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PAPER

A critical evaluation of the enhancement of mechanical properties of epoxy modified using CNTs

Robert W Bedsole[1], **Cheol Park**[2], **Philip B Bogert**[3] **and Hareesh V Tippur**[1]

[1] Department of Mechanical Engineering, Auburn University, AL 36849, USA
[2] Advanced Materials and Processing, NASA-LaRC, Hampton, VA 23681-2199, USA
[3] Structural Mechanics and Concepts, NASA-LaRC, Hampton, VA 23681-2199, USA

E-mail: tippuhv@auburn.edu

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Abstract

Carbon nanotubes (CNTs) have been widely shown in the literature to improve mechanical properties of epoxy, such as tensile strength, elastic modulus, strain to failure, and fracture toughness. These improvements in nanocomposite properties have been attributed to the extraordinary properties of the nanotubes, as well as the quality of their dispersion within and adhesion to the epoxy matrix. However, many authors have also struggled to show significant mechanical improvements using similar methodologies and despite, in some cases, showing qualitative improvements in dispersion with optical microscopy. These authors have frequently resorted to other methods for improving the mechanical properties of CNT/epoxy, such as electrically aligning CNTs, using different types of CNTs, or modifying the stoichiometry. The current work examines many different dispersion techniques, types of CNTs, types of epoxies, curing cycles, and other variables in an attempt to improve the mechanical properties of neat epoxy with CNTs. Despite seeing significant changes in the microscopy, no significant improvements in tensile or fracture properties have been attributed to CNTs in this work.

1. Introduction

Carbon nanotubes (CNTs) have exceptional thermal, electrical, and mechanical properties. CNTs are thermally stable up to 2800 °C (in vacuum or 400 °C in air) and possess twice the thermal conductivity of diamond. They have 1000 times higher electric-current-carrying capacity than copper wire. They have elastic modulus greater than 1000 GPa, at least ten times the strength of steel, and high ductility (because of adiabatic deformation through the sp^2 network), as large nonlinear deformations have been observed before CNT fracture. CNTs therefore have high potential in future multifunctional materials and should theoretically provide great enhancement in composite materials [1].

Epoxies have been used widely (as adhesives and as the matrix material in composites) for their mechanical properties (high stiffness, strength, and hardness), durability (strong chemical and wear resistance), and good adhesion to fillers. However, they are relatively brittle and have poor resistance to crack growth [2, 3]. Therefore many authors have attempted to improve the fracture toughness (K_{IC}) of epoxy by adding CNTs [2, 4–25] (table 1). Their improvements in fracture toughness[4] have been widely attributed to the extraordinary mechanical properties of CNTs [5–14, 16–20, 22–25], the quality of dispersion within the epoxy matrix [2, 4–18, 20, 22–24], and the strength of the bond between CNTs and epoxy [2, 4, 5, 7–10, 12–14, 17, 18, 23]. Many different types of CNTs have been used to achieve these improvements in K_{IC}, including functionalized (FN) and unfunctionalized (UFN) CNTs, single-walled (SWCNT) and multi-walled (MWCNT), and a wide array of weight percentages (0.1–3 wt%). Additionally, many different dispersion techniques have been used to improve K_{IC}, including various types of sonication and high shear techniques, often used in some combination

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[4] Note that crack initiation SIFs are typically reported in the literature as 'fracture toughness'.

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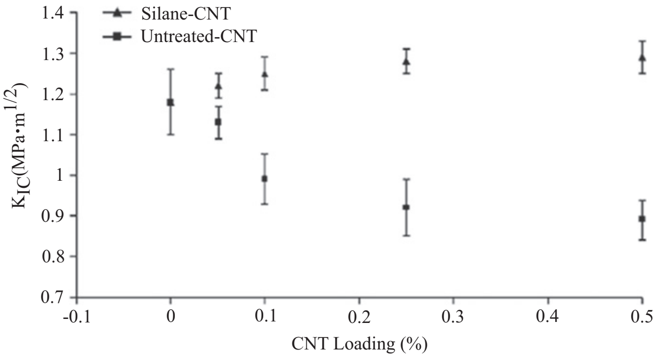

Figure 1. Variations of fracture toughness (K_{IC}) of nanocomposites with different CNT contents. (Reprinted from Ma, Kim and Tang 2007 Effects of silane functionalization on the properties of carbon nanotube/epoxy nanocomposites *Compos. Sci. Technol.* **67** 2965–72, with permission from Elsevier.)

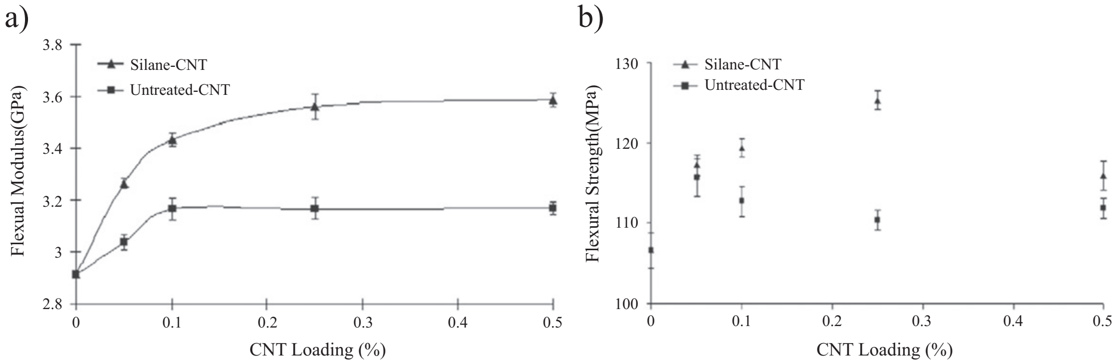

Figure 2. Variations of (a) flexural modulus and (b) flexural strength of nanocomposites with different CNT contents.(Reprinted from Ma, Kim and Tang 2007 Effects of silane functionalization on the properties of carbon nanotube/epoxy nanocomposites *Compos. Sci. Technol.* **67** 2965–72, with permission from Elsevier.)

with each other. Many of these techniques will be explained further in dispersion techniques (section 3), including several different types of sonication and calendering with a masterbatch. Reported improvements in K_{IC} range from 0% to 214%, compared to neat epoxies with an initial untoughened (neat) K_{IC} ranging from 0.35 to 3.7 $\mathrm{MPa}\sqrt{\mathrm{m}}$, with an average of 1.0 $\mathrm{MPa}\sqrt{\mathrm{m}}$ and a median of 0.7 $\mathrm{MPa}\sqrt{\mathrm{m}}$. Nine of the 23 CNT-modified K_{IC} values in table 1 are actually lower than the average initial toughness of neat epoxy in table 1, indicating both the wide range of epoxies available commercially and the wide range of reported outcomes in the literature. In a practical sense, the improvement of 214% from 0.7 $\mathrm{MPa}\sqrt{\mathrm{m}}$ to 2.2 $\mathrm{MPa}\sqrt{\mathrm{m}}$ of Gkikas *et al* [7] by adding 0.5 wt% unfunctionalized MWCNTs using probe tip sonication (PS) is much more significant than the nine reported CNT-modified epoxy K_{IC} values less than 1 $\mathrm{MPa}\sqrt{\mathrm{m}}$.

For the sake of this review, significant improvement is defined as improvement beyond the reported error bars, typically one standard deviation outside the mean value for K_{IC}. With this as the measure, many authors were unable to significantly improve the fracture toughness of neat epoxy with CNTs [14, 15, 19]. Several of the authors who showed improvements in K_{IC} with functionalized CNTs also reported no significant improvement with unfunctionalized CNTs [2, 13], and Ma *et al* [14] even reported a significant decrease in K_{IC} when using unfunctionalized CNTs (figure 1). Ma *et al* [14] did, however, report significant improvements in flexural modulus for both functionalized and unfuctionalized CNTs, a significant improvement in flexural strength with functionalized CNTs, and a significant decrease in flexural strength with unfunctionalized CNTs (figure 2).

