Dynamic Mechanical Property of Kaolinite/Styrene-Butadiene Rubber Composites

Yinmin Zhang¹, Hongli Song², Qinfu Liu¹,а, Shilong Zhang¹, Yude Zhang³

1 – School of Geoscience and Surveying Engineering, China University of Mining & Technology, Beijing, 100083 China
2 – School of Geoscience and Engineering, Hebei University of Engineering, Handan, 056000 China
3 – School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China
а – pzqm163@163.com

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ABSTRACT. The dynamic properties of kaolinite/styrene-butadiene rubber (SBR) composites filled by kaolinite were investigated to evaluate their real-world engineering applications. The results of field emission scanning electron microscopy (SEM), and transmission electron microscopy (TEM) revealed that the rubber chains were confined within the interparticle space of kaolinites, and that the nanoscale kaolinites exhibited a fine and physical dispersion in the SBR matrix. The dynamic properties of kaolinite/SBR composites were investigated by performing dynamic mechanical analysis (DMA) and rubber processing analysis (RPA). Both the decrease in kaolinite particle size and the increase in kaolinite content can greatly improve the storage modulus and reinforcing effect of kaolinite/SBR composites. A small particle size and a low filled content of kaolinite filler is favourable for the dynamic properties of kaolinite/SBR composites for tire products. The filler networking phenomenon attributed to the agglomeration-de-agglomeration of filler particles intensified as the kaolinite particle size was reduced and the kaolinite content was increased, which resulted from the increase in the unit volume fraction of kaolinite in the rubber matrix and the stronger interaction of kaolinite particles in the composite matrix.

Introduction. Layered clay minerals/polymer nanocomposites have received considerable attention from the industry and academic researchers because these materials have exhibited remarkably improved properties, such as improved mechanical properties and thermal ability, enhanced barrier property, and decreased flammability [1-7]. In particular, rubber is an important class of polymer materials because of its outstanding characteristics and special applications [8]. Many researchers have applied different approaches to modify clay minerals, which are then incorporated into rubber matrix by latex blending and simple melt mixing [5, 9]. Such practices have achieved slight improvements in the mechanical, thermal, and barrier properties of clay/rubber composites [6, 8, 10, 11].

The dynamic mechanical property is one of the important physical properties of rubber compounds, particularly for tire applications and for other dynamic rubber products; this property reflects the actual performance of rubber products[12]. Of considerable significance is the dynamic mechanical behavior of rubber materials determined under a wide range of frequencies and temperatures. This behavior can be evaluated by the storage modulus (𝐸’), the loss modulus (𝐸’’), and the loss tangent (tan δ) defined by 𝜋tan δ = 𝐸’’/𝐸’, where 𝐸’ is the storage modulus resulting from the stored elastic energy in the materials and 𝐸’’ is the loss modulus resulting from viscous dissipation [13-15]. Many studies have investigated dynamic mechanical properties of rubber polymer materials based on various modified fillers, including the carbon black, silica, graphite, cellulose, and organoclay [16-18].
Previous works on the dynamic mechanical properties of clay minerals/rubber polymer nanocomposites have mostly focused on montmorillonite, and only a few studies have explored kaolinite. Kaolinite is the most commonly 1:1 (two-sheet) type clay mineral with its basic unit consisting of a tetrahedral sheet of SiO$_2$ siloxane units and an octahedral sheet of AlO$_2$ (OH)$_4$ [11, 19-21]. After modification, kaolinite particles can become evenly dispersed in the rubber matrix and be used as a functional filler for rubber because of its light color, special stratified structure, and availability [10]. The present study is the first to report on the dynamic mechanical properties of kaolinite/styrene-butadiene rubber (SBR) composite as well as the effect of kaolinite particle size and content on the dynamic properties of these composites. The modified kaolinite and kaolinite/SBR composites are characterized by X-ray diffraction pattern (XRD), Fourier transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM).

**Experimental**

**Materials.** The rubber matrix is styrene-butadiene rubber (SBR 1500E), which was supplied by ShenHua Chemical Company of Nantong Jiangsu, China, and its Mooney viscosity is 47–57 $M_r^{100^\circ C}$. The kaolinite sample was obtained from SanXing Advance-New Material Company of Zaozhuang Shandong, China; the sample was a type of sedimentary kaolin with disordered structure. The chemical component of this kaolin is 45.74% SiO$_2$, 35.61% Al$_2$O$_3$, 0.88% Fe$_2$O$_3$, 1.23% TiO$_2$, 0.41% Na$_2$O, 0.32% K$_2$O, 0.11% MgO, and 0.12% CaO. Kaolinite samples with different particle sizes were obtained using a disperser and relative material properties are presented in Table 1. The silane coupling agent bis-(γ-triethoxysilyl-propyl)-tetrasulfide (Si69) was supplied by ShuGuang Chemical Group Limited Company of Nanjing Jiangsu, China. Zinc oxide (ZnO), stearic acid, the accelerator N-tert-butylbenzothiazole-2-sulphenamide (NS), and sulfur were obtained commercially.

