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Mechanism of Fatigue Failure of Clay–Epoxy Nanocomposites

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This work investigates the fatigue behaviour and the mechanism of fatigue failure of an epoxy resin with a dispersion of modified layered silicates in the polymer matrix. The fatigue properties are very important for structural application of nanocomposite materials. Clay–epoxy nanocomposites were successfully synthesized with a commercially available 1-Methylimidazole curing agent. The XRD and TEM findings demonstrated a pattern of clay morphology typically found in nanocomposite systems. The fatigue performance and fatigue failure mechanism of the clay–epoxy materials were studied under repetitive bending loads. The results showed that the fatigue life of filled epoxy improved significantly at strain amplitudes below a threshold value. The E-SEM observations of the epoxy and the clay–epoxy fracture surfaces showed different patterns. In conclusion, the addition of silicate strongly determines the fracture mechanism and enhances the fatigue performance.

Keywords: Layered Silicates, Epoxy, Fatigue Properties, Mode of Fatigue Failure.

1. INTRODUCTION

Polymer nanocomposites filled with layered silicates have been studied extensively in the last decade because of the dramatic improvement in their performance with a silicate addition of only 5 wt% or less.[1,2] Montmorillonite or MMT, one of the common silicates, is a crystalline, 2:1 layered clay mineral in which a central alumina octahedral layer is sandwiched between two silica tetrahedral layers. The layers are separated by a regular spacing, which is commonly termed the gallery. The more expanded this gallery distance, the better the properties of clay-polymer nanocomposites, because the polymer matrix has intruded to a greater extent into the filler.

Two types of polymer nanocomposite structures can be obtained, namely intercalated and exfoliated structures. Intercalated structures are formed when a small increase of the gallery distance occurs. On the other hand, exfoliated structures are formed when the silicate layers are well separated and individually dispersed in the polymer matrix. Since the latter structure is more homogeneous than the former, exfoliated nanocomposites exhibit better properties. However, it is difficult to obtain an exfoliated structure by itself. In fact the majority of studies show that polymer nanocomposites possess mixed structures or an intercalated structure only.[3] That is, exfoliation rarely seems to occur completely.

It is reported that the modulus, strength, and toughness of different types of clay–epoxy systems improve significantly with the addition of 5 wt% clay.[4,5] In structural application, fatigue properties and fatigue failure mechanism are significant. In the present study, the fatigue performance and the mechanism of fatigue failure of epoxy and clay–epoxy materials will be investigated.

2. EXPERIMENTAL DETAILS

The material used in the present work was Diglycidyl ether of bisphenol A/DGEBA resin (Araldite Algy 9708-1) purchased from Ciba-Geigy combined with 1-Methylimidazole (1-MI), purchased from Aldrich, as the curing agent. The filler, which is a commercial MMT, Nanomer I.30E, was purchased from Nanocor Inc.

The epoxy and clay powder were dried overnight at 50 °C in a vacuum prior to sample production. Unfilled epoxy specimens were made by mixing the epoxy resin and 2.5 wt% hardener. Filled specimens were synthesized by mixing the desired amount of clay with epoxy resin at (76 ± 1) °C using an overhead stirrer for 30 min; 2.5 wt% of hardener was then added into the mixture and mixed in. The blend was poured into release-agent-coated-aluminum moulds with mylar-sheet-covered glass bases, then cured at 160 °C for 2 hrs, and followed by a post-cure at 180 °C for 2 hrs.

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The fatigue test samples were prepared using triangular moulds with a thickness of 4 mm. The triangular samples were then ground using sand paper of 180 grid followed by 1200 grid, to obtain a homogeneous thickness of 3 mm.

X-ray diffraction (XRD) analysis was performed using a Phillips PW 1130 generator. A voltage of 40 kV and current of 25 mA were employed for Cu Kα radiation. Measurements were performed in a range of $2\theta = 1°–30°$ for the unfilled and filled epoxy samples as well as the dried MMT powder.

