Predicting Young’s modulus of CNT-reinforced polymers

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Abstract

In this paper, a formulation for prediction of effective Young’s modulus of carbon nanotube (CNT) reinforced polymers is presented. Based on fuzzy logic, a novel bridging method between experimental and theoretical results is used. This method provides three steps to calculate the true value of the modulus. First, the Young’s modulus of a hypothetical representative volume element (RVE) is obtained. Since nanocomposites consist of volume elements (VE) with different alignment angles, in the next step, the rotation effects on the VE’s modulus are considered. Subsequently, these VEs are replaced with aligned VEs which have compatible volume percentages. Based on the obtained different volume percentages, a suitable RVE with equivalent volume percentage is developed. Using this equivalent RVE and referring to step one, the Young’s modulus of the nanocomposite is determined. The obtained results show a good agreement with the experimental ones and with those obtained by traditional methods. The advantage of the proposed formula compared with conventional ones is its applicability to a wide domain of volume percentage of CNT.

1. Introduction

Nanocomposites are new class of composite materials where each constituent has dimensions in the range of 1–100 nm [1]. Recent studies have shown that nanoparticles have dramatic effects on the mechanical properties of polymers [2–5]. CNTs are one of the important nanoparticles that are widely known for their exceptional properties. Therefore, CNT-reinforced polymers are key materials for numerous industries. Currently, different techniques are being applied to analyze the mechanical properties of nanocomposites. In this regard, the researches for investigating the mechanical properties of nanocomposite, are divided into two groups of experimental and theoretical/numerical studies.

Experimental works explore the effects of different dispersion states [6,7], waviness [8], length and aggregate size [7,9–11], structure/size [12–14], and volume percentage [15] of CNTs on the mechanical properties of CNT-reinforced polymers. The various effects of nanotube such as structure/size [16], waviness [17], Alignment [18], debonding [19], volume percentage [20], agglomeration [11,21,22] and interphase region behavior [5,22,23] on mechanical properties of nanocomposites have been studied based on several theoretical/numerical methods. These methods are based on continuum mechanics [24,25], finite element (FE) [23,24,26], equivalent continuum mechanics [27,28], multi-scale modeling [29–32] and hybrid FE-micromechanics [33].

According to the literature survey, it observed that there is a large gap between the values of nanocomposite Young’s modulus attained by experimental and theoretical/numeric approaches [11,14,21]. Therefore, in the present study, fuzzy logic clustering algorithm is utilized to develop some rules for estimation of the effective modulus of CNT-reinforced polymers. These rules construct a connection between the aforementioned approaches.

2. Theoretical method

Each nanotube and its surrounding matrix is considered as a volume element (VE). These VEs are supposed to have the same volume percentage as the nanocomposite. Therefore, a nanocomposite specimen is a set of several VEs with same volume percentages and different angles of alignment. For a nanocomposite, a representative volume element (RVE) can be defined which represents its mechanical properties. If all of the VEs are aligned, the corresponding RVE is the same as VEs. However, for a nanocomposite which consists of VEs with different angles of alignment, it is needed to define an equivalent RVE.

To study the Young’s modulus of nanocomposites, the effects of CNT volume percentage and the VE alignment on the nanocomposite specimen are considered in three steps.
In the first step, the Young’s modulus of hypothetical RVE versus volume percentage of CNT is formulated using the available numerical data [5] and fuzzy clustering algorithm. This numerical data is noted as \((u_i, w_i)\), where \(u_i\) and \(w_i\) are CNT volume percentage and Young’s modulus of the hypothetical RVE, respectively. The fuzzy subtractive clustering algorithm [34] (see Fig. 1), is utilized to find the clusters of the data. The detected clusters are used to construct a set of suitable fuzzy rules in order to extract the mathematical formulation for predicting Young’s modulus of the hypothetical RVE against CNT volume percentage.

The rule premises, \(A_i\) are represented by exponential membership functions:

\[
\mu_{A_i}(u) = \exp \left(-\frac{4}{r^2_a} \left(\frac{u - u_i^c}{u_M - u_m}\right)^2\right), \quad i = 1 \ldots k
\]  

where \(k\) is the number of clusters, \(u_M\) and \(u_m\) are the maximum and the minimum amounts of \(u_i^c\), the corresponding \(u_i\) for the \(i\)-th cluster, and \(r_a\) is the cluster radius.

