FLEXURAL STRENGTH AND FRACTURE TOUGHNESS OF CARBON NANOTUBES (CNTS) REINFORCED EPOXY COMPOSITES

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Abstract- The objective of this study is to optimize the processing parameters of CNTs reinforced epoxy composites using ultrasonication method by measuring flexural strength and fracture toughness. The effect of CNTs amount, sonication intensity, and sonication time on strength and toughness properties of epoxy composites were investigatedusing and the result show that the addition of CNTs in epoxy composites improved the flexural strength and fracture toughness of the composites.

Keywords- Carbon Nanotubes (CNTs); Epoxy Composites; Flexural Strength, Fracture Toughness, Optimization

I. INTRODUCTION

Nowadays, the incorporation of thermosetting polymer composites is becoming a common practice in aircraft manufacturing design. The utilization of this material in aviation industry is due to the remarkable advantages in strength and stiffness properties. However, the widespread use of thermoset polymer is still constrained because of its inherent brittleness and fracture toughness limitation. This circumstance had become an impediment to thermoset polymer to turn out to be dominant materials on aircraft structures. Over the years, many attempts have been made to toughen thermoset polymer by adding either micron-sized soft (elastomeric or thermoplastic) or rigid (glass or ceramic) particles into the epoxy resins. These filler particles have been used to provide extrinsic toughening mechanism within the epoxy matrix.

As the advancement of nanotechnology, carbon nanotubes (CNTs) have attracted a great interest for nano-particle reinforcing candidates to substitute previous reinforcing particles due to its proven superior mechanical, electronic and thermal properties. The advantage of CNTs compared to previous toughening agent is stretched out on the fact that CNTs are composed of very small diameter in nanometer scale with high aspect ratio and thus have extremely large surface area for stress transfer within epoxy matrix. Since then, a number of research works have been conducted to discover the strength characteristic of these nano-polymer composite.

The objective of this paper is to determine the effect of adding CNTs using ultrasonication method to the flexural strength and fracture toughness properties of aviation grade epoxy. Experimental investigations were carried out on the influence of three processing factors: CNTs amount (in term of weight percentage, wt%), sonication intensity (in term of amplitude percentage, %) and sonication time (in term of hour, hr), which are the most relevant parameters to be considered. CNTs amount would indicate how much the CNTs needed to significantly enhance the flexural strength and fracture toughness simultaneously. Sonication intensity and time would identify the appropriate condition and duration for maximum effectiveness without any adverse effect to CNTs or epoxy resin.

II. METHODOLOGY

Aviation grade epoxy named Hysol EA9390 A/B obtained from Henkel Corporation Aerospace Group, USA was used for this experiment. It is a two component adhesive, Part A (resin) and Part B (hardener) with the viscosity of 60-120 Pa.s (Pascal-second @ kg/ms) and 0.06-0.12 Pa.s, respectively. The mix ratio is 100:56 and the pot life of this epoxy resin is 120 minutes. CNTs used for the this experiment was an industrial grade Multi-Walled Carbon Nanotubes (MWCNTs) obtained from Chengdu Organic Chemical Co Ltd (Timesnano), China. These CNTs were produced by natural gas catalytic decomposition over Ni/Al203. It has >90 % purity, outer diameter of 10-30 nm, and length of 10-30nm.

The samples for this experiment were fabricated according to Composite Material Handbook (MIL-HDBK-17-1F). ASTM D790-10 was used as the guideline for flexural tests under three point bending configuration and ASTM D5054, Single Edge Notch

Bending (SENB) was used for fracture toughness test. The sample's figures and dimensions are shown in Fig. 1.

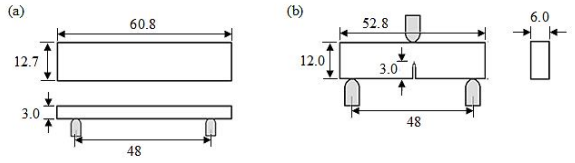


Fig. 1. Specimen figures and dimensions (a) Flexural test sample according to ASTM D790-10; (b) Fracture toughness test sample according to ASTM D5054 (unit in mm).

