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**Numerical Prediction of Young's Modulus of MWCNTs/MnO<sub>2</sub> Nanocomposite**

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**ABSTRACT**

*This paper presents numerical analysis of Young's modulus of MWCNTs/MnO<sub>2</sub> nanocomposite. The solution method has been used to fabricate of 5, 10 and 15 wt% of MWCNTs/MnO<sub>2</sub> nanocomposite powder. The Young's modulus of MWCNTs/MnO<sub>2</sub> nanocomposites was determined using analytical models include Voigt and Reuss bounds, Hashin and Shtrikman bounds, Halpin-Tsai model, Hui-Shia model. Voigt upper bound, Halpin-Tsai and Hui-Shia models predict nearly same Young's modulus of MWCNTs/MnO<sub>2</sub> nanocomposite in longitudinal direction. The various models also indicate that incorporating MWCNTs in MnO<sub>2</sub> matrix can potentially improve mechanical properties composites significantly. Halpin and Tsai proposed the equations for discontinuous short CNTs, randomly oriented in a matrix; the effective Young's modulus of the nanocomposite also increases with wt% of MWCNTs.*

**Keywords:** *Multi-Walled Carbon Nanotubes (MWCNTs); Manganese Di-Oxide (MnO<sub>2</sub>); Voigt and Reuss Model; Hashin and Shtrikman Bounds; Halpin-Tsai; Hui-Shia Model etc.*

**1.0 Introduction**

The discovery of carbon nano-tubes by Sumio Iijima in 1991 [1], it has high aspect ratio, large surface area, low density, excellent mechanical, electrical, thermal and tribological properties have attracted researchers used as a filler material nano-composite material. Composite materials with at least one of their constituent being less than 100 nm are commonly known as nano-composites. The experimental based research can ideally be used to determine the elastic properties of nano-composites, with the help of advanced fabrication process and testing equipment. Computational approach can play a vital role in the development of CNT based nano-composites and requires proper selection of mathematical models for the materials under investigation.

Manganese dioxide is used because of its low cost, eco friendly [2] and its electronic structure can exhibit metallic, semiconductor, or insulator behaviour. Most of the literature related to electrical properties of CNT/MnO<sub>2</sub> nano-composite, continuous

study of the mechanical properties of the nano composite could lead to useful multifunctional materials with simultaneous mechanical and electrochemical properties. So in near future manganese dioxide can be widely use as an engineering material. Hurang Hu et al. presented a critical review of recent experimental work, theory of micro nano-mechanics, and numerical analysis on mechanical properties of nano-composites material [3]. Amir Mostafa et al. [4] fabricated thermoplastic polyolefin elastomeric nano composites and investigated the effect of different pin geometries on clay dispersion. They applied three micromechanical models Halpin-Tsai, inverse rule of mixture and linear rule of mixture to investigate the Young's modulus of nano composites. They found that there was a significant difference between the Young's modulus obtained from these models and that obtained from experimental value. Hong Gun Kim et al. derived a closed form solution of the shear lag theory and predicted elastic modulus of short fiber reinforced discontinuous composite materials [5] and derive an analytical model for the stress transfer in

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acomposite. The predictions of the theoretical model to predict the composite Young's modulus are fairly consistent with the experimental result of SiC-Al metal matrix composite. In this study, a numerical prediction of Young's modulus of MWCNTs/ MnO<sub>2</sub> nanocomposites is done.

**2.0 Mathematical Modelling**

**2.1 Mathematical modelling of nanocomposites**

Many models can be applied to describe the effect of carbon nanotubes on composite materials. Common models are Voigt and Reuss bounds, Hashin and Shtrikman bounds, Halpin-Tsai model, Hui-Shia models.

**2.2 Numerical analysis of young's modulus of MWCNTs/ MnO<sub>2</sub> nano composite**

**2.2.1 Voigt upper bound and Reuss lower bound**

Voigt assumed that the reinforcement material and matrix are subjected to equal uniform strain in the fiber direction and predicted Young's modulus in the fiber direction called rule of mixture upper bound Equation and also known as the parallel coupling formula as shown (1) [7]

$$E_L = \phi_{MWCNTs} \times E_{MWCNTs} + (1-\phi) \times E_{MnO_2} \quad (1)$$

Where E is the Young's modulus and  $\phi$  is the volume fraction of reinforcement material

