

# The Influence of Montmorillonite on the Anti-Reversion in the Rubber–Clay Composites

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**ABSTRACT:** The influence of organically modified montmorillonate (OMMT) on the curing reversion of natural rubber (NR) and polychloroprene rubber (CR) blend has been demonstrated in this article. Characteristics of the NR/CR/OMMT hybrid composite were undertaken by combining the cure kinetics, thermal stability, and the detection of phase morphology. Compared to the neat rubber blend, thermal gravity analysis has shown improved thermal stability results during degradation for the nanofiller filled ones. Differential scanning calorimetry study has offered cure kinetic results; among which blending with NR has lifted the cure activation temperature of CR low toward.

Meanwhile, transmission electron microscopy has shown the intercalation and immobilization of OMMT in the CR phase formed a barrier to NR phase. In addition, to discover the reversion source, infrared spectroscopy has been applied to trace the oxygenic function units in the neat NR vulcanizate. All of the experimental results and related analysis has offered us the base to explain the improvement of the anti-reversion of the rubber blends. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 306–311, 2010

**Key words:** anti-reversion; montmorillonate; natural rubber; polychloroprene rubber

## INTRODUCTION

To improve the weather or oil resistance of natural rubber (NR), the well-known technique is blending with chloroprene rubber (CR). However, the provoking cure reversion has always been a tricky problem for the preparation of the blend.<sup>1</sup> In detail, as far as the sulfur-vulcanized NR considered, for one side, reversion is attributed to the conversion of multi-sulfuric bonds into double- or mono-sulfuric bonds; for the other side, because of the presence of the trans-methine butadiene-like structure<sup>2</sup> and the existence of slight amount of oxygen will promote the degradation of the main chain molecule, whereas the sulfur-vulcanized CR shows no cure reversion due to its unique vulcanization mechanism. The distinction of the two lies that metal oxides, commonly zinc oxide (ZnO) and magnesium oxide (MgO), play crucial part in the vulcanization of CR<sup>3</sup> for either ZnO or MgO can interact with the vulcanization coproduct hydro chloride (HCl), which initiates and promotes the vulcanization of CR. Gardner and

Mcneill<sup>4</sup> have pointed out that the release of HCl was due to the inclusion of allylic chloride which is most liable to degrade under high temperature. However, to discover the cause of blending in CR will aggregate the cure reversion of NR, it is necessary to detect the interaction of NR and CR. And it is tempting to infer that the vulcanize coproduct of NR will diffuse into CR and promote the release of HCl because NR may introduce much oxygen during mastication.<sup>5</sup> And the component identification work is achieved by Infrared spectroscopy (IR) techniques for which with recent developments in attenuated total reflection (ATR) has provided a means for spectroscopic monitoring the composition change in rubber blend.<sup>6</sup> Although Marynard and Mochel<sup>7</sup> have pointed out that there initially less than 1.6% 1,2-configuration exists in CR and which varies with the polymerization temperature. The existence of oxygen will make a dominant acceleration of dihydrochloride which may refer to the second and third crosslinking of 3,4- and 1,4-units, namely, more production of hydrochloride.

To verify the function of montmorillonate (MMT) on anti-reversion in the rubber–clay composite, it is suggested to take up with its bulk structure and dispersion status. Because as one of the most common two-dimensional nanofillers, MMT has been widely applied in the polymer-filler hybrid systems,<sup>8,9</sup> among which the usual improved tensile modulus,<sup>10</sup> barrier properties,<sup>11,12</sup> thermal stability and flammability<sup>13,14</sup> were achieved, and these have been elucidated to be the function of the bulk layer structure and dispersion of

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MMT in the polymer matrix. In fact, MMT belongs to the general family of 2 : 1 layered or phyllosilicates, i.e., two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide, and there is also gallery space between them. For polymer materials, the introduction of the high aspect ratio layered silicates not only can achieve reinforcement in both parallel and perpendicular of the tensile direction but also create a maze or "tortuous path," which retards the progress of gas or liquid molecules through the polymer matrix.<sup>8,15,16</sup> And this efficiency of reinforcement or barrier properties is much closely related to the dispersion status of MMT, namely, intercalated type, flocculated type, or exfoliated type, in the polymer matrix.<sup>8,17</sup> For the intercalated/fully exfoliated nanocomposites, properties of which typically resemble that of ceramic materials and much more complete protection was offered due to the insertion of polymer molecules than flocculated ones.

