

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.

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1. Introduction

Halloysite is a naturally occurring aluminosilicate, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, 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 = $\sim 60 \text{ m}^2/\text{g}$) [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 radical 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 overheating. 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 K α 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 $\times$ 48 mm $\times$ 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_{IC}). 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

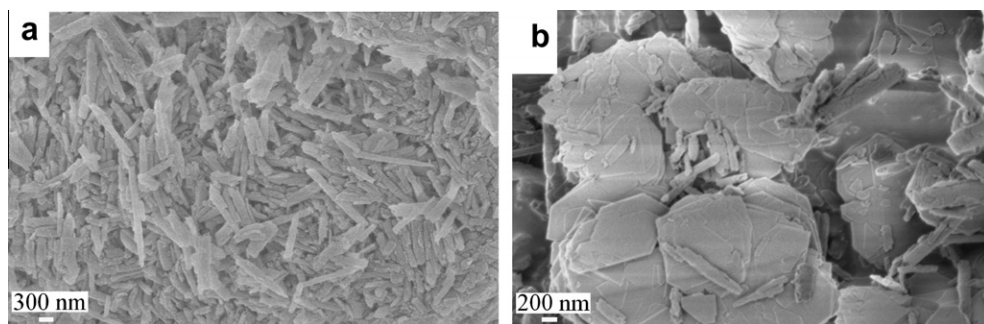


Fig. 1. SEM images of (a) as-received and (b) 100 h-PPA-treated halloysite.

difficult to homogeneously disperse them in polymers. On the contrary, short halloysite nanotubes (HNTs) were straight and individually separated, without entanglement between them, which potentially make easy to obtain good dispersion of HNTs in viscous polymers. Indeed, HNTs are in the form of rolling tubes [20], consisting of a number of aluminosilicate sheets, curved and closely packed with each other. After the PPA intercalation, the large layer expansion would unfold some, or most of the curved tubes, which may provide the opportunity for exfoliation of individual layers, similar to that for organically modified MMTs. As shown in Fig. 1b, after the PPA treatment of 100 h, most of the halloysite particles became platelets, with some of them even being dispersed flakes (exfoliated aluminosilicate sheets).

After halloysites incorporated with epoxy by direct mixing or ball milling and cured, the typical cross-sections of CT specimen with direct mixing and ball milling are shown in Fig. 2. The specimens made by direct mixing (Fig. 2a) shows that oversized halloysite clusters deposit at the bottom of the cured specimen, forming a halloysite-rich layer of about 1 mm. These oversized halloysite particle clusters in the bottom surface layer would cause premature failure of specimen under tension, with greatly reduced

strength and failure strain, as report previous by our group [3,4]. However, the specimens made by ball milling (Fig. 2b) presented macroscopic homogenous dispersion of halloysite in epoxy matrix. With the aid of ball mill homogenization, the halloysite cluster sizes were reduced greatly and minimized deposition of halloysite particle clusters to the bottom, accompanied by further enhancements in mechanical performance, which will be elaborated later in this study. So, practically, once the specimens were cooled and removed from the moulds they were milled using a surface grinder on both top and bottom surfaces to ensure flatness of specimens

