Analytical and Numerical Micromechanical Modelling of Carbon Nano Tubes/ Poly-L-Lactic Acid Composites for Bone Scaffold Application.

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Abstract

Composites comprising Carbon Nano Tube (CNT)s and the biocompatible polymers are of special interest due to their potential for specific biomedical applications. Pure biocompatible polymers such as poly-L-lactic acid (PLLA) does not have adequate mechanical properties for certain medical applications such as bone scaffolds or bone fixture; therefore new studies have been conducted. In this paper, we discussed on reinforcing the biodegradable polymers with carbon nanotubes as filler. We prepared mixture of single walled CNT (SWCNT) in PLLA for bone scaffolds application with a simple mixing method. We discovered that an addition up to 0.5 wt.% SWCNT found to increase the elastic modulus in factor of 4 and tend to decrease after an addition of 0.7 wt.% . Here, we report both analytical and numerical micromechanical model for elastic modulus compared with the experimental data. The analytical models covered the simplest model such as mixing rule (Voigt and Reuss model) and more advanced one such as Halpin-Tsai model. On the other hand, the numerical model elucidated a model of representative volume element (RVE) of the CNT/polymers. Additionally, particle orientations were also investigated in the random and aligned direction for analytical and numerical model. In the end, volume element simulation results of Ec/Em (stiffness ratio) are compared with the analytical model solution. The result shows that numerical simulation with aligned particle orientation gave best result for estimating the stiffness ratio of SWCNT up to 0.5 wt.%. The scanning electron microscope images also pictured to verify the alignment of particles in the polymer matrix.

Keywords:*CNT composites, biocompatible polymer, analytical micromechanical model, numerical micromechanical model.*

Introduction

In this paper, we discussed on reinforcing the synthetic biodegradable polymers with carbon nanotubes as filler. The unique properties of CNTs such as extremely high strength, low density and high electric conductivity offer advantages over other nano-fillers (An et al 2004, Meyyappan 2005). Moreover CNTs have dimensions which are comparable to ECM molecules such as collagen and laminin, and are reported to sup- port cell adhesion (Freire et al 2002, Kleinman et al 1985, Luckenbill-Edds 1997, He and Bellamkonda 2005). Carbon nanotubes are in fact extensively explored for biomedical applications (Balasubramanian and Burghard 2006, Harrison and Atala 2007, Zhang et al 2005), particularly those involving scaffolds for neural and bone tissue. For example neurons grown on a CNT network are reported to exhibit better signal transmission (Lovat et al 2005), possibly due to the fact that CNTs form tight contacts with neuron membranes leading to electrical shortcuts (Cilia et al 2008). Moreover, as CNTs behave like an inert matrix, combined with other natural or synthetic materials in biocomposites, they can be effective in bone tissue engineering applications. Carbon nanotube based substrates have been shown to support the growth of osteoblastic cells which can be expected to become functional bone (Li et al 2005, Zhang et al 2005, Pankratz et al 2009).

However, the effective utilization of the excellent properties of nanotubes in composite applications strongly depends on the ability to disperse CNTs homogeneously throughout the matrix, as well as on the interfacial bonding and the content of nanotubes in the matrix. Producing well-dispersed carbon nanotubes in a composite is difficult because the addition of solid 'powder' (carbon) in a liquid polymer in the early mixing stages often leads to phase separation between the carbon and the polymer matrix due to low interfacial bonding between the two. Several methods for enhancing interfacial adhesion between CNT and the polymer matrix are described (Coleman et al 2006). Following a simple two-solvent mixing method, a tolerable dispersion with low content of CNT in a polymer matrix has been reported by the authors (Pioggia et al 2007).

Here, we investigate suitable models both analytical and numerical that explain the mechanical property of the composite as candidate material for bone scaffolds.

Analytical Micromechanical Models

In the simplest possible case a composite can be modelled as an isotropic, elastic matrix filled with aligned elastic fibres that span the full length of the specimen. It assumes that the matrix and fibres are very well-bonded. Then, on application of a stress in the fibre alignment direction, the matrix and fibres will be equally strained and the total stress is the sum of the contributions. Under these circumstances, the composite tensile modulus in the alignment direction, Ec, is given by

$$E_C = (E_f - E_m)V_f + E_m \qquad (1)$$

where Ef is the fibre modulus, Em is the matrix modulus and Vf is the fibre volume fraction. This is the well-known Voigt's rule of mixtures (Callister 2003). Voigt model assumes a parallel connection between two moduli whereas Reuss uses series connection. Therefore, Reuss model is also applied and given by:

$$Ec = \left[\frac{Vf}{Ef} + \frac{(1-Vf)}{Em}\right]^{-1} \qquad (2)$$

In most cases these parallel and series models serve as an estimate of the upper and lower bounds of the blend modulus. However, this describes a rather idealised situation; fibres are generally much shorter than the specimen length. Additionally, above models were lack in considering the fibres dimension and orientation.

