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Cluster size effect in hardness of nanoclay/epoxy composites

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Abstract

The mechanical and thermal properties of nanoclay polymer composites have been experimentally investigated over the last decade. Most of the research has been focused mainly on the control of their interplanar structures, which govern the global properties of the composites. In reality, these structures (both exfoliated and intercalated patterns) are hardly achieved through the use of conventional manufacturing process for plastic products. Different sizes of clusters mixed by nanoclays and matrix would be easily formed, particularly in the extrusion of polymer-based components. This paper experimentally studied the hardness and interlaminar shear properties of nanoclay/epoxy composites with different amount of nanoclay content, which formed different sizes of nanoclay/epoxy clusters after mixing in an extruder. The results showed that the micro-hardness of the composites could be enhanced when a small amount of nanoclay was added into the epoxy. However, there was an optimal limit in which the hardness was dropped by continuously increasing the nanoclay content. Microscopic observation on the fracture surfaces showed that the size of the clusters varied with the amount of nanoclays used in the composites. Although previous literatures have reported that the use of nanoclays in polymer-based composites could enhance their mechanical properties, the interlaminar shear test indicated that the short beam shear strength of the composites decreased after adding the nanoclays into the matrix.
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1. Introduction

Recently, the developments on mechanical, bio-medical engineering and aeronautical components have been miniaturised into different scale levels. Due to the increasing need of micro/nano-sized devices and structural members in the nano-tech and space industries, the development of new advanced materials, which are able to sustain their strength in any extreme temperature and chemical environments without being mechanically, chemically or thermally degraded and to be manufactured to high degree of defect-free properties, particularly for space and automotive applications becomes a new challenge in the current decade.

In past few years, National Aeronautics and Space Administration (NASA) and John Space Centre (JSC) have

driven breakthrough technologies to expand human exploration of space [1]. One of the most important focuses in achieving this goal is to develop new materials, which possess strength-to-weight ratio that far exceeds any of today's materials. Nanocomposites have emerged as very efficient strategy to upgrade properties of synthetic polymers to the level where performance of these nanocomposites largely exceed the ones of conventional composites. Veprek and Argon [2], Veprek and Jilek [3] and Veprek [4] have found that nanocomposites exhibit superior hardness and elastic properties, and high level of thermal stability. Carbon nanotube and nanoclay composites have been recognised as the best nano-fillers for the composites to fulfil aforementioned requirements [5–7]. Successful use of nanotube/polymer and nanotube/metal composites in space applications is highly dependent on the structural integrity and mechanical performances of the composites in extreme low temperature, heat and radiation, and vacuum environments, particularly for reusable launch vehicles [8,9]. However, many literatures have reported that the nanotubes

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have a poor bonding strength to aerospace-used polymer matrices because of their perfect hexagonal atomic architecture on the nanotubes' surface [10–13]. It has been proofed that a good bonding strength between internal reinforcements and matrix is one of the dominant factors that attribute the outstanding mechanical properties of advanced composite structures [14–17]. Adding chemical catalysts to enhance the bonding strength of composite systems may damage the carbon–carbon bond that attributes to extraordinary mechanical and electrical properties of nanotubes.

