In this work, effects of silane coupling agents on the tribological properties of bentonite/nitrile butadiene rubber (NBR) composites were investigated. The composites were fabricated with a facile method. Three silane coupling agents, (3-mercaptopropyl)trimethoxysilane (MPTMS), bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPT) and [3-(2-aminoethylamino)propyl]triethoxysilane (AEAPTMS) were employed in our research. The short sulfur bonds formed between MPTMS and macromolecules in the matrices limited the extension of the contact interface between rubber matrices and glass plate, which contributed to the reduction in friction coefficient. With TESPT and AEAPTMS, the adhesion force of the composites was remarkably reinforced, further leading to the increase in friction coefficient. In the wear test, bentonite/silane/NBR composites showed better wear resistance compared to the specimens fabricated without silanes. By investigation on the morphological features of the worn surfaces, different wear mechanisms for composites with/without silane coupling agents were illustrated in detail. Generally, the effects of silanes to adhesion force, hysteresis loss ratio and hardness all contributed to the friction coefficients of the composites. In wear test, the effects of the silanes on hysteresis force were prominent. Incorporated with MPTMS, the composite showed poor wear resistance due to its high hysteresis loss ratio. POLYM. COMPOS., 00:000–000, 2015. © 2015 Society of Plastics Engineers

INTRODUCTION

In recent decades, inorganic-polymeric composites have been extensively utilized in industry area, showing outstanding properties in many aspects [1–4]. As one of the most important inorganic fillers for the fabrication of polymer composites, clay is economical and abundant in nature. Considering its prominent reinforcing effect for polymer materials, clay/polymer composites now play an important role in world composites market [5]. Among the clay/polymer composites, clay/rubber composites have been investigated since years ago due to their excellent performances in the academia and in industrial application [6–9].

Belonging to the family of clay, bentonite is mainly composed of montmorillonite, which is commonly utilized in the fabrication of clay/rubber composites. Exfoliated montmorillonite performs as an excellent reinforcement for rubbery materials originated from its nanoscopic dimensions, high aspect ratio [10] and high surface area-to-volume ratio [11]. Therefore, improvement in the dispersion state of bentonite in rubber matrices becomes an important issue. Another problem in the application of bentonite in rubber industry is the hydrophilicity of the silicate layers, which leads to serious phase separation between bentonite and hydrophobic matrices. To overcome these problems, compatibilizers and modifiers have been developed and utilized [12–14]. Thereinto, the effect of silane coupling agents on the dispersion of clay in the organic matrices is attractive while the filler–polymer interfaces could be reinforced by various chemical interactions from silane coupling agents [15, 16]. Mathialagan and Ismail [17] applied 3-aminopropyltrietoxysilane (APTES) in the preparation of bentonite filled EPDM composites. The results showed that the dispersion of bentonite in EPDM matrices was greatly improved while the interfacial interaction between EPDM and bentonite was also enhanced. Thus, in their research work, reinforced mechanical properties of the composites could be achieved. In previous researches, the influences of silane coupling agents on mechanical properties, thermal behaviors or gas permeabilities etc [18, 19] of rubber are subjects of general concern in the academia.

Undoubtedly, tribological properties are substantially important for the application of clay/polymer composites [20, 21]. However, until now, understanding on the mechanism of friction and wear is still insufficient. Frequently, theories related to the mechanism of friction or wear focus on two forces composing the friction force: adhesion force and hysteresis force [22, 23]. Grosch [24] provided two mechanisms which contributed to the friction between rubber and hard surfaces: first, the adhesion between rubber and the hard surface; second, the energy losses during the
deformation of rubber. He also found that at low sliding velocities, the friction of rubber was almost independent of velocity and temperature, while at high sliding velocities, the friction coefficient became a function of velocity.

