



# Reinforcement of waterborne polyurethane with chitosan-modified halloysite nanotubes



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## ABSTRACT

Waterborne polyurethane/halloysite nanotubes nanocomposites were prepared by modified halloysite nanotubes (HTs) with chitosan (CS). Modified HTs were characterized by Fourier transform infrared spectroscopy, elemental analysis, and thermogravimetry, which verified that CS was successfully assembled onto the HTs surface. The chitosan-modified halloysite nanotubes (CHTs) were uniformly dispersed in WPU matrix through the reaction with polyurethane prepolymer, and acted as chain cross-linker as well as reinforcing filler, which increased the cross-linking density of nanocomposites. The experimental results showed that the strong interfacial interaction and hydrogen bonding interaction between CHTs and WPU improved the degree of micro-phase separation, thermal properties, mechanical properties and surface properties of nanocomposites. The tensile strength and elongation at break were simultaneously enhanced when the CHTs loading was below 2 wt%.

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## 1. Introduction

Owing to the excellent elasticity, flexibility, low volatile organic compound (VOC), abrasion resistance and broad substrate suitability, waterborne polyurethane (WPU) has been widely used as environment-friendly material in various industrial fields [1]. However, compared with solvent-based polyurethane, WPU has inferior mechanical properties and thermal stability. To overcome these problems, WPU needs to be modified. There are many reports about modification of WPU, inorganic nanomaterials modification is a good method. Inorganic nanomaterials such as nano SiO<sub>2</sub> [2], carbon nanotubes [3], graphene [4], nanoclays [5], etc., were used in modification of WPU, these inorganic nanomaterials increased the mechanical properties of WPU.

Halloysite nanotube (HT), Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>·nH<sub>2</sub>O, is a new kind of prominent nanomaterials composed of multi-walled nanotubular-shaped crystalline nanostructures. In each halloysite nanotube, the external surface is composed of siloxane (Si–O–Si) groups, whereas the internal surface consists of a gibbsite-like array of aluminol (Al–OH) groups [6]. Halloysite nanotubes (HTs) have been used as catalyst carriers, drug deliverer and filler reinforcements due to their unusual shape, surface properties, chemical formation and readily availability [7]. Moreover, halloysite nanotubes have a similar structure of carbon nanotubes, which makes

them suitable substitute of expensive carbon nanotubes [8]. Unfortunately, the compatibility between HTs and polymer matrix is poor, the surface structure of HTs needs to be modified. In recent years, the functionalization of HTs with silane coupling agent has attracted considerable interest, and the silanized HTs can significantly improve the comprehensive properties of polymers [9]. However, the relatively low hydroxyl group content on the surface of HTs limits the reactive sites for covalent bonding, making covalent functionalization difficult. Therefore, more and more studies focused on the non-covalent surface modification of HTs [7].

Chitosan (CS) is a linear biopolymer of glucosamine with abundant amino groups, which is widely used in different types of composites due to its excellent mechanical, thermal, anti-bacterial properties and biological activities [10]. The amino and hydroxyl groups on CS chains can serve as electrostatic interaction and coordination sites, respectively. Furthermore, CS can effectively bond to the negatively charged outer surface of the HTs under acid condition [11]. The chitosan-modified halloysite nanotubes perfectly combine the advantages of inorganic and organic materials. There is no report on using chitosan as coupling agent to form effective linkages between HTs and polyurethane.

In the present work, chitosan was used as a biopolymer coupling agent, and chitosan-modified halloysite nanotubes (CHTs) were prepared. The structure and morphology of CHTs were investigated. Then novel waterborne polyurethane/chitosan-modified halloysite nanotubes nanocomposites were synthesized via prepolymerization process using CHTs as cross-linker as well as reinforcing filler. The structure and morphology of the WPU/CHTs nanocomposites

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were characterized by FTIR, XRD and SEM. The effect of the CHTs content on the thermal and mechanical properties of WPU/CHTs nanocomposites was characterized by TGA, DMA and tensile test machine. And the surface properties of WPU/CHTs nanocomposites were also investigated. The strong interfacial interaction and hydrogen bonds between CHTs and WPU increased the degree of micro-phase separation, thermal properties, mechanical properties and surface properties of nanocomposites.

## 2. Experimental

### 2.1. Materials

Halloysite nanotubes (HTs, Yanbo, China), hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) were purchased from Bayer, Germany. 1,4-butylene adipate glycol (PBA, Mn=2000) (supplied by Donghao Resine, China). Dimethylolbutanoic acid (DMBA, Tianyu, China), *n*-methyl pyrrolidone (NMP, Fuchen, China), triethylamine (TEA, Lingfeng, China) and dibutyltin dilaurate (DBTDL, Lingfeng, China) were all purchased in AR grade. Acetone was supplied by Guangzhou Fine Chemical Factory, China. Chitosan with a deacetylation degree of 90% was purchased from Aladdin, China.

### 2.2. Preparation of chitosan-modified halloysite nanotubes

1 g of CS was added to 100 mL of 2 wt% acetic acid solution and stirred until CS was completely dissolved, then 1 g of HTs powder was added to CS solution and mixed under ultrasound for 30 min to get a homogeneous mixture. The solution mixture was continuously stirred at 60 °C for 12 h. After that, the mixture was centrifuged and the solid was added into sodium carbonate solution (1 M) for 1 h. The solid was subsequently soaked in 100 mL sodium borohydride solution (0.2 M) for 5 h at room temperature. Finally, the chitosan-modified halloysite nanotubes (CHTs) were obtained by centrifugation and washed with deionized water for three times. Then the CHTs were dried at 60 °C for 48 h, and grounded in an agate mortar and passed through a 200-mesh sieve before use.