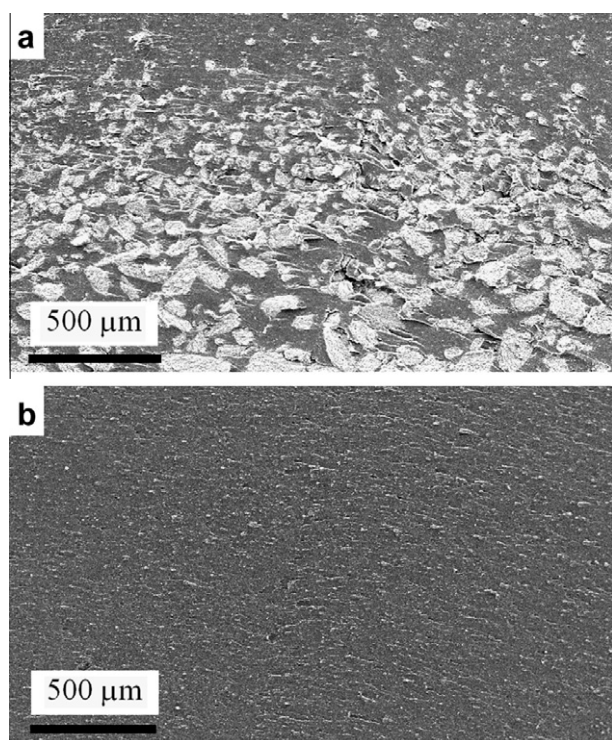


Fig. 2. SEM images of cross-section of 10 wt.% as-received halloysite-epoxy nanocomposites prepared by (a) mechanical mixing and (b) ball milling methods.

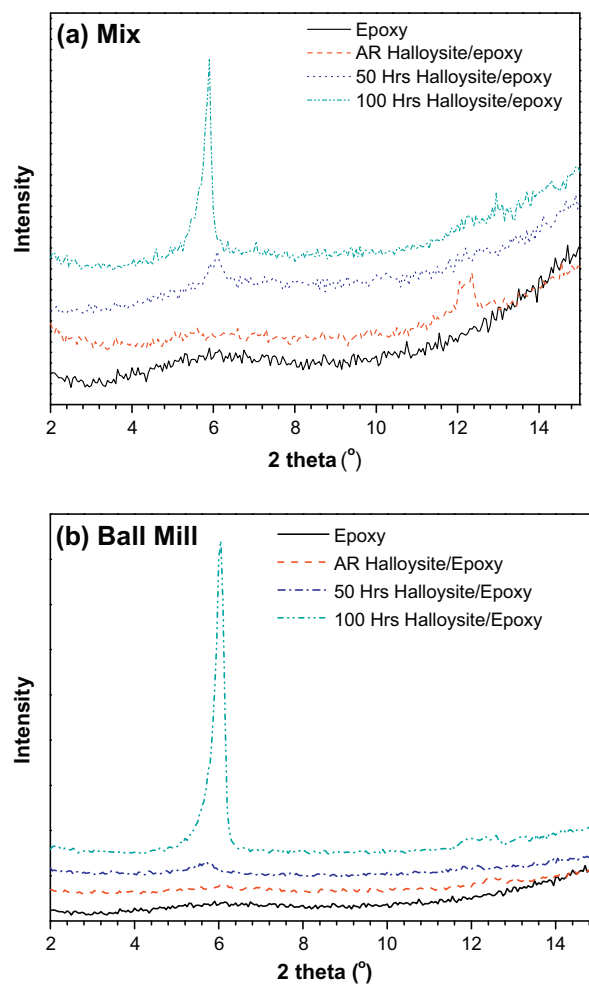


Fig. 3. WAXRD curves of neat epoxy and halloysites (with different treating times)-epoxy nanocomposites by different processing methods of (a) mechanical mixing and (b) ball milling.

