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Mechanical properties of attapulgite clay reinforced polyurethane shape-memory nanocomposites

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ABSTRACT

Nanocomposites based on attapulgite clay and shape-memory polyurethane were fabricated by mechanical mixing. The mechanical properties of samples were evaluated using a micro-indentation tester. The untreated commercial attapulgite clay resulted in a significant decrease in glass transition temperature and hardness of the nanocomposite due to the presence of moisture as well as the clay's amorphous structure and surface hydroxyl groups. The attapulgite nanoparticles were heat-treated at 850 °C, which resulted in crystallization of the particles and formation of layered attapulgite structure. The hardness of the nanocomposites composed of the heat treated clay powder dramatically increased as a function of clay content, which is attributed to the homogeneous dispersion of the nanofillers in the polymer matrix and strong filler–polymer interactions. Shape recovery of indentations has been demonstrated upon heating.

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1. Introduction

Recently, organic–inorganic nanocomposites have attracted considerable attention for the enhanced performance in mechanical, electrical, optical and other functional properties [1–4]. The polymer matrices that have been widely used in the nanocomposite design include poly(vinyl alcohol), styrene–butadiene rubber, epoxy resins, polyethylene, polyurethanes, polyamides and polyimides, etc. [5–10]. Different types of nanofillers (including ceramic and metallic nanopowders, nano-clay, carbon nanotubes (CNTs) and nano-SiO_2, etc.) have been used to reinforce the polymer matrix [11–14]. Attapulgite is a natural hydrated magnesium–aluminium silicate clay consisting of a three-dimensional network of densely packed rods with a diameter less than 100 nm and a length ranging from hundreds of nanometers to several micrometers for each single rod [15,16].

Shape-memory polymers (SMPs) have the capability of recovering their shape upon application of external stimulus such as thermal treatment or joule heating, light, or chemicals [17–21]. The mechanism of shape recovery in the SMPs can be attributed to 'shrinkage' or movements of polymer chains above either a melting or glass transition temperature [22]. The advantages of SMPs over other shape memory (SM) materials (in particular shape-memory alloys) include their lower cost, low density, high shape recoverability (up to 400%), and easy processability [23,24]. One disadvantage of SMPs is their low stiffness and strength compared to shape-memory alloys or ceramics. Therefore, a rising number of studies currently search for nano-size fillers to enhance the mechanical and shape-memory recovery properties of SMPs [25–28]. In this paper, attapulgite has been used to enhance the mechanical properties of polyurethane (PU), one of the most commonly used SMPs. We find that pre-treatment

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of attapulgite powder has a dramatic influence on the mechanical, thermal and shape-memory properties of the PU matrix nanocomposite.

2. Experimental

Commercial polyurethane MM5520 pellets from Mitsubishi Heavy Industries and attapulgite clay nanoparticles, $(Mg,Al)_2Si_4O_{10}(OH)\cdot 4(H_2O)$ were used in this study. Some of the attapulgite clay powder was heat-treated in an oven (in air) at 850 °C for 2 h. A Haake Rheocord 90 Torque Mixer was used for the mechanical mixing of the PU and attapulgite powders at 200 °C, and the SMP nanocomposite samples were prepared by a hot press. More information can be found in Ref. [29].

Scanning electron microscopy (SEM, Philips XL30-FEG) and high resolution transmission electron microscopy (HR-TEM, JEOL 2010F operating at 200 kV) were used to study the morphology of the attapulgite powders. The powder samples were dispersed in isopropanol in an ultrasonic bath for 10 min before SEM and TEM observations. A Fourier transform infrared spectrometer (Satellite FTIR Spectrometer, Mattson) was used to detect the absorption peaks of untreated and thermally treated attapulgite powders. The samples were prepared using the KBr pellet technique. Thermogravimetric analysis (TGA) of the commercial clay powder was carried out using a TA Instrument TGA 2950, and a 5 mg sample was heated in an alumina crucible with a heating rate of 10 °C/min from room temperature to 900 °C under N_2 atmosphere. Differential scanning calorimetry (DSC) analyses were performed with a Thermal Advantage DSC 2010 at a heating rate of 10 °C/min under a constant nitrogen flow. Microhardness (Vickers) testing was performed on the SMP and nanocomposite samples with average hardness readings calculated from at least five indentation tests. The indentation loads were varied between 98 to 980 mN and the indentation time was fixed at 20 s. The temperature dependence of hardness of SMP nanocomposite samples was tested using a Peltier heater beneath the composites. A profilometer (DEKTAK 3) was used for scanning the profile of the indents during shape recovery by heating.

