

# 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 the micro- and nano-scale deformation and fracture behaviour of a crosslink unsaturated polyester (UPE)-based nanocomposites is presented. Nanocomposites from well-dispersed MMT and UPE are prepared by a combination of mechanical stirrer and ultrasonication process. Fracture toughness represented by critical stress intensity factor ( $K_{Ic}$ ) based on linear elastic fracture mechanics (LEFM) and compact tension (CT) configuration is evaluated. Morphological characteristics for all nanocomposites are examined by using TEM, and the fracture surface and the toughening mechanisms of materials are identified by SEM analysis. The morphological characterization showed an intercalation/partially exfoliation structure of UPE/MMT nanocomposite with a moderate enhancement in fracture toughness in nanocomposite. The UPE/ 3 wt. % clay nanocomposite had the highest  $K_{Ic}$  by a 61 % improvement over the neat UPE. The incorporation of clay nanofiller into the crosslink UPE demonstrated a shift in toughening mechanism from a highly brittle fracture for the UPE into shear bands and particles' debonding and decohesion for nanocomposites.

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

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## 1. Introduction

In general, polymer-clay nanocomposites (PCNs) properties are directly dependent on the state of nanoparticles dispersion 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 play a role in constraining the mobility of polymer matrix and delay the crack initiation and propagation and consequently induce reasonable mechanical strength and toughness [4, 5]. Fracture toughness is a critical mechanical property which characterizes the resistance of a material to crack propagation or to fracture. The toughness of materials is directly dependent on the energy dissipation, or on the energy absorbed in fracturing the part.

Unsaturated thermoset polyester resin (UPE) is one of the most used thermosetting polymers in different industrial applications due to its good mechanical properties and low cost and density [6]. However, the brittleness of this class of materials because of a radical polymerisation process between unsaturated prepolymer and styrene is one of their major drawbacks [7]. Hence numerous studies have been done on the introduction of second phase particles in them in order to control the toughness of thermoset polymers. For instance, Evora et al. [8] embedded small loadings of TiO<sub>2</sub> nanoparticles in the unsaturated polyester resin. The presence of the particles had the greatest effect on fracture toughness and tensile strength. Baskaran et al. [9] found that the fracture toughness of UPE resin has improved when 5 wt. % of Alumina (Al<sub>2</sub>O<sub>3</sub>) particles was added. Moreover, the investigation of the fracture behaviour and toughening mechanisms were done on the introduction

of multiwall carbon nanotubes in unsaturated polyester [10, 11], and halloysite nanotubes (HNTs) in epoxy [12]. It was found that the use of nanoparticulates with polymers are effectively increased their fracture toughness without sacrificing other properties such as strength, modulus and glass transition temperature.

As a result of the abovementioned works, several toughening mechanisms have been observed in polymers filled by micro- and nano-particles such as multiple craze-like banding with dilatation (dilation) [13]. Crack-pinning mechanism while the crack front bows out between the filler particles and remains pinned at the particles [14]. Microcracking mechanism is another mechanism in which the toughness increases due to the incorporation of rubber or nano-scale particles into polymers [7]. Localized shear yielding (or shear banding) mechanism which 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. However, increase in tendency to shear yield in nanocomposites may cause an increase in energy absorption prior to fracture [15]. Also, there is a massive shear-banding mechanism which occurs due to the reduction in yield stress by the stress concentration of the compliant nano-scale or rubber particles that facilitate shear yielding. Additionally, particle bridging (rigid particles) mechanism in which a rigid or ductile particle plays as a bridging particle that applies compressive traction in the crack wake and the ductile particle deforms plastically in the material surrounding the crack tip, which provides additional crack shielding. The particle bridging provides most of the improvements in toughness since it remain intact for some distance behind the crack-front [16]. In this study, the attempt is made to investigate the relationship between well-dispersed structure nanocomposites and the fracture behaviour of unsaturated polyester (UPE), and to understand to what extent clay particles can inhabit crack initiation, crack growth, and then enhance the fracture toughness of the networked UPE.

