Rubber/clay nanocomposites by combined latex compounding and melt mixing: A masterbatch process

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Rubber/Ca-montmorillonite (Ca-MMT) nanocomposites with well exfoliated Ca-MMT layers were prepared by combination of latex compounding and melt mixing. Firstly, a high Ca-MMT content masterbatch was co-coagulated by natural rubber (NR) latex and modified Ca-MMT aqueous suspension through latex compounding. The masterbatch was added in the system of styrene butadiene rubber (SBR) and epoxidized natural rubber (ENR) by melt mixing subsequently. The X-ray diffraction (XRD) and transmission electronic microscopy (TEM) results showed that intercalated and exfoliated nanocomposites were obtained by the masterbatch technique. The effects of modified Ca-MMT introduction into the rubber matrix, via the masterbatch technique, on the properties of the resulting composites were studied. It was found that the vulcanization was hindered by the incorporation of modified Ca-MMT, while mechanical performances, thermal stability and aging resistance were improved. The increasingly glass transition temperature and the storage modulus with the loading of modified Ca-MMT were measured by dynamic mechanical analysis (DMA).

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1. Introduction

In recent years, polymer–clay nanocomposites are of great interest for both academic researches and industrial applications because they frequently exhibit unexpected properties synergistically derived from the two components [1–3]. Among these properties are higher strength and modulus, better thermal stability and improved barrier and chemical resistance [4–7]. The essence of this development is the nanoscale dispersion [8] and the very high aspect ratio of the clay platelets [9,10]. Basically three different levels of exfoliation of nanoclay are seen in polymer matrices: a non-exfoliated system where nanoclay particles are seen to remain as a stacked structure consisting of a very large number of platelets with interlayer spacing equivalent to that of neat nanoclay, an intercalated case wherein an expansion of clay platelets is observed resultant of polymer chain penetration into the interlayer spacing, and partly to complete exfoliation with individual silicate layers dispersed in the matrix [6]. Engineering performance of nanocomposites is observed to be maximal when coexistence of intercalated–exfoliated structures is achieved, in which intercalated and exfoliated of nanoclays into single and couple platelets homogeneously dispersed throughout the polymer. Simple incorporation of clay minerals into a polymer matrix, however, does not always result in the significant improvements in the mechanical properties of the matrix. This is due to the poor dispersion of the clay minerals in the matrix and the lack of affinity between the layered silicate minerals and the organic polymers. Hence, the sound dispersion of clay and good interfacial adhesion between clay and polymer matrix is indispensable for the preparation of high-performance polymer–clay nanocomposites. Recently, the most common methods for the preparation of polymer–clay nanocomposites are solution blending, melt mixing, in situ polymerization, and latex compounding [6,7,11]. Among them, the melt mixing is the most widely used method. This is because: first, this method is environmentally benign due to the absence of organic solvents; second, it is compatible with current industrial process, such as extrusion and injection molding. However, the dispersion of the clay in the polymer prepared by the melt mixing is not as good as that by the latex compounding [7]. Many researches reported that the clay layers can be exfoliated and homogeneously dispersed in polymer matrix at a nanolevel by the latex compounding method [12–14]. The respective advantages of melt mixing and latex compounding inspire us to prepare nanocomposites by combination of the two methods through a masterbatch process. Using a clay masterbatch to achieve intercalation/exfoliation structure in the preparation of nanocomposites is reported recently. The masterbatch is usually prepared with a specific surfactant or low molar mass polymer, with structures compatible to that of the polymeric matrix [15,16]. In this technique the clay masterbatch is directly compounded with the polymer. The preparation of nylon/clay [16], epoxy/clay [4,7,18], silicone/clay [15] and poly(ε-lactide)/clay [19] composites using a clay masterbatch...
have been described recently. The basic idea is to increase the clay interlayer spacing during the first stage of the process, by polymerization of monomers or suspension of the clay in water/solvents or low molar mass polymers. Then, the polymeric matrix intercalates in this enlarged clay spacing. Based on the existing researches, the work on preparation of a clay masterbatch from rubber latex and clay aqueous suspension through latex compounding has not been published.