Transmission electron microscope samples were cut using a Leica Reichert Ultracut S Microtome with a Diatome diamond knife, which was placed at an angle of 6°. The 70 nm thickness of sections were collected on hexagonal 300 mesh copper grids. The images were obtained from a Phillips EM 420 Transmission Electron Microscope (TEM), which was operated in bright field mode at 100 kV.

The fatigue tests were carried out at ambient temperature, using both an Instron machine for zero-cycle fatigue tests and a cantilever-bending machine. The fracture surfaces were observed using an Environmental-Scanning Electron Microscope (E-SEM) FEI Quanta 200 equipped with EDX apparatus. This microscope was operated at 20 kV at a low vacuum mode.

3. RESULTS AND DISCUSSION

Epoxy based nanocomposites were successfully synthesized by *in-situ* polymerisation. Four different clay loadings: 2.5 wt%, 5 wt%, 7.5 wt%, and 10 wt%, were prepared to produce the MMT–epoxy systems.

The structures of the specimens were examined by XRD and TEM. A typical XRD pattern of MMT and clay–epoxy nanocomposites is shown in Figure 1(a). A powder diffractogram of pure MMT, showing a strong peak due to the (001) reflection corresponding to a *d*-spacing of 2.2 nm, with the (002) and (101) peaks also quite evident. The diffractrogram of the pristine epoxy and MMT–epoxy materials are shown above the MMT XRD pattern. For the MMT–epoxy nanocomposites only a very weak (001) peak can be observed indicating that this system is largely exfoliated for all clay contents. It is also clear that the (101) peak can be observed and its intensity increases with the clay content. This shows that XRD is sensitive enough to detect the presence of the organoclay, and that the (001) of the clay is diminished relative to the (101) when in the epoxy.

Figure 1(b) shows the TEM image of the 2.5 wt% MMT–epoxy materials which is illustrated a typical image of organoclay in epoxy. The images of all MMT–epoxy samples exhibit a number of parallel organoclay layers. It was calculated that the average inter-layer distance was between 4.2 and 11.1 nm for all clay contents and a minimum layer distance of 2.5 nm. This indicates that these materials possess a mixture of exfoliated and intercalated structure, where exfoliation is at best partial.

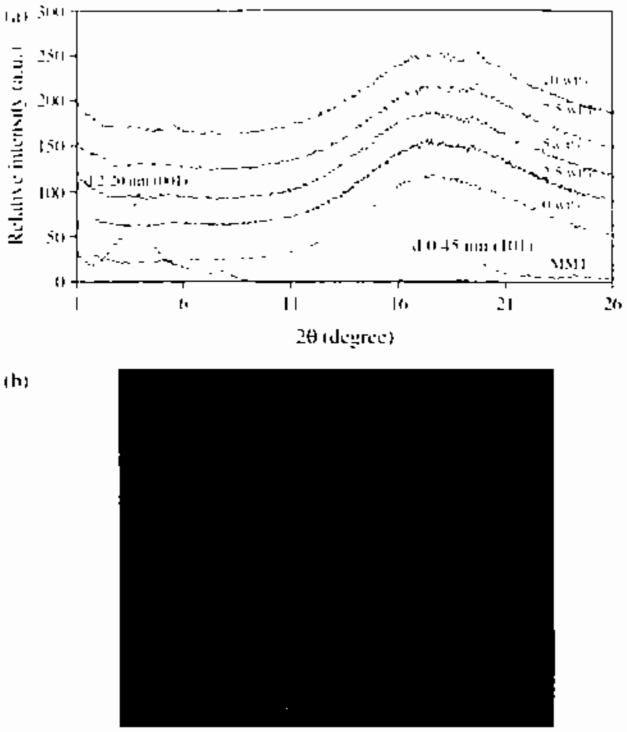

Fig. 1. (a) XRD patterns of MMT and epoxy and MMT–epoxy nanocomposites, (b) TEM image of 2.5 wt% I30E-epoxy material.