Sumfleth *et al* [21] dispersed three different types of unfunctionalized CNTs at three different weight percentages. The CNTs caused decreases in K_{IC} in five of the nine nanocomposites (one of which was a significant decrease), while only one nanocomposite led to a significant improvement in K_{IC} compared to neat epoxy.

Khan *et al* [12] found a modest but significant (~20%) improvement in K_{IC} using randomly oriented CNTs; however, after electrically aligning the CNTs perpendicular to the crack tip, a +51% improvement in K_{IC} was observed (figure 3). Significant improvements in Young's modulus were found both for randomly-oriented and aligned CNTs (figure 4), although the aligned CNTs gave much greater improvements in Young's modulus.

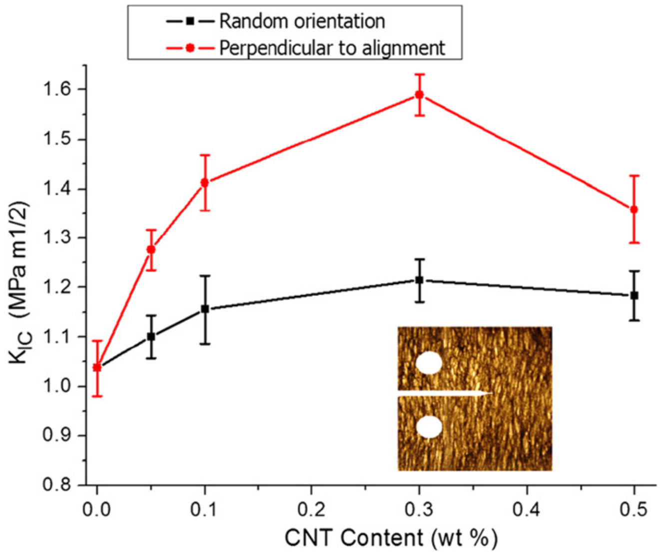

Figure 3. Quasi-static fracture toughness of nancomposites as a function of CNT content. (For interpretation of the references to color in these figure legends, the reader is referred to the web version of this article.) (Reprinted from Khan, Pothnis and Kim 2013 Effects of carbon nanotube alignment on electrical and mechanical properties of epoxy nanocomposites *Composites* A **49** 26–34, with permission from Elsevier.)

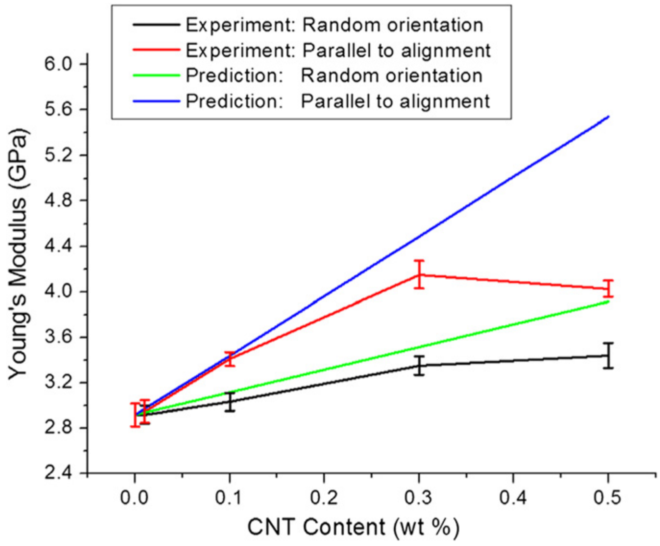

Figure 4. Young's modulus of nanocomposites as a function of CNT content. The predictions are based on the Halpin–Tsai model. (For interpretation of the references to color in these figure legends, the reader is referred to the web version of this article.) (Reprinted from Khan, Pothnis and Kim 2013 Effects of carbon nanotube alignment on electrical and mechanical properties of epoxy nanocomposites *Composites* A **49** 26–34, with permission from Elsevier.)

Mirjalili *et al* [15] used a hot stage with optical microscope to observe changes in dispersion during curing. *They observed significant reagglomeration of the CNTs when curing at high temperatures* (IPD = high temperature hardener) (figures 5(a) and (b)), which led to a reduction in K_{IC} (figure 6(a)). When adding a catalyst (N3), less reagglomeration was observed during curing (figures 5(c) and (d)), and this led to the best improvements in K_{IC} (figure 6(a)), although the significance with respect to the error bars is difficult to assess. When using a room temperature cure (TETA = triethylenetriamine hardener), minimal reagglomeration was observed (figures 5(e) and (f)), yet there was almost no corresponding improvement in K_{IC} (figure 6(a)). When using a combination of IPD and TETA, again minimal reagglomeration occurred (figures 5(g) and (h)), and yet almost no improvement in K_{IC} occurred (figure 6(b)). Mirjalili *et al* [15] quantified the dispersion as:

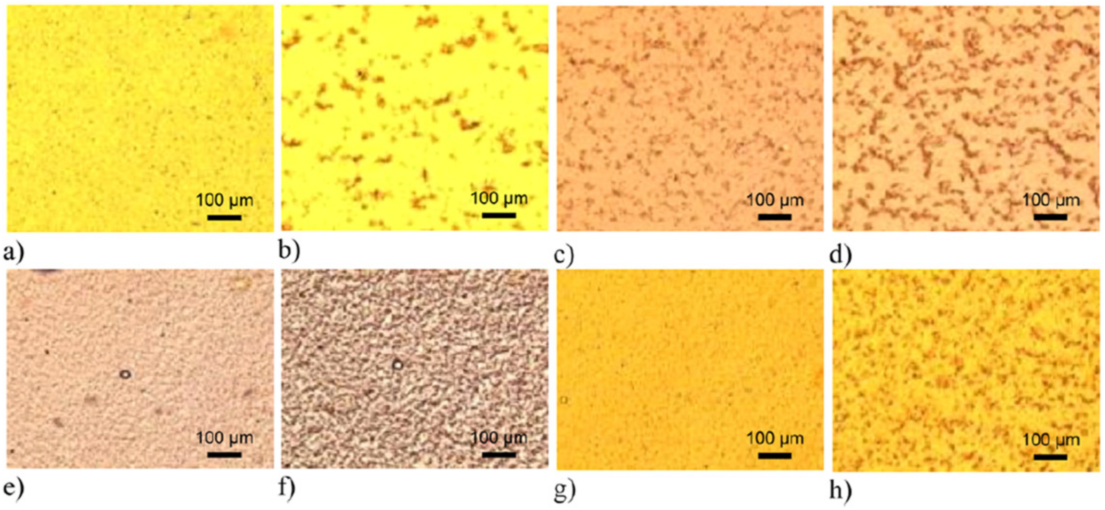

Figure 5. Dispersion quality evolution during the cure for different hardeners. (a) IPD at 25 °C; (b) IPD at 75 °C; (c) IPD/N3 at 25 °C; (d) IPD/N3 at 75 °C; (e) TETA at 25 °C; (f) TETA after 24 h at 25 °C followed by 2 h at 150 °C; (g) IPD/TETA at 25 °C; (h) IPD/TETA after 24 h at 25 °C. (Reprinted from Mirjalili, Yourdkhani and Hubert 2012 Dispersion stability in carbon nanotube modified polymers and its effect on the fracture toughness *Nanotechnology* **23** 1–8, © IOP Publishing. Reproduced by permission of IOP Publishing. All rights reserved.)

