Fracture toughness and toughening mechanisms of unsaturated polyester-based clay nanocomposites

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Abstract

In this study, the role of nanoclay particles (MMT) on micro- and nano-scale deformation and fracture behaviour of a crosslinked unsaturated polyester (UPE)-based nanocomposites is explored. Nanocomposites from well-dispersed MMT particles and the UPE resin were prepared by a combination of mechanical mixing and ultrasonication process. The morphological characteristics of nanocomposites were examined by TEM. Critical stress intensity factor (K_{Ic}) based on linear elastic fracture mechanics (LEFM) and compact tension (CT) configuration is evaluated. The fracture modes and toughening mechanisms of the fractured-surfaces were identified by SEM analysis. An intercalation/partially exfoliation structure of UPE/MMT nanocomposite with moderate enhancement in fracture toughness is observed. The addition of 3 wt. % MMT exhibits the highest K_{Ic} value of nanocomposite by a 61 % improvement over the neat UPE. The fracture surface of the neat UPE seems to be a highly brittle fracture without crazing and a coarser surface with the appearance of plastic deformation zones of the nanocomposites.

Keywords: fracture toughness; toughening mechanisms; unsaturated polyester; clay nanocomposites.

1. Introduction

In general, the properties of polymer-clay nanocomposites (PCNs) are directly dependent on the dispersion state of nanoparticles in the polymeric matrix, whether it is immiscible, intercalated or exfoliated nanocomposites [1-3]. The exfoliated/intercalated nanostructure and the strong interaction between clay nanolayers and polymer chains tend to constrain the mobility of polymer matrix, delay the crack initiation and propagation and consequently induce higher mechanical strength and toughness [4, 5]. Fracture toughness is a critical mechanical property which characterizes the resistance of material to crack propagation or to fracture. The toughness of materials is directly affected by the energy dissipation and energy absorbed in fracturing the part.

Unsaturated polyester (UPE) resins are one of the most used thermosetting polymers in different industrial applications for their good mechanical properties and low density [6]. However, the brittleness is the major drawback of thermosets, resulting from the radical polymerisation process between unsaturated prepolymer and styrene that produces crosslinking (three dimensional network of bonds) [7]. Introducing nanoparticles as a second phase into polymers was thought to effectively increase their fracture toughness and alleviate their brittleness without sacrificing other properties such as strength, modulus or glass transition temperature. Hence numerous studies were done on using different nanofillers with thermosets such as Evora et al. [8] embedded small amounts of TiO_2 nanoparticles in the UPE resin. The fracture toughness and tensile strength of the nanocomposite significantly improved with introducing TiO_2 particles. Baskaran et al. [9] found that fracture toughness of the UPE resin increased with the addition of 5 wt. % alumina (Al_2O_3) nanoparticles.

The fracture toughness and toughening mechanisms of multiwalled carbon nanotubes (MWCNT) with UPE [10, 11], and halloysite nanotubes (HNTs) with epoxy [12] were also reported. From the literature, different toughening mechanisms can be characterized such as microcracking mechanism that occurs during combining rubber or nano-scale particles with polymers [7]. Multiple craze-like banding with dilatation (dilation) [13]. Crack-pinning where the crack front bows out between nanoparticles and remained pinned of the particles [14]. Localized shear yielding (or shear banding) characterizes as narrow zone of intense shearing strain, forms either from material instability or abrupt loss of homogeneity of deformation [15]. Massive shear-banding mechanism also appears in polymer-based nanocomposites which occurs during the reduction of yield stress by stress concentration. It normally forms from the compliant nanoscale or rubber particles that facilitate shear yielding.

Additionally, particle bridging (rigid particles) is another mechanism of toughening occurs in polymer nanocomposites [16]. Rigid or ductile particles work as a bridging particles that provide most of toughness improvements while they remain intact for some distances behind the crack-front. This study aims to investigate the relationship between the structural behaviour and fracture properties of UPE/MMT nanocomposites. The role of MMT particles on improving toughness of nanocomposites due to restricting crack initiation and crack growth is explored.