This work is prepared to find out the source of cure reversion and function mechanism of MMT in the rubber-clay composite and mainly mentions four parts, i.e., the confirmation of the cure reversion, the identification of the inclusion of hydroxyl or carbonylic units in NR vulcanizate, further detail study on the vulcanization or degradation course of NR/CR blend with or without organically modified montmorillonite (OMMT), and the phase morphology of NR/CR/OMMT vulcanizate. Among which, the cure rheology, thermal gravity analysis (TGA), differential scanning calorimeter (DSC), attenuated total reflection infrared spectroscopy (ATR-IR), and transmission electron microscopy (TEM) studies were undertaken. As a well-founded result, we first connect the oxygenic groups of NR and hydrochloride of CR with the reversion of rubber blend and discover the unique function of montmorillonite on anti-reversion in our study subject.

## EXPERIMENTS

### Materials, preparation, and curing rheology

The related materials, sample preparation, and curing rheology test parts were mentioned in the previous work,<sup>1</sup> except that the blending ratio for NR and CR is 50/50 in this work. Besides, neat NR sample for ATR-IR test was also prepared as a composition-NR (RSS-1, Indonesia), 100 parts; antioxidant (4020) 1 part; zinc oxide, 5 parts; stearic acid, 1 part; sulfur, 2.5 parts; Vulcanizing accelerator M, 0.8 part; and the sample was cured for 10 min at 143°C.

### Cure kinetics using DSC

Neat CR and NR/CR blend in gross state were cured heating up from 80 to 300°C under nitrogen environment in a NETZSCH differential scanning

calorimeter; model DSC-204, to obtain the curing curves. Temperature ramp was 10°C/min during dynamical heating course.

### Thermal behavior using TGA

Thermal analysis was undertaken for gross NR/CR with OMMT or not and also their component rubber on a TA thermal gravity analysis, model SDT Q-600. Approximately 20 mg samples, placed in an alumina pan, were used and the heating procedure was from 35 to 600°C with a ramp 10°C per min under nitrogen.

### ATR-IR absorptions of NR

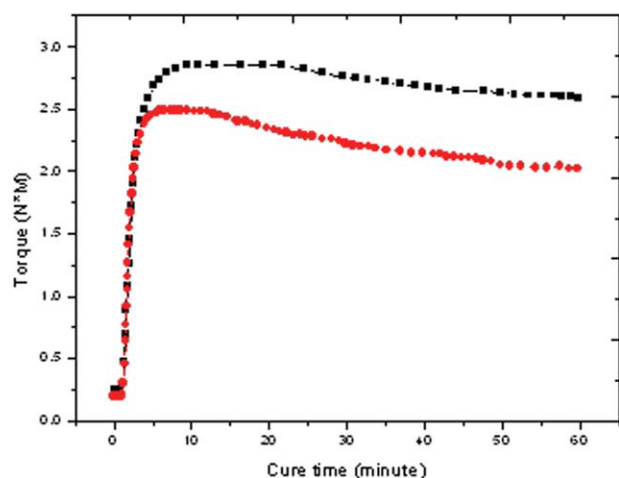
The neat NR sample was prepared individually and the Infrared spectrum was tested on a Nicolet spectrometer, model 560. And for the need of ATR, additional solid probe system was applied. The spectrum was recorded at a resolution of 4 cm<sup>-1</sup> with a total of 100 scans.

### Dispersion using TEM

Phase compatibility and OMMT dispersion locating around phase boundary were detected by TEM applying a JEOL - 2010 with an accelerating voltage 100 keV. The specimens were prepared using an Ultra cut R (Leica) ultra microtome. Thin sections about 100-nm thicknesses were cut with a diamond knife at ~ -100°C.