Numerous micromechanical models (Eshelby 1957, Hill 1965, Mori and Tanaka 1973, Ashton et al 1983, Halpin 1969, Halpin and Kardos 1976) have been proposed to predict the elastic constants of discontinuous fibre composites. These models generally depend on parameters including particle/matrix stiffness ratio Ep/Em; particle volume fraction Vf; particle aspect ratio L/D; and orientation. In applications relevant to the present study, the particles and the matrix are assumed to be linearly elastic. Here, Ep and Em denote the elastic moduli of the particle and the matrix, respectively.

Tucker provides a good review of the application of several classes of micromechanical models to discontinuous fiber-reinforced polymers (Tucker and Liang 1999). He noted that, of the existing models, the widely used Halpin–Tsai equations (Ashton et al 1969, Halpin 1969, Halpin and Kardos 1976) give reasonable estimates for effective stiffness. On the other hand, the Mori–Tanaka type models (Mori and Tanaka 1973, Tandon and Weng 1984) give the best results for large- aspect-ratio fillers. Therefore, we focus on prediction based on Halpin-Tsai model.

For aligned fibre composites, the Halpin–Tsai model gives the composite modulus to be:

$$E_c = E_m \frac{1+2(L/D)V_f\eta}{1- V_f\eta} \qquad (3.a)$$

$$\eta = \frac{(E_p/E_m)-1}{(E_p/E_m)+2(L/D)} \qquad (3.b)$$

For randomly orientated composites the expression becomes:

$$\frac{E_c}{E_m} = \frac{3}{8}\left[\frac{1+2(L/D)\eta_L V_f}{1-\eta_L V_f}\right] + \frac{5}{8}\left[\frac{1+2\eta_T V_f}{1-\eta_T V_f}\right] \qquad (4.a)$$

where

$$\eta_L = \frac{(E_p/E_m)-1}{(E_p/E_m)+2(L/D)} \qquad (4.b)$$

and

$$\eta_T = \frac{(E_p/E_m)-1}{(E_p/E_m)+2} \qquad (4.c)$$

Both rule of mixtures and the Halpin–Tsai equations were taking Em = 500 GPa and l/D = 500. A number of the systems studied report values in this range (Coleman et al 2004, Kearns and Shambaugh 2002, Putz et al 2002). It should be emphasized here that L is not the true or actual length of the nanotubes in the composite, but it can be considered as the effective nanotube length responsible for reinforcement in the composite system.

Note that any difference in the calculated and measured values in different composites can be attributed to differences in interfacial strength in different systems or in the same system at different nanotube loading.

As predicted, Voigt model which take into account the total stress of fibres and matrix correspondingly, shows a much higher values than experimental data (figure 1). On the other hand, Reuss model, as lower bound of rule mixture, gives closer prediction. However, Reuss model failed in following the trend of elastic modulus with increasing CNT. The Reuss' estimates were quasi-constant during the addition of 0.2-1.3% CNT (figure 1.a). On the other hand, Halpin-Tsai random model gave closer prediction to experimental data. Therefore, Halpin-Tsai random and aligned models were then taken into account in estimating the composite systems.

