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Modeling of Storage Modulus of Graphene-Epoxy Nanocomposites

Alperen Acar, Ozgen Colak Cakir and Deniz Uzunsoy

Abstract— **In this work, the storage modulus of epoxy and graphene-epoxy nanocomposites are modeled using a temperature and rate dependent modulus formulation. The stiffening effect of reinforcements is included to the elastic modulus formulation for the modeling of nanocomposite materials. Simulation results are compared to experimental data from Acar et al. [1].**

***Keywords*—graphene, epoxy, storage modulus.**

I. Introduction

Graphene, a two-dimensional carbon nanofiller with a one-atom-thick sheet of sp^2 bonded carbon atoms, which is densely packed in a honeycomb crystal has attracted much attention due to the distinguished mechanical, electrical, optical and thermal properties. For fabrication and design of new class of polymer nano-composites, it has been used as the nanofiller.

Modeling of materials under different loading conditions is an important issue in the mechanics. Development of material models for different materials is also needed for structural analysis. Even though there are large number of works about metallic material modeling, due to the viscoelastic and viscoplastic properties of polymers, it is not easy to model polymeric and composites materials.

In this work, storage modulus of epoxy and graphene-nanocomposite is modeled using the temperature and strain rate dependent elasticity modulus formulation.

Alperen Acar
Yildiz Technical University
Turkey

Ozgen Çolak Çakir
Yildiz Technical University
Turkey

Prof. Dr. Deniz Uzunsoy
Bursa University
Turkey

II. Dynamic Mechanical Analysis

To study the viscoelastic behavior of polymers, Dynamic mechanical analysis (DMA) has been used extensively. By applying a sinusoidal stress, the strain in the material is measured. Storage and loss modulus of the material is determined with respect to temperature. This approach is used to locate the glass transition temperature of the material, as well as to identify transitions.

In the previous work by Acar et al. [1], graphene-epoxy nancomposites are manufactued using soft molding method. The well known fabrication process contains the following steps: Dispersion of graphene in acetone using sonicator, mixing epoxy resin and graphene, heating in a vacuum oven to remove asetone, adding curing agent, degassing and curing in an oven. To characterize the mechanical behaviors of graphene-epoxy nanocomposite, tension experiments and DMA are performed for epoxy and graphene-epoxy nanacomposite.

The viscoelastic responses of the epoxy and nanocomposite samples were examined using a Dynamic Mechanical Thermal Analysis Instrument (DMA - TA Instruments Q800) in the three point bending mode. The experiments are carried out at a frequency of 1 Hz. Typical dimensions for DMA samples were 35 mm (length) x 13.5 mm (width) x 3.2 mm (thickness). DMA measurements were carried out at a temperature range from room temperature to 200°C with a heating rate of 5°C/min, Acar et al. [1].

III. Modeling Storage Modulus

Apart from metallic material, the mechanical properties of polymeric materials significantly change with temperature and strain rate since they exhibit viscoelastic and viscoplastic behavior even at room temperature.

DMA have reveal that amorphous polymers undergoes three main transitions which are beta relaxation, glass transition and flow. They are characterized by the associated transition temperatures, $T_{\beta,}$ T_g, T_f, Colak et al. [2]. Richeton et al. [3] used the elasticity modulus equation defined by Mahieux and Reifsnider [4], [5] and extended this theory to include rate and temperature effects. Temperature and rate dependent elasticity modulus is given in Equation (1) and (2).

$$E(\theta,\dot{\varepsilon}) = (E_1(\dot{\varepsilon}) - E_2(\dot{\varepsilon})exp\left[\left(\frac{\theta}{T_\beta(\dot{\varepsilon})}\right)^{m_1}\right] + (E_2(\dot{\varepsilon}) - E_3(\dot{\varepsilon})exp\left[\left(\frac{\theta}{T_g(\dot{\varepsilon})}\right)^{m_2}\right] + E_3(\dot{\varepsilon})exp\left[\left(\frac{\theta}{T_f(\dot{\varepsilon})}\right)^{m_3}\right] \quad (1)$$

The three transition temperatures and instantaneous modulus are defined as followings,

$$\frac{1}{T_\beta} = \frac{1}{T_\beta^{ref}} + \frac{k}{\Delta H_\beta} ln\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}^{ref}}\right)$$

$$T_g = T_g^{ref} + \frac{-c_2^g log\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}^{ref}}\right)}{c_1^g + log\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}^{ref}}\right)}$$

$$T_f = T_f^{ref}\left[1 + 0.01 log\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}^{ref}}\right)\right]$$

$$E_i = E_i^{eff}\left(1 + s.log\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}^{ref}}\right)\right) \quad (2)$$

T_β, T_g, T_f are transition temperatures at a reference strain rate ($\dot{\varepsilon}^{ref}$), used as parameters in the equations. c_1^g and c_2^g are the Williams–Landel–Ferry (WFL) parameters.

