# Optimization of Micromechanical Theories for Nanocomposites Reinforced with Carbon Nanotubes

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## Abstract

Several micromechanical theories exist that can be used to predict composite material properties. Short fibre composite micromechanical models have also been used to predict nanocomposite modulus. However, the reasons for selecting particular models were not provided. Also, the sensitivity of the micromechanical models had not been considered. There are few studies that predict damping for composite materials using micromechanical models and they have never before been used to predict nanocomposite damping over a wide temperature range.

In this work, to find a better micromechanical model for nanocomposite materials, predictions from the theories have been compared with three previous experimental nanocomposite works. It was observed that the Lavengood theory showed the closest results to the experimental results, as a result of its suitability for low volume fraction reinforcement of fibres in the composite. The sensitivity of fibres aspect ratio was considered too, it was found that Lavengood theory exhibit less sensitivity that others.

**Keywords:** Nanocomposites, Micromechanic theories, Composite Materials, Nanotechnology.

## 1. Introduction

As the use of composite materials has increased, the need to predict performance more accurately has resulted in the development of many micromechanical models. These theories are primarily used to assess and predict analytically the elastic stiffness of different composite materials considering their microstructure [1]. Models have been developed that deal with various types of fibre reinforcement including long fibres, unidirectional and random short fibre. However, the suitability of such models for predicting the properties of nanocomposites is uncertain, as the micromechanical theories assume perfect bonding between fibre and matrix while in reality the level of adhesion between the matrix and nanoscale reinfocement is not well understood. The other reason is related to the high aspect ratio for fibres in a nanocomposite compared to the fibres in composite materials. In addition, the suitability of micromechanical theories to predict modulus as temperature changes is not known.

A few studies have been done on the suitability of micromechanical theories to predict the damping of composite materials. Shokrieh et al [2] compared the experimental results of glass fibre/epoxy with micromechanical theories at room temperature. They found good agreement between experimental results with the Halpin-Tsai model. However, there is uncertainty about the suitability of micromechanical models to predict the composite and nancocomposite damping, especially as temperature changes.

In this work, several micromechanical theories are presented and used to predict the longitudinal Young's modulus and damping for the nanocomposites and composite materials at different volume fractions and temperature range.

## 2. Continuous fibre reinforced matrix

"Continuous fibres" means fibres that extend over the entire dimension of a part without a break or interruption. However, there are different theories for the limit of aspect ratio between continuous and short discontinuous fibres [3, 4]. For a matrix reinforced with long and straight fibres, two models are commonly used depending on the orientation of the load to the fibres.

2.1 The Rule of Mixtures:

This model is used to calculate mechanical properties, such as Young's modulus, thermal expansion and density for composites reinforced with unidirectional continuous fibres when the load direction is parallel to the fibre direction. It assumes no slip and perfect fibre-matrix bonding. This model is of one dimension; therefore it neglects the Poisson ratio of the composite content [5,6]. The modulus formula for the rule-of-mixtures is:

$$E_c = E_f\, v_f + E_m v_m \qquad 1$$

$$v_m = 1 - v_f$$

where, $E_c$ is the Young's modulus of the composite, $E_f$ is the Young's modulus of the fibre, $E_m$ is the Young's modulus of the matrix, $v_f$ is the volume fraction of the fibre and $v_m$ is the volume fraction of the matrix.

2.2 Reuss model:

This model is used to find the transverse modulus for composites reinforced with unidirectional continuous fibre. It is used when the loading direction is perpendicular to the fibres and assumes no slip between fibre and matrix [6, 7]. The formula for the modulus of the composite is:

$$\frac{1}{E_c} = \frac{v_f}{E_f} + \frac{v_m}{E_m} \qquad 2$$

## 3. Short fibre reinforced matrix

A short fibre composite involves discontinuous fibres embedded in a matrix. The fibres can have either random orientation or be aligned in a particular direction.

