Material Properties

Cross-property interaction between stiffness, damage and thermal conductivity in particulate nanocomposite

Addis Tessema, Addis Kidane*

Department of Mechanical Engineering, University of South Carolina, 300 Main Street, Columbia, SC 29208, United States

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A nanocomposite made from epoxy and nano silica particles was subjected to compressive fatigue loading and the resulting interaction between stiffness, damage and thermal conductivity investigated. First, the thermal conductivity (K) and the elastic modulus (E) of the as-fabricated materials were measured prior to any fatigue loading. Then, the samples were subjected to cyclic loading, and the thermal conductivity and the modulus of elasticity of the specimens were measured after every 5 to 10 thousand cycle intervals until a significant change in the response of the material was observed. In addition, a semi-analytical model is proposed to quantify damage in the material by taking the modulus of elasticity and thermal conductivity data obtained from the experiment. Finally, the cross-property relation between the modulus of elasticity, the thermal conductivity and the damage density in the material at any state of the fatigue cycle is investigated.

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1. Introduction

Nanocomposite materials, as a result of their tailored properties, are expected to have multiple and improved functions beyond their parent materials [1–3]. For example, polymer nanocomposites made from different nano-sized constituents are being effectively used in electronic, energy, automotive and bio-material industries. However, there are many challenges related to processing, dispersion of nanoparticles, characterization and modeling the matrix-nanoparticle interaction in nanocomposites. These challenges have attracted many researchers for the last three decades.

Nanocomposites are heterogeneous and their mechanical, thermal or electromagnetic responses are influenced by the combined response of the matrix as well as the particles and the interface layers between them [4]. Under a given loading condition, the constituents, both the matrix and nano-filler, have contribution in the overall response [5–10]. Usually, because of property mismatch between nanoparticles and the matrix material, the interface layers are made up of weak Van der Waals bonds. Moreover, a higher number of voids are found to be concentrated around the interface layers which could induce stress concentration within the material. Thus, the interface layers are usually weaker than the nano-filler or the matrix material [4,10,11].

Under mechanical loading, interface debonding, matrix micro-cracking and filler particles crushing are among the well-known types of damage occurred in nanocomposites [12,13]. During loading, the formation of microcracks is a gradual process and the residual mechanical, thermal and electrical response of nanocomposites are altered by the extent of this damage. The elastic modulus is found to degrade gradually as the level of damage increases [14–18]. When a nanocomposite is subjected to fatigue loading, cracks usually start to emerge at the interface. As the loading cycles increase, the number and size of cracks grow, which results in reduction in stiffness.

The quantity and size of the damage is related to the number of fatigue cycles, whereas the type of damage initiated is observed to depend on the amplitude and frequency of the cycles [12–14,19]. Under low stress-high cycle fatigue loading conditions, matrix micro-cracking is observed to be dominant. On the other hand, under high stress-low cycle loading conditions, the matrix-particle interface damage occurred prior to matrix micro-cracking [15,16]. Analytical and numerical studies have shown that thermal conductivity of nanocomposites is also affected by the presence of damage [3,15,16,18,20–24]. It is shown that the volume and shape of cracks have a direct influence on the effective thermal conductivity of nanocomposites [17,22]. Song et al. [20] investigated the relation between thermal conductivity and stiffness in composites with aligned fibers and planar randomly oriented fibers using a
A self-consistent Mori-Tanaka model. An explicit correlation between the thermal conductivity and the modulus of elasticity was observed.

Apart from these few studies, a detailed experimental study on the effect of damage on the thermal conductivity and modulus of elasticity of nanocomposites and their cross-relation under fatigue loading is missing. This study is focused on understanding the effect of fatigue damage on the thermal conductivity and elastic modulus in a nanocomposite and developing an explicit correlation between the two material properties. A polymer nanocomposite was fabricated from epoxy and silicon particles, and the change in the thermal conductivity and modulus of elasticity as a function of fatigue loading was investigated experimentally. In addition, a mathematical model that interrelates the damage quantity with effective thermal conductivity and elastic modulus is developed.

