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Numerical Prediction of Young's Modulus of MWCNTs/MnO_2 Nanocomposite

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ABSTRACT

This paper presents numerical analysis of Young's modulus of MWCNTs/MnO_2nanocomposite. The solution method has been usedto fabricate of 5, 10 and 15 wt% of MWCNTs/MnO_2nanocomposite powder. The Young's modulus of MWCNTs/MnO_2nanocomposites 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_2 nanocomposite in longitudinal direction. The various models also indicate that incorporating MWCNTSs in MnO_2 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_2); 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 Ijima 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 than100 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_2 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 andpredicted 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 predictthe composite Young's modulus are fairly consistentwith the experimental result of SiC-Al metal matrix composite. In this study, a numerical prediction of Young's modulus of MWCNTs/ MnO_2 nanocomposites is done.

2.0 Mathematical Modelling

2.1Mathematical modelling of nanocomposites

Many models can be appliedto 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_2 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]

$$EL=\varphi_{MWCNTs}\times E_{MWCNTs}+(1-\varphi)\times E_{MnO2} \quad (1)$$

Where E is the Young's modulus and φ 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]:

$$ET=\frac{1}{\left(\frac{\Phi_{MWCNT}}{E_{MWCNT}}+\frac{\Phi_{MnO2}}{E_{MnO2}}\right)} \quad (2)$$

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)

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

The lower bound bulk modulus as shown (4)

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

The upper bound shear modulus as shown (5)

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

The lower bound shear modulus as shown (6)

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

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 theequations for aligned fiber-reinforced composite materialsand predictedthe elastic modulus based Hermans and Hill equation [10].

According toHalpin-Tsai model, the longitudinal and transverse modulus isshown by (9) and (10):

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

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

Where

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

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)

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

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

Where

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

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

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

3.0 Materials and Synthesis of Nano-Composite

3.1 Materials

The reinforcing material used was Multiwall Carbon nanotubes and$KMnO_4$ used as oxidising agent.

3.2 Synthesis of 10 wt% MWCNTs/ MnO_2 nanocomposite

The solution method [15, 16] has been applied to fabricate MWCNTS/MnO_2 nanocomposite powder. In shortly the process is described as--

In a beaker, 0.2 gram multi wall nano-tube immersed in 2M boiling H_2SO_4 (aq) solution. After 3 hours of dispersion, 4 gram $KMnO_4$ was added at 85^0C.

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 65^0C 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_2nanocomposites 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_2nanocomposites 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-Kα 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 α-MnO_2, group: I4/m (87 as shown in fig:3.

It is confirmed that the MWCNTS/MnO_2 nano-composite is formed and MnO_2 as a single crystal structure called α-MnO_2 [14, 15].

Fig 1: Yield of Different wt% MWCNTS/MnO2 Nano-Composite Powder.

Fig 2: XRD Pattern of MWCNTs

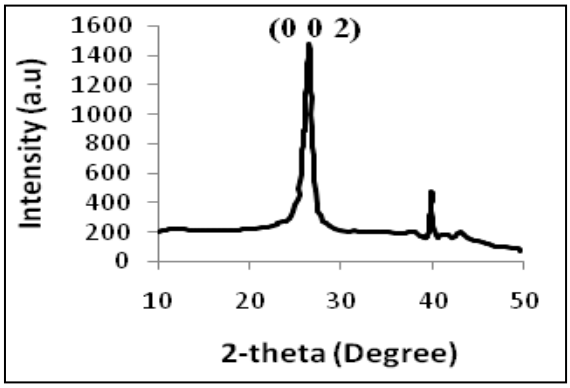
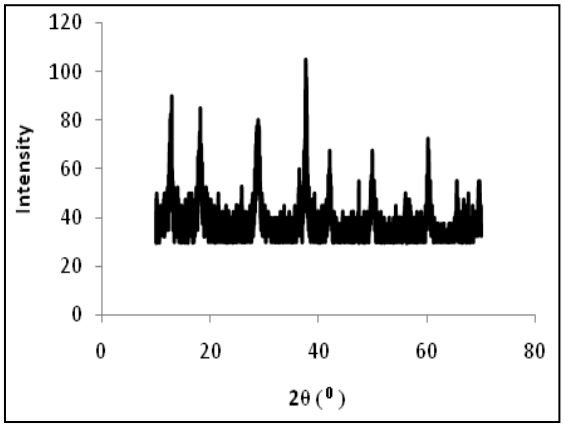