Klüppel and Heinrich [25] further proved that a broad maximum of friction coefficient could be achieved as the sliding velocity kept increased. There are also some research works on other important factors of the friction. Persson [26] developed a theory of the hysteretic contribution to rubber friction. He argued that the local pressure was large enough to squeeze the rubber into the small “cavities” at the top of large asperities, but not at the bottom of large cavities. Eriksson and Jacobson [27] further explored the relationship between geometric factors and friction force. They found that the entirely geometric contribution, including the changes of contact angle, considerably increased the friction coefficient. Generally, it is believed that the mechanism of friction is complex and still in debate. Concerning the compatibilizers and modifiers in the fabrication of clay/polymer composites, there are some reports [21, 28, 29] on the study of tribology with silane coupling agents applied in composite materials. However, to our best knowledge, the literature dedicated to the effects of silane coupling agents applied in composite materials. However, to our best knowledge, the literature dedicated to the effects of silane coupling agents applied in composite materials. However, to our best knowledge, the literature dedicated to the effects of silane coupling agents applied in composite materials. However, to our best knowledge, the literature dedicated to the effects of silane coupling agents applied in composite materials. However, to our best knowledge, the literature dedicated to the effects of silane coupling agents applied in composite materials.

In our previous work, a facile method for the fabrication of bentonite/silane/NBR composites was developed [30]. In the present work, three silane coupling agents with different functional groups (shown in Scheme 1) were selected and a series of composites were prepared and compared. Thus, the effects of different interactions between the silanes and the matrices could be evaluated. In the three applied silanes, MPTMS and TESPT are able to form chemical bonds (short or long sulfur bonds) with the macromolecules in the matrices while AEAPTMS mainly forms ion-molecule interaction. Friction coefficients and wear losses of the composites were determined. Characteristics of mechanical properties were also measured. The effect of various silanes on the tribological properties of the composites was discussed in detail while the wear losses of the composites were correlated with the tensile properties by Ratner-Lancaster model [31]. The viscoelastic properties of the representative composites were further evaluated and investigated with dynamic mechanical analysis.

**EXPERIMENTAL**

**Materials**

Bentonite (Bt, ≥95%; water content, <3%; Na⁺-montmorillonite content, ≥95%; cation exchange capacity, 0.85 meq/g) was purchased from YAKURI Pure Chem, Japan. Acrylonitrile butadiene rubber (NBR) latex (KNB 35L, solid content: 20.3%, w/v; acrylonitrile content: 34%) was provided by Kumho Petrochemical, Korea. (3-Mercaptopropyl) trimethoxysilane (MPTMS, 95%), [3-(2-aminoethylamino) propyl] triethoxysilane (AEAPTMS, ≥80%) and bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPT, ≥90%) were purchased from Sigma-Aldrich, USA; Dodecylbenzenesulfonic acid, sodium salt (DBS-Na, 50.0%) was manufactured by Samchun Pure Chem, Korea. Ammonia water (28.0%, w/w) was supplied by Duksan Pure Chem, Korea. All other chemicals were of reagent grade and used as received: 2,2′-dibenzothiazolyl disulfide (DM) was supplied by WAKO Pure Chem, Japan; stearic acid (above 95.0%), ZnO (above 99.0%) and sulfur powder (above 99.0%) were supplied by Daejung Chem, Korea; N-Cyclohexyl-2-benzothiazolylsulfenamide (CBS) was supplied by TCI, Japan.

**Synthesis of the Composites**

With the optimization on the reaction factors in advance, a typical procedure for the synthesis is provided: 0.035 mol of silane coupling agent was added dropwise into 500 mL of NBR latex (stabilized by DBS-Na) and mixed for 30 min. Subsequently, aqueous suspension of bentonite (0.1 g/mL) was blended with NBR latex. 3.0 mL of ammonia aqueous solution (25.0 wt%) was finally added as a catalyst. The reaction was held for 2 h at room temperature. After the synthesis, the slurry was coagulated with 1,000 mL of calcium chloride aqueous solution (0.09 × 10⁻³ mol/mL) and dehydrated in vacuum at 70°C until a constant weight was obtained. A series of composites with different silane coupling agents were fabricated. Bentonite/NBR composite was prepared in the absence of any silane while neat NBR was fabricated by directly precipitating NBR latex in CaCl₂ aqueous solution. The composites and neat NBR were then blended with other ingredients on a two-roll mill at 40°C. The formulations for synthesis and compounding are summarized in Table 1. In the last step, the vulcanized composites with a thickness of 2 mm were achieved under a pressure of 10 MPa in a hydraulic press (Auto hydraulic press type, Ocean Science) at 160°C.