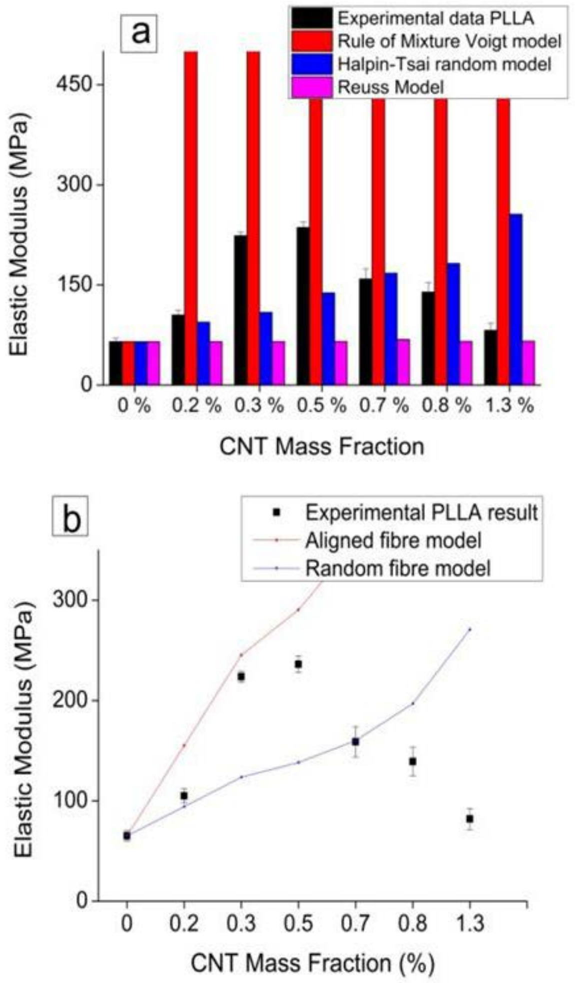

Figure 1. (a) Comparative studies of experimental elastic modulus with prediction using Halpin-Tsai model, Voigt and Reuss model and (b) prediction of elastic modulus using Halpin-Tsai both aligned and random calculation for PLLA composites.

Moreover, figure 1.b depicts that the real values were in the range between aligned and random fibre composites model, except for PLGA +0.5 wt.% CNT. However, at higher nanotube volume fractions (more than 0.8 wt.%) the deviations are greater. The reason for this difference is that the models are not suitable for massive CNT agglomeration in polymer matrix. Halpin-Tsai equation is derived based on the assumption that stress transfer between polymer matrix and nanotube is perfect. The interfacial shear strength is an important parameter for any fibre-reinforced composite and many studies have been devoted to it. The first thing to determine is whether any stress is transferred to the nanotubes at all. Hence, non-uniform dispersion of CNT leads to poor stress transfers to the matrix.

Numerical Micromechanical Models

Models of representative volume element (RVE) of the CNT/polymers were constructed. The construction can be described by a set of geometric features of such as particle volume fraction, particle aspect ratio, and particle orientation distribution. In this work, we focus our attention on the simplified case of uniform, well-aligned in an isotropic matrix. A typical RVE (filler fraction=0.01, L/D=1000) used in the finite element method (FEM) of this paper is shown in figure 2.

Several assumptions are made for theoretical modelling. Firstly, CNTs are homogeneously dispersed in the CNT/ polymer composites and have uniform dimensions including their length, inner, and outer diameters. Secondly, there is no direct interaction between the adjacent CNTs.

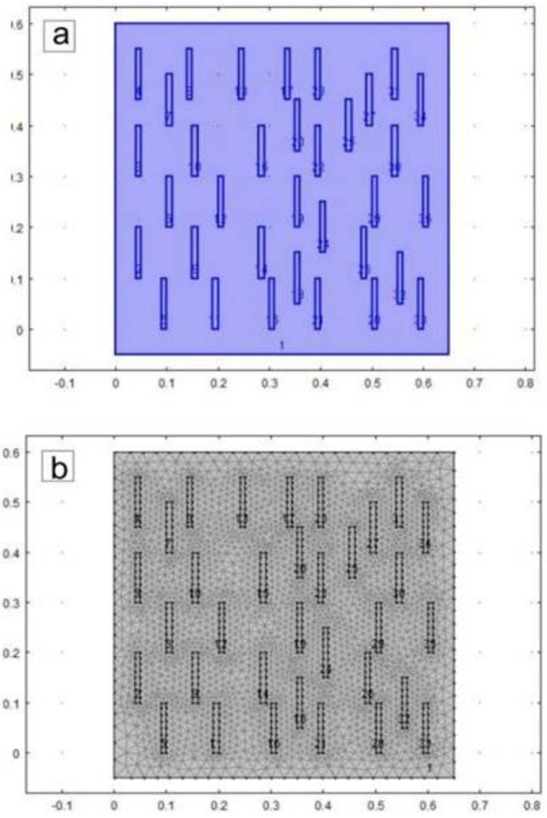

Figure 2. A typical RVE for FEM micromechanical simulation (fp =0:02; L/D= 1000; number of particles in the RVE=36).

The RVE dimensions are large compared to the characteristic size of the particle; the number of particles included in the RVE is sufficient enough (~40). The dimensions used and parameters for the full square RVE are listed in table 1.

