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Triglycidyl *para*-aminophenol modified montmorillonites for epoxy nanocomposites and multi-scale carbon fiber reinforced composites with superior mechanical properties

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ABSTRACT

Multi-scale carbon fiber reinforced polymer (CFRP) composites with continuous carbon fiber as the primary reinforcement and nanoscale fillers as the secondary reinforcement have attracted great research interests in the last decade. Herein we report a new organically modified montmorillonite (MMT) for epoxy nanocomposites and multi-scale CFRP composites with superior mechanical properties. The organically modified MMT is prepared by ion-exchanging natural MMT with the hydrochlorate of triglycidyl *para*-aminophenol (TGPAP), a tertiary amine-type epoxy oligomer used as a CFRP matrix for the aerospace industry. The TGPAP-modified MMTs disperse uniformly in the matrix as thin stacks of intercalated nanoplatelets and exfoliated single-layer nanoplatelets, and are reactive with the epoxy matrices, thus remarkably enhance the mechanical properties of the nanocomposites and multi-scale CFRP composites. In contrast to reference CFRP composites, the incorporation TGPAP-modified MMTs greatly retards the propagation of inter-layer delamination, and fiber breakage becomes the major damage mode in the three-point bending tests. In particular, 4 wt% of TGPAP-modified MMTs increases the interlaminar shear strength of the multi-scale CFRP composites by 52%, and the flexural strength by 52.3%, which is superior to those of MMT-containing CFRP composites ever reported.

1. Introduction

Carbon fiber reinforced polymer (CFRP) composites are widely used in aerospace, defense and automobile industries, because of their high specific strength, modulus, stiffness and low density. The mechanical properties of CFRP composites are governed by the properties of the polymer matrix, the carbon fibers (CF) and the quality of fiber/resin interfacial adhesion [1]. In the last decade, “multi-scale” composites containing continuous microscale fibers as the primary reinforcement and discontinuous nanoscale fillers, such as carbon nanotubes [2–6] and nanofibers [7], nanoclays [8–21] and graphene derivatives [22–26], as the secondary reinforcement have attracted great research interest. It is expected that strengthening of the matrices by the nanoscale fillers can increase the performance of the multi-scale CFRP composites, especially the flexural strength that is matrix-dominated rather than fiber-dominated [27,28]. For example, we previously demonstrated that incorporation of reduced graphene oxide (rGO) greatly increased the mechanical properties of epoxy resin and its corresponding CFRP composites [25]. When the rGO content is 0.2 wt% in epoxy, the flexural strength of the multi-scale epoxy/rGO/CF composites is 32% greater than that of the epoxy/CF composite and the flexural modulus is increased by approximately 15%. However, the preparation of graphene oxide requires rather complicated and dangerous chemical reactions, and extremely time-consuming purification and separation processes.

Montmorillonite (MMT), after being transferred from hydrophilic to liophilic by ion-exchange with cationic surfactants, is considered to be the most attractive nanoclay as the secondary reinforcing materials for CFRP composites [8–21]. Miyagawa [13] investigated the effect of MMTs on the mechanical and thermophysical properties of a CF reinforced biobased epoxy composite. Dynamic mechanical analysis (DMA) showed an increase of 0.9 GPa for the storage modulus at 30 °C with the addition of 5.0 wt% exfoliated MMT nanoplatelets. The interlaminar shear strength (ILSS) of the CFRP composites was also increased. Chowdhury et al.

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[14] studied the effect of MMTs on the flexural and thermal properties of woven CF reinforced polymers manufactured by the vacuum assisted resin infusion molding process. The maximum improvements in the flexural strength and modulus are 13.7% and 9.35%, respectively, for 2 wt% MMT loading. Phonthammachai et al. [15] fabricated multilayer CFRP laminates from a silanized MMTs/epoxy nanocomposite by a slurry compounding technique. At low silanized MMT content (0.6 vol%), the flexural modulus and tensile modulus are 24% and 16% higher than those of neat epoxy CFRP composite, respectively. Xu et al. [16] manufactured CF reinforced epoxy/MMTs composites by hot melt lay-up plus autoclave process. The results showed that the interlaminar fracture toughness was increased by 85% by the introduction of 4 phr MMTs in the epoxy matrix, and the flexural strength was increased by 38% by the introduction of 2 phr MMTs. Zhou et al. [17] fabricated epoxy/MMTs/CF composites by vacuum assisted resin transfer molding and showed that incorporation of MMTs increased the glass transition temperature (Tg) by 5 °C, decomposition temperature by 6 °C and flexural strength by 13.5%. Khan et al. [18] studied the influence of MMTs on the fracture resistance and mechanical properties of epoxy nanocomposites and the corresponding CFRP composites. It was found that the incorporation of MMTs enhanced the impact and quasi-static fracture resistance, as well as the flexural strength and modulus of the CFRP composites. Besides the increased mechanical properties, MMTs also endow composites with other increased properties. Campbell et al. [19] reported that MMTs reduced the helium leak rate of CFRP cryotanks by fivefold. Fatigue crack propagation behaviors of CFRP composites are important in engineering components that are exposed to cyclic loading. Khan et al. [20] found a significant improvement (74%) in fatigue life for 3 wt% MMT reinforced CFRP composites. Timmerman et al. [21] utilized MMTs to efficiently eliminate the delamination, microcracking and potholing of CFRP composites caused by cryogenic cycling.