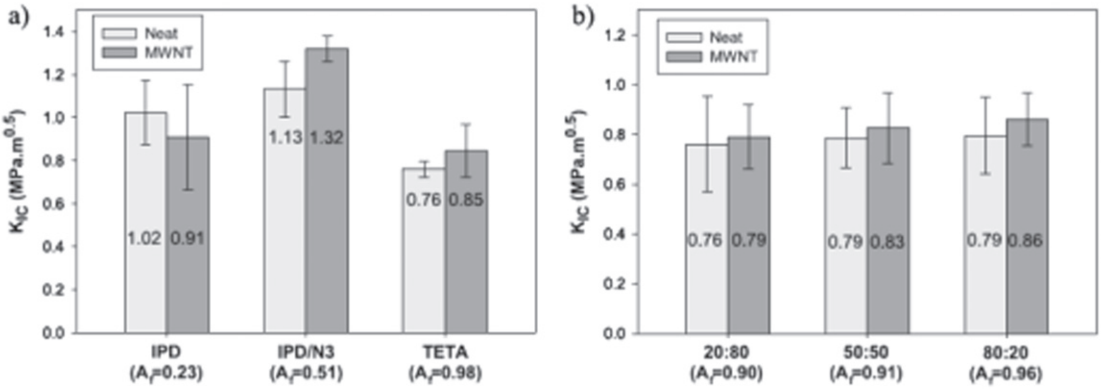

Figure 6. Fracture toughness test results. (a) Bisphenol-A with 0.3 wt% MWNT and different types of hardener; (b) bisphenol-A with 0.3 wt% MWNT with different IPD:TETA ratio. (Reprinted from Mirjalili, Yourdkhani and Hubert 2012 Dispersion stability in carbon nanotube modified polymers and its effect on the fracture toughness *Nanotechnology* **23** 1–8, © IOP Publishing. Reproduced by permission of IOP Publishing. All rights reserved.)

$$A_f = \frac{\text{Area of CNT agglomerates (dark area)}}{\text{Total area}}, \tag{1}$$

where A_f values are the area fraction where CNTs are present (figure 6). If improvement in dispersion (A_f values) corresponds with increasing fracture toughness, it does so only up to a point in this case.

Gupta *et al* [3] also reported qualitative changes in dispersion via optical microscopy (figure 7) and the resulting effect on tensile strength (figure 8). They dispersed 0.5 wt% unfunctionalized MWCNTs into Epon 862 and Epikure W, the same resin system used in the current work, by several different dispersion techniques. The only reported (insignificant) improvement in tensile strength (figure 8) corresponds to figure 7(e).

Ashrafi *et al* [2] synthesized SWCNTs and then functionalized them (r-SWCNT). When 0.2 wt% CNTs were added at the manufacturer recommended stoichiometry of 1:0.8 molar ratio of resin:hardener, K_{IC} increased insignificantly from 1.10 $\text{MPa}\sqrt{\text{m}}$ to 1.33 $\text{MPa}\sqrt{\text{m}}$ (table 2). Then they considered a case where 25% more hardener was added to reach a molar ratio of 1:1. While K_{IC} of neat epoxy did not change, a statistically significant increase in K_{IC} of r-SWCNT was found (1.51 $\text{MPa}\sqrt{\text{m}}$). This composition containing 0.2 wt% r-SWCNT and 1:1 molar ratio of resin:hardener gave them significant increases in ultimate tensile strength, ultimate tensile strain, and tensile toughness, as well as an insignificant increase in elastic modulus, when compared to the manufacturer-recommended neat epoxy (table 3). This material also gave significant increases in ultimate tensile strength, ultimate tensile strain, and tensile toughness, as well as an insignificant decrease in

Table 1. K_{IC} of epoxy toughened with CNTs.

Author	Neat K_{IC} (MPa$\sqrt{m}$)	CNT-modified K_{IC} (MPa$\sqrt{m}$)	CNT type	Dispersion technique
Alishahi *et al* 2013	2.1	2.6 (+24%)	0.5 wt% UFN MWCNT	probe tip sonication
Ashrafi *et al* 2013	1.09	1.51 (+39%)	0.2 wt% FN SWCNT	bath and probe tip sonication
Ayatollahi *et al* 2011	1.62	2.05 (+27%)	0.5 wt% UFN MWCNT	probe tip sonication
Chatterjee *et al* 2012	0.5	0.9 (+80%)	0.5 wt% COOH MWCNT	bath sonication, homogenizer, and calender
Gkikas *et al* 2012	0.7	2.2 (+214%)	0.5 wt% UFN MWCNT	probe tip sonication
Gojny *et al* 2005	0.65	0.93 (+43%)	0.5 wt% NH_2 DWCNT	calender
Hsieh *et al* 2011	0.69	0.98 (+42%)	0.5 wt% UFN MWCNT	probe tip sonication
Hu *et al* 2012	0.6	1.2 (+100%)	2 wt% UFN MWCNT	planetary mixer
Jyotishkumar *et al* 2012	0.35	0.48 (+37%)	0.22 wt% UFN MWCNT	sonication
Khan *et al* 2013	1.0	1.2 (+20%)	0.3 wt% FN MWCNT	sonication and calender
Lachman and Wagner 2010	0.67	1.23 (+84%)	0.34 wt% NH_2 MWCNT	probe tip sonication
Ma *et al* 2007	1.2	1.3 (+8%)	0.5 wt% Silane MWCNT	sonication
Mirjalili *et al* 2012	1.13	1.32 (+17%)	0.3 wt% FN MWCNT	high shear mixer
Miyagawa *et al* 2005	0.55	0.75 (+36%)	0.2 wt% F SWCNT	sonication
Rahman *et al* 2012[a]	1.9	2.7 (+42%)	0.3 wt% NH_2 MWCNT	probe tip and calender
Shtein *et al* 2013	0.9	2 (+122%)	0.1 vol% UFN MWCNT	probe tip sonication
Solodilov *et al* 2012	0.4	0.4 (+0%)	0.3–1.0 wt% UFN MWCNT	probe tip sonication
Srikanth *et al* 2012	0.96	1.28 (+33%)	0.5 wt% NH_2 MWCNT	probe tip and ball mill
Sumfleth *et al* 2010	0.58	0.67 (+16%)	0.5 wt% UFN MWCNT	calender w/ masterbatch
Tang *et al* 2013	0.548	0.698 (+27%)	1 wt% UFN MWCNT	ball mill w/ masterbatch
Thostenson and Chou 2006[a, b]	0.7	1.2 (+71%)	0.25 wt% UFN MWCNT	calender
Yu *et al* 2008	0.45	0.72 (+60%)	3 wt% UFN MWCNT	sonication
Zhou *et al* 2008[a, b, c]	3.6	4.7 (+31%)	0.3 wt% UF MWCNT	probe tip sonication
Average	**1.00**	**1.29 (+51%)**[d]		

[a] Recreated similar methodology during this research.

[b] Used Epon 862/Epikure W.

[c] Converted from MPa$\sqrt{mm}$ to MPa$\sqrt{m}$.

[d] The average % improvement is much higher than the improvement of average neat epoxy versus average CNT-modified epoxy. This is due to the large improvements of a few outliers such as Gkikas *et al* [7] and Shtein *et al* [18].