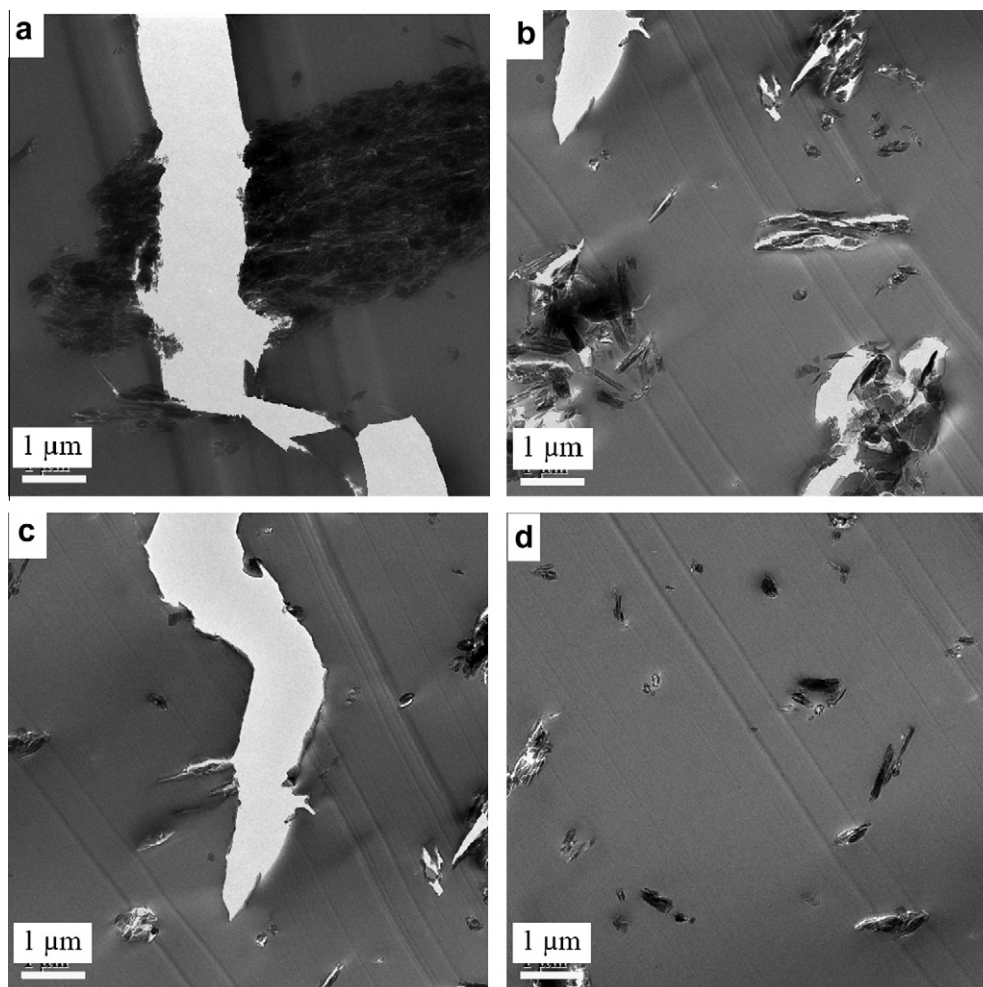


Fig. 4. TEM images of the typical cross-sections of CT specimens near the crack tips of as-received halloysites-epoxy nanocomposites by different processing methods of (a and b) mechanical mixing and (c and d) ball milling.

and to remove possible oversized halloysite particle aggregates, which may sink to the bottom during curing.

WAXD patterns of directly mixed and ball milled halloysite-epoxy composite samples after grinding are shown in Fig. 3a and b respectively. The basal spacing [001] of the as-received halloysite is approximately 7.2 Å, based on the diffraction angle for the peak at $2\theta = 11.9^\circ$. After PPA treatment, a new diffraction peak appeared at $2\theta = 5.8^\circ$, which was due to the PPA intercalation to the halloysite interlayer positions, causing expansion of layers in the direction perpendicular to the base plane with a final basal spacing of 15.1 Å. Clearly, a peak at $2\theta = 11.9^\circ$ can be seen for the untreated halloysite-epoxy composite while the peak at $2\theta = 5.8^\circ$ is invisible. Broadened low peaks appeared at both $2\theta = 5.8^\circ$ and $2\theta = 11.9^\circ$ for the halloysite-epoxy composite sample with halloysite being treated for 50 h using PPA. With increasing treating time, the peaks at $2\theta = 5.8^\circ$ became clearer and sharper, while the peaks at $2\theta = 11.9^\circ$ almost disappeared for the composites with PPA-treated halloysite for 100 h, indicating that intercalated structure of halloysite was still preserved in the halloysite-epoxy composites.

