# PREDICTION OF MODULUS AND FRACTURE TOUGHNESS OF THE CARBON NANOTUBES /POLYMER COMPOSITES BY USING MODIFIED HALPIN-TSAI EQUATIONS

Bin Ya[1], Bingwen Zhou[2], Linggang Meng[3] and Xingguo Zhang[4]

[1] Dalian University of Technology, Dalian, yabin@mail.dlut.edu.cn
[2] Dalian University of Technology, Dalian, zbw@dlut.edu.cn
[3] Dalian University of Technology, Dalian, menglg@dlut.edu.cn
[4] Dalian University of Technology, Dalian, zxgwj@dlut.edu.cn

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## ABSTRACT

Modified Halpin-Tsai equations to fit experimental data on the mechanical characteristics, such as modulus and fracture toughness of random orientation nanotubes-polymer composites at high volume fractions of the CNT fillers are discussed. Through extensive literature survey, we postulate a semi-empirical parameter p, related to the degree of CNT aggregation with increasing the volume content. Such analyses have been used to predict the value of modulus and fracture toughness of CNTs/polymer composites. Experimental data and predict value of modulus and fracture toughness of CNTs/polymer composites from literature listed in this paper. Results show that the modified Halpin-Tsai equations can not only predict the modulus but also fracture toughness of CNTs/polymer composites when the matrix is brittle and the differences between the experimental data from different publications and the predicted value are mostly around ±5% and ±10% respectively for modulus and fracture toughness of CNTs/polymer composites.

## 1 INTRODUCTION

The superior mechanical [1-3], thermal [4-7] and electrical [3, 7-10] properties of carbon nanotubes (CNTs), compared with conventional fillers such as carbon black, glass, carbon fiber, and rubber, etc. have attracted a lot of interest in their use as fillers in polymer matrices [11]. Given that the diameter of CNTs is only a few nanometers, and the length may be in the micrometer range, this results in a large aspect ratio and interfacial area [12]. However, there are still two major challenges in obtaining optimal characteristics of CNT-polymer composites, i.e.,: a) poor dispersion of CNTs; and b) weak bonding the CNTs and the matrix.

The elastic modulus and fracture toughness are important parameters tocharacterize the mechanical properties of CNT-polymer composites. A common model used to predict modulus of CNTs/polymer composites was developed by Halpin and Tsai [13, 14]. The work was originally developed for continuous fiber composites and followed the work of Hill [15].

For aligned fiber composites, Hill assumed a composite cylinder model in which the embedded phase consisted of continuous and perfectly aligned cylindrical fibers. Both the materials were assumed to be homogeneous and isotropic about the fiber direction. The composite was treated by assuming each fiber to behave as though it were surrounded by a cylinder of pure matrix. Then the Halpin-Tsai model gives the composite modulus also for the short fibers or carbon nanotubes [16]:

$$E_c = E_m \frac{(1+\xi\eta V_f)}{(1-\eta V_f)} \tag{1}$$

where Ec and Em is the composites and matrix modulus respectively.

$$\xi = 2l/d \tag{2}$$

where $l$ and d is the length and the diameter of the fiber.

$$\eta = \frac{E_f/E_m - 1}{E_f/E_m + 1} \tag{3}$$

where $E_f$ is the fiber modulus.

For randomly orientated composites the corresponding expression is [17]:

$$\frac{E_c}{E_m} = \frac{3}{8}\left[\frac{1+\xi\eta_L V_f}{1-\eta_L V_f}\right] + \frac{5}{8}\left[\frac{1+2\eta_T V_f}{1-\eta_T V_f}\right] \tag{4}$$

