Constitutive modelling of viscoelastic behaviour of CNT/Polymer composites

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Abstract
The nanocomposites exhibit high electrical conductivity, significant third order non-linear optical behaviour and electroluminescence, while having substantially improved mechanical strength relative to the neat polymer. Since the experimental techniques are so expensive, the development of analytical models those are capable of predicting the time-dependent viscoelastic behaviour of such nanocomposites is essential. In this paper, the constitutive relation and linear viscoelastic behaviour of NTRPC are studied using methods of micromechanics and nanomechanics. First, the effects of volume fraction, aspect ratio and orientation of carbon nanotubes (CNTs), on the overall elastic properties of NTRPC are obtained through a variety of micromechanical techniques. Secondly, by incorporating the Dynamic Correspondence Principle (DCP), the elastic solution is extended to solve the related linear viscoelastic problem.

Keywords:
Carbon nanotubes, Nanocomposites, Viscoelasticity, Mechanical properties

1 Introduction

Polymer composites reinforced by carbon nanotubes (CNTs) have been extensively researched for their high strength and stiffness properties [1]. The high strength and elastic modulus, fibrous shape and large aspect ratios of these nanotubes (NTs) make them a very promising candidate as the ideal reinforcing fibers for advanced composites with high strength and low density [2]. The nanocomposites exhibit high electrical conductivity, significant third order non-linear optical behavior and electroluminescence, while having substantially improved mechanical strength relative to the neat polymer. However, very limited attention has been paid to the viscoelastic behavior of nanotubes reinforced polymer composites (NTRPC). Since the experimental techniques are so expensive, there is a need to develop analytical models that are capable of predicting the time-dependent viscoelastic behavior of such nanocomposites.

In this paper, the constitutive relation and linear viscoelastic behavior of NTRPC are studied using methods of micromechanics. First, the effects of volume fraction, shape, aspect ratio and orientation of carbon nanotubes (CNTs), on the overall elastic properties of NTRPC are obtained. Secondly, by incorporating the Dynamic Correspondence Principle (DCP), the elastic solution is extended to solve the related linear viscoelastic problem.

2 Geometric structure of SWCNTs

Carbon nanotubes are the fourth allotrope of condensed carbon. Two varieties of these tubes have been distinguished, the single walled carbon nanotubes (SWCNTs) and the multi-walled carbon nanotube (MWCNTs). The SWCNTs are generated by rolling up a Graphene sheet into a seamless cylinder with a constant radius. The atomic structure of nanotubes depends on tube chirality, which is defined by the Chiral vector C_h and the Chiral angle θ as shown in Fig 1. The Chiral vector and Chiral angle can be defined in terms of the lattice translation indices (n, m) and the basic vectors a_1 and a_2 of the hexagonal lattice as follows:

$$C_h = na_1 + ma_2 \tag{1}$$

$$\theta = \sin^{-1}\left[\frac{\sqrt{3}m}{2\left(\sqrt{m^2+mn+n^2}\right)}\right] \tag{2}$$

Using this (n, m) naming scheme, the three types of orientation of the carbon atoms around the nanotube circumference are specified as Armchair, Zigzag, or Chiral. The chirality of nanotubes has significant impact on its transport properties, particularly the electronic properties [3].

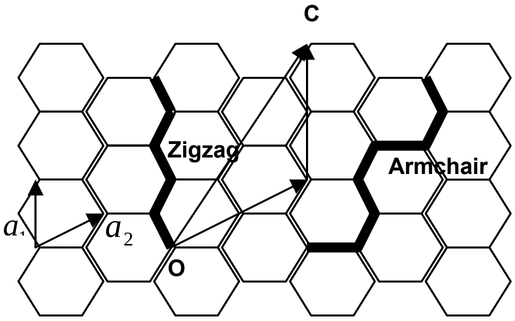

Fig. 1 Schematic of the hexagonal lattice of Graphene sheet

3 MICROMECHANICAL ANALYSIS

The first research on viscoelastic behaviour of composites is return to the works of Hashin [4] and Schapery [5]. After that, many researches oriented toward the investigation of the effects of fibre orientation [6] and intermediate phase [7] on the mechanical properties of composites. In the following we are going to derive the constitute relation for viscoelastic behaviour of nanocomposites reinforced with CNTs. To achieve this goal we have considered the following assumptions:

- The CNTs are straight and the effects of waviness are ignored
- We consider two cases:
  - (a) Random dispersion of NTs which leads to isotropic behaviour and
  - (b) Uniform dispersion of NTs which leads to transverse isotropic behaviour of nanocomposites
    - The interphase region (between NT and neat polymer) is modelled as the elastic and transverse isotropic material which the mechanical properties are determined through the Equivalent Continuum Modelling (ECM) technique [8].
    - The overall behaviour of nanocomposites is modelled as linear viscoelastic
    - The mechanical properties of NTs and polymer are independent of temperature
    - The micromechanical model is based on the Mori -Tanaka approach [9]

The stress-strain relation for linear viscoelastic material is defined as [10]

$$\sigma(t)=\int_0^t L(t-\tau)\dot{\varepsilon}(\tau)d\tau, \quad \varepsilon(t)=\int_0^t M(t-\tau)\dot{\sigma}(\tau)d\tau$$

(3)

where the dot denotes the differentiation with respect to time (t), and L(t) and M(t) are the stress relaxation stiffness and creep compliance tensors, respectively.

By applying the Laplace-Carson transformation as:

$$\hat{f}(s)=s\int_0^\infty e^{-s\tau} f(\tau)d\tau$$

(4)

to Eq. (3) gives

$$\hat{\sigma}(s)=\hat{L}(s)\hat{\varepsilon}(s), \qquad \hat{\varepsilon}(s)=\hat{M}(s)\hat{\sigma}(s)$$

(5)

where the hat indicates the transformed function in the Carson domain, and s is the transform variable. In fact, according to the Correspondence Principle in viscoelasticity (e.g., [11–13]), if a Laplace transformable, analytical solution exists for a problem in linear elasticity, the solution for the corresponding problem in linear viscoelasticity in the Carson (transformed) domain can be directly obtained from the former by replacing stiffness and compliance tensors with its viscoelastic counterpart $\hat{L}(s)$ or $\hat{M}(s)$, respectively. In particular, for a transversely isotropic composite containing unidirectionally aligned, identical CNTs the Eq. (5) is written as:

$$\begin{cases}\hat{\sigma}_{11}=\hat{L}_{11}\hat{\varepsilon}_{11}+\hat{L}_{12}\hat{\varepsilon}_{22}+\hat{L}_{12}\hat{\varepsilon}_{33},\\ \hat{\sigma}_{22}=\hat{L}_{12}\hat{\varepsilon}_{11}+\hat{L}_{22}\hat{\varepsilon}_{22}+\hat{L}_{23}\hat{\varepsilon}_{33},\\ \hat{\sigma}_{33}=\hat{L}_{12}\hat{\varepsilon}_{11}+\hat{L}_{23}\hat{\varepsilon}_{22}+\hat{L}_{22}\hat{\varepsilon}_{33},\\ \hat{\sigma}_{12}=2\hat{L}_{44}\hat{\varepsilon}_{12},\\ \hat{\sigma}_{23}=2\hat{L}_{66}\hat{\varepsilon}_{23}=\left(\hat{L}_{22}-\hat{L}_{23}\right)\hat{\varepsilon}_{23},\\ \hat{\sigma}_{31}=2\hat{L}_{44}\hat{\varepsilon}_{31},\end{cases}$$

(6)