2. Material and sample preparation

2.1. Materials used

A nanocomposite, epoxy reinforced with nanosilica filler, was fabricated for this study. Bisphenol-A epoxy (Buehler Epothin 2 Resin, Part-A) was used as a resin. Following the manufacturer's recommendation, Bisphenol-B epoxy (Bueler Epothin 2 Hardener, Part-B) was used as a hardener. Silica nano-powder was selected as nano filler. The silica nanofiller, 99.5 trace metal basis, was purchased from Sigma Aldrich, and has spherical shape with particle size of 10—20 nm (BET). Nanocomposite with 2% of silica nanoparticles, by weight, was fabricated following a procedure outlined in the next section.

2.2. Sample preparation

First, as-received epoxy resin (Part-A) and silica nano-powders were weighed based on the predetermined weight ratio (98 and 2 by weight respectively). The weighed epoxy resin and silica nanopowder were poured into a glass beaker and mixed mechanically until the mixture turned to a uniform color. The mixture was also subjected to ultrasonic mixing to obtain better dispersion of the nano-particles in the matrix. Next, the air trapped during mechanical and ultrasonic mixing was removed by using a vacuum chamber. The hardener (Buehler Epothin 2, Part-B) was then added to the mixture, mixed mechanically and ultrasonically, and vacuumed until the air trapped was removed. Finally, the mixture was poured into cylindrical shaped molds coated with a release agent and placed in a condition controlled hood for 24 h. Once completely dried, the material was taken out of the mold, machined to the right size, and the top and bottom surfaces were polished. Further, two holes were drilled along the radial direction (perpendicular to the cylinder axis) to place thermocouples during the thermal conductivity test.

3. Experimental method

Two sets of experiments were conducted to characterize the thermal conductivity and mechanical properties and are detailed below.

3.1. Thermal conductivity

The thermal conductivity experiments were performed based on ASTM C177 using a linear unidirectional heat transfer apparatus. As shown in Fig. 1, the apparatus has a 25.4 mm brass cylindrical bar at the top of the assembly which is attached to an electrical heat source. It has another 25.4 mm brass cylindrical bar located at the bottom of the assembly connected with running water and serve as a heat sink. Usually, the specimen would be sandwiched between the two brass rods. However, since the thermal conductivity of the nanocomposite is expected to be very low compared to the brass, two polycarbonate cylinders were inserted between the two brass bars and the specimen was sandwiched between them. The thermal conductivity of polycarbonate is as low as the nanocomposite, and hence the heat loss in the interface due to material mismatch can be minimized. A total of eight thermocouples (T1-T8) were inserted into the polycarbonate bars and the specimen, to monitor the temperature across the axis of heat flow, as shown on Fig. 1 (b).

The amount of heat supplied was controlled by adjusting the source voltage of the electrical heater. In this work, all the experiments were conducted at an average temperature of about \( T = 30 \degree C \), which corresponds to a 5 V electric power supply. This temperature was selected to keep the specimen below the glass transition temperature (\( T_g = 43 \degree C \)) and avoid the effect of phase transformation. From the temperature data measured by the thermocouples, the thermal conductivity of each specimen can be
calculated using the well known steady state heat conduction equation given in Eq. (1).

\[
K_{\text{Speci}} = K_{\text{PC}} \left[ \frac{(\Delta X_{\text{Speci}})^* \left( (T_2 - T_3) + (T_6 - T_7) \right)}{2^* \left( \Delta X_{\text{PC}} \right)^* \left( T_4 - T_5 \right)} \right]^{1/2}
\]

where \(K_{\text{PC}}\) is the thermal conductivity of the polycarbonate bars, \(\Delta X_{\text{PC}} = 15\) mm is the distance between the thermocouples \(T_2\) and \(T_3\) and \(T_6\) and \(T_7\), \(\Delta X_{\text{Speci}} = 13\) mm is the distance between the thermocouples \(T_4\) and \(T_5\) within the specimen. To improve the accuracy of the thermal conductivity measurement, the average temperature measured from the top and bottom polycarbonate bars were used in the analysis.

3.2. Fatigue loading

To generate and progressively grow the damage/micro-cracks in the specimen, the samples were subjected to a compression-compression fatigue loading at a constant amplitude fluctuating between 445 and 4450 N, at a frequency of 2 Hz. A material testing system (MTS 810) was used under load control mode. As shown in Fig. 2, the specimen was sandwiched between two flat aluminum fixtures and a thin layer of lubricating grease was put on the contacting faces to reduce friction.