### *3.1 Aligned short fibre composite*

To find the Young's modulus of aligned short fibres in a composite, the following micromechanical theories are used:

#### 3.1.1 Shear-Lag Model

Shear lag theory was originally proposed by Cox in 1952. Cox's analysis was relatively simple, assuming that stress transfer between fibre and matrix is entirely due to matrix shear. This method is commonly used in micromechanics models for oriented short fibre composites. It is often used to predict the elastic longitudinal modulus $E_{11}$ for composite materials fully bonded between the fibre and the matrix. Also, the stress transfer through the fibre ends was neglecte[8, 9].

Cox suggested a one-dimensional equation to explain the stress transfer between the matrix and the fibre. So, the model considers a single fibre of length $l$ and radius $r_f$ encapsulated in a concentric cylindrical shell of matrix having radius *R*. The following expression is obtained for the longitudinal modulus:

$$E_{11} = \eta_1 v_f E_f + (1 - v_f)E_m \qquad 3$$

where,

$$\eta_1 = 1 - \frac{\tanh(\frac{\beta l}{2})}{\frac{\beta l}{2}}$$

$$\beta = (\frac{H}{\pi r_f^2 E_f})^{1/2}$$

$$H = \frac{2\pi G_m}{\ln(\frac{R}{r_f})}$$

$$R = r_f\sqrt{\frac{K_R}{v_f}}$$

Here, $E_f$ and $E_m$ are the moduli of the fibre and the matrix, respectively. $G_m$ is the shear modulus of the matrix and $\eta_1$ is the length-dependent efficiency factor. For Cox's model, $K_R$ is a constant and is equal to the value 3.628.

### 3.1.2 Halpin-Tsai Equations

The Halpin-Tsai equations are based on the self-consistent micromechanics method, which assumes an effective modulus for the matrix and perfect bonding between matrix and fibre. Also, they assume that both of the inclusion and the medium are homogeneous and elastic, and the fibre behaves as if surrounded by a cylinder of pure and homogeneous matrix. The Halpin-Tsai equations are used to calculate the longitudinal and transverse modulus and strength of unidirectional short fibre composites, and transverse mechanical properties of long fibre reinforced composites [10, 11].

The Halpin Tsai model demonstrates that the geometry of the reinforcement has significant effect on the composite stiffness [12]. It is equation can be expressed in a common form:

$$\frac{p}{p_m} = \frac{1 + \xi\eta v_f}{1 - \eta v_f} \qquad 4$$

where,

$$\eta = \frac{\frac{p_f}{p_m} - 1}{\frac{p_f}{p_m} + \xi}$$

where, $p$ represents any one of the composite moduli, such as $E_{11}$ (longitudinal modulus), $E_{22}$ (transverse modulus which is perpendicular to the fibre direction). The corresponding moduli of the fibre and the matrix are $p_f$ and $p_m$ respectively, while $\xi$ is a parameter that depends on the particular elastic property being considered. It expressed in the combination of differences in Poisson ratio's and elastic constants [12, 13].

For the longitudinal modulus $\xi = 2l/d$.

For the lateral modulus $\xi$=2.

The Halpin-Tsai equations are known provide reliable predictions at low volume fractions. It has also been noted that they sometimes under-predict stiffness at high volume fractions.

### 3.1.3 Comparison between Shear Lag and Halpin-Tsai models

To find the Young's modulus for a nanocomposite material by both theories of shear lag and Halpin-Tsai, a composite material of properties as shown in Table 1 was used for the calculations. The properties were assumed according to data from the M-RECT project.

The Young's modulus at different volume fractions for aligned short fibre composites were predicted using both shear lag and Halpin-Tsai models, as shown in Figure 1.

Table 1: Composite constituents mechanical properties.

| Material | Young's modulus, GPa | Shear modulus, GPa | Poisson ratio | Diameter, nm | Length, µm |
|---|---|---|---|---|---|
| CNT | 1000 | n/a | 0.2 | 20 | 0.5 |
| PEEK | 3.9 | 1.9 | 0.4 | n/a | n/a |