Tabel 1. Parameters for FEM simulation in COMSOL environment.

Parameter	Polymer matrix	CNT	units
Length	600	1	µm
Width	600	--	
Diameter	--	1	nm
Young modulus, E	0.065	500	GPa
Poisson's ratio, ν	0.45	0.33	
Density , δ	1120	1800	Kg/m3

Two-dimensional plane strain simulations of well-oriented random particle distributions are subject to small- strain axial tensile loading. Periodic boundary conditions expressed in terms of the macroscopic strain tensor ε are applied to the RVE. The macroscopic normal strain εm is used to drive the deformation of the entire RVE.

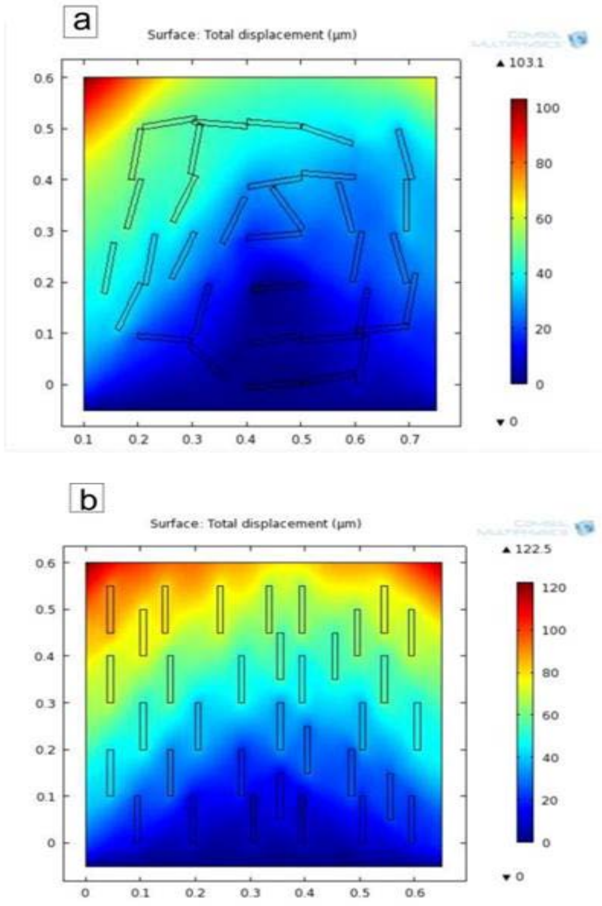

Figure 3. The axial strain contour in a RVE loaded to ε = 0.08 for (a) random particle orientation and (b) aligned orientation.

The model shows that the deformation was different for the composites with random and aligned model. The result in figure 3 was established by inserting parameters in table 1 to simulate deformation in polymer film with CNT particle fraction of 0.01 (v/v). The principle of virtual work has been used to calculate the mechanical response of the RVE by following Danielsson et al (2002). Practically, we were taking into account of small deformation gradients. The stress σ is derived from forces of two 'auxiliary nodes' with respect to the 'displacement' as strain ε.

The plane strain FEM simulation results of Ec/Em are compared with the analytical random Halpin-Tsai model solution in figure 4. In particular, Ec/Em is predicted to increase almost linearly with CNT mass fraction by both FEM simulations and the Halpin-Tsai model.

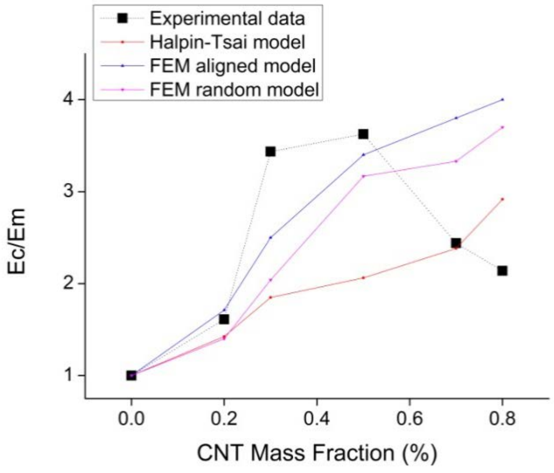

Figure 4. Predictions of the effective longitudinal modulus for CNT/PLLA composites

Conclusion

We have compared the experimental data with simulation both from various analytical and FEM numerical models. The model of Halpin-Tsai random fibres gave the most accurate among the analytical models. However, the numerical FEM model gave more precise predictions than the Halpin-Tsai model provided that the parameters used were available.

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