Fig. 4 shows TEM images of dispersion of halloysite particles in epoxy by directly mechanical mixing and ball milling homogenization. To show the interactions between crack tip and halloysites, the TEM sections were taken from the vicinity in front of the arrested crack tip in specimens with 90% of individual average peak load for unstable fracture. In Fig. 4a and b, with only mechanical mixing, a large halloysite particle clusters with agglomeration size above 1 μm existed and formed a halloysite-rich region. This

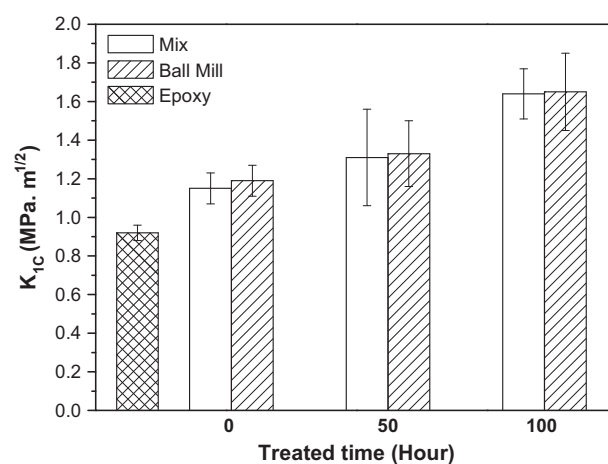


Fig. 5. Fracture toughness of neat epoxy and halloysites (with different treating times)-epoxy nanocomposites with different processing methods (mechanical mixing and ball milling).

phenomenon was also identified by other researchers [2,3]. The dispersion of halloysite particles in the epoxy matrix by direct mixing is still not sufficiently homogenous in nano-scale, even in micro-scale, in spite of the fact that the halloysite nanoparticles in the clusters are fully surrounded by the matrix resin [3]. Therefore,

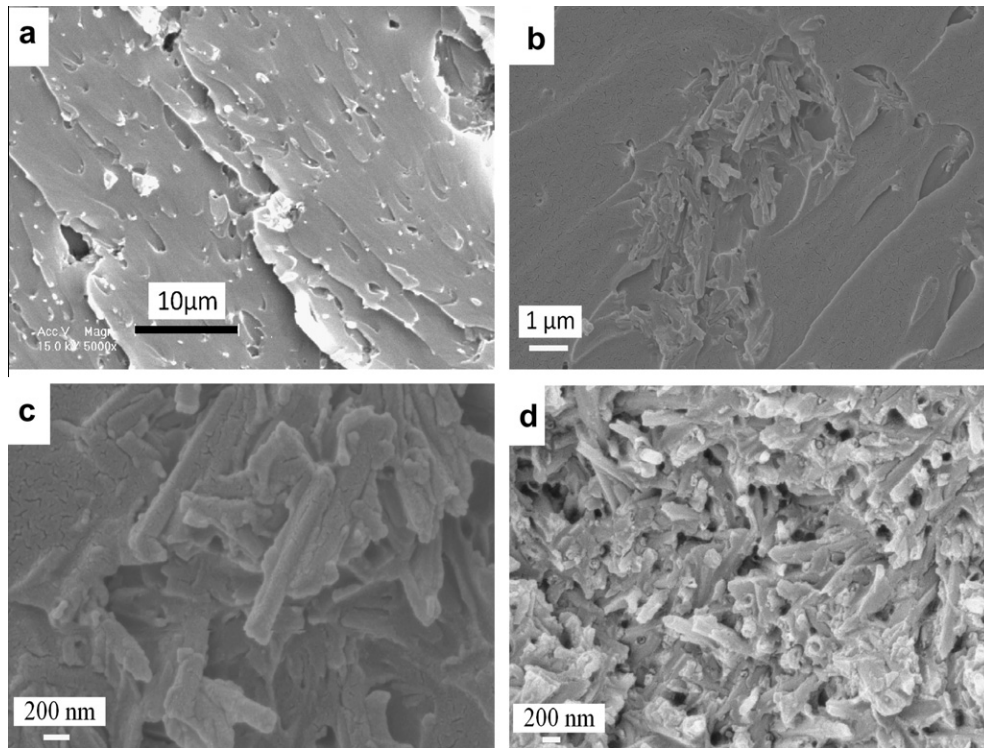


Fig. 6. SEM images of fracture surfaces near crack tip of as-received halloysite-epoxy nanocomposite prepared by mechanical mixing.