3. Results and discussions

3.1. Clay powder analysis

Fig. 1 shows an SEM image of the commercial attapulgite clay powder revealing a loose fiber bundle structure. The length of each fiber varies from submicrometer to few micrometers and the diameter is about tens of nanometers. The TEM micrograph in Fig. 2a shows that the commercial attapulgite particles are highly dispersed individual rod-like, without any aggregations. Selected area electron diffraction (SAED, not shown) reveals its amorphous nature, confirmed by the HR-TEM image in Fig. 2b and c. The diameter of individual fibers is about 20–50 nm, whereas the average length is a few micron. The mean value of the aspect ratios of the fibers (L/d) is in the range of 40–100.

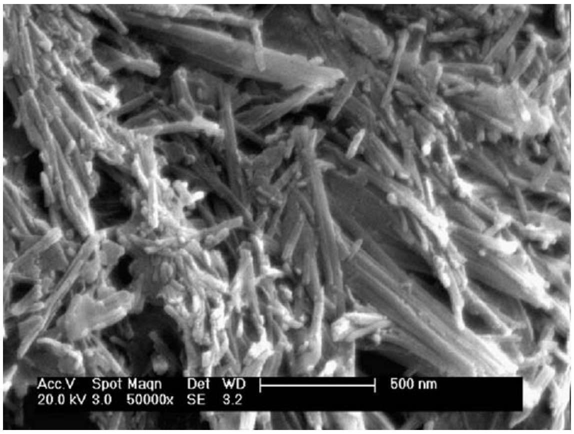

Fig. 1. SEM observation of the commercial clay revealing a loose fiber bundle structure, with the length of fibers varying from submicrometer to few micrometers and the diameter about tens of nanometer.

After heat treatment, the attapulgite fibers reconstruct and combine together to form a bundled structure (see Fig. 3a), which could no longer be broken even by ultrasonication for an extended time. The ring-like scattered diffraction spots reveal the nanocrystalline feature as shown by the inset SAED pattern of Fig. 3a. The corresponding HR-TEM images in Fig. 3b and c confirm this new feature. Individual crystallites are embedded in the amorphous matrix with a separation of around 5 nm.

Fig. 4 shows the FTIR results of the commercial and heat-treated attapulgite powders. There are two types of molecules containing hydroxyl groups associated with the natural attapulgite. The peak at 3430 cm^{-1} corresponds to the hydroxyl stretching vibrations of absorbed moisture [30]. Absorbance peak at 3552 cm^{-1} can be attributed to the anti-symmetric stretching modes of molecular water coordinated with the magnesium at the edges of the channel [31]. The peak at 1654 cm^{-1} is associated with the hydroxyl deformation mode of zeolitic water, and the peak at 984 cm^{-1} with the bending vibration of —OH group [32].

In comparison with the spectrum of the commercial attapulgite powder, the FTIR spectrum of the heat-treated clay revealed a broadening of the peak at 3436 cm^{-1}, whereas the 1654 cm^{-1} mode was lost. This suggests that heat treatment had removed most inter-fibrillar water, and reduced most of the —OH group content in attapulgite. As shown in Fig. 4, the decrease in —OH group content led to absorbance peaks at 1074 and 984 cm^{-1} which can be attributed to the symmetric and anti-symmetric Si—O—Si stretching vibrations [33,34]. The peak at 800 cm^{-1} indicates the presence of Si—O—Al and O—Al bonds [34]. It should be pointed out that the peak at 3436 cm^{-1} is still pronounced but shifted from 3430 cm^{-1} after the heat treatment. This is due to the O—H stretch formed after removing the inter-fibrillar water [35].

The TGA result of the commercial powder is shown in Fig. 5 and reveals a three-stage change during heating. The first stage at a temperature of about 100 °C corresponds to the loss of moisture which may exist in attapulgite powder as the free water. The second stage

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