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# Toughening of brittle polyester with functionalized halloysite nanocomposites

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ARTICLE INFO	A B S T R A C T		
<i>Ceywords:</i> -Alloysite nanotubes -Balane Fhermoset Nanocomposites Fracture toughness Foughening mechanisms	This study presents the role of pristine halloysite nanotubes (HNT) and silane-functionalized halloysite (s-HNT) on toughening mechanisms and initiating plastic deformation in unsaturated polyester (UPE) nanocomposite. The critical stress intensity factor ( $K_{Ic}$ ) and the critical strain energy release rate ( $G_{Ic}$ ) as fracture toughness indications were measured and the relationship between the morphological structures and toughening mechanisms was identified. The results indicated that the fracture toughness values exhibited a steady-state increasing trend with the incorporation of up to 5 wt % HNT or s-HNT into the UPE resin. The 3% HNT or 3% s-HNT composites were found to obtain the highest toughness values supported with uniformly dispersed particles. The SEM observations showed different energy dissipation mechanisms are; zone shielding and shear yielding with a presence of full particle debonding with the HNT addition; and river line patterns, a tail-like		

structure and the formation of micro-cracks mechanisms were observed with the addition of s-HNT.

# 1. Introduction

Understanding of material's resistance to the crack initiation and propagation in thermosets nanocomposites has become a prominent area in the most recent research. This is because thermosets have a gaint macromolecule covalently bonded network structure with a high crosslink density and a little dissipated energy i.e., plastic deformation in front of the crack tip is localized leading to a catastrophic brittle failure [1-4]. Hence, much effort has been devoted to initiate localized energy absorbing mechanism in the fracture process zone of such a material to reduce plastic resistance and delay reaching brittle strength [5-12]. For instance, Bilisik and Sapanci [13] experimentally determined the fracture toughness of epoxy-based multiwall carbon nanotube. It was found that the fracture toughness resistance to arrest the crack growth in the nanocomposite was due to fiber bridging. Similarly, He et al. [14] toughened epoxy nanocomposites by multi-walled carbon nanotubes (MWCNTs) to enhance the micro-cracks resistance of carbon fiber reinforced epoxy composite at 77 K. It was revealled that the mechanical properties and the micro-cracks resistance of the composite have improved. The fracture toughness of epoxy/nanosilica (NS) composites increased with increasing NS content due to zone shielding mechanism that involves plastic deformation. While, no significant change in the toughness was noticed with changing particle sizes of NS [15]. Four toughening mechanisms were observed in the epoxy/NS composites are particle debonding, matrix ligament bridging, matrix dilation bands and matrix shear banding.

In general, the resistance of a material to crack propagation is representing by the fracture toughness, either the critical stress intensity factor ( $K_{Ic}$ ) or the critical strain energy release rate ( $G_{Ic}$ ) values. The  $K_{Ic}$ or G<sub>Ic</sub> values at which crack propagation occurs depend upon many factors such as loading conditions, temperature, material and geometry of the specimen as well as the crack length and stress concentration [16]. However, a complete imagination of toughening mechanisms and fracture energy (stress) in thermosets toughened by rigid micro- or nano-sized fillers is still not well understood. This is because thermosets having a three-dimensional molecular structure that demonstrates inherent brittle fracture mode with unstable crack propagation and limited yielding under plane-strain conditions. The present study aims to identify the toughening mechanisms occurring in the brittle UPE-nanocomposites after HNT and s-HNT incorporation in order to comprehensively grasp the role of good adhesion salinized halloysite on the UPE matrix in changing the fracture mechanics. Fracture toughness of UPE/HNT or UPE/s-HNT nanocomposites was conducted in terms of KIC and G<sub>Ic</sub>. The novelty of this study lays on understanding whether the improved wettability and adhesion between functionalized HNTs particles with the UPE matrix would change the fracture modes or would have bridged or deflected the crack initiated in the polymer-nanocomposite.

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#### 2. Experimental

#### 2.1. Materials used

Halloysite nanotubes (HNT) with a length of (0.5-3.0 µm), an exterior diameter of (50-70 nm) and an internal diameter of (15-30 nm) and specific gravity of 2.26, were provided by Applied Mineral Inc. The unsaturated polyester (UPE) provided by Nupol, was used as polymer matrix. The UPE resin has a low viscosity of 350 cp to permit better compatibility with the nanofiller and a high styrene of 45% to promote the polymerization. The Methyl Ethyl Ketone Peroxide (MEKP/ Butanox-M50) contains 33% peroxide content was used as catalyst at 1.5% of the UPE weight percent to initiate the crosslinking of the UPE resin. Vinyltrimethoxysilane (VTMS) - 98% solution with a linear formula of C5H12O3Si and a molecular weight of 148.23 purchased from Sigma, Aldrich was used as coupling agent to improve the dispersibility of halloysite and improve its affinity with the organic polymer matrix. Sol-gel process was applied to functionalize pristine as-received HNT surface with VTMS that was discussed in details in a previous study [17]. In brief, 50 g of HNT and 12 g of VTMS were dissolved in a 500 ml of ethanol absolute under agitation to produce s-HNT. One ml of acetic acid and 50 ml of distilled water were then added to the aqueous solution to keep the pH value in the range of 4.5-5.5. The solution was mixed for 3 h at 50 °C on a hotplate with a magnetic stirrer. The final product was filtered and washed by deionised water until neutral, and dried under a fuming hood overnight and later at 100 °C for 8 h to remove any remnant of the solvent. The dried product (slurry) was ground in a porcelain mortar and pestle to primary powders to crush the bulk aggregates and sieved using different fine metal sieves to exclude micro- and nanoparticles of the primary filler.

