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Frequency and amplitude dependence of complex moduli of composite material reinforced with nanofibers

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A micromechanical model is developed to determine effective inelastic properties of nanocomposite under monoharmonic deformation by taking into account detailed micro-structural geometries and constitutive models of the constituents. By using the Correspondence Principle in Viscoelasticity and the modified Mori-Tanaka method, the effects of interface between inclusion and matrix is taken into account. By applying the presently developed model, a numerical analysis for determination of complex moduli for polymeric nanocomposite reinforced by nanofibers composed from carbon nanotubes (CNTs) is conducted at the isothermal conditions. Analysis of the complex moduli dependence on frequency and amplitude of strain intensity is performed. Composites reinforced with both unidirectionally aligned and randomly oriented nanofibers are considered. Results demonstrate a weak dependence of loss moduli on the frequency of the loading within the wide range of it.

Keywords: complex moduli of material, storage modulus, loss modulus, monoharmonic loading, nanocomposite, nanofiber.

Introduction. Cyclic loading is one of the most important and widely used types of loading imposed on structural elements. Materials of structures and their members experiencing cyclic deformation can exhibit specific time dependent properties and can be deformed inelastically being exposed to high stress levels. At the present, there are two approaches to address and characterization this behavior. In the frame of the first approach, the complex set of constitutive equations governing response of numerous internal parameters is introduced while within the second approach, the approximate amplitude relations are used to characterize the cyclic response of the material, i.e. the relations between amplitudes of the main mechanical field parameters over the cycle [1-3]. The key point of the amplitude theories is concept of complex moduli [2]. For an inelastic (particularly viscoelastic) material, the modulus governing the relation between strain and stress amplitudes is represented by a complex quantity with real and imaginary parts referred to as storage and loss modulus respectively.

Under relatively high stress levels, polymeric composites exhibit time-dependent and inelastic deformations. The time-dependent and inelastic deformations become more pronounced at elevated temperatures and environmental conditions. As mentioned above, depending on the applications, composites are often subjected to

harmonic loading. To accurately predict an overall performance and lifetime of polymer composites, it is necessary to model time dependent and inelastic responses of the constituents (inclusions and polymer) and to incorporate microstructural characteristics of the composites, such as size, shape, and compositions of the constituents. While micromechanical formulations that include detailed micro-structural characteristics can give good response characteristics, it is often difficult to obtain exact closed form solutions especially when material nonlinearity is also considered. Limited experimental studies have been done on understanding the inelastic behavior of particulate reinforced polymer composites under cyclic loading.

In present investigation, the analytical modeling approach based on micromechanical modeling concept which allows incorporating various micro-structural geometries and properties of the constituents to evaluate the effective inelastic responses of composites is employed. This micromechanical model is formulated in terms of exact stress-strain fields of the micro-structural geometries. However, it is often difficult to obtain the exact closed form solutions especially when material nonlinearity or inelastic behavior is also considered. Some of the micromechanical models have been extended to predict inelastic or viscoplastic behaviors of polymer based composites [4-9]. Weng [10] used the self-consistent method for analyzing effective creep behavior of composites. It was assumed that inclusion and matrix exhibit elastic and linear viscoelastic behavior, respectively. Levesque et al. [11] proposed a linearized homogenization scheme for predicting nonlinear viscoelastic responses of particulate reinforced composites. In this scheme, the homogenized micromechanical model of the Mori and Tanaka [12] was used. The particle was modeled as linear elastic, while the Schapery nonlinear viscoelastic model [13] was applied for the matrix phase. Li and Gao [14] investigated viscoelastic responses of carbon nanotube (CNT) particles embedded in polyamide. The viscoelastic response of nanocomposite was obtained via the Mori-Tanaka model while the matrix and inclusion was considered viscoelastic and elastic materials, respectively.

Weng and co-worker [15] have presented a homogenization scheme, and applied it to uncover the interface effect on its time-dependent behavior, and storage and loss moduli at various CNTs loadings. They used the Burgers four parameter model for the description time dependent behavior of polypropylene according to the Maxwell and Voigt spring and dashpot models. It is important to notice that, some polymers used as constituents in composite systems exhibit combined viscoelastic-viscoplastic responses, e.g. high density polyethylene and polycarbonate and Epoxy resins. These combined responses can occur at early loading (small stress/strain levels). Aboudi [16] has developed a micromechanical model to predict the viscoelastic-viscoplastic responses of multiphase materials. The viscoelastic-viscoplastic model for polymer developed by Frank and Brockman [17] is implemented in the multiphase composites.

This paper is devoted to the modeling and characterization of cyclic response of PR-520 (Epoxy resin) reinforced by nanofiber composed of CNTs subjected to monoharmonic kinematic loading. To predict the inelastic behavior of the polymeric matrix, the Goldberg constitutive model is used. To simulate the response in terms of amplitudes at different frequencies, the relations between the amplitudes of main field

variables are established with making use of complex moduli concept (the approximate amplitude relations). We have developed a micromechanical model to predict the inelastic responses of multiphase nanocomposites by taking to account effects of the interface condition by using Qu model [18].