where

$$\eta_L = \frac{E_f/E_m - 1}{E_f/E_m + \xi} \tag{5}$$

and

$$\eta_T = \frac{E_f/E_m - 1}{E_f/E_m + 2} \tag{6}$$

The Halpin-Tsai model is known to fit data very well at low CNT filler volume fractions, but the differences between experimental and predicted value are large at high content. Chen et al. [18] studied the modulus of amine functionalized multi-walled CNTs (MWNT-NH2) reinforced nylon 6 composites by using Halpin-Tsai equations but found discrepancies between the theoretically predicted values and the experimental data, especially when the content of the MWNT-NH2 was beyond 0.5 wt%. Díez-Pascual [19] also compared the experimental modulus results of SWCNTs/Poly(ether ether ketone) (PEEK) and Halpin-Tsai model calculated values. When the contents of SWCNTs were low (0.1-0.5 wt %), the elastic modulus differences between experimental data and the predicted value were ~10%, but when the content of SWCNTs increased to ~0.9 wt %, the difference was as large as 65.7%.

In order to obtain better prediction of the modulus of the CNTs/polymer composites at high content of carbon nanotubes, we tried to modify the Halpin-Tsai equations. Taking into account aggregation of carbon nanotubes in polymer composites, Park [20] used for the equation (2):

$$\xi = 2\frac{l_{cnt}}{r_{cnt}} \times \frac{1}{p} \tag{7}$$

where $l_{cnt}$ and $r_{cnt}$ are the CNT length and radius, p is related to the degree of CNT aggregation. The p was introduced to be a semi-empirical parameter, related to the bundle length (b) and diameter (a), and p=b/a. For functionalized SWCNTs with a diameter of 1.5nm and length of 5-20μm, p was found to be 18, and 67 for unfunctionalized SWCNT impregnated polymer composites. In MWCNT/polymer composites, p was approximately equal to 10.

Yeh et al. [21] also modified equation (2) to fit the nonlinear curve of the Young's modulus with CNT volume fractions taking account of the aggregation of carbon nanotubes in the phenolic based composites:

$$\xi = 2\frac{l}{d}e^{-75v_f - 1.0} \quad \text{for network MWNTs} \tag{8}$$

$$\xi = 2\frac{l}{d}e^{-55v_f - 0.5} \quad \text{for dispersed MWNTs} \tag{9}$$

Moreover, the Halpin-Tsai equations have never been used to predict the fracture toughness of CNTs/polymer composites. However, there are still some other models to calculate the fracture toughness [22-24]. One of the important toughening mechanisms is crack bridging [25]. Mirjalili [26] modeled the fracture toughness enhancement using J-integral theory with a critical fiber length lc:

$$\frac{l_c}{r} = \frac{\sigma_u}{\tau} \tag{10}$$

where r is the nanotube radius, $\sigma_u$ is the nanotube ultimate strength (20~40 GPa for MWCNT), and $\tau$ is the interfacial shear stress between the nanotube and the polymer matrix (47MPa [27] or smaller at 20MPa [1, 28] if the interfacial bonding is poor). If the length of carbon nanotube $l \leq l_c$, CNT

pulling-out will occur. CNTs rupturing and pulling-out may both increase the toughness when the length of carbon nanotube l>lc.

In this work, we aim to modify the Halpin-Tsai equations based on Park's work [20] to fit experimental data across the literature, with high content of carbon nanotubes. We also discuss whether the Halpin-Tsai equations can be used to predict the fracture toughness of CNTs/polymer composites.

## 2 PREDICTION OF MODULUS OF CNTS/POLYMER COMPOSITES

The Halpin-Tsai equations may only be applied to predict modulus of CNTs/polymer composites when the CNTs are uniformly dispersed in the matrix. But such dispersion of CNTs has been by far the most significant challenge in the field of CNTs-reinforced composites [29]. Both twisting and aggregation of CNTs can be found in polymer composites [30-32]. Additionally at increasing the volume fraction of CNTs, the dispersion becomes worse [32]. So the parameter p in equation (7) changes with the volume fractions.