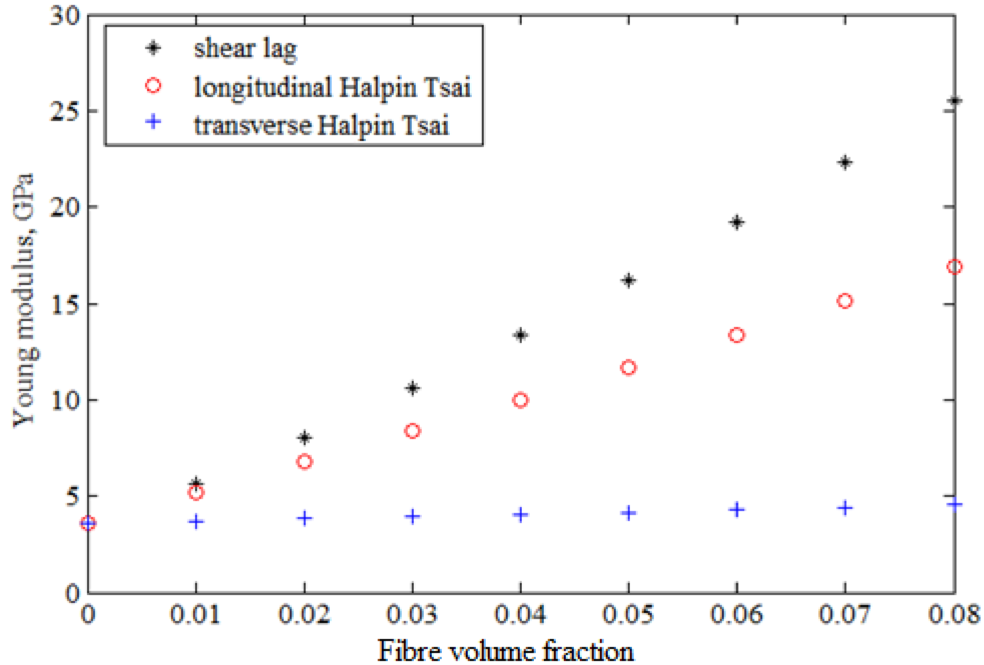


Figure 1: Young's modulus for aligned CNT-PEEK nanocomposites.

It can be seen that the longitudinal modulus predicted by the shear lag model is higher than that predicted by Halpin-Tsai and the difference between them increases with volume fraction. The transverse modulus predicted by Halpin-Tsai is significantly lower than the longitudinal modulus.

### *3.2 Random short fibre composite*

Several micromechanical models have been developed to estimate the Young's modulus for a random orientation of short fibres in a matrix. These theories are derived from the micromechanical theories used for long fibre and aligned short fibre composites.

#### 3.2.1 Lavengood and Goettler model

Lavengood and Goettler modified the Halpin-Tsai model by developing a technique to compute the average elastic modulus for short fibre composite by integrating over the fibre inclination distribution[14]. This theory is suitable for investigating the stiffness in two and three-dimensional random fibre distributions. It requires fibres to be relatively long and the volume fraction to be low. Also, it is assumed that all the elements in the composite are under the same values of stress and strain. They compared their theory with experimental results for an epoxy composite and achieved agreement [4]. They derived the following equation [14]:

$$E_{3d} = \left(\frac{1}{5}\right) E_{11} + \left(\frac{4}{5}\right) E_{22} \tag{5}$$

where $E_{11}$ and $E_{22}$ are longitudinal and transverse Young's modulus calculated using Halpin-Tsai with unidirectional orientation and the same fibre aspect ratio and volume fraction.

### 3.2.2 Fibre Density Function -Pan's Model

Pan developed a new approach to predict the elastic constants of randomly oriented fibre composites. His idea was based on constructing a relation between fibre volume fraction and area fraction for random fibres through using fibre orientation. For that purpose, he developed a density function to describe the fibre orientation through two angles in a curvilinear coordinate system. His theory is dependent on the composite material content properties only and neglects the geometry effect of the composite constituents. He started with the rule-of-mixtures for a unidirectional composite to calculate composite modulus [15, 16].

For the case of three-dimensional random fibre orientation, the tensile modulus is given by:

$$E_c = E_f \frac{v_f}{2\pi} + E_m\left(1 - \frac{v_f}{2\pi}\right) \tag{6}$$

Pan's model has no restriction on the fibre volume fraction. Also, this theory can be applied to cases other than random fibre orientation as long as the fibre orientation density function is available.