1. Procedure of complex moduli derivation

In this investigation, the approximate model of inelastic behavior developed in [1, 2] for the case of proportional harmonic loading has been used. In this case, the cyclic properties of the polymer are described in terms of complex moduli. It is important to notice that the inelastic deformation is considered to be incompressible and thermal expansion is dilatational, it may be more convenient in some applications to separate the isotropic stress-strain relations into deviatoric and dilatational components that can be shown by equations as

$$s_{ij} = 2G\left(e_{ij} - \varepsilon_{ij}^{in}\right), \quad \sigma_{kk} = 3K_V\left(\varepsilon_{kk} - \varepsilon^{\theta}\right),$$

where G is the shear modulus, K_V is the bulk modulus, i, j, $k = 1,2,3$ and repeated index implies a summation over. Due to incompressibility of plastic deformation, $\dot{\varepsilon}_{kk}^{in} = 0$, i.e. the plastic strain rate is deviatoric: $\dot{\varepsilon}_{ij}^{in} = \dot{e}_{ij}^{in}$. According to this model, if a body as a system subjected to harmonic deformation or loading, then its response is also close to harmonic law

$$e_{ij}(t) = e'_{ij}\cos\omega t - e''_{ij}\sin\omega t, \quad s_{ij}(t) = s'_{ij}\cos\omega t - s''_{ij}\sin\omega t.$$

The complex amplitudes of the deviator of total strain, $\tilde{e}_{ij}$, inelastic strain, $\tilde{e}_{ij}^{in}$, and the stress deviator, s_{ij}, are related in the N^{th} cycle by the complex shear modulus, $\tilde{G}_N$, and plasticity factor, $\tilde{\lambda}_N$, as shown below

$$\tilde{s}_{ij} = 2\tilde{G}\,\tilde{e}_{ij}, \quad \tilde{e}_{ij}^{in} = \tilde{\lambda}\,\tilde{e}_{ij},$$

here $\tilde{e}_{ij} = e'_{ij} + ie''_{ij}$, $\tilde{s}_{ij} = s'_{ij} + is''_{ij}$, $\tilde{e}_{ij}^{in} = e'^{in}_{ij} + ie''^{in}_{ij}$, $\tilde{G} = G'_N + iG''_N$, $\tilde{\lambda} = \lambda'_N + i\lambda''_N$ and N is the cycle number, $N = 1, 2, 3, \ldots$; $(\cdot)'$ and $(\cdot)''$ denote the real and imaginary parts of complex quantities.

The shear modulus and plasticity factor are functions of the intensity of the strain-range tensor, frequency and temperature

$$\tilde{G}_N = \tilde{G}_N(e_0, \omega, \theta), \quad \tilde{\lambda}_N = \tilde{\lambda}_N(e_0, \omega, \theta), \tag{1}$$

where the square of the intensity of strain-range tensor is calculated as $e_0^2 = e'_{ij}e'_{ij} + e''_{ij}e''_{ij}$.

The imaginary parts of the complex moduli are determined from the condition of equality of the energies dissipated over a period and are calculated according to the formula

$$G_N'' = \frac{\langle D' \rangle_N}{\omega\, e_0^2}, \quad \lambda_N'' = \frac{G_N''}{G_0}, \quad \langle (\cdot) \rangle_N = \frac{1}{T}\int_{T(N-1)}^{TN} (\cdot)dt, \quad T = \frac{2\pi}{\omega}, \tag{2}$$

where D' is the rate of dissipation of mechanical energy, G_0 is the elastic shear modulus. The real parts are found with making use of the condition that generalized cyclic diagrams $s_{aN} = s_{aN}(e_0, \omega)$ and $e_{paN} = e_{paN}(e_0, \omega)$, which relate the ranges of the stress and plastic-strain intensities in the N^{th} cycle, coincide in the frame of the complete and approximate approaches

$$G_N'(e_0, \omega) = \left[\frac{s_{aN}^2(e_0, \omega)}{4e_0^2} - G_N''^2(e_0, \omega) \right]^{1/2},$$

$$\lambda_N'(e_0, \omega) = \left[\frac{e_{paN}^2(e_0, \omega)}{4e_0^2} - \lambda_N''^2(e_0, \omega) \right]^{1/2}. \tag{3}$$

where G_N' and λ_N' are the sought-for real part of shear modulus and plasticity factor.

In spite of the fact that the single-frequency approximation based on harmonic linearization has a good agreement with precise model of nonlinear behavior, it's necessary to analyze its practical accuracy for specific classes of problems.

As mentioned in the beginning of this section, the second approach is based on the concept of complex moduli, which are determined by standard and modified techniques of equivalent linearization. It is important to notice that, the imaginary parts of complex moduli are defined by the exact expression for rate of dissipation averaged over the period of cyclic loading while to improve the accuracy of real parts of complex moduli the modified approach is proposed as shown in equation (3). According to equation (1), the complex moduli for isothermal loading case depend on the frequency and amplitude of kinematic loading only. The purpose of this investigation is to study the influence of these parameters on complex moduli of polymeric nanocomposites.

2. Description of mechanical behavior of matrix, nanofiber and interface

Inclusions are very stiff and their mechanical response can be assumed as predominantly elastic. Nonlinear or inelastic isothermal behavior of polymer matrix will be represented by Goldberg model [19] under kinematic harmonic loading at the wide range of amplitudes. The condition of load transfer in interface of inclusion and matrix will be modeled by a displacement jump that was proposed by Qu [18]. Though the interface has negligibly small volume concentration, the effects of interface can significantly lower the overall stiffness and properties of the nanocomposite at the high volume fraction of inclusions [20].

3. Mechanical response of nanofiber

According to reported effective elastic properties for nanofiber composed of unidirectionally oriented carbon nanotubes, it is considered as transversely isotropic.

