A Novel Method to Decrease Micro-residual Stresses of Fibrous Composites by Adding Carbon Nanotube

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Abstract
In this research, a novel method to decrease micro-residual stresses of fibrous composites by adding carbon nanotubes (CNTs) is proposed in detail. The negative coefficient of thermal expansion and the high young's modulus of CNTs can be utilized to counterbalance the process induced residual stresses in composites. To this end, first, the effects of adding CNTs to the matrix of fibrous composites in reducing the coefficient of thermal expansion (CTE) and increasing of young's modulus of matrix are studied theoretically. Then, a three phase micromechanical model (the energy method) is used to model the effect of CNT in reducing the residual stresses of fibrous composites. The results show that by addition of CNTs, enhancements in properties of matrix are obtained and lead to decrease in micro-residual stresses of matrix and fiber up to 72%.

Keywords: Residual Stress; Carbon Nanotube; Fibrous Composite; Polymer

1. Introduction

Residual stress in fiber reinforced polymer composites (FRP) is caused due to high contraction of polymer matrix in comparison with fibers during curing and cooling stages of fabrication. Such a phenomenon is almost observed in any FRP to some extent as a result of natural inconsistency of physical and mechanical properties of composite contents. On the micromechanical level or constituent level, the mismatch in coefficient of thermal expansion between the fibers and the matrix is the governing parameter [1, 2]. Assuming that bonding between the fiber and matrix leads to compressive and radial residual stresses in the fiber and tensile; and radial residual stresses in the matrix. Such stresses are often ignored or neglected in design of composites. Thus, misinterpretation may happen in characterizing mechanical properties of composites [3].

There have been already some procedures to control the dimensional stability and decrease residual stresses. However, all these approaches are confined to changing in layers arrangement or curing cycles [4]. Nowadays, nano-science has attracted many attentions. A novel approach is to utilize the outstanding properties of carbon nanotubes (CNTs). High Young's modulus and negative thermal expansion of CNTs have made them suitable candidates to fabricate residual stresses free nanocomposites [5, 6]. In many researches, increase in young's modulus and decrease in thermal expansion of polymers due to addition of CNTs are reported [6-10].

In this study, by presenting a modeling approach, it is shown how decrease in the thermal expansion and increase in the young's modulus of polymer matrix as results of addition of CNTs influences the reduction of micro-residual stresses of the matrix and fiber in CNT/carbon fiber/polymer nanocomposite.

2. Calculations

2.1. Effect of CNTs on coefficient of thermal expansion and Young's modulus of polymers

Theoretically, Young's modulus of CNT is about 1 *TPa*. The reported longitudinal coefficient of thermal expansion (CTE) for CNT is -1.5E-6 $°C^{-1}$. Despite this fact, the CNT radial CTE is about 15E-6 $°C^{-1}$ [5]. There are two key points to be investigated about the CNTs/polymer nanocomposites. First is the dispersion state of CNTs in the matrix and the other is the possible reactions

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of CNTs with polymer chains. In many researches, decreased CTE of polymers due to addition of CNTs are reported experimentally, but no nanoscale model has been already reported for the predication of CTE of CNT/polymer nanocomposites. To estimate the CTE of CNT/epoxy nanocomposite, a micromechanical equation is utilized [5, 11].

$$\alpha_{nc} = \frac{\alpha_{CNT} V_{CNT} E_{CNT} + \alpha_m (1 - V_{CNT}) E_m}{V_{CNT} E_{CNT} + (1 - V_{CNT}) E_m} \tag{1}$$

In which α_{nc}, α_{CNT}, α_m are CTE of nanocomposites, CNT and matrix, respectively. E_m and E_{CNT} are young's modulus of matrix and CNT. V_{CNT} is the CNT volume fraction. Equation 1 does not take into account the distribution of the nanotubes, but assumes a perfect reinforcement of the matrix with a perfect alignment and interfacial bonding of the nanotubes.