Designation: bentonite/NBR composites with different bentonite loading were designated as “B2NC, B5NC,
TABLE 1. Formulations for the synthesis and compounding.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Neat NBR</th>
<th>Bentonite/NBR</th>
<th>Bentonite/silane/NBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR (phr)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Bentonite (phr)</td>
<td>0</td>
<td>2, 5, 10, 20</td>
<td>20</td>
</tr>
<tr>
<td>Silane coupling agents (mol)</td>
<td>0</td>
<td>0.017, 0.035b</td>
<td>0</td>
</tr>
<tr>
<td>DBS-Na (phr)</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>ZnO (phr)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid (phr)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>DM (phr)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CBS (phr)</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Sulfur powder (phr)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*a phr, parts per hundreds of rubber.

b0.0085 mol and 0.017 mol for TESPT.

B10NC, B20NC”, in which the numbers after the letter “B” present bentonite loading in the unit of phr. For bentonite/silane/NBR composites, letters “M,” “T,” and “A” present MPTMS, TESPT and AEAPTMS while letters “a” and “b” present composites prepared with 0.017 mol of silanes and 0.035 mol of silanes, respectively. For instance, “AB20NCa” presents the composite prepared with 0.017 mol of AEAPTMS and 20 phr of bentonite.

CHARACTERIZATION

X-Ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) was performed with Empyrean (manufactured by PANalytical) X-ray diffractometer. The specimens (with the same weight of 4.0 g) were all determined at a generator voltage of 40 kV and a generator current of 30 mA with copper as the radiation source. XRD data were collected over the range 4–11°(2θ) a rate of 2°/min.

Swelling Test

Swelling ratio is always measured for the evaluation of crosslinking density of composite materials. In our work, equilibrium swelling ratio was determined. The specimens were swelled in toluene for 72 h according to ASTM D471-79 standard [30]. The equilibrium swelling ratio (S) of the composites was computed with the following equation:

\[ S = \frac{(W_w - W_u)}{W_u/\rho_r} \times 100\% \] (1)

where \( W_w \) is the weight of swollen specimens, \( W_u \) is the original weight of the specimens in air, \( \rho_r \) is the density of toluene (0.867 g/cm³) and \( \rho_r \) is the density of the specimens.

Mechanical Properties

For tensile test, the specimens cut from the vulcanizate sheets were all in standard dumb-bell shape with dimensions 25 mm × 6 mm × 1 mm. Then the tensile properties were determined with a Tinius Olsen H5KT-0401 testing machine according to ASTM D412 standard. Shore A hardness of the specimens was obtained with Shore Durometer Type A according to ASTM D2240. Hysteresis test was performed till 100% strain and the hysteresis loss ratio (\( h_r \)) was calculated by dividing loop area with the area of work performed by extension deformation [32].

Friction Coefficient Test

Static friction coefficient (\( \mu_s \)) and dynamic friction coefficient (\( \mu_d \)) of the vulcanized composites were measured with Test One friction testing machine TO-100-IC according to ASTM 1894 (apparatus shown in Scheme 2a). Relevant parameters were shown as follows: sample size 63.5 mm × 63.5 mm × 1.0 mm, normal load 2/4.5/7 N, sliding velocity 300 mm/min. All the surfaces of the specimens were cleaned up in advance by sonication in acetone for 10 min.

Taber Abrasion Wear Test

Taber abrasion wear test was performed on a standard Taber abrasion tester (Taber Industries) with two Genuine Taber abrasive wheels (Calibrase®, CS-10). The test was operated at a rotary speed of 80 cycles/min according to ASTM D1044. The wear loss was recorded for every 1,000 cycles and totally 10,000 cycles of rubbing was carried out for each specimen. A 250 g load was located...
on the arms connecting with each wheel for balancing (see Scheme 2b).