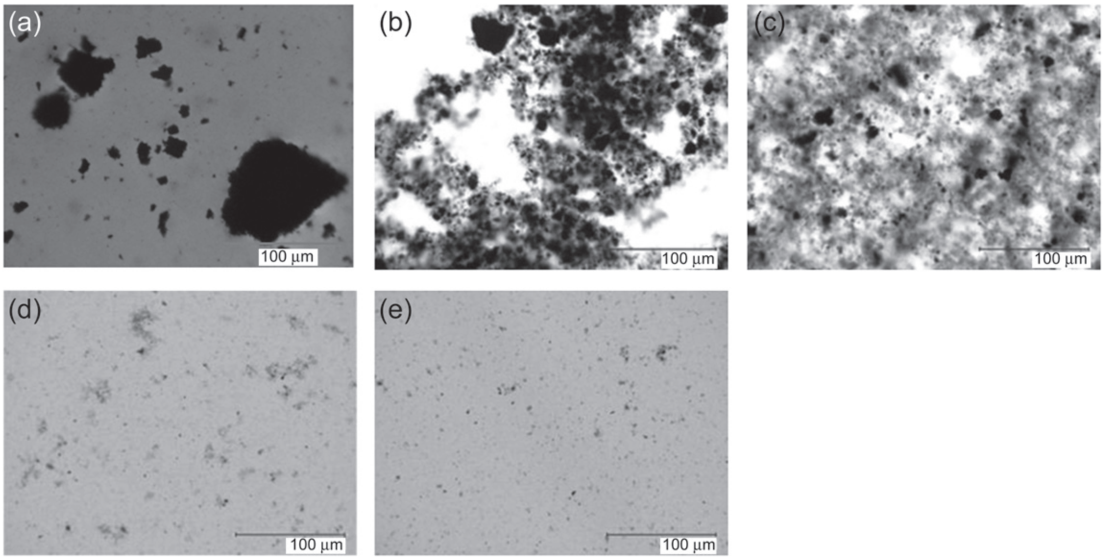

Figure 7. Effect of processing methods on dispersion of pristine MWCNT in epoxy resin (a) US; (b) PSM; (c) US + PSM; (d) MF; and (e) MF + PSM. (US = ultrasound, PSM = planetary shear mixing, MF = microfluidizer). (Reprinted from Gupta *et al* 2013 The effect of mixing methods on the dispersion of carbon nanotubes during the solvent-free processing of multiwalled carbon nanotube/epoxy composites *J. Polym. Sci.* B **51** 410–20, with permission from Wiley.)

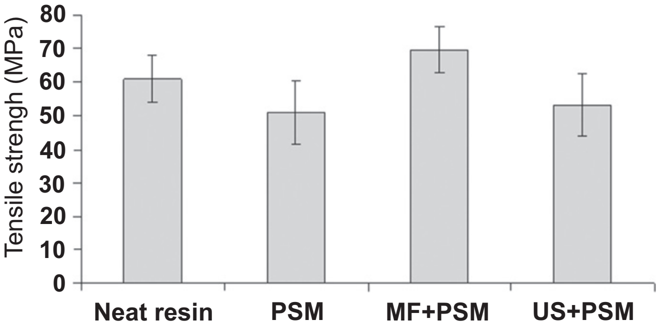

Figure 8. Tensile strength data (MPa) for MWCNTs/epoxy nanocomposites processed by different methods. (Reprinted from Gupta *et al* 2013 The effect of mixing methods on the dispersion of carbon nanotubes during the solvent-free processing of multiwalled carbon nanotube/epoxy composites *J. Polym. Sci.* B **51** 410–420, with permission from Wiley.)

Table 2. Fracture toughness of epoxy resins and their composites. (Reprinted from Ashrafi *et al* 2013 Influence of the reaction stoichiometry on the mechanical and thermal properties of SWCNT-modified epoxy composites *Nanotechnology* **24** 1–9, © IOP Publishing. Reproduced by permission of IOP Publishing. All rights reserved.)

	Sample names	Fracture toughness, K_{IC} (MPa $\sqrt{m}$)	K_{IC} increase/decrease (%)	Reduction in variation of K_{IC} (%)
1:0.8 molar ratio	Epoxy	1.10 ± 0.34		
	0.06 wt% r-SWCNT	1.19 ± 0.24	+8 [0.65][a]	29
	0.2 wt% r-SWCNT	1.33 ± 0.10	+20 [0.19]	70
	0.2 wt% u-SWCNT	0.80 ± 0.18	$\underline{-28}$[b] [0.10]	47
1:1 molar ratio	Epoxy	1.09 ± 0.30		
	0.06 wt% r-SWCNT	1.31 ± 0.28	+20 [0.28]	5
	0.2 wt% r-SWCNT	1.51 ± 0.06	$\underline{+38}$ [0.017]	80
	0.2 wt% u-SWCNT	1.15 ± 0.20	+5 [0.74]	33
1:1.1 molar ratio	Epoxy	1.51 ± 0.44		
	0.06 wt% r-SWCNT	1.42 ± 0.19	−5 [0.72]	56
	0.2 wt% r-SWCNT	1.17 ± 0.13	−23 [0.14]	71
	0.2 wt% u-SWCNT	1.09 ± 0.10	$\underline{-28}$ [0.075]	78

[a] The numbers in brackets giving the results of Student's T-test (p value) for probability of null hypothesis.

[b] The underscored number suggesting a statistically significant difference based on a 10% probability of null hypothesis or less ($p \leqslant 0.1$).

Table 3. Tensile properties of epoxy resins and their composites. (Reprinted from Ashrafi *et al* 2013 Influence of the reaction stoichiometry on the mechanical and thermal properties of SWCNT-modified epoxy composites *Nanotechnology* **24** 1–9, © IOP Publishing. Reproduced by permission of IOP Publishing. All rights reserved.)

Samples	Tensile modulus, E (GPa)	Ultimate tensile strength, UTS (MPa)	Ultimate tensile strain, $\varepsilon_{\max}$ (%)	Tensile toughness, G (MPa)
Epoxy (1:0.8)[a]	4.02 ± 0.16	92.2 ± 8.9	3.21 ± 0.54	1.73 ± 0.49
Epoxy (1:1)	4.32 ± 0.30	87.7 ± 14.2	2.76 ± 0.67	1.34 ± 0.55
Epoxy (1:1.1)	4.27 ± 0.26	48.1 ± 20.9	1.31 ± 0.68	0.41 ± 0.25
0.2 wt% r-SWCNT (1:0.8)	4.08 ± 0.45	81.0 ± 7.7	2.72 ± 0.38	1.28 ± 0.35
Changes	+1.5% [0.79][b]	$\underline{-12\%}$[c] [0.08]	−16% [0.17]	−26% [0.17]
0.2 wt% r-SWCNT (1:1)	4.13 ± 0.07	117.8 ± 2.4	4.15 ± 0.20	2.83 ± 0.18
Changes	−4.4% [0.34]	$\underline{+34\%}$ [0.013]	$\underline{+56\%}$ [0.01]	$\underline{+111\%}$ [0.004]
0.06 wt% r-SWCNT (1:1)	4.31 ± 0.31	110.6 ± 15.0	3.81 ± 0.70	2.49 ± 0.77
Changes	−0.2% [0.96]	$\underline{+26\%}$ [0.039]	$\underline{+43\%}$ [0.029]	$\underline{+85\%}$ [0.027]
0.2 wt% u-SWCNT (1:0.8)	4.4 ± 0.5	71.2 ± 2.5	2.28 ± 0.15	0.94 ± 0.10
Changes	$\underline{+7\%}$ [0.02]	$\underline{-23\%}$ [0.003]	$-\underline{29\%}$ [0.013]	$\underline{-46\%}$ [0.016]
0.2 wt% u-SWCNT (1:1)	4.28 ± 0.13	86.3 ± 4.5	2.59 ± 0.10	1.25 ± 0.13
Changes	−4.4% [0.34]	−1.7% [0.87]	−2.7% [0.86]	−6.8% [0.79]

[a] The numbers in parenthesis are the resin-to-hardener molar ratios.

[b] The numbers in brackets giving the results of Student's T-test (p value) for the probability of null hypothesis.

[c] The underscored number suggesting a statistically significant difference based on a 10% probability of null hypothesis or less ($p < 0.1$).

elastic modulus, when compared to the 1:1 molar ratio neat epoxy. When the molar ratio of *neat* epoxy was increased to 1:1.1, K_{IC} increased to the same value ($1.51\ \mathrm{MPa}\sqrt{\mathrm{m}}$) as 1:1 molar ratio 0.2 wt% r-SWCNT, but with much more scatter. In addition, the ultimate tensile strength and ultimate tensile strain decreased significantly, and the elastic modulus increased insignificantly compared to the manufacturer-recommended molar ratio (1:0.8) of neat epoxy. When unfunctionalized nanotubes (u-SWCNT) were added to epoxies at different stoichiometries, improvements were found in elastic modulus, while improvements were not found in K_{IC}, ultimate tensile stress, ultimate tensile strain, or tensile toughness.