Recent researches have found that commercial organo-clays (layered silicates such as montmorillonite which has a fairly large aspect ratio, hereafter called 'nanoclays') could be used to make aerospace epoxy nanocomposites, which possess excellent mechanical strength and low coefficient of thermal expansion with relatively low cost and ease of fabrication [18,19]. Companies such as Nanocor, Southern Clay Products and Zhejian Fenfhong Clay Chemicals Co. in the US, Japan and China have patented technologies for production of nanoclays. Several polymer companies both in the US and Japan are producing nylon nanocomposites for automotive and packaging applications. A few weight percentages of nanoclays with a thickness of about 1 nm in polymer boots the heat distortion temperature by 80 °C making possible structural applications under conditions where the pristine polymer would normally fail [19–21]. The existence of silicate platelets inhibits the polymer chain rotation that influences the mechanical and thermal properties of the nanocomposites. In some extents, these platelets could inhibit the crack propagation due to the formation of micro-voids when the nanocomposites are under-stressed, thus increasing the fracture toughness [22]. Alexandre and Dubois [19] and Lau et al. [23] have proofed that the mechanical and thermal properties of composites could be modulated by nano-fabrication process of intermetallic compounds. A latest literature also revealed that inter-calated and exfoliated morphologies of nanoclay/polymer composites are highly affected by the manufacturing time and temperature, which in turn influenced the cross-linking interaction of polymer. The amount of nanoclays inside the polymer also appeared different with mechanical, thermal and electrical properties of nano-composites. The per-meability of water, oxygen and other gases of the nanoclay composites also decreased making these composites ideal for building up advanced composite fuel tanks for tomorrow's reusable launch vehicles. Timmerman et al. [24] clearly demonstrated that the number of transverse cracking of carbon fibre/epoxy laminates as a response to cryogenic cycling was significantly reduced when nano-fillers were used. The development of these polymer-based nanocomposite materials enables to make advanced struc-tures with high strength and thermal stability. It thus minimises the risk of geometrical and thermal distortions due to the changes of ambient temperature and therefore maintains the aerodynamic profiles of the structures. Due to

layered silicate nanocomposites achieving composite prop-erties at much lower volume fraction of reinforcements, they avoid many of the costly and cumbersome fabrication techniques common to conventional fibre-reinforced poly-mer materials [18].

An appropriate addition of a small amount of nanoclays, typically in the range of 3–5 wt%, could provide an efficient upgrade on the mechanical and thermal performances of conventional polymer-based composites [25,26]. In an industrial point of view, these lightest particles could be effectively used to produce high stiffness and thermal stability structural components with having low cost and no subjection to weight penalty. Recently, many product manufacturing organisations and commercial companies have started to deeply investigate the possibility of producing this type of nanocomposites in order to fabricate plastic products with high strength and low thermal distortion [27–29]. However, these properties are highly dependent on the dispersion property and interplanar arrangements of nanoclays inside the composites [30].

It has been reported that the impact and wear resistance, as well as fracture toughness of advanced composites, could be improved by mixing an optimal amount of nanoclays [31–33]. The optimal amount of the nanoclays in the composites is dependent on the particle size and shape, homogeneity, dispersion property and interfacial bonding properties between the particles and matrix. Practically, both exfoliated and intercalated planar structures can only be found in laboratory studies, which is in fact difficultly achieved during product moulding processes. To the best knowledge of the authors to date, no detailed report has been published presently to study the dispersion properties of nanoclays in polymer-based materials after extrusion. Practically, the formation of micro-size nanoclay/polymer clusters always appears in the composite. These clusters, in turn, would influence the intrinsic material and mechanical properties of the composites. To look at the cluster size effects to the properties of the composites, micro-hardness and interlaminar shear tests were conducted in this work. Different amounts of nanoclays were added into epoxy-based resin to form nanoclay/epoxy composites. The micro-hard-ness of testing samples was examined by using micro-hardness tester (Vicker type). The microscopic observation on the fractured surface of these samples was also conducted to measure the cluster size and study their effect to the hardness of the composites. An interlaminar shear test was also carried out to investigate the short beam shear properties that have not been discussed previously elsewhere of the composites. The effect co-relating to the size of nanoclay/epoxy clusters was also discussed in this paper.