In previously reported MMT nanocomposites, MMTs are modified with amine derivatives, such as quaternary ammonium cationic surfactants with nonreactive hydrocarbon chains [29,30] and/or reactive hydroxyethyl chains of different lengths [31–33], 2,4,6-tris-(dimethylaminomethyl) phenol (an accelerator for epoxy curing) [34], and poly(oxyalkylene) amine (a curing agent of epoxy) [35,36]. In this study, a new type of organically modified MMTs was prepared by ion-exchanging MMTs with the hydrochlorate of triglycidyl *para*-aminophenol (TGPAP), a liquid tertiary amine-type epoxy oligomer used as the CFRP matrix for the aerospace industry. To the best of our knowledge, the tertiary amine-type epoxy was for the first time used for the modification of MMTs. The TGPAP-modified MMTs were incorporated into epoxy to prepare nanocomposites and multi-scale CFRP composites. TGPAP modification endows the MMT platelets with great dispersion uniformity in the epoxy matrix and reactivity towards the crosslinking of epoxy. The morphology and dispersion of the TGPAP-modified MMTs in the epoxy nanocomposites were observed. The flexural properties, tensile properties and thermomechanical properties of the MMTs/epoxy nanocomposites and the influence of the TGPAP-modified MMTs on the mechanical properties of muti-scale CFRP composites were investigated systematically.

2. Experimental

2.1. Materials

Na^+ montmorillonite (Na-MMT) was obtained from Zhejiang Huate New material Co., Ltd. (China) and the cation exchange capacity value of Na-MMT was 79 mmol/100 g. TGPAP was supplied by Shanghai Research Institute of Synthetic Resins (China). 3,5-Dimethylthio-2,4-toluenediamine (DMTDA), from Tianjin Zhongxin Chemtech Co., Ltd. (China), was used as the curing agent. Other chemicals were of reagent grade and purchased from Shanghai Chemical Reagents Company (China). Unidirectionally aligned CF fabrics (T700-12 K) were purchased from Toray (Japan).

2.2. Preparation of TGPAP modified Na-MMT

40 g of Na-MMT was dispersed in 320 mL of deionized water by stirring and sonication. The aqueous solution of the hydrochlorate of TGPAP was obtained by adding 13.3 g of TGPAP to 80 g of diluted HCl (0.6 mol/L). The Na-MMT suspension was mixed with the TGPAP·HCl solution and stirred vigorously for 2 h. The precipitation TGPAP-modified MMTs was separated by centrifuging, washed with large amount of water and then freeze-dried for 2 days.

2.3. Preparation of MMTs/epoxy nanocomposites

To prepare the MMTs/epoxy nanocomposites with various MMT contents, the above TGPAP-modified MMTs were added into various amounts of the mixture of TGPAP and DMTDA, and mechanically stirred vigorously until homogeneous mixtures were obtained. The mass ratio of TGPAP versus DMTDA in the final mixture was set at 2:1. The above MMTs/epoxy mixtures were heated and pre-cured in a steel mold at 120 °C for 0.5 h, 150 °C for 0.5 h, 170 °C for 2.5 h, and then post-cured at 200 °C for 1 h. The MMT contents varied from 2 to 8 wt% in the nanocomposites.

2.4. Preparation of the multi-scale CFRP composites

The multi-scale CFRP composites were prepared by hand lay-up and compression molding. The MMTs/epoxy mixtures with various MMT contents were first coated onto the two sides of CF fabrics at 80 °C and then cooled to room temperature to obtain CF prepregs. 10 layers of the CF prepregs were stacked and degassed in a vacuum oven. The temperature of the oven was increased from room temperature to 80 °C in half an hour and maintained at 80 °C for 2 h. After degassing, the stacked prepregs were taken out of the vacuum oven and then hot pressed at 10 MPa and then heated for curing. The curing scheme is the same to that for the above-mentioned MMTs/epoxy nanocomposites. The content of carbon fibers in the composites is about 66 wt% for all the samples.

2.5. Characterization

Wide-angle X-ray diffraction (XRD) patterns were obtained with a PANalytical X'Pert PRO MPD diffraction system (The Netherlands) equipped with Cu Kα radiation ($\lambda = 1.542$ Å). The dispersion of MMTs in the epoxy matrix was observed by transmission electron microscopy (TEM) (JEM-1200EX, JEOL, Japan) and high resolution electron microscopy (HRTEM) (CM200UT, Philips, The Netherlands). Ultrathin sections of approximately 100 nm were microtomed at ambient temperature by ultramicrotom (Power Tome PC, RMC, USA) with a diamond knife. A Hitachi S-4800 (Hitachi, Japan) scanning electron microscope (SEM) was used to examine the micro-morphology of the fracture surfaces of the MMTs/epoxy nanocomposites and the multi-scale CFRP composites. Prior to the SEM examination, the samples were sputter-coated with gold to avoid charge accumulations. Dynamic mechanical analysis (DMA) for the MMTs/epoxy nanocomposites was performed in a three-point-bending mode using DMA (Q800, TA Instruments, U.S.A.), which was operated at 1 Hz at a constant heating rate of 3 °C/min and temperatures from 30 to 250 °C. Rectangular specimens with dimensions of $20 \times 5 \times 2$ mm^3 were used for the DMA measurement. Tensile, flexural properties and ILSS values