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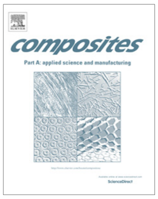

Effect of clay and PEO-PPO-PEO block copolymer on the microstructure and properties of cyanate ester/epoxy composite

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ABSTRACT

In this study, processing, morphology and properties of poly (ethylene oxide)-block-poly (propylene oxide)-block-poly (ethylene oxide) (PEO-PPO-PEO) triblock copolymer and clay modified cyanate ester/epoxy hybrid nanocomposites were investigated. The PEO-PPO-PEO triblock copolymer preferentially reaction-induced microphase separate into spherical micelles in the cyanate ester/epoxy matrix. PEO-PPO-PEO was used as both nanostructuring agent for cyanate ester/epoxy blended resin and thus the predominantly intercalated and few exfoliated platelets of were also observed with clay, which successfully reduced the brittleness of the cyanate ester/epoxy blended resin increasing the toughness of designed materials. The stiffness and heat resistance of the neat BCE/EP resin could be retained in the BCE/EP/F68/clay hybrid nanocomposites. The optimum property enhancement was observed in the hybrid nanocomposites containing 5 wt% PEO-PPO-PEO and 3 wt% clay. The thermo/mechanical properties of the hybrid nanocomposites depend on microstructure, dispersion state and the ratio between organic and inorganic modifiers content.

1. Introduction

Cyanate ester/epoxy blended resins (CE/EPs) are a well-known high-performance thermosetting resin with good thermal and hydrothermal properties so CE/EPs have been considered as a good candidate for fabricating structural and functional materials [1,2]. But like most thermosetting resins, the biggest shortcoming of pure CE/EP resin is its brittleness, which limits its application in the fabrication of materials with high toughness. To improve its toughness, many methods have been developed to modify thermosetting resin, such as binary or ternary blending with engineering thermoplastics or liquid rubber [3,4]. Nevertheless, one disadvantage of the modifiers is the risk of sacrificing the stiffness and heat resistance of thermosetting matrix [5].

In recent years, there has been considerable interest in hybrid composites blending both toughening material (thermoplastic/liquid rubber/block copolymer particle) and inorganic nanoparticles. A new kind of polymeric material with remarkable properties will be generated by the incorporation both toughening material and inorganic nanoparticles in thermosetting matrix. The incorporation of inorganic nanoparticles into the thermosetting matrix can improve its thermo/mechanical behaviors by lowering the plasticization effect obtained with organic additives [6–8]. In addition, the block copolymer (BCP) has been used in several works as nanostructuring agent and simultaneously as template for inorganic nanoparticles [9,10]. Bashar et al. prepared a ternary system based on epoxy, acrylic triblock copolymer M52N and clay [11]. It was found that block copolymer act as nanotemplates lead to better dispersion of clay throughout the matrix because the microphase separation of P(MMA-co-DMA) block domains prevents their agglomeration. The use of a ternary mixture of epoxy/M52N/clay has represented as a good strategy to achieve a balance of modulus and toughness. The influence of alumina nanoparticles (Al_2O_3) on thermal mechanical properties in diglycidyl ether of bisphenol A/poly(styrene-b-butadiene-b-styrene) (SBS) epoxidized triblock copolymer blends has been studied [12]. The nanostructured epoxy systems based on SBS epoxidized triblock copolymer and well-dispersed Al_2O_3 nanoparticles allowed an increase in fracture toughness maintaining the transparency and stiffness of neat epoxy. Based on the above findings, it is recognized that the hybrid composites containing both inorganic nanoparticles and

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block copolymer can open a new strategy for preparation of high performance thermosetting materials.

In this study, CE/EP/clay/BCP hybrid nanocomposites were prepared. BCP are used not only as nanostructuring agent for the CE/EP resin but also as dispersion agent for clay. Even though there have been a few studies on the preparation and mechanical properties of epoxy modified with both BCP and clay [11,13], still the research in this field is inadequate to comprehensively evaluate and explain the effect of both BCP and clay on the properties of the thermosetting resin. The focus of this study is to systematically investigate the synergistic effects of both BCP and clay on the properties of the resulting hybrid nanocomposites. The present study involved characterizing the nanocomposites by various morphological examinations. The structure–property relationships of the CE/EP/clay/BCP hybrid nanocomposites were also studied by exploring the effect that clay dispersion and block copolymer phase structures may have on the flexural and thermomechanical properties.