Reuss applied the same uniform stress in the transverse direction, and predicted the modulus in the transverse direction called inverse rule of mixtures, also known as series coupling formula as shown (2) [8]:

$$E_T = \frac{1}{\left(\frac{\phi_{MWCNT}}{E_{MWCNT}} + \frac{\phi_{MnO_2}}{E_{MnO_2}}\right)} \quad (2)$$

**2.2.2 Hashin and shtrikman upper and lower bounds**

Hashin and Shtrikman [9] assumed that the material is macroscopically isotropy and homogeneous, and predicted the elastic constant of the composite are as given below

The upper bound Bulk modulus as shown (3)

$$k_{upper} = k_f + (1-\phi) \frac{1}{\left[\frac{1}{k_m - k_f} + \frac{3\phi}{3k_f + 4G_f}\right]} \quad (3)$$

The lower bound bulk modulus as shown (4)

$$k_{lower} = k_m + \phi \frac{1}{\left[\frac{1}{k_f - k_m} + \frac{3(1-\phi)}{3k_m + 4G_m}\right]} \quad (4)$$

The upper bound shear modulus as shown (5)

$$G_{upper} = G_f + (1-\phi) \frac{1}{\left[\frac{1}{G_m - G_f} + \frac{6\phi(k_f + 2G_f)}{5G_f(3k_f + 4G_f)}\right]} \quad (5)$$

The lower bound shear modulus as shown (6)

$$G_{lower} = G_m + \phi \times \frac{1}{\left[\frac{1}{G_f - G_m} + \frac{6(1-\phi)(k_m + 2G_m)}{5G_m(3k_m + 4G_m)}\right]} \quad (6)$$

The lower bound Young's modulus as shown (7)

$$E_{lower} = \frac{9K_{lower}G_{lower}}{3K_{lower} + G_{lower}} \quad (7)$$

The upper bound Young's modulus as shown (8)

$$E_{upper} = \frac{9K_{upper}G_{upper}}{3K_{upper} + G_{upper}} \quad (8)$$

**2.2.3 Halpin-tsai model**

Halpin and Tsai [10, 11] developed the equations for aligned fiber-reinforced composite materials and predicted the elastic modulus based Hermans and Hill equation [10].

According to Halpin-Tsai model, the longitudinal and transverse modulus is shown by (9) and (10):

$$E_L = \frac{1 + 2\left(\frac{l}{d}\right)\phi\eta_L}{1 - \phi\eta_L} E_m \quad (9)$$

$$E_T = \frac{1 + 2\phi\eta_T}{1 - \phi\eta_T} E_m \quad (10)$$

Where

$$\eta_L = \frac{E_f - E_m}{E_f + 2\left(\frac{l}{d}\right)E_m}, \quad \eta_T = \frac{E_f - E_m}{E_f + 2E_m}$$

When the reinforcing materials are discontinuous short CNTs, randomly oriented in a matrix, Halpin and Tsai proposed the equations to estimate the effective Young's modulus as [12]

$$E_{em} = \frac{3}{8} E_L + \frac{5}{8} E_T$$

**2.2.4 Hui-shia model**

Hui and Shia and Shia et al. [13] derived formulas for predicting the overall modulus of composites with aligned reinforcements with fiber and flake like reinforcements. They found that the theoretical predictions agreed with experimental results. The Hui-Shia model presents the Young's modulus as shown by equation (11) and (12)

$$E_L = E_m \left[ \frac{1-\phi}{1-\frac{\phi}{\xi}} \right] \quad (11)$$

$$E_T = E_m \left[ \frac{1}{1 - \frac{\phi}{4} \left( \frac{1}{\xi} + \frac{3}{\xi + \lambda} \right)} \right] \quad (12)$$

Where

$$\xi = \varphi + \frac{E_m}{E_f + E_m} + 3(1 - \varphi) \left[ \frac{(1-g)\alpha^2 - \frac{g}{2}}{\alpha^2 - 1} \right]$$

$$\Lambda = (1 - \varphi) \left[ \frac{3(\alpha^2 + 0.25)g - 2\alpha^2}{\alpha^2 - 1} \right]$$

$$g = \frac{\alpha}{(\alpha^2 - 1)^{3/2}} \left[ \alpha \sqrt{\alpha^2 - 1} - \cosh^{-1} \alpha \right]$$

### 3.0 Materials and Synthesis of Nano-Composite

#### 3.1 Materials

The reinforcing material used was Multiwall Carbon nanotubes and KMnO<sub>4</sub> used as oxidising agent.