### 3.2.3 Krenchel's rule of mixture

Krenchel modified the rule-of-mixtures to find the Young's modulus of discontinuous random distribution of fibres reinforced composites. He used an efficiency factor for orientation to predict the orientation effect of the fibres. He also used a fibre length factor to be suitable for short fibre composites [17, 18]. The general formula for this theory is as below:

$$E_c = (\eta_o \eta_1 E_f - E_m)v_f + E_m \quad 7$$

$$\eta_o = a_n cos^4(\theta) \quad 8$$

where $a_n$ is proportional to total fibre content, $\theta$ is angle of the fibre, $\eta_o$is the orientation factor, and $\eta_1$the length efficiency factor.

Also $\eta_1$ approaches 1 for $l/d$>10, and $\eta_0$ =1/5 for randomly oriented fibre.

## 4 Comparison between conventional micromechanical theories for random fibre composite and previous nanocomposite experimental results

In this section, the experimental results of composite materials of carbon fibre/PEEK and the experimental results of three different published studies on random carbon nanotube reinforced composites are compared with the theoretical micromechanical models for random fibre composites. This comparison is necessary to find suitable micromechanical theory for the nanocomposites and composite material. So, the classical micromechanical theories are compared with the following experimental results:

### *4.1 Nanocomposite of SWCNT/PEEK*

In this previous study [17], the dispersion of SWCNTs that was used to reinforce PEEK was enhanced by functionalizing CNTs with polysulfones to increase the bonding between composite contents. To find the mechanical properties of the composite, tensile testing was carried out at room temperature with speed 1mm/min for specimens of dog bone shape (Type V) and according to UNE-EN ISO 527-1 standard. The nanocomposite constituents' properties are shown in Table .

Table 2: Properties of constituents for the nanocomposite material [7].

| Material | Young's modulus, GPa | Poisson's ratio | Diameter, nm | Length, µm |
|---|---|---|---|---|
| SWCNT | 1000 | 0.2 | 1 | 0.1 |
| PEEK | 4.1 | 0.4 | n/a | n/a |

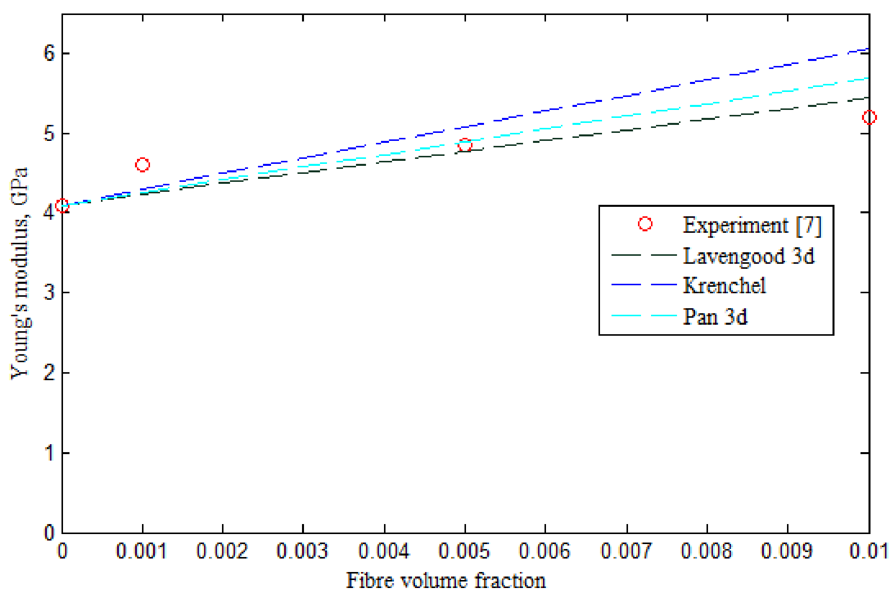


Figure 2: Young's modulus of composite of CNT/ PEEK with changing nanotube content.

The same properties of the nanocomposite constituents for the specimen in experimental work [17] were used in the classical micromechanical theories to obtain Young's modulus results at different fibre content, which are shown in Figure 2.