Based on the first-order Sugeno model [35], the appropriate fuzzy rules can be written as:

\[
R_i: \text{If } u \text{ is } A_i \text{ then } w_i(u) = p_{i0} + p_{i1}u_i, \quad i = 1 \ldots k
\]  

The unknown coefficients \(p_{i0}\) and \(p_{i1}\) can be evaluated using least square estimation [35] as follows:

\[
\beta_i = \frac{\mu_{A_i}(u_j)}{\sum_{j=1}^{k} \mu_{A_j}(u_j)}, \quad P = (B^T B)^{-1} B^T W
\]  

The mathematical formulation for Young’s modulus of the hypothetical RVE can be expressed as:

\[
w(u) = \frac{\sum_{i=1}^{k} \mu_{A_i}(u) w_i(u)}{\sum_{i=1}^{k} \mu_{A_i}(u)}
\]

So at the end of the first step, Young’s modulus of the hypothetical RVE in a range of a pre-assumed CNT volume percentage is calculated. By using the available data of longitudinal (transverse) Young’s modulus and CNT volume percentage for finding the

**Fig. 1.** Fuzzy clustering algorithm.
clusters and incorporating Eqs. (1)-(5), the mathematical formulation for longitudinal (transverse) Young’s modulus is obtained; i.e. 
\( w(u) = w_{1}(u) = E_{11}^{0}, \quad w(u) = w_{22}(u) = E_{22}^{0}. \) Take note that \( w_{1}(w_{2}) \) is the Young’s modulus of the hypothetical RVE in direction 1 (2) which is different from \( w_{1}(w_{2}) \) obtained from Eqs. (2)-(4).

In the second step, the effects of the rotation of VE on its longitudinal modulus are investigated. An aligned isolated VE can be treated the same as hypothetical RVE, so the developed formulation, in step one, is used to predict the Young’s modulus of VE. This means that for a given CNT volume percentage of nanocomposite (which is same for all of the VEs), the Young’s modulus of only aligned VEs can be calculated by using the extracted mathematical formulation in step one.

The calculated Young’s moduli of aligned VE, in the directions of axis-1 and axis-2, are denoted as \( E_{11}^{0} \) and \( E_{22}^{0} \). (axis-1 and axis-2 are the longitudinal and transverse directions, respectively). Because of different elastic moduli in the aforementioned directions, VE has different values of stiffness in the corresponding directions assumed to be \( K_{1} \) and \( K_{2}. \) If VE is rotated by angle of \( \theta, \) the stiffness in direction of axis-1 can be calculated as:

\[
K_{1}^{\theta} = K_{1} \cos (\theta)^{2} + K_{2} \sin (\theta)^{2}
\]

Based on Eq. (6), the longitudinal tensile modulus of rotated VE can be obtained as:

\[
E_{11}^{\theta} = E_{11}^{0} \cos (\theta)^{2} + E_{22}^{0} \sin (\theta)^{2} = w_{1}(u) \cos (\theta)^{2} + w_{2}(u) \sin (\theta)^{2}
\]

At the end of the second step, longitudinal tensile modulus of all VEs with all possible angles are calculated.

The third step consists of three sections. Firstly, VEs with \( E_{11}^{0} \) are replaced with equivalent aligned VEs (\( \theta = 0 \)) which have new reduced volume percentages and same longitudinal tensile modulus \( (E_{11}^{0}) \). At the end of the first section, i.e. Eq. (8a), the main nanocomposite, which consists of VEs with identical volume fraction and different angles of rotation, is converted to a nanocomposite which now consists of equivalent aligned VEs with reduced volume percentages and same longitudinal tensile modulus. Since the rotated VEs are replaced with aligned VEs with the same longitudinal Young’s modulus, therefore, along this conversion, the longitudinal Young’s modulus of nanocomposite is not changed.

In the second section, i.e. Eq. (8b), all the aligned VEs of the converted nanocomposite are combined and a new refined CNT volume percentage for converted nanocomposite is obtained. The converted nanocomposite is supposed to have an equivalent RVE with the refined CNT volume percentage. Note that because of the isotropic property of nanocomposite [27], the distribution percentage of each alignment angle is considered the same.

Finally, for the developed equivalent RVE with refined CNT volume percentage, it is possible to calculate the Young’s modulus using the extracted mathematical formulation in the first step (Eq. (8c)). Whereas, the longitudinal Young’s modulus was kept fixed along the conversion, it is only allowed to utilize the mathematical formulation for longitudinal Young’s modulus.

The procedure of the third step is summarized as follows:

\[
\varphi_{\theta} = w_{1}(E_{11}^{\theta}) \quad \text{or} \quad \varphi = \frac{\int_{0}^{180} \varphi_{\theta} \, d\theta}{180}, \quad \varphi = \frac{\int_{0}^{\pi} W_{1}(E_{11}^{\theta} \cos (\theta)^{2} + E_{22}^{0} \sin (\theta)^{2}) \, d\theta}{\int_{0}^{\pi} d\theta} \quad \text{(8b)}
\]

\[
E_{NC} = w_{1}(E_{11}^{0}) \quad \text{(8c)}
\]

where \( \varphi_{\theta} \) is CNT volume percentage of equivalent aligned VE, \( \varphi \) and \( E_{NC} \) are the CNT volume percentage of equivalent RVE and the Young’s modulus of nanocomposite, respectively.