Consequently, the stress-strain relations are determined by five independent elastic constants. By using the Hill's notation, symmetric fourth-order stiffness tensor for inclusion can be represented by the equation [21]:

$$\mathbf{L}^{\mathrm{P}} = \mathbf{L}^{\mathrm{P}}\left(2k_p, l_p, n_p, 2m_p, 2p_p\right),$$

where $\mathbf{L}^{\mathrm{P}}$ is the elastic stiffness tensor and n_p, k_p, l_p, m_p and p_p are the Hill's elastic moduli for particle, which they indicate the uniaxial tension modulus, the plane-strain bulk modulus, the associated cross modulus, the transverse shear modulus and the axial shear modulus, respectively. It can be presented in terms of the common engineering constants as $\mathbf{L}^{\mathrm{P}} = \mathbf{L}^{\mathrm{P}}\left(2K_{23}, C_{12}, C_{11}, 2G_{23}, 2G_{12}\right)$, when the CNTs are aligned in direction x_1. Considering this notation, the all moduli and major Poisson's ratio, ν_{12}, are given by:

$$E_{11} = n_p - {l_p}^2 / k_p, \quad \nu_{12} = l_p / 2k_p, \quad K_{23} = k_p,$$
$$E_{22} = \frac{4m_p\left(k_p m_p - {l_p}^2\right)}{k_p n_p - {l_p}^2 + m_p n_p}, \quad G_{12} = p_p, \quad G_{23} = m_p.$$

The relation between Hill's constants and components of elastic stiffness tensor, L^P_{ijkl}, can be rearranged as follows:

$$k_p = \frac{\left(C_{22} + C_{23}\right)}{2},\ l_p = C_{12},\ n_p = C_{11},\ m_p = \frac{\left(C_{22} - C_{23}\right)}{2},\ p_p = C_{66}.$$

Consequently, if the nanofiber is considered to be isotropic, the stress-strain relations are governed by two independent elastic constants and isotropic stiffness tensor can also be represented using the Hill's notation and the aforementioned quantities are defined as:

$$k_p = K + G/3, \quad l_p = K - 2G/3, \quad n_p = K + 4G/3, \quad m_p = p = G,$$

where K and G are bulk and shear modulus, respectively.

3.1. Effects of the interface

In the model developed by Qu [18], the interface can be introduced by using a layer of negligible thickness in which traction remains continuous and displacement becomes discontinuous. The equations that model the interfacial traction continuity and the displacement jump were introduced in [18]. The second order compliance tensor of the spring layer, η_{ij}, was proposed by Qu in the same paper. According to it, if the tensor η_{ij} tends to zero (infinite stiffness) then the displacement jump is zero and continuity in displacements are recovered. This tensor is chosen to be symmetric and positive definite and components of second order compliance tensor can be expressed in the form [20]

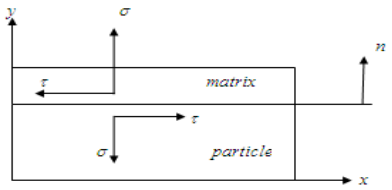

Fig. 1. Scheme for matrix and inclusion location

$$\eta_{ij} = \gamma\delta_{ij} + (\beta - \gamma) n_i n_j, \tag{4}$$

where δ_{ij} is the Kronecker delta and n_i represents the unit outward normal vector. It is important to address the physical meaning of the parameters γ and β. They are the quantities that represent the compliance in the tangential and normal directions respectively as shown in Fig.1. These terms are usually defined through the analysis of a scheme where a horizontal surface divides the matrix and the inclusion material [18] (see Fig. 1).

3.2. Constitutive equations of the polymer matrix

To accurately predict an overall performance and lifetime of polymer, it is necessary to model time dependent and inelastic responses. Viscoelastic materials such as polymer materials have the particularity of possessing viscous, elastic and, under some conditions, plastic behavior. Constitutive material models of viscoelastic solids have been proposed for isotropic materials undergoing small deformation gradients whereas the inelastic strain can be calculated as the difference of the total strain and elastic strain.

Goldberg et al. [19-22] proposed a model for predicting the viscoplastic response of neat polymers, utilizing a set of state variables as an indication of the resistance of polymeric chains against flow. It should also be mentioned that polymer's mechanical properties and loading/strain rate are the two main parameters that govern the nonlinear response of the polymer.

According to this model, the inelastic strain components can be expressed in terms of the deviatoric stress components as follows

$$\dot{\varepsilon}_{ij}^{in} = 2D_0 \exp\left(-\frac{1}{2}\left(\frac{Z}{\sigma_e}\right)\right)^{2n}\left(\frac{s_{ij}}{2\sqrt{J_2}} + \alpha\delta_{ij}\right), \tag{5}$$

where, $\dot{\varepsilon}_{ij}^{in}$ is the inelastic strain rate tensor which can be defined as a function of deviatoric stress and Z and α are the state variables; J_2 is the second invariant of the deviatoric stress tensor that can be expressed as a function of σ_{ij}; the variable α is a state variable which controls the level of the hydrostatic stress effects; D_0 and n are material constants; D_0 represents the maximum inelastic strain rate and n controls

the rate dependency of the material. The effective stress, σ_e, also be defined as a function of the mean stress, such that the summation of the normal stress components σ_{kk} is three times of the mean stress. The evolution of the internal stress state variable Z and the hydrostatic stress state variable α are defined by the equations

$$\dot{Z} = q(Z_1 - Z)\dot{e}_e^{in}, \quad \dot{\alpha} = q(\alpha_1 - \alpha)\dot{e}_e^{in}, \tag{6}$$

where q is a material constant representing the "hardening" rate, and Z_1 and α_1 are material constants representing the maximum values of Z and α, respectively. The initial values of Z and α are defined by the material constants Z_0 and α_0. The term $\dot{e}_e^{in}$ in equations (6) represents the effective deviatoric inelastic strain rate.

4. The viscoelastic response of nanocomposite and modified Mori-Tanaka (MT) approach

By employing the Correspondence Principle in Viscoelasticity the constitutive relations for the behavior of the viscoelastic material can be represented by:

$$\hat{\boldsymbol{\sigma}}(s) = \hat{\mathbf{L}}(s)\hat{\boldsymbol{\varepsilon}}(s), \quad \hat{\boldsymbol{\varepsilon}}(s) = \hat{\mathbf{M}}(s)\hat{\boldsymbol{\sigma}}(s),$$

where $\hat{\mathbf{L}}(s)$ and $\hat{\mathbf{M}}(s)$ are the stress relaxation stiffness and creep compliance tensors in transformed domain, respectively. Every symbol with hat indicates the transformed function in the transformed domain, and s is the transform variable.