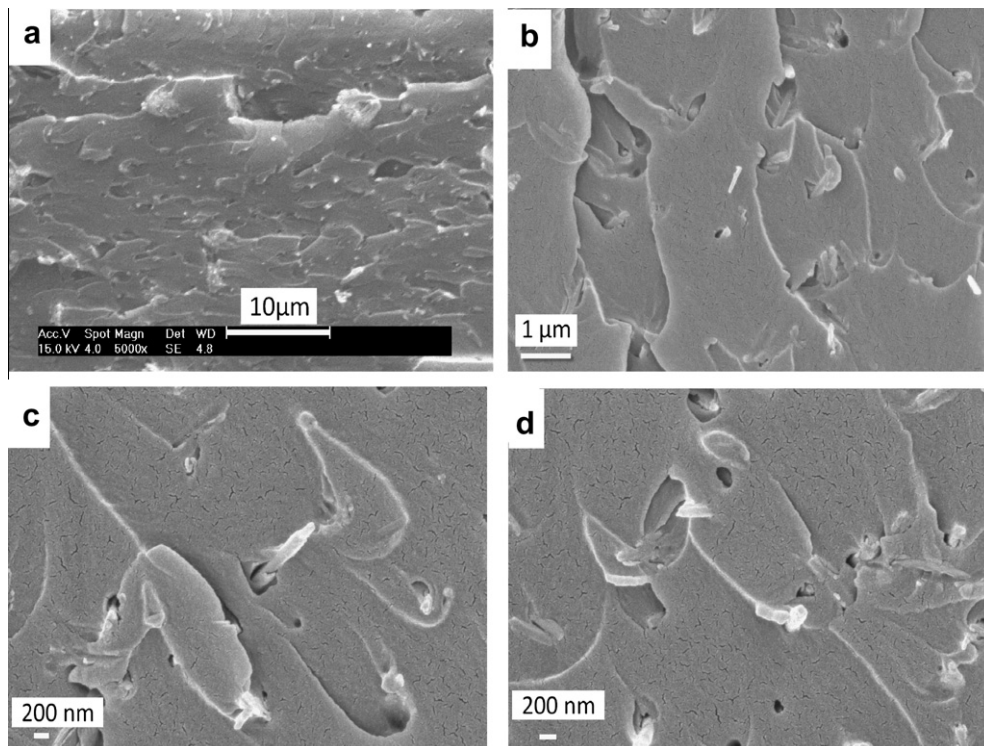


Fig. 7. SEM images of fracture surfaces near crack tip of as-received halloysite-epoxy nanocomposite prepared by ball milling.

improvements in mixing methods, such as here by ball mill homogenization are expected to produce more homogeneous nanocomposites with reduce cluster sizes. As shown in Fig. 4c and d, after ball milling, the size of the halloysite particle clusters reduced greatly to sub-micrometer level with more uniform distribution of halloysites.

3.2. Processing methods and PPA-treatment on mechanical behaviour of composites

The mechanical properties of halloysite-epoxy composites with different kinds of halloysite and prepared by two different processing methods are shown in Fig. 5. Obviously, the magnitudes of the