## RESULTS AND DISCUSSION

As illustrated in Figure 1, a bigger torque value, an extended cure platform and much less reversion is obtained for the OMMT-filled NR/CR blend. Bigger maximum torque of OMMT-filled NR/CR blend than the neat one implies that the filler may affect the apparent crosslinking density of the rubber vulcanizates and introduce additional "bound rubber" interaction including intercalation and exfoliation of OMMT and rubber. Further analysis by combining with the fact that, in OMMT-filled NR/CR sample, the progression of the primary torque is in accord with that of NR/CR, indicating the filler shows less effect on the rubber vulcanization in initial stage, so the bigger maximum torque is mainly ascribed to the interaction of rubber and clay which reduces the mobility of the macromolecule chains. And exact dispersion will be shown in the TEM images which will be offered in the next part. Because CR shows no reversion in the vulcanization, the extended cure platform indicates the improvement of the thermal stability, which can only be attributed to the improvement of NR.<sup>1</sup> Most importantly, resemble high torque retention of NR/CR blend with different blend ratios is observed, indicating that the blending



**Figure 1** Curing curves of NR/CR blend filled with 5 wt % OMMT (filled square one) or not (filled circle one). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ratio shows no vital influence on the interaction of NR and CR during vulcanization, i.e., the OMMT can improve the anti-reversion of NR/CR blend is a common phenomenon. Besides, vulcanization parameters for rubber blend with or without OMMT is shown in Table I, from which it is found that the torque value has increased from 0.23 to 2.85 for the rubber–clay composite, while the torque increases from 0.19 N\*M to 2.49 N\*M. As a measure of dynamic shear modulus, torque difference indirectly relates to the crosslinking density.<sup>18</sup> And as a confirmation, the addition of OMMT accurately improves the anti-reversion of NR/CR blend.

To explore the function of OMMT, the binary rubber blend vulcanizate reversion mechanism study was first undertaken on the basis of TGA and DSC. Although the fine vulcanization mechanism of CR has not been classified, the rearrangement of allylic of 1,2-polymerized units in CR and release of hydrochloride has been well elucidated<sup>3</sup> to be the crucial acting part. In the previous work, Gardner et al.<sup>4</sup> have pointed out the dehydrochlorination during thermal degradation occurs less readily unless oxy-

gen is present, and it is not a self-accelerated reaction which is different from the thermal degradation behavior of polyvinyl chloride (PVC). And in this work, the thermal stability of unvulcanized rubber—NR, CR, NR/CR blend, and OMMT-filled NR/CR rubber compounds—was undertaken. The corresponding TGA results are shown in Figure 2 and the related degradation parameters, i.e., maximum degradation peaks, which are shown in Table II. It is easy to find that the binary blend of CR and NR has lifted the derivative weight peaks at 316 and 374°C, which respectively belongs to the maximum degradation peaks of NR and CR, to high temperatures. So compared with the neat rubber vulcanizates, NR/CR blend vulcanizates show better high temperature stability by enhanced maximum degradation peak temperatures. Besides, the introduction of a few load of OMMT into CR, as shown in NR/CR/OMMT curve, has enhanced the thermal stability by slowing down the degradation rate at temperatures between the maximum degradation peaks of CR and NR. The NR/CR/OMMT system hereby shows much better thermal stability at high temperatures. And these results are in accordance with some previous work.<sup>13,14</sup> Figure 3 gives the low temperature range, from 120 to 220°C, special concern, and offers crude but useful information on the weight loss during vulcanization of rubber which will be discussed combining with the corresponding DSC results.

On the assumption that the heat flow is only attributed to the cure reaction and is proportional to the rate of conversion,<sup>3,19</sup> DSC has been applied to give a further illustration of the rubber blend vulcanization and the results are shown in Figure 4 in which, a broad exothermic peak between 130 and 220°C with vary maximum peaks depending on the component is shown. Compared with the neat CR sample, blending with NR has lead to the initial peak position shifts toward lower temperature, which is in the range of 130–140°C. This range is in line with the initial degradation peak temperature of allylic bonds and much lower than the corresponding one of CR, i.e., about 155°C. Similar

**TABLE I**  
Vulcanization Parameters for Rubber Blend with or Without OMMT

Sample	ML <sup>a</sup> (N*M)	MH <sup>b</sup> (N*M)	$\Delta M^c$ (N*M)	$T_{10}^d$ (m : s)	$T_{90}^e$ (m : s)	$\Delta M_{97}^f$ (m : s)	$\Delta M_{93}^g$ (m : s)
NR/CR without OMMT	0.19	2.49	2.30	1 : 19	3 : 21	15 : 38	21 : 28
NR/CR with OMMT	0.23	2.85	2.62	1 : 21	4 : 21	28 : 55	43 : 49

<sup>a</sup> Minimum torque.