# 2.2. Nanocomposite preparation

Nanocomposites based on different weight percentages (1, 3, 5, 7, and 9 wt %) of pristine halloysite (HNT) or silanized halloysite (s-HNT) and the UPE resin were prepared by using a combination of direct mechanical stirrer rotated at 2000 rpm and ultra-sonication process at ambient temperature. The mixing process of halloysite particles in the liquid UPE resin was done for 30 min at 24 °C. During the rotation process, the halloysite particles were slowly added to avoid particles agglomeration and to ensure good dispersion. The produced mixture was later placed under ultrasonic probe at a frequency of 25 KHz for 2 h to agitate halloysite particles well inside the resin and remove the air bubbles. Interestingly, the ultrasonic probe was operated intermittently to avoid overheating and styrene emission.

The processed mixture was then cast into the pre-designed moulds having cavities match the desired finishing dimensions. The samples were cured at room temperature for 24 h and post-cured at 60 °C for 2 h in the oven and later by at 90 °C for 2 h to ensure a fully polymerization of the network. Samples of the neat UPE were prepared following the same curing process as a baseline for comparing the results. Upon completion of the curing process, the specimens were removed from the moulds and finally set up in accordance to the required testing.

#### 2.3. Fracture toughness measurement

In this study, values of fracture toughness are measured following the linear elastic fracture mechanics (LEFM) described in ASTM D 5045 [18]. Two common testing geometries, single-edge notch bending (SENB) and compact tension (CT) configuration are applied. The SENB geometry is more popular because it requires less material without complicated machining compared to the CT sample geometry. The CT geometry gives more accurate plain-strain fracture toughness since it gives more space for the crack propagation. The SENB and CT configurations are illustrated in Fig. 1. For the both test geometries, a precrack was generated by tapping a fresh razor blade into the notch tip with a drop weight to maintain an accurate fracture toughness values. The crack length-to-width ratio (a/w) is limited to 0.5 and loading rate of 5 mm/min. In case of SENB specimen, the span-to-specimen width ratio (s/w) is maintained of 4, loaded in three-point bending (3PB).

The critical stress intensity factor ( $K_{Ic}$ ) was calculated of at least five samples as per the following formulas and the averaged was taken:

$$K_{Q} = \frac{P_{Q}}{BW^{1/2}} f\left(\frac{a}{w}\right)$$
(1)  
$$f\left(\frac{a}{w}\right) = 6\left(\frac{a}{w}\right)^{1/2} \times \frac{\left[1.99 - \frac{a}{w}\left(1 - \frac{a}{w}\right)\left(2.15 - 3.93\frac{a}{w} + 2.7\left(\frac{a}{w}\right)^{2}\right)\right]}{\left(1 + 2\frac{a}{w}\right)\left(1 - \frac{a}{w}\right)^{3/2}}$$
(2)

where  $P_Q$  is the maximum load determined from the load-displacement curve, *B* is the specimen thickness.

For the single-edge notch specimen under three point bending (SEN-3PB) testing, the general principle of the bend-test fixture is illustrated in Fig. 2 a & b. As shown in Fig. 2 a, the line of action of the applied load will pass midway between the support roll centres, the span (S = 4 W = 48 mm). The bend-test was performed at room temperature and the load versus loading-point displacement curve was obtained.

The determination of the energy per unit area of crack surface or the critical strain energy release rate ( $G_{Ic}$ ) of neat UPE and its nanocomposites was determined using the following formula:

$$G_{lc} = \frac{K_{lc}^2}{E}$$
(3)

The above equation was applied as for the SENB geometry and plane stress conditions.

The E is the obtained elastic modulus of a material at the same time and temperature conditions as the fracture test. The  $K_{Ic}$  is the same obtained from Eq. (1).

In terms of using compact tension (CT) geometry, the plain-strain fracture toughness test was measured under the opening mode as follows:

$$K_{Q} = \frac{P}{BW^{1/2}} f\left(\frac{a}{w}\right)$$

$$f\left(\frac{a}{w}\right)$$

$$= \frac{\left(2 + \frac{a}{w}\right) \left\{ 0.886 + 4.64 \left(\frac{a}{w}\right) - 13.32 \left(\frac{a}{w}\right)^{2} + 14.72 \left(\frac{a}{w}\right)^{3} - 5.6 \left(\frac{a}{w}\right)^{4} \right\}}{\left(1 - \frac{a}{w}\right)^{3/2}}$$
(5)

In order to determine a valid plain-strain fracture toughness,  $K_{Ic}$  in accordance with this test method, the conditional  $K_Q$  that obtained from Eq. (4) with the use of **P** as the maximum load needs to be checked with the satisfaction of specimen thickness used against:

$$B, a, (w - a) > 2.5(K_0 / \sigma_v)^2$$
(6)

Where  $K_Q$  is the conditional or trial fracture toughness, and  $\sigma_y$  is the yield strength (MPa).

After checking the conditional result  $K_Q$  against the size criteria following Eq. (6). The calculated fracture toughness ( $K_{Ic}$ ) is valid since the quantity of  $2.5(K_Q/\sigma_y)^2$  is less than the values of specimen thickness (B), the crack length (*a*), and the ligament (*w* – *a*).