We can derive from equations (4), (5), (6) and (7)

$$\xi = \frac{N\frac{E_f}{E_m} - M}{1 - N} = 2\frac{l_{cnt}}{r_{cnt}} \times \frac{1}{p} \tag{11}$$

where

$$\mathrm{M} = \frac{8}{3}\left\{\frac{E_c}{E_m} - \frac{5}{8}\left[\frac{1+2\eta_T v_f}{1-\eta_T v_f}\right]\right\} \tag{12}$$

$$\mathrm{N} = \frac{M-1}{v_f(\frac{E_f}{E_m}-1)} \tag{13}$$

If we know the modulus of the matrix, CNTs and the CNT-polymer composites, and the content of CNT fillers, this may be used to calculate the value of parameter p. However the modulus of the CNTs are quite different from each other due to different synthesis methods and related processing parameters. There are some experimental studies of the elastic modulus of carbon nanotubes, and the results are quite different with each other[15, 33-35]. So we assume that the Young's modulus of the used CNTs (EF) are in the range of 0.7 TPa to 1.8TPa.

We can calculate the value of $p$ by using equations (11), and the volume fractions were calculated by using

$$v_f = \rho_m w_f / (\rho_f - \rho_f w_f + \rho_m w_f) \tag{14}$$

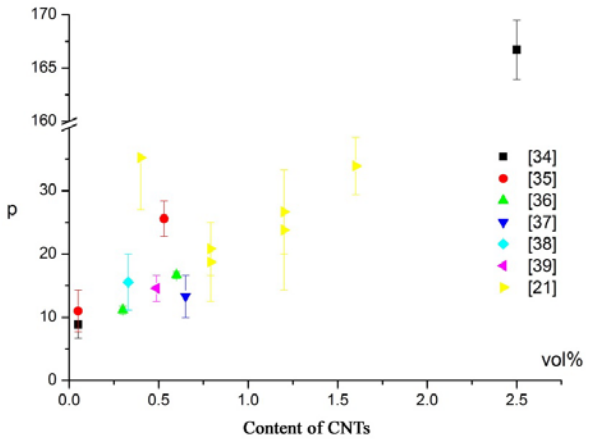


Figure 1: The parameter p changes with volume fractions of CNTs

Figure 1 indicates the relationship between the parameter p and the volume fraction of CNTs. As shown in Figure 1, we can see that with increasing the content of CNTs, the extent of aggregation also

increases. When the volume fraction of CNTs is lower than 0.3%, the value of p is ~10. If 0.3 %< vf <1.5%, p is ~20, but if the content of CNTs is higher than 1.5 vol%, the value of p increases to ~150. So, approximately:

$$p = \begin{cases} 10 & v_f \le 0.3\% \\ 20 & 0.3\% < v_f \le 1.5\% \\ 150 & v_f > 1.5\% \end{cases} \quad (15)$$

Table. 1 lists some experiment data and predicted value that calculated by using modified Halpin-Tsai euqations(4-7) and (15). Most of the differences between the experiment data and predicted value are lower than 5%, especially when the content of CNTs is low. With increasing the volume fraction of CNTs (>1.5 vol %), the differences become discrete. But the value is still lower than 15%. Therefore, the modified Halpin-Tsai equations can be applied to calculate the modulus of the CNTs/polymer composites.