Usually, Young's modulus of nano-filler is high. Experimental results about CNTs show that as the weight loading of CNTs in matrix increases, Young's modulus of matrix increases in a linear manner. By more increase in the weight loadings, Young's modulus increasing trend falls due to difficulties of CNTs dispersion in matrix and agglomeration generation. Generally, Young's modulus of polymer reinforced with CNTs is calculated by the use of Young's characteristics of components (CNT and matrix), aspect ratio and CNT volume fraction. Since the CNT Young's modulus is usually higher than that of polymeric matrices, through polymer reinforcement by CNT, composite modulus increases.

For modeling of a matrix reinforced with nano-fillers, there are currently different experimental and semi experimental methods. Depending on the nano-fillers geometry and structure, it is possible to use modified micromechanics equations with these nano-fillers. Also, in studies conducted for replacement of CNTs with an effective modulus, a mathematical model for estimation of Young's modulus of polymeric matrices reinforced with CNTs has been presented. A model to estimate the Young's modulus of CNT reinforced polymer is presented [12]. While these equations are simple, they match experimental data. In this model, through effective modulus definition and considering interphase properties using Halpin-Tsai equations, nanocomposite Young's modulus is estimated as below:

$$\eta_1 = \frac{\frac{(E_{Eff.NF})_{Long}}{E_m} - 1}{\frac{(E_{Eff.NF})_{Long}}{E_m} + \frac{L}{R_{NT}}} \Rightarrow E_{11} = E_m \left(\frac{1 + \frac{L}{R_{NT}} \eta_1 v_f}{1 - \eta_1 v_f} \right)$$

$$\eta_2 = \frac{\frac{(E_{Eff.NF})_{Tran}}{E_m} - 1}{\frac{(E_{Eff.NF})_{Tran}}{E_m} + 2} \Rightarrow E_{22} = E_m \left(\frac{1 + 2\eta_2 v_f}{1 - \eta_2 v_f} \right) \tag{2}$$

where L is CNT length, R_{NT} is CNT radius, E_m is matrix Young's modulus, V_f is CNT volume fraction and $(E_{EFF.NT})_{Long}$ and $(E_{EFF.NT})_{Tran}$ are effective CNT longitudinal and transverse Young's modulus, respectively. And finally, Young's modulus of composite reinforced by CNT is:

$$E = \frac{3}{8} E_{11} + \frac{5}{8} E_{22} \tag{3}$$

2.2. CTE and Young's modulus of CNT/epoxy nanocomposite

Equation 1 is used to calculate the CTE of CNT/epoxy nanocomposite at various weight ratios for epoxy resin (LY556 supplied by Huntsman Co.) with thermal expansion of 70E-6 $°C^{-1}$ and Young's modulus of 2.5 *GPa* and Poisson's ratio of 0.28 enhanced with single-wall carbon nanotubes (SWNT) with Young's modulus of 1 T*Pa* and CTE of -1.5E-6 $°C^{-1}$. Fig.1 presents the CTE of nanocomposite for various CNT contents. The micromechanical model shows a decrease of 70% of CTE for CNT/epoxy at 1 *wt.%* SWNT.

To estimate the Young's modulus of above composites, Shokrieh and Mahdavi's model is employed [12]. To use this model, length of SWNT is considered to be 15 *µm*. Thickness of CNT wall and its radius are 0.34 *nm* and 2 *nm*, respectively. The results of Young's modulus of CNT/epoxy are illustrated in Figure 2. As can be seen in Figure 2, Young's modulus has an increase of 30% at 1 wt.% SWNT.

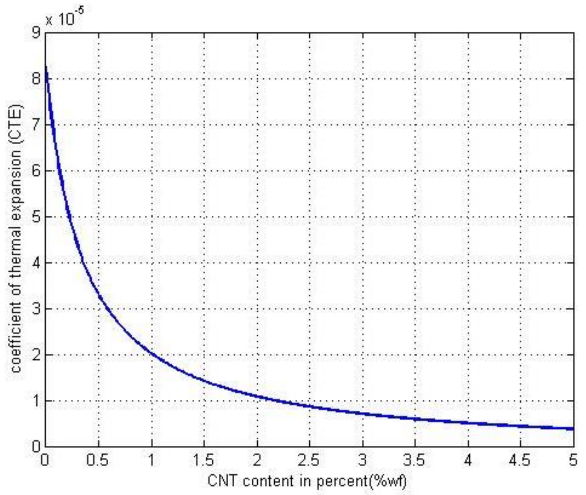


Fig. 1. CTE of SWNT/Epoxy (LY 556) nanocomposite at various filler contents.

