**Communication:** The preparation, characterization and properties of novel millable polyurethane/organoclay nanocomposites are reported. Clay treated with methyl tallow bis(2-hydroxyethyl) quaternary ammonium chloride was used as an organoclay for nanocomposite preparation. X-ray diffraction indicated the intercalation of polymer chains inside the interlayer spacings of the clay. Dynamic mechanical analysis showed a significant increase in storage modulus, and tensile strength increases with increased organoclay loading.

![X-ray diffraction patterns of millable polyurethane/organoclay nanocomposites.](image)

**New Millable Polyurethane/Organoclay Nanocomposite: Preparation, Characterization and Properties**

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**Introduction**

Manufacturers usually compound polymers with fillers in order to improve the stiffness and toughness of materials, to enhance their barrier properties, to improve flame retardance, and to reduce cost. Addition of particulate fillers sometimes imparts drawbacks to the resulting composites such as brittleness and opacity. Nanocomposites are a new class of composites that are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range. They show better physical properties such as thermal, mechanical, and barrier properties because of the much stronger interfacial force between the well-dispersed nanometer-sized domain than the conventional polymer/filler composite.[1–7] Depending on the structure of the dispersed clay particles in the polymer matrix, the composite can be classified as either intercalated or exfoliated nanocomposites. In an intercalated nanocomposite clay particles are dispersed in an ordered lamellar structure with larger gallery height, whereas in an exfoliated nanocomposite, each silicate layer is delaminated and dispersed in a continuous polymer matrix.

Polyurethane elastomers are noted for their toughness, flexibility, strength, abrasion resistance, and chemical resistance. Since they are relatively expensive compared to other elastomers, they are primarily used in demanding applications such as automotive bumpers, covers/trim, solid fire industrial rollers, shoe soles, sports goods, and various mechanical goods. Solid polyurethane elastomers can be divided into three categories, namely cast, millable, and thermoplastic elastomers. In the casting technique a liquid reaction mixture comprising of low-molecular-weight material is poured into a heated mold, wherein the material is converted into a solid, high-molecular-weight elastomeric product. Millable elastomers are rubbers like gums, which may be compounded in ordinary rubber processing equipment with other ingredients. Cast and thermoplastic elastomers gain their hardness and modulus as a result of
phase separation between hard and soft segments in the polymer chains, whereas the millable polyurethane elastomer develops hardness and modulus through the addition of fillers (phase separation while present, is secondary). Plenty of studies have already been conducted regarding polyurethane nanocomposites based on cast and thermoplastic elastomers\[8–14\] but there is no paper available to date concerning millable polyurethane-based nanocomposites. This paper highlights the preparation and the properties of the millable polyurethane/organoclay nanocomposite. For the previous preparative route to silicate/polyurethane nanocomposites, the approach was to physically mix alkyl- or aromatic-modified silicate with a polyurethane prepolymer or polyurethane urea polymer in appropriate solvents.\[15–18\] In the present study, the millable polyurethane/organoclay nanocomposite is prepared by mechanical mixing followed by the vulcanization method.\[19,20\]

**Experimental Part**

**Materials**

The millable polyurethane used was Urepan R 6404, which was kindly donated by Rhein Chemie, Germany. (There must be a terminal hydroxyl group in the millable gum.)

Dicumyl peroxide (DCP) and stearic acid were purchased from Aldrich Chemical Co. Cloisite 30B was procured from Southern Clay. The structure of the organic modifier is shown below, where T represents the hydrogenated tallow (≈65% C18, ≈30% C16, ≈5% C14).

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Polyurethane (phr)</th>
<th>DCP (phr)</th>
<th>Stearic acid (phr)</th>
<th>Cloisite 30B</th>
<th>Maximum torque (lb · in⁻¹)</th>
<th>Optimum cure time (t₀) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPU</td>
<td>100</td>
<td>4</td>
<td>0.25</td>
<td>–</td>
<td>27.7</td>
<td>7.2</td>
</tr>
<tr>
<td>MPU₅</td>
<td>100</td>
<td>4</td>
<td>0.25</td>
<td>5</td>
<td>28.4</td>
<td>13.2</td>
</tr>
<tr>
<td>MPU₁₀</td>
<td>100</td>
<td>4</td>
<td>0.25</td>
<td>10</td>
<td>27.1</td>
<td>15.3</td>
</tr>
<tr>
<td>MPU₁₅</td>
<td>100</td>
<td>4</td>
<td>0.25</td>
<td>15</td>
<td>28.1</td>
<td>18.1</td>
</tr>
</tbody>
</table>