<sup>b</sup> Maximum torque.

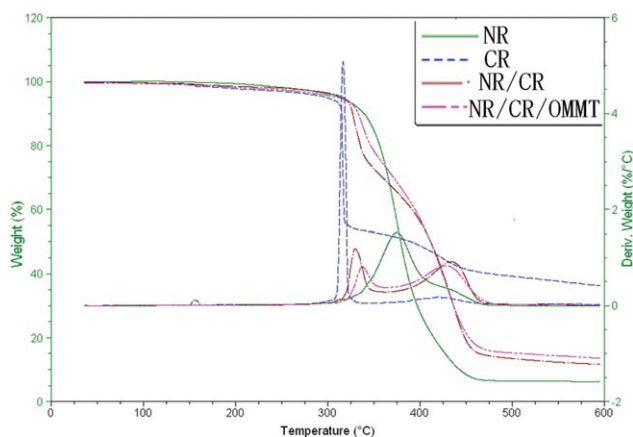
<sup>c</sup> Torque variance.

<sup>d</sup> Scorch time.

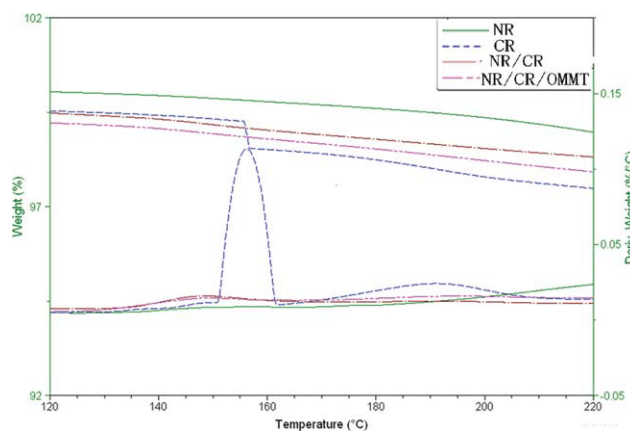
<sup>e</sup> Optimum cure time.

<sup>f</sup> Torque reverts to 97% of torque variance.

<sup>g</sup> Torque reverts to 93% of torque variance.



**Figure 2** TGA and DTGA curves of gross rubbers, i.e., NR, CR, NR/CR blend, and OMMT-filled rubber blend. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 3** TGA and DTGA curves, vulcanization temperature range (120–220°C) of gross rubbers, i.e., NR, CR, NR/CR blend, and OMMT-filled rubber blend. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

phenomenon is also observed in the TG/DTG curves, i.e., Figure 3 gives a big degradation peak with the midpoint at about 155°C for the sole CR sample and saint degradation peaks at 140°C for rubber blends. Here, the degradation peaks are attributed to the elimination of hydrochloride.<sup>4,20</sup> So the blending of NR has promoted the rearrangement of allylic functionalities and earlier release of hydrochloride than CR.

As a consecutive elucidation, the identification of the NR vulcanizate components was undertaken by ATR-IR analysis. And Figure 5 shows the infrared spectrum of NR vulcanizate, which exhibited absorption bands at around 835  $\text{cm}^{-1}$ , assigned to C=CH deformation, 1447  $\text{cm}^{-1}$ , CH<sub>3</sub> and CH<sub>2</sub> deformations, and 1374  $\text{cm}^{-1}$ , CH<sub>3</sub> deformation. All of that are characteristic absorption bands of NR.<sup>21</sup> Besides, the absorption band at around 1720  $\text{cm}^{-1}$ , assigned to C=O stretch, and the absorption band around 1084  $\text{cm}^{-1}$ , due to carbon/oxygen functionalities.<sup>2,22</sup> It is easy to conclude that the infrared spectrum suggests that the material was influenced by oxidation during mastication or vulcanization. And the elucidation of the residue of lots of free oxygen has been referred in other works related to rubber mastication.<sup>5,23</sup>

Although the existence of free oxygen plays great role to the mastication of NR and the introduction of