2. Experimental setup

2.1 Materials and nanocomposites preparation

Organoclay platelets (MMT, Cloisite® 30B) provided by Southern Clay Products, Inc. via Jim Chambers and Associates, Australia) were used at different amounts (1, 3, 5, 7, and 9 wt. %) to toughen unsaturated polyester (UPE, AROPOL®-1472PLSE, Nupol, Australia with 45 % styrene). The nanocomposites were prepared by means of shear mixing followed by sonication (agitation) to drive the air bubbles off. After mixing, the catalyst Methyl Ethyl Ketone Peroxide (MEKP/Butanox-M50) was added to the mixture at 2 % of the UPE weight and manually stirred for 1 min. Finally, the mixture was cast in special moulds having the identical dimensions of the compact tension samples and cured at room temperature for 24 hr and post cured at 60 °C for 2 hr followed by 2 hr at 90 °C following an increment rate of 10°C/30 min.

2.2 Morphological characterization

Transmission electron microscope (TEM) was used to observe the dispersion of clay platelets in the UPE resin. Ultra-thin sections of an approximately 70 nm in thickness were cut by a diamond knife at room temperature. The TEM analysis was examined using a JEOL (JEM-1010) TEM instrument at an acceleration voltage of 100 KV. Scanning Electron Microscope (SEM, Philip XL-30) examination was utilized to identify the failure modes and toughening mechanisms of the nanocomposites. The compact tension-fractured surfaces were sputter coated by platinum before doing the SEM examination to improve their electrical conductivity.

2.3 Fracture mechanisms

The stress intensity factor (K_{Ic}) and strain energy release rate (G_{Ic}) of the cured neat UPE and UPE-based MMT nanocomposites were evaluated using compact tension (CT) configuration. The

CT specimens were prepared according to ASTM D5045 as shown in **Fig. 1**. A pre-crack was created by tapping a fresh razor blade into the notch tip with a drop weight to maintain an accurate K_{Ic} values. The loading rate was adapted at 5 mm/min and the following relationships were used to measure the K_{Ic}:

$$K_{Ic} = \frac{P_Q}{BW^{1/2}} \cdot f\left(\frac{a}{W}\right) \tag{1}$$

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

where P_Q is the load determined from load-displacement curve, B is the specimen thickness. The

calculated K_{Ic} values were tested against: B, a, (W-a) > 2.5 $(K_{Ic}/\sigma_y)^2$ (3)
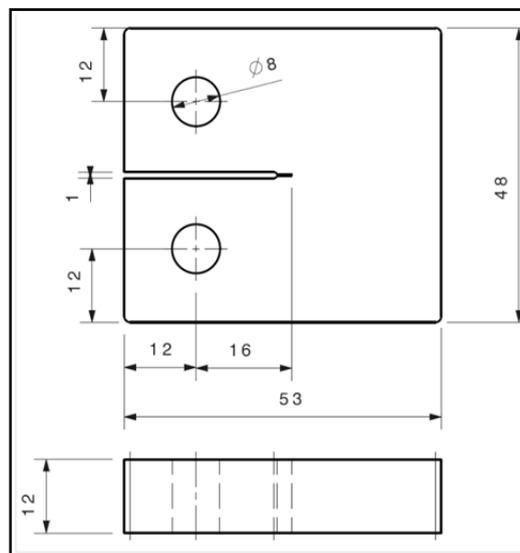
Fig. 1 Dimensions of the compact tension (CT) specimen.