This paper aims at reporting on a new approach for the preparation of rubber—clay nanocomposites by combining the latex compounding and the melt mixing with a masterbatch process. A highly filled organo-Ca-montmorillonite (Ca-MMT)/natural rubber (NR) masterbatch is first prepared by co-coagulating of NR latex and modified Ca-MMT aqueous suspension, followed by melt mixing with the rubber matrix accompanied with carbon black: styrene butadiene rubber (SBR) and epoxidized natural rubber (ENR). This method allows preparing nanocomposites with a high degree of exfoliation. In order to strengthen the interface between Ca-MMT and rubber, bis[3-triethoxysilylpropyl]-tetrasulfide (TESPT) was used to in situ modify Ca-MMT during the preparation of the masterbatch. The dispersion of the Ca-MMT in masterbatch and nanocomposites made by the masterbatch was characterized by X-ray diffraction (XRD) and transmission electronic microscopy (TEM). The effects of modified Ca-MMT content on the properties of the nanocomposites were researched.

2. Experimental procedure

2.1. Materials

The Ca-MMT, with a cationic exchange capacity of 93 meq/100 g, is supplied by Nanhui Inorganic Factory (China, Guangdong). NR latex (solid content: 60%) is from Rubber Institute of Guangzhou (China). Apart from NR latex, NR ISNR-3 from Rubber Institute of Guangzhou was also used in the compound formulations. Unpublished work in our laboratory indicates that the gum properties of both these NR are similar and thus NR ISNR-3 was used for dose adjustment during compound formulation as described later. SBR, with trademark SBR1502 (styrene content 23.5 wt.%), was manufactured by Jilin Chemical Industry Company, China. ENR, with 25 mol% epoxide groups, was supplied by the Tropical Crops Research Center of Zhanjiang (China). Carbon black (N220) and TESPT were provided by Rubber Institute of Guangzhou. Other rubber additives were industrial grade and used as received.

2.2. Preparation of NR/modified Ca-MMT nanocompound masterbatch

At first, Ca-MMT was dispersed in water with vigorous stirring (3% dispersed) to obtain the Ca-MMT aqueous suspension. While, the TESPT was added to the pre-blended solution of ethanol and water, after 30 min ultrasound, the solution was slowly added into the Ca-MMT aqueous suspension (The amount of TESPT is 5 wt.% of Ca-MMT). The mixture was vigorously stirred at 70 °C for 30 min. To study the properties of Ca-MMT modified by the TESPT, some of the modified Ca-MMT was treated with acetone extraction and dried at 100 °C for Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) tests.

Then the cooled organic clay aqueous suspension was mixed together with the NR latex and vigorously stirred for a period of time. After that, the mixture was co-coagulated in 10% calcium chloride solution, washed with water until its pH was about 7, and dried in an oven for 20 h at 60 °C. Then the NR/modified Ca-MMT nanocompound masterbatch was obtained. The content of the Ca-MMT filler in the NR/modified Ca-MMT nanocompound masterbatch is 26 wt.% which is indicated by TGA.

2.3. Sample preparation

The NR/modified Ca-MMT nanocompound masterbatch, NR, ENR, SBR, N220, vulcanizing ingredients and other additives were mixed on a 6-in. two-roll mill, according to the recipe listed in Table 1, where the amount of the NR/modified Ca-MMT masterbatch is decided by its Ca-MMT content and the NR dose was adjusted by adding NR ISNR-3 from outside during mixing. Then the compounds were vulcanized in a standard mold at 150 °C for optimum vulcanization time, which was determined by the U-CAN UR-2030 vulcameter (Taipei, Taiwan).

2.4. Characterizations

XRD was used to characterize the Ca-MMT and to study the dispersions of the Ca-MMT in the NR/modified Ca-MMT masterbatch and nanocomposites prepared by the masterbatch process. The XRD experiments were conducted at ambient temperature on a Rigaku Dmax/III diffractometer (Rigaku Corporation, Tokyo, Japan) using a Cu Kα radiation (λ = 1.54 Å). The generator was operated at 40 kV and 30 mA. The samples of different shapes were scanned from 1° to 10°, with a step length of 0.02°.