For the determination of fracture toughness measurements of neat UPE and its different nanocomposites using compact tension (CT) geometry, the tension-testing clevis and set up the test fixture (Fig. 3). Both ends of the CT specimen (Fig. 3 b) are held by special clevises and loaded through pins to provide rolling contact between the loading pins and the clevis holes. Afterwards, the CT specimen was loaded at rate of 5 mm/min. The measurement of critical strain energy release rate ( $G_{Ic}$ )



Fig. 1. Specimen configuration as used for fracture toughness measurements (a) SENB sample, and (b) CT geometry.



Fig. 2. Bending rig (a) and single-edge notch bend geometry (b) used in this study.



Fig. 3. (a) Tension test and clevis design used for compact tension (CT) geometry (b).

of materials was determined as for the CT specimen geometry and plane strain condition as follows:

$$G_{Ic} = \frac{K_{Ic}^2 (1 - v^2)}{E}$$
(7)

The **E** is the elastic modulus of material obtained at the same time and temperature conditions as the fracture test. The  $K_{Ic}$  is obtained from Eq. (4), and v is the measured Poisson's ratio of unsaturated polyester resin (v = 0.35).

#### 2.4. Morphological characteristics

The microstructural characteristics of nanocomposites were identified by transmission electron microscope (TEM, JEOL-1010) with 100 kV acceleration voltage. Ultrathin sections were cut from each nanocomposite with a diamond knife at room temperature and placed on carbon-coated copper grids. The effect of HNT and s-HNT addition on fracture surface and toughening mechanism of UPE nanocomposites was examined by using Scanning Electron Microscope (SEM, Philip XL-30). The SEM specimens were sputter coated with platinum to improve the conductivity before the examination. X-ray diffraction (XRD) scans were performed using advance Bruker D-8 X-ray diffractometer and CuK $\alpha$  radiation generated at 40 KV and 30 mA. Energy-dispersive X-ray spectroscopy (EDX or EDS) was used to figure out the elemental analysis or chemical characterization of halloysite particles before and after salinization.

Fourier Transform-Infrared (FT-IR) spectroscopy was used to characterise the molecular structures of the nanocomposites and identify the vibrational states of the chemical bonds obtained after curing process. The FT-IR test was also carried out to determine the role of silanized halloysite on the bending vibration of C–H groups and C–C bonds of the neat UPE resin. Differential scanning calorimeter (DSC-Q200) was used to measure the glass transition temperature (T<sub>g</sub>) and the heat capacity of phase change for neat UPE and its different HNT and s-HNT nanocomposites.

#### 3. Results and discussion

#### 3.1. Morphology of halloysite nanotubes

TEM micrographs were utilized to assess the morphology of treated and untreated halloysite nanotubes. Fig. 4 a & b depicts large tactoids of untreated HNT due to poor dispersion, and a decreased tactoid size of s-HNT particle for a better dispersion. Another observation can be depicted in Fig. 4, that is, lengths of s-HNT seem to be shorter and their aspect ratios (length/diameter) lower than these for the HNT [19]. Similar observation was depicted in the TEM images of CdS–Fe<sub>3</sub>O<sub>4</sub> nanostructure [20]. The energy dispersive spectroscopy (EDS) analysis was conducted to identify the chemical composition of halloysite before and after salinization. Fig. 5a shows the SEM image of a tensile-fractured surface for the UPE/5% HNT composite. Fig. 5b shows the EDS analysis of the major phase in the SEM image, showing the UPE resin, and Fig. 5c shows the analysis of the HNT particles. Based on the EDS analysis, the interaction (affinity) of HNT particles to the UPE resin seems to be relatively reasonable. In the major phase, there was a characteristic peak of C, corresponding to the polymer matrix, associated with a short fluctuation of Al and Si, corresponding to the presence of halloysite in the matrix. However, several elements—Ca, Na and O—besides Al and Si appeared in the HNT composition, but disappeared in the major phase. The sharp peaks of Pt represent the sputter coating of surface with platinum before completing the SEM analysis.

The EDS analysis of UPE/s-HNT nanocomposite as shown in Fig. 6, almost demonstrated the same fluctuations of elements as per the HNT particles. The indistinctive difference between the EDS analysis for HNT and s-HNT particles is, in the latter particles, that the fluctuations of Na, Al, Si, and Ca seem to be a little shorter and the fluctuations of C higher than in the former particles. This phenomenon can either indicate a better interaction between the halloysite and the UPE matrix particle, or the s-HNT surface covered by multilayer silane structure, which may shorten the fluctuations of the elements.

Wide-angle X-ray scattering (WAXS) scans of neat UPE, HNT and s-HNT loose powders are shown in Fig. 7. The XRD intensity pattern of neat UPE showed as a baseline diffraction pattern while the XRD intensity of HNT and s-HNT particles revealed a sharp basal reflection due to the random orientation of HNT. The treatment of HNT surface resulted in changing its crystalline structure and consequently higher order reflection peaks in the XRD patterns, indicating a high degree of nanotube orientation and high alignment of HNT tactoids in the flow direction. The basal spacing (001) of HNT and s-HNT were approximately similar at 7.42 Å, based on a diffraction angle of  $2\theta = 11.92^{\circ}$ and wavelength of Cu K $\alpha$  ( $\lambda = 1.54$  Å).