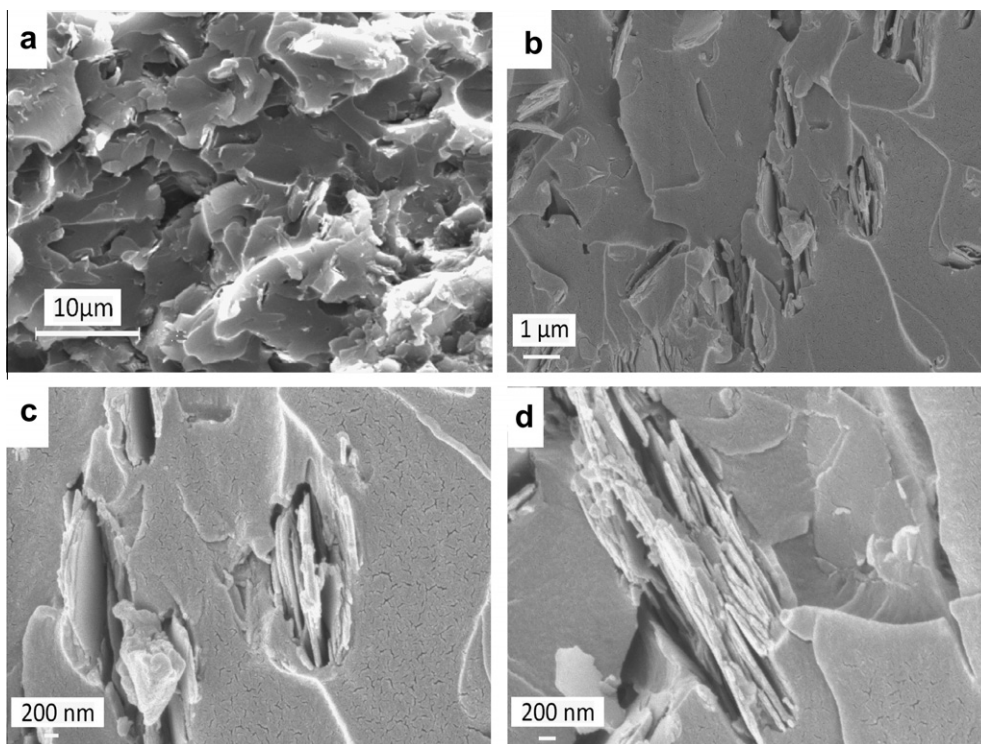


Fig. 8. SEM images of fracture surfaces near crack tip of 100-h PPA-treated halloysite-epoxy nanocomposite prepared by mechanical mixing.

critical stress intensity factor (K_{IC}) of the modified epoxies were significantly improved after halloysite particles were incorporated, especially with treated halloysite particles. The treated halloysite-epoxy composites have relatively higher K_{IC} than as-received halloysite-epoxy composites. Because, in the composites with the

intercalated halloysite, there was a substantial increase of the total contact area between halloysite and epoxy, as a result the morphology change from nanotubes to nanoplatelets. The treated halloysite nanoparticles also achieved a better dispersion in the epoxy matrix and, on the other hand, promote the formation of a large

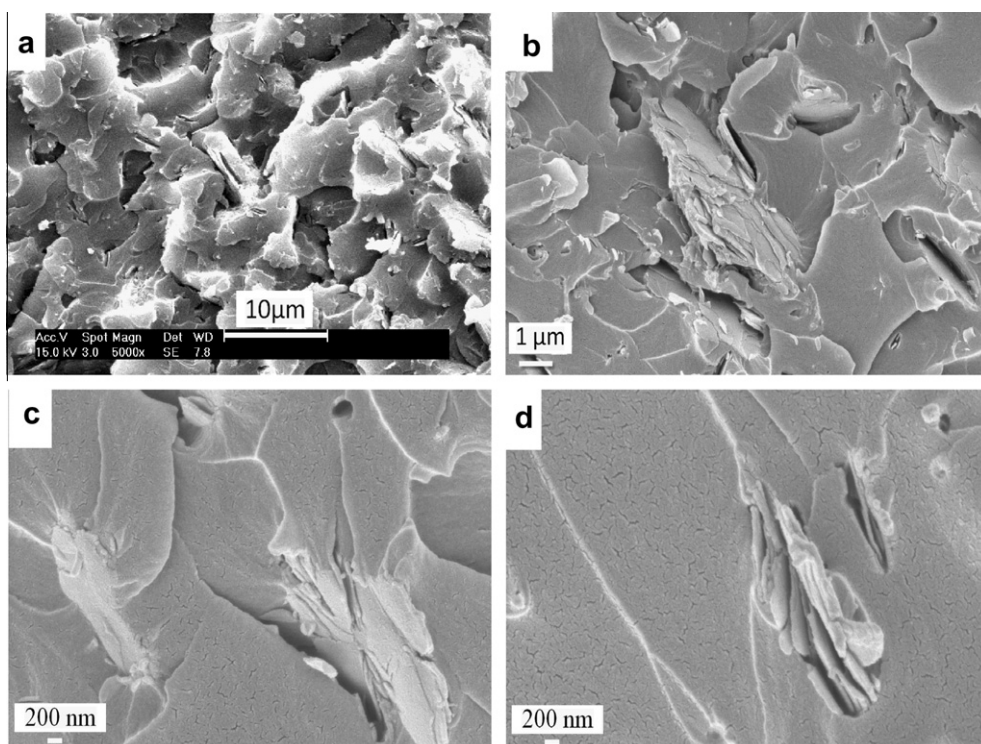


Fig. 9. SEM images of fracture surfaces near crack tip of 100-h PPA-treated halloysite-epoxy nanocomposite prepared by ball milling.