| composites | Volume fraction (vol %) | Aspect ratio of CNTs | $E_c$ Experiment data (GPa) | $E_c$ Predicted value (GPa) | Difference (%) |
|---|---|---|---|---|---|
| DWCNT/Epoxy [42] | 0.025 | 3333 | 2.5 | 2.50±0.03 | 0.09±1.10 |
| MWCNT/ Epoxy [37] | 0.05 | 715 | 3.24 | 3.25±0.02 | 0.19±0.60 |
| MWCNT/ Polypropylene [36] | 0.05 | 800 | 1.67 | 1.67±0.01 | -0.19±0.58 |
| DWCNT/ Epoxy [42] | 0.05 | 3333 | 2.9 | 2.58±0.05 | -10.9±1.88 |
| DWCNT/ Epoxy [43] | 0.05 | 3571 | 3.35 | 3.48±0.05 | 3.95±2.05 |
| MWCNT/ Epoxy [40] | 0.06 | 833 | 3 | 3.02±0.07 | 0.66±0.84 |
| MWCNT Epoxy [42] | 0.15 | 3333 | 3.2 | 2.91±0.16 | -8.87±5.14 |
| MWCNT/ Epoxy [23] | 0.17 | 416 | 1.6 | 1.46±0.01 | -8.61±0.60 |
| MWCNT/ Epoxy [40] | 0.2 | 833 | 3.3 | 3.30±0.08 | -0.02±2.55 |
| MWCNT/ Epoxy [37] | 0.26 | 715 | 3.51 | 3.65±0.11 | 4.02±2.90 |
| MWCNT/ Polypropylene [38] | 0.3 | 400 | 0.87 | 0.88±0.01 | 0.70±0.66 |
| SWCNT/ Phenylene sulphide [39] | 0.32 | 1000 | 2.8 | 2.59±0.05 | -7.52±1.81 |
| MWCNT/ Epoxy [40] | 0.33 | 833 | 3.4 | 3.33±0.05 | -1.98±1.76 |
| MWCNT/ Phenolic [21] | 0.4 | 743 | 5.71 | 5.84±0.13 | 3.48±2.31 |
| MWCNT/ Epoxy [44] | 0.487 | 446 | 1.62 | 1.38±0.01 | -14.86±0.5 |
| MWCNT/Epoxy [37] | 0.53 | 715 | 3.69 | 3.82±0.09 | 3.43±2.38 |
| MWCNT/ Polypropylene [38] | 0.6 | 400 | 0.92 | 0.89±0.01 | -3.46±0.36 |
| SWCNT/ Phenylene sulphide [39] | 0.65 | 1000 | 3.2 | 2.99±0.10 | -6.47±3.24 |
| MWCNT/ Phenolic [21] | 0.79 | 743 | 6.4 | 6.54±0.26 | 2.32±4.05 |
| MWCNT/ Phenolic [21] | 0.79 | 743 | 6.49 | 6.54±0.26 | 0.90±3.99 |
| SWCNT/ Epoxy [45] | 0.89 | 1000 | 3.27 | 4.04±0.19 | 23.44±5.94 |
| MWCNT/ Phenolic [21] | 1.2 | 743 | 7.08 | 7.29±0.40 | 2.97±5.58 |
| SWCNT/ Phenylene sulphide [37] | 1.29 | 1000 | 3.8 | 3.78±0.21 | -0.50±5.46 |
| MWCNT/ Phenolic [21] | 1.6 | 743 | 6.96 | 6.69±0.07 | -3.74±0.97 |
| MWCNT/ Phenolic [21] | 2.4 | 743 | 7.25 | 7.50±0.10 | 3.5±1.42 |
| MWCNT/ Phenolic [21] | 2.4 | 743 | 7.69 | 7.50±0.10 | -2.5±1.34 |
| MWCNT/ Polypropylene [36] | 2.46 | 800 | 1.99 | 2.47±0.01 | 24.1±0.67 |
| MWCNT/ Polypropylene [38] | 2.8 | 400 | 1.05 | 1.00±0.001 | -4.78±0.09 |
| MWCNT/ Phenolic [21] | 3.2 | 743 | 7.53 | 8.32±0.14 | 10.43±1.85 |

Table 1: Experiment data and predicted value of modulus of CNT/polymer composites

## 3 PREDITION OF FRACTURE TOUGHNESS OF CNTS/POLYMER COMPOSITES

Griffith theory states that a crack will propagate when the reduction in potential energy that occurs on crack growth is greater than or equal to the increase in surface energy due to the creation of new surfaces.

$$\sigma = \sqrt{\frac{2E\gamma}{\pi a}} \tag{16}$$

where $\sigma$ is the stress, E is the Young's modulus, $\gamma$ is the surface energy (per unit area), and $a$ is the interior crack length.