3. Results and discussion

3.1 Morphology

Fig. 2 (a-d) illustrates representative TEM micrographs of the cured UPE/MMT nanocomposites. They show a number of clay clusters in the liquid resin and there are more of these clusters appear in the higher filler nanocomposites. The appearance of clay aggregates may be attributed to the structure of the clay platelets that composes of an inner octahedral layer surrounded by two silicate tetrahedral layers, or may be to the natural state of clay that exists as stacks of many platelets at several hundred nanometres, those long and wide separated by an interlayer distance of ~1-3 nm which might not be separated by using direct mechanical mixing [5, 17].
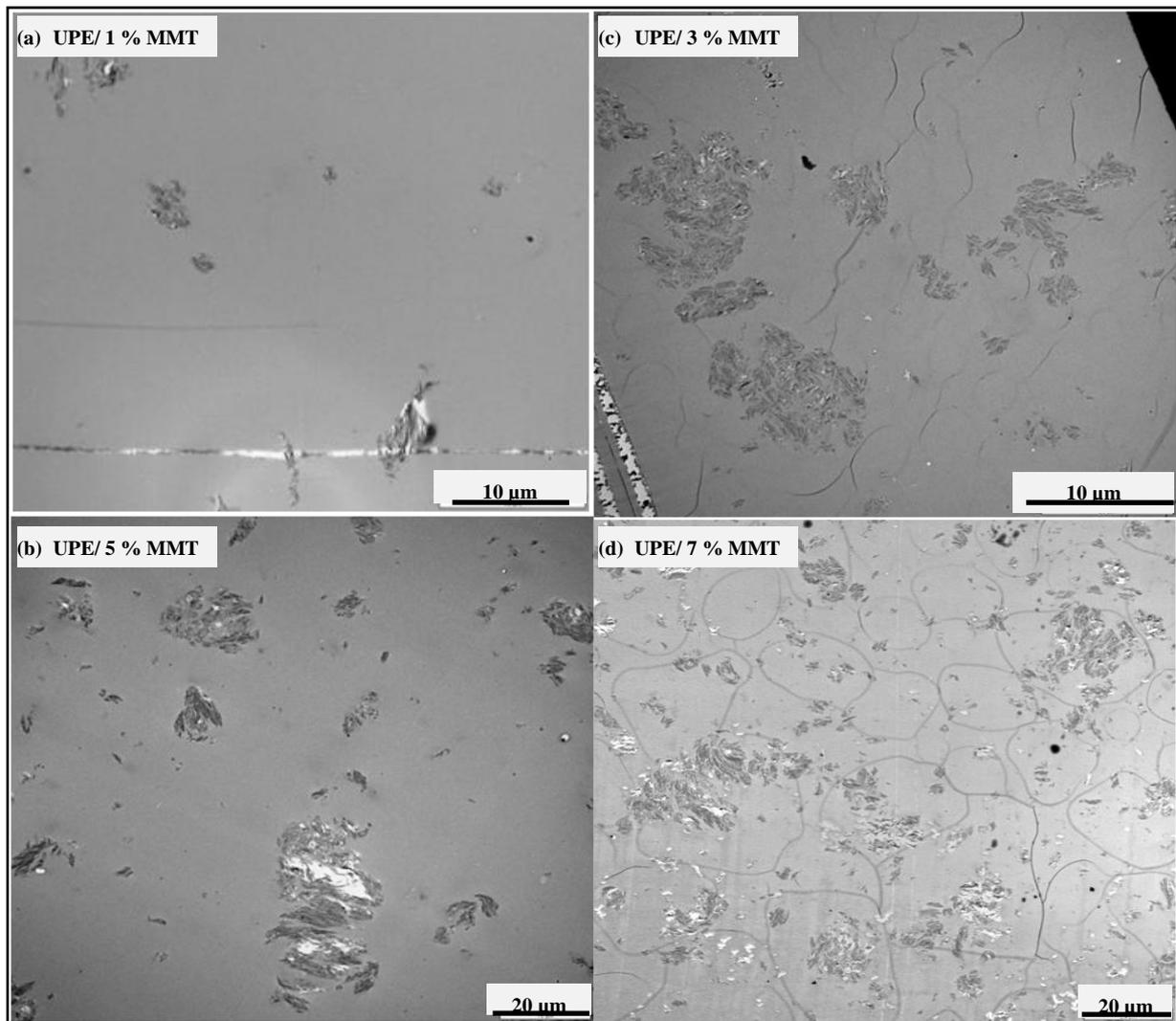
Fig. 2 TEM photomicrographs of UPE-based different MMT nanocomposites.