## **2. Experimental setup**

### **2.1 Materials and nanocomposites preparation**

Organoclay platelets (MMT, Cloisite<sup>®</sup> 30B, provided by Southern Clay Products, Inc. via Jim Chambers & Associates, Australia) were introduced into unsaturated polyester resin (UPE, AROPOL<sup>®</sup>-1472PLSE, Nupol, Australia having 45 % styrene) at different amounts (1, 3, 5, 7, and 9 wt. %). Nanocomposites from MMT/UPE were prepared by means of high 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 UPE weight and stirred manually for 1 min as per the instructions of the supplied company. Later, the mixture was poured in a special plastic moulds having the fracture specimens geometry, and cured at room temperature for 24 h and post cured at 60°C for 2h followed by 90°C for 2h 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 layers in the UPE polymer resin. Ultra-thin sections of approximately 70 nm in thickness were cut by diamond knife from the nanocomposites at room temperature and examined using a JEOL (JEM-1010) TEM instrument at an acceleration voltage of 100KV. Scanning Electron Microscope (SEM, Philip XL-30)

was utilized to identify the failure modes and toughening mechanism. SEM observations were carried out on the fracture surfaces of compact tension fracture specimens after sputter coating with a thin layer of platinum to increase electric conductivity.

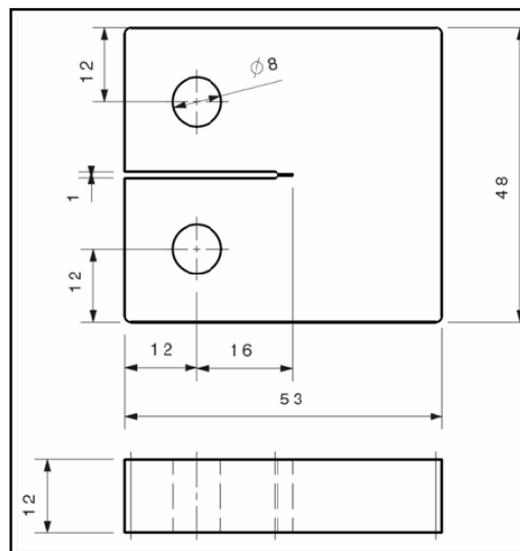
### 2.3 Fracture mechanisms study

The stress intensity factor ( $K_{Ic}$ ) and the strain energy release rate ( $G_{Ic}$ ) of the cured neat UPE and the UPE/nanocomposites were evaluated using the compact tension (CT) configurations. The CT fracture specimens were prepared according to ASTM D5045 as shown in **Fig. 1**. A pre-crack was generated by tapping a fresh razor blade into the notch tip with a drop weight to maintain an accurate  $K_{Ic}$  values. 5 mm/min is adapted as loading rate and the following relationships are used to measure the  $K_{Ic}$ :

$$K_{Ic} = \frac{P_Q}{B W^{3/2}} \cdot f\left(\frac{a}{W}\right) \quad (1)$$

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

Where  $P_Q$  is the load determined from the load-displacement curve, B the specimen thickness. The calculated  $K_{Ic}$  values were checked against:  $B, a, (W-a) > 2.5 (K_{Ic}/\sigma_y)^2$  (3)