The whole experimental process followed a loop: first the thermal conductivity and the elastic modulus of the as-fabricated specimen were measured. Then, the specimen was subjected to fatigue loading and, after every 10,000 fatigue cycles (sometime 5000 cycles if damage was observed), the thermal conductivity and the elastic modulus were measured. The process was continued until each specimen was subjected to 200,000 cycles of fatigue loading.

4. Results and discussion

4.1. Modulus of elasticity

The modulus of elasticity (E) of the nanocomposite measured at different fatigue cycles was recorded and depicted in Fig. 3. From the results, it is clear that the modulus of elasticity of the nanocomposite deteriorated approximately linearly with the fatigue cycles. This is not a surprising result, it was documented that the rate of stiffness degradation has a direct association with the state of damage in the material [14] [23].

4.2. Thermal conductivity

The thermal conductivity of the nanocomposite measured at different loading cycles is depicted in Fig. 4. The thermal conductivity of the silica epoxy nanocomposite before being subjected to fatigue loading was 0.45 W/mK and was higher than the plain epoxy (about 0.35 W/mK, measured independently). This is expected, as the nano-filler would enhance the heat flow by serving as an additional heat channel [5,8]. Once the samples were subjected to fatigue loading, the thermal conductivity of the nanocomposite was observed to decrease gradually with fatigue cycles.

The discontinuities and microcracks in the material due to damage could interrupt the continuity of phonon vibration. The interruption could result in phonon scattering, and hence lower the efficiency of heat flow in the material and reduce the thermal conductivity. Evidently, as shown in Fig. 4, the thermal conductivity decreased gradually as the loading cycle increased. The fact that the thermal conductivity and the elastic modulus decreased with loading cycles can indicate a possible relation between them. The following sections will focus on developing the relation between damage, thermal conductivity and elastic modulus of the nanocomposite.

5. Damage analysis

5.1. Semi-analytical approximation

The damage within the composite is usually described by a damage parameter \((D_k)\), which defines the change in stiffness at any apparent loading cycle relative to the initial modulus. In general, the damage parameter \((D_k)\) is a dimensionless quantity and can be expressed as:

\[
D_k = \frac{E_0 - E_n}{E_0}
\]

where \(E_0\) and \(E_n\) are the modulus of elasticity at pre-fatigue and at any \(n\) fatigue cycles state, respectively.
The apparent modulus of elasticity at any \( n \) cycles \( (E_n) \) can be written as a function of initial state elastic modulus \( (E_0) \) by fitting the plot of the modulus of elasticity against the fatigue cycles shown in Fig. 3 with a three-parameter exponential function, as also shown in Eq. (3).

\[ E_n = E_0 + Ae^{-Bn} \]  

(3)

where \( n \) is the number of cycles, and \( A \) and \( B \) are constants obtained from curve fitting.

By substituting Eq. (3) in to Eq. (2), the damage parameter can be described in terms of initial elastic modulus and the number of fatigue cycles as:

\[ D_s = \frac{-Ae^{-Bn}}{E_0} \]  

(4)

The expression given in Eq. (4) is important, since the damage

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Fig. 3. Modulus of elasticity \( (E) \) with fatigue cycles.

Fig. 4. Thermal conductivity \( (K) \) with fatigue cycles.
parameter of the material at any instant of the fatigue cycles is directly determined from initial modulus and fitting constants.

Similarly, the thermal conductivity data plotted in Fig. 4 is fitted with a three-parameter exponential function. The expression for thermal conductivity as a function of initial thermal conductivity and fatigue cycle is described as:

\[ K_n = K_0 + C e^{-Dn} \]  \hspace{1cm} (5)

where \( K_0 \) is the pre-fatigue thermal conductivity of the nano-composite, \( C \) and \( D \) are constants obtained from fitting of the experimental data.

As noted in Eq. (3) and Eq. (5), both the apparent elastic modulus and thermal conductivity are described in terms of the number of fatigue cycles \( n \), thus, the two properties can be related to each other as:

\[ E_n = E_0 + A e^{\frac{B}{C0} \ln \left( \frac{K_n}{K_0} \right)} \]  \hspace{1cm} (6)