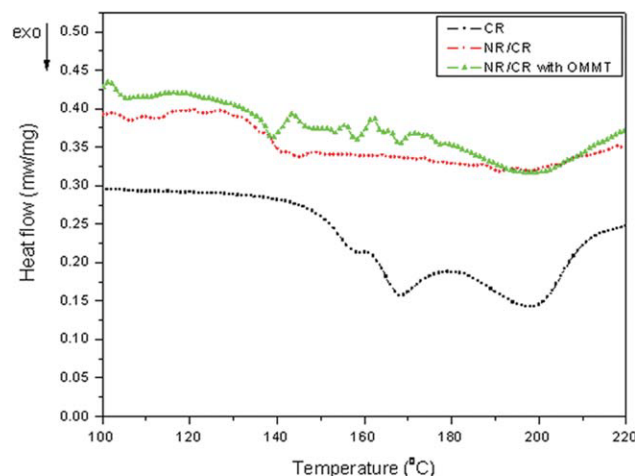
the carbon/oxygen functionalities does benefit to the later vulcanization,<sup>23</sup> it may also promote the dehydrochlorination in CR by diffusion under the function of high temperature. This presumption is in accordance with the cure rheology and DSC results. Contrast to the ascending trend of curing curve of CR, NR/CR blend shows dominant reversion. And in the NR/CR blend, the initial dehydrochlorination temperature of CR has moves from about 158°C to less than 140°C.

However, the addition of MMT can offer superior barrier property and improve the thermal stability of polymer matrix as elucidated above. The TEM images of the rubber blend are shown in Figures 6 and 7. As shown in Figure 6, there are two separate phase, i.e., NR phase and CR phase, and most MMT staying in the CR phase gives the later less

**TABLE II**  
Degradation Parameters of Rubber compounds Relate to TGA curves

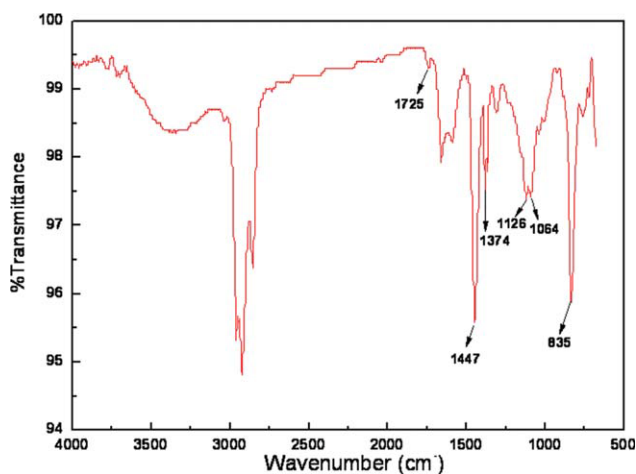
Sample	Main degradation peak temperature (°C)	
NR	–	374*
CR	316*	–
NR/CR	329*	434*
NR/CR with OMMT	337*	428*

\* The derivative weight peak value.



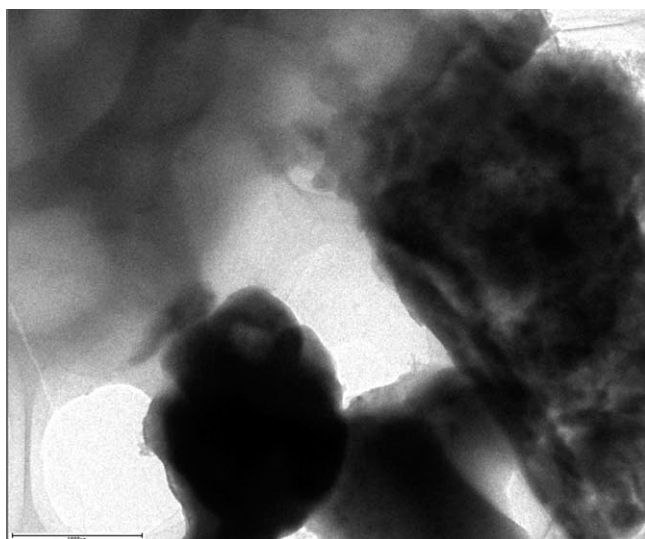
**Figure 4** DSC curves of gross rubbers, namely, CR, NR/CR blend, and OMMT-filled rubber blend. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