In fact, according to the Correspondence Principle in Viscoelasticity, if a Laplace transformable, analytical solution exists for a problem in linear elasticity, the solution for the corresponding problem in linear viscoelasticity in the transformed domain can be directly obtained from the former by replacing $\mathbf{L}$ or $\mathbf{M}$ with its viscoelastic counterpart $\hat{\mathbf{L}}$ or $\hat{\mathbf{M}}$.

As mentioned in section 3, by using the approximate amplitude relations, the complex shear moduli are derived at different frequency for various strain amplitudes. Also, due to incompressibility of plastic deformation, the bulk modulus of polymer is considered to be constant and real. Then the stress relaxation stiffness tensor of polymer matrix, $\hat{\mathbf{L}}^{\mathrm{M}}$, is determined as function of frequency and amplitude.

After introducing the effect of interface into the equivalent inclusion method, a modified expression for the Eshelby's tensor is found for the case of ellipsoidal inclusions with slightly weakened interfaces. The new expression is written as:

$$\hat{\mathbf{S}}^{\mathrm{M}} = \hat{\mathbf{S}} + \left(\mathbf{I} - \hat{\mathbf{S}}\right)\mathbf{H}\hat{\mathbf{L}}^{\mathrm{M}}\left(\mathbf{I} - \hat{\mathbf{S}}\right), \tag{7}$$

where $\hat{\mathbf{S}}$ is the original Eshelby's tensor in transformed domain that components of it are given in [26]. $\mathbf{I}$ and $\hat{\mathbf{L}}^{\mathrm{M}}$ are the fourth order identity tensor and the matrix relaxation stiffness tensor of matrix, respectively. The second term in the right hand

side of equation (7) is present to introduce the interface effects. The components of tensor $\mathbf{H}$ are presented as:

$$H_{ijkl} = \gamma P_{ijkl} + (\beta - \gamma) Q_{ijkl}, \tag{8}$$

expressions for components of tensor $\mathbf{P}$ and $\mathbf{Q}$ are given in [15].

Once the modified Eshelby's tensor based on equation (7) has been included into the analysis, the modified MT estimate is introduced. The expression for the modified MT estimation for a two phase aligned composite is obtained in transformed domain as:

$$\hat{\mathbf{L}}^{\mathrm{C}} = \left(c_0 \hat{\mathbf{L}}^{\mathrm{M}} + c_1 \mathbf{L}^{\mathrm{P}} \mathbf{A}^{dil}\right)\left(c_0 \mathbf{I} + c_1 \mathbf{A}^{dil} + c_1 \mathbf{H} \mathbf{L}^{\mathrm{P}} \mathbf{A}^{dil}\right)^{-1}, \tag{9}$$

where c_0 and c_1 are volume fraction of matrix and inclusion, respectively. Here $\hat{\mathbf{L}}^{\mathrm{C}}$ and $\mathbf{L}^{\mathrm{P}}$ are the relaxation stiffness tensor of composite and inclusion, respectively. Also the dilatation tensor $\mathbf{A}^{dil}$ is recalculated as:

$$\mathbf{A}^{dil} = \left[\mathbf{I} + \hat{\mathbf{S}}^{\mathrm{M}} \hat{\mathbf{L}}^{\mathrm{M}-1}\left(\mathbf{L}^{\mathrm{P}} - \hat{\mathbf{L}}^{\mathrm{M}}\right)\right]^{-1}.$$

According to equations (8) and (9) if the parameters γ and β are set to zero, the tensor $\mathbf{H}$ vanishes and the new expressions for the relaxation stiffness tensor of composite reduce to the original MT expression. It is worth mentioning that the expression for the effective elastic properties in equation (8) depends on the inclusion length in contrast to the original MT which is aspect ratio dependent.

When the randomly oriented inclusions are embedded to the matrix, determination of the effective viscoelastic properties can be obtained following the same procedure in transformed domain. Using the result obtained above for the total average strain, the MT expression with considered interface effects for the case of randomly oriented inclusions is:

$$\hat{\mathbf{L}}^{\mathrm{C}} = \left(c_0 \hat{\mathbf{L}}^{\mathrm{M}} + c_1 \left\{\mathbf{L}^{\mathrm{P}} \mathbf{A}^{dil}\right\}\right)\left(c_0 \mathbf{I} + c_1 \left\{\mathbf{A}^{dil}\right\} + c_1 \left\{\mathbf{A}^{dil} \mathbf{H} \mathbf{L}^{\mathrm{P}}\right\}\right)^{-1},$$

where the brackets $\{\cdot\}$ designate the average over all passible orientations. In particular, for a transversely isotropic composite containing unidirectionally aligned identical inclusions along the x_1 direction of a Cartesian coordinate system $Ox_1x_2x_3$, five independent parameters in the Laplace-transformed domain based on Hill's notation can be derived [14]. Also, when transversely isotropic inclusions are randomly oriented in a composite, only two properties are required to define the tensor completely. The bulk modulus and shear modulus of the composite in the transformed domain, $\hat{K}$ and $\hat{G}$ can be obtained from their corresponding elastic counterparts, respectively [21].

Once these two quantities are obtained, we can form the new isotropic tensor by using Hill's notation in transformed domain.

