Materials Science and Engineering A 528 (2011) 7999–8005

Contents lists available at ScienceDirect

Materials Science and Engineering A

journal homepage: www.elsevier.com/locate/msea

Microstructures and toughening mechanisms of organoclay/polyethersulphone/epoxy hybrid nanocomposites

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ARTICLE INFO

Article history:
Received 2 May 2011
Accepted 7 July 2011
Available online 18 July 2011

Keywords:
Hybrid nanocomposites
Organoclay
Fracture toughness
Toughening mechanism

ABSTRACT

Hybrid nanocomposites (HNCs) with high fracture toughness were successfully prepared by incorporating polyethersulphone (PES) and organoclay into epoxy resin. Their microstructures were studied. They were composed of homogeneous PES/epoxy matrices and micron-scale organoclay agglomerates. These agglomerates consisted of smaller tactoid-like regions which were comprised of ordered exfoliated nanolayers. The toughening mechanisms of the two tougheners were also studied and then related to their microstructures. For one thing, the PES which was dissolved in the epoxy resin homogeneously improved the ductility of the epoxy resin and made it easier to deform. For another, the organoclay agglomerates induced crack front bowing, crack bridging, crack deflection, crack bifurcation and plastic deformation of the matrices on the micron-scale, respectively. These toughening processes were achieved by the ordered exfoliated nanolayers with various orientations, which debonded from the matrices, bridged the cracks and induced the plastic deformation of the matrices on the nanoscale.

1. Introduction

As the matrices of fiber-reinforced composites, epoxy resins were often toughened by a secondary phase [1]. Since 1980s, significant progress has been made in improving their fracture toughness with inorganic particle [2], liquid rubber [3], thermoplastic [4,5], etc.

With the development of nanotechnology, the incorporation of nanoparticles such as nanoclay was regarded as an effective way to toughen epoxy resins [6,7]. The nanoclay could improve their fracture toughness without leading to a dramatic decrease in other desirable mechanical properties such as modulus or strength. However, its dispersion and morphology could markedly affect the mechanical properties of the synthesized nanocomposites [8].

In recent years, to incorporate two tougheners into epoxy resins simultaneously has been deemed to be a better strategy for getting a further improvement in their mechanical properties, particularly in their fracture toughness. As one of the promising components in these ternary hybrid nanocomposites (HNCs), nanoclay is playing an increasingly significant role in toughening epoxy resins [9–11].

With the widespread use of various tougheners, their toughening mechanisms were also studied. Crack deflection, crack front bowing (including crack pinning), crack tip bifurcating (i.e., branching), microcracking, crack tip blunting, crack bridging and micro-shear banding are the well-known toughening mechanisms which have been applied to various polymer systems up to now [6,12–17]. A variety of single-toughener systems have been researched and each toughener usually has more than one toughening mechanism, while the toughening mechanisms of two-toughener systems are more complicated and the synergistic toughening effect of the two tougheners is hard to attain. Accordingly, further research should be done on the two-toughener systems to reveal the complicated mechanisms for getting better mechanical properties.

In this study, our objective is to prepare organoclay-reinforced PES-modified epoxy-based hybrid nanocomposites (i.e., organoclay/PES/epoxy HNCs) with high fracture toughness, reveal the microstructures of the two tougheners in them and dig out their toughening mechanisms.

2. Experimental

2.1. Preparation of samples

In order to prepare the HNCs, PES (5 wt%, Sumitomo Corporation) and epoxy oligomer (DER331®, Dow Chemical Company) were completely dissolved in methylene chloride (Tianjin Kermel Chemical Reagent Co., Ltd.) at room temperature. Then organoclay (1 wt% or 3 wt%, I.30E, Nanocor) was dispersed in the solution with vigorous mechanical stir and the mixture was sonicated for at least 30 min. The translucent mixture was then placed into a water bath and a hot vacuum oven to drive off the solvent. In the next stage,

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doi:10.1016/j.msea.2011.07.009

the stoichiometric amount of the hot DDS (SUZHOU YINSHENG Chemical Co., Ltd.) was added to the mixture with a fierce stir. Subsequently, the mixture was cast into a preheated mould treated with a release agent (Frekote 44-NC, Loctite Corporation). At last, the mould was cured at 120 °C for 24 h and subsequently post-cured at 180 °C for additional 2 h.

This preparing method was also used to synthesize the nanocomposites, the PES/epoxy blend and the neat cured epoxy resin by omitting the incorporation of PES, organoclay and both of them, respectively. The same curing schedule was applied.

2.2. Physical measurement

Dynamic mechanical properties of all the samples were measured by a DMA Q800 analyzer produced by TA Instruments Corporation at a fixed frequency of 1 Hz and a heating rate of 3 °C/min. The tests were conducted under dual cantilever mode for the samples of size 60 mm × 6 mm × 3 mm.

X-ray diffraction (XRD) measurements were performed on a D/max-γB diffractometer with a Cu Kα radiation (λ = 0.154 nm) produced by Rigaku Corporation. The acceleration voltage and acceleration current were 40 kV and 20 mA, respectively. The scanning speed and the step length were 0.6° min^{-1} and 0.006°, respectively. The 2θ ranged from 0.6° to 10°.

For scanning electron microscope (SEM) observation, all the fractured specimens were coated with a layer of gold around 200 Å thick and observed by a scanning electron microscope (Philips XL-30).

