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Study on mechanical properties of polyurethane-attapulgite nanocomposites

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Among the clay minerals, those of fibrous morphology, such as attapulgite, are less abundant than those of platy habit, such as kaolinite, montmorillonite, and illite [1]. Fibrous clay minerals find extensive use in industrial and commercial applications which exploit the unusual behavior arising from their physicochemical and structural properties [2, 3].

Polyurethanes (PU) are becoming increasingly important as engineering materials, because of their high abrasion resistance, tear strength, excellent shock absorption, flexibility and elasticity. Conventional PU, however, is known to exhibit poor resistance to heat and barrier properties. To overcome these disadvantages, various experiments aimed at improving both the mechanical properties and thermal stability of PU have been conducted. One method to improve mechanical properties of PU involved dispersing inorganic or organic fillers into the PU matrix [4, 5].

Attapulgite was classified as a three-layer inverted mineral of fibrous habit whose structure comprises a complete planar sheet of oxygen atoms arranged in exactly the same manner as that in micas and other clay minerals [6]. However, the distinguishing feature of the structure is that the Si—O tetrahedras form long strips, each an amphibole unit wide on alternate sides of the oxygen sheet in a manner which confers a regular corrugated Si—O structure. Octahedral units of MgO positioned parallel with these corrugations produce open ended (but otherwise enclosed) rectangular channels, equivalent to about one amphibole unit wide (0.6 nm) and one brucite unit high (0.37 nm), and consequently the structure has a more distinct 3-dimensional structure than platy clays (where basal faces exhibit 2-D symmetry). Attapulgite has the structural formula $[(OH_2)_4(Mg,Al,Fe,)_5(OH)\cdot 2Si_8O_{20}\cdot 4H_2O$. Fig. 1 shows the schematic diagram of attapulgite [7]. Since attapulgite is hydrophilic and lacks affinity with hydrophobic organic polymers, it was usually treaded with various organic agents such as acetalation to create a partial hydrophobic character on the originally hydrophilic silicate surfaces [8]. In this letter, we report the preparation and mechanic properties of PU/O-ATPG nanocomposites.

4,4′-Diphenylmethane diisocyanate (MDI, Aldrich), polytetramethylene glycol (PTMEG, Mn = 2000, Aldrich) were dehydrated under vacuum at 60 °C for 24 h. Dimethylforamide (DMF, 99%, Tianjing Chemical Reagent Co.,) and 1,2-diaminopropane (Shanghai Chemical Reagent Co.) were dried over calcium hydride for two days and then distilled under vacuum Attapulgite (ATPG, Huiying Attapulgite Co.) and N-[3-(trimethoxysilyl)propyl]ethylenediamine (Tianjing Chemical Reagent Co.) were used as received.

20 g of the screened attapulgite was gradually added to a previously prepared solution of 50 g N-[3-(trimethoxysilyl)propyl]ethylenediamine dissolved in 500×10^{-6} m^3 of dehydrated toluene, and refluxed at 130 °C for 6 h. The precipitate formed was then isolated by filtration, suspended in 400×10^{-6} m^3 of alcohol and stirred for 2 h, then washed repeatedly with alcohol. The product was finally filtered and dried in vacuum at 80 °C for 24 h, ground and screened with a 300-mesh sieve to obtain the O-ATPG.

Different amounts of O-ATPG were used as a part of chain extenders replacing a part of 1,2-diaminopropane to form O-ATPG/PU nanocomposites.5 g of 4,4′-Diphenylmethane diisocyanate (MDI) and 19.5 g of polytetramethylene glycol (PTMEG) at a molar ratio of 2:1 were dissolved in DMF solvent, the whole solution was mixed under nitrogen atmosphere for 2 h at 90 °C to form a pre-polymer. Then the O-APTG (1, 2, 3 wt% etc.) was mixed with 20×10^{-6} m^3 DMF and then added to the prepolymer with vigorous stirring at room temperature for 2 h. Subsequently, 0.74 g of 1,2-diaminopropane was gradually added to the mixture with vigorous stirring for 4 h to complete the reaction. The O-ATPG/PU films were formed by casting the solution onto glass plates and then removing the solvent in vacuum at 70 °C for 36 h.

X-ray diffraction measurements (XRD) were performed with a D/Max-2400 Rigaku diffractometer with Ni-filtered Cu K_α radiation ($\lambda = 0.15418$ nm). The scanning rate was 2°/min over a range of $2\theta = 2$–15 °. Differential scanning calorimetry (DSC) was performed with a DSC822E under N_2 atmosphere with a heating rate of 10 °C/min. Tensile properties of the sample were tested with an Instron mechanical tester (model DY-35) at a crosshead speed of 500 mm/min. The I-shaped specimens had a dimension of 4 mm in width, 16 mm in length and 0.2 mm in thickness. For each datum point, five samples were tested and the average value was taken.