For the fabrication of control sample (epoxy without CNTs, 0 wt% CNTs), neat resin sample was prepared by mixing the resin and hardener thoroughly according to the mix ratio. The slurry was then stirred using mechanical stirrer for 5 minutes at 150 RPM. Then, it was placed inside a vacuum chamber for 30 minutes to remove entrapped air before transferring it into a mold for further curing process. The samples were allowed to cure at 93^{o}C for 4 hours and cooled at room temperature before being removed from the mold.

For the fabrication of CNTs-epoxy, CNTs were dispersed into Part B hardener via ultrasonication method using Qsonica Q700 machine. For this process, the beaker was submerged in ice to keep the temperature at low level as shown in Fig. 2. After completion the sonication process, Part A resin was added into the mixture. Then, the mixture went through the process of stir, vacuum, mold and cure as a control sample.

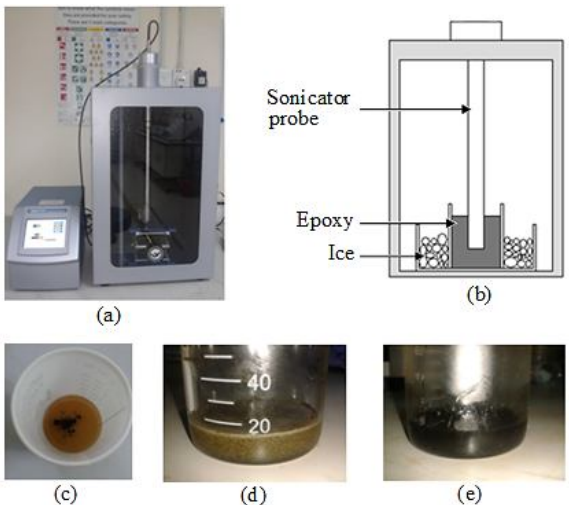


Fig. 2. CNTs reinforced hardener process. (a) Qsonica Q700 machine. (b) Sonication process in ice bath. (c) Hardener with 0.1 wt% CNTs inclusion. (d) CNTs-hardener using hand stir result. (e) CNTs-hardener using ultrasonication result.

For mechanical test, both flexural and fracture tests were conducted on a 50kN INSTRON 5569A servo-hydraulic testing machine at room temperature. The test fixtures are shown in Fig. 3.After the samples tested, the fracture surface of each sample condition was examined through Field Emission Scanning Electron Microscopic (FESEM) using Zeiss Supra 55VP machine.

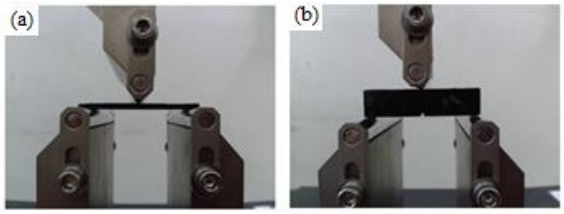


Fig. 3. Test fixtures of (a) flexural strength test, and (b) fracture toughness test.

III. RESULTS AND DISCUSSION

III.I. The effect of CNTs amount

Table 1 and Fig. 4 show the result of flexural strength and fracture toughness test of CNTs fibre reinforced epoxy composites as a function of CNTs amount. The conditions selected are at constant sonication time (1.25 hours) and sonication intensity (45% sonication amplitude). The graph depicts that CNTs amount has a positive correlation with both properties. Flexural strength was increased significantly within 0.2 wt% to 0.6 wt% and less significant when the amount exceed beyond 0.6 wt%. For fracture toughness, the value was increased significantly from 0.1 wt% to 0.6 wt% and then slightly decreased after 0.6 wt%. These results show that the best composition of CNTs amount for this epoxy resin is at 0.6 wt% with an improvement of 77.5% and 25.1% in flexural strength and fracture toughness, respectively.