Irwin [46, 47] modified the Griffith theory to make it applicable to ductile materials. For a given applied stress, $\sigma$, and pre-existing crack size, a, from equation (16) the net energy release rate, G

$$G = \frac{\pi\sigma^2 a}{E} \tag{17}$$

For Gc, the critical energy release rate, when fracture to occur.

$$G_c = \frac{\pi\sigma_{cr}^2 a}{E} \tag{18}$$

where $\sigma_{cr}$ is critical stress for fracture, and a is the given pre-existing crack size.

So, for CNTs/polymer composites,

$$\frac{G_{c,c}}{G_{c,m}} = \frac{\frac{\pi\sigma_c^2 a}{E_c}}{\frac{\pi\sigma_m^2 a}{E_m}} = \frac{\sigma_c^2}{\sigma_m^2}\frac{E_m}{E_c} \tag{19}$$

where Gc,c, Gc,m are the strain energy release rate of the composites and the matrix respectively. $\sigma_c$, $\sigma_m$ are the fracture stress of the composites and the matrix respectively.

As the relationship between the modulus of the composites is known which has been discussed in the previous section, so we can calculate Gc,c if the relationship of the fracture stress between the matrix and the composites is known.

According to the properties of brittle materials, we can assume that the polymer matrix is brittle and the stress-strain curve of CNTs/polymer composites is linear, and during tensile testing, the strain does not change. In Gojny's study [43], the strain of epoxy matrix and 0.1wt% DWCNT/epoxy composites are almost the same. Similar experimental results have been also published from Hedia et al [48]. Linear tensile strength and strain curve was obtained, and the strain improved only from1% to 1.2% after adding 1wt% MWCNTs. So we assume that $\varepsilon_m = \varepsilon_c$.

$$\text{Consequently, } \frac{E_c}{E_m} = \frac{\frac{\sigma_c}{\varepsilon_c}}{\frac{\sigma_m}{\varepsilon_m}} = \frac{\sigma_c}{\sigma_m} = \frac{3}{8}\left[\frac{1+\xi\eta_L V_f}{1-\eta_L V_f}\right] + \frac{5}{8}\left[\frac{1+2\eta_T V_f}{1-\eta_T V_f}\right] \tag{20}$$

We set c= $\frac{3}{8}\left[\frac{1+\xi\eta_L V_f}{1-\eta_L V_f}\right] + \frac{5}{8}\left[\frac{1+2\eta_T V_f}{1-\eta_T V_f}\right]$, so we can derive from equation (19)

$$\frac{G_{c,c}}{G_{c,m}} = \frac{\sigma_c^2}{\sigma_m^2}\frac{E_m}{E_c} = c^2\frac{1}{c} = c \tag{21}$$

We also know the relationship between critical stress intensity factor (Kc) and, the critical energy release rate (Gc)[49]:

$$Kc = (EGc)^{0.5} \tag{22}$$

So,

$$\frac{K_{Ic,c}}{K_{Ic,m}} = \frac{(E_c\, G_{c,c})^{0.5}}{(E_m\, G_{c,m})^{0.5}} = \left(\frac{E_c}{E_m}\cdot\frac{G_{c,c}}{G_{c,m}}\right)^{0.5} = (c^2)^{0.5} = c \tag{23}$$

According to the equation (23), the modified Halpin-Tsai model can also be used to calculate the fracture toughness of CNT-polymer composites if the polymer matrix is assumed to be brittle, e.g. as

in the case of epoxy polymer matrices. Table. 2 lists some experimental data and predicted value that calculated by using equations (23).