2. Experimental investigation

Araldite GY 251 epoxy resin and hardener HY 956 in the ratio of 5:1 were used to form base polymer materials.
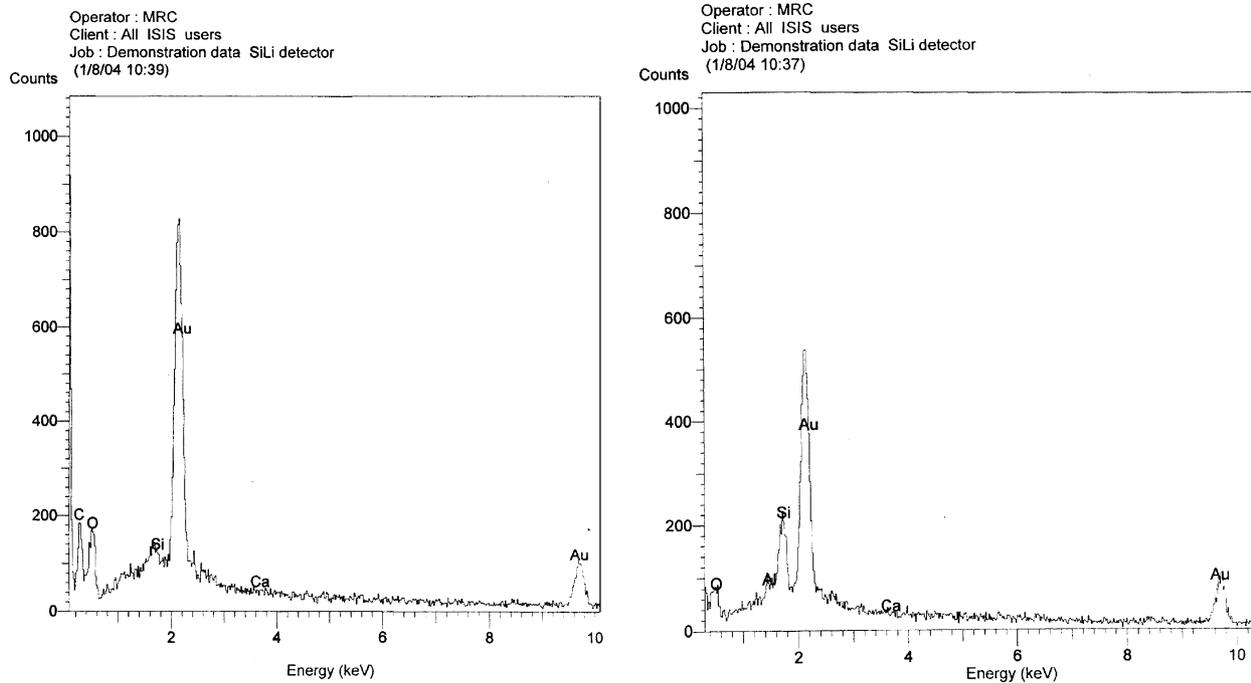
Fig. 1. Diagrams captured from EDX: location away from the cluster (left) and the center of the cluster (right).

Nanoclay particles (SiO_2, Nanolin DK1 series from the Zhejiang FH Nanoclay Chemical Technology Company) were then added into the materials to form nanoclay/epoxy nanocomposites. The mean diameter, density and moisture content of the nanoclays were 25 nm, less than 3% and 0.45 g/cm^3 with more than 95% of SiO_2, respectively. At the beginning of the nanocomposite manufacturing process, the predetermined amount of nanoclays was added into the resin by mechanical stirring and followed by sonication for 1 h at room temperature in order to provide a uniformly dispersed nanoclay/epoxy uncured mixture. The hardener was then added into the mixture by appropriate ratio followed by mechanical stirring and afterward vacuuming for another 24 h. This step was to remove air-bubbles that were trapped inside the nanocomposites before curing. Six types of sample were made in this study; they were pure epoxy (0 wt% nanoclay content), and nanocomposites with 2, 4, 6, 10 and 15 wt% of nanoclays.

Micro-hardness test was conducted to all samples and a total of 10 indentation points were measured on the samples' surface. Micro-hardness tester (FM-7E) of the Future-Test Corporation from Tokyo, Japan was used in the test. To increase the accuracy of measurement, all samples' surfaces were well polished using high-grade sandpapers prior to the test. To observe the dispersion and mixing properties of the nanoclays in the nanocomposites with different amounts of nanoclay content, all samples were broken into two pieces by undergoing a bending test. The fractured surfaces were then examined by using Leica Stereoscan 440 model scanning electron microscopy (SEM). X-ray spectroscopy (EDX) was also used to verify the validity of the location of the nanoclay particles (Fig. 1).

Since most of the previous study was mainly focused on the tensile and bending strengths of nanotube/polymer composites, the interfacial shear properties of these composites have not yet been investigated elsewhere. In our work, similar samples as for the micro-hardness test were also made for interlaminar shear test to investigate the short beam shear strength of the nanocomposites and study the effect to their cluster sizes. The size of the samples was 10 mm $\times$ 10 mm $\times$ 2 mm.

