

# 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.

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## 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 nanocomposites are manufactured 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 acetone, 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 nanocomposite.

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).

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

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

$$\begin{aligned} \frac{1}{T_\beta} &= \frac{1}{T_\beta^{ref}} + \frac{k}{\Delta H_\beta} \ln \left( \frac{\dot{\epsilon}}{\dot{\epsilon}^{ref}} \right) \\ T_g &= T_g^{ref} + \frac{-c_2^g \log \left( \frac{\dot{\epsilon}}{\dot{\epsilon}^{ref}} \right)}{c_1^g + \log \left( \frac{\dot{\epsilon}}{\dot{\epsilon}^{ref}} \right)} \\ T_f &= T_f^{ref} \left[ 1 + 0.01 \log \left( \frac{\dot{\epsilon}}{\dot{\epsilon}^{ref}} \right) \right] \\ E_i &= E_i^{eff} \left( 1 + s \cdot \log \left( \frac{\dot{\epsilon}}{\dot{\epsilon}^{ref}} \right) \right) \end{aligned} \quad (2)$$

$T_\beta, T_g, T_f$  are transition temperatures at a reference strain rate ( $\dot{\epsilon}^{ref}$ ), used as parameters in the equations.  $c_1^g$  and  $c_2^g$  are the Williams–Landel–Ferry (WLF) 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  $\alpha_r, \beta_r, \delta_r$  and  $\eta_r$  are defined as

$$\begin{aligned} \alpha_r &= \frac{3k_m + 2n_r - 2l_r}{3n_r} \\ \beta_r &= \frac{4\mu_m + 7n_r + 2l_r}{15n_r} + \frac{2\mu_m}{5p_r} \\ \delta_r &= \frac{3k_m(n_r + 2l_r) + 4(k_r n_r - l_r^2)}{3n_r} \end{aligned}$$

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

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,  $\mu$  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.

$\xi = \frac{V_{agglomer}}{V}, \quad \zeta = \frac{V_r^{agglomer}}{V_r}$  Naturally, the volume fractions of those two phases are needed to be defined. They are defined by two parameters as;

$$\quad (4)$$

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

$$\begin{aligned} \kappa_{agglomer} &= \kappa_m + \frac{(\delta_r - 3\kappa_m \alpha_r) c_r \zeta}{3(\xi - c_r \zeta + c_r \zeta \alpha_r)} \\ \kappa_{out} &= \kappa_m + \frac{c_r (\delta_r - 3\kappa_m \alpha_r) (1 - \zeta)}{3[1 - \xi - c_r(1 - \zeta) + c_r(1 - \zeta) \alpha_r]} \\ \mu_{agglomer} &= \mu_m + \frac{c_r \zeta (\eta_r - 2\mu_m \beta_r)}{2(\xi - c_r \zeta + c_r \zeta \beta_r)} \\ \mu_{out} &= \mu_m + \frac{c_r (1 - \zeta) (\eta_r - 2\mu_m \beta_r)}{2[1 - \xi - c_r(1 - \zeta) + c_r(1 - \zeta) \beta_r]} \end{aligned} \quad (5)$$

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

$$\begin{aligned} \kappa^{eff} &= \kappa_{out} \left[ 1 + \frac{\xi \left( \left( \frac{\kappa_{agglomer}}{\kappa_{out}} \right) - 1 \right)}{1 + \alpha(1 - \xi) \left( \left( \frac{\kappa_{agglomer}}{\kappa_{out}} \right) - 1 \right)} \right] \\ \mu^{eff} &= \mu_{out} \left[ 1 + \frac{\xi \left( \left( \frac{\mu_{agglomer}}{\mu_{out}} \right) - 1 \right)}{1 + \beta(1 - \xi) \left( \left( \frac{\mu_{agglomer}}{\mu_{out}} \right) - 1 \right)} \right] \end{aligned} \quad (6)$$

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.

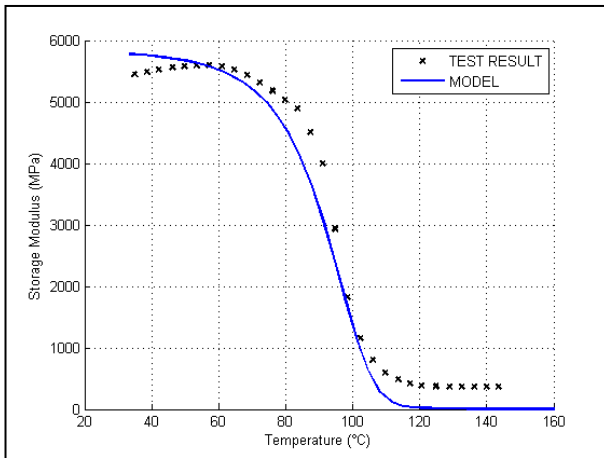


Figure 1. Modeling of storage modulus of epoxy with respect to temperature. Experimental data is taken from Acar et al. (2015).

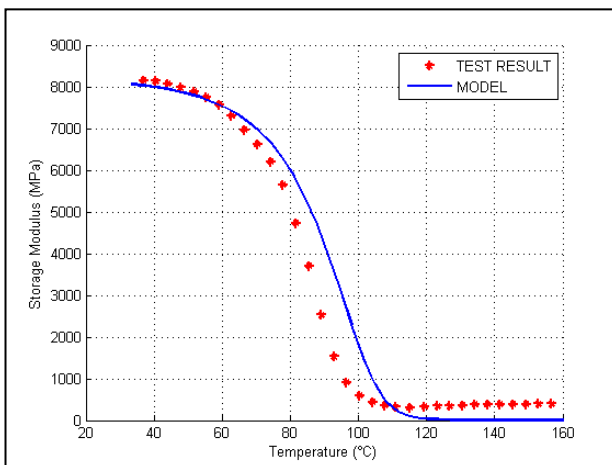


Figure 2. Modeling of storage modulus of graphene-epoxy nanocomposite with respect to temperature, (0.5 wt. % graphene). Experimental data is taken from Acar et al. (2015).

## 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.

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