TGA was carried out in a TA Q20 (New Castle, America) thermogravimetric analyzer over a temperature range from room temperature to 650 °C at a heating rate of 10 °C min⁻¹. Nitrogen is used as purging gas.

FTIR was recorded on a Nicolet Fourier-transform infrared spectrophotometer. Clay powder was pressed with KBr powder for FTIR measurement in transmission mode at a resolution of 4 cm⁻¹. Dynamic mechanical analysis (DMA) spectra of the samples were obtained by using EPLEXOR® @ 500 N/1500 N advanced dynamic mechanical spectrometer (GABO Company, Germany). The specimens with the size of 30 mm × 6 mm × 4 mm were analyzed in tensile mode at a constant frequency of 10 Hz, a strain of 0.5%, and a temperature range from −80 to 100 °C at a heating rate of 3 °C min⁻¹.

The curing characteristics of the compounds were determined at 150 °C by U-CAN UR-2030 vulcameter.

Tensile tests including 100% modulus, tensile strength, elongation at break and permanent set were performed following ASTM D412 [20] using U-CAN UT-2060 (Taipei, Taiwan) instrument and the strain rate was 500 mm/min. The 100% modulus is the stress value when the strain is 100%; The permanent set is defined as following: the extension remaining after a specimen has been broken in a normal tensile strength test, which is measured by fitting the two broken dumbbell pieces together at the point of rupture 10 min after the specimen is broken and expressed as a percentage.

<table>
<thead>
<tr>
<th>Table 1: Formulation of the mixtures.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
</tr>
<tr>
<td>NR/ENR/SBR</td>
</tr>
<tr>
<td>TESPT modified Ca-MMT (from nanocomposite masterbatch)</td>
</tr>
<tr>
<td>N220</td>
</tr>
<tr>
<td>Zinc oxide</td>
</tr>
<tr>
<td>Stearic acid</td>
</tr>
<tr>
<td>Accelerator CZ</td>
</tr>
<tr>
<td>Accelerator DM</td>
</tr>
<tr>
<td>Antioxidant 4010NA</td>
</tr>
<tr>
<td>Sulfur</td>
</tr>
<tr>
<td>Processing oil</td>
</tr>
</tbody>
</table>

* CZ: N-cyclohexyl-2-benzothiazole sulfonamide.
* DM: 2,2′-dibenzothiazole disulfide.
* 4010NA: N-isopropyl-N′-phenyl-p-phenylene diamine.
of the original length. The permanent set is also called tensile set-after-break.

The tear strength was measured according to ASTM D624 [21] specifications by U-CAN UT-2060 instrument. An unnicked 90° angle specimen is used. The unnicked angle tear strength is defined as following: the maximum force required to rupture a specified angle-shaped test piece, divided by the thickness of the test piece, the force acting in a direction substantially along the length of the test piece. The rate of separation of the grips is 500 mm/min and five test pieces per sample were tested.

Shore A hardness was performed following ASTM D2240 [22] using A type shore durometer (Shanghai, China). The needle indenter with taper angle of 35° truncated cone and top plane cone diameter of 0.79 mm was used.

Air aging of the samples was performed by a 401-A air aging oven (Shanghai instrument factory, China) according to ASTM D865 [23]. The samples were placed in the air aging oven at 100 °C for 72 h. When the heating period is complete, remove the samples from the oven and condition them for 16 h in a strain-free condition in the atmosphere, and then the tensile tests were carried out.

The specimens were ultramicrotommed into thin pieces of about 120 nm thickness with a Leica EM UC6 (Wetzlar, Germany). Then the TEM observations were done using a Philips Tecnai 12 TEM (Amsterdam, Netherlands) at an accelerating voltage of 30 kV.