Eq. (6), expresses the apparent modulus of elasticity at \( n \) fatigue cycles as a function of elastic modulus \( E_0 \) and thermal conductivity \( K_0 \) at \( n \) cycles. The material constants in Eq. (3), Eq. (5) and Eq. (6) are presented in Table 1. This expression offers a glimpse of the possibility of estimating the apparent modulus of elasticity \( E_n \) of the material based on initial conditions and the apparent thermal conductivity \( K_n \), without ever needing to know the number of cycles. This relation is critical due to the fact that, with known initial thermal conductivity and elastic modulus, the residual elastic modulus \( E_n \) at any time can be monitored by measuring the apparent thermal conductivity \( K_n \). Similarly, the thermal conductivity of the material can be expressed in terms of the modulus of elasticity. This cross-property interaction between the two properties is essential as it helps to estimate one property by measuring the other property more convenient to measure. The elastic modulus estimated from the semi-analytical/exponential model (Eq. (6)) is in good agreement with the experimental measured value as shown in Fig. 5.

Furthermore, by substituting the expression of modulus of elasticity in Eq. (6) into Eq. (2), the damage parameter \( D_s \) can be expressed in terms of thermal conductivity as shown in Eq. (7):

\[ D_s = A \left( \frac{E_0}{E_0} \right) e^{\frac{B}{C0} \ln \left( \frac{K_n}{K_0} \right)} \]  \hspace{1cm} (7)

where \( A, B, C \) and \( D \) are constants obtained from the experimental data.

From Eq. (7), the state of damage at any instant of loading cycles can be estimated based on the elastic modulus and thermal conductivity measured at pre-fatigue state and the thermal conductivity at any fatigue cycle. As depicted in Fig. 6, substantial agreement is observed between the experimental result and the semi-analytical model given by Eq. (7). This is a simple but interesting relation as it can serve as a way of estimating damage in the material without ever dealing with additional mechanical testing at any loading cycle.

Table 1
Curve fitting parameters for the elastic modulus and thermal conductivity.

<table>
<thead>
<tr>
<th>Const. terms</th>
<th>( E_0 )</th>
<th>( A )</th>
<th>( B )</th>
<th>( K_0 )</th>
<th>( C )</th>
<th>( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica Epoxy (SE)</td>
<td>( 7.55 \times 10^7 )</td>
<td>( -2.3 \times 10^7 )</td>
<td>( 1.6 \times 10^5 )</td>
<td>( 0.445 )</td>
<td>( -1.1 \times 10^{-2} )</td>
<td>( 8.5 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

Fig. 5. The modulus of elasticity \( (E) \) with fatigue cycles based on experimental and semi-analytical approximation.
5.2. Differential scheme

Numerous micromechanics models have been developed in the past. These models are based on the assumption of non-interacting particles within the homogenous material to estimate the thermal, electrical and mechanical properties of particulate composites [3,21]. The differential scheme is one of them and has been effectively implemented to estimate the effective electrical conductivity of nanocomposites [3,18,20]. This model is constructed by modifying the self-consistent model by an infinitesimally increasing progression of cracks or inhomogeneity. This modified model is considered as an ideal model for a particle filled composite. The model takes the parameters such as density, shape and level of inhomogeneity into account. Assuming an initially homogenized material system and later by introducing a gradual increasing inhomogeneity (micro-cracks), in this work, the differential scheme is adopted to describe the effective modulus of elasticity and the effective thermal conductivity. By considering the nanocomposite as isotropic material, the effective modulus of elasticity can be written as [22,25]:

\[ E_n = E_0 \left( 1 - \frac{1}{C_0 d} \right)^{\varepsilon(\gamma, n_0)} \]  

(8)

where \( E_n \) and \( E_0 \) are the apparent and initial elastic modulus respectively and \( \varepsilon(\gamma, n_0) \) is a shape factor that described as:

\[ \varepsilon(\gamma, n_0) = \frac{1 - (2v_0)}{\pi \gamma} \]

\( \gamma \) is the crack aspect ratio and \( d \) is the crack density. Note, the change in Poisson’s ratio due to crack is very small and assumed to be negligible in this model.

Rearranging the terms in Eq. (8) and using modulus of elasticity (\( E_n \) and \( E_0 \)) data obtained from our experiments, the crack density (\( d \)) can be extracted for a certain form of crack shape. In our case, by considering an oblate shaped crack with aspect ratio (\( \gamma \)) of 0.2, the crack volume ratio (\( d \)) at different fatigue cycle is obtained and depicted in Fig. 7. As shown in Fig. 7, the crack density (\( d \)) in the silica epoxy nanocomposites is increased almost linearly with fatigue cycles.