The role of HNT and s-HNT particles on the wettability and glass transition of nanocomposites was investigated by measuring the glass transition temperature (Tg) by using DSC spectra in the heating mode. The incorporation of HNT or s-HNT nanoparticles in the crosslinked UPE resulted in a marginal reduction in Tg values, with a slight shifting in the initial formulation of a giant molecule network of the UPE matrix, as shown in Fig. 8. The Tg values of neat UPE and its HNT and s-HNT nanocomposites are given in Table 1.

Fig. 9 shows the FT-IR spectrum of neat UPE and its nanocomposites. Fig. 9a reveals the characteristic Si–O–Si absorption band occurred over a wide range of wave numbers in the region of  $701-1085 \text{ cm}^{-1}$ . Within the silanization process, hydrolysis and condensation reactions occur on bifunctional silane molecules [(RO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-X], leading to the generation of siloxane



Fig. 4. TEM images of untreated halloysite nanotubes (a), and silane-treated halloysite nanotubes (b).



Fig. 5. (a) SEM image of UPE/5% HNTs showing large clusters, (b) and (c) observing the energy dispersive X-ray (EDX) elemental analysis for different spots in the nanocomposite.



Fig. 6. SEM image of UPE/5 wt % s-HNT composite (a), and its EDS analysis (b).

(-Si-O-Si-) which creates a bridge bond between the hydroxyl (OH) group on the silanized surface. The silanol groups change the hydrophilic nature of these surfaces to a hydrophobic nature. The intensity of absorption in the IR spectrum is related to the change in dipole that occurs during the vibration. The vibrations leading to significant change in dipole (e.g., C=O stretch) cause more intense absorption

than the vibrations causing a modest or no change in dipole (e.g., C = C symmetric). The aromatic rings characteristic of C = C absorption appeared at 3625 cm<sup>-1</sup> and this was confirmed by the existing peak at 1600 cm<sup>-1</sup>. The rounded peaks of hydrogen bond stretches (O–H absorption) appeared in the region of 3200–3600 cm<sup>-1</sup>. The characteristic absorption bands of the C–H group occurred at 2937.9 cm<sup>-1</sup> and



Fig. 7. X-ray scans for neat UPE, untreated HNT and silane-treated s-HNT nanotubes.

the symmetric band at  $2983.5 \,\mathrm{cm}^{-1}$  was due to aliphatic hydrogen stretching.

Fig. 9b shows the characteristic peaks appeared in UPE/5% HNT and UPE/5% s-HNT nanocomposites. They are as follows: the carbonyl absorption (C=O) ester peaks at  $1729 \text{ cm}^{-1}$ , the C–H bending at  $1453 \text{ cm}^{-1}$ , the rounded peaks such as O–H peaks for the C–O ester in the range of  $1000-1280 \text{ cm}^{-1}$ , and the C–H out of plane and the

asymmetric C–H stretch at 744 and 701 cm<sup>-1</sup>, respectively. The C–H absorption of the methyl group (CH<sub>3</sub> symmetric deformation) appeared at 1396.8 cm<sup>-1</sup>.

# 3.2. Fracture toughness test

The load-displacement curves for the neat UPE and its HNT



Fig. 8. DSC thermograms of neat UPE and its nanocomposites.

#### Table 1

Nanocomposites	$K_{c} (MPa.\sqrt{m})$		G <sub>c</sub> (J/m <sup>2</sup> )	
	СТ	SENB	СТ	SENB
Neat UPE UPE/1% HNT (UPE/1% s-HNT) UPE/3% HNT (UPE/3% s-HNT) UPE/5% HNT (UPE/5% s-HNT) UPE/7% HNT (UPE/7% s-HNT) UPE/9% HNT (UPE/9% s-HNT)	$\begin{array}{l} 1.2 \pm 0.1 \\ 1.24 \pm 0.16 \ (1.28 \pm 0.13) \\ 1.4 \pm 0.4 \ (1.36 \pm 0.25) \\ 1.17 \pm 0.09 \ (1.3 \pm 0.1) \\ 1.09 \pm 0.12 \ (1.26 \pm 0.15) \\ 1.05 \pm 0.1 \ (1.16 \pm 0.2) \end{array}$	$\begin{array}{l} 2.04 \ \pm \ 0.13 \\ 2.1 \ \pm \ 0.2 \ (2.44 \ \pm \ 0.18) \\ 2.28 \ \pm \ 0.33 \ (3.33 \ \pm \ 0.41) \\ 2.28 \ \pm \ 0.45 \ (2.56 \ \pm \ 0.35) \\ 1.65 \ \pm \ 0.4 \ (2.4 \ \pm \ 0.25) \\ 1.42 \ \pm \ 0.15 \ (1.65 \ \pm \ 0.22) \end{array}$	$\begin{array}{l} 0.33  \pm  0.05 \\ 0.34  \pm  0.06  (0.34  \pm  0.08) \\ 0.411  \pm  0.12  (0.37  \pm  0.08) \\ 0.3  \pm  0.05  (0.35  \pm  0.07) \\ 0.27  \pm  0.04  (0.33  \pm  0.06) \\ 0.27  \pm  0.06  (0.3  \pm  0.05) \end{array}$	$\begin{array}{l} 0.94 \ \pm \ 0.09 \\ 0.97 \ \pm \ 0.09 \ (1.24 \ \pm \ 0.1) \\ 1.09 \ \pm \ 0.2 \ (2.23 \ \pm \ 0.32) \\ 1.14 \ \pm \ 0.09 \ (1.37 \ \pm \ 0.11) \\ 0.61 \ \pm \ 0.11 \ (1.2 \ \pm \ 0.12) \\ 0.48 \ \pm \ 0.05 \ (0.61 \ \pm \ 0.07) \end{array}$