### 2.3. Preparation of the WPU/CHTs nanocomposites

The WPU/CHTs nanocomposites were prepared by prepolymerization process. First, dehydrated PBA2000 and DMBA were added into a 500 mL four-necked flask equipped with a thermometer, mechanical stirrer, and nitrogen inlet. The mixture was heated at 65 °C for 30 min while stirring. Then, HDI, IPDI and the catalyst DBTDL were added into the flask under nitrogen atmosphere, the reaction was carried out at 75 °C for 3 h, then cooled down to 50 °C. After that, the ultrasonic-treated CHTs *n*-methyl pyrrolidone solution was added into the reactor. When the residual NCO content reached the expected value (determined by the standard dibutylamine back titration method [12]), acetone was added into the mixture to reduce the viscosity of prepolymer, then a certain amount of TEA was added to neutralize the carboxylic acid for 30 min at 40 °C. After that, the neutralized mixture was dispersed into deionized water with vigorous stirring. Finally, the WPU/CHTs composites with 30% solid content were obtained after removing the acetone by vacuum distillation. The molar ratio of HDI/IPDI/PBA2000/DMBA/TEA was 2/1/1.3/1.65/1.65. By changing the CHTs contents of 1 wt%, 2 wt%, and 3 wt%, a series of nanocomposites were prepared and designated as WPU/CHTs-1, WPU/CHTs-2, WPU/CHTs-3, respectively.

### 2.4. Film preparation

The films were prepared by pouring the WPU/CHTs nanocomposites onto a polytetrafluoroethylene (PTFE) mold and then dried at room temperature for 7 days. Before characterization, the films were placed in a vacuum oven at 50 °C for 24 h to remove the solvent completely.

### 2.5. Characterization

FTIR spectra were detected by Perkin–Elmer spectrum 2000 infrared spectrophotometer in the wavenumber range from 4000 to 400  $\text{cm}^{-1}$  at 25 °C. XRD analysis was carried out on a D8 Advance apparatus (Bruker, Germany) with a nickel-filtered Cu K-radiation ( $\lambda=0.154\text{ nm}$ ), the scanning rate was 0.2 s/step at the interval scanning of 0.04°. TGA was investigated by STGA449 C (Netzsch, Germany) at the heating rate of 10 °C/min from room temperature up to 600 °C under nitrogen atmosphere. The CHN elemental analysis was performed on an ElementarVario EL III Elemental Analyzer. The coated amount of CS ( $M_{\text{CS}}$ , mol chitosan  $\text{g}^{-1}$  halloysite) was calculated by  $M_{\text{CS}} = W_{\text{N}}M_{\text{CS}}/M_{\text{N}}$ , where  $W_{\text{N}}$  is the mass percentage (mass%) of N obtained by CHN analysis,  $M_{\text{CS}}$  is the molecular weight of the structural unit of chitosan, and  $M_{\text{N}}$  is the molar mass of N (14.007  $\text{g mol}^{-1}$ ) [6,13]. The morphology of the nanocomposites was characterized by SEM (Zeiss Merlin Compact). SEM were carried out after spraying gold onto the fracture surface under vacuum. DMA was analyzed by the DMA242C (Netzsch, Germany) under the tension mode from –100 to 70 °C with a frequency of 1 Hz and a heating rate of 2 °C/min. The thermal property of films was analyzed using a Netzsch 204F1 differential scanning calorimeter analyzer (DSC, Germany). The non-isothermal measurement was scanned from –80 to 80 °C with a heating rate of 10 °C/min. The mechanical properties of films were measured at 25 °C with the Instron tension meter Model 3367. A crosshead rate of 100 mm/min was used to determine the elongation at break and the ultimate tensile strength. The surface properties of films were measured by the contact angle goniometer (JC2000C1, Shanghai Zhongchen). Sessile-drop method was taken at room temperature, the average value of three replicates was taken.

## 3. Results and discussion

### 3.1. Characterization of chitosan-modified halloysite nanotubes

Fig. 1 showed the FTIR spectra of CS, HTs and CHTs. The spectrum of CS exhibited peaks at 3431  $\text{cm}^{-1}$  due to the overlapping of O–H and N–H stretching bands, 2925  $\text{cm}^{-1}$  for aliphatic C–H stretching, 1644 and 1599  $\text{cm}^{-1}$  for N–H bending. C–H bending around 1422  $\text{cm}^{-1}$  and C–O stretching around 1081  $\text{cm}^{-1}$  also can be seen. The spectra of HTs and CHTs both showed strong absorption peaks at 3693  $\text{cm}^{-1}$  and 3621  $\text{cm}^{-1}$  associated with the O–H stretching of inner surface hydroxyl groups and the inner hydroxyl groups, respectively. Other characteristic absorption peaks such as perpendicular Si–O stretching at 1094  $\text{cm}^{-1}$  and 1025  $\text{cm}^{-1}$ , O–H stretching of water at 3450  $\text{cm}^{-1}$ , the deformation Si–O–Al vibration at 543  $\text{cm}^{-1}$  and the deformation Si–O–Si vibration at 470  $\text{cm}^{-1}$  were observed in both samples. Compared with the spectrum of HTs, CHTs exhibited new peaks around 2930  $\text{cm}^{-1}$  and 1416  $\text{cm}^{-1}$ , which were assigned to the symmetric stretching of aliphatic C–H and C–N stretching vibration of CS, respectively. Moreover, the wide peak at 1573  $\text{cm}^{-1}$  in the spectrum of CHTs assigned to the –NH<sub>2</sub> groups deformation vibration at 1560  $\text{cm}^{-1}$  along with O–H deformation vibration at 1636  $\text{cm}^{-1}$  was detected. The new peaks in the CHTs spectrum indicated that the CS was coated on the surface of HTs.

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