| Composites | Volume fraction (vol %) | Aspect ratio of CNTs | $E_m$ Modulus of matrix (GPa) | $K_{Ic}$ Experiment data (MPa·$m^{0.5}$) | $K_{Ic}$ Predicted value (MPa·$m^{0.5}$) | Difference (%) |
|---|---|---|---|---|---|---|
| MWCNT/Epoxy[42] | 0.025 | 3333 | 2.4 | 0.59 | 0.52±0.01 | -12.34±1.0 |
| MWCNT/Epoxy[40] | 0.033 | 833 | 2.9 | 1.1 | 1.06±0.004 | -3.30±0.45 |
| MWCNT/Epoxy[42] | 0.05 | 3333 | 2.4 | 0.58 | 0.53±0.01 | -7.88±1.96 |
| MWCNT/Epoxy[37] | 0.05 | 715 | 3.15 | 1.86 | 1.67±0.01 | -10.09±0.6 |
| DWCNT/Epoxy[43] | 0.053 | 3571 | 3.29 | 0.75 | 0.64±0.01 | -13.91±1.7 |
| DWCNT/Epoxy[42] | 0.06 | 3571 | 2.4 | 0.55 | 0.54±0.01 | -1.79±2.46 |
| MWCNT/Epoxy[40] | 0.066 | 833 | 2.9 | 1.15 | 1.09±0.01 | -5.45±0.87 |
| DWCNT/Epoxy[42] | 0.12 | 3571 | 2.4 | 0.48 | 0.58±0.03 | 20.90±5.6 |
| MWCNT/Epoxy[42] | 0.15 | 3333 | 2.4 | 0.65 | 0.60±0.03 | -7.22±5.25 |
| MWCNT/Epoxy[23] | 0.17 | 416 | 1.34 | 0.8 | 0.73±0.003 | -8.57±0.60 |
| MWCNT/Epoxy[40] | 0.20 | 833 | 2.9 | 1.2 | 1.18±0.03 | -1.49±2.50 |
| MWCNT/Epoxy[37] | 0.27 | 715 | 3.15 | 2.05 | 1.88±0.05 | -8.17±2.60 |
| MWCNT/Epoxy[40] | 0.33 | 833 | 2.9 | 1.17 | 1.19±0.02 | 2.19±1.84 |
| DWCNT/Epoxy[42] | 0.35 | 3571 | 2.4 | 0.55 | 0.69±0.05 | 25.29±9.4 |
| MWCNT/Epoxy[50] | 0.40 | 875 | 1.97 | 2.8 | 2.53±0.05 | -9.62±1.68 |
| MWCNT/Epoxy[37] | 0.53 | 715 | 3.15 | 1.93 | 1.96±0.04 | 1.73±2.34 |
| MWCNT/Epoxy[50] | 0.68 | 50 | 1.97 | 2.2 | 2.18±0.002 | -0.67±0.03 |
| SWCNT/Epoxy[44] | 0.89 | 1000 | 0.56 | 0.58 | 0.82±0.04 | 41.20±6.80 |

Table 2: Experiment data and predicted value of fracture toughness of CNTs/epoxy composites

We can see that most of differences between the experimental data and the predicted value of fracture toughness are lower than ±10%.

## 4 EXPERIMENTAL

We fabricated MWCNTs reinforced epoxy (EP828) composites. The diameter of MWCNTs is about 8-13nm, and MWCNTs have a length in the range of 3-5μm. Epoxy with different content of MWCNTs (0.1wt-1.0wt%) and ethanol were mixed at 70℃ by using an ultrasonication for 10min (500W, 20 KHz). A pulsed ultrasound mode, 30s on/10s off, was applied. All the mixtures were kept in vacuum oven at 80℃ for 24h to remove excess ethanol. Then, adding the selected curing agent, 2-Ethyl-4-methylimidazole. After another 15min degassing, the mixtures were cast into mechanical testing specimen shape and cured at 80℃ for 1h and 120℃ for 3h. The mechanical properties of MWCNTs/epoxy composites were measured at room temperature using a universal testing machine (CSS-44200). Five specimens of each composition were prepared to obtain an average value. The comparison of experimental value and predicted value which are calculated by different methods is shown in Figure 2 and Figure 3.