Fracture properties of neat UPE and UPE/HNT nanocomposites. The values of UPE/s-HNT nanocomposites are shown in parentheses.

nanocomposites are shown in Fig. 10. In general, all nanocomposites tested in opening deformation mode (mode-I), using compact tension (CT) specimen geometry showed unstable crack propagation under a continuous loading condition, while the load dropped down to zero

after reaching the maximum, indicating a linear elastic and brittle behaviour. It is also implying that most energy is consumed in the initiation stage while little energy is dissipated in the rapid crack-propagation stage. After the tensile load was applied, the 1% s-HNT





Fig. 9. FT-IR spectra of different HNT nanocomposites (a), and FTIR spectres for UPE/5% HNT and UPE/5% s-HNT nanocomposites (Comparison study).





Fig. 10. Load-displacement curves of CT samples for (a) neat UPE and different UPE/HNT nanocomposites, and (b) neat UPE and different UPE/s-HNT fractured under tensile loads.

reinforced unsaturated polyester (UPE) suffered further extension (displacement) compared to the other nanocomposites. This is attributed to the crack initiated under load is deflected due to the interfacial adhesion that is certainly exist. As the crack grows, the load continues to rise, as shown in Fig. 10 b until it fails when the load reaches the strength of that specimen.

The 3% HNT (Fig. 10 a) and 3% s-HNT (Fig. 10 b) nanocomposites showed their ability to carry higher loads. This is due to presence of plastic deformation in the UPE composites imparted by the well-dispersed halloysite nanotubes (shown in TEM images, Fig. 11a), blunting the crack tip and reducing the local stress concentration and consequently allowing composites to carry higher loads before failure occurs. The capability of 3% s-HNT nanocomposites is larger than that of the 3% HNT nanocomposites. It is obvious that the improved wettability and adhesion between the s-HNT nanoparticles and the polymer matrix as well as perfect uniform dispersion (shown in TEM images, Fig. 11b) resulted in higher fracture force and higher crack opening displacement (COD) compared to the untreated HNT ones. The values of fracture toughness ( $K_c$ ) and the critical strain energy release rate ( $G_c$ ) determined using two kinds of specimen geometries (CT and SENB) are listed in Table 1.

The averaged values of all fracture properties were obtained from testing at least five specimens exhibited a deviation in the range of 0.04–0.4 for the K<sub>c</sub> values and 0.05–0.45 for the G<sub>c</sub> values. Regardless the specimen geometry, the incorporation of HNT and s-HNT into the UPE resin showed a significant improvement in the fracture toughness where the addition of 3 wt % HNT or 3 wt % s-HNT presented the highest values of K<sub>c</sub> and G<sub>c</sub> (see Table 1). For instance, with the use of SEN-3PB technique, the K<sub>c</sub> increased from 2.04 MPa m<sup>0.5</sup> for neat UPE to 2.28 MPa m<sup>0.5</sup> (11% improvement) and 3.33 MPa m<sup>0.5</sup> (63% improvement) for UPE/3% HNT and UPE/3% s-HNT nanocomposites, respectively. The values of G<sub>c</sub> also improved by 16% for UPE/3% HNT and 137% for UPE/3% s-HNT nanocomposites. However, further addition (> 5 wt %) of HNT or s-HNT particles reduced the toughness of the UPE nanocomposites.

The purpose of this measurement is to determine the consistency of



Fig. 11. TEM images of the cured 3% HNT-UPE composites (a), and the cured 3% silane treated HNT-UPE composites (b).

the fracture results with the size of the specimen and to elucidate the sequence of events that occurred during the fracture process i.e., to understand the mechanisms that contribute to the observed differences in toughness. As can be seen in Table 1 with increasing weight fraction of halloysite particles, the values of both  $K_{\rm Ic}$  and  $G_{\rm Ic}$  steadily increased. From the results obtained, it was observed that the UPE nanocomposites filled with silane-modified halloysite particles induced higher values of fracture toughness and fracture energy compared to the neat UPE or the UPE/HNT nanocomposites. These increases in toughness with the incorporation of up to 5 wt % of HNT or s-HNT nanoparticles have been attributed to the ability of particles to induce an increased extent of plastic deformation in front of the cracking path in the nanocomposite. The initiation of plastic deformation with the presence of hallovsite nanoparticles is one of the most dominant toughening mechanisms that can be noticed through toughening thermosetting polymers with nanoparticles. Furthermore, it was also believed that the presence of halloysite particles in the thermosetting UPE matrix that generated nonreactive surfaces and local free volume in the structure and then reduced the glass transition temperature (T<sub>g</sub>) are usually increased toughness and damage tolerance [17]. Nevertheless, further increase of halloysite content (> 5 wt %) induced lower values of both K<sub>Ic</sub> and G<sub>Ic</sub> and such that is related to the structure/property considerations. This means that the presence of higher contents of halloysite particles in the crosslinked UPE extremely toughened the UPE structure and involved that structure undergoing inhomogeneous, and raise from its ability to undergo strain-softening and leading to the localized nature of the plastic deformation [21].