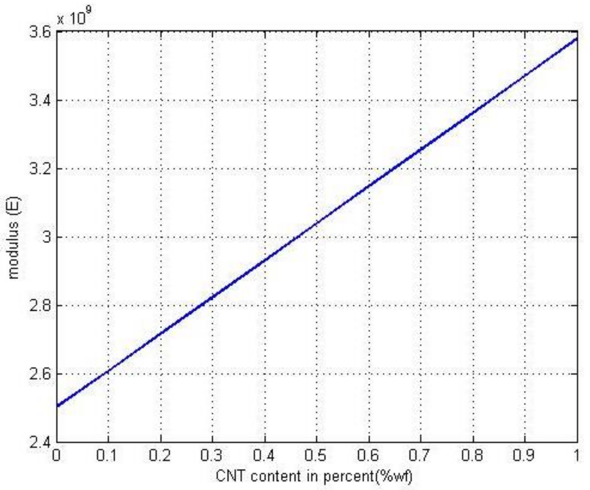


Fig. 2. Young's modulus of CNT/epoxy (LY556) nanocomposite at various filler contents.

3. Results and Discussion

3.1. Micro-residual stresses of CNT/carbon/epoxy nanocomposites

Several micro-analytical methods have been presented by various authors to determine residual stresses in a single fiber-matrix composite [13, 14]. Among them, Shokrieh and Safarabadi developed a model based on the energy method to determine the micro-residual stresses components in fibrous composites [15]. This method does not have the limiting assumptions of the other methods and provides a direct approach to obtain the micro-residual stresses rather than using an indirect approach.

With regard to good dispersion of CNTs through the matrix, one can assume a CNT/epoxy nanocomposite as a homogeneous matrix with enhanced properties [16]. Then, with ignorance of CNT effect on the interphase properties between the carbon fiber and the matrix, micro-residual stresses for CNT/carbon fiber/epoxy are modeled using three phase energy method.

3.2. Energy method

Shokrieh and Safarabadi proposed a three-dimensional closed-form solution which can be used for prediction of micro-residual stresses in a single fiber-interphase-matrix composite. The proposed solution is based on the energy method. First, the representative volume element (RVE) is considered as a single fiber-matrix composite with the interphase between them (Figure 3). Then, two suitable Airy stress functions are assumed (Eq.11). By applying the equilibrium equations and boundary conditions, the other stress components in the fiber and matrix are obtained in terms of the two assumed Airy stress functions. In the next step, using the stress-strain relations, all strain components for the three phases are calculated. Finally, the total strain energy is formulated and based on the minimum total complementary energy principle, the two unknown Airy stress functions are found and as a result the full state of residual stress components is obtained.

This method consists of some assumptions such as bonding between the matrix and fiber which is assumed to be imperfect. Also, all three phases (the fiber, matrix and the interphase) are homogeneous and linearly elastic. Moreover the fiber, matrix and interphase are modeled as isotropic materials.

In a cylindrical coordinate system the equilibrium equations are [17]:

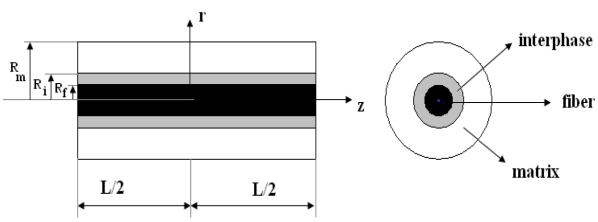


Fig. 3. The three-phase composite model [12].