Temperature and rate dependent elasticity modulus formulation is extended to model the behavior of nanocomposites in the work by Acar et al. [6].

The inclusive theory of Richeton et al.[3] is extended to cover the effect of graphene content by redefining the three modulus values "E_i" (the modulus values on the onset of three transition temperatures) which are used as scalars in Richeton's theory. In order to define modulus values as a function of graphene fraction, the Mori Tanaka scheme developed by Ji et al. [7] is used.

The stiffening effect of reinforcements is included for the modeling of nanocomposite materials. The properties of nanomaterials are highly affected by agglomeration of reinforcements. The work of Ji et. al [7] proposes an elasticity modulus definition which considers the agglomeration effect of graphene using Mori-Tanaka micromechanics method.

The Mori-Tanaka Method is applied to a system of graphene-polymer nanocomposite. Mori Tanaka expressions which are α_r , β_r , δ_r and η_r are defined as

$$\alpha_r = \frac{3k_m + 2n_r - 2l_r}{3n_r}$$

$$\beta_r = \frac{4\mu_m + 7n_r + 2l_r}{15n_r} + \frac{2\mu_m}{5p_r}$$

$$\delta_r = \frac{3k_m(n_r + 2l_r) + 4(k_r n_r - l_r^2)}{3n_r}$$

$$\eta_r = \frac{2}{15}\left(k_r + 6m_r 8\mu_m - \frac{l_r^2 + 2\mu_m l_r}{n_r}\right) \quad (3)$$

In eq (3) subscript r stands for the reinforcement (GNP and GPO in our case), and subscript m stands for the polymer matrix. k, m, n, l, p are parameters of the Hill's [10] moduli, μ is shear modulus.
In approach of Ji et. al. [7] mentioned above, the composite structure is divided into two phases as the agglomerated and the effective matrix phases.
$\xi = \frac{V_{agglomer}}{V}$, $\zeta = \frac{V_r^{agglomer}}{V_r}$ Naturally, the volume fractions of those two phases are needed to be defined. They are defined by two parameters as;

(4)

And now the Bulk and shear modulus of agglomerated and out (effective matrix) phases are calculated separately as;

$$\kappa_{agglomer} = \kappa_m + \frac{(\delta_r - 3\kappa_m\alpha_r)c_r\zeta}{3(\xi - c_r\zeta + c_r\zeta\alpha_r)}$$

$$\kappa_{out} = \kappa_m + \frac{c_r(\delta_r - 3\kappa_m\alpha_r)(1-\zeta)}{3[1 - \xi - c_r(1-\zeta) + c_r(1-\zeta)\alpha_r]}$$

$$\mu_{agglomer} = \mu_m + \frac{c_r\zeta(\eta_r - 2\mu_m\beta_r)}{2(\xi - c_r\zeta + c_r\zeta\beta_r)}$$

$$\mu_{out} = \mu_m + \frac{c_r(1-\zeta)(\eta_r - 2\mu_m\beta_r)}{2[1 - \xi - c_r(1-\zeta) + c_r(1-\zeta)\beta_r]} \quad (5)$$

And the expressions for the effective bulk modulus and shear modulus are;

$$\kappa^{eff} = \kappa_{out}\left[1 + \frac{\xi\left(\left(\frac{\kappa_{agglomer}}{\kappa_{out}}\right) - 1\right)}{1 + \alpha(1-\xi)\left(\left(\frac{\kappa_{agglomer}}{\kappa_{out}}\right) - 1\right)}\right]$$

$$\mu^{eff} = \mu_{out}\left[1 + \frac{\xi\left(\left(\frac{\mu_{agglomer}}{\mu_{out}}\right) - 1\right)}{1 + \beta(1-\xi)\left(\left(\frac{\mu_{agglomer}}{\mu_{out}}\right) - 1\right)}\right] \quad (6)$$

and now effective elastic moduli can easily be calculated as;

$$E_i^{eff} = \frac{9\kappa^{eff}\mu^{eff}}{3\kappa^{eff} + \mu^{eff}} \quad (7)$$

IV. Simulation Results

Storage modulus versus temperature curves are simulated using the above formulations. Experimental data obtained from Acar et al. (2015) is compared to simulation results and depicted in Figure 1 and 2. A good match is found.

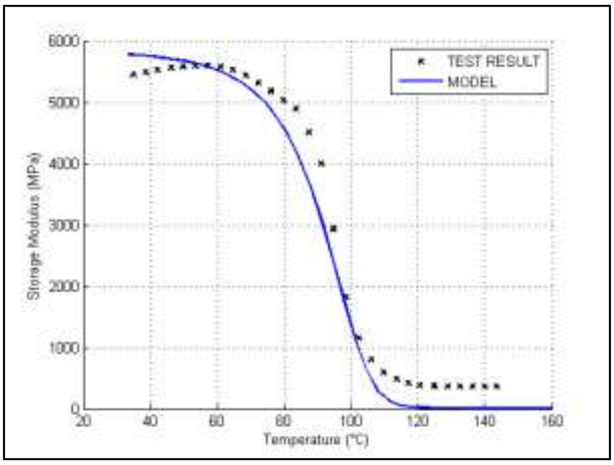

Figure 1. Modeling of storage modulus of epoxy with respect to temperature. Experimental data is taken from Acar et al. (2015).