3.2 Fracture toughness and mechanisms

Fig. 3 shows a set of typical load-crack opening displacement (COD) curves obtained from the CT fracture tests for the cured neat UPE and UPE-based different MMT nanocomposites. All samples underwent unstable straight line crack propagation when the maximum loading is reached. The addition of 3 wt. % MMT to the UPE resin manifested the highest applied load before fracture of nanocomposite. The fracture toughness (K_{Ic}) values versus different clay loadings (1-9 wt. %) are illustrated in **Fig. 4**. The magnitudes of K_{Ic} of the filled UPE modestly improved after introducing MMT platelets. Three weight percent of MMT addition appears the highest K_{Ic} by 61 % improvement over the neat UPE. Further increasing of MMT induces lower K_{Ic} values due to the appearance of clay aggregates and the weak interaction between clay layers and the polymer resin. These results are in similar with those reported in previous study [18]. A comparison on K_{Ic} values for UPE-based different nanoparticles is reviewed in **Table 1** to better understand the effect of incorporating different nano-sized particles into the crosslinked UPE resins on their fracture toughness.
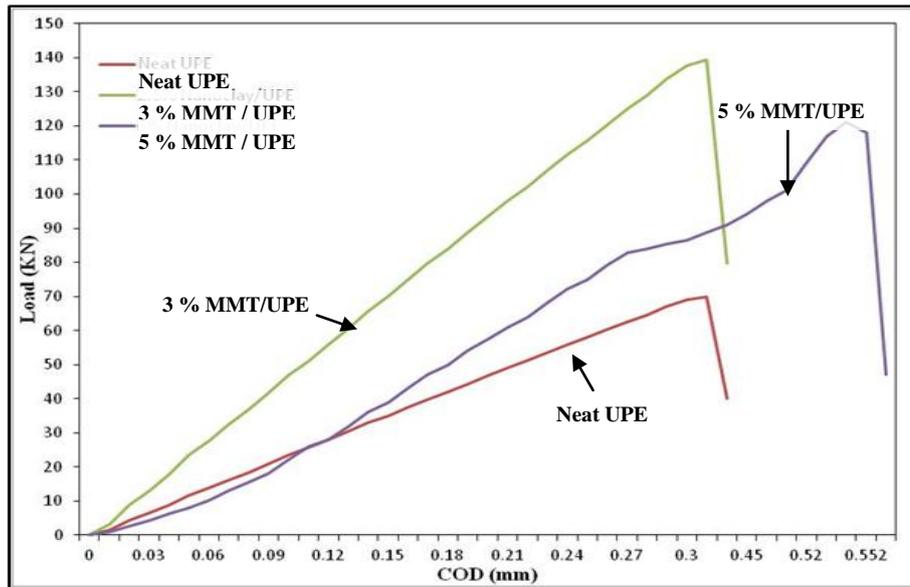
Fig. 3 The typical loads versus crack opening displacement (COD) curves.
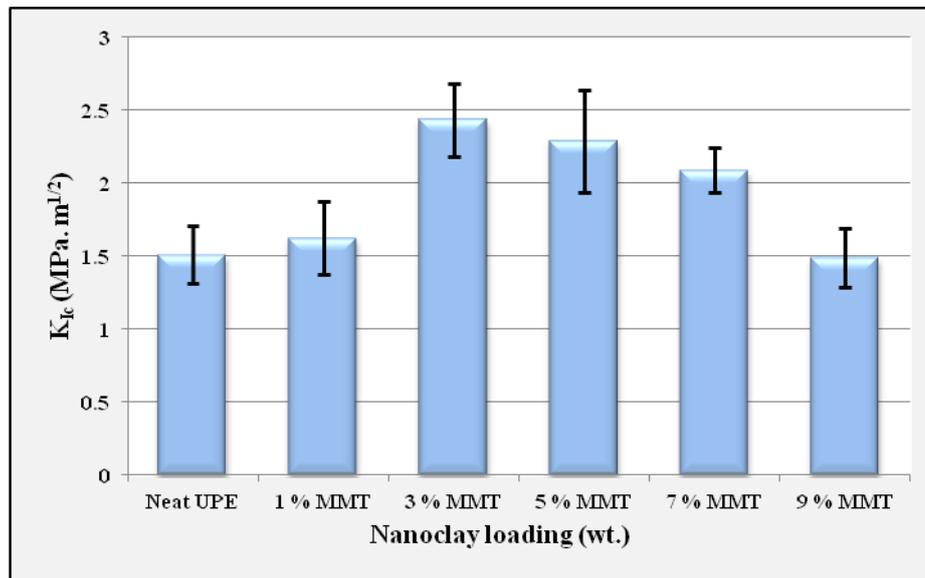
Fig. 4 Fracture toughness of the neat UPE and the UPE/MMT nanocomposites