5. Numerical technique and the material properties

In the present work, for the determination of the nonlinear response of matrix, the numerical integration of Goldberg equations was adopted. To solve the implicit equation (5), one should utilize an appropriate numerical integration technique. Three step scheme of attacking the problem of complex moduli determination was designed. At the first step, the elastic-viscoplastic response of the material to harmonic deformation was calculated numerically for different amplitudes of loading strain at various frequencies. At the second step, the stabilized cyclic stress-strain and inelastic-strain-strain diagrams were obtained for the whole set of calculated data. At the final step, the complex moduli were calculated by the averaging over the period of vibration of the results of direct integration and making use of cyclic diagrams and formulae (2) and (3). The system of nonlinear ordinary differential equations that describes the polymer response to harmonic loading in the case of pure shear consists of the one-dimensional equations of Goldberg model comprising equation (5) and evolutionary equations

$$\dot{\alpha} = \frac{2qD_0}{\sqrt{3}}\left(\alpha_1 - \alpha\right)\exp\left[-\frac{1}{2}\left(\frac{Z^2}{3S_{12}^2}\right)^n\right]\frac{S_{12}}{|S_{12}|},$$

$$\dot{Z} = \frac{2qD_0}{\sqrt{3}}\left(Z_1 - Z\right)\exp\left[-\frac{1}{2}\left(\frac{Z^2}{3S_{12}^2}\right)^n\right]\frac{S_{12}}{|S_{12}|},\quad \dot{\varepsilon}_{12}^{in} = 2D_0\exp\left[-\frac{1}{2}\left(\frac{Z^2}{3S_{12}^2}\right)^n\right]\frac{S_{12}}{2|S_{12}|}.$$

The law of strain deviator variation $e = e_0 \sin\omega t$, as well as Hooke law for shear stress $s_{12} = 2G\left(e_{12} - \varepsilon_{12}^{in}\right)$, should be added to the system. It is important to notice that the known relations between the complex-value moduli, $\tilde{E}$, $\tilde{G}$ and $\tilde{\nu}$, and real valued bulk modulus, K_V, exist in the form:

$$\tilde{E} = 2\tilde{G}\left(1 + \tilde{\nu}\right),\ \tilde{\nu} = \frac{3K_V - 2\tilde{G}}{6K_V + 2\tilde{G}}.$$

According to the Correspondence Principle in Viscoelasticity the relaxation stiffness tensor of matrix, $\hat{\mathbf{L}}^{\mathrm{M}}$, can be derived using two determined independent constants $\tilde{E}$ and $\tilde{\nu}$.

The modified MT method is applied here to obtain the effective viscoelastic properties of the nanocomposite. To obtain reasonable values for the parameter γ, we used the values which was obtained by Namilae and Chandra [24] with molecular dynamics. The value for the parameter γ is chosen for all cases in this section 0.01 nm/GPa and β is set to zero to prevent material interpenetration. In this investigation, computations for nancomposites reinforced by unidirectionally aligned or randomly oriented nanofibers composed of the unidirectionally aligned CNTs are presented.

The values of material constants for both RP-520 (Epoxy resin) that was used as matrix and CNTs used for calculations have been taken from [22-25]. The list of the

values is given below: $E = 3250$ MPa, $D_0 = 10^6$ s^{-1}, $n = 0.92$, $q = 253.6$, $Z_0 =$ $= 407.5$ MPa, $Z_1 = 768.6$ MPa, $\alpha_0 = 0.571$, $\alpha_1 = 0.122$, $\nu = 0.4$ and for CNTs $l_p = 10$ GPa, $k_p = 30$ GPa, $m_p = 1$ GPa, $n_p = 450$ GPa, $p_p = 1$ GPa, length and diameter of CNTs were chosen to be 6 and 1.7 nm, respectively.

6. Numerical results and discussion

In this section, the results of study for examining the viscoelastic behavior of polymeric nanocomposite reinforced with nanofibers under kinematic harmonic loading are presented. Controlling parameters include frequency, amplitude of loading, nanofiber volume fraction and orientation. Interval of frequency 1 to 100 Hz and volume fraction 3, 5 and 10 percent are considered, respectively. In this investigation for determination of nanofibers orientation effects, a transversely isotropic nanocomposite system containing unidirectionally aligned nanofibers and isotropic nanocomposite system with randomly oriented nanofibers are considered. According to microstructural geometry of CNTs, the nanofiber aspect ratio for both the transversely isotropic nanocomposites and the isotropic nanocomposites is chosen to be equal to 3.5.

It is important to notice that for the transversely isotropic nanocomposites, five independent paramerers, i.e., $\hat{E}_{11}$, $\hat{E}_{22}$, $\hat{G}_{12}$, $\hat{\nu}_{12}$ and $\hat{K}_{23}$, are used to illustrate their viscoelastic responses, while the behavior of the isotropic nanocomposites is characterized by two independent parameters, i.e., $\hat{E}$, $\hat{\nu}$.

For isotropic nanocomposites containing randomly oriented nanofibers, the effects of nanofiber volume fraction, V_f, and amplitude of harmonic loading on the complex shear moduli and complex axial moduli at the constant frequency, $f = 1$ Hz, are displayed in Fig. 2, 3. According to these results, both storage and loss moduli increase as the volume fraction increases. It is also seen, the strain intensity amplitude, which, the nonlinear behavior of nanocomposite starts at (about $e_i = 2.5\%$) does not change with the increase of the volume fraction of nanofiber because it is related to

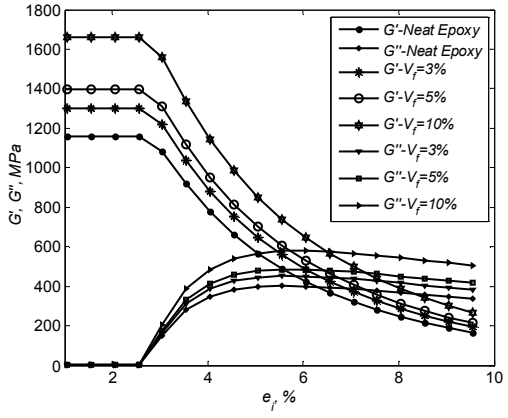

Fig. 2. The complex shear moduli at 1 Hz for nanocomposite with randomly oriented nanofibers