<table>
<thead>
<tr>
<th>Samples</th>
<th>D$_{10}$/μm</th>
<th>D$_{50}$/μm</th>
<th>D$_{90}$/μm</th>
<th>% ≤1 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite-1(K1)</td>
<td>1.06</td>
<td>6.49</td>
<td>22.19</td>
<td>9.05 %</td>
</tr>
<tr>
<td>Kaolinite-2(K2)</td>
<td>0.89</td>
<td>3.74</td>
<td>17.94</td>
<td>12.20 %</td>
</tr>
<tr>
<td>Kaolinite-3(K3)</td>
<td>0.63</td>
<td>1.93</td>
<td>4.98</td>
<td>22.75 %</td>
</tr>
<tr>
<td>Kaolinite-4(K4)</td>
<td>0.28</td>
<td>0.53</td>
<td>1.69</td>
<td>79.27 %</td>
</tr>
</tbody>
</table>

**Preparation of the modified kaolin**

The beneficiated kaolinite was dispersed into water at a content of 25%. Then, 0.5% sodium polyacrylate with an average molecular weight of 3000–3500 was added into the mixture as a dispersant. The pH level of the mixture was maintained at 10.0 by using a sodium hydroxide (NaOH) solution. Subsequently, 0.5% modifier was added into the resulting dispersion, and the dispersion was stirred for 1.5 h by using a mechanical mixer at approximately 60 °C. The modified kaolinite powder was obtained by spray drying at 120 °C [8].

**Preparation of the kaolinite/rubber nanocomposites**

The procedure of preparing kaolin/SBR nanocomposites is briefly described as follows [22, 23]: First, raw SBR was plasticized for 3–5 min in an SK-160B open mill at room temperature. The spacing between the two rolls was approximately 0.15 cm, and the roll rate was 6.98 m/min. ZnO, stearic acid, NS, and sulfur was added into the plasticized compound successively. The two roll spacing was
adjusted to 0.05 cm and uniform mixing was performed for 15 min. The formulation of the kaolin/SBR nanocomposites (phr) is as follows: SBR, 100.00; zinc oxide, 3.00; stearic acid, 1.00; accelerator NS, 1.00; sulfur, 1.75; kaolinite, variable. The optimal cure time was determined by using a ZWL-III non-rotor vulkameter. The kaolinite/SBR composites specimens were placed in a 150 mm \times 150 mm \times 2 mm mold and vulcanized in a 400 mm \times 400 mm 25TQLB vulcanizing machine at 153 °C and 10.0 MPa until the optimal cure time was obtained. The cured rubbers were rapidly cooled in air.

Characterization and Measurement

FT-IR spectroscopy was performed by a FT-IR spectrometer (Magna-IR 750 Nicolet) at a resolution of 4 cm−1 in the range of 4000–500 cm−1. The samples were prepared at potassium bromide (KBr) pellets (ca. 2% by mass in KBr).

The morphology of the kaolin/SBR nanocomposites was characterized by a scanning electron microscopy (SEM) using a S4800 low-temperature field emission electron microscope manufactured by Rigaku Corporation. The TEM images of the kaolinite/SBR composites were characterized by a JEM-2100 transmission electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. The samples were prepared by ultramicrotomy of the bulk cured composites to obtain a section of approximately 50 nm thickness.

The dynamic-mechanical properties were measured by utilizing a dynamic mechanical analyzer DMA 242C (Netzsch, Germany). The tests were conducted in the temperature range of −70 °C to 90 °C at a heating rate of 3 °C min−1. The rubber specimens were prepared as a cut strip with the size of 10.00 mm \times 3.95 mm \times 2.06 mm (length \times thickness \times width) under tension mode at a constant frequency of 10 Hz and a strain amplitude of 0.25%. The dynamic elastic modulus (E′) and the mechanical loss tangent (\tan \delta) as a function of temperature were measured. The temperature corresponding to the peak in \tan \delta versus the temperature plot was taken as the glass-to-rubber transition temperature (Tg).

