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Regular Article

Reinforced carbon fiber laminates with oriented carbon nanotube epoxy nanocomposites: Magnetic field assisted alignment and cryogenic temperature mechanical properties

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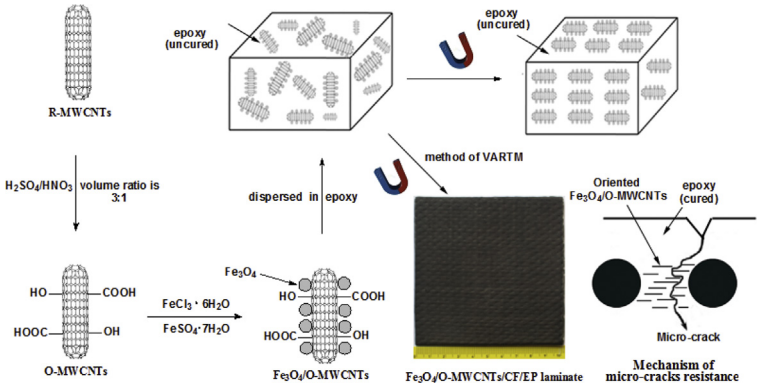
GRAPHICAL ABSTRACT



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ABSTRACT

The epoxy nanocomposites with ordered multi-walled carbon nanotubes (MWCNTs) were used to influence the micro-cracks resistance of carbon fiber reinforced epoxy (CF/EP) laminate at 77 K, Oxidized MWCNTs functionalized with Fe_3O_4 (Fe_3O_4/O-MWCNTs) with good magnetic properties were prepared by co-precipitation method and used to modify epoxy (EP) for cryogenic applications. Fe_3O_4/O-MWCNTs reinforced carbon fiber epoxy composites were also prepared through vacuum-assisted resin transfer molding (VARTM). The ordered Fe_3O_4/O-MWCNTs were observed to have effectively improved the mechanical properties of epoxy (EP) matrix at 77 K and reduce the coefficient of thermal expansion (CTE) of EP matrix. The ordered Fe_3O_4/O-MWCNTs also obviously improved the micro-cracks resistance of CF/EP composites at 77 K. Compared to neat EP, the CTE of ordered Fe_3O_4/O-MWCNTs modified CF/EP composites was decreased 37.6%. Compared to CF/EP composites, the micro-cracks density of ordered Fe_3O_4/O-MWCNTs modified CF/EP composites at 77 K was decreased 37.2%.

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1. Introduction

Carbon fiber reinforced epoxy resin (CF/EP) laminate, which is fabricated by using epoxy (EP) as matrix and continuous carbon fiber (CF) as reinforcing materials through prepreg, mould pressing and vacuum resin transfer mould (VARTM), has been proved to be one kind of advanced composites due to its superior properties, such as high specific strength and modulus, anti fatigue and corrosion, easy processing, and facile large-scale production. Thus, it is considered to be the most promising structural materials in cryogenic propellant tank for space shuttles [1–6]. When the CF/EP composite tank is used for cryogenic liquid storage and suffers from the process of low-temperature aging and temperature cycling from room temperature (RT) to cryogenic temperature (77 K), micro-cracks will appear and propagate in the composites, causing a variety of defects, such as fiber/matrix interface debonding, pore formation and delamination [7–9]. All these will result in a significant reduction in the performance of composites, leading to the leakage of liquid. Therefore, the CF/EP composites with excellent micro-crack resistance at low temperature are most critical for the design and development of reusable launch vehicles.

Generally, the micro-cracks of CF/EP composites developed during the temperature cycling mainly happen in the resin matrix and mainly arise from different thermal properties between carbon fibers and epoxy resin matrix. For example, the coefficient of thermal expansion (CTE) of epoxy is about $65 \times 10^{-6}\ ^{\circ}C^{-1}$ while about $-12 \times 10^{-6}\ ^{\circ}C^{-1}$ for the carbon fibers [10]. This vast difference will introduce a high internal stress in the composites during the temperature cycle, leading to the formation and growth of micro-cracks in the epoxy matrix. Therefore, the resistance to micro-crack of the CF/EP composites is largely determined by the performance of epoxy matrix, which is closely related to the property and the orientation of the fillers dispersed in the resin except the molecular structure of the epoxy resin.