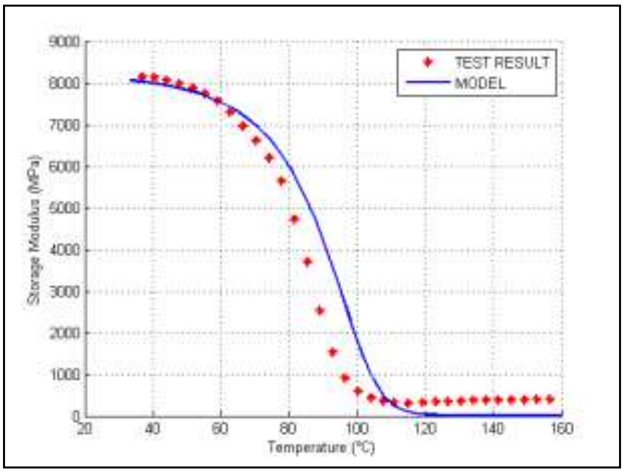

Figure 2. Modeling of storage modulus of graphene-epoxy nanocomposite with respect to temperature, (0.5 wt. % graphene). Experimental data is taken from Acar et al. (2015).

V. Conclusions

Viscoelastic behavior of amorphous polymer, epoxy and graphene reinforced epoxy nanocomposite is modeled using the newly introduced modulus formulation. In the following works, the stress-strain behavior of nanocomposite will be simulated.

References

[1] A. Acar, Ö. Ü. Çolak Çakir, and D. Uzunsoy, "Synthesis and characterization of graphene-epoxy nanocomposites," Material Testing, vol. 57 (11-12), pp. 1001-1005, 2015

[2] O. U. Çolak, S. Ahzi, and Y. Remond, "Cooperative viscoplasticity theory based on the overstress approach for modeling large deformation behavior of amorphous polymers: Cooperative viscoplasticity theory," *Polym. Int.*, p. n/a–n/a, Sep. 2013.

[3] J. Richeton, G. Schlatter, K. S. Vecchio, Y. Rémond, and S. Ahzi, "A unified model for stiffness modulus of amorphous polymers across transition temperatures and strain rates," *Polymer*, vol. 46, no. 19, pp. 8194–8201, Sep. 2005

[4] C. A. Mahieux and K. L. Reifsnider, "Property modeling across transition temperatures in polymers: a robust stiffness–temperature model," *Polymer*, vol. 42, no. 7, pp. 3281–3291, 2001.

[5] C. A. Mahieux and K. L. Reifsnider, "Property modeling across transition temperatures in polymers: application to thermoplastic systems," *J. Mater. Sci.*, vol. 37, no. 5, pp. 911–920, 2002.

[6] A. Acar, Ö. Ü. Çolak Çakir, and S. Ahzi, "Cooperative-VBO model for Graphene Nanocomposites", International Journal of Plasticity, under review.

[7] Ji Xiang-Ying, Cao Yan-Ping and Feng Xi-Qiao "Micromechanics prediction of the effective elasticmoduli of graphene sheet-reinforced polymer nanocomposites" Modelling Simul. Mater. Sci. Eng. 18 045005, 2010

About Author (s):

Özgen Çolak Çakır was born in Sivas, Turkey. She received her Ph.D. at Rensselaear Polytechnic Institute in 2001 under the supervision of Professor Erhard Krempl. She moved to Yildiz Technical University, Istanbul/ Turkey in Agust 2001 and serves as a full Professor since 2005.

Her research interests include material modeling, viscoelasticity, viscoplasticity and nanocomposites.

Alperen Acar, born in 1986, received his MSc degree in Mechanical Engineering from Istanbul Technical University, Turkey, in 2011, and is currently a PhD candidate atthe Graduate School of Natural and Applied Sciences of Yildiz Technical University in Istanbul. He has also been working as a research assistant in the Mechanical Engineering Department of Yildiz Technical University since 2009. His research interests include characterization and modeling of mechanical behavior of polymeric materials, viscoelasticity and finite element analysis.

Prof. Dr. Deniz Uzunsoy received her MSc and PhD degrees in Metallurgical and Materials Engineering from Yildiz Technical University, Istanbul, Turkey, and The University of Birmingham, UK, in 1997 and 2004, respectively. She is currently working at Bursa Technical University, Turkey, as a full Professor.

Her research expertise includes lightweight structures and materials, nano materials, automotive materials, graphene, lithium ion batteries and material characterization.