**Sample Preparation**

The mixing formulation is shown in Table 1. Before being used, the organoclay was dried overnight in an air circulatory oven at 80°C. The organoclay was mixed with millable polyurethane elastomer in a Haake Rheocorder mixer at a rotor speed of 50 rpm, at 120°C for 10 min. After that the polyurethane elastomer was removed from the Haake Rheocorder and then the organoclay-filled elastomer was mixed with DCP and stearic acid in a laboratory-made two-roll mill. The mixed sample was cured in a hot press at 160°C to their optimum cure time, which is shown in Table 1.

**Characterization**

The basal spacings of the organoclay were studied by means of a wide-angle X-ray diffractometer (WAXD; Rigaku D/max 2200 H) with Cu Kα radiation operating at 30 kV and 30 mA. A WAXD pattern of the thin film of the hybrid was obtained. The tensile properties of the samples were measured by a Universal Tester (hounsfield UL 25) at a strain rate 10 mm · min⁻¹ using five dogbone-shaped replicas for each sample. Dynamic mechanical analysis (DMA) of the samples was carried out by using a dynamic mechanical analyzer (Rheovibron DDV-25 F; Orientec Co.) in the tension mode with the following parameters: frequency 1 Hz, scan rate 5°C · min⁻¹, within a temperature range of −100 to +100°C.

**Results and Discussion**

**Torque Rheometry**

Cure characteristics of the rubber compounds filled with the organoclay were determined using a Monsanto Rheometer at 160°C. As shown in Table 1, vulcanization time (t₀) increases with increased organoclay loading, which is probably caused by the scavenging of radicals by fillers. The maximum torque value (T_max) of the millable polyurethane/organoclay compounds remains more or less the same as that for unfilled (without organoclay) rubber compounds. Thus, the filler is not influencing the apparent crosslink density of the rubber vulcanizates.

**Wide-Angle X-ray Diffraction Analysis (WAXD)**

Direct evidence of intercalation of the polymer chains into the silicate galleries is obtained from the WAXD patterns in the range of 2θ = 1.5–12° and is shown in Figure 1. The

Table 1. Mixing formulations and torque rheometry results of the millable polyurethane/organoclay nanocomposites.

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Figure 1. X-ray diffraction patterns of millable polyurethane/organoclay nanocomposites.

peak corresponding to the basal spacing ($d_{001}$) of the organically modified clay (Cloisite 30B) appears at $2\theta = 4.74^\circ$.

For all nanocomposites, the $d_{001}$ peak of the clay has been shifted to a low angle corresponding to an increase in the $d$ spacing from 1.9 to 3.45, 3.79, and 3.81 nm for MPUN$_5$, MPUN$_{10}$, and MPUN$_{15}$, respectively (MPU = millable polyurethane). The decrease in the intensity of the peak for the rubber/organoclay hybrid in comparison to pure Cloisite 30 B is because of the decrease in the coherent layer scattering. The intensity of the peak is substantially lower for MPUN$_5$, whereas for MPUN$_{10}$ and MPUN$_{15}$ intensity increases. The WXRD results can be explained on the basis of the intercalation of the polymer chains into the clay layers, which led to the disordering of the layered clay structure, thus a decrease in the WXRD coherent scattering intensity. For further addition of the organoclay, the intensity of the $d_{001}$ peak (MPUN$_{10}$ and MPUN$_{15}$) increased, confirming the intercalation of the polymer chains in the layers without disruption of the ordered structure. For all nanocomposites, peaks of a higher order (such as at 5.02, 7.34, and 9.2° for MPUN$_{15}$) are observed, confirming the order tactoid.

**Tensile Properties**

The mechanical properties of the millable polyurethane/organoclay nanocomposites are summarized in Table 2.