This literature review indicates that adding CNTs to epoxy does not always improve the fracture toughness, even when the dispersion is deemed good. Researchers have found that when straightforward techniques do not lead to significant improvements in K_{IC} of CNT-modified epoxy, these may be achieved by electrically aligning CNTs, using different types of CNTs, or adding additional hardener beyond the manufacturer-recommended stoichiometry.

In this work, many different CNT dispersion techniques are demonstrated for several types of CNTs. The corresponding effects on the quality of dispersion within the epoxy matrix and the mechanical properties of the resulting nanocomposite are detailed.

2. Experimental details

Quasi-static tension and fracture tests were performed for each type of nanocomposite and compared to neat epoxy resin. Specimen geometry is given in figure 9. Both tests were performed on a tensile tester (Instron 4465) in displacement control. Tension tests were performed at 1.27 mm min^{-1} according to ASTM D638 using a 6.25 mm gauge length extensometer to collect strain values. Three-point bend fracture tests were performed on single-edge notched samples at a cross-head speed of 0.6 mm min^{-1} after notches were sharpened using a razor blade. The quasi-static fracture toughness values (K_{IC}) were calculated based on the maximum recorded load using

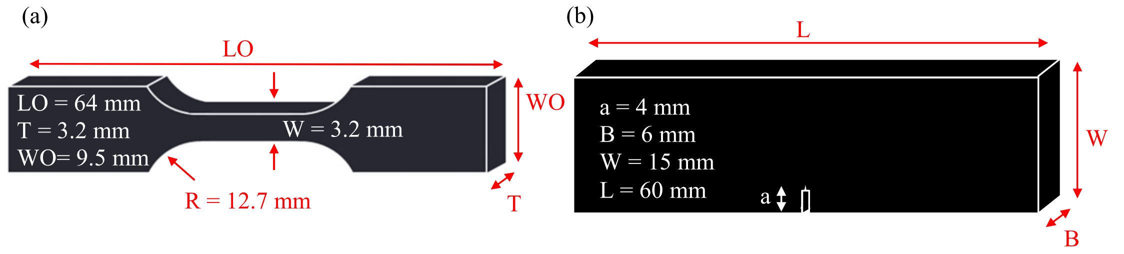

Figure 9. Specimen geometries used for quasi-static (a) tension and (b) fracture

$$K_{\mathrm{IC}} = \frac{\left(\frac{P_{\max}}{B\sqrt{W}}\right)\left(3\frac{S}{W}\sqrt{\frac{a}{W}}\right)}{2\left(1+2\frac{a}{W}\right)\left(1-\frac{a}{W}\right)^{3/2}}\left[1.99-\frac{a}{W}\left(1-\frac{a}{W}\right)\left\{2.15-3.93\left(\frac{a}{W}\right)+2.7\left(\frac{a}{W}\right)^{2}\right\}\right], \tag{2}$$

where $P_{\max}$ is peak load prior to fracture, B is thickness, W is width, S is span (50.4 mm), and a is crack length. Material preparation information is provided in the following section for each nanocomposite considered.

Dynamic mechanical analysis (DMA) was performed using a 5 °C min^{-1} ramp from room temperature to around 240 °C in dual cantilever beam mode with a frequency of 1 Hz and an amplitude of 15 μm (0.04% strain). Specimens were machined to 60 mm × 12 mm × 3 mm, and the span length was 35 mm.

3. Dispersion techniques

3.1. Bath sonication with mechanical stirring

3.1.1. Methods

Initial samples were prepared using Epon 862 resin and Epikure W hardener from Momentive Chemicals, USA. Because functionalization methods cannot yet be controlled, functionalization tends to occur at random defect sites, and functionalization has been shown to weaken the properties of CNTs [26], unfunctionalized MWCNTs (Baytubes C 150P) were initially dispersed into the epoxy matrix. Unfunctionalized CNTs are amphiphobic, so they do not interact well with epoxy resin; however, because of their amphoteric nature, they can accept electrons from the amine groups found in epoxy hardeners in order to achieve some level of compatibilization [26]. In addition to the thermodynamic approach of dispersing the CNTs first in the hardener (donor–acceptor interaction), the kinetic approach of simultaneous mechanical stirring at 400 rpm and 45 kHz bath sonication (dispersion via cavitational force) using an Elma Ultrasonics Transsonic Ti-H-6 bath sonicator at 80 °C for 30 min was employed. After that the stoichiometric amount (100 g resin:26.5 g hardener) of resin was added (manufacturer recommendation was a molar ratio of 1:1 resin:hardener), followed by an additional 30 min of mechanical stirring at 1500 rpm and 45 kHz bath sonication at 80 °C.

With the future goal of creating three-phase CNT/epoxy/carbon fiber nanocomposites in mind, the following cure schedule [27] was used. Samples were poured into a steel mold and degassed using a vacuum for 30 min at 80 °C. Samples were then heated to 80 °C for 30 min, cured at 120 °C for 2.5 h, and post-cured at 180 °C for 3 h. This degassing technique and cure schedule was applied to all Epon 862 and Epikure W samples presented in this work (except when stoichiometry was intentionally varied in section 3.5), although other cure schedules were also tried without successful mechanical enhancement of epoxy.

3.1.2. Results

Two types of neat samples (without CNTs) were produced. The first batch of neat samples was made using only hand-stirring (HS) of the resin and hardener. The stress versus strain response and load versus load-point deflection response measured for these samples are shown as solid red curves in figures 10(a) and 11(a) (the cross represents the breaking point). A second set of neat samples was made with the exact same methodology involving bath sonication and mechanical stirring applied during preparation of CNT-modified epoxy (BS/MS) (dashed red curves in figures 10(a) and 11(a)). The latter set of neat samples provides a strict one-to-one correspondence regarding the sample preparation protocol used for preparing CNT-modified material. The importance of applying the same methodology to the neat and CNT-modified sample preparation is demonstrated in figures 10(b), (c), and 11(b). Evidently, the matched protocol leads to an increase in Young's modulus, ultimate stress, and fracture toughness, respectively, even without the addition of CNTs. (This is a subtle but often overlooked or unreported aspect in many reports.) Therefore, all subsequent neat samples