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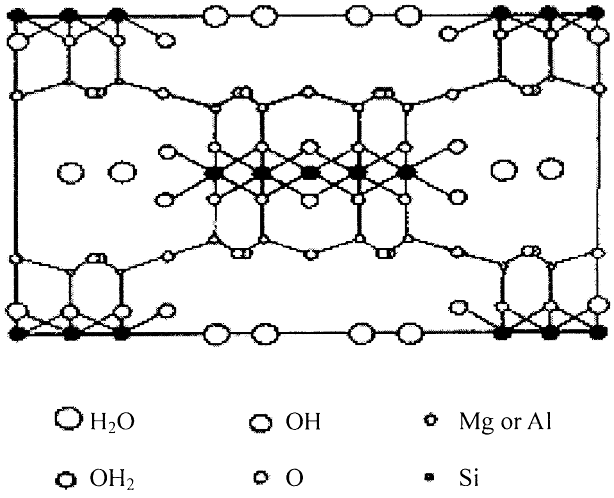

Figure 1 Schematic diagram of attapulgite.

The X-ray diffractograms of attapulgite, O-ATPG and O-ATPG/PU are shown in Fig. 2. It was shown that the first diffraction peak at $2\theta = 6.08^\circ$ corresponds to a basal spacing of the clay platelets of 1.43 nm. For O-ATPG, the peak at $2\theta = 6.08^\circ$ became broad and weak, this indicated that the silicate layer galleries in the attapulgite were intercalated by N-[3-(trimethoxysilyl)propyl]ethylenediamine. In the O-ATPG/PU spectrum, the peak at $2\theta = 6.08^\circ$ was totally absent, thus suggesting the exfoliation of the attapulgite clay platelets in the polymeric matrix [9]. The second diffraction peak of attapulgite, O-ATPG and O-ATPG/PU at $2\theta = 8.36^\circ$ corresponded to 1.0 nm in diameter of the fiber crystal structure of attapulgite.

The thermal properties of pure PU and O-ATPG/PU nanocomposites was detected by DSC, and the results are shown in Table I. The glass transition temperatures of ATPGT/PU nanocomposites were between −65.5 and −67.7 °C, being lower than that of pure PU at −61.5 °C. Endo peak 1 of O-ATPG/PU nanocomposites was between 8.1 and 10.8 °C, higher than that of pure PU at 2.6 °C. The fusion (ΔH) of O-ATPG/PU nanocomposites was between 36.4 and 46.8 $\text{J} \cdot \text{g}^{-1}$, being larger than that of pure PU at 7.5 $\text{J} \cdot \text{g}^{-1}$.

TABLE I T_g and T_m of pure PU and O-ATPG/PU nanocomposites

O-ATPG content (wt%)	T_g[a] (°C)	Endo 1 peak, T(°C)	ΔH ($\text{J} \cdot \text{g}^{-1}$)
0 (pure PU)	−61.5	2.6	7.5
2	−67.7	8.3	46.7
4	−67.7	8.1	40.3
6	−65.5	9.7	41.5
8	−66.5	7.9	36.4
10	−66.5	10.8	44.0
20	−65.5	9.6	43.3

[a] Glass transition temperatures.

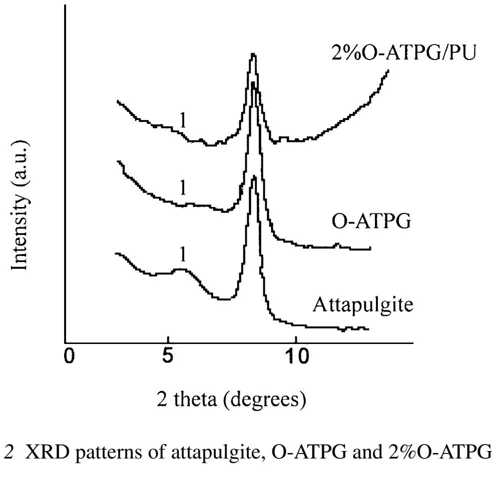

Figure 2 XRD patterns of attapulgite, O-ATPG and 2%O-ATPG/PU.

This trend might be explained because O-ATPG/PU was crystalline. When O-ATPG was used as chain extenders to replace a part of the 1,2-diaminopropane, the attapulgite was dispersed in the polymer matrix, and it might serve as nucleation seeds in the polymer matrix. Since attapulgite was a type of one dimensional nanocomposite having a layered silicate clay structure, its crystal was in the form of fiber. The chain motions of polymer molecules attached in the attapulgite silicate layers could be barred and limited. And the crystallizability of O-ATPG/PU nanocomposites was reduced. These factors caused Endo peak 1 and ΔH of O-ATPG/PU higher and T_g of O-ATPG/PU lower than that of pure PU.

The experimental results of the O-ATPG content on the tensile mechanical properties of the nanocomposites are shown in Fig. 3. It was found that the O-ATPG content had a remarkable effect on the mechanical properties of the nanocomposites. As shown in Fig. 3, both the tensile strength and the elongation at break of the O-ATPG/PU increased with the increasing O-ATPG content in the range of 1–3 wt%.Compared to the pure PU, the tensile strength and the elongation at break of the 3 wt% O-ATPG content were increased by more than 220 and 155% respectively. When the O-ATPG content was higher than 3 wt%, both the tensile strength and the elongation at break of the O-ATPG/PU decreased.