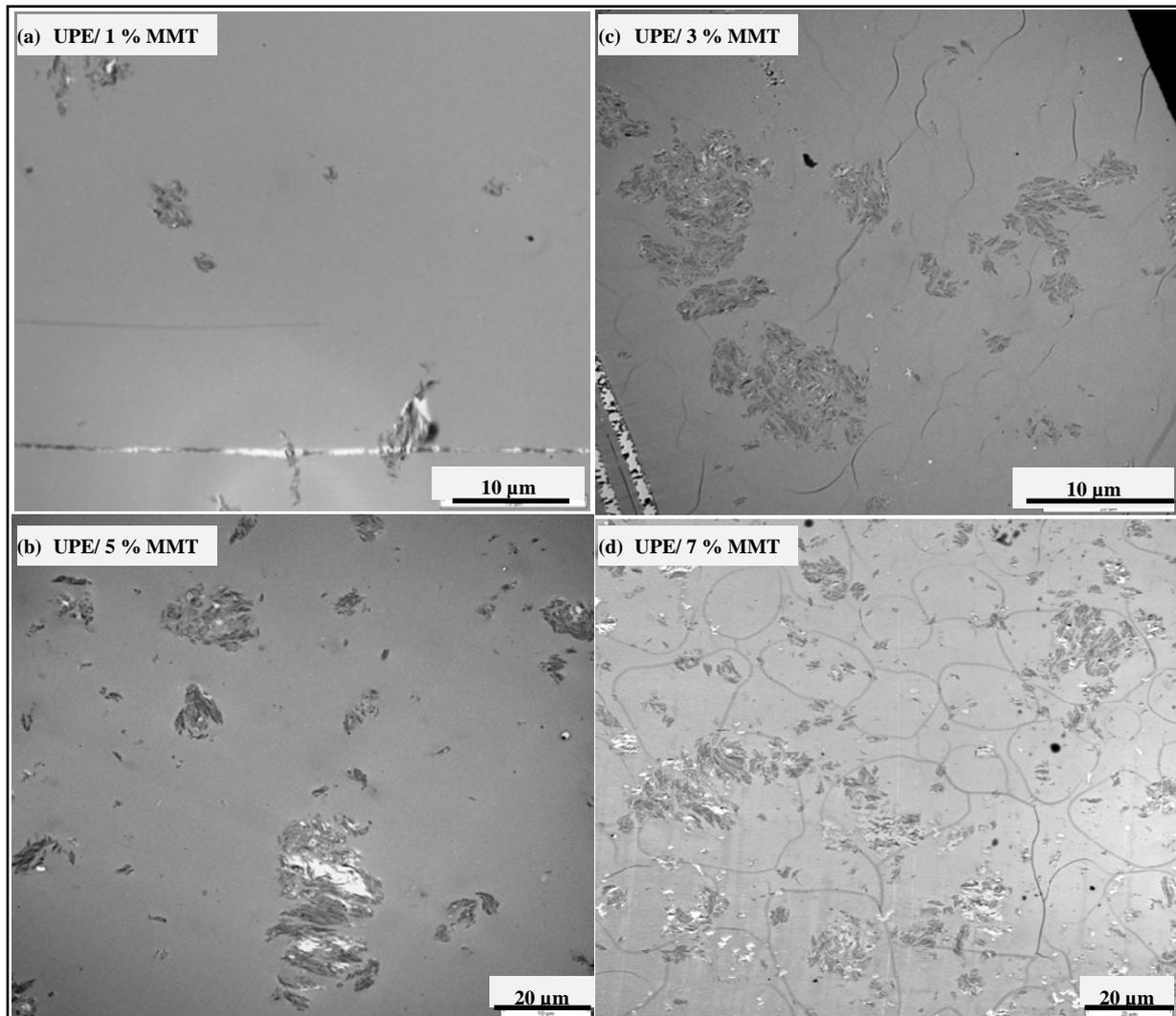
**Fig.1** Dimension of the compact tension (CT) specimen.

## 3. Results and discussion

### 3.1 Morphology

**Fig. 2** shows representative TEM micrographs of the cured unsaturated polyester (UPE) filled by different nanoclay loadings. From the figure, it can be noticed that a good dispersion of clay layers in the polymeric matrix with a plausible intercalation between nanoclay and the polymer chains has achieved by using direct high shear mixing and sonication. However, several agglomerates of micro-particles with thickness of 100 nm or greater are created at higher nanoclay loadings can also

be seen in **Fig. 2c**. The appearance of these clusters are attributed to the structure of clay that composed of platelets with an inner octahedral layer surrounded by two silicate tetrahedral layers and because of the natural state of clay which exists as stacks of many platelets at several hundred nanometres long and wide separated by an interlayer distance of  $\sim 1\text{-}3$  nm [5, 17].