Previous studies have shown that the micro-crack resistance of CF/EP composites in low temperature environment can be improved by adding fillers, such as alumina, clay, carbon nanotubes (CNTs) and graphene. For example, Timmerman et al. [11] and Khan et al. [12] adopted layered clays as fillers in the fiber-reinforced epoxy composites. The transverse cracking in the symmetric CF/EP composites as a response to cryogenic cycling was significantly reduced and the filler concentration used was much lower than that for the traditional fillers. The particle concentration and their distribution state in the matrix were also observed to be very important in maximizing the benefits of fillers reinforcement. Meanwhile, nanoclays can be easily used to modify the traditional fiber-reinforced composites and enhance their resistance to thermal cycling induced stress. For example, Kim et al. [13] and Yokozeki et al. [14] attempted to enhance the crack resistance of the carbon/epoxy composites by adding multi-walled carbon nanotubes (MWCNTs) into the resin. Due to the embrittlement of the epoxy resin at 77 K, the degree of fracture toughness enhancement obtained from the application of toughened epoxy at cryogenic temperature was less than that at room temperature. The MWCNTs-added carbon/epoxy unidirectional prepregs were fabricated via a filament winding method with different concentrations of MWCNTs (0.0, 0.2 and 0.7 wt%). The material systems blended with 0.2 and 0.7 wt% MWCNTs exhibited an enhanced fracture toughness and low crack density at the cryogenic temperature. The micro-cracks propagated normal to the fibers when viewed along their length through the epoxy matrix beginning at the outer edge of the laminate and ending at 0°/90° ply interface. The results were also reported by Nobelen et al. [15]. In our previous studies, slightly increased mechanical properties and significantly reduced CTE value of epoxy resin were obtained by adding MWCNTs [16]. All the above research results show that the randomly distributed nanofillers can improve the micro-cracks resistance of CF/EP laminates, but the effects of ordered nanofillers in matrix on the mechanical properties of CF/EP laminate at cryogenic temperature have not been reported yet.

Herein, the main purpose of this study is to investigate the effects of functionalized MWCNTs orderly distributed in the matrix on the mechanical properties of CF/EP laminate at 77 K. The optimized formulation of diglycidyl ether of bisphenol-A (DGEBA)/poly oxypropylenediamine (jeffamine D-230) with a low viscosity was selected as the epoxy matrix. Raw MWCNTs (R-MWCNTs), oxidized MWCNTs (O-MWCNTs) and Fe_3O_4/O-MWCNTs were used to modify epoxy. A magnetic induced approach was presented for the preparation of epoxy nanocomposites with Fe_3O_4/O-MWCNTs of ordered alignment. O-MWCNTs were first coated with magnetic Fe_3O_4 particles, and dispersed in epoxy matrix, and finally induced to be aligned by a magnetic force before the suspension was cross-linked. The tensile and impact mechanical properties of the modified epoxy composites at 77 K were studied and compared with those at RT. The mechanisms of CNTs modifiers on the cryogenic toughening and micro-cracks resistance behaviors of modified CF/EP laminates under cryogenic thermal cycling were investigated.

2. Experiments

2.1. Materials

Raw MWCNTs (R-MWCNTs) used in the study were synthesized by catalytic chemical vapor deposition (CM-95, Hanhwa Nanotech, Korea). The epoxy resin was YD-128 (DGEBA, Kukdo Chemical Co. Ltd), which had an epoxide equivalent weight (EEW) of 185-190 eq-1. The curing agent (jeffamine D-230) was provided by New Seoul Chemical Co. Ltd. The reagents used for the acid treatment were nitric acid (60–62%, Junsei Chemical, Japan), and sulfuric acid (95%, Junsei Chemical). Ammonia solution (25%), ethanol (99.5%), iron chloride hexahydrate (99.0%, $FeCl_3{\cdot}6H_2O$), iron sulfate heptahydrate (99.0%, $FeSO_4{\cdot}7H_2O$) and monodispersed magnetite microspheres (99.0%, Fe_3O_4) were purchased from Aladdin regent Co. Ltd, Shanghai, China. All the chemicals and reagents were used without any further treatment. Unidirectional carbon fibers (CARBONEX CF-730, Hankuk Carbon Ltd., Korea) were used as reinforcement for the composites.

2.2. Preparation of O-MWCNTs and Fe_3O_4/O-MWCNTs

Oxidization of MWCNTs (O-MWCNTs): Certain amount of R-MWCNTs was weighed and transferred into a 500 mL flask, then mixed with acid (volume ratio of sulfuric acid and nitric acid was 3:1, carefully added along the wall of the flask). The mixture was heated to 110 °C under strong magnetic stirring and then maintained at this temperature for an additional hour. The O-MWCNTs were separated by using cellulose acetate membrane and repeatedly washed with distilled water until the pH value was 7. Finally, the collected O-MWCNTs were dried in a vacuum oven at 60 °C.

Fe_3O_4/O-MWCNTs: The Fe_3O_4/O-MWCNTs were synthesized by an in-situ chemical oxidation and co-precipitation method, which was slightly modified from the reported method [17]. Briefly, 40 mg O-MWCNTs were dispersed ultrasonically with 150 mL DI water in the flask for one hour. Then, the flask was purged with N_2 for 30 min. A solution of $FeCl_3{\cdot}6H_2O$ (48.0 mg) and $FeSO_4{\cdot}7H_2O$ (247.1 mg) in DI water (50 mL) was purged with N_2 for 30 min and then added to the flask. The flask was transferred to a water bath at