It can be noticed that the Young's modulus of nanocomposite increased slightly with increasing fibre content for all micromechanics theories. Also, in comparison between the experimental results with the theoretical models, the Lavengood three-dimensional theory gives the best fit. In addition, Pan model and Krenchel are close to the experimental results, especially at low fibre content. The reason of that belongs to the suitability of Lavengood for low fibre content in composite and Pan considered the effect of efficiency density function for the fibres.

### *4.2 Nanocomposite of multi-walled carbon nanotube/polypropylene*

In this previous experimental study [19], MWCNT/polypropylene nanocomposite specimens were produced at different fibre contents. Also, to produce homogeneous specimen, the packing pressure, mould temperature and melting temperature were controlled.

The properties of the constituents of the composite are shown in Table .

Table 3: Nanocomposite material constituents (CNT/polypropylene) [19].

| Material | Young's modulus, GPa | Poisson's ratio | Diameter, nm | Length, µm |
|---|---|---|---|---|
| MWCNT | 1200 | 0.2 | 20 | 0.5 |
| Polypropylene | 0.6 | 0.42 | n/a | n/a |

The experimental results of the Young's modulus as a function of CNT content for different CNT /polypropylene composites is shown in Figure 3. The same properties of the fibre and the matrix of the specimen in the experimental test were applied to the theories of short fibres in composite.

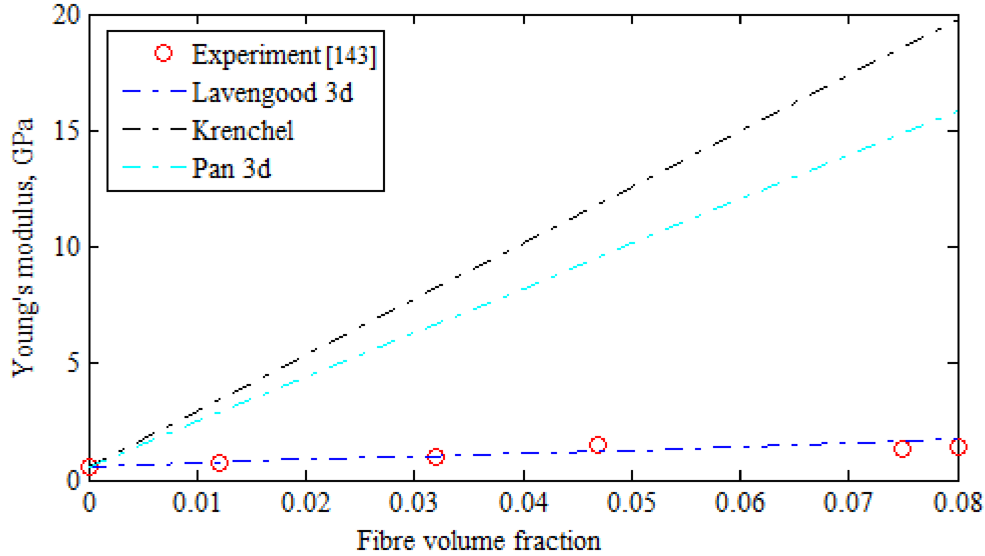


Figure 3: Young’s modulus of CNT /polypropylene with changing nanotube content.

The results show that the experimental Young’s modulus values of the composite fit with the Lavengood theory. The results of both of Pan theory and Krenchel theory are far from the experimental results as the Lavengood model is derived to be suitable for low fibre content.

### *4.3 Nanocomposite of MWCNT/Epoxy*

In this previous study [20], MWCNT and epoxy were mixed by an ultrasonic process to get a good dispersion of the constituents. By this method, a uniform dispersion of the fibres was observed.

The composite mixtures were cured at 170 °C for 4 hours in a convection oven. The prepared specimens were tested in flexure using a 10 kN servo hydraulic machine. The machine worked under displacement control with a crosshead speed of 2 mm/min at room temperature. The properties of the constituents composite are as in Table .

Table 4: Nanocomposite material constituent’s properties (CNT/Epoxy) [20].

| Material | Young’s modulus, GPa | Shear modulus, | Poisson’s ratio | Diameter, nm | Length, μm |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| | | GPa | | | |
| MWCNT | 1000 | n/a | 0.2 | 40 | 3 |
| Epoxy | 2.46 | 1 | 0.25 | n/a | n/a |

Comparison between the micromechanical theories and experimental results are shown in Figure 4.