3. Results and discussion

Table 1 shows the experimental measurements of micro-hardness of the nanocomposites with different nanoclay

Table 1
Results of the micro-harness measurements at different nanoclay compositions

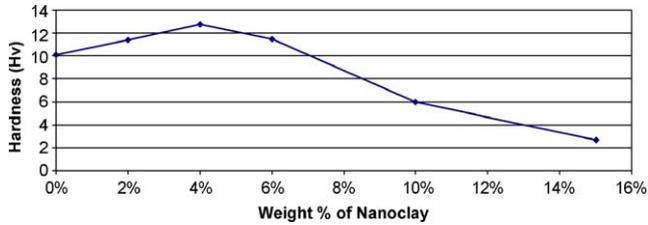| Hardness (Hv)	0%	2%	4%	6%	10%	15%
1	9.9	10.8	11.7	11.7	8.2	1.5
2	9.2	11.6	12.9	10.4	5.1	1.5
3	9.6	10.1	11.9	11.1	5.5	2.3
4	9.4	11.9	14.4	10.9	6.2	3.5
5	9.5	12.3	12.8	12.9	6.1	5.1
6	10.1	11.8	12.7	12.5	6.1	2.9
7	10.6	10.1	12.1	10.9	4.8	3.2
8	11.4	12.2	13.1	11.8	5.3	2.6
9	10.5	12	13	12	6.1	2.2
10	10.6	11.3	12.9	10.2	6.3	2
Average	10.08	11.41	12.75	11.44	5.97	2.68
Maximum	11.4	12.3	14.4	12.9	8.2	5.1
Minimum	9.2	10.1	11.7	10.2	4.8	1.5

Fig. 2. Average value of the micro-hardness test at different weight % of nanoclay.

contents. An average hardness was calculated by 10 indentation measurements and a plot of the results of each type of samples is shown in Fig. 2. At the beginning, it is obvious that the hardness increases with increasing nanoclay content. The maximum hardness was measured where the nanoclay content reached 4 wt%. A decline of the hardness also appears on further increasing the nanoclay content; the hardness decreases in a drastic manner from 12.75 Hv (4 wt% of nanoclay) to 2.68 Hv (15 wt% of nanoclay). In most previous literatures, it has been indicated that adding a small amount of nanoclays into polymer-based materials could potentially enhance their strength, like hardness of the current samples with the nanoclay content less than 4 wt%. However, it is also reasonable to believe that it should have an optimal limit since the physical properties between these nano-structural materials and matrix are different. In the current study, it was demonstrated that the hardness was dropped if the amount of the nanoclays was beyond 4 wt%. Besides, for the sample with more nanoclay content, the time required for solidification was also longer as well as the surface of the sample was relatively soft compared with other samples with lower nanoclay contents. It was suspected that the nanoclays might retard the chemical reaction, and so cause incomplete curing process of the composites. For all samples with high nanoclay content, the matrix might not be fully cured. By looking at the trend presented in Fig. 2, it is worthwhile to study in detail the physical mechanism that governs this contrary effect in hardness of the nanocomposites.
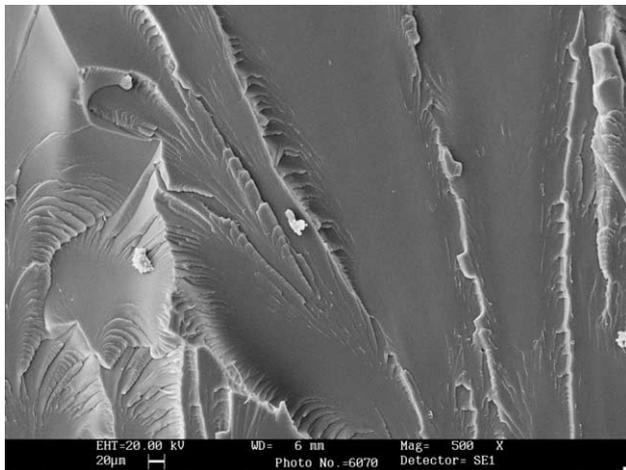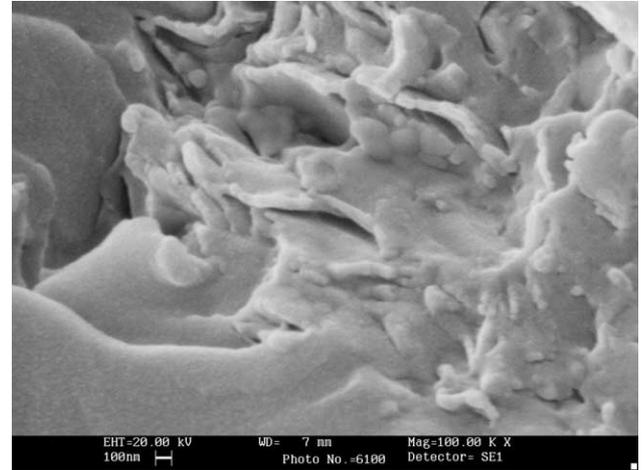

