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Influences of processing methods and chemical treatments on fracture toughness of halloysite–epoxy composites

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ABSTRACT

This study presented experimental reports on effects of processing methods (mechanical mixing and ball milling homogenization) on the fracture toughness of as-received and phenylphosphonic acid (PPA) treated halloysite–epoxy composites. It was demonstrated that with halloysite added, the composites held higher fracture toughness value than that of neat epoxy. Large-sized particle clusters occurred during mechanical mixing process can significantly decrease by ball milling homogenization and much more uniform dispersion was obtained in the cured composites. With PPA treatment, the morphology of halloysite changed from nanotubes to nanoplatelets with a substantial increase in the total contact area between halloysite and epoxy, it further enhanced fracture toughness in PPA-treated composites. The fracture toughness mechanisms of each nanocomposite with different processing methods and chemical treatments have been illustrated.

1. Introduction

Halloysite is a naturally occurring aluminosilicate, $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$, chemically similar to kaolinite, dickite or nacrite, differing mainly in the morphology of crystal. Halloysite is a layered clay mineral, consisting of one alumina octahedron sheet and one silica tetrahedron sheet in a 1:1 stoichiometric ratio. The halloysite particle can adopt a variety of morphologies, but the most common form is an elongated hollow tubular structure with a large aspect ratio, similar to that of carbon nanotubes (CNTs), due to its structural defects, particularly in layer stacking of the neighbouring alumina and silica layers, and their hydrated waters [1]. In recent years, halloysite particles have been investigated as an alternative type of additive for polymers [2–10], because halloysite particles are readily obtainable and are much cheaper than other nanoparticles such as CNTs [11,12]. More importantly, the unique crystal structure of halloysite nanotubes resembles that of CNTs, and therefore halloysite particles may have the potential to provide cheap alternatives to expensive CNTs because of their tubular structure in nano-scale. Moreover, due to its similarity to other layered clay minerals such as montmorillonite (MMT) [13], halloysite has the potential to be further intercalated or exfoliated chemically or physically [14].

Preliminary results have demonstrated that blending epoxies (EPs) with a certain amount of halloysite nanotube (HNT) can noticeably increase their fracture toughness, strength and modulus, without sacrificing their thermal mechanical properties such as glass transition temperature [2–4], however, achieving homogeneous dispersion of HNTs in epoxies remains a challenge due to agglomeration of large particle clusters [3]. It is believed that the agglomeration of HNTs is caused mainly by their relatively large surface energy because their tiny particle size results in a large surface area (specific area = $\sim$60 m^2/g) [1]. As a result, HNTs tend to agglomerate under the influence of the van der Waals force. The moderate shear stresses provided by the conventional mechanical blending methods, such as ultrasonic vibration and shear mixing using a stirrer or a magnetic bar, are unlikely to fully eliminate particle agglomeration. However, the use of severe shear stresses, such as the use of ball mill with epoxy [4] or melt extrusion with polyamide 6 [15], may break-up the agglomerates and achieve a homogeneous dispersion of HNTs in the polymer matrix.

Meanwhile, surface modifications to HNTs may produce the opportunity to expand the basal spacing of HNTs by the intercalation or exfoliation of inorganic and organic compounds in their interlayers, which may make it easy to produce a homogeneous mixture of HNTs with polymers during blending [16]. HNTs grafted with different polymers by chemical synthesis were reported

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recently [7,17]. Polystyrene (PS) grafted HNTs and polyacrylonitrile (PAN) grafted HNTs were synthesized by atom transfer radial polymerization (ATRP) which can be used as a nonwoven porous fabric after crosslinking to tightly entrap water droplets [7]. HNTs grafted with polymethyl methacrylate (PMMA) were synthesized via radical polymerization and poly(vinyl chloride)/PMMA-grafted HNTs show effective improved toughness, strength and modulus [17].

As specified to HNT/EP system, Deng et al. [4] reported experimental studies aimed to achieve homogeneous mixtures of halloysite nanotubes with epoxies through ball mill homogenization and chemical treatments. It was demonstrated that chemical treatments by using potassium acetate (PA), silane or cetyl trimethyl ammonium chloride (CTAC) were unable to intercalate the already dehydrated halloysite. However, it was demonstrated that ball mill homogenization and PA treatment were effective approaches to reduce the size of halloysite particles clusters in the epoxy matrix, while silane and CTAC treatments were found to increase the possibility of particle agglomeration. With the improvement in particle dispersion in epoxies, enhancements in the mechanical properties of the halloysite–epoxy nanocomposites were achieved. Recently, Tang et al. [16] reported that phenylphosphonic acid (PPA) was successfully used to unfold and intercalate halloysite, resulting in an increase of basal spacing from 7.2 Å to 15.1 Å, accompanied by the morphology change of most particles from nanotubes to nanoplatelets. The halloysite particles were combined with an epoxy to form partially and fully intercalated nanocomposites. It was found that better dispersion in the epoxy was achieved using the unfolded and intercalated halloysite than using the as-received halloysite. There was a significant increase in fracture toughness for the epoxy composites with unfolded and intercalated halloysite particles, without sacrificing other properties such as strength, modulus, glass transition temperature and thermal stability. The fracture toughness of the halloysite–epoxy composites was markedly increased with an increase in the intercalation levels.