Fig 3: XRD Pattern of 10 wt% MWCNTS/MnO2



5.0 Result and Discussion

5.1 Elastic constants of MWCNTs and MnO_2

Table1 and Table 2 shows the physical and mechanical properties of MWCNTs and MnO_2

Table 1: Properties of MWCNTS Synthesized by CVD

Parameters	Properties
Density g/cm^3	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_2

Parameter	MnO_2[19]
Density(ρm) [g/cm^3]	4.55
Poisson's ratio(μm)	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+μ) (13)

G≅ 197GPa

Bulk modulus of MWCNTs is shown (14)

E=3K(1-2μ) (14)

K≅ 208.33GPa

5.1.2 Theoretical elastic constants of MnO_2

Young's modulus of matrix material MnO_2 is given by (Em)=3Km(1-2μm)=45.40 GPa

Young's modulus of matrix material (E_m)=2Gm(1+μ_m)

Shear modulus (G_m)≅ 17.73 GPa

5.2 Numerical determination of young's modulus of MWCNTs/ MnO_2 nano composite

5.2.1Numerical model of 5% MWCNTs/MnO_2 nano composite

5.2.1.1 Volume fraction of MWCNTs

The yield 5 wt% MWCNTs/MnO_2 nano composite was obtained 1.96g by using solution method.

Volume of MWCNTS (Vf) $=\frac{m_f}{\rho_f}=\frac{0.1}{1.34}=$ 0.07462

Vol. of MnO_2 (Vm)=$\frac{m_m}{\rho_m}=\frac{1.86}{4.55}$ =0.4087

Volume fraction of MWCNTS (φf) = $\frac{V_f}{v_m+v_f}=\frac{0.07462}{0.0762+0.4087}$=0.15388

5.2.1.2 Young's Modulus of 5% wt MWCNTS/MnO2 nanocomposite

5.2.1.2.1 Voigt upper bound and Reuss lower bound model

Longitudinal Young's modulus of 5 wt% MWCNTS/MnO2 nanocomposite

ELC=φ MWCNTS×EMWCNTS + (1-φ) ×EMnO2 =107.65GPa

Transverse Young's modulus of 5 wt% MWCNTS/MnO2 nano-composite

ETC=$\frac{1}{(\frac{\Phi_{MWCNT}}{E_{MWCNT}}+\frac{\Phi_{MnO2}}{E_{MnO2}})}$ =52.70 GPa

5.2.1.2.2 Hashin and Shtrikman upper and lower bounds

$k_{upper}=k_f+(1-\varphi)$=208.33+(1-.15439)$\frac{1}{\frac{1}{34.4-208.33}+\frac{3\times0.15439}{3\times208.33+4\times197.36}}$ =52.36 GPa

$k_{lower}=k_m+\varphi\frac{1}{[\frac{1}{k_f-k_m}+\frac{3(1-\varphi)}{3k_m+4G_m}]}$=34.4+0.15439 $\frac{1}{\frac{1}{208.33-34.4}+\frac{3(1-0.15439)}{3\times34.4+4\times17.33}}$=42.0 GPa

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

$=197.36+(1-0.15439)\frac{1}{[\frac{1}{17.73-197.36}+\frac{6\times0.15439(208.33+2\times197.36)}{5\times197.36(3\times208.33+4\times197.36)}]}$=33.696 GP

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

$$=17.73+0.15439\times\frac{1}{[\frac{1}{197.36-17.73}+\frac{6(1-0.15439)(34.4+2\times17.73)}{5\times17.73(3\times34.4+4\times17.73)}]}$$

=83.23 GPa

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

$$E_{lower} = \frac{9\times42\times23.14}{3\times42+23.14}=58.64GPa$$

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

5.2.1.2.3 Halpin-tsai model

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

$$= \frac{0.45\times10^3 - 45.40}{.45\times10^3 + 2\times1000\times45.40}$$

$$= 4.4339\times10^{-3}$$

$$\eta_T = \frac{E_f - E_m}{E_f + 2E_m}\eta_T = \frac{0.45\times10^3 - 45.40}{0.45\times10^3 + 2\times45.40}=0.74815$$

$$E_L = \frac{1+2(\frac{l}{d})\varphi\eta_L}{1-\varphi\eta_L}E_m = \frac{1+2\times1000\times0.15439\times4.4339\times10^{-3}}{1-0.15439\times4.339\times10^{-3}}=107.62\ GPa$$

$$E_T = \frac{1+2\varphi\eta_T}{1-\varphi\eta_T}E_m = \frac{1+2\times0.15439\times0.74815}{1-0.15439\times0.74815}\times 45.40 = 63.186GPa$$