3. Results and discussion

3.1. Characterization of TESPT modified Ca-MMT

3.1.1. FTIR analysis results

Fig. 1 shows the FTIR spectra of Ca-MMT and TESPT modified Ca-MMT. Ca-MMT presents two typical peaks. A strong absorption band at 1030 cm⁻¹ is observed, corresponding to the Si–O stretching vibration of the silicate. The band observed at 1634 cm⁻¹ is assigned to the deformation vibrations of the interlayer water of the Ca-MMT. Note that in the case of the TESPT modified Ca-MMT, two new peaks appear in the FTIR spectrum. Bands at 2934 cm⁻¹ are attributed to the C–H stretching vibrations of TESPT. The band at 1418 cm⁻¹ corresponds to the –CH₂– asymmetric deformation vibration of TESPT. Furthermore, the deformation vibration of the interlayer water of the modified Ca-MMT is shift to 1566 cm⁻¹, which is assumed that the TESPT has reacted with the water in the interlayer.

3.1.2. TGA analysis results

TGA and derivative thermogravimetry (DTG) thermograms of Ca-MMT and TESPT modified Ca-MMT are presented in Fig. 2. From the results, it can be seen that when the temperature is up to 180 °C, the weight loss of the Ca-MMT is about 15%, which corresponds to the escape of surface and interlayer adsorbed water. At 600 °C, the total weight loss of the Ca-MMT is about 18%. As for TESPT modified Ca-MMT, the decomposition of the organoclay is characterized by two steps. The first one, which is the decomposition of the surface and interlayer adsorbed water, decreases to 10% loss weight below 180 °C. The second one has a total weight loss of about 4.5%, which is due to the decomposition of TESPT. This is different from the Ca-MMT. These results from FTIR and TGA confirm that the TESPT has reacted with the surface groups of Ca-MMT in the TESPT modified Ca-MMT.

3.2. Characterization of NR/modified Ca-MMT masterbatch and nanocomposites with 8 phr modified Ca-MMT prepared by the masterbatch process

3.2.1. XRD analysis results

The XRD patterns of Ca-MMT, NR/modified Ca-MMT nanocompound masterbatch and nanocomposite containing 8 phr modified Ca-MMT and prepared by melt blending a masterbatch with SBR and ENR are presented in Fig. 3, where diffraction peaks correspond to the (0 0 1) plane reflections of the clay. From Fig. 3, the pristine Ca-MMT (a in Fig. 3) shows a peak at around 2θ = 5.8°, corresponding to (0 0 1) basal spacing of 1.5 nm. The X-ray pattern for the NR/modified Ca-MMT nanocompound masterbatch (b in Fig. 3) reveals a low broad peak at around 2θ = 5.8°, that suggests this system has a mixed morphology consisting of regions of stacked clay tactoids and regions of exfoliated clay platelets [24]. The substantial decrease of the peak intensity at around 2θ = 5.8° compared with that of the pristine Ca-MMT powder indicates that most of

![Fig. 1. The FTIR spectra of Ca-MMT and TESPT modified Ca-MMT.](image1)

![Fig. 2. TGA and DTG thermograms of Ca-MMT and TESPT modified Ca-MMT.](image2)

![Fig. 3. X-ray diffraction patterns for (a) pristine Ca-MMT, (b) NR/modified Ca-MMT masterbatch and (c) nanocomposite with 8 phr modified Ca-MMT prepared from masterbatch. Notes: the position of the (0 0 1) reflex is indicated by line marks.](image3)
the modified Ca-MMT layers have been exfoliated and form a nano-separated system in the masterbatch. It is well known that
the interlayer spacing of the Na-montmorillonite (Na-MMT) is lar-
ger than Ca-MMT and many studies have reported formation of
intercalated and exfoliated nanocomposites based on Na-MMT [25,26]. Little work, however, has been devoted to nanocomposites
based on the Ca-MMT. It can be seen from the XRD results that the
modified Ca-MMT layers are exfoliated successfully by the latex
compounding method, leading to an exfoliated structure in the nanocomposites. In the nanocomposite containing 8 phr modified
Ca-MMT (c in Fig. 3), a peak presents at 2θ = 1.8° appears, which
corresponds to an interlayer distance of 4.8 nm, indicating that
the initial stacked clay tactoids brought in by the masterbatch are
intercalated by the rubber chains during the process of mixing and
curing. The weak peak at 2θ = 5.5° (corresponding interlayer
distance 1.6 nm) suggests that a few stacked clay tactoids still exist
in the vulcanized sample, but most exfoliated structure achieved in
the masterbatch is preserved, which is further confirmed by TEM
analysis discussed later. It is interesting that a distinct peak appears at 2θ = 6.8°, which corresponds to an interlayer distance of
1.3 nm. This maybe is caused by the extraction of water in the
interlayer of modified Ca-MMT during the mixing and thermal set-
ting process [27].