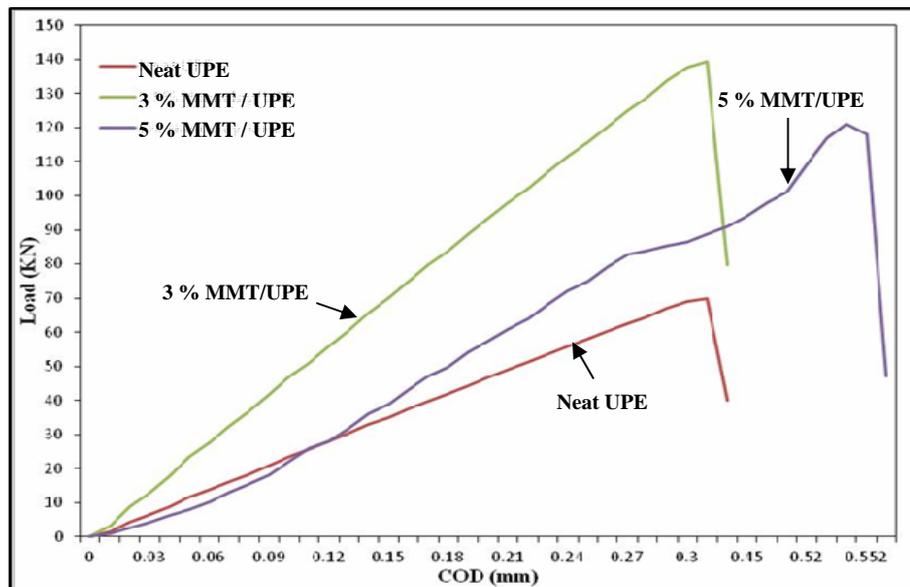
**Fig. 2** TEM photomicrographs of UPE filled by different clay nanocomposites.

### 3.2 Fracture toughness and mechanism

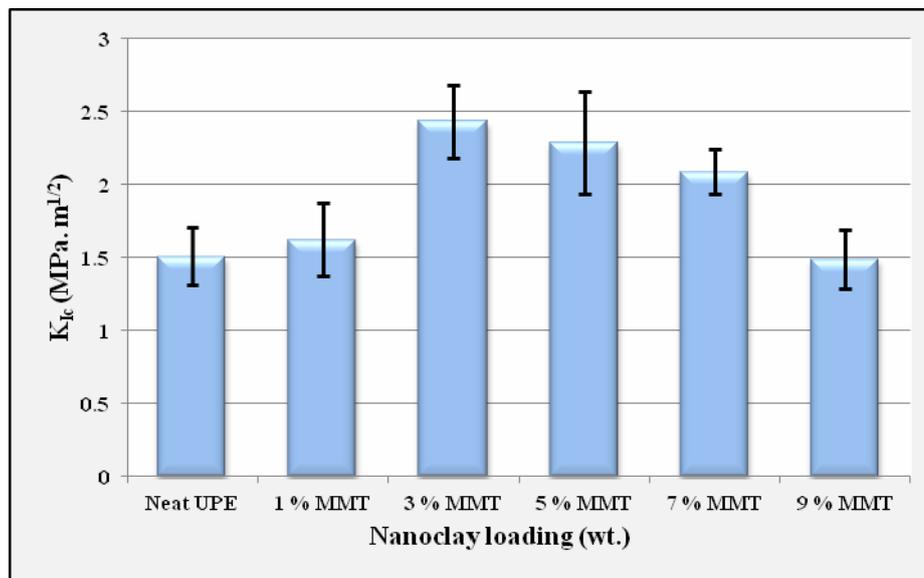
**Fig. 3** shows a set of typical load-crack opening displacement (COD) curves obtained from the CT fracture tests for the cured neat unsaturated polyester (UPE) and UPE filled by different contents of 3 wt. % and 5 wt clay nanocomposites. It can be found that all samples have undergone unstable crack propagation with a straight line when the maximum load is reached due to the high crosslink density of the UPE and its prone to fast fracture. Meanwhile, the UPE-based 3 wt. % MMT nanocomposites manifested their ability to carry higher loads with lesser displacements (COD) whereas the addition of 5 wt % MMT showed lower loads with higher displacements compared to the neat UPE resin.