Table 1 Fracture toughness for different nanoparticles-filled unsaturated polyester (UPE)

Materials	K_{IC} (MPa m$^{1/2}$) {test specimen type }	Comments and Reference
UPE/ 3 wt. % MMT	2.435 [1.51: Neat UPE] {CT}	The current study
UPE/ 1 wt. % TiO_2	0.85 [0.5: Neat UPE] {SENB}	Direct ultrasonification method, [8]
UPE / 40 % Bamboo fibre	1.2 [0.5: Neat UPE] {CT}	Laminating lay-up process, [19]
UPE / 1 wt. % Alumina	1.42 [1: Neat UPE] {SENB}	Prepared using direct mixing approach, [20]

CT: Compact tension, SENB: Single-edge notched bending.

SEM examination was used to identify the fracture mechanics and toughening mechanisms of UPE/MMT nanocomposites ruptured at ambient temperature. The fracture mode of the neat UPE (**Fig. 5a**) seems to be a highly brittle failure without crazing. Introducing clay particles to the networked UPE resin tends to form a localized shear yielding mechanism with a better absorbing of energy. The appearance of isolated shear bands as an energy absorption mechanism occurs due to introducing a second phase material into single-phase polymers. This mechanism is associated with a better plastic deformation [21].

The addition of nanoclay platelets to the UPE resin also causes in presence of crack pinning mechanism (see **Fig. 5c**). The fracture surface of 5 % MMT/UPE nanocomposite shown in **Figure 5d,** characterizes various directions of crack