2. Experimentation

2.1. Materials

Diglycidyl ether of bisphenol A epoxy resin (DGEBA) with epoxide equivalent weight of 185–210 was supplied by Baling petrochemical of Hunan in China. A commercial Bisphenol A dicyanate ester, 2,2′-bis(4-cyanatophenyl) isopropylidene (BCE) with molecular weight of 278.6 was obtained from Wuqiao Resin plant of Jiangsu in China. PEO-PPO-PEO triblock copolymer (Pluronic F68) with molecular weight of 8600 was purchased from Haian Pertrochemical plant of Jiangsu in China. A commercially available GK-5 clay functionalised with an alkylammonium salt was purchased from Gukang New Materials CO., LTD of Jiangxi in China. The characteristics of materials used are shown in Table 1.

2.2. Preparation of BCE/EP hybrid nanocomposites

BCE/EP resin containing 0 wt%, 1 wt%, 3 wt% and 5 wt% clay particles are named along the manuscript as BE, BE-1, BE-3 and BE-5, respectively. BCE/EP resin modified with 5 wt% F68 containing 0 wt %, 1 wt%, 3 wt% and 5 wt% clay particles are named as 5F, 5F-1, 5F-3 and 5F-5, respectively. BCE/EP resin modified with 10 wt% F68 containing 0 wt%, 1 wt%, 3 wt% and 5 wt% clay particles are named as 10F, 10F-1, 10F-3 and 10F-5, respectively. In Table 2 the tested materials are listed.

BCE/EP/F68 nanocomposites were prepared in the following way. Firstly, F68 was added to BCE/EP prepolymer at 110 °C and stirred for mixing until a homogeneous blend was achieved. Then the mixture was degassed to remove the entrapped air at 100 °C in a vacuum oven for 0.5 h, followed by casting the mixture into a Teflon mold for curing via the procedure of 120 °C/2 h + 150 °C/2 h + 180 °C/2 h + 200 °C/2 h and postcuring at 220 °C for 3 h, allowing them to cool gradually to room temperature.

Table 2
Tested materials.

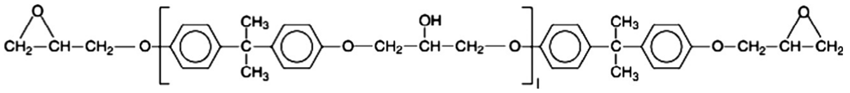
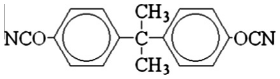
Material system	Clay content (wt%)	F68 content (wt%)
BE	0	0
BE-1	1	0
BE-3	3	0
BE-5	5	0
5F	0	5
5F-1	1	5
5F-3	3	5
5F-5	5	5
10F	0	10
10F-1	1	10
10F-3	3	10
10EPE-5	5	10

Preparation of the BCE/EP/clay or F68/BCE/EP/clay nanocomposites: the desired amount of the GK-5 clay, dried at 120 °C for a period of 24 h. Clay and F68 were mixed with BCE/EP prepolymer at 100 °C using magnetic stirrer for 40 min. The above mixture was mixed using sonication (200 W maximum power; 28 kHz maximum frequency) for 40 min. During the process, the temperature of the mixture was maintained at about 80 °C by using a water bath. All the mixtures were degassed in a vacuum chamber for 40 min. The samples were cured via the procedure of 120 °C/2h + 150 °C/2 h + 180 °C/2 h + 200 °C/2 h and post-cured at 220 °C for 3 h, allowing them to cool gradually to room temperature.

2.3. Characterization methods

Wide angle X-ray diffraction (WAXD) studies of the nanocomposites were performed using a X'Pert PRO (PAN alytical Corporation, Holland) diffractometer with a vertical goniometer. The diffractometer is fitted with a Cotube as an X-ray source and a graphite monochromator to filter K-beta wavelength. Tests were run at 60 kV and 60 mA, and samples were scanned between $2\theta = 2 - 10^o$ by changing the angle of incidence at a rate of 0.008 $2\theta^{-1}$. Differential scanning calorimetry (DSC) measurements were performed with a Q200 DSC (TA Instruments, USA) for the analysis of curing kinetics. All experiments were conducted at a heating rate of 10 °C/min under a nitrogen flow of 10 cm^3/min, working with 5–7 mg samples in aluminium pans. The curing enthalpy (ΔH) was obtained by integrating the DSC exothermic peak area, using TA instrument software. Microstructure of the cured nanocomposites was studied by transmission electron microscope (TEM) and atomic force microscopy (AFM) measurements. Samples were prepared by using an ultramicrotome Leica UC6 instrument equipped with a diamond knife at room temperature. A Libra 200FE transmission electron microscope operated at 200 kV with resolution of 2.4 Å was used. AFM images were obtained using a

Table 1
Chemical structures of materials used.

Material	Chemical structure
DGEBA	
BCE	
F68