**Scanning Electron Microscopy (SEM)**

The tensile fractured surfaces and worn surfaces of the specimens sputter-coated with a thin film of gold were examined using field emission scanning electron microscopy (FE-SEM) with a model number of JSM-7500 (JEOL) under accelerating voltage of 10.0 kV.

**Dynamic Mechanical Analysis (DMA)**

The dynamic mechanical properties of representative composites were characterized with a dynamic mechanical analyzer with a model number of Q800 (TA Instrument). The specimens with dimensions 40mm × 10mm × 1mm were determined with dual-cantilever bending mode in a temperature range of −80 to 120°C. A sinusoidal strain with a frequency of 1 Hz was applied.

**RESULTS**

**XRD Analysis**

The interlayer spaces of bentonite were characterized with XRD as shown in Fig. 1. It could be seen that the original distance between stacked layers of pure bentonite is 1.27 nm [33], presented by the peak at 6.9° in Fig. 1a. For the bentonite/NBR composites, the interlayer space was expanded to approximately 1.43 nm (6.2°). The intensity of the peak kept enhanced as bentonite loading increased from 2 to 20 phr. With silane coupling agents incorporated (see Fig. 1b), the peak at 6.2° was significantly weakened compared to B20NC, especially for MPTMS. Interestingly, for AEAPTMS, the peak at 6.2° shifted to 4.8°, presenting an expanded interlayer distance of 1.84 nm. Meanwhile, different from the other two silanes, as the incorporated AEAPTMS increased from 0.017 to 0.035 mol, the intensity of the peak at 4.8° was significantly enhanced.

**Swelling Ratio**

The values of swelling ratio were important for the evaluation of swelling resistance in organic solvent as well as the crosslinking density of the composites. As shown in Table 2, with bentonite incorporated, the swelling ratio of the composite decreased from 217% to 172%. It is also revealed that the silane coupling agents influenced the swelling ratio in different ways: MPTMS led to a much lower swelling ratio of MB20NCb, which was only 138%, indicating a significant increase in crosslinking density. However, with TESPT and AEAPTMS applied in the preparation of the composites, the changes in swelling ratio were marginal (174% for TB20NCb and 172% for AB20NCb).

**Friction Coefficient**

The static and dynamic friction coefficients ($\mu_s$ and $\mu_d$) of the composites with various bentonite loadings are shown out in Fig. 2. The relationships among the bentonite loading, the loading force and the friction coefficient were exhibited in the figure. It is revealed that as the

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Swelling ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat NBR</td>
<td>217</td>
</tr>
<tr>
<td>B20NC</td>
<td>172</td>
</tr>
<tr>
<td>MB20NCb</td>
<td>138</td>
</tr>
<tr>
<td>TB20NCb</td>
<td>174</td>
</tr>
<tr>
<td>AB20NCb</td>
<td>179</td>
</tr>
</tbody>
</table>

**FIG. 1.** XRD patterns of representative vulcanizates. (a) Pure bentonite and bentonite/NBR composites with different bentonite loadings; (b) bentonite/silane/NBR composites with different silane coupling agents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
bentonite loading increased from 0 to 10 phr, both $\mu_s$ and $\mu_d$ were remarkably elevated up. However, excess bentonite led to a reverse trend of the friction coefficients. In Fig. 3, the influences of different silane coupling agents on the friction coefficient of the composites are presented. Among the three silanes, MPTMS led to much lower friction coefficients compared to neat NBR while the other two silanes resulted in higher friction coefficient values.

Wear Loss

From the wear volume loss shown in Fig. 4a, it is exhibited that higher content of bentonite in NBR matrices showed detrimental effect to the wear resistance of the materials. For B10NC, the wear volume loss was more than 200% higher compared to neat NBR and for B20NC, more than 400%. With silane coupling agents added (see Fig. 4b), the wear resistance of the composites was recovered to some extent. However, the loss rate and total volume losses (shown in Table 3) of the bentonite/silane/NBR composites were still higher than those values of neat NBR.