Figure 2 shows the fatigue life of the epoxy and MMT–epoxy materials, which in general, can be divided into four different areas of strain amplitude. The four areas are the strain amplitude for zero-cycle fatigue; the high strain amplitudes with a small number of cycles; the medium strain amplitudes with a medium number of cycles, where

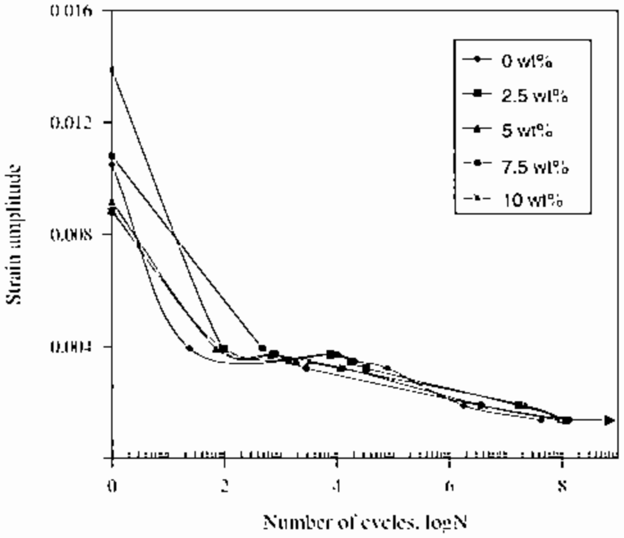

Fig. 2. Fatigue life of MMT–epoxy nanocomposites.

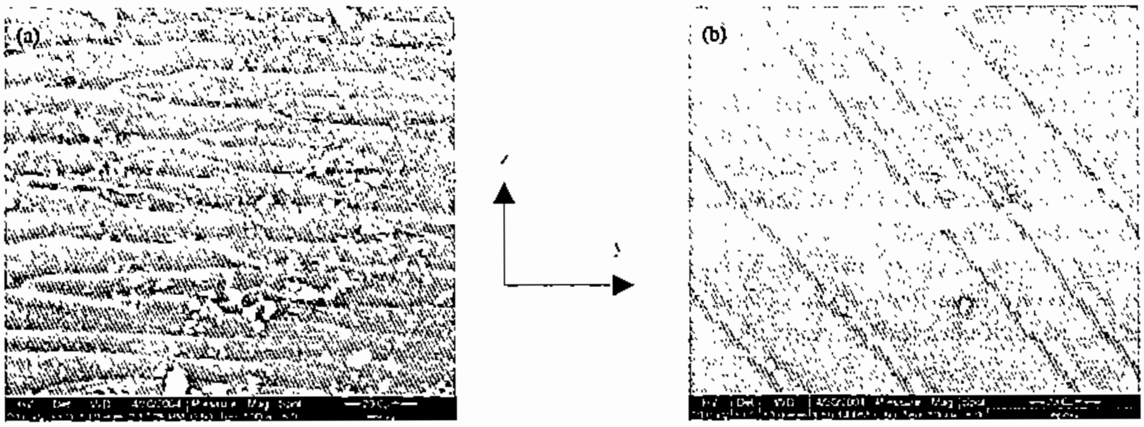

Fig. 3. E-SEM images of fracture surface of epoxy (a) on the edge and (b) on the center of fatigue-loaded samples.

the plateaus occur; and the low strain amplitudes with a large number of cycles.

It can be seen that the zero-cycle fatigue property (the strain that can be withstood in a monotonic test) does not improve significantly with clay addition. For the high strain amplitudes, there is an improvement of fatigue endurance of the filled epoxy compared to that of the unfilled epoxy. For the medium strain amplitudes, plateaus occur and these plateaus show critical conditions. In this region, there is no consistent pattern of fatigue life improvement. For the low strain amplitudes, there is a significant improvement of the fatigue life of the filled epoxy compared to that of the unfilled epoxy. It is obvious that the unfilled epoxy fails at about 42 million cycles and the filled epoxy does not fail at up to 110 million cycles.