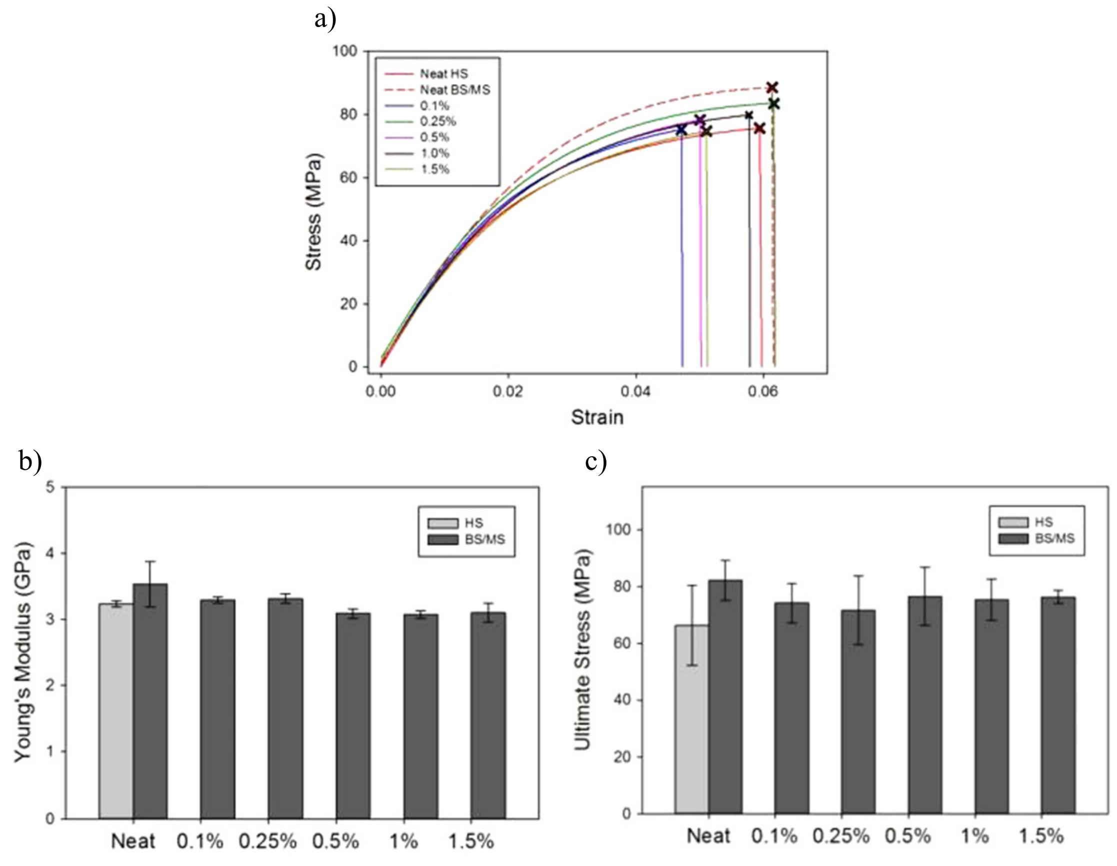

Figure 10. Results from quasi-static tension tests using hand-stirring (HS) or bath sonication with mechanical stirring (BS/MS) for 0–1.5 wt% CNTs. (a) representative stress–strain curves ('x' indicates failure point), (b) average Young's modulus, and (c) average ultimate stress. Error bars here and throughout indicate one standard deviation from the mean.

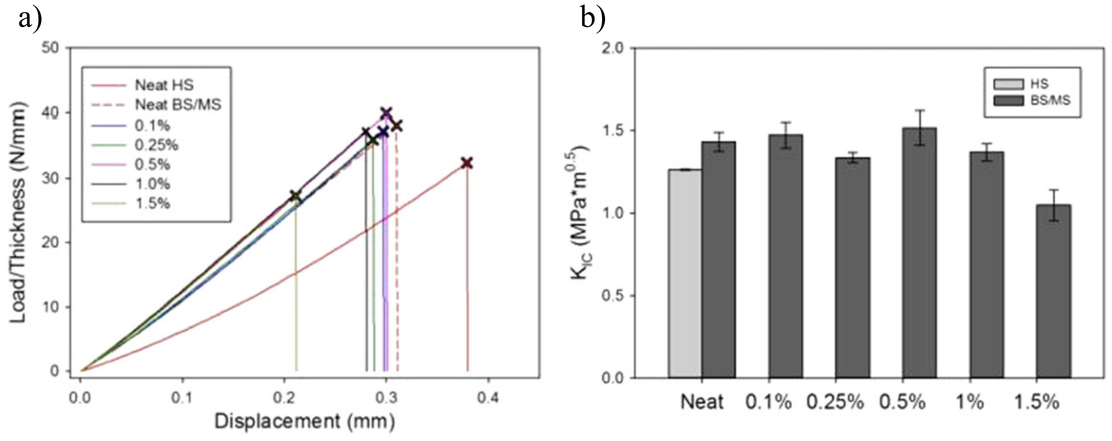

Figure 11. Results from quasi-static fracture tests using hand-stirring (HS) or bath sonication with mechanical stirring (BS/MS) for 0–1.5 wt% CNTs. (a) representative load–displacement curves normalized by specimen thickness, where 'x' indicates crack initiation, and (b) average fracture toughness (K_{IC}). K_{IC} of neat epoxy increases from 1.26 MPa$\sqrt{m}$ to 1.43 MPa$\sqrt{m}$ when the control sample is mechanically stirred and bath sonicated instead of only hand-stirred.

presented in this work have been processed in the same way that the corresponding CNT-modified samples are prepared.

The addition of CNTs over a wide range of weight percentages (0.1–1.5 wt%) caused an insignificant decrease in Young's modulus and ultimate strength (figure 10) and no significant improvement in fracture toughness (K_{IC}) (figure 11). The largest improvement in K_{IC} was approximately +6% at 0.5 wt% CNTs.

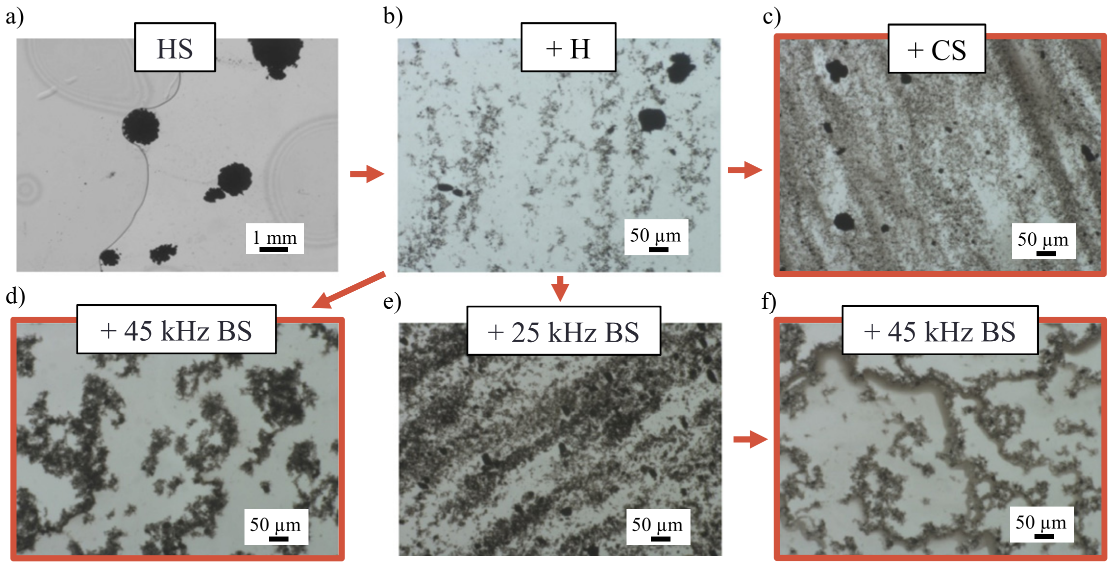

Figure 12. Optical microscopy of optimization process of 0.1 wt% Baytubes dispersed into Epikure W: (a) hand-stirring (HS); (b) hand-stirring and homogenization (HS + H); (c) hand-stirring, homogenization, and cup horn sonication (HS + H + CS); (d) hand-stirring, homogenization, and 45 kHz bath sonication (HS + H + BS); (e) hand-stirring, homogenization, and 25 kHz bath sonication; and (f) hand-stirring, homogenization, 25 kHz bath sonication, and 45 kHz bath sonication. ▭ indicates a final step in the optimization process.

3.2. Optimization of dispersion with optical micrographs

3.2.1. Methods

CNT dispersion was optimized based on optical micrographs using smaller batch sizes (~20 g) with 0.1 wt% CNTs. (Note that, even when only CNTs and hardener are present, 0.1 wt% CNTs is calculated according to the final formulation including the resin; therefore, 0.1 wt% CNTs and Epikure W is actually ~0.5 wt% CNTs prior to the addition of resin.) As in section 3.1, Baytubes were dispersed into Epikure W for achieving the thermodynamic effect before adding Epon 862 resin. A Cole Parmer Labgen 7 homogenizer (250 μm gap between rotating blade and stationary blade) was used to initially break up large agglomerates in the CNT-hardener mixture. Its speed was varied between 5000 and 35 000 rpm. Mechanical stirring was again performed simultaneously with bath sonication (either with 25 or 45 kHz setting). Cup horn sonication (CS) (Misonix Sonicator 3000, 20 kHz) with higher cavitation intensity than bath sonication, was varied between 25 and 160 W. Drops of CNT/hardener were collected from the batch onto glass slides periodically in order to monitor the effect of each of these dispersion techniques over time. The results are summarized in figure 12.