Mechanical Properties

The values of tensile stress ($\sigma$), strain at break ($\varepsilon$), hysteresis loss ratio ($h_r$) and shore A hardness of presentative composites are all tabularly summarized in Table 4. The reinforcing effect of bentonite in the tensile strength of NBR matrices was prominent. At high loading of bentonite, strain at break of the composites decreased slightly comparing to the other bentonite/NBR composites. Among the bentonite/silane/NBR composites, there was a drastically decreasing in $\varepsilon$ value for MB20NCb. However, its $\sigma$ value reached 13.8 MPa, which was comparable with TB20NCb. It is also revealed that higher content of bentonite led to enhanced hardness. The incorporation of MPTMS remarkably increased the hardness of MB20NCb to 69.0. With same bentonite loading, TB20NCb and
AB20NCb showed lower hardness (51.7 and 50.6, respectively) than B20NC and MB20NCb. Hysteresis phenomenon, commonly occurs during the deformation of elastomeric materials, significantly influences the tribological properties of rubber. Hysteresis loss presents the energy dissipated during the recovery of elastomer after extension. Therefore, hysteresis loss ratio \((h_r)\), which is the ratio of the center area of the hysteresis loop and the area under the tensile curve, becomes a significant value for the evaluation of hysteresis force. As shown in Table 4, \(h_r\) increased accordingly with bentonite loading, reaching to 0.27 for B20NC. Silane coupling agents showed different effects on \(h_r\). MPTMS further elevated up that value to 0.35. However, both TESPT and AEAPTMS led to a decline of \(h_r\). For TB20NCb and AB20NCb, the \(h_r\) values were only 0.16 and 0.19, respectively.

**Morphology**

SEM micrographs of representative specimens were provided as shown in Figs. 5 and 6. It could be found that for TB20NCb and AB20NCb, the worn surfaces were smoother compared with the undulated surfaces of neat NBR, B10NC, B20NC and MB20NCb. With silane coupling agents, some small but deep grooves could be observed on the surfaces, as could be seen in Figs. 5 and 6. More aggregations of bentonite could be found for B20NC and AB20NCb while the gaps between the aggregations and the matrices were distinct for B20NC. In Fig. 6, peeled particles could be observed on the worn surfaces. Obviously, for bentonite/silane/NBR composites, the particle sizes were smaller compared to B20NC.

Tensile fractured surfaces of neat NBR, B20NC and bentonite/silane/NBR composites were also investigated with SEM, as shown in Fig. 7. Compared with the uniform fractured surfaces of neat NBR, B20NC showed highly corrugated structure with tortuous paths on the fractured surface. Meanwhile, large-size bentonite aggregates could be observed, separated off from the surface. Bentonite/silane/NBR composites showed smoother surfaces, especially for AB20NCb. Aggregated bentonite could still be found in bentonite/silane/NBR composites but in much smaller size compared to B20NC.

**Dynamic Mechanical Analysis**

By DMA, the storage modulus, loss modulus and tan\(\delta\) of representative specimens were determined and showed in Fig. 8. Meanwhile, from the curves of tan\(\delta\) vs