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

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

5.2.1.2.4 Hui-Shia model

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

$$\xi=0.15439+\frac{45.40}{450+45.40} + 3(1-0.15439)[\frac{(1-0.9999)1000^2-\frac{0.9999}{2}}{1000^2-1}]=0.26684$$

$$\Lambda=(1-\varphi)[\frac{3(\alpha^2+0.25)g-2\alpha^2}{\alpha^2-1}]=(1-0.15439)[\frac{3(1000^2+0.25)0.9999-2\times1000^2}{1000^2-1}]=0.84535$$

$$g=\frac{\alpha}{(\alpha^2-1)^{3/2}}[\alpha\sqrt{\alpha^2-1}-\cosh^{-1}\alpha=\frac{1000}{(1000^2-1)^{3/2}}[1000\sqrt{1000^2-1}-\cosh^{-1}1000=0.9999$$

$$E_L = E_m[\frac{1}{1-\frac{\varphi}{\xi}}] = 45.40[\frac{1}{1-\frac{0.15439}{0.26684}}]=107.73\ GPa$$

$$E_T = E_m[\frac{1}{1-\frac{\varphi}{4}(\frac{1}{\xi}+\frac{3}{\xi+\Lambda})}] = 45.40[\frac{1}{1-\frac{0.15439}{4}(\frac{1}{0.26684}+\frac{3}{0.26684+0.84535})}]=60.44\ GPa$$

Similarly, the theoretical Young's modulus of 10 and 15 wt% were calculated. Table:3 shows the theoretical Young's modulus of MWCNTs/MnO_2nanocomposites calculated using different models.

Table 3: Theoretical Young's Modulus of MWCNTSs/ 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_{lower}=58.64GPa	E_{lower} =71.63GPa	E_{lower}=83.03
	E_{upper}=83.23 GPa	E_{upper}=115.27 GPa	E_{upper}=141.35
Halpin-Tsai model	E_L=107.47	E_L=154.158	E_L=189.144
	E_T=63.186GPa	E_T=79.97GPa	E_T =94.90
Halpin-Tsai model (discount. randomly oriented fiber)	Eem=79.848 GPa	Eem=107.92	Eem=130.241
Hui-Shia model	E_L=107.73	E_L =154.69	E_L =189.32
	E_T=60.44	E_T=75.469	E_T =79.699

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

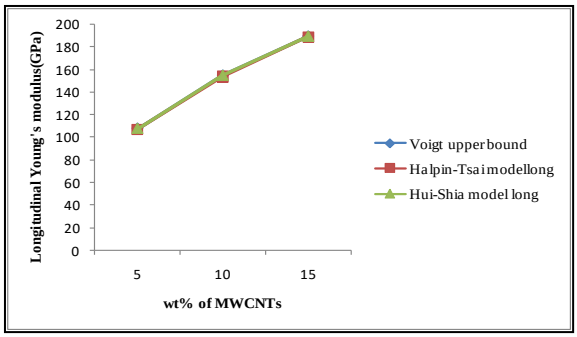
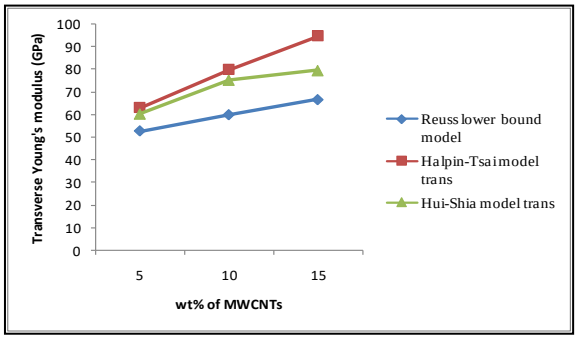


Fig 5: Variation of Transverse Young's Modulus with wt% of MWCNTS



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 MWCNTSs/MnO_2 nanon composite in longitudinal direction.

6.0 Conclusions

In the present work, numerical analysis of Young's modulus of MWCNTs/MnO_2nanocomposite at different weight fraction of MWCNTSs 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 MWCNTSs. 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/ MnO2 nano composite in longitudinal direction and there is a significant difference in transverse direction.The various models also indicate that incorporating MWCNTSs in MnO2 matrix can potentially improve mechanical properties composites significantly.

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