Table 1.The effect of CNTs amount in epoxy composites

No	CNTs amount (wt%)	Sonication intensity (%)	Sonication time (hr)	Flexural strength (MPa)	Fracture toughness (MPa.m$^{1/2}$)
1	0	0	0	62.67	3.803
2	0.2	45	1.25	65.00	4.533
3	0.6	45	1.25	111.21	4.758
4	1.0	45	1.25	112.70	3.850

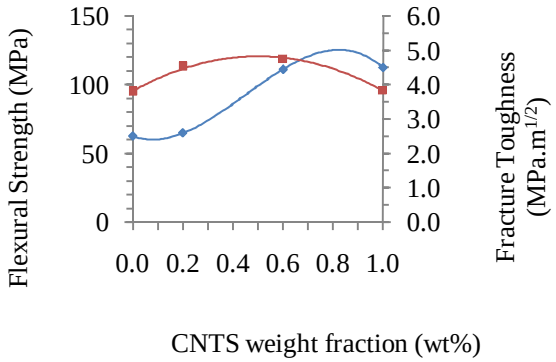


Fig. 4.The effect of CNTs amount in epoxy composites (Fracture toughness = square; Flexural strength = diamond).

Fig. 5 shows the FESEM images of the fracture surface of epoxy with and without CNTs. The cleavage steps, which are characterized by the distance between the 'rivers lines', were used to compare the

fractographic feature of the fracture surface. It was observed that the epoxy composites with CNTs inclusion exhibit rougher fracture surface than neat epoxy. It was clearly shown that the cleavage steps of the epoxy fracture surface were more narrowed as the increased of CNTs content. The decrease of cleavage steps was correspond to the crack branching due to the dispersed CNTs forced the crack path to propagate. As a consequence, the divergence of the cracks by the CNTs causes enhancement of resistance to crack propagation process. This scenario also has been reported in literatures.

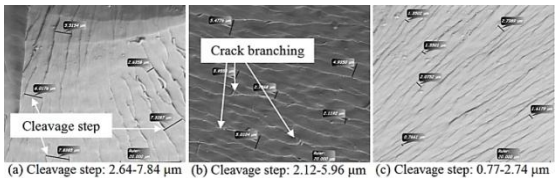


Fig. 5.Fracture surface of (a) neat epoxy, (b)epoxycomposites with 0.2 wt% CNTs, and (c) epoxy composites with 0.6 wt% CNTs, at 1000X magnification.

Fig. 6 is the FESEM image of epoxy with 1.0 wt%. While there is generally uniform distribution of the CNTs in the epoxy composites, a few unwell separated clung of CNTs were observed. This image indicates the presence of CNTs agglomeration in the epoxy composites when reinforced with high CNTs content, and became a location of stress concentration. When the concentrated stress exceeds the materials strength, it triggers cracksfrom accumulated nano-scale cracks and caused the sample to failmore quickly. Therefore, it became the cause of the decrease in the flexural strength and fracture toughness.

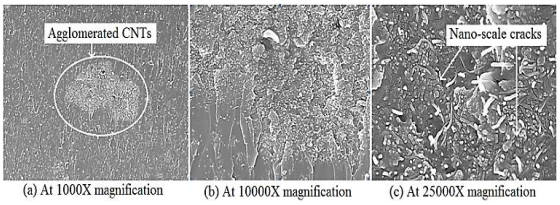


Fig. 6.FESEM images of the epoxy composites with 1.0 wt% CNTs, showing the portion of agglomerated CNTs.

III.II. The effect of sonication intensity

Table 2 and Fig. 7 show the results of epoxy composites with respect to sonication intensity factor at constant CNTs amount (0.6 wt%) and sonication time (1.25 hours). A significant positive linear correlation of sonication amplitude was observed for both properties. The graph shows that the higher amplitude of sonication intensity, the higher improvement in flexural strength and fracture toughness. Sonication at 70% amplitude shows the highest improvement with 113.6% and 37.3% in flexural strength and fracture toughness properties, respectively. At this particular processing condition, the results show that there is no indication of CNTs damage.

