.
28. Smith, S. R.; Koenig, J. K. Macromolecules 1991, 24, 3496.
29. Fülber, C.; Unseld, K. Colloid Polym Sci 1996, 274, 191.
30. Chang, J. H.; An, Y. U. J Polym Sci Part B: Polym Phys 2002, 40, 670.
31. Chang, J. H.; An, Y. U.; Sur, G. S. J Polym Sci Part B: Polym Phys 2003, 41, 94.