It is essential here to further discuss the difference in toughness due using different thicknesses of specimen geometry (CT and SENB). According to ASTM D 5045 standard test method for plain-strain fracture toughness and strain energy release rate of plastic materials [18]. The validity of calculated  $K_{Ic}$  and the size criteria must be satisfied to Eq. (6). In the case of using the configuration SENB geometry, that quantity was not satisfied with the size criteria required by the ASTM standard test method. As a result, it is obviously that the values of stress intensity factor ( $K_c$ ) calculated with the SENB-3PB under plain stress conditions are higher than those calculated with the use of CT specimens under plain-strain conditions [22].

# 3.3. Toughening mechanisms

The morphology of different fracture surfaces for nanocomposites filled with untreated and silane-treated halloysites was conducted by SEM examination in order to quantitatively understand the toughening mechanisms took part. According to experimental observations in various previous studies [8,21,23–26], it was revealed that the improvements in both fracture toughness and fracture energy shown by nanofilled-polymers are strictly related to the large amount of energy



Fig. 12. SEM images of different fractured surfaces for unfilled brittle UPE matrix fractured under different loads and specimen geometries.



Fig. 13. Fractography of mode I fracture toughness using CT geometry for 5% HNT/UPE composite. The yellow arrows represent the decohesion and black arrows indicate the direction of the crack propagation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

dissipated by the initiation of different plastic deformation mechanisms and different damaging mechanisms taking place at the nanoscale.

The fractoraphic analysis of the fractured-surface for unfilled UPE matrix tested with both the CT geometry under tension and the SEN-3PB under bending showed a highly smooth brittle fracture, as depicted in Fig. 12. The surface topography of the unfilled UPE matrix exhibited both smooth and rough surface features. The smooth one represented by mist regions while the rough surfaces represented by hackle regions (see Fig. 12 b). Hackle regions frequently appear in areas where the stress field (direction or magnitude) is changing rapidly or the stress state changes from plain strain to plain stress [27]. In the current case, the hackle regions appeared in the region of a specimen subjected to bending on the compression side of the specimen but changes to tension as the crack approaches from the tension side. Furthermore, different directions of crack propagation were observed in the morphology of the unmodified brittle UPE matrix irrespective the applied loads or specimen geometries.

The presence of rigid particles in the thermosetting polymer matrix undoubtedly contributed in the initiation of various mechanisms of energy absorption before the appearance of the first crack [28]. These energy dissipation mechanisms can be described as the addition of HNT into the UPE matrix introduces more local plastic deformation near the crack tip (see Fig. 13a). This induces its importance in toughening behaviour and improving fracture energy since the energy absorbed by the creation of additional fracture surface area necessitates additional energy to be input to the system to continually drive crack growth [29]. The fracture surfaces of 5% HNT/UPE near the precrack front region were examined under SEM. The white arrows at the down left image in Fig. 13 b indicate the crack growth direction while the yellow arrows in the same image refer to the decohesion (inter-granular fracture) which probably occurs along the weakened hydrophilic particle and the polymer interface. Similarly, in Ref. [5] revealed that the plastic deformation that verified in a lightly cross-linked epoxy matrix includes shear yielding and matrix dilation. This finding also agree well with [30] findings where a small birefringent zone was found associated with the creation of an obvious dilatation zone under loading, indicating local matrix deformation. Dilatation refers to an expansion in volume of a material under stress.

The zone shielding toughening mechanism represented by the formation of micro-voids around the crack tip was observed as shown in Fig. 14. In general, there are three different mechanisms categorized under zone shielding mechanisms are: the transformation that occurs when the crack actually changes the crystalline structure of the surrounding material to inhibit crack growth; the microcrack formation and the crack field void formation [5]. Numerous micro-cracks or micro-voids form simultaneously in a brittle material when the applied loads reach a certain level. The distribution of these micro-cracks depends essentially on the local stress concentration and the material



Fig. 14. Fracture surface for UPE/3% HNT composite showing the microvoids occurred due to the particle-polymer interface debonding.

heterogeneity where the formation of either micro-cracks or microvoids around the crack tip reduces its stress concentration and interferes with crack propagation. In contrast, the presence of stress concentration can lead to shear yielding around every particle and hence throughout a large volume of material rather than just at the crack tip [31]. Hence the polymer matrix absorbs a large amount of energy during deformation and is toughened due to the initiation of matrix shear yielding mechanism.

The matrix shear yielding mechanism was observed in the fracture surface of untreated halloysite composite, as depicted in Fig. 15. This mechanism is also thought to be initiated by the stress concentrations around the periphery of the nanoparticles [21]. Furthermore, clear evidence of halloysite particle debonding can be found in the untreated

system (Fig. 16 a, b), but not in the silanized system. On the fracture surface of the silanized nanocomposite, partially debonded or even fully debonded halloysite particles were found (Fig. 17 a, b), but much less commonly compared to the case of the untreated composite. Interestingly, contributing the total fracture energy, the presence of particles debonding considers one of the pre-requisites to activate void expansion and matrix shear deformation energy dissipation mechanisms [32].

Nevertheless, discussions of these energy dissipation mechanisms have been mainly qualitative and hence the qualitative observation of increased toughness and quantitative increase in the fracture energy in this study appear to agree with interface debonding, shear yielding and with the theory that states the initiation of stress concentration in the surrounding area of halloysite particles. To this end, stress fields are



Fig. 15. Fracture surface of (a) 1% HNT/UPE composite, (b) 3% HNT/UPE, and (c) 5% HNT/UPE tested with the SENB geometry under bending, showing shear yielding mechanism.