In this study, as received and PPA-treated halloysite will be compared characterized by using mechanical mixing and ball milling processing methods. Effects of processing methods and PPA-treatment on the fracture toughness of halloysite–epoxy nanocomposites will be illustrated and with proper material design, halloysite/epoxy nanocomposites can achieve a much higher fracture toughness value. The proposed fracture toughness mechanisms will be discussed at the end.

2. Experimental details

2.1. Sample preparation

The chemical treatment of halloysite nanotubes by using phenylphosphonic acid (PPA) has been reported previous [16]. The as-received and PPA-treated halloysite particles were separately combined with a diglycidyl ether of bisphenol A (DGEBA) epoxy resin, Araldite-F (Ciba-Geigy, Australia) to form composites. Both the as-received and the PPA-treated halloysite particles in 10 wt.% were separately added into the epoxy resin, by means of mechanical mixing or ball milling. For mechanical mixing, the mixture stirred at 100 °C on a hotplate stirrer (IKA C-Mag HS7) for 5 h to obtain homogeneous mixtures. The mixtures were then degassed in a vacuum oven (about −100 kPa) for at least 30 min. For ball mill homogenisation, a planetary ball mill, Pulverisette 5 (Fritsch, Germany), was used to mix as-received or PPA-treated HNTs with epoxies. Prior to ball milling, the halloysites were mechanically mixed with DGEBA epoxy resin at 60 °C using a mechanical mixer and then transferred into grinding bowls for further mixing using the ball mill. The ball mill consisted of four grinding bowls vertically positioned on a rotating supporting disc. The cavity of each grinding bowl is 500 ml with an inner diameter of 100 mm at the upper end. The halloysite–epoxy mixture was prepared with the use of 15 WC-Co grinding balls in 20 mm in diameter. A rotation speed of 200 rpm was used and the homogenisation process was programmed to run for 48 h with a 10 min break every 50 min to avoid overhearing. After that, the mixture was transferred to a beaker and heated with mechanical stirring at 100 °C, then degassed in a vacuum oven for at least 30 min. After that, a hardener, Piperidine (Sigma–Aldrich, Australia), was added to the mixtures in a ratio of 100:5 by weight, while stirring slowly. Following further degassing for 10 min the vacuum was released and the liquid mixtures were cast into the specimen cavities of pre-heated silicon rubber moulds and cured at 120 °C for 16 h. For the designated mechanical tests, rubber moulds were prepared to produce compact tension specimens.

2.2. Characterizations

Scanning electron microscopes (SEMs) (Philips XL30 SEM, the Netherlands and Zeiss ULTRA Plus Field Emission SEM, Germany) were utilized to identify the morphology of halloysite particles, the homogeneity of halloysite particles in the epoxy nanocomposites, and failure modes of compact tension (CT) fracture specimens. Wide angle X-ray diffraction (WAXD) was conducted on halloysite–epoxy nanocomposites using an X-ray diffraction unit (Model D5000, Siemens, Germany) with Cu Kα radiation (wavelength = 1.54056 Å). Transmission electron microscopy (TEM) images of halloysite–epoxy nanocomposites were obtained using a transmission electron microscope (JEOL 2010, Japan) at 200 kV. For the preparation of the TEM specimens, halloysite–epoxy nanocomposites were ultramicrotomed using glass knives on an ultra-cut microtome (Leica ultracut-R ultramicrotomed, Germany) to produce thin sections with a nominal thickness of 100 nm. The sections were transferred onto Cu grids for TEM observation.

A universal material testing machine (Instron, Mode 5567. USA) was used for all fracture toughness tests. All mechanical tests were conducted at room temperature. The fracture toughness of the cured neat epoxy and halloysite-epoxy nanocomposites was measured using the compact tension (CT) specimens according to ASTM D5045 [18]. A CT specimen has a nominal dimension of 48 mm × 48 mm × 10 mm. To minimize the effects of residual stress and residual plastic deformation around the pre-crack tip, a sharp pre-crack was introduced to each CT specimen by inserting a fresh razor blade at the tip of the machined crack and tapping gently with a light hammer [19]. A loading rate of 2 mm/min was adopted for all fracture tests, as recommended by ASTM D5045. As there are strict requirements for specimen geometry and crack length for the accurate measurement of the fracture toughness using CT tests according to the ASTM criteria, only those specimens which fulfilled the condition $a/W = 0.45–0.55$ (a is the pre-crack length and W is the distance between the centre of the loading pin to the edge of the CT specimen) were used to calculate the critical stress intensity factor (K_{1C}). At least 8 CT specimens were successfully tested for each group of materials.

3. Results and discussion

3.1. Morphology and dispersion of halloysites in composites

As shown in Fig. 1a, the as-received halloysite particles used in this study were basically in the form of short small tubes (nanotubes) with a length of 100–2000 nm and a diameter of 50–150 nm, geometrically similar to multiwalled CNTs. However, long CNTs always tend to entangle with each other, forming agglomerates that make