propagation on the cleavage surface. These directions of crack advancement oriented from top to bottom with irregular curved paths. Further addition of MMT to the thermosetting UPE induces mixed failure mechanisms of cleavage and void-coalescence mechanisms (**Fig. 5 e and f**).
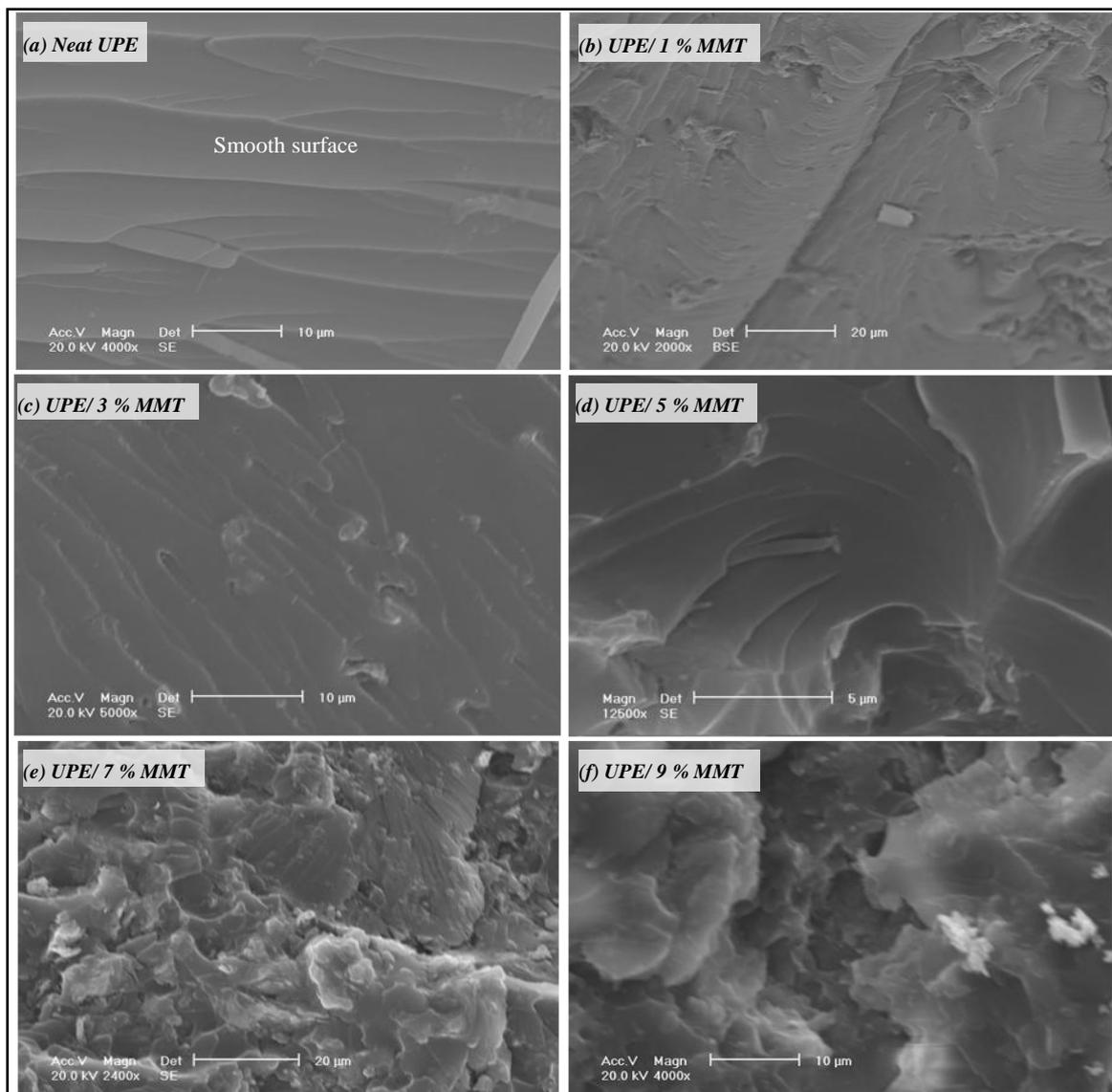
Fig. 5 SEM images showing the failure mechanisms of fracture surface obtained from the CT specimens for the neat UPE and UPE-based different MMT nanocomposites.

Conclusion

The nano-effect of clay nanoparticles (MMT) on the fracture toughness and toughening mechanisms of a highly crosslinked unsaturated polyester (UPE) was experimentally investigated. The morphological behaviour was described by TEM examination. The mode I fracture toughness of compact tension samples ruptured at room temperature was characterized according to ASTM D5045, and their fractured-surfaces were identified by SEM analysis. Intercalation structure of UPE/MMT nanocomposites is observed. The incorporation of MMT up to 3 wt. % MMT into the UPE resin showed the highest stress intensity factor (K_{Ic}) by a 61 % higher than the neat UPE. The deformation mechanisms of material transferred from a highly brittle fracture without crazing for the neat UPE to shear yielding deformation with plausible energy absorption for the nanocomposites.

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