Fig. 16. SEM images illustrating the fracture surface of 3% HNT/UPE composite (a), and 5% HNT/UPE (b) after debonding.



Fig. 17. SEM images illustrating the fracture surface of: (a) 1% s-HNT/UPE nanocomposite, and (b) 3% s-HNT/UPE nanocomposite after debonding.



Fig. 18. Fracture surfaces from SENB geometries of: (a) 3% s-HNT/UPE, and (b) 5% s-HNT/UPE nanocomposite showing matrix shear band mechanism.

formed due to the difference in strength modulus and Poisson's ratio between halloysite and unsaturated polyester.

On the other hand, the topography analysis of fracture surfaces of the silanized halloysite composites although they apparently seem similar to those of the untreated halloysite systems; they relatively show finer with complex features. This is perhaps for the formation of multiple interfacial bonding sites on the surface of silanized halloysite. Such multiple sites normally form during the hydrolysis process, and they can act as a thick interfacial bridge between particles-silane-polymer. Before identifying the toughening mechanisms in the s-HNT nanocomposites, it is necessary to clarify the fracture behaviour that can be expected to observe in such nanocomposites. As the s-HNT particles are much stronger than the pristine HNT and have a strong interface with the UPE matrix, particle deformation, internal cavitation and particlepolymer interface debonding would unlikely occur under loading. However, as discussed above that a partially particle debonding was observed in the silanized halloysite composites versus a fully debonding in the un-silanized halloysite composites (see again Fig. 16 and Fig. 17). This means that the particles debonding and the subsequent void growth as well as the matrix shear band are also played roles in the toughening of silanized halloysite nanocomposites [5,21]. reported that the matrix shear band contributed more to the fracture toughness than the plastic void growth effect.

The matrix shear yielding or matrix shear banding is also observed



Fig. 19. Fracture surfaces from SENB geometry of 7% s-HNT/UPE nanocomposite showing the massive shear yielding mechanism.

in the topography analysis of silanized halloysite nanocomposite. It is an energy absorption mechanism associated with polymer failure. It occurs when localized plastic flow starts in response to an applied stress at approximately 45° to the applied load (Fig. 18). Such plastic flow may spread shear bands in the whole sample, absorbing a significant quantity of energy or may lead to localized yielding. Localized shear yielding is a narrow zone of intense shearing strain forming due to a material instability i.e. corresponding to an abrupt loss of homogeneity of deformation. Increase in tendency to shear yield in nanocomposites results in isolated shear bands and increase the energy absorption prior to fracture [32]. Usually, spread shear yielding or shear bands is initiated by debonding of inorganic nanoparticles whereas debonding of particles trigger spread shear yielding around the cavity of the matrix left by debonded particles. The size of both dilational bands and shear bands increases with increasing halloysite content.

In the view of the role of silanized halloysite (s-HNT) particles on the initiation of shear yielding, the higher contents of s-HNT caused in the initiation of the massive shear banding, as can be observed in the fracture surface of 7 wt % s-HNT nanocomposites, Fig. 19.

The massive shear banding mechanism is a crack-tip shielding occurs due to the reduction in yield stress by the stress concentration of the compliant nano-scale particles that facilitate shear yielding. Similar observation of micro-shear banding, shear yielding and massive shear yielding mechanisms have been reported in the literature [30,33,34]. Later [29], reported that the size of shear bands increases with increasing filler content whereas it does not significantly affect with the use of different particle sizes.

Despite the inherit interdependence of the shear yielding



**Fig. 21.** The fracture surfaces near crack tip after SEN-3PB testing of 3% s-HNT/UPE composite, showing the crack initiation zone at different magnifications with a local deformation process. White arrows indicate the direction of crack propagation.

toughening mechanisms described above, the energy dissipation through this mechanism was thought to be insufficient to be responsible for the overall increased toughness in the thermosetting polymers nanocomposites. Other energy dissipation mechanisms such as crack pinning, crack deflection/bifurcation effects, twisting and immobilised polymer around the particles as well as river patterns and matrix ligament bridging are thought to be as a dominant mechanism highly contributed to overall toughness in the UPE nanocomposites.

To this end, in the current investigation, it was found that the well dispersed s-HNT particles in the polymer matrix associated with their high aspect ratios are aid in promoting crack bridging and deflecting the advancing crack and force growth to deviate from the existing



Fig. 20. SEM images of fracture surfaces near crack tip of (a) 5% s-HNT/UPE, and (b) 7% s-HNT/UPE nanocomposites showing crack bridging mechanism.



Fig. 22. The fracture surface of 5% s-HNT/UPE nanocomposite after SEN-3PB testing, showing crack initiation zone at different magnifications with river liners.



Fig. 23. The fracture surface of UPE reinforced with (a) 3 wt % s-HNT, and (b) 5 wt % s-HNT nanocomposites, demonstrating the tail-like structures.