Fig. 4. SEM photograph of 4 wt% of nanoclay/epoxy composite.

In Figs. 3 and 4, morphological observations on the fractured surfaces of the nanoclay/epoxy samples are shown. It is obvious that clusters were formed in the sample with 4 wt% nanoclay particles. The average diameter of the clusters measured throughout the whole sample at different locations was about 125 nm. The clusters were evenly distributed throughout the sample, which reflected that those small nanoparticles intended to agglomerate with each other. This phenomenal observation denoted that those nanoclay particles could not be easily dispersed although it was subjected to sonication. This might be due to the fact that the viscosity of the room temperature cured resin could not be low enough to allow the diffusion of monomers into planar structures of the nanoclay particles. This agglomeration may be caused during the curing process of the composites. The nanoclay particles moved toward others and partly bonded with epoxy matrix to form clusters. The size of the clusters was dependent on the amount of nanoclay particles inside the uncured matrix.

In Fig. 5, a micrograph of the sample with 15 wt% of nanoclay particles is also shown. Comparing with Fig. 4,

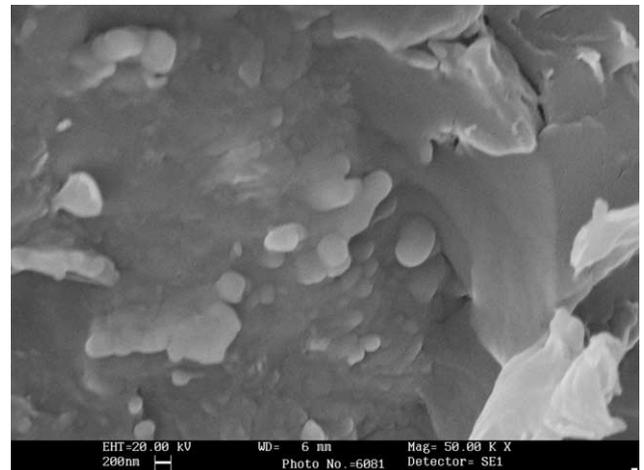Fig. 3. SEM photograph of pure epoxy.

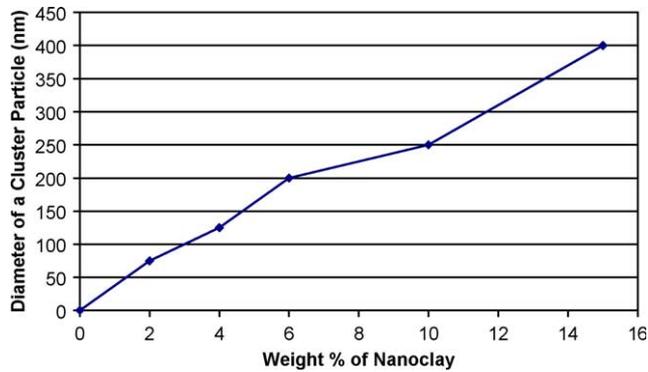Fig. 5. SEM photograph of 15 wt% of nanoclay/epoxy composite.