The experiment on strain sweeps were conducted by using a RPA 2000 (ALPHA, America). A slight excess in testing materials was needed to ensure the testing cavity house was full. The tests were performed under pressured conditions to ensure that porosity did not develop in the samples during the tests. The temperature was maintained at 60 °C before the uncured samples were subjected into the cavity house for conducting stain sweep. Subsequently, the temperature was raised to 170 °C to vulcanize the samples for their optimal cure time (t90). After curing, the temperature was cooled down to 60 °C again. Strain sweep was performed from 0.26%–100% and the frequency was kept at 1.0 Hz.

Results and Discussion

FT-IR analysis of kaolinite and modified kaolinite

The FT-IR spectra of the kaolinite and the organic modified kaolinite are presented in Fig. 1. In the spectrum of virgin kaolinite, well-resolved absorbed bands were located at 3695, 3652, and 3620 cm−1. The 3695 and 3652 cm−1 bands were attributed to the stretching vibration of the surface hydroxyl groups, whereas the 3620 cm−1 was attributed to the vibration of the inner surface hydroxyl groups[24]. The stretching vibration bands of Si-O are observed at 1101, 1034, and 1009 cm−1. The spectrum showed the bending vibration of -OH at 913 cm−1, and the stretching and bending vibration of Si-O-Al was found at 696 and 538 cm−1 respectively[20, 25, 26]. Four additional bands at 3450, 2920, 1634, and 1457 cm−1 are observed in the spectrum of the organic modified kaolinite. The bands at 3450 and 1634 cm−1 are attributed to the stretching and bending vibration mode of H2O, respectively, whereas the bands at 2920 and 1457 cm−1 are ascribed to the vibration mode of -CH2 derived from the silane coupling agent [27]. The results indicated that the silane coupling agent have interacted with kaolinite and modified the surface property of the kaolinite particles.
Fig. 1. FT-IR spectra of kaolinite and modified kaolinite.

**Microstructure of kaolinite/SBR composites**

The microstructure of a kaolinite/SBR composite is shown in Fig. 2. The layer-like particles of kaolinite exhibited noteworthy characteristics with diameters ranging from 300 nm to 700 nm and thicknesses ranging from 50 nm to 200 nm. The average distances between the layer-like particles ranged from dozens of nanometers to hundreds of nanometers. The TEM images of the kaolinite/SBR composite with kaolinite are shown in Fig. 3. The kaolinite particles were finely dispersed in the SBR matrix. No significant aggregation occurred among the layered-like particles kaolinite. The kaolinite had a thickness of approximately dozens of nanometers and a diameter of 500 nm; the average distances between the layer-like particles ranged from dozens of nanometers to hundreds of nanometers.

Fig. 2. SEM images of kaolinite/SBR composite.
Dynamic properties of kaolinite/SBR composites

To evaluate the effect of kaolinite particle size and content on the dynamic mechanical behaviours of kaolinite/SBR composites, dynamic mechanical analyses were conducted on cross-linked systems and rubber compounds without crosslinking among the polymer chains.

Cross-linked systems were subjected to dynamic mechanical analysis by applying the temperature sweep methodology described in the Experimental section. The influences of kaolinite particle size on the dynamic storage modulus ($E'$, in the tensile model) and the loss tangent (tan δ) as a function of temperature for kaolinite/SBR nanocomposites are presented in Figs. 4 and 5. The storage modulus represents the elastic component and is an indicator of the capacity of a material to store the input mechanical energy [15]. As shown in Fig. 4, as the temperature increased from −60 °C to 10 °C, the storage modulus for all samples rapidly decreased, eventually reaching a constant value; this behaviour may be attributed to the glass transition phenomenon. In the low-temperature region, the storage modulus of the vulcanizate samples increased as the particle size of kaolinite decreased; this behavior is ascribed to the reinforcement of kaolinite and the stronger interaction between polymer chains and kaolinite particles as the particle size was reduced [28]. Consequently, the restriction on the motion of molecular chains increased. The storage modulus for vulcanizate samples in the given temperature region decreased more rapidly as the kaolinite particle size was reduced, indicating that the low-temperature rigidity of these vulcanizate were susceptible to the increase in temperature.

Fig. 4. The dynamic storage modulus as a function of temperature for kaolinite/SBR nanocomposites filled with different particle sized kaolinite.
Table 2. $\tan \delta$ and $T_g$ of SBR/kaolinite composites filled with kaolinite with different size.