The following two effects could explain all these results: (1) Favorite interactions between the polymer and the silicate in nanocomposites lead to the organic and inorganic phases being dispersed at the nanometer level. Due to size features, nanocomposites possess unique properties. (2) Due to the layer orientation, nanocomposites exhibited better mechanic properties. When the O-ATPG content was less than 3%, the tensile strength and the elongation at break of the O-ATPG/PU both increased by increasing the O-ATPG contents. When the O-ATPG content attained the range of 3–20 wt%, the tensile strength and the elongation at break of the O-ATPG/PU decreased by increasing the O-ATPG contents. The tensile strength and the elongation at break of the O-ATPG/PU attained was maximum when the O-ATPG content was 3%.

High tensile strength and high elongation at break PU nanocomposites were synthesized successfully with the attapulgite treated by N-[3-(trimethoxysilyl)propyl] ethylenediamine used as chain extenders to replace a part of 1,2-diaminopropane. The tensile mechanical properties of these O-ATPG/PU nanocomposites were dramatically improved. Compared to the pure PU, the tensile strength and the elongation at break of the 3 wt% O-ATPG content were increased by more than three

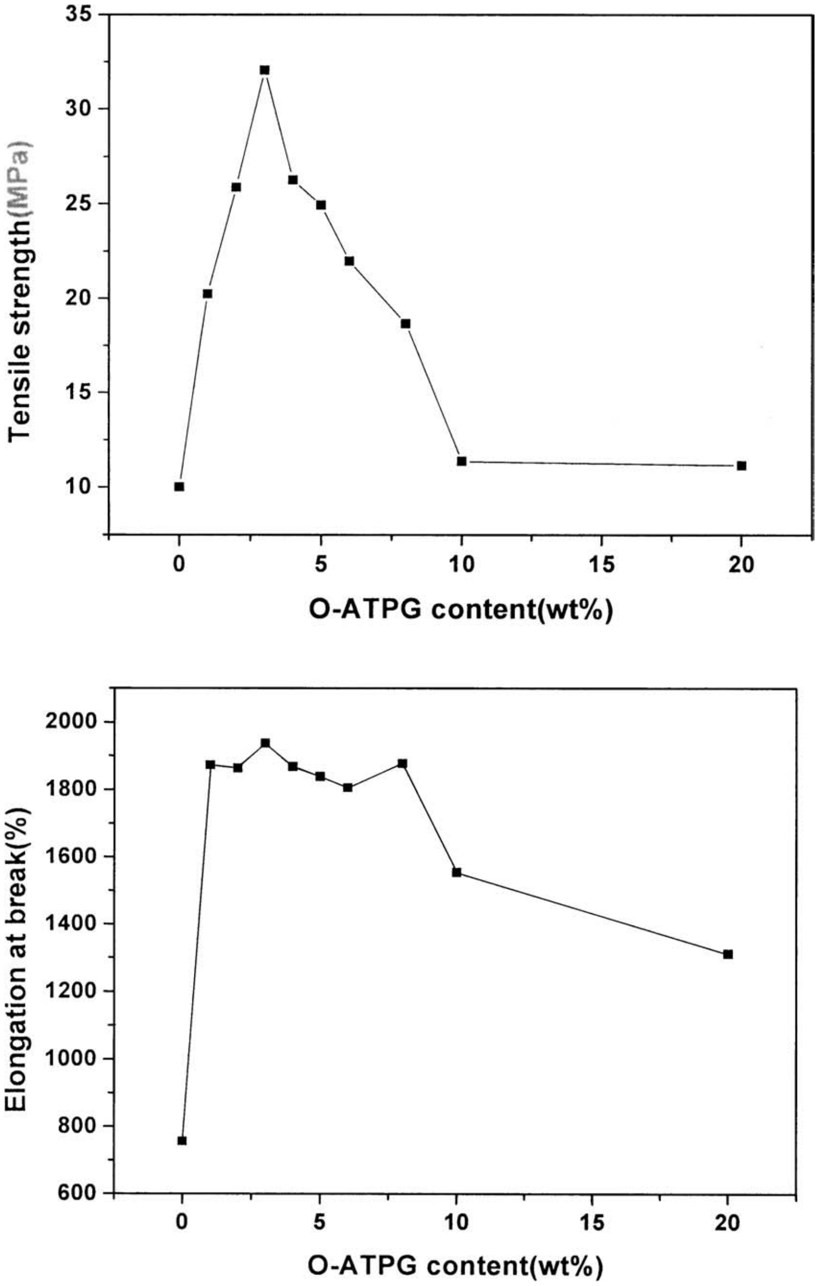

Figure 3 Effect of the O-ATPG content on the tensile mechanical properties of O-ATPG/PU nanocomposites.

times and two times respectively. The thermal properties of O-MMT/PU nanocomposites were also higher than that of the pure PU.

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