The interaction between Epikure W and Baytubes is not strong enough compared to that between nanotube and nanotube in order to break up the CNT agglomerates (>1 mm) effectively by HS (figure 12(a)). Subsequent homogenization (H) dispersed some of the CNTs well but continued to leave behind large agglomerates (>50 μm) (figure 12(b)). Subsequent CS dispersed some CNTs even more thoroughly, although large agglomerates (<50 μm) remained (figure 12(c)). Instead of CS, when the sample was hand-stirred, homogenized, and then bath sonicated at 45 kHz (figure 12(d)), the largest agglomerates were reduced to around 10 μm in diameter, but the CNTs appeared to remain tightly packed. Instead, if the sample was first bath sonicated at 25 kHz (figure 12(e)) and then the frequency was increased to 45 kHz, the final dispersion (figure 12(f)) produced the 'fluffy-loosely-packed' description of good dispersion noted in [26].

This final methodology (figure 12(f)) was chosen as the optimized methodology, with the following details: 15 min of homogenization (first 10 min at 35 000 rpm, then 5 min at 25 000 rpm), 45 min of simultaneous mechanical stirring at 400 rpm and 25 kHz bath sonication at 80 °C, and 60 min of simultaneous mechanical stirring at 400 rpm and 45 kHz bath sonication at 80 °C. Then the resin was hand-stirred in, and the entire mixture was simultaneously stirred mechanically at 1500 rpm and bath sonicated at 45 kHz for another 30 min at 80 °C.

The succession of dispersion in the optimized methods is explained as follows: homogenization caused large CNT aggregates to be broken down into smaller pieces using extremely high shear stress within the narrow homogenizer gap. Next, 25 kHz bath sonication was used to break these CNT aggregates into smaller and looser aggregates with simultaneous mechanical stirring. Note that 25 kHz sonication offers greater size cavitation than 45 kHz with a higher force among greater size interfaces. (The cavity size and force are inversely proportional to the sonication frequency.) The 25 kHz sonication frequency provides higher cavitation forces but cannot break

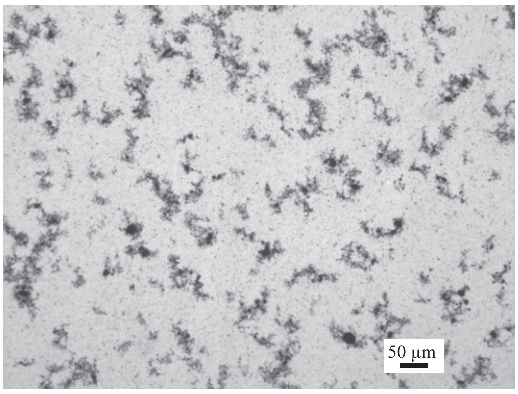

Figure 13. Optical microscope image from the optimized methodology of uncured Epon 862, Epikure W, and 0.2 wt% Baytubes.

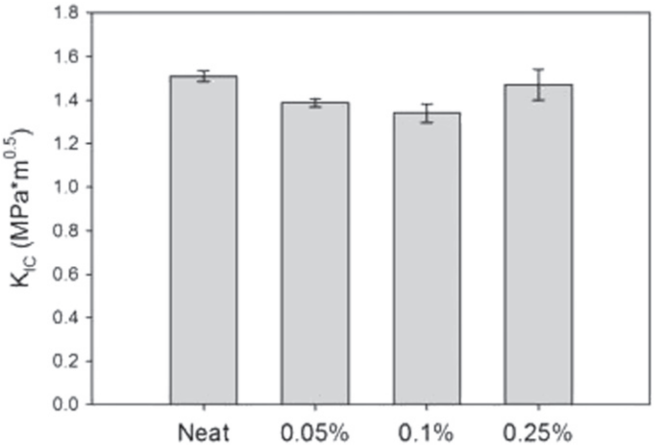

Figure 14. Fracture toughness for samples from the optimized methodology samples. No improvements in K_{IC} for 0.05–0.25 wt% CNTs are evident.

up small-scale aggregates because the cavity size is too big to form within small scale interfaces. Therefore, 45 kHz sonication with smaller size cavitation was used next to break the loosened small aggregates further, creating the loose, fluffy CNT dispersion in figure 12(f). The final dispersion after scaling up to full batch sizes and doubling the final CNT wt% is shown in figure 13. This figure closely resembles figures 5(c) and (d), which led to the greatest improvement in K_{IC} (figure 6(a)) found by Mirjalili *et al* [15].

3.2.2. Results

The fracture toughness results from the sample preparation methods described above are presented in figure 14. Despite apparent improvements in CNT dispersion, no improvements were found in fracture toughness for nanocomposites with 0.05–0.25 wt% CNTs. Also the optimized methodology applied to the neat sample improved K_{IC} to 1.51 $\mathrm{MPa}\sqrt{\mathrm{m}}$, compared to 1.43 $\mathrm{MPa}\sqrt{\mathrm{m}}$ for the original methods (section 3.1). Perhaps the dispersion level achieved here (figure 13) is not good enough to effectively improve the toughness, or the nanotubes may be damaged during processing, thereby degrading their properties. This image (figure 13) shows separated (localized), loosened, fluffy CNTs, instead of evenly dispersed CNTs throughout the entire matrix. This dispersion level was later improved upon by introducing calendering (section 3.4).

3.3. Other methodologies for dispersing CNTs into hardener first

3.3.1. Methods

When the technique optimized by optical microscopy observation did not result in any increase in the fracture toughness beyond that of neat epoxy with the same processing steps, several other methodologies were attempted based on the optimization study (figure 12) using Epon 862 and Epikure W.

Samples similar to the optimized methods but with less bath sonication time (to minimize potential damage of nanotubes) were produced (figure 12(d)), both with 0.2 wt% Baytubes and with 0.2 wt% of a second type of

