Contents lists available at ScienceDirect

Composites Science and Technology

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

Morphological structure and mechanical properties of epoxy/polysulfone/cellulose nanofiber ternary nanocomposites

Yan Zhang [a], Ping'an Song [a,*], Shenyuan Fu [a,*], Fenghua Chen [b]

[a] Department of Materials, College of Engineering, Zhejiang Agriculture & Forestry University, Hangzhou 311300, China
[b] Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

ABSTRACT

Despite some work on epoxy resin/cellulose nanofiber (CNF) system, it remains unclear how CNF affects microstructure and mechanical properties of epoxy/polysulfone (PSF) binary blends so far. We herein introduced CNF into the blends via a combination of solvent exchange and melt mixing. Results show that epoxy/PSF binary blends display three distinct types of phase separated structures but slightly affecting mechanical properties because of poor interfacial adhesion. However, only adding small amount of CNF can enhance impact toughness and tensile strength due to improved interfacial adhesion, probably arising from hydrogen bonding interactions between CNF surfaces and matrix polymers, and penetrating and bridging effects of CNF between different phases. For example, compared with the epoxy/PSF blends, adding 0.2 wt% of CNF can increase impact strength by ~49%. Additionally, 0.3 wt% of CNF can increase the glass transition temperature by ~18 °C relative to the epoxy resin.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Epoxy resins are a class of significant thermosetting polymers which are often used as matrices for creating high-performance composites in aerospace and automotive industrial fields because of their high modulus, excellent adhesion properties and chemical resistance, good dimensional and thermal stability, etc. [1,2]. However, inherent brittleness extremely limits their wide applications in industrial fields. Incorporating thermoplastic polymers has been proven to be one of the most effective approaches to address the drawback. For example, epoxy resins are widely modified with polysulfone (PSF) [3], poly(ether sulfone) (PES) [4], polyetherimide (PEI) [5] etc. Owing to relatively high glass transition temperature (T_g) and high modulus of the thermoplastic polymers, the toughness of the epoxy resins can be usually enhanced without any significant loss of T_g and modulus [3–6]. The epoxy/thermoplastic (TP) binary system is generally homogeneous before curing and the phase separation normally occurs due to the increase in molecular weight of the epoxy and the decrease in miscibility of the TP with the crosslinked epoxy upon curing [7]. Various morphological structures, such as sea-island, bicontinuous, nodular and layered structures, have been observed with the increase of TP contents, mainly depending on the competition between the curing reaction and phase separation [8–11]. For the epoxy/TP binary system, it is well-known that achieving superior mechanical properties normally requires a fine phase-separated structure with phase domains in proper sizes and good interfacial adhesions between two separated phases. Thus, to obtain optimal morphological structure and performances for the thermoplastic modified epoxy system, tremendous research has been devoted to the mechanism and kinetics of the reaction induced phase separation, and to the relationship of morphological structure and mechanical property [4–6,12–15].

Recently, many different micro or nano-sized fillers like silica particles, graphene, carbon nanotubes, carbon nanofibers or nanoclay have been incorporated into epoxy/TP binary systems to control the morphology and proprieties of the cured materials due to their unique characteristics [16–21]. Cellulose nanofiber (CNF), a new kind of expanded high-volume cellulose fiber with the diameters in the range of 10–100 nm and lengths varying from several to tens of micrometers, has been attracting particular interest in both academic and industrial fields due to its advantages of abundance, renewable nature and outstanding mechanical properties [22–24]. Although the effect of CNF on mechanical property and the curing reaction of the neat epoxy have been studied over the past years [25–28], there are few related studies reported the

---

* Corresponding authors.
E-mail addresses: songyu19800919@163.com (P. Song), fshenyuan@sina.com (S. Fu).

effects of CNF on microstructure and mechanical properties of epoxy/TP binary systems.

Our earlier studies have discussed in detail the reaction-induced phase separation of the epoxy/TP blends while the mechanical properties have not been investigated yet [29–31]. Therefore, in the present work, the relationship between morphology and mechanical properties of the epoxy/PSF system was initially discussed. Meanwhile, to tailor the morphology and mechanical properties of the epoxy/PSF blends, the CNF was introduced. The epoxy/PSF/CNF nanocomposites were prepared by a combination method of solvent exchange and melt mixing in this work, and the influence of the CNF at low loading level on the morphology and mechanical properties was studied.

2. Experimental section

2.1. Materials

Liquid diglycidyl ether of bisphenol A (DGEBA), a difunctional epoxy resin (E-51) with epoxide equivalent weight of 185–200 g/eq was supplied by Jinhong Adhensives (Hangzhou, China). 4,4′-diaminodiphenyl sulfone (DDS, purity > 99%), the curing agent, was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Polysulfone (PSF) (Udel P1700, M_n = 38,000 g/mol, M_w = 62,000 g/mol), the thermoplastic polymer, was provided by Solvay Co. Ltd. The cellulose nanofiber (CNF, KY100), was provided by Daicel Chemical Industries, Ltd. (Japan), which is a 25 wt% solid content in water suspension.

