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Facile hydroxylation of halloysite nanotubes for epoxy nanocomposite applications

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ABSTRACT

Polymer nanocomposites have been extensively investigated over the past two decades, resulting in a wide range of applications because of their excellent performance. Halloysite, a type of naturally occurring aluminosilicate, has attracted increasing interest in polymer nanocomposite applications, especially for the enhancement of mechanical properties owing to its tubular structure. Herein, we report a facile approach to achieve a high level of dispersion of halloysite nanotubes (HNTs) in epoxy by treating HNTs with a low concentration of sodium hydroxide (NaOH). The NaOH treatment resulted in the formation of hydroxyl groups on the surface of HNTs, leading to a much higher level of dispersion of HNTs in water, organic polar solvents, and epoxy matrix. The higher density of external silanol groups (Si–OH) of hydroxylated HNTs (h-HNTs) was confirmed by X-ray photoelectron spectroscopy (XPS) characterization. Such a higher level of dispersion and stronger interface led to simultaneous enhancement in both the stiffness and the toughness of epoxy/h-HNT nanocomposites. Systematic characterizations were performed to investigate the related stiffening and toughening mechanism. The implication of the present findings is discussed.

1. Introduction

Incorporation of nanofillers into polymer matrices such as epoxy to prepare nanocomposites have been studied intensively with the aim to enhance mechanical and barrier properties and/or to introduce new functionalities such as magnetic and electrical properties [1–4]. The dispersion of nanofillers in the host material and their interaction with the host greatly influence the final properties of nanocomposite [5]. A uniform dispersion of nanofillers will lead to a much larger interface area, allowing the nanofillers to effectively carry the load from matrix. Surface modification of nanofillers can be adapted to achieve this purpose [6]. Various nanofillers, including zero dimensional nanoparticles [7–16], one dimensional carbon nanotubes (CNTs) [17–22] and carbon nanofibers [23,24], and two dimensional montmorillonite (MMT) [25–27], graphite [28–34], α-zirconium phosphate [35–42], have been widely used due to their excellent mechanical and thermal properties. Among them, MMT nanosheets and CNTs are two most popular nanofillers. However, MMT need be exfoliated before being incorporated into a polymer matrix, which requires additional processing cost and time. CNTs are known for high mechanical strength with a high aspect ratio. However, at this stage it's impractical to adopt CNTs into scalable production as they remain expensive [43].

Halloysite nanotubes (HNTs) are a naturally occurring material that consists of 1:1 aluminosilicate layers rolled into tubular structures as shown in Fig. 1. They have notable advantages as compared to CNTs and MMT. HNTs can be easily re-dispersed in aqueous and organic solvents after being dried. The aluminosilicate composition of HNTs is chemically non-toxic and is durable in high strength shearing, thus making them a viable candidate for applications where bio-compatibility is of high priority [44]. In addition, HNTs are available in large quantities and thus they are of a much lower price than CNTs [45]. Therefore, HNTs are a promising alternative to CNTs for potential commercial composite applications.

However, some engineering challenges remain to be solved in processing HNTs. First, HNTs tend to agglomerate into clusters

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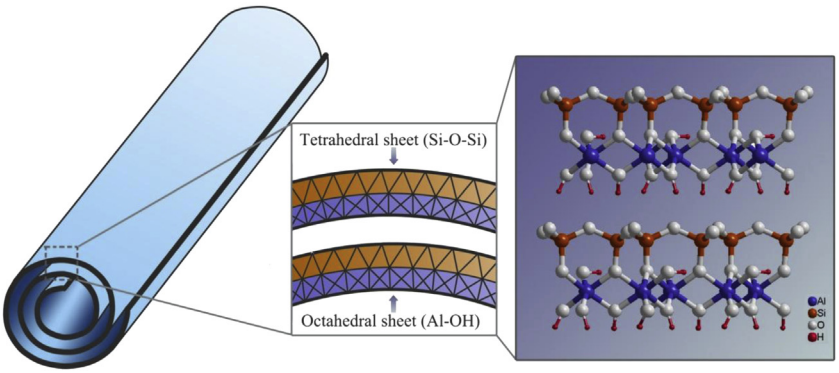

Fig. 1. Schematic structure of HNTs from single tubular appearance to crystalline structure.

during the preparation of nanocomposites. Second, the interfacial adhesion between the HNT phase and some polymer matrices such as epoxy is not ideal due to the low concentration of polar functional groups on the external surface of HNTs. Both of these issues must be addressed and optimized before the full potential of HNTs can be realized. Since the density of hydroxyl groups on the external surface of HNTs is much lower than that of alumina lumen, HNTs tend to agglomerate into undesirable clusters when being dispersed in polar chemicals. Thus, it's necessary to explore an effective method to increase the hydroxyl group density on the external surface of HNTs, which is very critical to bring out the full potential of HNTs for composite applications.