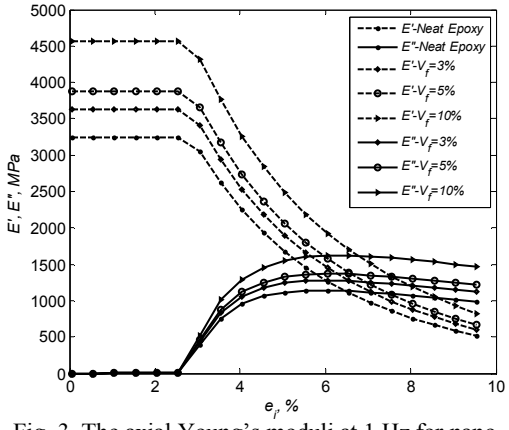

Fig. 3. The axial Young's moduli at 1 Hz for nanocomposite with randomly oriented nanofibers

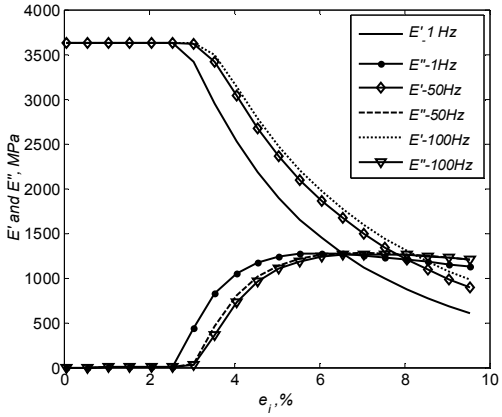

Fig. 4. The effects of frequency on complex axial Young's moduli for nanocomposite with randomly oriented nanofibers at $V_f = 3\%$

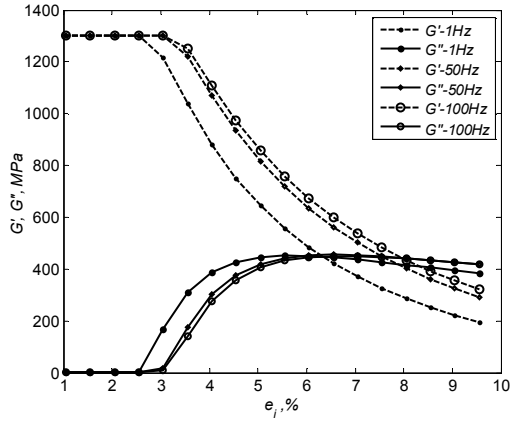

Fig. 5. The effects of frequency on complex shear moduli for nanocomposite with randomly oriented nanofibers at $V_f = 3\ \%$

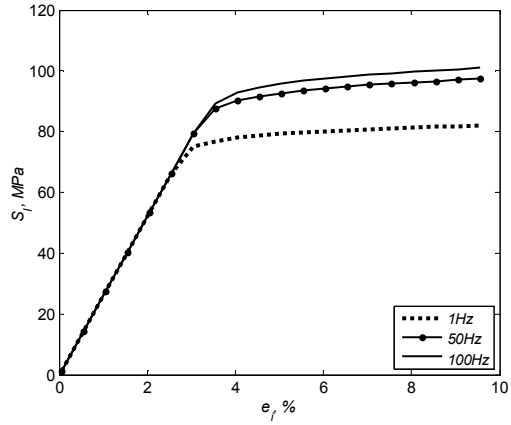

Fig. 6. The effects of frequency on cyclic diagrams for nanocomposite with randomly oriented nanofibers at $V_f = 3\ \%$

nonlinear behavior of matrix. It is interesting to notice, that the maxima of the loss moduli for various volume fraction occur at the same amplitude of harmonic loading (about $e_i = 6\ \%$).

The effect of frequency is easily observable. In Fig. 4, 5 the effects of frequency on complex shear moduli and axial moduli are shown. According to the presented results in complex shear moduli diagram, the storage moduli increase as the frequency increases in the inelastic region at the constant volume fraction of the nanofibers, while the loss modulus decreases slightly as the frequency increases below the value of strain intensity amplitude providing its maximum. The maximum values of the loss modulus increase insignificantly and occur later with frequency increasing. The cyclic diagrams at stabilized stage of the vibration are shown in Fig. 6. The curves are calculated for cyclic pure shear loading for 3% nanofibers volume fraction for different frequencies (1, 50, 100 Hz) at 25°C.

For the transversely isotropic nanocomposites reinforced with unidirectionally aligned nanofibers, the effects of volume fraction, V_f, and amplitude of harmonic loading on the complex axial Young's moduli, $\hat{E}_{11}$, complex transverse Young's moduli, $\hat{E}_{22}$, Poisson ratio, $\hat{\nu}_{12}$, and complex axial shear moduli, $\hat{G}_{12}$, at the constant frequency (f = 1 Hz) are displayed in Fig. 7-9.

These figures show that nanofibers volume fraction has little effect on the complex axial shear moduli, $\hat{G}_{12}$, and the transverse Young's moduli, $\hat{E}_{22}$, while its influence on the complex axial Young's moduli, $\hat{E}_{11}$, is profound. In Fig. 9, the effect of volume fraction on real and imaginary parts of Poisson ratio, $\hat{\nu}_{12}$, are presented.

These results indicate that the influence of V_f for both the unidirectionally aligned fibers and randomly oriented fibers on the Poisson ratio is small.