Table 2.The effect of sonication intensity in epoxy composites

No	CNTs amount (wt%)	Sonication intensity (%)	Sonication time (hr)	Flexural strength (MPa)	Fracture toughness (MPa.m$^{1/2}$)
1	0	0	0	62.67	3.803
2	0.6	20	1.25	87.84	4.332
3	0.6	45	1.25	111.21	4.758
4	0.6	70	1.25	133.85	5.221

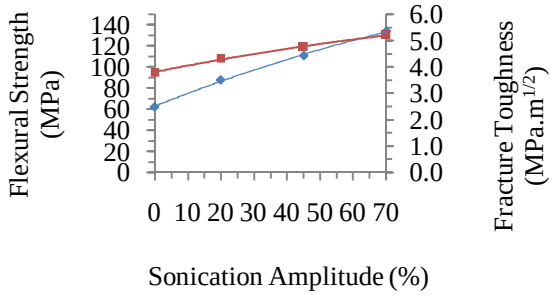


Fig. 7.The effect of sonication intensity in epoxy composites (square = Fracture toughness) (diamond = Flexural strength)

Fig. 8 shows the representative FESEM image for CNTs-epoxy composite samples processed at 45% and 70% sonication amplitudes. Based on the observation, the CNTs pull-out is more apparent in the epoxy composite sample processed at 45% sonication amplitude. Meanwhile, CNTs breakage was found to be the dominant failure mechanism in the epoxy composite sample processed at 70% sonication amplitude. The pull-out CNTs indicate that the interfacial bonding between epoxy and CNTs surface is weak, while CNTs breakage indicate a firm and strong interfacial bonding exists between epoxy and CNTs.

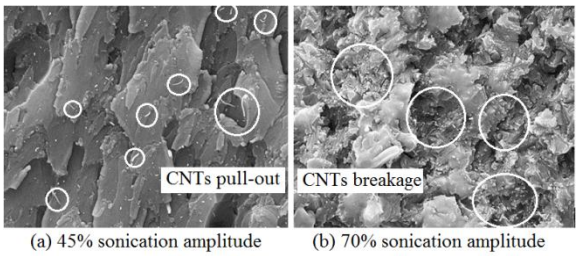


Fig. 8.A comparison of 0.6 wt% CNTs in epoxy composites at different sonication amplitudes, for 1.25 hours of sonication time.

III.IV. The effect of sonication time

For the investigation on the effect of sonication time, two different cases were selected, which are the effect of sonication at low and high CNTs contents. Table 3 and Fig. 9 show the results of epoxy composites at low CNTs content (0.36 wt%). In the case of low CNTs content, alteration in both sonication time and amplitude show insignificant effect to both responses. Only a moderate increment was observed in both properties (16-32.3% improvement in flexural strength and 0.5-8.5% improvement in fracture toughness).

Table 3.The effect of sonication time in epoxy composites at low CNTs content

No	CNTs amount (wt%)	Sonication intensity (%)	Sonication time (hr)	Flexural strength (MPa)	Fracture toughness ($MPa.m^{1/2}$)
1	0	0	0	62.67	3.803
2	0.36	30	0.8	72.67	3.805
3	0.36	30	1.7	75.70	4.068
4	0.36	60	0.8	77.36	4.127
5	0.36	60	1.7	82.92	3.988

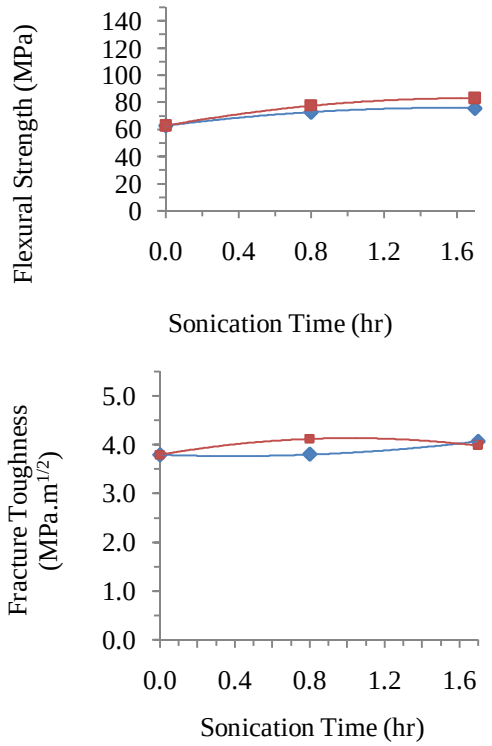


Fig. 9.The effect of sonication time in epoxy composites at low CNTs content.(Top: flexural strength, bottom: fracture toughness (red curve (top-square) = 30% sonication amplitude; blue curve = (bottom-diamond) 60% sonication amplitude)