#### 3.2 Synthesis of 10 wt% MWCNTs/ MnO<sub>2</sub> nanocomposite

The solution method [15, 16] has been applied to fabricate MWCNTs/MnO<sub>2</sub> nanocomposite powder. In shortly the process is described as--

In a beaker, 0.2 gram multi wall nano-tube immersed in 2M boiling H<sub>2</sub>SO<sub>4</sub> (aq) solution. After 3 hours of dispersion, 4 gram KMnO<sub>4</sub> was added at 85°C.

The solution color changed from purple to brown and precipitates was obtained.

The obtained black yield was washed with de-ionized water and then dried at 65°C in a laboratory oven for 4 hours. The obtained black yield was 2.03 g.

Similar, the experiments were carried out for 5 wt% and 15 wt% MWCNTs/MnO<sub>2</sub> nanocomposites powder.

The yield obtained were 1.96gm, 2.03 gm and 2.14 gm for 5 wt%, 10 wt% and 15 wt% of MWCNTs/ MnO<sub>2</sub> nanocomposites powder respectively as shown in figure 1.

#### 4.0 Chemical Characterization

The chemical structure of the nano-composite was investigated using Mini Flex, with Cu-K $\alpha$  radiation. The XRD pattern of the MWCNTs is as shown in figure 2. Diffraction peaks at 26.550 can be indexed as (002) plane and it is also reflections of graphite [15, 16, and 17].

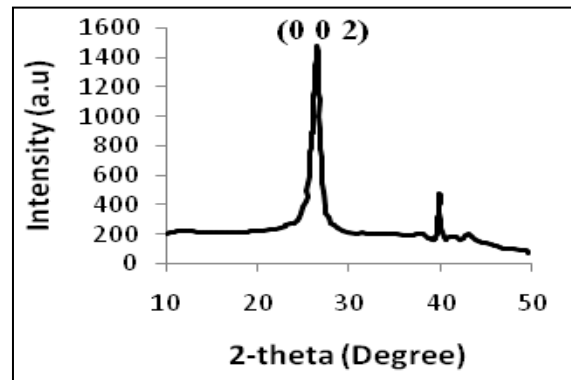
The other diffraction peaks can be indexed to the tetragonal  $\alpha$ -MnO<sub>2</sub>, group: I4/m (87 as shown in fig:3.

It is confirmed that the MWCNTs/MnO<sub>2</sub> nano-composite is formed and MnO<sub>2</sub> as a single crystal structure called  $\alpha$ -MnO<sub>2</sub> [14, 15].

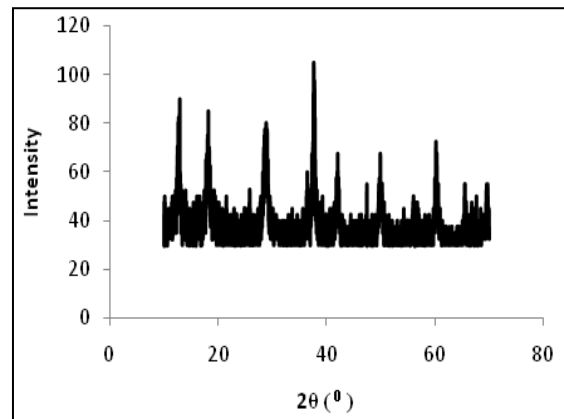
**Fig 1: Yield of Different wt% MWCNTs/MnO<sub>2</sub> Nano-Composite Powder.**



**Fig 2: XRD Pattern of MWCNTs**



**Fig 3: XRD Pattern of 10 wt% MWCNTs/MnO<sub>2</sub>**



**5.0 Result and Discussion**

**5.1 Elastic constants of MWCNTs and MnO<sub>2</sub>**

Table 1 and Table 2 shows the physical and mechanical properties of MWCNTs and MnO<sub>2</sub>

**Table 1: Properties of MWCNTs Synthesized by CVD**

Parameter	Properties
Density g/cm <sup>3</sup>	1.33-1.4[15,17,18]
Young's modulus TPa	0.45[15,17]
Poisson's ratio	0.14

**Table 2: Properties of MnO<sub>2</sub>**

Parameter	MnO <sub>2</sub> [19]
Density(ρ <sub>m</sub> ) [g/cm <sup>3</sup> ]	4.55
Poisson's ratio(μ <sub>m</sub> )	0.28
Bulk Modulus, K [GPa]	34.4

**5.1.1 Theoretical elastic constants of MWCNTs**

Consider the MWCNTs are isotropic.