As shown in Figure 2, when the content of MWCNTs is low (<0.3 wt%), the experimental value of modulus of MWCNTs/epoxy composites is close to the low limit of predicted value calculated by Halpin-Tsai euqations. But with increasing the content of MWCNTs, the differences become higher. When MWCNTs is 1.0wt%, the differences between experimental value and predicted value is around 45%. But by using modified Halpin-Tsai equations, the differences decrease to about 10%. The modified Halpin-Tsai equations fits the experimental value better according to the analysis above.

Similar results can be found in Figure 3 to compare the fracture toughness.

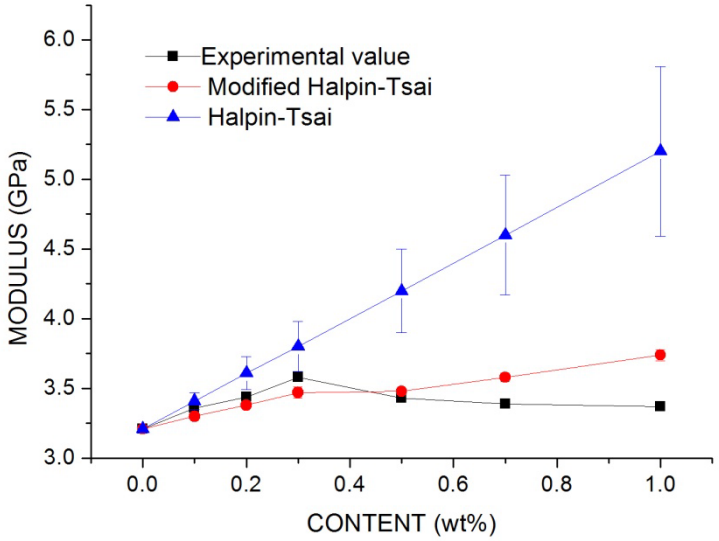


Figure 2: Comparison between experimental data of modulus of MWCNTs/epoxy composites and predictions

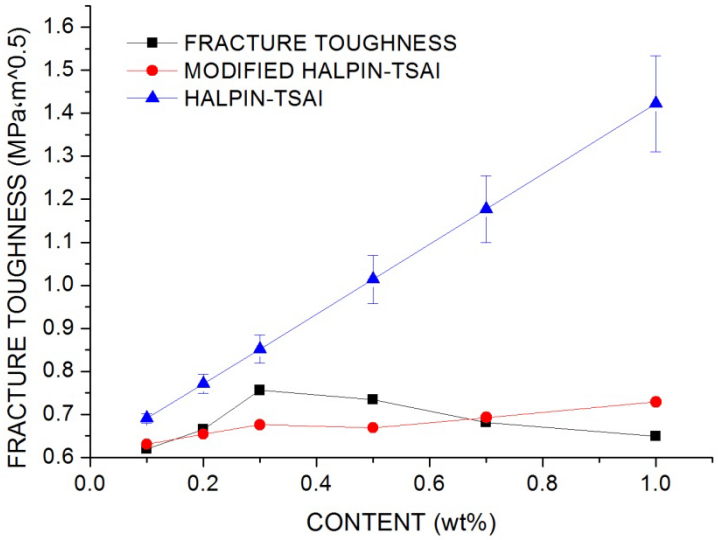


Figure 3: Comparison between experimental data of fracture toughness of MWCNTs/epoxy composites and predictions

## 5 CONCLUSION

We have showed that the modification of classic Halpin-Tsai equations through a semi-empirical parameter p, which is related the degree of CNTs aggregation can be used to predict the elastic modulus and the fracture toughness of CNT-polymer composites. The modified equations fit the experimental composites modulus results very well especially when the content of the CNT is lower than 1.5 vol%. Analysing the properties and the linear stress-strain curve of brittle matrix materials, we can also understand that the modified Halpin-Tsai equations can also be used to calculate the fracture toughness of the composites. The differences between the experimental data and the predicted

value are of the order of/less than mostly around ±15%. The accumulation of data on the density and aspect ratio of the CNTs, would enable further prediction of the fracture toughness at high CNT filler content.

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