Micro observations of the epoxy and MMT–epoxy fracture surfaces can be seen in Figures 3 and 4, respectively. Figures 3(a) and (b) show striations of the epoxy fracture surface on the edge and on the center, respectively. A striation is a common fracture pattern of a brittle epoxy material. It is clear that the striations are close together on the edge of the fracture surface and considerably further apart on the center of the fracture surface. With a careful examination, it suggests that the crack started from the edge of the samples; the crack then propagated to both sides along the edge (z-direction). Then, the crack moved towards the center in y-z direction to the other edge until the sample was totally broken.

Figures 4(a) and (b) show the 2.5 wt% MMT–epoxy fracture surface on the edge and on the center, respectively. Striations and clumps are observed in these images. Comparing these images, the striations on the edge and on the center part of the fracture surface are similar, in which the crack propagated in z-direction. Moreover, comparing Figures 3(a), (b), 4(a) and (b), the mechanism of failure on the edge of the filled epoxy is similar to that of the unfilled epoxy. However, the striation patterns and the directions of the crack propagation on the centre part of the fracture surfaces between the unfilled and filled epoxy materials are different. This indicates that clay addition changed the pattern of the striation and the direction of crack propagation on the center part of the sample. Moreover, clay addition also changed the morphology of the material by the appearance of the clumps. From EDX observations, it was found that the clumps were clay aggregates in the size range 7.6–14.8 μm.

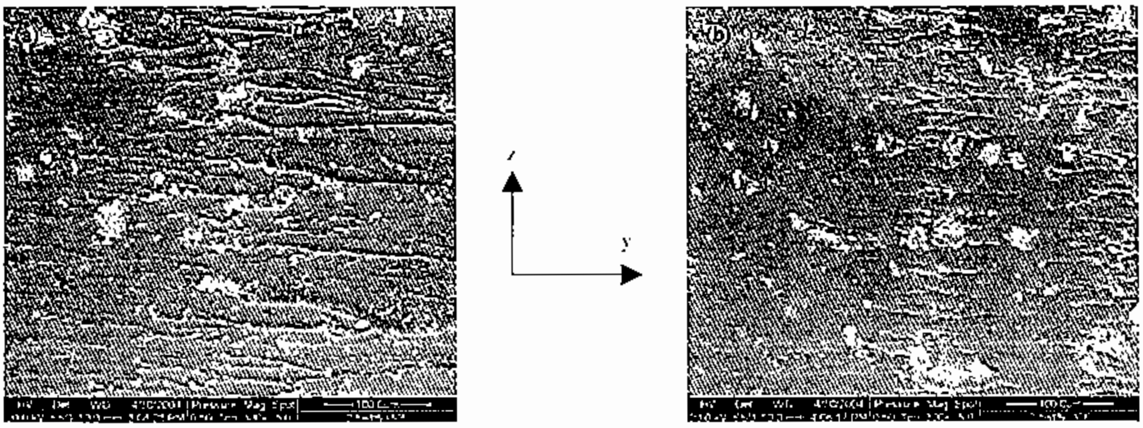

Fig. 4. E-SEM images of fracture surface of 2.5 wt% MMT–epoxy (a) on the edge and (b) on the center of fatigue-loaded samples.

4. CONCLUSIONS

An aggregate-intercalated-exfoliated structure is formed in the MMT–epoxy nanocomposites. Clay addition generally improves the fatigue endurance for a given strain amplitude. More notably, below a threshold amplitude, filled epoxy has a fatigue endurance of about three times higher than the unfilled epoxy.

The mode of failure of epoxy and clay–epoxy is similar, which is fracture behaviour typical of brittle epoxy. However, clay addition changes the morphology and the pattern of striation on the fracture surfaces as well as the direction of crack propagation.

References and Notes

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