The fracture toughness values ( $K_{Ic}$ ) versus different clay loadings (1-9 wt. %) with respect to the

neat resin value were illustrated in **Fig. 4**. The magnitudes of  $K_{Ic}$  of the modified UPE have modestly improved after nanoclay platelets were incorporated where the introduction of 3 wt % MMT content showed the highest  $K_{Ic}$  value by 61% higher than the neat UPE. However, these values have decreased at higher nanofiller contents due to the appearance of clay aggregates and the weak interaction between clay layers and polymer resin thereof with the increase of clay contents. These results are in conformance with these reported in the literature [18]. A comparison of different studies where  $K_{Ic}$  values have been obtained is addressed in **Table 1**. From the table, it can be noted that the incorporation of even low levels of nanoparticle into unsaturated polyester resin resulted in noticeable changes in fracture toughness of the produced materials over the neat resin due to the presence of nanoparticles.



**Fig. 3** Typical load vs. crack opening displacement (COD) curves.



**Fig. 4** Fracture toughness of the neat UPE and the UPE/MMT nanocomposites

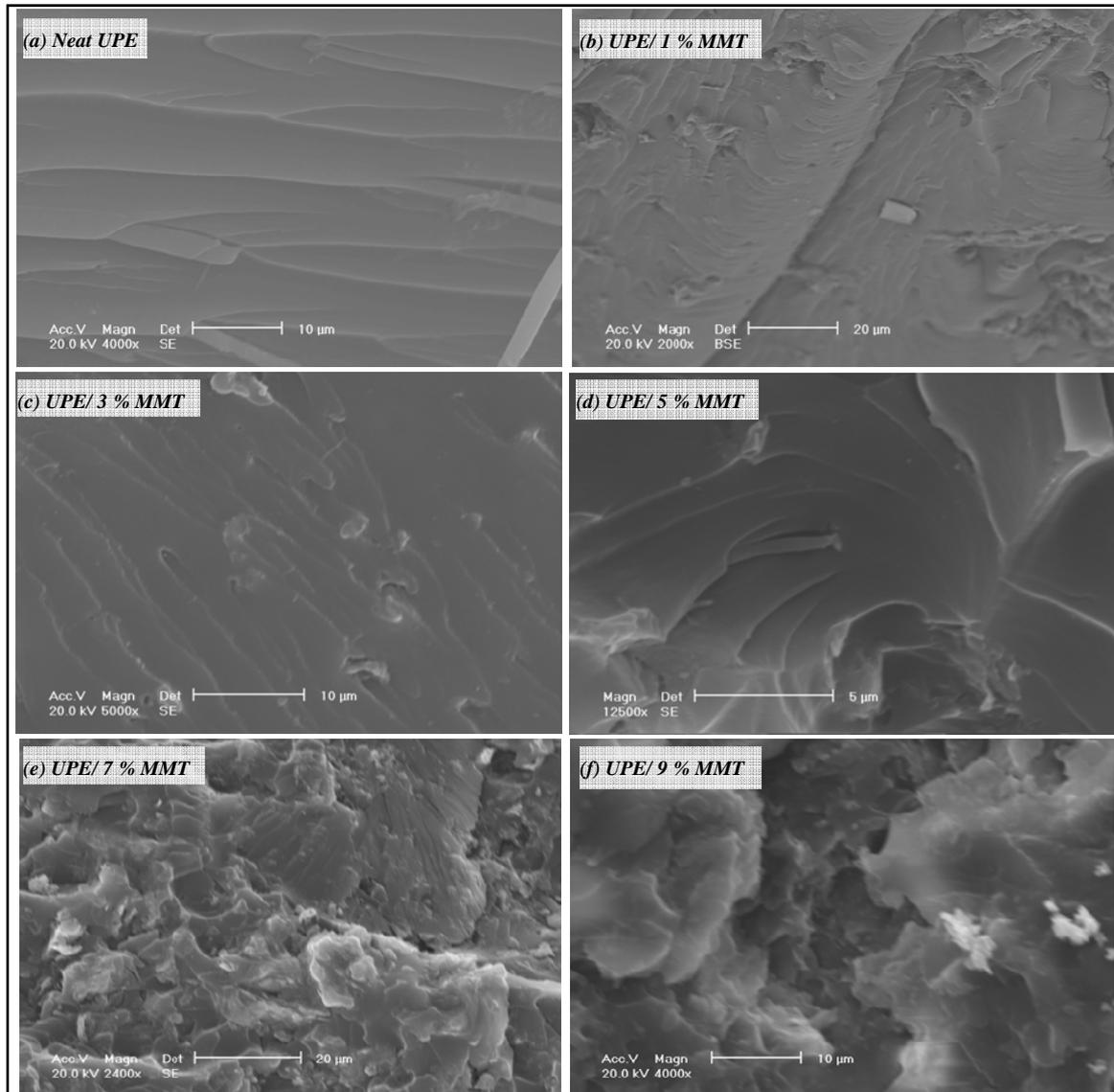
**Table 1** Fracture toughness for different nanoparticles-filled unsaturated polyester (UPE)