3.3. Properties of nanocomposites prepared by the masterbatch
process

3.3.1. Curing characteristics

The vulcanization characteristics of the nanocomposites pre-
pared by the masterbatch technique are shown in the Table 2. As
can be observed, nanocomposite with 4 phr modified Ca-MMT
shows a maximum torque (S_{max}) value of 26.02 dNm, which is
higher than that of the unfilled Ca-MMT nanocomposites. While
with more modified Ca-MMT loading when the content of modi-
cated Ca-MMT is more than 8 phr, the torque of the vulcanize is
decreased and is lower than that of the unfilled Ca-MMT nanocom-
posites. The scorch time (t_s2) and the vulcanization time (T_{90}) are
increased by the incorporating of modified Ca-MMT, which indi-
cates that modified Ca-MMT hinders vulcanization. The curing rate
index (CRI), indicating the rate of cure of the compounds, is defined
as 100/(T_{90} - t_s2). The inclusion of modified Ca-MMT delays the vul-
canization process and the curing rate decreases with modified Ca-
MMT content. However, a possible mechanism for explaining this
phenomenon is still obscure at present.

3.3.2. Mechanical properties and aging properties

The effects of the modified Ca-MMT content on the mechanical
properties and aging properties of nanocomposites prepared by the
masterbatch process are shown in Table 3 and the stress–strain
curves are presented in Fig. 5. It can be seen that the optimum
modulus at 300%, tensile strength and shore A hardness are
achieved at 6 phr of modified Ca-MMT loading, 30%, 27% and 11%
increases in modulus at 300%, tensile strength and shore A hard-
ness are achieved compared with those of the unfilled Ca-MMT
vulcanize. The significantly enhanced mechanical properties
can be ascribed to the dispersed structure of modified Ca-MMT in
the nanolevel, the high aspect ratio, and the much improved
polymer–filler interaction. The dispersed structure of modified
Ca-MMT at the nanolevel in the matrix is brought about by the
NR/modified Ca-MMT masterbatch in which the modified Ca-
MMT dispersed evenly during the latex compounding, and the en-
hanced rubber–Ca-MMT interfacial adhesion is achieved by the
reaction of TESPT with rubber matrix and Ca-MMT. However, at
higher than 6 phr of modified Ca-MMT loading, modulus at 300%,
tensile strength and shore A hardness start to reduce due to
agglomeration of the clay [27]. The elongation at break of the nano-
composites increases consistently with the addition of modified
Ca-MMT. The increase in elongation at break is due to better filler
dispersion and strong filler–rubber interaction. The tear strength
increases with the modified Ca-MMT loading increasing. Interest-
ingly enough, when the modified Ca-MMT increases from 6 phr
to 8 phr, the value of tear strength is almost doubled. The improved
tear strength with the addition of clay is also reported by Wu [28].
The crack growth is related to the tearing energy of the nanocom-
posites and the fine filler could act as a barrier to crack propagation
during the tear process, so the tear strength is improved greatly
[29,30]. Clearly, the nanocomposites prepared by the masterbatch
technique display superior mechanical properties compared to un-
filled composites.