The Shear modulus of MWCNTs is shown (13)

$$E=2G(1+\mu) \tag{13}$$

$$G \cong 197\text{GPa}$$

Bulk modulus of MWCNTs is shown (14)

$$E=3K(1-2\mu) \tag{14}$$

$$K \cong 208.33\text{GPa}$$

**5.1.2 Theoretical elastic constants of MnO<sub>2</sub>**

Young's modulus of matrix material MnO<sub>2</sub> is given by (E<sub>m</sub>)=3K<sub>m</sub>(1-2μ<sub>m</sub>)=45.40 GPa

Young's modulus of matrix material (E<sub>m</sub>)=2G<sub>m</sub>(1+μ<sub>m</sub>)

$$\text{Shear modulus } (G_m) \cong 17.73 \text{ GPa}$$

**5.2 Numerical determination of young's modulus of MWCNTs/ MnO<sub>2</sub> nano composite**

**5.2.1 Numerical model of 5% MWCNTs/MnO<sub>2</sub> nano composite**

**5.2.1.1 Volume fraction of MWCNTs**

The yield 5 wt% MWCNTs/MnO<sub>2</sub> nano composite was obtained 1.96g by using solution method.

$$\text{Volume of MWCNTs } (V_f) = \frac{m_f}{\rho_f} = \frac{0.1}{1.34} = 0.07462$$

$$\text{Vol. of MnO}_2 (V_m) = \frac{m_m}{\rho_m} = \frac{1.86}{4.55} = 0.4087$$

$$\text{Volume fraction of MWCNTs } (\phi_f) = \frac{V_f}{V_m + V_f} = \frac{0.07462}{0.07462 + 0.4087} = 0.15388$$

**5.2.1.2 Young's Modulus of 5% wt MWCNTs/MnO<sub>2</sub> nanocomposite**

**5.2.1.2.1 Voigt upper bound and Reuss lower bound model**

Longitudinal Young's modulus of 5 wt% MWCNTs/MnO<sub>2</sub> nanocomposite

$$E_{LC} = \phi \text{ MWCNTs} \times E_{\text{MWCNTs}} + (1-\phi) \times E_{\text{MnO}_2} = 107.65\text{GPa}$$

Transverse Young's modulus of 5 wt% MWCNTs/MnO<sub>2</sub> nano-composite

$$E_{TC} = \frac{1}{\left(\frac{\phi_{\text{MWCNT}}}{E_{\text{MWCNT}}} + \frac{\phi_{\text{MnO}_2}}{E_{\text{MnO}_2}}\right)} = 52.70 \text{ GPa}$$

**5.2.1.2.2 Hashin and Shtrikman upper and lower bounds**

$$k_{\text{upper}} = k_f + (1 - \phi) = 208.33 + (1 - 0.15439) \frac{1}{\frac{1}{34.4 - 208.33} + \frac{3 \times 0.15439}{3 \times 208.33 + 4 \times 197.36}} = 52.36 \text{ GPa}$$

$$k_{\text{lower}} = k_m + \phi \frac{1}{\left[\frac{1}{k_f - k_m} + \frac{3(1-\phi)}{3k_m + 4G_m}\right]} = 34.4 + 0.15439 \frac{1}{\frac{1}{208.33 - 34.4} + \frac{3(1-0.15439)}{3 \times 34.4 + 4 \times 17.33}} = 42.0 \text{ GPa}$$

$$G_{\text{upper}} = G_f + (1 - \phi) \frac{1}{\left[\frac{1}{G_m - G_f} + \frac{6\phi(k_f + 2G_f)}{5G_f(3k_f + 4G_f)}\right]}$$

$$= 197.36 + (1 - 0.15439) \frac{1}{\left[\frac{1}{17.73 - 197.36} + \frac{6 \times 0.15439(208.33 + 2 \times 197.36)}{5 \times 197.36(3 \times 208.33 + 4 \times 197.36)}\right]} = 33.696 \text{ GP}$$

$$G_{\text{lower}} = G_m + \phi \times \frac{1}{\left[\frac{1}{G_f - G_m} + \frac{6(1 - \phi)(K_m + 2G_m)}{5G_m(3k_m + 4G_m)}\right]} G_{\text{lower}}$$