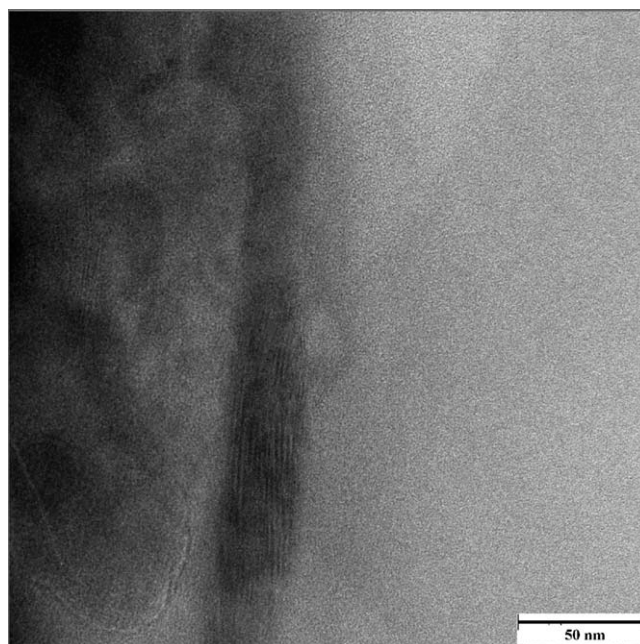


**Figure 5** Attenuated total reflection infrared spectrum (ATR-IR) of NR vulcanizate. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

transparency in the TEM image. Figure 7 offers information of the dispersion of OMMT around the phase boundary. It is dominant to find that the layered clay lies oriented along the rubber phase boundary with no intercalation or exfoliation, whereas the CR phase, there visualizes an even dark scene which indicates a better intercalation state is achieved. The different dispersion state for OMMT in CR phase and binary phase boundary is introduced by the strong anisotropy in the shape of the clay sheets and the abrupt change of the rheology condition due to the incompatible of CR and NR. Because the proper high aspect ratio, MMT can



**Figure 6** TEM image of dispersion of OMMT in the rubber blend (The scaled bar is 1000 nm).

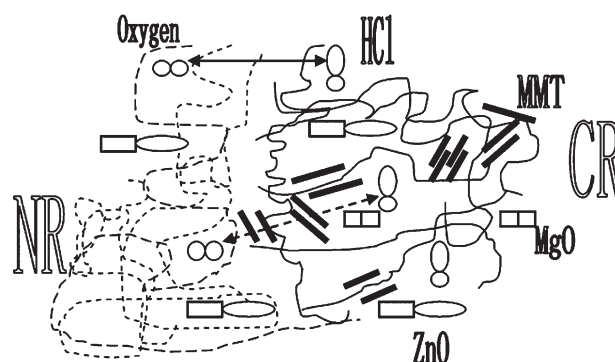


**Figure 7** TEM image of dispersion of OMMT in the interface of rubber blend.

introduce “tortuous path”<sup>8,15,16</sup> to retard the interdiffusion of oxygen and hydrochloride after well dispersion in the CR phase or the phase boundary of NR and CR, we have enough confidence to attribute the improvement of the anti-reversion for NR/CR blend to that the barrier property of OMMT can inhibit the phenomenon that oxygen diffuses from NR phase to CR phase and adverse diffuse route of HCl. And a schematic photo is shown as Figure 8.

## CONCLUSIONS

A sound study on the function of OMMT on the anti-reversion mechanism of OMMT in the NR/CR



**Figure 8** The schematic figure of barrier function of OMMT (oxygen indicates the free oxygen and movable carbon/oxygen functionalities in NR; solid arrow line indicates the possible diffuse route of HCl and oxygen lies between NR and CR; dotted arrow line indicates the diffuse route is obstructed by MMT).

blend was undertaken and the inherent relation is first discovered. These are the main points:

1. The degradation of rubber blend is mainly due to the thermal destruction of main chain of NR while the add product of CR, i.e., hydrochloride, can promote this course.
2. The sole CR is not readily to dehydrochlorination except for the function of oxygen and high temperature. And the much remaining oxygen or generated oxygenic function units during roll-mill mastication of NR can be the accelerating source.
3. OMMT staying mainly in the CR phase and mainly being in intercalated case introduces a better thermal stability for the NR/CR blend and gives a barrier wall for the interdiffusion of both oxygen and hydrochloride. This is the key function of OMMT on the improvement of the anti-reversion in the NR/CR blend.

By solving the cure reversion of NR/CR blend, we find the possibility to get high-performance NR/CR blend which will be demonstrated in the following papers.

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