Sodium hydroxide is universally applied to maximize the density of hydroxyl groups on silica [46,47]. Since the external surface of HNTs is structurally similar to silica, we explored to use sodium hydroxide to hydroxylate the external surface of HNTs [48]. Herein, we report this very simple approach to improve the dispersibility of HNTs in the epoxy-based nanocomposites through the facile NaOH treatment. The higher level of dispersion of HNTs in epoxy led to considerable enhancement in both stiffness and toughness of the resultant nanocomposites.

2. Experimental

2.1. Materials

Halloysite in a powder form was obtained from Applied Minerals, Inc. Hydrogen peroxide (H_2O_2, 34–37%) was purchased from Fisher. Sodium hydroxide was ordered from VWR. Epoxy resin EPON 862 and curing agent EPICURE W were obtained from Momentive Corporation. All chemicals were used as received without further treatment.

2.2. Preparation of hydroxylated HNTs (h-HNTs)

Since the organic contamination has a negative effect on the compatibility of the HNTs with the epoxy matrix [49], the as-received HNTs were treated by H_2O_2 to remove organic impurities. Typically, 30.0 g of the as-received HNTs was added into 200 mL 30% H_2O_2 aqueous solution and magnetically stirred for 1 h. The HNTs dispersion was then ultrasonicated for 10 min prior to the centrifugation treatment to separate HNTs from the liquid phase. The resultant purified HNTs (p-HNTs) were first dried at 110 °C for 12 h in an oven and then dried at 60 °C in a vacuum oven for 12 h. To enhance the dispersion of HNTs into epoxy matrix, the p-HNTs were then treated by NaOH. Typically, 2.00 g of p-HNTs was dispersed in 100 mL deionized water. Subsequently, 0.058 g NaOH was added and the mixture was magnetically stirred for 24 h at room temperature. The resultant hydroxylated HNTs (h-HNTs) solid phase was then separated by centrifugation and rinsed several times with water until the pH reached 7. The prepared h-HNTs were first dried at 110 °C for 12 h in an oven and then dried at 60 °C in a vacuum oven for 12 h.

2.3. Preparation of epoxy/h-HNT nanocomposites

A sample of h-HNTs (1.00 g) was dispersed in 100 mL acetone and ultrasonicated for 20 min to obtain a uniform dispersion. The h-HNTs in acetone were then mixed with epoxy resin EPON 862 to achieve 1.0 and 4.8 wt% of h-HNTs in epoxy resin. Ultrasonication was applied to achieve a high level of dispersion. Subsequently, the mixture was added into a rotary evaporator to remove acetone. The curing agent EPICURE W (epoxy resin:curing agent = 100:26.4 in mass ratio) was then added into the system. The resultant translucent mixture was then cast into a silicone mold. The resin mixture was then cured in an oven at 80 °C for 1 h, followed by 121 °C for 1 h and 2.5 h of post-cure at 181 °C. For comparison, a neat epoxy and epoxy samples with 1.0 and 4.8 wt % p-HNTs were prepared following the same procedures.

2.4. Characterization

Turbidity experiments were performed on an ultraviolet-visible (UV–Vis) spectrophotometer (VARIAN CARY 5000) at 600 nm using a quartz cuvette. To determine the kinetics of sedimentation, the p-HNTs and h-HNTs aqueous dispersions (1.0 mg/mL) were prepared and stirred vigorously for 5 min before the start of the experiments.

Zeta potential and Z average size measurements of HNTs were tested by using an aqueous electrolyte solution (0.001 M KCl) with a concentration 0.1 mg/mL HNTs at 25 °C in a Malvern Zetasizer Nano ZS. The h-HNTs aqueous electrolyte was injected into a disposable cuvette with a metal electrode specific for zeta potential and size test.

X-ray diffraction (XRD) patterns were recorded on a Bruker D2 diffractometer with a graphite monochromator with Cu Kα radiation.

X-ray photoelectron spectroscopy (XPS) of the p-HNTs and h-HNTs were recorded on a PHI 595 Multiprobe System with an Al Kα source (1486.6 eV). A survey scan (pass energy: 160 eV) was conducted for all the samples. High resolution spectra (pass energy: 50 eV) were recorded at corresponding regions for silicon and carbon. All the spectra were calibrated using the C 1s peak (284.6 eV) [50].

JEOL 2010 FASTEM® transmission electron microscope was applied to investigate the particle size and tubular structure of the p-HNTs and h-HNTs. To prepare the TEM specimens, HNTs particles

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