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Tensile stress (MPa)</th>
<th>Stress at break (MPa)</th>
<th>Strain at break (%)</th>
<th>Hysteresis ratio</th>
<th>Shore A hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat NBR</td>
<td>4.90</td>
<td>4.85</td>
<td>676</td>
<td>0.15</td>
<td>45.1</td>
</tr>
<tr>
<td>B2NC</td>
<td>6.38</td>
<td>6.27</td>
<td>773</td>
<td>0.18</td>
<td>48.4</td>
</tr>
<tr>
<td>B5NC</td>
<td>7.15</td>
<td>7.09</td>
<td>734</td>
<td>0.19</td>
<td>48.2</td>
</tr>
<tr>
<td>B10NC</td>
<td>7.58</td>
<td>7.48</td>
<td>716</td>
<td>0.22</td>
<td>54.6</td>
</tr>
<tr>
<td>B20NC</td>
<td>8.44</td>
<td>8.39</td>
<td>558</td>
<td>0.27</td>
<td>58.7</td>
</tr>
<tr>
<td>MB20NCb</td>
<td>13.8</td>
<td>12.6</td>
<td>170</td>
<td>0.35</td>
<td>69.0</td>
</tr>
<tr>
<td>TB20NCb</td>
<td>13.8</td>
<td>13.6</td>
<td>629</td>
<td>0.16</td>
<td>51.7</td>
</tr>
<tr>
<td>AB20NCb</td>
<td>13.1</td>
<td>13.1</td>
<td>596</td>
<td>0.19</td>
<td>50.6</td>
</tr>
</tbody>
</table>
temperature, the glass transition temperature ($T_g$) and maximum value of tan$\delta$ (tan$\delta_{\text{max}}$) were achieved and summarized in Table 5. As shown in Fig. 8a, in the glassy region, TB20NCb showed the highest value of storage modulus among the specimens. The storage modulus of B20NC and AB20CNb were a little lower than neat NBR. MB20NCb exhibited the lowest storage modulus value in glassy region, however declined much slower than the other specimens as the temperature was elevated. In Fig. 8b, MB20NCb showed a broader and lower peak compared to the other specimens. Generally, the curves of loss modulus vs temperature and tan $\delta$ vs. temperature (Fig. 8a) showed similar trends. Compared to B20NC, the $T_g$ of MB20NCb was elevated up to $\sim 18.8^\circ\text{C}$ while for
TB20CNb and AB20NCb, the values of $T_g$ decreased to $-25.5$ and $-27.5^\circ$C, respectively (see Table 5).

**DISCUSSION**

**Intercalated/Exfoliated Structure of Bentonite in NBR Matrices**

Due to the abundant ions existing in the interlayer spaces, the interlayer distance of bentonite was expanded as suspended in water phase. It is also revealed that at low loading of bentonite (2 phr), the peak slightly shifted to left, showing out that bentonite was more thoroughly swelled in water at lower concentration. The incorporation of silanes obviously affected the intercalated/exfoliated structure of bentonite layers, as shown in Fig. 1b. In the applied silanes, MPTMS was apparently more effective in exfoliating bentonite layers compared to TESPT (see Fig. 1b). With AEAPTMS, the interlayer distance was expanded while higher content of AEAPTMS remarkably enhanced the peak at 4.8°. Considering the molecular length of AEAPTMS (approximately 0.6 nm), triple-layer structure of AEAPTMS possibly formed in between the bentonite layers. As supported by Jia [15] and his coworkers, the amino groups in AEAPTMS could be ionized in water phase, generating $-$NH$_3^+$, further interacted with hydroxyl groups on the interfaces of bentonite layers, which hindered further exfoliation of the layers. That was supposed to be the main reason for the high intensity of AB20NCb at 4.8°. By this mean, more aggregations observed on the worn surface and fractured surface of AB20NCb (see Figs. 5 and 7) could also be explained.

**Friction Coefficient**

It has been reported in previous works that during sliding on a dry elastomer/rigid contact interface without wear, the friction force ($F_f$) was composed of two factors for polymeric materials: adhesion force ($F_a$) and hysteresis force ($F_h$) [23, 34].

In our study, friction coefficient test and Taber abrasion test were carried out, respectively. In these tests, two different surfaces from the rigid materials were involved: smooth surface for friction coefficient determination (glass) and rough surface for abrasion test (Genuine Taber abrading wheels composed of vitrified binder and silicon carbide abrasive particles). According to the values of $h_r$ in Table 4, the contribution of $F_h$ to $F_f$ could be evaluated. Subsequently, the effect of $F_a$ could also be predicted. Due to the incorporation of bentonite, $h_r$ was elevated up (Table 4), which mainly contributed to the increase in friction coefficient (Fig. 2). Normally, $\mu_a$ and $\mu_h$ kept constant under enhanced normal load force. However, it is found that there was an increasing trend as normal load force was elevated up. It is possibly due to the “front edge effect” during the test. The rubber block tilted during moving on the glass plate, leading to an abnormal increment in friction coefficient.