$$= 17.73 + 0.15439$$

$$\times \frac{1}{\left[\frac{1}{197.36 - 17.73} + \frac{6(1 - 0.15439)(34.4 + 2 \times 17.73)}{5 \times 17.73(3 \times 34.4 + 4 \times 17.73)}\right]} = 83.23 \text{ GPa}$$

$$E_{\text{lower}} = \frac{9K_{\text{lower}}G_{\text{lower}}}{3K_{\text{lower}} + G_{\text{lower}}}$$

$$E_{\text{lower}} = \frac{9 \times 42 \times 23.14}{3 \times 42 + 23.14} = 58.64 \text{ GPa}$$

$$E_{\text{upper}} = \frac{9K_{\text{upper}}G_{\text{upper}}}{3K_{\text{upper}} + G_{\text{upper}}} = 83.23 \text{ GPa}$$

### 5.2.1.2.3 Halpin-tsai model

$$\eta_L = \frac{E_f - E_m}{E_f + 2\left(\frac{l}{d}\right)E_m} \eta_L$$

$$= \frac{0.45 \times 10^3 - 45.40}{0.45 \times 10^3 + 2 \times 1000 \times 45.40}$$

$$= 4.4339 \times 10^{-3}$$

$$\eta_T = \frac{E_f - E_m}{E_f + 2E_m} \eta_T = \frac{0.45 \times 10^3 - 45.40}{0.45 \times 10^3 + 2 \times 45.40} = 0.74815$$

$$E_L = \frac{1 + 2\left(\frac{l}{d}\right)\eta_L}{1 - \eta_L} E_m =$$

$$\frac{1 + 2 \times 1000 \times 0.15439 \times 4.4339 \times 10^{-3}}{1 - 0.15439 \times 4.4339 \times 10^{-3}} = 107.62 \text{ GPa}$$

$$E_T = \frac{1 + 2\eta_T}{1 - \eta_T} E_m = \frac{1 + 2 \times 0.15439 \times 0.74815}{1 - 0.15439 \times 0.74815} \times 45.40$$

$$= 63.186 \text{ GPa}$$

When the reinforcing materials are discontinuous short CNTs, randomly oriented in a matrix, Halpin and Tsai proposed the equations for discontinuous short CNTs, randomly oriented in a matrix to estimate the effective Young's modulus

$$E_m = \frac{3}{8} E_L + \frac{5}{8} E_T = \frac{3}{8} \times 107.62 + \frac{5}{8} \times 63.186 = 79.848 \text{ GPa}$$

### 5.2.1.2.4 Hui-Shia model

$$\xi = \phi + \frac{E_m}{E_f + E_m} + 3(1 - \phi) \left[ \frac{(1-g)\alpha^2 - \frac{g}{2}}{\alpha^2 - 1} \right]$$

$$\xi = 0.15439 + \frac{45.40}{450 + 45.40} +$$

$$3(1 - 0.15439) \left[ \frac{(1 - 0.9999)1000^2 - \frac{0.9999}{2}}{1000^2 - 1} \right] = 0.26684$$

$$\Lambda = (1 - \phi) \left[ \frac{3(\alpha^2 + 0.25)g - 2\alpha^2}{\alpha^2 - 1} \right] = (1 -$$

$$0.15439) \left[ \frac{3(1000^2 + 0.25)0.9999 - 2 \times 1000^2}{1000^2 - 1} \right] = 0.84535$$

$$g = \frac{\alpha}{(\alpha^2 - 1)^{3/2}} [\alpha \sqrt{\alpha^2 - 1} -$$

$$\cosh^{-1} \alpha] = \frac{1000}{(1000^2 - 1)^{3/2}} [1000 \sqrt{1000^2 - 1} -$$

$$\cosh^{-1} 1000] = 0.9999$$

$$E_L = E_m \left[ \frac{1}{1 - \frac{\phi}{\xi}} \right] = 45.40 \left[ \frac{1}{1 - \frac{0.15439}{0.26684}} \right] = 107.73 \text{ GPa}$$

$$E_T = E_m \left[ \frac{1}{1 - \frac{\phi}{\frac{1}{4}\xi + \xi + \Lambda}} \right] =$$

$$45.40 \left[ \frac{1}{1 - \frac{0.15439}{4 \left( \frac{1}{0.26684} + \frac{3}{0.26684 + 0.84535} \right)}} \right] = 60.44 \text{ GPa}$$

