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Reduction of thermal residual stresses of laminated polymer composites by addition of carbon nanotubes

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ABSTRACT

This paper studies the effects of multi-walled carbon nanotubes (MWCNTs) on the thermal residual stresses in polymeric fibrous composites. Reinforced ML-506 epoxy nanocomposites with different amounts of homogeneously dispersed MWCNTs (0.1 wt.%, 0.5 wt.% and 1 wt.%) were fabricated using the sonication technique. Thermo-mechanical analysis and tensile tests of the specimens were carried out to characterize the thermal and mechanical properties of MWCNTs/epoxy composites. Due to the negative thermal expansion and high modulus of MWCNTs, addition of MWCNTs resulted in a great reduction of the coefficient of thermal expansion (CTE) of epoxy. The MWCNTs also moderately increased the Young's modulus of the epoxy. Then, the effects of adding MWCNTs on micro and macro-residual stresses in carbon fiber (CF)/epoxy laminated composites were investigated using the energy method and the classical lamination theory (CLT), respectively. The results indicated that the addition of low amounts of MWCNTs leads to a considerable reduction in thermal residual stress components in both micro and macro levels.

1. Introduction

In laminated polymer composites, due to their inherent inhomogeneous nature, residual stresses are generated during the curing process. These stresses adversely influence dimensional stability and strength of composite laminates and could result in premature failure, delamination, warpage and matrix cracking [1–3]. Thus, it is important to develop techniques to reduce these stresses. The most approaches employed so far for this purpose are confined to modifying curing cycles [4–8].

Residual stresses in laminated composites, based on their resources, are studied from two points of view; micro residual stresses in a unidirectional ply and macro residual stresses in laminated composites. Micro and macro residual stresses originate from independent sources. The residual stress in micro-scale is mainly the result of the mismatch in coefficient of thermal expansion (CTE) and Young's modulus between the fibers and the matrix, while at the macro-mechanical level, expansion and contraction of different layers with different orientations is the major source of residual stresses. Therefore, residual stresses in each layer of laminated polymer composites can be determined separately on the micro- and macro-scales.

In recent years, an increasing number of materials with negative thermal expansion have been discovered. One of the most important applications of the negative thermal expansion materials is to compensate for undesirable effects of high thermal expansion of other materials. Regarding this fact, addition of nano-additives with negative CTE to polymer matrix is a potential approach to effectively reduce thermal residual stresses in fiber-reinforced polymer composites. The thermal residual stresses are mainly functions of CTE and Young's modulus of the composite constituents. Compared with polymer matrix, nano-additives like CNTs and CNFs have much higher Young's modulus and much lower CTE. Thus, these nano-additives could be dispersed into the polymer to modify its thermal and elastic behavior.

Numerous experimental studies demonstrated the great capability of CNTs for the modification of thermal and mechanical properties of the polymer matrix [9–12]. Compared with two-phase composites (nano-additive and matrix), less studies have been carried out on the thermal and mechanical properties of three-phase composites (nano-additive, fibers and matrix). Some researchers reported significant reduction of CTE of fibrous composites due to addition of small amounts of nano-additives [13,14].

On the other hand, very little research has so far been conducted on the nano-additives effects on thermal residual stresses of composites. Nishino et al. [15] studied the effect of tungstate zirconium phosphate (ZWP) particles on CTE of polyether ether ketone (PEEK) polymers. They experimentally showed that by

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incorporating 40 vol.% ZWP particles with negative CTE, the CTE of the ZWP/PEEK composite reduces about 62% and becomes identical to the CTE of aluminum. This reduction in CTE was found to be effective for the decrease of the residual stress at the interface between aluminum plate and the ZWP/PEEK composites. Also, Hsiao and Gangireddy [16] showed that the use of CNFs results in the reduction of the spring-in phenomenon in *L*-shaped glass/polyester composite parts. Badrinarayanan et al. [17] could remarkably reduce the warpage of un-symmetric carbon fiber-reinforced composite laminates by using zirconium tungstate (ZrW_2O_8) nanoparticles. Although these studies show that the enhancement of dimensional stability in composite components could be accomplished by using nano-additives, but no previous work, to the best of the authors' knowledge, has quantitatively studied the effect of nano-additives on the micro and macro residual stresses distribution in the laminated polymer composites.

This paper presents a study on MWCNTs effects on thermal residual stresses in polymeric fibrous composites. For this purpose, the CLT and the energy method are coupled with the experimental characterization results to study MWCNTs effects on the thermo-mechanical properties of MWCNTs/epoxy and MWCNTs/CF/epoxy nanocomposites as well as, ultimately, on the micro- and macro-residual stress components. A significant trend of reduction in both micro and macro-residual stresses was found when the MWCNTs weight fraction increased. These findings confirm that MWCNTs possess excellent potential to be used as a thermal expansion compensator for the modification of the thermal behavior of the epoxy and to reduce the thermal residual stresses of the fiber/epoxy laminated composites.