As silane coupling agents applied, the tribological properties of the composites were affected in diverse ways. Actually, all of MPTMS, TESPT and AEAPTMS could provide lone pair electrons due to the existence of S and N atoms, which are substantial to the enhancement of $F_a$. However, with MPTMS, the hardness of the composite was remarkably enhanced compared to B20NC. That was the main reason limiting the extension of the composite surface, resulting in low contacting area for MB20NCa or MB20NCb against the glass plate. Consequently, the friction coefficients...
of those two composites were low at different loading forces. The prominent hardnesses of MB20NCa and MB20NCb were probably related to their high crosslinking densities (see the data in Table 2) originated from the formation of S—C bonds between mercapto groups and macromolecules in the matrices.

Wear Resistance

As mentioned above, during the wear loss test, rough-surface abrading wheels were employed. Gabriel [22] and Fuller [35] supported the idea that \( F_a \) is negligible for rough contact interface. In that condition, \( F_h \) was the only factor influencing \( F_F \). Generally, wear volume loss and the number of abrading circles showed a linear relationship (Fig. 4), indicating the wear rates were constant during the test. MB20NCb showed the highest value of \( h_r \) (0.35) among all the specimens while its wear volume loss reached 0.11 cm\(^3\) (see Table 3). However, its wear volume loss was a little lower than B20NC, implying that friction coefficient was not the only effective factor for wear loss. It is believed that the reinforced filler–matrices interaction of the composite due to the incorporation of MPTMS [30] also contributed to the wear resistance of the composite. Concerning TB20NCb and AB20NCb, their wear loss almost doubled the value of neat NBR (but much lower than MB20NCb and B20NC due to their low \( h_r \) values), showing out that hybrid composites performed poorly compared with neat rubber materials in the aspect of wear resistance. The wear mechanisms will be further discussed in the following section.

Morphology

In Fig. 5, the wear asperities become more corrugated as bentonite loading increased from 0 to 20 phr, which could be attributed to the poor compatibility of bentonite in NBR matrices. The highly corrugated worn surface of MB20NCb (Figs. 5 and 6) could be attributed to the high content of short sulfur bonds formed during vulcanization between MPTMS and rubber matrices. Deep and small grooves could be observed on the worn surfaces of bentonite/silane/NBR composites, which were circled in red in Fig. 5. That could be explained by the differences in the dispersion states of bentonite, as shown in Scheme 3. Without silane coupling agents, large-size aggregations of bentonite could be easily flaked off from the matrices.

TABLE 5. \( T_g \) and Tan \( \delta_{\text{max}} \) of representative specimens.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( T_g )</th>
<th>Tan ( \delta_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat NBR</td>
<td>-24.2</td>
<td>0.74</td>
</tr>
<tr>
<td>B20NC</td>
<td>-24.4</td>
<td>0.76</td>
</tr>
<tr>
<td>MB20NCb</td>
<td>-18.8</td>
<td>0.57</td>
</tr>
<tr>
<td>TB20NCb</td>
<td>-25.7</td>
<td>1.12</td>
</tr>
<tr>
<td>AB20NCb</td>
<td>-27.5</td>
<td>1.32</td>
</tr>
</tbody>
</table>

FIG. 8. Dynamic mechanical analysis of representative specimens. (a) Storage modulus and loss modulus of the specimens; (b) Tan\( \delta \) of the specimens. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surface (circled in red in Fig. 6), which led to a high wear loss rate. However, for bentonite/silane/NBR composites, the dispersion of bentonite was significantly improved. During abrading, thin flakes of bentonite were pulled out, left only deep and small grooves. Apparently, geometry of the wear asperities was influential to the wear loss, which was supported by Gabriel [22]. He argued that the depth of penetration of the rigid surface into the elastomer changed the angle of contact between both surfaces, thus significantly increased the friction force. As shown in Figs. 5 and 6, the highly corrugated wear asperity of MB20NCb drastically aggravated the wearing, resulting in a high wear loss. Meanwhile, for TB20NCb and AB20NCb, the relatively smoother wear asperities implied that there were only mild abrasive wear on these two surfaces. For the specimens with lower hardnesses, e.g. neat NBR, TB20NCb and AB20NCb, it was probable for the particulates peeled off from the matrices to embed into the asperities on the counterface, forming a transfer film. By that mean, the asperities became rounded and smoothed, leading to the reduction of wear. The phenomenon was observed during our research (not shown) and it was also supported by Dasari [36].