Table 4 and Fig. 10 show the result of epoxy composites at high CNTs content (0.84 wt%). In this case, sonication time and amplitude showed significant effect to both properties. However, a significant improvement was observed on the flexural strength only, but not to fracture toughness properties. These results are also contrary with previous findings. At high content of CNTs, although the graph shows an improvement in flexural strength as the increase of sonication time, but the lower amplitude of sonication sample has showed a better result than the higher amplitude. Furthermore, fracture toughness test result didnot exhibit an improvement at all, neither at high nor at low amplitude of sonication.

Table 4.The effect of sonication time in epoxy composites at high CNTs content.

No	CNTs amount (wt%)	Sonication intensity (%)	Sonication time (hr)	Flexural strength (MPa)	Fracture toughness ($MPa.m^{1/2}$)
1	0	0	0	62.67	3.803
2	0.84	30	0.8	133.55	3.353
3	0.84	30	1.7	147.48	3.233
4	0.84	60	0.8	98.91	3.176
5	0.84	60	1.7	111.46	3.108

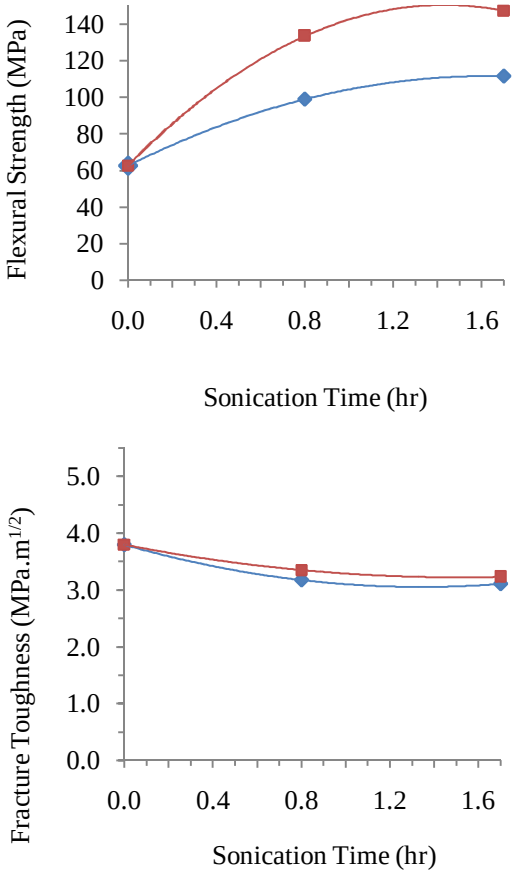


Fig. 10.The effect of sonication time in epoxy composites at high CNTs content..(Top: flexural strength, bottom: fracture toughness (red curve (top-square) = 30% sonication amplitude; blue curve = (bottom-diamond) 60% sonication amplitude)

CONCLUSIONS

From the analysis of the experiment, the fundamental understandings of the processing performance relations are summarized as follows;

(i)CNTs inclusion in the epoxy composites improved the flexural strength and fracture toughness of epoxy composites. But, when the content of CNTs is higher than 0.6 wt%, they tend to agglomerate.

Appropriate processing condition is required to ensure a good state of dispersion within the matrix. If not, it will diminish their potential as a toughening agent for epoxy composites.

(ii) There is a limitation for CNTs and epoxy to be exposed to sonication wave. The high power of the sonication waves should have a time constraint.

Inadequate sonication power and time combination will damage the interface interaction of the CNTs and epoxy surface region.

However, there was no evidence that is observed in this study to prove the mechanism of CNTs damage.

These findings show the need to optimize the sonication process in order to maintain balance between the state of dispersion and the damage imposed on the CNTs because of the sonication waves.

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