Materials	$K_{IC}$ (MPa m <sup>1/2</sup> ) {test specimen type }	Comments and Reference
UPE/ 3 wt. % MMT	2.435 [1.51: Neat UPE] {CT}	The current study
UPE/ 1 wt.% TiO <sub>2</sub>	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,

The fracture modes and toughening mechanisms in the thermosetting unsaturated polyester (UPE) toughened by clay nanomaterials ruptured at ambient temperature are identified by using SEM analysis as shown in **Fig. 5**. The SEM micrograph (**Fig. 5a**) showed the failure mechanism of the fracture surface of the neat UPE is a highly brittle failure mode without crazing. However, the introduction of clay particles into the networked UPE resin associated with better absorbing of energy, leading to localized shear yielding. Similarly, the authors in [21] referred to the appearance of isolated shear bands as an energy absorption mechanism accompanied with better plastic deformation in the failure mode of polymer having a second phase. Furthermore, the addition of nanofiller into the UPE resin resulted in particle pinning of the crack (**Fig. 5c**) leaving behind tail-like structure. SEM image (**Fig. 5d**) of the fracture surface of UPE-5 wt. % clay nanocomposite depicts various crack propagation directions on the cleavage surface. The direction of crack advancement is from top to bottom with an irregular curved path. Further clay nanoparticles (> 5 wt. % MMT) incorporation into the crosslink UPE resin accompanied with mixed failure mechanism represented by cleavage and void-coalescence as shown in **Fig. 5 e and f**.

Additionally, in order to fully understand the nano-effect of clay particles on the fracture surface of UPE/clay nanocomposite, SEM images with different magnifications (**Fig. 6**) for the fracture surface of UPE- 3 wt % MMT nanocomposite were taken. This sample was chosen because of its relative higher fracture toughness. **Fig. 6a** illustrates the fracture topography at low magnification, showing the crack-initiation and crack-propagation zones. Another SEM view (**Fig. 6b**) at low magnification, showing the first zone of crack growth (zone 2A), in which the formation of microcracks can be noted. The tearing of the connected material (the particle-matrix interface) and decohesion occurred at the weakest locations in zone 2A (**Fig. 6c**) [22]. Comparatively, zone 2B (**Fig. 6d and e**), showing a similar flat cleavage along the fracture planes. The intergranular fracture mechanism or decohesion can also be observed in zone 2c (**Fig. 6f**).