2. Experimental procedure

In this study, two-phase MWCNTs/epoxy composites and three-phase MWCNTs/CF/epoxy composites were fabricated and characterized. The MWCNTs were dispersed into the epoxy matrix with three weight ratios of 0.1%, 0.5% and 1% which were then reinforced with carbon fibers. A detailed description of these experiments is presented in the following sections.

2.1. Raw materials and nanocomposites fabrication

The MWCNT (purity >95%) in this study was provided by Neutrino Company and had an average diameter of 8–15 nm, a length of 0.5–2 μm and a density of 1.65 g/cc. The diglycidyl ether of Bisphenol-B epoxy resin, ML-506 (Mokarrar Engineering Materials, Iran) and the curing agent, Aradur-830 (Huntsman, Germany) were used at 100:60 ratio for fabrication of nanocomposites.

The ML-506 epoxy was mixed with Aradur-830 hardener thoroughly. The mixture was stirred for 30 min at 250 rpm. Then, the mixture was placed under a vacuum chamber for 30 min to remove air bubbles. The MWCNTs/epoxy nanocomposite specimens reinforced with three different contents of MWCNTs were fabricated with the aid of the sonication technique. First, ML-506 epoxy were premixed with MWCNTs by shaking and stirred for 30 min at 2000 rpm. Then, in order to break the residual aggregates and obtain a homogeneous dispersed mixture of epoxy resin and MWCNTs, the mixtures containing 0.1, 0.5 and 1 wt.% MWCNTs were sonicated (Hielscher UP400S, Teltow, Germany) at 200 W with a probe of 14 mm diameter for 40, 60 and 80 min, respectively [18]. During the sonication, the mixture container cooled in an ice-bath. Once the sonication was completed, the curing agent was added to the mixture and stirred for 20 min at 250 rpm. Then, air bubbles were removed by degassing the solution in a vacuum chamber for 15 min. Finally, the bubble free mixtures of MWCNTs/epoxy and neat resin were cast into steel molds and cured for 6 h at 100 °C followed by 6 *h* at 120 °C. A mold-releasing agent was added to the mold surface to allow an easy release of the cured specimens. The cured specimens were then allowed to cool slowly.

Three-phase MWCNTs/CF/epoxy composites were manufactured using the hand lay-up method. The MWCNTs/epoxy composite was used in the manufacturing of MWCNTs/CF/epoxy composites. Subsequently, the curing agent was added to MWCNTs/epoxy mixture and the multi-phase composite was fabricated by the hand lay-up method. In addition, the same cure process as the two-phase composites was employed for the three-phase composites. A roller was used to remove the air entrapped during the hand lay-up process and to uniformly distribute the resin between all layers. The volume fraction of the carbon fibers in final laminates was approximately 45% for all composite specimens, measured by burn-off tests.

2.2. Characterization of nanocomposites

2.2.1. Young's modulus characterization of nanocomposites

The Young's modulus of the fabricated MWCNTs/epoxy specimens was obtained using tensile tests, performed according to ASTM: D638-10. In order to perform the tensile test, a universal testing apparatus (STM-150, Santam, Iran) with a 50 kN load cell was used. The machine was run under the displacement control mode at a crosshead speed of 1.0 mm/min. An extensometer of 50 mm gauge length was used for strain measurement. Both ends of each specimen were clamped by the pneumatics grips of the testing machine with an inter-grip distance of 40.0 mm. Prior to the tensile test, all samples were mechanically polished to minimize the influence of surface flaws, especially the porosity. At least five samples were tested for each MWCNTs contents; the final property was the average result of the five tests. Prepared samples for tensile tests are shown in Fig. 1.

In the macro residual stress analysis by the CLT, the elastic constants of the unidirectional MWCNTs/CF/epoxy composites are required. Static strength tests in the longitudinal and transverse directions were performed for the unidirectional MWCNTs/CF/epoxy laminates as three-phase composites, according to ASTM: D3039 M-08. The dimensions of 0° unidirectional specimens were about 250 mm in length, 15 mm in width and 1.2 mm in thickness. The dimensions of the 90° unidirectional specimens were about 175 mm in length, 25 mm in width and 2.1 mm in thickness. For each weight fraction of MWCNTs, five specimens were tested.

2.2.2. CTE characterization of nanocomposites

In order to investigate the MWCNTs effects on the CTE of composites, the CTE of the neat resin and, MWCNTs/epoxy specimens was measured by a thermo-mechanical analyzer (TMA). The CTE values were determined by measuring the inclination of the thermal strains vs the temperature according to ASTM: E831-12:

Fig. 1. (a) MWCNTs/epoxy, (b) Neat epoxy, (c) longitudinal MWCNTs/CF/epoxy and (d) transverse MWCNTs/CF/epoxy specimens prepared for the tensile test.