A JOEL JEM-2100F transmission electron microscope (TEM) was used at an accelerating voltage of 200 kV to observe the microtomed thin-section specimens of 50–60 nm thickness. Before the observation, the samples were first fractured according to the double-notched four-point bending (DN-4PB) test [18]. The subcritical crack tip damage zones were then carefully polished, trimmed and microtomed for being observed on 200 mesh copper grids.

2.3. Mechanical properties

The fracture toughness of all the cured resins was measured from the critical stress intensity factor (K_{IC}) in the single-edge notched three-point bending (SEN-3PB) test according to ASTM D5045-99. The dimensions of each sample were 70 mm (L) × 10 mm (W) × 5 mm (B) and the span was 40 mm (S). A screw-driven Instron machine (Instron 5569) was used at a crosshead speed of 0.5 mm/min. At least 5 specimens of each composition were tested.

3. Results and discussions

3.1. Microstructures of PES and organoclay in the HNCs

In this study, 5 wt% PES was added to the epoxy resins for preparing the organoclay/PES/epoxy HNCs and the PES/epoxy blend. DMTA was then used to observe the phase morphologies in them. As shown in Fig. 1, all the curves have single peaks, which is the characteristic of homogeneous phase morphology. It demonstrates that the PES was dissolved in the epoxy resins homogeneously and phase decomposition between them was suppressed greatly.

The morphology of the dispersed organoclay in the nanocomposites and the HNCs was investigated with XRD (Fig. 2) and TEM (Fig. 3). It can be seen from Fig. 2 that there are no peaks in the XRD curves, which indicates that the organoclay was all exfoliated. Since 2θ is ranging from 0.6° to 10°, the d-spacing of the dispersed organoclay is all larger than 12 nm in accordance with the Bragg's relation [7]. Fig. 3 shows that the organoclay possesses mainly ordered exfoliated structure in the HNCs and the d-spacing is more than 12 nm.

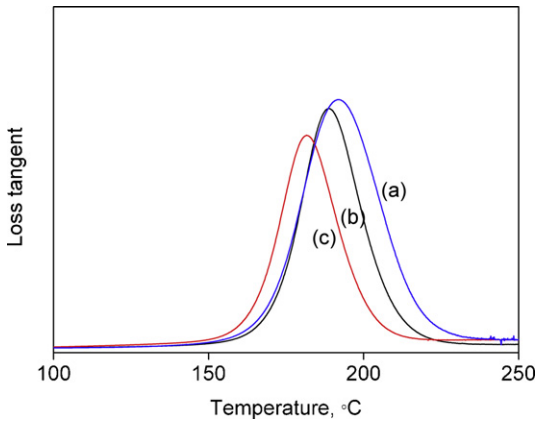

Fig. 1. DMTA curves of Loss tangent vs. temperature for three samples: (a) the PES/epoxy blend; (b) the organoclay (1 wt%)/PES/epoxy HNC; (c) the organoclay (3 wt%)/PES/epoxy HNC.

The TEM images of the organoclay in the nanocomposites which are not demonstrated here show similar patterns. It should be noted that the organoclay was still close to each other to form various micron-scale agglomerates (Fig. 3(c)). These agglomerates with loose structure inside are commonly composed of many smaller tactoid-like regions ca. 1 μm in diameter with ordered exfoliated nanolayers parallel to each other. Since there are no electrostatic attractive force and van der Waals force between the nanolayers whose d-spacing exceeds 8 nm [7], these tactoid-like regions are easy to be fractured and separated from each other by the external stress. Particularly, the tactoid-like regions have various orientations which are predicted to influence the fracture behaviour and thus the fracture toughness of the HNCs. In this study, the orientation of an organoclay nanolayer is defined as the direction its end surface faces and the orientation of a tactoid-like region is regarded as the orientation of most of its nanolayers.

3.2. Toughening mechanisms of the HNCs

Table 1 presents the Model-I fracture toughness values (K_{IC}) of the prepared neat cured epoxy resin, PES/epoxy blend, nanocomposites and HNCs. It shows that the K_{IC} values of the HNCs are the highest two and therefore the PES and the organoclay have a marked synergistic toughening effect on the epoxy resin. Since phase decomposition was greatly suppressed in the HNCs, the toughening mechanisms mainly relate to the ductility of the

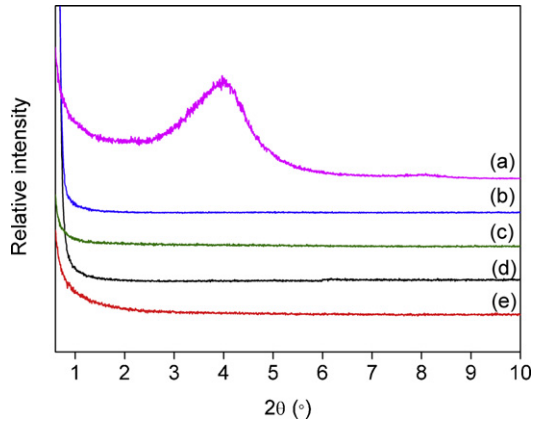

Fig. 2. XRD patterns of the specimens: (a) the organoclay; (b) the organoclay (1 wt%)/epoxy nanocomposite; (c) the organoclay (3 wt%)/epoxy nanocomposite; (d) the organoclay (1 wt%)/PES/epoxy HNC; (e) the organoclay (3 wt%)/PES/epoxy HNC.