Fig. 24. Fracture surface morphology after SEN-3PB test of 5% HNT/UPE nanocomposite (a), and 5% s-HNT/UPE nanocomposite (b).

fracture plane during the crack propagation. However, the better dispersion of the s-HNT particles and the further preparation processes to functionalize them tended to a reduction in their aspect ratio and this reduction is obviously reduced the possible effect of crack bridging and crack path deflection. Generally speaking, in the particles bridging toughening mechanism, the additive rigid particles act as bridging particles granting compressive grip in the crack path. While, the additive soft or flexible particles such as rubber deform plastically in the material surrounding the crack tip providing additional crack shielding [35]. To further understand the bridging mechanism in this study, Fig. 20 depicts the bridging mechanism of particles in the UPE thermosetting nanocomposite. Fig. 20 b shows that a large cluster of silanized halloysite particles appeared with further addition of filler content, bridging the crack when it passes through, resisting the advanced of the crack. However, such large clusters may also result in reducing the threshold of carrying loads and then cause premature failure (see Table 1). This finding was also supported by Refs. [36,37] where the former authors reported that functionalized carbon nanotubes (CNTs) was a good additive for fracture toughness enhancement of the polymethylmethacrylate (PMMA) nanocomposites. Where, the CNTs are playing a key role in dissipating energy associated with the crack growth via promoting crack bridging and crack deflection mechanisms, but that can be only observed with a high CNTs content and at high aspect ratio.



Fig. 25. Fracture surface morphology after SEN-3PB test of 5% s-HNT/UPE nanocomposite, showing macro-cracks (a) and micro-crack (b).



Fig. 26. The fracture surface for: (a) 7% s-HNT/UPE and (b) 9% s-HNT/UPE nanocomposites.

In light of the above findings and discussions, the fracture surface of 3% s-HNT/UPE nanocomposite after SEN-3PB testing showed a semicircular region of well-defined local plastic deformation process occurred around the crack initiation zone, as shown in Fig. 21. Such deformation process is to involve some toughness enhancement via blunting the crack tip and increase the size of the plastic zone. With further increase of silanized halloysite, instead of the occurrence of local deformation process in the crack initiation zone and crack propagation zone, river liner markings (Fig. 22) leading to the initial site of crack growth were detected in the topography of 5% s-HNT nanocomposite but substantial indications of plastic deformation in the control group were not noted. Hence, the lack of observed plastic deformation process and a smooth fracture surface agree well with the relatively low measured toughness of the nanocomposite. River pattern is a mechanism in which a pattern similar to a river and its branches are generated on the new cleavage plane at slightly different elevations. As the crack then propagated, these levels combined to form a crack advancing on fewer parallel planes [16].

Furthermore, characteristic tail-like structures formed behind halloysite aggregates in the process zone on the fracture surface can be observed in Fig. 23, which are often observed in particles filled epoxy systems [38,39]. The tail-like structures are in reality steps, which are formed when two secondary crack fronts divided by the aggregates meet with each other. With an increase of HNT content, the aerial density of these steps increases (see Fig. 23 b) and the fracture surface became rougher and more characteristic tails appeared and interconnected with each other (Fig. 24). The [40] suggested that characteristic tail structure usually forms when the two secondary crack fronts separated by a particle meet with each other after crack front bowing.

Nevertheless, there is no qualitative interpretation of Fig. 24 was found in the literature. The [41] claimed that a combination of well dispersed nanotubes with well impregnated smaller agglomerates leading to trigger void nucleation and/or micro-crack coalescences at the interface between nanotubes and the surrounding matrix resin. Later [42], reported that treated halloysite in the epoxy nanocomposite manifest small crack trajectories that are deflected and meander through the matrix, giving rise to the increased resistance to crack propagation. However, the particle agglomerates may also promote premature failure ahead of crack. Our point of view actually aligns with both observations where micro- and macro-cracks were found in the treated halloysite-unsaturated polyester composites, formed along the matrix-halloysite interfaces (see Fig. 25).

The formation of large number of micro-cracks and the increase in the fracture surface area due to crack deflection. Meanwhile, this is the suitable answer for the early allocated question about whether the nanoparticles in the thermosetting polymers deflect or bridge the crack. The formation of micro-cracks cause tensile yielding and then a large tensile deformation are aid to deflect the crack path. However, when these micro-cracks open, voids will result and permit large strains and consequently, the micro-cracks will effectively lower the modulus in the frontal zone around the crack tip, and thus effectively reduce the stress intensity factor.

The situation of topography analysis (Fig. 26) is much complicated for nanocomposites containing higher halloysite contents where the fracture surface is very rough and filled with scale-like steps, indicating that the presence of halloysite layers forced the crack to propagate along a very tortuous path (see Fig. 26 a). This observation was supported by Ref. [25] where the curved path of crack growth can be due to the fact that the maximum tangential stress direction changes as the crack advances. At each step of crack propagation, the crack plane rotates and grows in a new direction that has the maximum tangential stress.

#### 4. Conclusion

The role of untreated and silanized halloysite nanotubes on fracture toughness and toughening mechanisms of thermosetting unsaturated polyester (UPE) nanocomposites was experimentally investigated in this study. The addition HNT or s-HNT into the UPE matrix improved their ability to carry the loads and resulted in significant improvements in toughness and fracture energy. The silane-treatment on halloysite surface played a key role in improving the particles dispersion and interfacial adhesion between the particles and the polymer matrix and consequently in further enhancing toughness. The toughness improvement was attributed to the presence of plastic deformation that blunts the crack tip and reduces the local stress concentration and consequently allowing composites to carry higher loads before failure occurs. The SEM micrographs showed a highly smooth brittle fracture in the fractured surface of the neat UPE. The addition of rigid HNT or s-HNT particles into the UPE matrix contributed in the initiation of various mechanisms of energy absorption before the appearance of the first crack while different major and minor toughening mechanisms have generated.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesb.2018.10.032.

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