Fig. 6. Variation of the cluster size at different wt% of nanoclay.

the size of the clusters was apparently bigger than that of the one with only 4 wt% nanoclay particles. The diameter of the sample with 15 wt% of nanoclay particles measured from the SEM was about 400 nm. In fact, this phenomenon is explainable. As the wt% of the nanoclay particles increases, the free volume allows for nanoclay particles to move around would be decreased. Therefore, the mechanical stirring and ultrasonic separation techniques cannot be effectively used to separate the agglomerations of the nanoclays, as higher the wt% of nanoclay particles in the epoxy resin, the less the free volume for each nanoclay particles to live in. At the same time, the cross-link density of the nanocomposites then increased and it therefore resulted in increasing the tendency for the nanoclay particles to form pairs or clusters [10]. As the amount of nanoclay particles increases in the composites, the inertia for the nanoclay particles to form agglomeration is also increased. Therefore, larger clusters of nanoclay would be easily formed. The average cluster sizes of nanocomposites with different amounts of nanoclay particles are plotted in Fig. 6. The cluster size increased with increasing the wt% of the nanoclay particles.

In Fig. 7, there is a long plastic yielding zone appearing in a pure epoxy sample after the interlaminar shear test. From the long yielding zone of the pure epoxy, it is obvious that the fracture energy consumption and toughness of the pure epoxy are quite high. However, it is apparently different compared with others after adding nanoclay
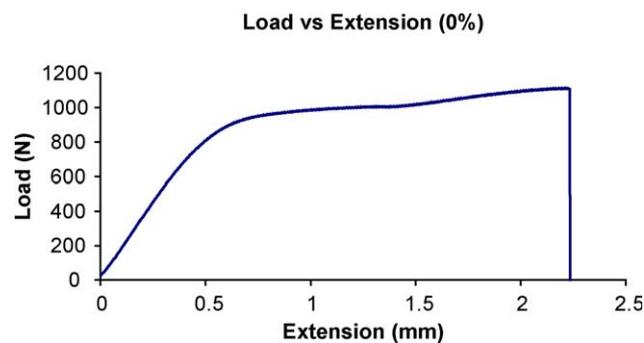

Fig. 7. Load–deflection curve extracted from the interlaminar shear test of pure epoxy.
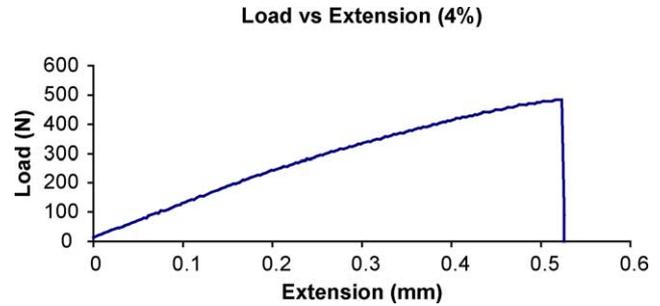

Fig. 8. Load–deflection curve extracted from the interlaminar shear test of nanocomposites with 4 wt% of nanoclay particles.

particles. In Figs. 8 and 9, the load–deflection relationships captured during the interlaminar shear test of nanoclay/epoxy samples are shown. In these figures, it is obvious that the ductility of the epoxy-based samples dropped after mixing with nanoclay particles. In Fig. 8, no plastic deformation of a nanocomposite with 4 wt% of nanoclays is shown. However, for another sample with 15 wt% of nanoclays, the sample became softer and the short beam shear strength is also lower than the one with 4 wt% of nanoclay particles and pure epoxy.