2.2. Sample preparation

Both the epoxy/PSF binary and epoxy/PSF/CNF ternary composites were prepared. The ratio of DGEBA/DDS was fixed at 1:0.27 w/w, i.e., 0.8 hydrogens of amino groups per epoxide group. As for the identification, the epoxy/PSF binary and epoxy/PSF/CNF ternary composites are named by PSFx (x = 10, 15, and 20) and PSFx–CNFy (x = 10, y = 0.1, 0.2, and 0.3), respectively. For instance, PSF10 and PSF10-CNF0.1 respectively refer to the epoxy/PSF binary system containing 10 wt% PSF, and the epoxy/PSF/CNF ternary system containing 10 wt% PSF and 0.1 wt% CNF.

Epoxy/PSF blends were prepared using melt mixing technique [5]. PSF was firstly dissolved in the epoxy resin at 140 °C with constant stirring until complete dissolution. DDS was added to the above mixture at 120 °C and stirred vigorously for about 15 min. Homogeneous samples with different PSF concentrations were thus obtained.

The epoxy/PSF/CNF blends were prepared using a combination method of solvent exchange and melt mixing [5,25]. To introduce the CNF into the specific epoxy/PSF blends, the solvent exchange method was used firstly. After the CNF was diluted with water, ultrasonic treating and strong stirring were used to destroy the hydrogen-bonding interactions among nanofibers to promote the dispersion. The aqueous suspension was then solvent exchanged with ethanol 5 times to remove the water completely. The desired amount epoxy was added into the ethanol suspension of CNF, sonicated for about 10 min and stirred for 5 h. The suspension was heated at 80 °C while stirring for 4 h in an electric oven and then was degassed in a vacuum oven for another 4 h at the same temperature to remove the ethanol completely. Afterwards, the PSF was added into the mixture and stirred at 140 °C until fully dissolved. Subsequently, DDS was added and stirred at 120 °C until it dissolved in the mixture completely. The resulting composites were poured into an open mould. A three-step curing schedule was used: 6 h at 160 °C, afterwards 2 h at 180 °C and finally 2 h at 200 °C.

2.3. Characterizations

Morphological structures of fractured surfaces for the cured samples were examined using the scanning electron microscope (SEM, ShimadzuSS-550 and Hitachi Ultra-high SU8000). All the sample surfaces were coated with platinum before observation.

The morphology of CNF was observed by transmission electron microscopy (TEM, JEOL JEM-1230). A drop of a diluted CNF suspension was deposited on a carbon-coated grid and allowed to dry at room temperature for TEM observation.

The tensile properties of cured composites were measured at room temperature (23 ± 2 °C) by means of a SANSCMT-6104 universal testing machine (Shenzhen, China) according to GB/T 1040.2-2006. The specimens for tensile testing were standard dog-bone shaped with a 25 mm gauge length. A load cell of 10 KN was employed and the crosshead speed was 2 mm/min. At least six tests were conducted for each sample, from which average values and standard deviations were derived.

The Charpy impact strength of the composites was measured by means of a Charpy impact test, according to the specification GB/T 1043-93 using unnotched rectangular specimen testing. The dimensions of the specimens were $80 \times 10 \times 4$ mm^3. At least ten tests were conducted for each sample and the results were averaged.

The dynamic mechanical analysis (DMA) of cured samples was determined using a TA Instruments DMA Q800 dynamic mechanical thermal analyzer. Rectangular specimens of $60 \times 10 \times 3$ mm^3 were used. The DMA tests were performed in a dual cantilever mode at a frequency of 1 Hz and the temperature was raised from 30 °C to 250 °C at a heating rate of 3 °C/min.

3. Results and discussion

3.1. Morphology and mechanical properties of the epoxy/PSF blends

Fig. 1 presents the SEM images of the fractured surfaces of the neat epoxy and epoxy/PSF blends at different PSF weight fractions. The left images at low magnification shown in Fig. 1 in each panel had a full view of the surface structure. The thickness of the sample presented here was about 3 mm, which was much larger than the previously studied thin films with the thickness of about 100 μm [11,30]. For the neat epoxy (PSF0), a flat and homogeneous surface was shown, while for the PSF modified epoxy system, heterogeneous morphology was observed because of the curing reaction induced phase separation. At a relatively low content of PSF (PSF10), PSF-rich spherical domains formed and dispersed in the epoxy matrix. The size of the discrete PSF-rich particles was around 1 μm, while at a relatively high PSF content (PSF20), a nodular structure evolved, where the inter-connected epoxy-rich spherical particles (the nodules) with the diameter about 5 μm were tightly wrapped by the continuous PSF-rich network-like domains. By contrast, PSF15 shows a three-layered morphological structure. For the upper and lower layers, similar morphology that the PSF-rich particles dispersed in the epoxy-rich matrix generated and the thickness of each layer was in the range of 100–150 μm. For the middle layer, most of the PSF-rich domains were located and a typical dual phase was observed, where the size of the phase separated domains were much larger, up to several hundred microns.

The mechanical properties in terms of impact and tensile strength of the neat epoxy and epoxy/PSF blends were displayed in Fig. 2. The results showed that the impact strength increased slightly at low PSF contents (PSF10) while the tensile strength slightly decreased compared with the neat epoxy. However, when the PSF content was increased to a relatively high value (PSF15 and