$$\frac{\partial \sigma_{zz}}{\partial z}+\frac{\partial \tau_{rz}}{\partial r}+\frac{\tau_{rz}}{r}=0 \tag{4}$$

$$\frac{\partial \sigma_{rr}}{\partial r}+\frac{\partial \tau_{rz}}{\partial z}+\frac{\sigma_{rr}-\sigma_{\theta\theta}}{r}=0 \tag{5}$$

For an axi-symmetric problem, the stress components in terms of the Airy stress function ϕ are given by:

$$\sigma_{rr}=\frac{1}{r}\frac{\partial \phi}{\partial r}+\frac{\partial^2 \phi}{\partial z^2} \tag{6}$$

$$\sigma_{\theta\theta}=\frac{\partial^2 \phi}{\partial z^2} \tag{7}$$

$$\sigma_{zz}=\frac{\partial^2 \phi}{\partial r^2}+\frac{1}{r}\frac{\partial \phi}{\partial r} \tag{8}$$

$$\tau_{rz}=-\frac{\partial^2 \phi}{\partial r \partial z} \tag{9}$$

$$\tau_{z\theta}=\tau_{r\theta}=0 \tag{10}$$

Here, because of the axi-symmetry, Airy stress functions can be assumed as:

$$\phi_j(r,z)=f_n(r).g_n(z) \qquad n=1,2,3 \quad , \quad j=f,m,i \tag{11}$$

The subscripts $j=f,m,i$ refer to the fiber, matrix and interphase respectively. Also the functions $f_n(r)$ and $g_n(z)$ are functions of radial and axial coordinates, respectively. Thus, using equations 6-9 the stresses in the three phases can be written as:

$$\sigma_{rr}^{j}=\frac{1}{r}\frac{df_n(r)}{dr}g_n(z)+f_n(r)\frac{d^2 g_n(z)}{dz^2} \tag{12}$$

$$\sigma_{\theta\theta}^{j}=f_n(r)\frac{d^2 g_n(z)}{dz^2} \tag{13}$$

$$\sigma_{zz}^{j}=(\frac{d^2 f_n(r)}{dr^2}+\frac{1}{r}\frac{df_n(r)}{dr})g_n(z) \tag{14}$$

$$\tau_{rz}^{j}=-\frac{df_n(r)}{dr}\frac{dg_n(z)}{dz} \tag{15}$$

Due to the stress-free state of the boundary conditions and the stress continuity at the fiber-interphase and interphase-matrix interfaces along radial direction, the number of unknown functions $f_n(r)$ decreases. Also, the axial stresses in the composite constituents are maximum at the plane of symmetry and zero at the ends of the composite. Thus the functions $f_1(r)$, $f_2(r)$ and $f_3(r)$ can be written as an unknown constant A_1 [18]. Consequently, with respect to equation 14 the axial stresses in the fiber and matrix are:

$$\sigma_{zz}^{f}=A_1 g_1(z) \tag{16}$$

$$\sigma_{zz}^{i}=A_2 g_2(z) \tag{17}$$

$$\sigma_{zz}^{m}=A_3 g_3(z) \tag{18}$$

On the other hand, the equilibrium equation in axial direction yields:

$$\sigma_{zz}^{f}V_f+\sigma_{zz}^{i}V_i+\sigma_{zz}^{m}V_m=0 \tag{19}$$

where V_f, V_m, V_i are the fiber, matrix and interphase volume fractions, respectively. Substituting equations 16, 17, 18 in to equation 19 gives:

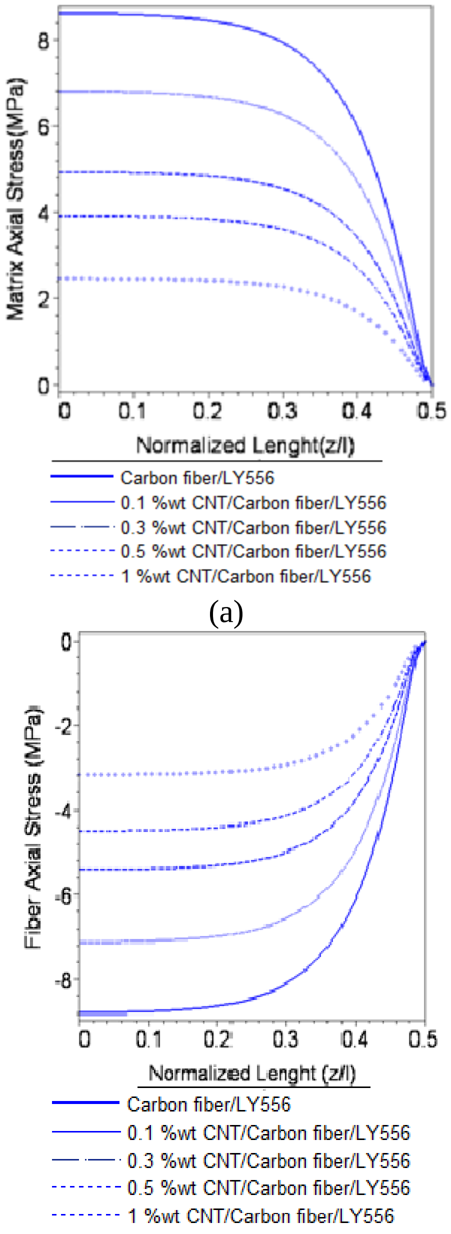
$$A_1 g_1(z)V_f+A_2 g_2(z)V_m+A_3 g_3(z)V_i=0 \tag{20}$$

Equation 20 relates the three unknown functions $g_1(z), g_2(z), g_3(z)$ to each other. So, there are actually two unknown functions. Using the total complementary energy principle, these two functions will be determined and the third one will be found from equation 20. So the axial, shear, radial and tangential stress components can be obtained in the composite constituents. A comprehensive description of three dimensional analysis of micro-residual stresses is shown in reference 15.

3.3. Results of micro-residual stresses for CNT/carbon/epoxy nanocomposites

With utilization of CTE and Young's modulus results, micro-residual stresses of the fiber and matrix in the nanocomposite are calculated and compared with the residual stress of carbon/epoxy composites using a MAPLE code written from the energy method.

Figs. 4a and 4b show the distribution of residual stress in the matrix and fiber, respectively. As can be seen, with increase in



(a)

(b)

Fig. 4. (a) Fiber axial residual stress distribution; (b) Matrix axial residual stress distribution.

Table 1. Decrease of the maximum residual stress in fiber and matrix.

CNT content (wt.%)	0. 1	0.3	0.5	1
Decrease of the Maximum fiber axial residual stress (%)	21	44	50	69
Decrease of the Maximum matrix axial residual stress (%)	23	46	64	72

the CNT content, maximum axial stress in the fiber and matrix is decreased. The reduction of axial residual stress of fiber and matrix at 1 *wt.%* SWNT are 69% and 72%, respectively which are considerable. Table 1 presents the amounts of decrease in the residual stress of CNT-Carbon/Epoxy for different CNT contents.

4. Conclusions

In this research, the effect of CNT on distribution of micro-residual stresses in fibrous CNT/carbon/epoxy nanocomposite was investigated. With the aid of available macro and nano-mechanic equations, Young's modulus and coefficient of thermal expansion in presence of CNT were calculated. It was seen that addition of the CNTs to the epoxy matrix led to an increase in the Young's modulus and a decrease in the CTE of the polymer. By using energy based model, micro-residual stresses of fibrous nanocomposite at various CNT contents were calculated. As it was expected, by addition of CNTs, enhancements in the properties of matrix were obtained and led to considerable amount of decrease in the micro-residual stresses of the matrix and fiber. By obtaining a good dispersion of the CNTs, which is usually achieved at weight ratios below 1 *wt.%*, the results indicated that reduction of 72% in microscale residual stress in the matrix and fiber was obtainable. It is noteworthy that the CNT influence on the interphase properties and reaction of CNT particles with the polymer chain, are ignored in the energy model. However, such phenomena may lead to the presence of the residual stress. Therefore, considering them needs further studies.

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