Although Section 2 shows that the hardness of nanoclay/epoxy composites could be enhanced and the maximum hardness could be achieved by adding 4 wt% nanoclays into epoxy composites, the results from the interlaminar shear strength test showed that the short beam shear strength of all nanoclay/epoxy composites decreased. In the 4 wt% of nanoclay sample, there were more tiny nanoclay clusters as shown in Fig. 4. These tiny nanoclay clusters of about 125 nm in diameter would squeeze into the polymer chains of the epoxy and loosen the interaction between them. In addition, from the crack surface of the sample, the clusters' shape appeared like a sphere. From the mirror-like interface between the nanoclay clusters and the epoxy, it reflects that the interfacial bonding strength between the nanoclay clusters and the epoxy was weak. As a result, when there is an external force applied, debond at the interface between the nanoclays and matrix would easily occur. Hence, the short beam shear strength of the epoxy decreased with
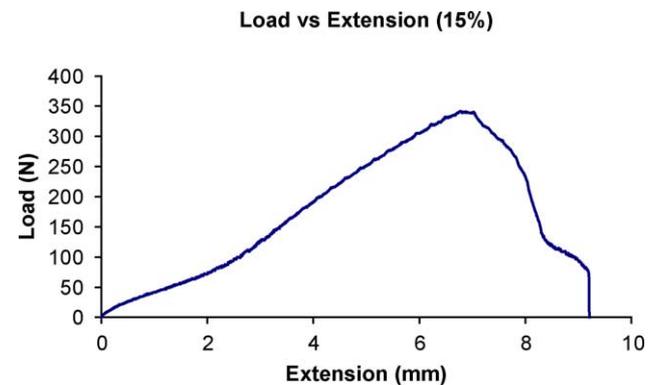

Fig. 9. Load–deflection curve extracted from the interlaminar shear test of nanocomposites with 15 wt% of nanoclay particles

nanoclay added. At 15 wt% of nanoclay, the load–deflection behaviour appeared in a strange way as shown in Fig. 9. It does not possess a clear fracture point after the maximum load appears. This is due to the fact that the amount of nanoclay content has been greatly increased and the mechanical behaviour is determined by the nanoclay particles interaction rather than the epoxy–nanoclay interface mechanisms. The epoxy now acts like 'glue' between the nanoclay particles. As the cluster size becomes larger, the breaking paths of the applied load become rougher and in a 'zig–zag' manner. Hence, the fracture toughness of the 15 wt% of nanoclay becomes higher and more difficult to fracture than the pure epoxy. Thus, the micro-hardness of the 15 wt% of nanoclay sample was much lower than the other samples as the deformability of the 15 wt% of nanoclays was the highest. Therefore, it becomes obvious to understand the trend of the micro-hardness behaviour as shown in Fig. 2 and the existence of the optimal amount of the addition of nanoclay.

According to the results obtained from the micro-hardness test, the cluster size attributed the properties of the nanocomposites. Increasing the amount of the nanoclay particles in the nanocomposites represents that the quantity of the nano-reinforcements increases, and therefore the overall strength is also increased. However, it would have an optimal limit since the size of the cluster increases and subsequently the total number of the clusters, as nano/micro-reinforcements are decreased. The distance between these nano-size or micro-size clusters is also decreased which eventually reduces the effectiveness of strengthening the nanocomposites. This is an important aspect since most of previous literatures were mainly focused on the production of exfoliated and intercalated nanoclay structures for nanocomposites. The effect due to the formation of clusters is normally neglected. However, in real practice, it is extremely difficult to control the nano-structures of the nanoclay particles in the general product manufacturing process. Although the formation of clusters, in some points would induce adverse effects to the product, the use of appropriate amount of nanoclay particles, which produce a pre-determined size of clusters after the manufacturing process, may give optimal mechanical and thermal properties to the whole structures.

4. Conclusion

This paper studies the hardness of nanoclay/epoxy composites with different amounts of nanoclay particles. The influence of the hardness due to the formation of clusters is also explained in the paper. Microscopic observation using SEM was conducted to measure the cluster size of the nanocomposites. It was found that the hardness of the nanocomposites increased with increasing nanoclay content. However, it was also seen that there was an optimal limit. This might be due to the size of the clusters

reaching a crucial limit and therefore the reinforcing function of the nanoclays decreased. Interlaminar shear test showed the short beam shear strength of the epoxy decreased after adding few percents of nanoclay particles. A shiny surface of the clusters, captured from the fractured samples also revealed that a weak bonding interfacial existed between the cluster and matrix, which led to a poor short beam strength of the composites. However, it would not affect the hardness of the composites during different stress transfer mechanisms between the hardness and shear properties of materials. Further work is under processing to study in detail the mechanical and thermal properties of nanoclay/polymer composites due to formation of clusters.

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