3. Results and discussions

The available data [5] and fuzzy clustering algorithm (Fig. 1) are used to explore the variations of the non-dimensional longitudinal and transverse tensile modulus of hypothetical RVE versus volume percentage of CNT (Fig. 2, the first step). The Young’s modulus of matrix, i.e. \( E_{M} \), is used for normalizing the longitudinal and transverse tensile modulus of hypothetical RVE. It can be seen in Fig. 2 that the normalized moduli trends, determined based on the current model, match very well with the available data [5].

For a rotated VE, the longitudinal modulus is determined using Eq. (7). The variations of the longitudinal Young’s modulus versus angle of rotation and CNT volume percentage is shown in Fig. 3 (the second step).

Following the third step, based on Eq. (8), first, the volume percentages of equivalent VEs are obtained. Then, volume percentage of equivalent RVE and the corresponding modulus are determined. This modulus for nanocomposite is obtained with regard to a pre-assumed CNT volume percentage. If the pre-assumed volume percentage is changed, the modulus differs. Therefore, fuzzy clustering algorithm (Fig. 1), is utilized again to extract a new formulation for the Young’s modulus of nanocomposite as a function of CNT volume percentage:

\[
E_{NC} = \frac{0.22 \varphi_{0.12}^{0.96} - 3.7 \varphi_{0.12}^{0.96} + 0.42 \varphi + 2.8}{1 + \varphi_{0.12}^{0.96}} E_{M} \quad \text{(9)}
\]

In Fig. 4, a comparison between the results of the current proposed formula (Eq. (9)), traditional Halpin–Tsai approximation [21], Lorentz estimation [12] and experimental data [21] is illustrated. Halpin–Tsai approximation is valid for low weight fraction (less than 1%) [14] or CNT volume percentage less than 0.5% (magnified zone in Fig. 4), while Lorentz estimation uses experimental results to take the volume distribution of CNT into account and modifies the Halpin–Tsai approximation. This modification extends the range of validity to 7.5% of CNT volume percentage [12].
The obtained results show a good agreement within the domain of validity of Halpin–Tsai and Lorentz approximations. The superiority of the current proposed formulation compared to the aforementioned approximations, is that the proposed formulation is applicable for low and high CNT volume percentages, while those approximations are valid for low CNT volume percentages. Moreover, the presented formula is independent of CNT aspect ratio. In addition, the comparison of the obtained results and available experimental data in higher range of CNT volume percentages, proves the accuracy of the proposed formula. Therefore, the gap between the values of nanocomposite Young’s modulus obtained from current study with experimental data and results of Halpin–Tsai and Lorenz approximations.

Fig. 3. Non-dimensional Young’s modulus of rotated VE as a function of rotation angle and CNT volume percentage.

Fig. 4. Comparison of the normalized nanocomposite Young’s modulus versus CNT volume percentage obtained from current study with experimental data and results of Halpin–Tsai and Lorenz approximations.

The results presented in Fig. 4 indicate a good agreement within the domain of validity of Halpin–Tsai and Lorentz approximations. As previously mentioned, the aforementioned approximations are valid for low CNT volume percentages, while the proposed formula is applicable for high CNT volume percentages as well. Moreover, the presented formula is independent of the aspect ratio of CNT while in Halpin–Tsai and Lorentz approximations, the aspect ratio is one of the important parameters in predicting the Young’s modulus. The latter advantage becomes important because Tserpes and Chanteli [5] have shown that for aspect ratios more than 20, the Young’s modulus of nanocomposite does not change significantly. In addition, the comparison of the obtained results and available experimental data in higher range of CNT volume percentages reflects the ability and accuracy of the proposed formula in the prediction of effective modulus.

4. Conclusions

This paper presents a formulation for prediction of effective modulus of CNT-reinforced polymers using a fuzzy logic approach. For this purpose, firstly, the longitudinal and transverse tensile modulus of hypothetical RVE versus percentage of CNT are calculated. Secondly, the effects of alignment of constitutive VEs on their modulus are considered. Then, equivalent RVE with refined CNT volume percentage is developed for nanocomposite by considering all of the possible cooperative angles. Lastly, the Young’s modulus of nanocomposite is formulated using the equivalent RVE and fuzzy clustering algorithm.

The obtained results show a good agreement within the domain of validity of Halpin–Tsai and Lorentz approximations. The superiority of the current proposed formulation compared to the aforementioned approximations, is that the proposed formulation is applicable for low and high CNT volume percentages, while those approximations are valid for low CNT volume percentages. Moreover, the presented formula is independent of CNT aspect ratio. In addition, the comparison of the obtained results and available experimental data in higher range of CNT volume percentages, proves the accuracy of the proposed formula. Therefore, the gap between the values of nanocomposite Young’s modulus attained by experimental and theoretical/numeric approaches can be filled with the presented formula.

References