<table>
<thead>
<tr>
<th>Samples</th>
<th>K1-SBR</th>
<th>K2-SBR</th>
<th>K3-SBR</th>
<th>K4-SBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tan \delta(0^\circ C)$</td>
<td>0.29</td>
<td>0.28</td>
<td>0.26</td>
<td>0.324</td>
</tr>
<tr>
<td>$\tan \delta(60^\circ C)$</td>
<td>0.098</td>
<td>0.135</td>
<td>0.119</td>
<td>0.125</td>
</tr>
<tr>
<td>$T_g/{^\circ C}$</td>
<td>-19.8</td>
<td>-20.1</td>
<td>-20.43</td>
<td>-20.34</td>
</tr>
</tbody>
</table>

Fig. 5. The loss tangent as a function of temperature for kaolinite/SBR nanocomposites filled with different particle sized kaolinite.

The $\tan \delta$ as a function of temperature is shown in Fig. 5. Table 2 summarizes the values of different glass transition temperatures and the loss tangent at 0 °C and 60 °C. The temperature corresponding to the maximum of $\tan \delta$ values is generally related to the glass transition temperature ($T_g$). The $\tan \delta$ values at 0 °C and 60 °C are generally considered to be correlated with wet traction and rolling resistance, respectively. For vulcanized rubber materials, the higher $\tan \delta$ values at 0 °C indicate a desirable wet traction property, whereas the lower $\tan \delta$ values at 60 °C correspond to a lower rolling resistance property. In this study, we use the $\tan \delta$ values at 0 °C and 60 °C to assess the wet traction and rolling resistance of kaolinite/SBR composites.

The $\tan \delta$ values at $T_g$ for vulcanize samples decreased as the kaolinite particle size was reduced; this behavior is due to the favorable dispersion of kaolinite particles and the interaction between filler particles and rubber chains in the composite matrix. This finding is in agreement with those obtained by similar studies mentioned above. However, the $T_g$ for all vulcanization samples were found to be about at -20 °C, which presented no obvious change. Overall, the vulcanize rubber sample filled by the smaller-particle-sized kaolinite presented higher $\tan \delta$ values at 0 °C and 60 °C, which indicating that smaller-particle-sized kaolinite can improve the wet traction property but is not conducive to the rolling resistance property of rubber materials.

The influences of kaolinite content on the dynamic storage modulus and $\tan \delta$ as a function of
temperature for kaolinite/SBR nanocomposites are presented in Figs. 6 and 7. Table 3 summarizes the values of different glass transition temperatures and loss tangents at 0 °C and 60 °C for kaolinite/SBR composites filled by different contents of kaolinite. As shown in Fig. 6, the storage modulus of vulcanize samples increased as the kaolinite content increased in the low-temperature region; this effect is also attributed to the reinforcement of kaolinite and the stronger restriction on molecular chains motion as a result of the increase in the volume fraction of kaolinite. A more rapid decrease in the storage modulus was observed in the vulcanize samples with a higher amount of kaolinite at the temperature range of −60 °C to −20 °C. As could be seen in Fig. 7. The tanδ values at Tg for vulcanize samples decreased as the kaolinite content increased; this effect is attributed to the increase in the unit volume fraction of kaolinite in the composite matrix. Consequently, the hysteresis of the composite is decreased in the low-temperature region. The tanδ values at 0 °C for vulcanize samples decreased as the kaolinite content increased, thereby showing the low wet traction of the samples with high amounts of kaolinite. However, the tanδ values at 60 °C for vulcanize samples increased as the kaolinite content increased, demonstrating the higher rolling resistance of samples with high amounts of kaolinite. These results indicate that the increase in kaolinite content can improve the storage modulus and validates the reinforcing effect of kaolin/SBR composites. However, a high kaolinite content is not beneficial for the wet traction and rolling resistance of vulcanize rubber materials.