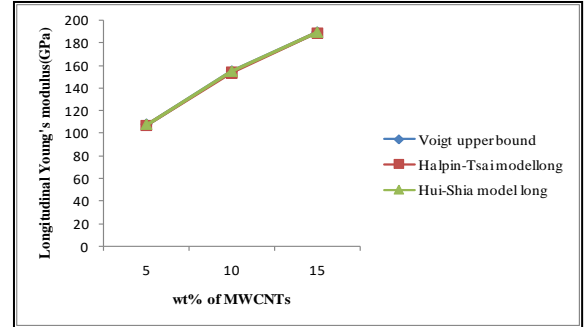
Similarly, the theoretical Young's modulus of 10 and 15 wt% were calculated. Table:3 shows the

theoretical Young's modulus of MWCNTs/MnO<sub>2</sub> nanocomposites calculated using different models.

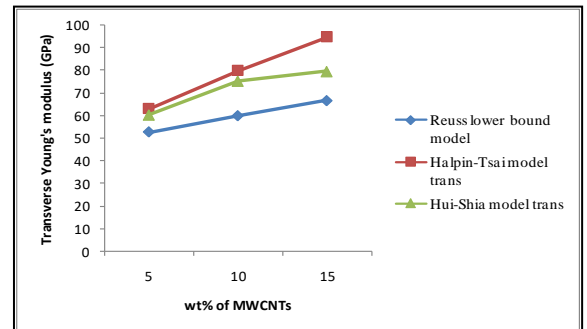
**Table 3: Theoretical Young's Modulus of MWCNTs/ MnO2 Nano-Composites**

Model	5wt% MWCNTs/MnO 2 nanocomposite	10 wt% MWCNTs/MnO2 nanocomposite	15 wt% MWCNTs/MnO2 nanocomposite
Voigt upper bound and Reuss lower bound model	EL=107.65GPa	EL=154.88GPa	EL= 189.55GPa
	ET=52.70 GPa	ET=59.99 GPa	ET=66.79 GPa
Hashin and Shtrikman upper and lower bounds	E <sub>lower</sub> =58.64GPa	E <sub>lower</sub> =71.63GPa	E <sub>lower</sub> =83.03
	E <sub>upper</sub> =83.23 GPa	E <sub>upper</sub> =115.27 GPa	E <sub>upper</sub> =141.35
Halpin-Tsai model	E <sub>L</sub> =107.47	E <sub>L</sub> =154.158	E <sub>L</sub> =189.144
	E <sub>T</sub> =63.186GPa	E <sub>T</sub> =79.97GPa	E <sub>T</sub> =94.90
Halpin-Tsai model (discount. randomly oriented fiber)	E <sub>m</sub> =79.848 GPa	E <sub>m</sub> =107.92	E <sub>m</sub> =130.241
Hui-Shia model	E <sub>L</sub> =107.73	E <sub>L</sub> =154.69	E <sub>L</sub> =189.32
	E <sub>T</sub> =60.44	E <sub>T</sub> =75.469	E <sub>T</sub> =79.699

**Fig 4: Variation of Longitudinal Young's Modulus with wt% of MWCNTS**



**Fig 5: Variation of Transverse Young's Modulus with wt% of MWCNTS**



### 5.3 Variation of young's modulus with wt% of MWCNTs

The Young's modulus in longitudinal direction is nearly same for the models Voigt upper bound Halpin-Tsai and Hui-Shia. But it is slightly different in transverse direction. The variation of Young's modulus in longitudinal and transverse direction is shown in figure 4 and figure 5 respectively. These three models may be conveniently used to determine Young's modulus of MWCNTs/MnO<sub>2</sub> nanocomposite in longitudinal direction.

### 6.0 Conclusions

In the present work, numerical analysis of Young's modulus of MWCNTs/MnO<sub>2</sub> nanocomposite at different weight fraction of MWCNTs varying from 5 to 15% is investigated. It is observed that Voigt upper bound, Halpin-Tsai model and Hui-Shia models gives similar results of Young's modulus in longitudinal direction at different wt% of MWCNTs. This also shows that Voigt upper bound, Halpin-Tsai model or Hui-Shia models can only used to predict theoretical Young's modulus of MWCNTs/MnO<sub>2</sub> nano composite in longitudinal direction and there is a significant difference in transverse direction. The various models also indicate that incorporating MWCNTs in MnO<sub>2</sub> matrix can potentially improve mechanical properties composites significantly.

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