The results of aging test demonstrate that the mechanical prop-
erties of nanocomposites after aging in air for 72 h at (100 ± 1) °C
are better than that of unfilled Ca-MMT vulcanize. The antiaging
properties are improved with clay loading. However, too much clay
deteriorates antiaging properties. The studies on the improvement
of aging resistance by polymer–clay nanocomposites have been

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**Table 2**

<table>
<thead>
<tr>
<th>Modified Ca-MMT loading (phr)</th>
<th>t_s2 (min)</th>
<th>T_{90} (min)</th>
<th>S_{min} (dNm)</th>
<th>S_{max} (dNm)</th>
<th>CRI (min^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.65</td>
<td>6.20</td>
<td>1.67</td>
<td>24.44</td>
<td>28.17</td>
</tr>
<tr>
<td>4</td>
<td>3.17</td>
<td>8.42</td>
<td>1.77</td>
<td>26.02</td>
<td>19.05</td>
</tr>
<tr>
<td>6</td>
<td>3.25</td>
<td>9.32</td>
<td>1.89</td>
<td>24.52</td>
<td>16.47</td>
</tr>
<tr>
<td>8</td>
<td>3.12</td>
<td>9.37</td>
<td>2.40</td>
<td>24.41</td>
<td>16.00</td>
</tr>
<tr>
<td>10</td>
<td>3.12</td>
<td>10.32</td>
<td>2.24</td>
<td>23.43</td>
<td>13.89</td>
</tr>
<tr>
<td>12</td>
<td>3.17</td>
<td>11.27</td>
<td>2.39</td>
<td>23.00</td>
<td>12.35</td>
</tr>
</tbody>
</table>

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![TEM image of the nanocomposite with 8 phr modified Ca-MMT prepared by the masterbatch.](image)
extensively reported [8,31,32]. Generally, this is because the sound dispersed clay can act as a superior insulator and mass transport barrier to both oxygen and the volatile products generated during decomposition. But too much clay will lead to the clay aggregates, which bring more defects and form the stress concentration point.

3.3.3. TGA analysis results

The thermal stability of the unfilled and filled nanocomposites with different modified Ca-MMT loading prepared by the masterbatch process has been studied by TGA. Fig. 6 presents the DTG curves of unfilled and filled nanocomposites with different modified Ca-MMT loading. Table 4 shows the thermal degradation characteristics of nanocomposites. The results show that the 5%, 50% weight loss and peak degradation temperature \( T_{\text{max}} \) of the temperature corresponding to the maximum value in the derivative thermogram shifts to the higher values with increasing modified Ca-MMT loading, compared with the unfilled Ca-MMT vulcanize. A notable shift of \( T_{\text{50}} \) by 8.7 °C to higher temperature can be observed in the case of 4 phr modified Ca-MMT filled nanocomposite. A substantial reduction in peak degradation rate from 2.15%/°C in unfilled Ca-MMT vulcanize to 1.81%/°C in nanocomposites filled with 8 phr modified Ca-MMT also can be seen. The reduction in degradation rate, which is a measure of relative thermal stability, together with the increase in \( T_{\text{50}} \), \( T_{\text{max}} \) and \( T_{\text{d}} \), respectively, to better thermal stability in the nanocomposites compared to the unfilled Ca-MMT vulcanize, which is consistent with the results from aging test. It has been reported that the thermal stability is a function of not only clay dispersion and polymer–filler interaction, but also clay content [9]. Hence, the nanocomposites with relatively higher modified Ca-MMT loadings have better thermal stability in contrast to the mechanical properties, which are discussed before. Additionally, the formation of enhanced char yield in the high temperature region with increasing clay content also contributes to the enhancement of thermal stability.