Where L_{ij} are the components of the stiffness tensor. Therefore the normal and transverse Young's modulus, shear modulus and in plane and out of plane Poisson's ration can be determined as:

$$\begin{cases} \hat{E}_{11} = \hat{L}_{11} - \dfrac{2\left(\hat{L}_{12}\right)^2}{\hat{L}_{22}+\hat{L}_{23}}, \\ \hat{E}_{22} = \hat{L}_{22} + \dfrac{\left(\hat{L}_{12}\right)^2\left(\hat{L}_{23}-\hat{L}_{22}\right) + \hat{L}_{23}\left[\left(\hat{L}_{12}\right)^2 - \hat{L}_{11}\hat{L}_{23}\right]}{\hat{L}_{11}\hat{L}_{22} - \left(\hat{L}_{12}\right)^2}, \\ \hat{G}_{12}=\hat{L}_{44}, \quad \hat{\upsilon}_{12} = \dfrac{\hat{L}_{12}}{\hat{L}_{22}+\hat{L}_{23}}, \quad \hat{\upsilon}_{23} = \dfrac{\left[\hat{L}_{11}\hat{L}_{23} - \left(\hat{L}_{12}\right)^2\right]}{\hat{L}_{11}\hat{L}_{22}-\left(\hat{L}_{12}\right)^2}, \end{cases}$$

(7)

For isotropic composites containing randomly oriented NTs, the above five independent constants are reduced to only two independent constants.

4 NuMERICAL RESULTS

In this section the effects of aspect ratio and volume fraction for isotropic and transversely isotropic composite are investigated.

a. Isotropic behaviour

In the case of randomly oriented NTs, the overall behaviour of composite will be isotropic.

In Fig. 2 the effect of aspect ratio (ratio of the length to diameter of NTs) on the axial creep compliance (inverse of Young's modulus) is shown. As it is seen with increasing the aspect ratio, the creep compliance of composite is reduced.

In Fig. 3 the effect of volume fraction on the shear creep compliance (the inverse of shear modulus) is shown. By increasing the volume fraction, the shear creep compliance is decreased. By comparing the Fig. 2 and 3, we can see that the effect of aspect ratio is higher than volume fraction.

It should be mentioned that with passing the time the shear and axial creep compliance are increased.

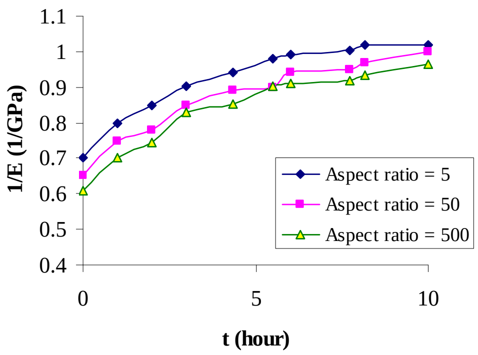

Fig. 2 variation of axial creep compliance with time for different values of aspect ratio

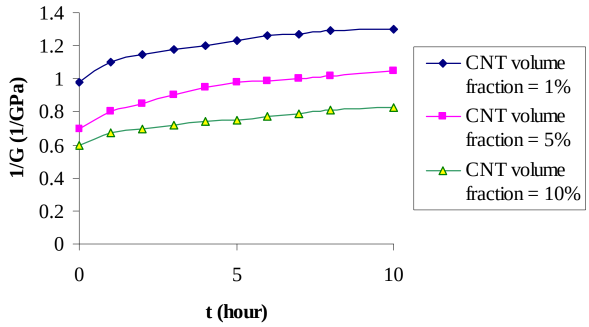

Fig. 3 variation of shear creep compliance with time for different values of volume fraction

b. Transverse isotropic behaviour

In the case of uniformly distributed NTs, the overall behaviour of composite will be transversely isotropic with five independent material constants.

In Fig. 4 the effect of aspect ratio on the axial creep compliance M11 and axial shear creep compliance M44 is shown. As it is seen with increasing the aspect ratio, the creep compliance of composite is reduced. Of course the effect of aspect ratio on M11 is clearly higher than M44.

In Fig. 5 the effect of aspect ratio on the transverse creep compliance (M22) and the plane strain bulk modulus (k23) is shown. With increasing the aspect ratio, the transverse creep compliance is decreased. However aspect ration has almost no effect on the plane strain bulk modulus