A similar non-interacting differential scheme is developed to obtain the effective thermal conductivity as [22,25]:

\[ K_n = K_0 \left( 1 - d \right)^{\eta(\gamma)} \]  

(9)

where \( K_n \) is the apparent thermal conductivity, \( K_0 \) is the thermal conductivity of initially homogenized material, \( \eta(\gamma) \) is the shape factor parameter which is expressed as:

\[ \eta = d \left( A_1(\gamma) + A_2(\gamma) \right) \frac{3}{2} \]

where \( A_1(\gamma) = \frac{1}{1 - f_0(\gamma)} \) and \( A_2(\gamma) = \frac{1 - 3f_0(\gamma)}{2f_0(\gamma)(1 - f_0(\gamma))} \)

The Eshleby’s tensor factor \( f_0(\gamma) \) is written as:

\[ f_0 = \frac{\gamma^2(1 - \gamma^2)}{\pi(1 - \gamma^2) \arctan \left( \frac{\sqrt{1 - \gamma^2}}{\gamma} \right)} \]

By inserting the thermal conductivity data from the experiment into Eq. (9), the crack density (\( d \)) for oblate shaped cracks with aspect ratio (\( \gamma \)) of 0.2 is determined and plotted in Fig. 8. For the purpose of comparison, the crack density obtained from Eq. (8) (using the modulus of elasticity data) is also plotted in Fig. 8. It is observed that the crack volume ratio obtained from the modulus of elasticity (Eq. (8)) is fairly consistent with that obtained from thermal conductivity data (Eq. (9)). This result indicates that the differential scheme is an effective method to estimate the effective thermal conductivity, elastic modulus, and crack density of the material used.

Further, noting that the differential scheme model depicted in Eq. (8) and Eq. (9) holds crack density (\( d \)) as a common term, an explicit relation between the thermal conductivity and the elastic modulus can be obtained by combining them as:
\[ E_n = E_0 \left( \frac{K_n}{K_0} \right)^{\frac{1}{4}} \]  

(10)

Similar to the semi-analytical expression (Eq. (6)) discussed above, this explicit relation can be used to obtain the elastic modulus at any fatigue cycle based on the initial materials properties and the thermal conductivity measured at that stage of fatigue cycle. The elastic modulus estimated based on Eq. (10) is plotted in Fig. 9 along with the experimental results and the estimation from Eq. (6). Note, the property estimated by Eq. (6) (a semi-analytical method) is fully based on a curve fitting of the experimental data, whereas, Eq. (10) (differential scheme) is based on a micromechanics model assuming non-interacting inhomogeneity with isotropic material. From the result shown in the Fig. 9, both models have followed a similar pattern and are in good agreement with the elastic modulus obtained experimentally.
Finally, using Eq. (2) and Eq. (10), the damage parameter ($D_s$) can be described in terms of the thermal conductivity as:

$$D_s = \frac{1}{C_0} K_n^{\eta} K_o^{1/\eta}$$  \hspace{1cm} (11)

This model enables determination of the damage parameter reasonably without testing the apparent elastic modulus ($E_a$). As shown in Fig. 10, both the differential scheme (Eq. (11)) and the semi-analytical model (Eq. (7)) have estimated the damage parameter reasonably well and are in good agreement with the experimental value.

6. Summary

A detailed study on the cross-relation between, damage, elastic modulus, and thermal conductivity in nanocomposites was...
conducted experimentally. The degradation of the modulus of elasticity was observed to be gradual and considered as an indication for the occurrence of damage within the material. Similarly, a gradual reduction in the thermal conductivity was observed as the loading cycle increases. The experimental results were approximated by three parameter exponential functions for both the thermal conductivity and elastic modulus as a function of fatigue cycles. A semi-analytical model is also proposed to estimate the elastic modulus and damage parameter based on initial properties and thermal conductivity at any stage.

On the other hand, a differential scheme model was used to describe the thermal conductivity and elastic modulus as a function of crack density. The density of crackwas estimated based on differential scheme using thermal conductivity and elastic modulus data independently. Both schemes gave an excellent estimate of the crack density. The density of crack was estimated based on different data independently. Both schemes gave an excellent estimate of the crack density compared with the experimental results.

In conclusion, damage, elastic modulus and thermal conductivity of the investigated nanocomposites are eminently interrelated, and the models can be used to describe one property based on the other.

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