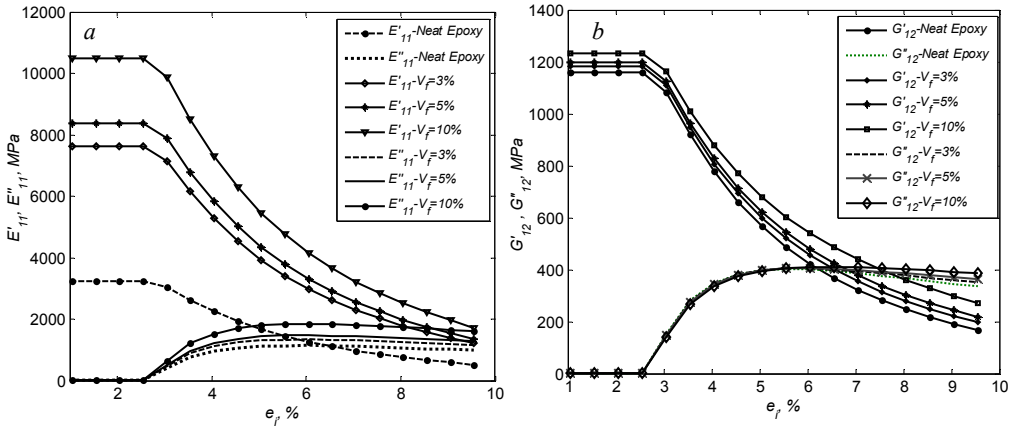

Fig. 7. Macroscopically transversely isotropic nanocomposite with uniaxially oriented nanofibers at 1 Hz
a) complex axial Young's moduli, b) axial shear moduli

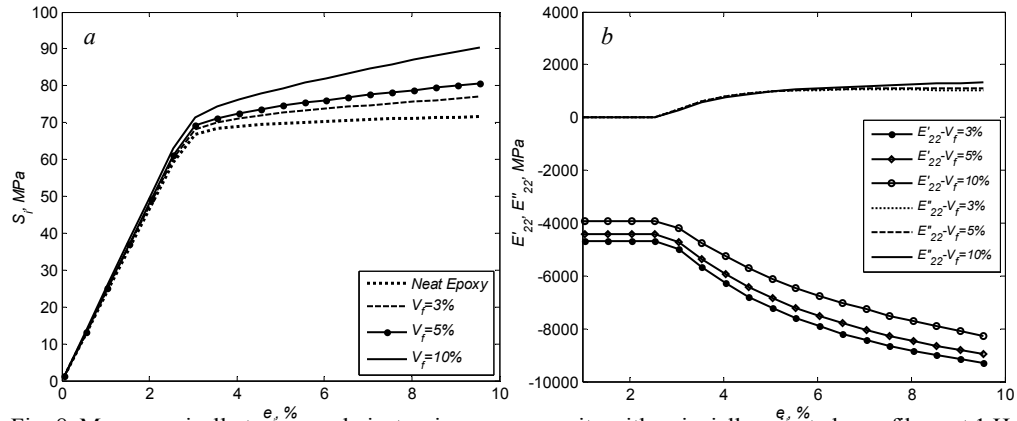

Fig. 8. Macroscopically transversely isotropic nanocomposite with uniaxially oriented nanofibers at 1 Hz
a) cyclic diagrams, b) complex transverse Young's moduli

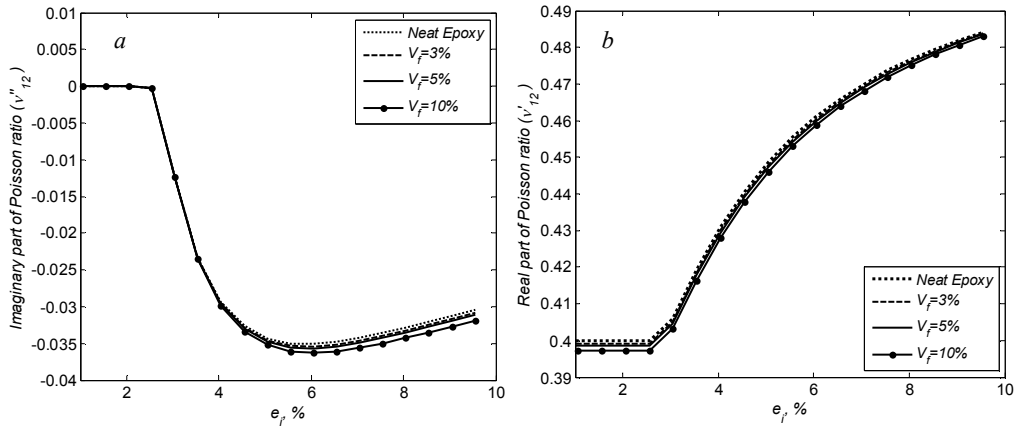

Fig. 9. Macroscopically transversely isotropic nanocomposite with uniaxially oriented nanofibers at 1 Hz *a*) imaginary parts of Poisson ratio, *b*) real parts of Poisson ratio

The cyclic diagrams for neat polymer and nanocomposites with different volume fraction at 1 Hz and 25°C are shown in Fig. 8a. The effect of nanofiber volume fraction is easily observable. It is worth mentioning that real and imaginary parts of complex Poisson ratio exhibit weak dependence on the V_f (see small difference in curves in Fig. 9).

In Fig. 10 the influence of frequency at the constant volume fraction on the complex axial shear modulus, $\hat{G}_{12}$, and the complex axial Young's modulus, $\hat{E}_{11}$, are shown. The storage moduli increase with increasing frequency in the inelastic region, while the loss moduli decrease slightly as frequency increases in interval of strain intensity below the value, which provides the maximum for the modulus.