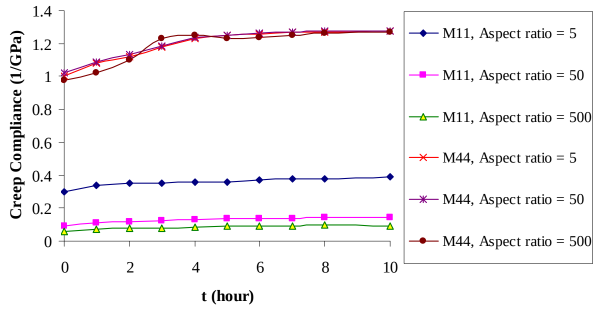

Fig. 4 variation of axial and shear creep compliance with time for different values of aspect ratio

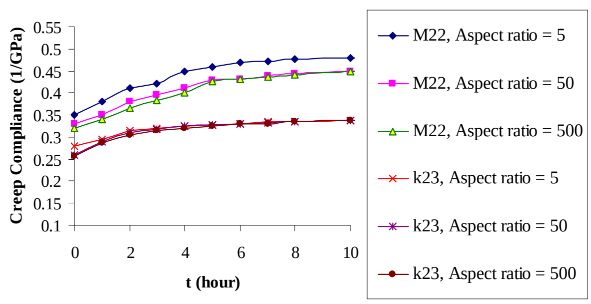

Fig. 5 variation of transverse creep compliance and the plane strain bulk modulus with time for different values of aspect ratio

In Fig. 6 and 7 the effect of volume fraction on the axial creep compliance (M11), the axial shear creep compliance (M44), transverse creep compliance (M22) and the plane strain bulk modulus (k23) are shown. With increasing the volume fraction, M11 and M44 are decreased; however k23 and M22 are almost constant. These trends are in good agreement with previous results [14, 15]. Furthermore, with 0% and 100% volume fraction of NTs we get the mechanical properties of neat polymer and NTs respectively.

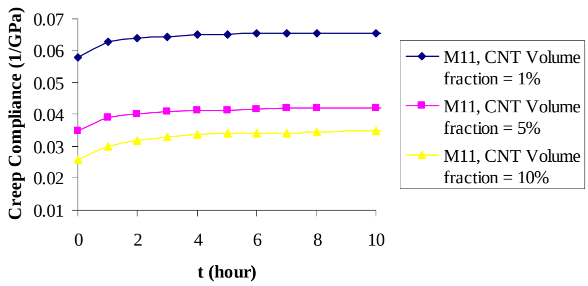

Fig. 6 variation of the axial creep compliance with time for different values of volume fraction

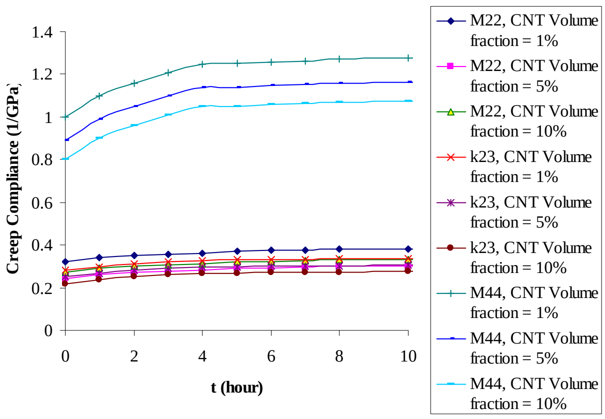

Fig. 7 variation of transverse creep compliance, axial shear creep compliance and the plane strain bulk modulus with time for different values of volume fraction

5 CONCLUSIONS

Based on the Dynamic Correspondence Principle (DCP) and the method of micromechanics, the effect of volume fraction, aspect ratio and orientation of NTs on the viscoelastic behaviour of polymer composites reinforced with NTs are obtained. The computational results have lead to the following conclusions:

- For randomly oriented NTs,

6 By increasing volume fraction or aspect ratio the M44 and M11 are decreased.

7 The effect of volume fraction is higher than aspect ratio

- For uniformly distributed NTs

(a) The effect of aspect ratio on M44 and k23 is insignificant but has a great effect on M11.

(b) By increasing the aspect ratio, the axial stiffness of the composite is improved

(c) By increasing of the volume fraction M11 is decreased however other mechanical properties are almost constant.

Investigation the effects of agglomeration and waviness of NTs and the variation of temperature on the viscoelastic properties on nanocomposites, can be studied in future.

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