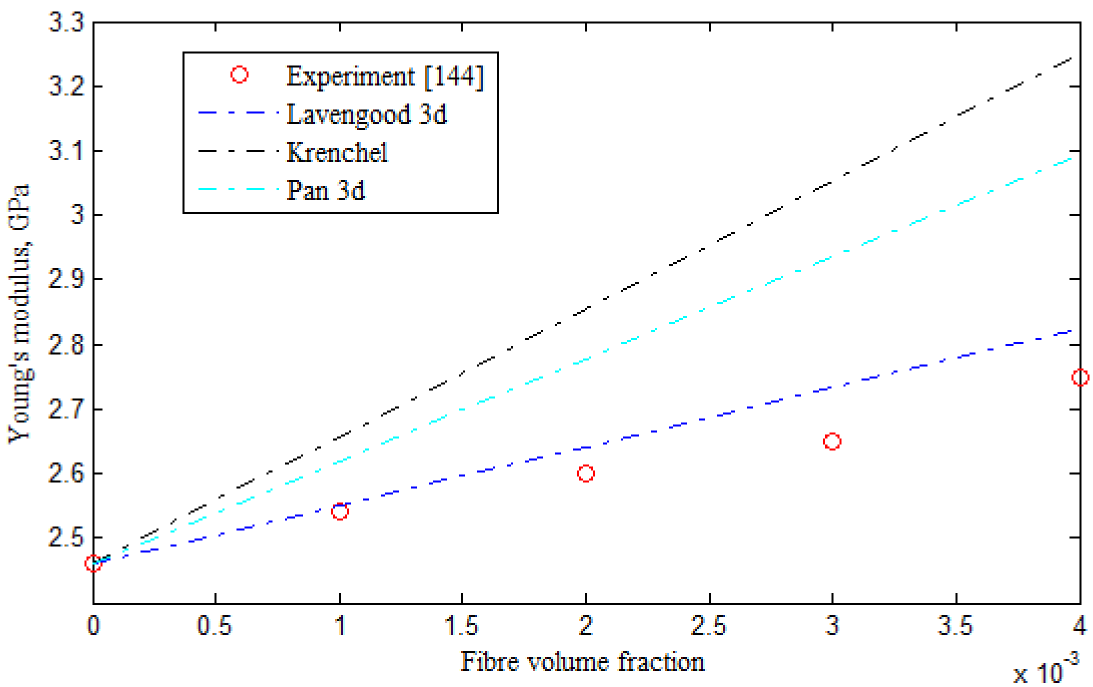


Figure 4: Young's modulus of MWCNT/Epoxy with increasing volume fraction of nanotubes.

It can be seen that the Lavengood model fits the experimental results best, especially at low fibre content. There are some difference between experiment results with both Pan and Krenchel and this difference increases with rising fibre content proportionally.

These results indicate that both Krenchel and Pan model are not suitable for nanocomposites. However, the Lavengood theory gives best fit for nanocomposite materials, as it was derived to be suitable for composite with low volume fraction.

## 5 Sensitivity of micromechanical theories

From the micromechanical theories, it can be observed that the theories are dependent on different properties of composite material contents such as modulus or fibre aspect ratio.

To find the influence of fibre aspect ratio on modulus, the micromechanical theories for random fibre composite materials were compared at different fibre aspect ratio (for the composite defined in Table 1. Results are shown in Figure 5.