![Graph](image)

**Fig. 6. The dynamic storage modulus as a function of temperature for kaolinite/SBR nanocomposites filled with different kaolinite contents.**

**Table 3. tanδ and Tg of SBR kaolinite composites filled with different contents.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>tanδ(0°C)</th>
<th>tanδ(60°C)</th>
<th>Tg/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK-20-SBR</td>
<td>0.332</td>
<td>0.107</td>
<td>-21.20</td>
</tr>
<tr>
<td>MK-30-SBR</td>
<td>0.302</td>
<td>0.112</td>
<td>-21.37</td>
</tr>
<tr>
<td>MK-40-SBR</td>
<td>0.326</td>
<td>0.119</td>
<td>-19.2</td>
</tr>
<tr>
<td>MK-50-SBR</td>
<td>0.324</td>
<td>0.125</td>
<td>-20.43</td>
</tr>
<tr>
<td>MK-60-SBR</td>
<td>0.311</td>
<td>0.129</td>
<td>-20.16</td>
</tr>
<tr>
<td>MK-70-SBR</td>
<td>0.308</td>
<td>0.131</td>
<td>-20.2</td>
</tr>
<tr>
<td>MK-80-SBR</td>
<td>0.307</td>
<td>0.144</td>
<td>-18.9</td>
</tr>
</tbody>
</table>
Filler network structure of kaolinite/SBR composites

The effect of kaolinite particle size and content on the storage modulus (G', in the shear model) as a function of shear strain for kaolinite/SBR compounds without crosslinking were evaluated. The storage modulus as a function of shear strain for SBR filled by kaolinite with different particle size is presented in Fig. 8. The G' values of all SBR filled with kaolinite are higher than that of pure SBR over the entire span of shear strain amplitudes, thus verifying that a significant reinforcement has occurred; this finding is in agreement with the above data. All of the composites displayed a reduction of G' with the shear strain. This effect was more pronounced as the filler particle size decreased; however, this effect can be ignored in pure SBR. The decrease in the storage modulus with the applied shear strain for rubber melts containing reinforcing fillers is a non-linearity behaviour known as the Payne effect [17, 29]. Such an effect is considered an indication of the occurrence of the so-called filler networking phenomenon, which is attributed to an agglomeration-deagglomeration process of the filler particles above the filler percolation threshold [30]. The reduction of kaolinite particle size resulted in the increase in special surface, surface energy, and the unit volume fraction of fillers in the rubber matrix. These changes enhanced the interaction between the filler particles and intensified the agglomeration-deagglomeration process. Thus, a larger Payne effect was observed for the SBR filled with smaller-particle-sized kaolinite. These results show that the agglomeration-deagglomeration process of kaolinite particles would be intensified as the particle size is reduced and indicates that modifications are necessary to improve the dispersion of fillers in the rubber matrix.

The storage modulus as a function of shear strain for SBR filled by different contents of kaolinite is presented in Fig. 9. The G' values of composites increased as the kaolinite content increased over the entire span of shear strain amplitudes; this behaviour is attributed to the stronger restriction of kaolinite particles on molecular chains motion as result of the increase in the unit volume fraction of kaolinite and the interaction between kaolinite particles and rubber chains. The Payne effect of kaolinite/SBR composites exhibited an enhanced tendency as the kaolinite content increased, indicating that the agglomeration-deagglomeration of filler particles intensified because of the relative increase in the unit volume fraction of kaolinite in the composite matrix.

Fig. 7. The loss tangent as a function of temperature for kaolinite/SBR nanocomposites filled with different kaolinite contents.
Fig. 8. The storage modulus ($G'$) as a function of strain for kaolinite/SBR nanocomposites filled with different particle sized kaolinite.

Fig. 9. The storage modulus ($G'$) as a function of temperature for kaolinite/SBR nanocomposites filled with different kaolinite contents.

Summary. A series of SBR composites filled with modified kaolinite was prepared by melt blending. The influences of kaolinite particle size and content on the dynamic mechanical properties of kaolinite/SBR composites were investigated. The results of SEM and TEM revealed that the rubber chains were confined within the interparticle space of kaolinite, and that micro-scale kaolinite particles exhibited a physical dispersion in the SBR matrix. Both the decrease in kaolinite particle size and the increase in kaolinite content can greatly improve the storage modulus and reinforcing effect of kaolinite/SBR composites. The reduction of kaolinite particle size is beneficial for the wet traction property but undesirable for the rolling resistance property of kaolinite/SBR composites. However, the increase in kaolinite content is unfavourable for both the wet traction and rolling resistance of the vulcanized rubber samples. The results indicate that smaller particle size and low filled content of kaolinite filler is favourable for the dynamic properties of SBR materials for tire products. The filler networking phenomenon ascribed to the agglomeration-deagglomeration of filler particles was intensified as the particle size was reduced and the kaolinite content was increased as a result of the increase in the unit volume fraction of kaolinite in the rubber matrix and the stronger interaction between kaolinite particles in the composite matrix.
Acknowledgments
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Cite the paper