Table 2. Mechanical properties of polyurethane/organoclay nanocomposites.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Tensile strength</th>
<th>100% tensile stress</th>
<th>Elongation at break</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPa</td>
<td>Mpa</td>
<td>%</td>
</tr>
<tr>
<td>MPU</td>
<td>6.9</td>
<td>1.4</td>
<td>528</td>
</tr>
<tr>
<td>MPUN$_5$</td>
<td>8.4</td>
<td>2.0</td>
<td>694</td>
</tr>
<tr>
<td>MPUN$_{10}$</td>
<td>9.5</td>
<td>2.3</td>
<td>720</td>
</tr>
<tr>
<td>MPUN$_{15}$</td>
<td>9.8</td>
<td>2.8</td>
<td>750</td>
</tr>
</tbody>
</table>

Tensile strength as well as 100% tensile stress increase with increased organoclay loading. The tensile strength of MPUN$_{10}$ (10 phr clay-filled polyurethane) is 1.46 times higher than the tensile strength of MPU. The elongations at break for all samples are also found to increase with increased organoclay amounts. The elongation at break of MPUN$_{10}$ is 1.36 times higher than that of MPU. When an inorganic filler is added (which forms a microcomposite) to a polyurethane elastomer (to reduce cost and to improve stiffness) the elongation at break is found to decrease.

The simultaneous enhancement of the tensile strength and elongation at break, which is occurring in this millable polyurethane nanocomposite, also shows a good agreement with other polyurethane elastomer systems studied by Pinnavaia et al. The intercalation of the polymer chains inside the organoclay gallery increases the surface area between the organoclay and polymer chains, which results in the enhancement of polar interactions between the silicate layer and polymer chains. These increased polar interactions are responsible for the improvement of the tensile strength of the nanocomposites. The enhancement in the elongation at break of the polyurethane elastomer nanocomposite may be attributed, in part, to the plasticizing effect of the gallery onium ions and to their contribution to the formation of dangling chains, but also probably to conformational effects at the polymer/clay interface. The combination of improved stiffness and elasticity are quite exceptional and make elastomeric nanocomposites a new family of high-performance materials.

**Dynamic Mechanical Analysis (DMA)**

The storage modulus of the samples over a wide temperature range of $-100$ to $+100$ °C is displayed in Figure 2. The results are shown in Table 3. It is observed that reinforcement is prominent above the glass transition temperature of the millable polyurethane, when the material is soft and flexible, thus causing significant improvement in the storage modulus above the glass transition temperature. It is observed from Table 3 that the storage modulus (25 °C) of MPUN$_{10}$ is 2.9 times higher than that of the MPU. The enhancement of the storage modulus depends on the degree of intercalation of the polymer inside the chains and the aspect ratio of the filler.
The tan\( \delta \) curves of millable polyurethane clay hybrids are shown in Figure 3. The tan\( \delta \) curve shows a peak at about \(-2.1\) °C (MPU), which is attributed to the glass transition temperature \( (T_g) \) of the unfilled elastomer. For all nanocomposites tan\( \delta \) is shifted to a slightly higher temperature. This shift of the tan\( \delta \) peak is because of the hindered cooperative motion of the polymer chains. The value of tan\( \delta \) at \( T_g \) was also found to decrease with increased organoclay content. This is because of the strong interfacial interaction between the matrix rubber and filler and is also observable in the other rubbery microcomposites.\(^\text{[22,23]}\)

Conclusions

We have successfully prepared new millable polyurethane/organoclay nanocomposites. The WAXD results of the nanocomposites showed a shift in the peak position with reduced intensity in comparison to the organoclay, suggesting thereby the intercalation of the polymer inside the silicate layer. Tensile strength, 100% stress, and elongation at break of the nanocomposites were found to be higher than those of their pristine counterparts. Storage moduli of the nanocomposites increase with increased organoclay contents above the \( T_g \) of the millable polyurethane.

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Table 3. Results from dynamic mechanical analysis.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Storage modulus at 25 °C (MPa)</th>
<th>tan( \delta )</th>
<th>Intensity of the peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPU</td>
<td>( 4.63 \times 10^6 )</td>
<td>-2.08</td>
<td>1.45</td>
</tr>
<tr>
<td>MPU_5</td>
<td>( 7.89 \times 10^6 )</td>
<td>-0.24</td>
<td>1.05</td>
</tr>
<tr>
<td>MPU_10</td>
<td>( 13.43 \times 10^6 )</td>
<td>-0.86</td>
<td>0.65</td>
</tr>
<tr>
<td>MPU_15</td>
<td>( 32.69 \times 10^6 )</td>
<td>-1.68</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Figure 2. Variation of dynamic storage moduli with temperature for unfilled millable polyurethane elastomer and nanocomposites.

Figure 3. Variation of tan\( \delta \) with temperature for unfilled millable polyurethane elastomer and nanocomposites.