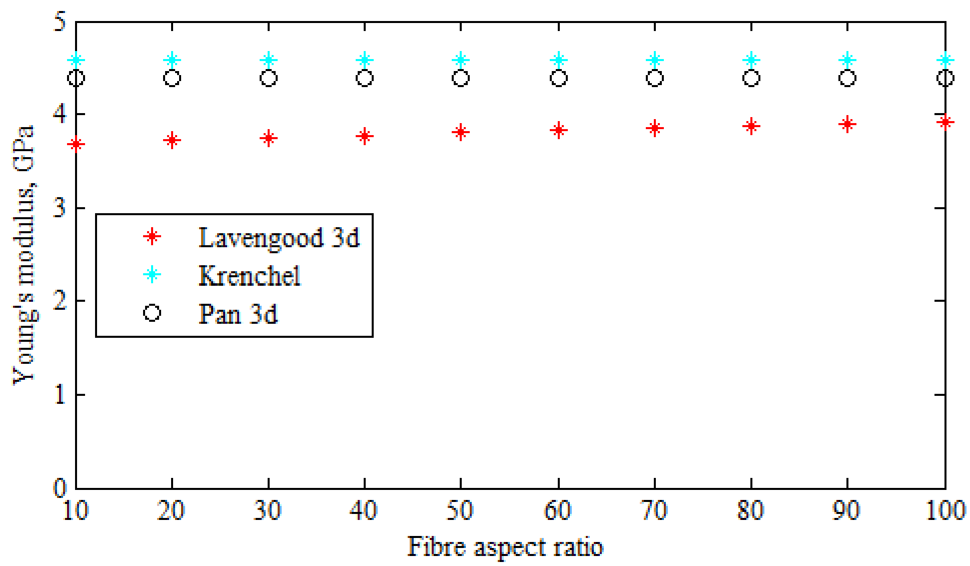


Figure 5: Effect of fibre aspect ratio on modulus of CNT-PEEK nanocomposite contain 0.5% $v_f$ of CNT.

It can be seen that fibre aspect ratio has influence on Lavengood theory only. However, it does not have effect on either Pan or Krenchel theories as they depend on the composite material constituents moduli and fibre content only. This is because the Lavengood model was derived from Halpin-Tsai that is fibre geometry dependent. However, Krenchel and Pan model were derived from rule-of-mixture and they neglect the effect of fibre geometry.

The Young’s modulus for composite material was found at different fibre modulus to clarify micromechanical theories sensitivity with fibre modulus. The results are shown in Figure 6.

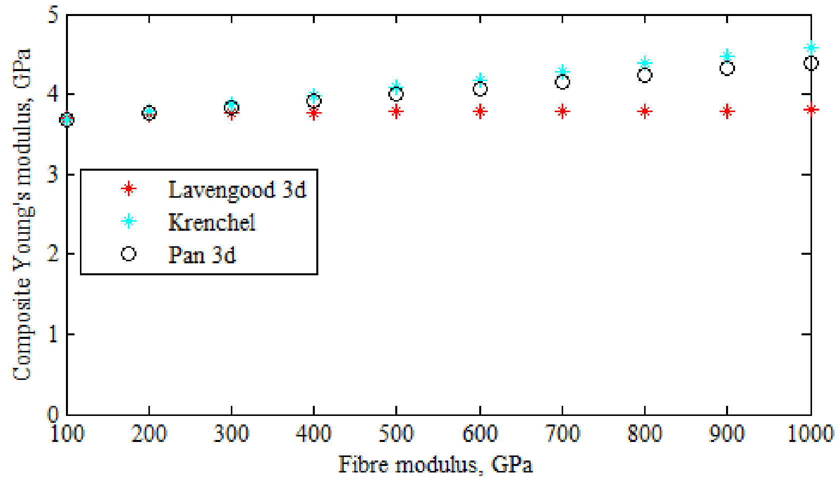


Figure 6: Effect of fibre modulus on modulus of CNT-PEEK nanocomposite contain 0.5%
$v_f$ of CNT.

It can be observed that all the theories are affected by fibre modulus change differently. So, the fibre modulus has higher effect on both Pan and Krenchel. However, it’s effect on Lavengood theory is only slight.

## 6 Conclusion

From the comparison between three experimenta; theories with exists micromechanical theories, it was concluded that Lavengood theory is giving best fit to the experimental results.

It was found also micromechanical theories are sensitive to properties, such as fibre aspect ratio and fibre modulus. Lavengood model shows slight sensitivity to fibre aspect ratio but Krenchel and Pan model do not. Also, it was noticed that all mechanical theories were affected by changes in fibre modulus differently. Krenchel was affected more than others and Lavengood recorded less sensitivity.

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