3.3.4. DMA analysis results

The temperature dependence of tan \( \delta \) for the nanocomposites with different modified Ca-MMT loading prepared by the masterbatch process is presented in Fig. 7. The tan \( \delta \) of the nanocomposites exhibit three peaks at \(-50°C, -39°C\) and \(-15°C\), which correspond to the glass transition temperature \( T_{\text{g}} \) of NR, SBR and ENR, respectively. With the modified Ca-MMT increasing, a noticeable reduction in tan \( \delta \) peak height at \(-15°C\) can be observed. The peak height of tan \( \delta \) curve at \(-15°C\) decreases from 0.65 in unfilled Ca-MMT vulcanize to 0.60 for nanocomposite filled with 8 phr modified Ca-MMT. The reduction in the tan \( \delta \) peak height with the addition of modified Ca-MMT can be attributed to the enhanced polymer–nanoclay interaction, which results in restricted segmental mobility of the polymer chains. The peak height of tan \( \delta \) curve at \(-50°C\) and \(-39°C\) decreases with modified Ca-MMT increasing, except for the nanocomposite with 8 phr modified Ca-MMT. The \( T_{\text{g}} \) of NR, SBR and ENR show a modest increase in the addition of modified Ca-MMT. As discussed above, this

### Table 3

Effect of modified Ca-MMT content on mechanical properties and aging properties of the nanocomposites.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Modified Ca-MMT content (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Modulus at 300% (MPa)</td>
<td>10.2 ± 0.1</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>22.4 ± 0.9</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>465 ± 15</td>
</tr>
<tr>
<td>Permanence set (%)</td>
<td>16 ± 0.7</td>
</tr>
<tr>
<td>Tear strength (kN/m)</td>
<td>42.4 ± 1.0</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>57</td>
</tr>
<tr>
<td>Aging in air (100 ± 1 °C, 72 h)</td>
<td>73.7</td>
</tr>
<tr>
<td>Property descend ratio (%)</td>
<td>0.65</td>
</tr>
</tbody>
</table>

* Property descend ratio = \((\text{tensile strength} \times \text{elongation at break})_{\text{before aging}} - (\text{tensile strength} \times \text{elongation at break})_{\text{after aging}}\)/\((\text{tensile strength} \times \text{elongation at break})_{\text{before aging}}\) × 100%. 

### Table 4

Thermal degradation characteristics of nanocomposites with different modified Ca-MMT loading.

<table>
<thead>
<tr>
<th>Modified Ca-MMT loading (phr)</th>
<th>( T_{\text{50}} ) (°C)</th>
<th>( T_{\text{max}} ) (°C)</th>
<th>( T_{\text{d}} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>317.4 ± 0.7</td>
<td>361.5 ± 0.5</td>
<td>362.2 ± 0.6</td>
</tr>
<tr>
<td>4</td>
<td>326.1 ± 0.6</td>
<td>368.5 ± 0.7</td>
<td>367.6 ± 0.5</td>
</tr>
<tr>
<td>6</td>
<td>325.1 ± 0.5</td>
<td>368.3 ± 0.4</td>
<td>366.7 ± 0.2</td>
</tr>
<tr>
<td>8</td>
<td>325.3 ± 0.6</td>
<td>370.1 ± 0.4</td>
<td>367.6 ± 0.5</td>
</tr>
</tbody>
</table>
is believed to be due to the enhanced polymer–nanoclay interaction. The curves of storage modulus \( E' \) versus the temperature for nanocomposites with different modified Ca-MMT loading are presented in Fig. 8. The \( E' \) of the nanocomposite filled with modified Ca-MMT shows a higher value than the unfilled Ca-MMT vulcanize over the whole temperature range, which shows that the addition of modified Ca-MMT into compound results in an increase of stiffness. That further reflects the strong confinement of nanodispersed silicate layers on the rubber chains.

4. Conclusions

Rubber/Ca-MMT nanocomposites with well exfoliated Ca-MMT layers have been prepared by combination of latex compounding and melt mixing. The FTIR and TGA tests showed that the TESPT reaction with the surface groups of Ca-MMT by the in situ modification. An exfoliated structure in the masterbatch and a coexistence of intercalated–exfoliated structures in the vulcanize were assessed by XRD and TEM. The incorporation of modified Ca-MMT shows a higher value than the unfilled Ca-MMT vulcanize over the whole temperature range, which shows that the addition of modified Ca-MMT into compound results in an increase of stiffness. That further reflects the strong confinement of nanodispersed silicate layers on the rubber chains.

References