Different from the wear asperities with both bentonite and rubber particles, there were only bentonite aggregates observed on the tensile fractured surfaces (Fig. 7). For bentonite/silane/NBR composites, the separated bentonite particles could be hardly observed or in much smaller size, showing the effect of silane coupling agents in improving the dispersion of bentonite and filler–rubber interactions.

**Ratner-Lancaster Correlation**

It has been a long time since researchers found that there is a relationship between wear resistance and mechanical properties. During the past years, a number of models have been proposed. Ratner-Lancaster correlation [32] is a commonly employed among the models, which is shown as follow:

$$ W = \frac{k \mu}{H \sigma \varepsilon} $$

(1)

in which $W$ is the wear volume loss, $\mu$ is the friction coefficient, $H$ is the hardness, $\sigma$ is the stress at break and $\varepsilon$ is the strain at break. Lancaster [37] further illustrated the proportional relationship between wear rate and the product of $\sigma$ and $\varepsilon$. The wear volume losses versus $\frac{1}{\sigma \varepsilon}$ are shown in Fig. 9, exhibiting reasonable linear correlation for most of the specimens. It is revealed that the values of $\varepsilon$ for TB20NCb, AB20NCb and MB20NCb became dominant parameters in the correlation. High rigidity of the macromolecules originated from the short sulfur bonds formed by MPTMS resulted in low value of $\varepsilon$ and high wear loss. For TB20NCb and AB20NCb, the macromolecules in the matrices showed better flexibility, which provided higher values of $\varepsilon$ and reinforced wear resistance compared to the other specimens. It could also be seen that the prediction for neat NBR and B20NC was inaccurate. The wear mechanisms for B20NC with highly agglomerated bentonite and neat NBR matrices might be different compared with other specimens, which still need further exploration.

**Dynamic Mechanical Analysis**

As shown in Fig. 8a, the values of storage modulus in rubbery region of different specimens were in the order: MB20NCb > B20NC > TB20NCb > AB20NCb > neat NBR, which was accordance with the orders of hardness and Young’s modulus. However, the wear resistance of the specimens showed an opposite trend. In the glassy region, most of the composites showed lower storage modulus compared with neat NBR, especially for MB20NCb. Considering the short sulfur bonds in MB20NCb, the mobility of the macromolecules in NBR was significantly restricted during glass transition, which interrupted the tight packing of the macromolecules. The aggregations of bentonite (see XRD patterns in Fig. 1) were possibly the main reason for the low storage modulus of B20NC and AB20NCb. As the temperature was elevated, drastic energy losses of TB20NCb and AB20NCb could be observed in the curves of loss modulus versus temperature, which could be attributed to the flexibility of the multi-sulfur bonds formed by TESPT [38, 39] and the reversible ion-molecule interaction from AEAPTMS with the macromolecules in the matrices [40]. Oppositely, for MB20NCb, the peak of loss modulus was lower and broader. Good dispersion of bentonite and short sulfur bonds formed by MPTMS were the two reasons for that, which restricted the movement of the macromolecules. These could be further evidenced by tanδ-temperature...
CONCLUSION

Generally, all the three silane coupling agents provided low pair electrons which reinforced the adhesion force of the composites. However, by forming networks with the macromolecules in the matrices during vulcanization, they influenced the hardness of the materials in different ways. With MPTMS, the deformation of the composite hardly occurred which led to a limited contact area of the interface, which resulted in low friction coefficients. It could be concluded that hysteresis loss ratio was more effective to the wear resistance of the composites. Meanwhile, the reinforced filler-rubber interactions also contributed to the enhancement in wear resistance of the composites. From the results of DMA, it could be found that MPTMS facilitated the restriction of the molecular movement in the matrices, which was also helpful for the understanding in the tribological properties of the composites.

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