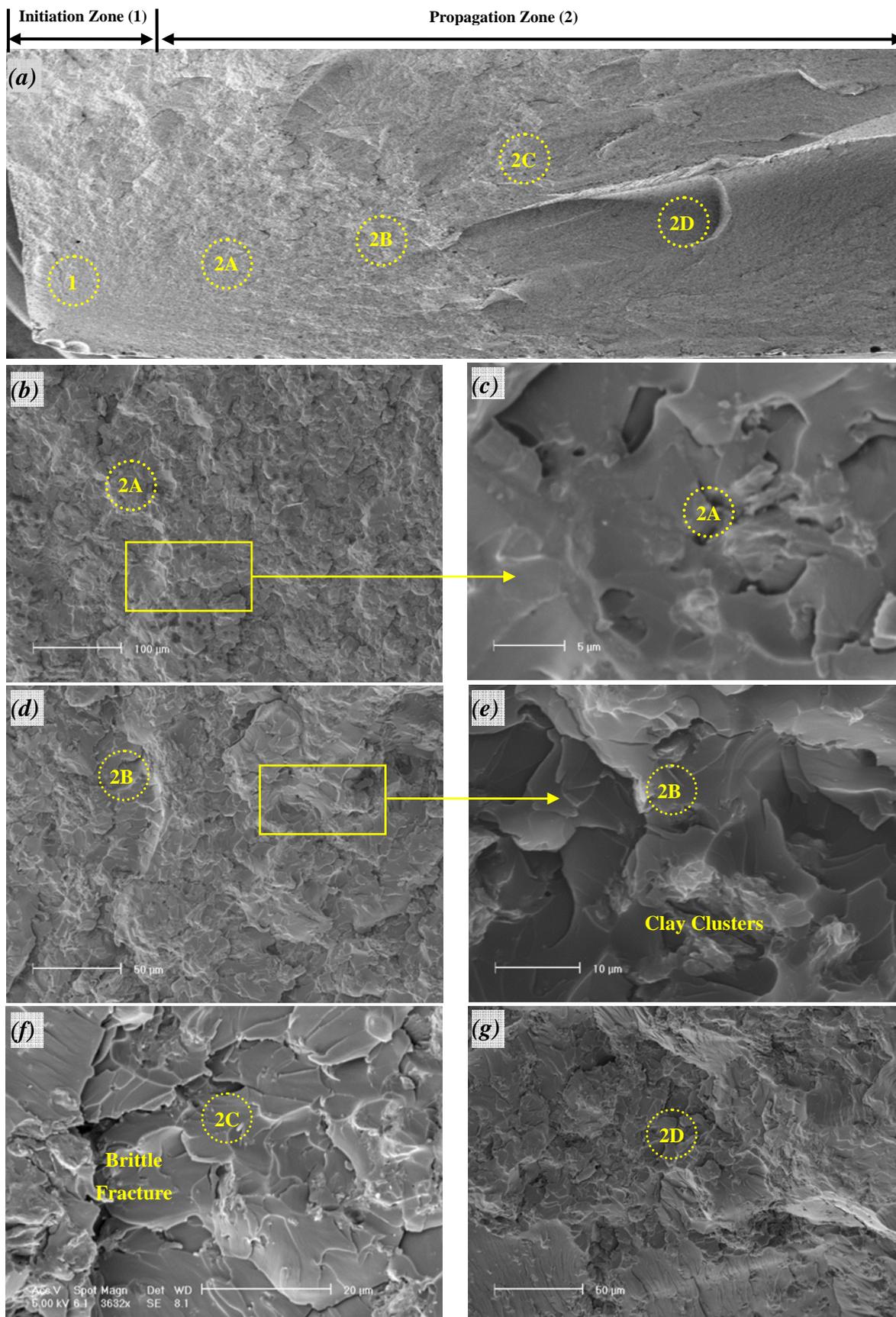


**Fig. 5** SEM micrographs showing the failure mechanisms of the fracture surface obtained from the compact tension specimens of the neat UPE and the UPE-filled by different clay nanocomposites.

## Conclusion

The nano-effect of clay nanoparticles on the fracture toughness and toughening mechanisms of fully crosslink thermoset unsaturated polyester (UPE) was experimentally investigated in this study. The morphological characterization was described by using TEM examination and the failure modes of the fracture surfaces of compact tension samples ruptured at room temperature was also identified by using SEM analysis. An intercalation structure with a uniform dispersion of UPE/clay nanocomposites prepared by direct high shear mixing and sonication process were observed. The incorporation of MMT into UPE resin induced higher fracture toughness where nanocomposites containing UPE and 3 wt. % MMT showed a higher stress intensity factor ( $K_{Ic}$ ) by a 61 % increase over the neat UPE. The role of nanofiller on the deformation mechanism demonstrated a shift from

highly brittle fracture mode without crazing for the neat UPE into shear yielding deformation mechanism with plausible energy absorption for nanocomposites.



**Fig. 6** SEM micrographs of the fracture surface of UPE-3 wt. % clay nanocomposites ruptured at room temperature showing initiation and different crack propagation zones.

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