The maximum values of the moduli increase insignificantly and occur later with increasing frequency. It is worth to mention here, that this behavior is governed by the nonlinear response of matrix. This indicates that the stiffness of material increases as

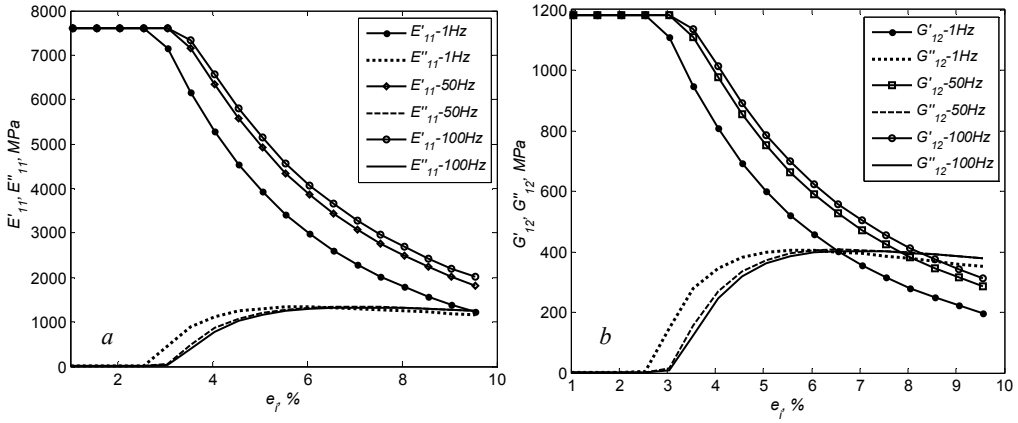

Fig. 10. The effects of frequency for the transversely isotropic nanocomposites at V_f=3 % *a*) complex axial Young's moduli, *b*) complex axial shear moduli

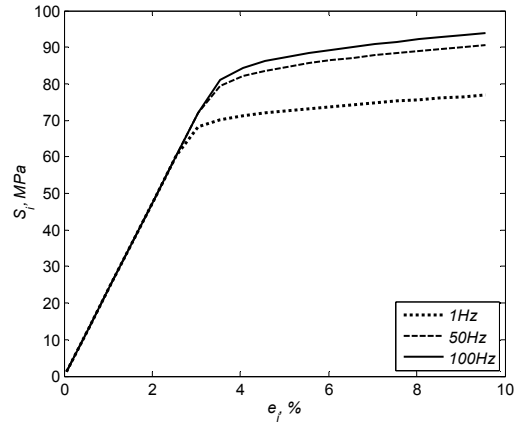

Fig. 11. The cyclic diagrams for different frequencies for nanocomposite with uniaxially oriented nanofibers (macroscopically transversely isotropic material) at $V_f = 3$ %

the frequency increases. The cyclic diagrams are shown in Fig. 11. The curves are calculated for cyclic pure shear loading for 3 % of volume fraction of the nanofibers at different frequencies (1, 50, 100 Hz) under isothermal condition. According to Fig. 7*a* and cyclic diagram for neat polymer, increasing of volume fraction for the transversely isotropic nanocomposites has little effect on complex axial shear modulus.

Conclusions. In the paper, a micromechanics model is developed to determine effective inelastic properties of nanocomposite under monoharmonic loading by taking into account detailed micro-structural geometries and constitutive models of the constituents. By using the Correspondence Principle in viscoelasticity, the modified Mori-Tanaka method and effects of interface between inclusion and matrix is extended to the transformed domain. By applying the presently developed model, a numerical analysis for determination of the complex moduli of polymeric nanocomposite reinforced with nanofibers is conducted under the isothermal condition. Characterization of the complex moduli dependence on frequency and amplitude of strain intensity is performed. Composites reinforced with both unidirectionally aligned and randomly oriented nanofibers are considered. The volume fraction and orientation of nanofiber are considered as the controlling parameters. Results demonstrate the weak dependence of loss moduli on the frequency of the loading within the wide interval of it. For nanocomposites containing unidirectionally aligned nanofibers, numerical results indicate that the increase of the nanofibers volume fraction significantly enhances their axial complex moduli but has insignificant influences on their transverse, shear and plane strain bulk complex moduli. It is found that the random orientation of nanofibers provides more effective plane strain bulk complex moduli but less effective axial complex moduli than the aligned orientation. In addition, the effect of the nanofiber orientation on the shear complex moduli is negligibly small. Furthermore, for nanocomposites with uniaxially aligned or randomly oriented nanofibers, both the storage and loss moduli are found to increase monotonically with the increase of the nanofiber volume fraction.

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Частотні й амплітудні залежності комплексних модулів композитного матеріалу, зміцненого нановолокнами

Ярослав Жук, Мохамед Хашемі

Розвинуто мікромеханічну модель для визначення ефективних непружних властивостей нанокомпозиту у разі моногармонічного деформування, в якій враховуються особливості мікроструктурної геометрії та визначальні моделі поведінки складників. За допомогою принципу відповідності для в'язкопружності та модифікованого методу Морі-Танака враховано вплив інтерфейсу між включенням і матрицею на ефективні модулі. Із застосуванням розвинутої моделі й числової процедури визначено комплексні модулі полімерного нанокомпозиту, армованого нановолокнами з вуглецевих нанотрубок, в умовах сталої температури. Проведено аналіз залежності комплексних модулів від амплітуди інтенсивності деформації та частоти моногармонічного деформування. Розглянуто нанокомпозити, армовані як однонаправленими волокнами, так і волокнами, орієнтованими випадковим чином. Отримані результати демонструють слабку залежність модуля втрат від частоти в широкому інтервалі її зміни.

Частотные и амплитудные зависимости комплексных модулей композитного материала, упрочненного нановолокнами

Ярослав Жук, Мохамед Хашеми

Развита микромеханическая модель для определения эффективных неупругих свойств нанокомпозита при моногармоническом деформировании, в которой учитываются особенности микроструктурной геометрии и определяющие модели поведения составляющих. При помощи принципа соответствия для вязкоупругости и модифицированного метода Мори-Танака учитывается влияние интерфейса между включением и матрицей на эффективные модули. С применением развитой модели и численной процедуры определены комплексные модули полимерного нанокомпозита, армированного нановолокнами из углеродных нанотрубок, в условиях постоянной температуры. Проведен анализ зависимости комплексных модулей от амплитуды интенсивности деформации и частоты моногармонического деформирования. Рассмотрены нанокомпозиты, армированные как однонаправленными волокнами, так и волокнами, ориентированными случайным образом. Полученные результаты демонстрируют слабую зависимость модуля потерь от частоты в широком интервале ее изменения.

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