number of microcracks and plastic deformations in the intercalated halloysite–epoxy interfaces, resulting in a further improvement in fracture toughness [16]. Also, composite with ball mill process has slight higher K_{IC} than that processed by directly mixing under the same conditions with as-received or PPA-treated HNTs.

Typical fracture surface of CT specimens for the 10 wt.% halloysite–epoxy composites using as-received halloysite and 100 h-PPA-treated halloysite and prepared by mechanical mixing and ball mill homogenization are shown in Figs. 6–9. Figs. 6 and 7 show as-received halloysite–epoxy composites prepared by two different process methods and Figs. 8 and 9 show 100 h-PPA-treated halloysite–epoxy composites prepared by two different process methods. In Figs. 6a and 8a, the dispersion of halloysites in the composite generally uniform, though most were in the form of particle clusters of different sizes, shown in Fig. 6b and 8b. There were also some isolated particle clusters of relatively large size up to several microns, particularly for the composite containing as-received halloysite. As shown in Figs. 7 and 9, the use of ball mill homogenisation greatly reduced the size of the halloysite particle clusters and resulted in more uniform distribution of halloysites.

For the as-received halloysite–epoxy composites prepared by mechanical mixing (Fig. 6) and ball milling (Fig. 7), the improvements in fracture toughness can be attributed to mechanisms such as halloysite particle clusters (heavily existed in direct mixing process) can interact with the crack, bridging the crack when it passes through, resisting the advanced of the crack and thus resulting in an increase in fracture toughness (Figs. 4a and 6b) or several broken halloysites on the fracture surface with obvious separations from the matrix (debonding) or pull-out of halloysites from the matrix and halloysites left in the matrix (heavily existed in ball milling homogenization process). As halloysites are much stronger and stiffer than the epoxy matrix, fibre breakage, fibre–matrix interface debonding and fibre pull-out from the epoxy matrix would consume extra energy, therefore it is understandable that if the particles were evenly distributed in the matrix without the presence of large aggregations to cause premature failure (Fig. 7c and d), K_{IC} was enhanced.

For the PPA-treated halloysite–epoxy composite prepared by mechanical mixing (Fig. 8) and ball milling (Fig. 9), the improvements in fracture toughness might be attributed to further enhanced dispersion due to the morphology change. The fracture toughness mechanisms are different from as-received halloysite–epoxy composites but similar to intercalated or exfoliated organo-clay in epoxy matrices [21,22], which promote the formation of a large number of microcracks and fracture energy absorptions in the intercalated halloysite–epoxy interfaces, resulting in a further improvement in fracture toughness [16]. With ball milling homogenization, treated halloysites have fewer layers stacking together (Fig. 9c and d) than these from mechanical mixing (Fig. 8c and d), which created more promoting a large number of microcracks and plastic deformations when the specimen was loaded.

4. Conclusions

On the basis of the current results, it appears that the ball mill homogenization method was effective in achieving homogeneous mixtures of halloysite with epoxies with halloysite contents of 10 wt.%. Large-sized particle clusters occurred during mechanical mixing process can significantly decrease by ball milling method. With PPA treatment on halloysite to change the structure morphology from tube-form to platelet-form created additional particle surfaces due to the release of some internal surface areas concealed by

the rolled layers of the nanotubes. The increased halloysite–epoxy contact surfaces could provide extra sites for interactions between halloysite and epoxy matrix under stress. The improved dispersion of halloysite particles in the epoxy due to PPA intercalation and ball milling homogenization contributed to a further increase in the fracture toughness of the halloysite–epoxy composites compared with those of the composite with as-received halloysite and even treated halloysite with mechanical mixing process.

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