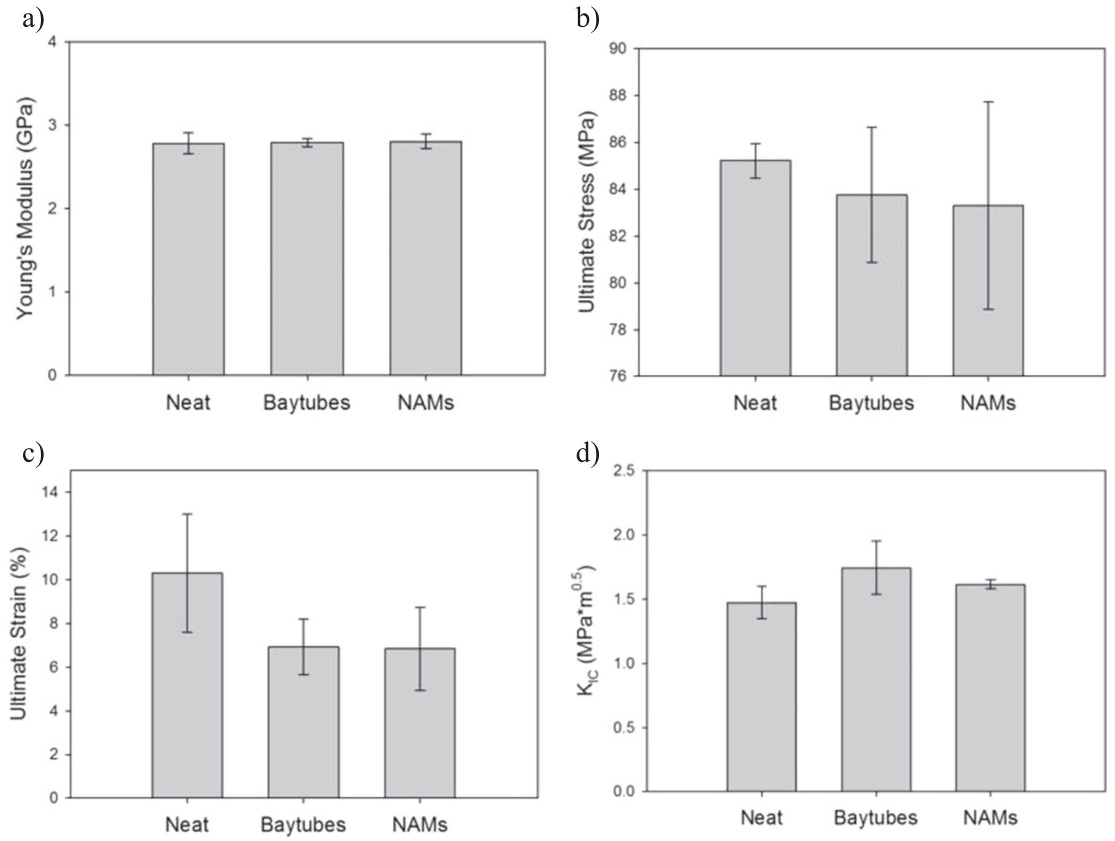

Figure 15. Results of quasi-static tension and fracture tests of methods involving homogenization and less bath sonication time than the optimized methods (HBS) with two different types of unfunctionalized 0.2 wt% CNTs (Baytubes and NAMs). No change is observed in (a) Young's modulus, and decreases in (b) ultimate stress and (c) ultimate strain are not significant. Improvements in (d) fracture toughness are not significant with respect to the error bars.

unfunctionalized CNTs from Nanostructured and Amorphous Materials, Inc (NAMs). This method included 15 min of homogenization (first 10 min at 35 000 rpm, then 5 min at 25 000 rpm) and 30 min of simultaneous mechanical stirring at 400 rpm and 45 kHz bath sonication at 80 °C. Then the resin was hand-stirred into the mixture, and the entire batch was simultaneously mechanically stirred at 1500 rpm and bath sonicated at 45 kHz for another 30 min at 80 °C. Note that this is the same methodology as presented in section 3.1 but with the addition of homogenization.

Two additional methodologies were attempted with higher cavitation intensity with greater cavity sizes using 0.2 wt% Baytubes. The cup horn sonication (figure 12(c)) uses a water medium between the horn and the sample, while PS involves placing the probe tip directly into the sample for even higher, but very localized, cavitation intensity. In both cases, CNTs were dispersed with 15 min of homogenization (first 10 min at 35 000 rpm, then 5 min at 25 000 rpm), 2 h of high cavitation intensity sonication (cup horn sonication or probe tip sonication) at 5 s 'on'/5 s 'off' cycling for 1 h of 'on time,' and 30 min of simultaneous mechanical stirring at 400 rpm and 45 kHz bath sonication at 80 °C. Then the resin was hand-stirred in, and the entire mixture was simultaneously mechanically stirred at 1500 rpm and bath sonicated at 45 kHz for another 30 min at 80 °C. The cup horn sonicator was set to an amplitude of 3.5, which delivered ~80 W of power. The probe tip sonicator (Vibracell VCX 750) was set to an amplitude of 35%, which delivered ~260 W of power.

3.3.2. Results

Figure 15 gives the results of the mechanical tests (stress versus strain and load versus load-point deflection graphs are not shown for brevity) of samples with homogenization and less bath sonication time than the optimized methods described in section 3.2. These samples were homogenized and then processed in the same way as in section 3.1. In the tension tests, there is no change in Young's modulus, and the decreases in ultimate strength and ultimate strain are insignificant. While both Baytubes and NAMs gave improvements in K_{IC} (+27% and +14%, respectively), neither improvement is considered significant with respect to the associated error bars due to large scatter in the data.

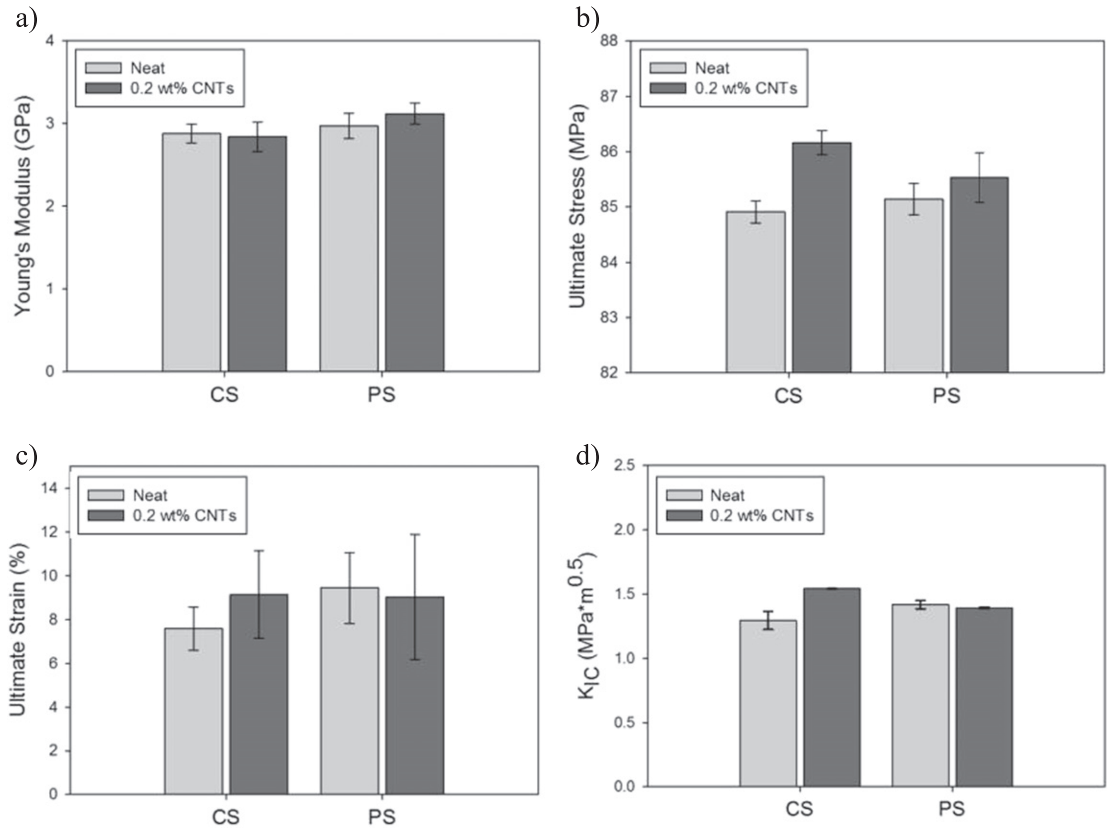

Figure 16. Results of quasi-static tension and fracture tests of methods involving higher cavitation intensity (CS = cup horn sonication, PS = probe tip sonication) using 0.2 wt% Baytubes. No significant changes are observed in (a) Young's modulus or (c) ultimate strain. Improvements in (b) ultimate stress and (d) fracture toughness are significant with respect to the error bars using the CS methodology.

Table 4. Summary of important K_{IC} results when dispersing CNTs into the hardener first.

Dispersion technique	CNT type	Neat K_{IC} (MPa$\sqrt{m}$)[a]	CNT K_{IC} (MPa$\sqrt{m}$)	+% K_{IC}
BS/MS	0.5 wt% Baytubes	1.43 ± 0.06	1.52 ± 0.10	6
Optimized	0.25 wt% Baytubes	1.51 ± 0.02	1.47 ± 0.07	−3
HBS	0.2 wt% Baytubes	1.47 ± 0.13	1.74 ± 0.21	27
HBS	0.2 wt% NAMs	1.47 ± 0.13	1.62 ± 0.04	14
CS	0.2 wt% Baytubes	1.29 ± 0.07	1.54 ± 0.002	19
PS	0.2 wt% Baytubes	1.42 ± 0.03	1.39 ± 0.005	−2

[a] Note that all CNT-modified samples show significant improvement in K_{IC} compared to the original hand-stirred neat sample from section 3.1 (K_{IC} = 1.26 ± 0.01 MPa$\sqrt{m}$).

Figure 16 shows the mechanical test results for the cases of higher cavitation intensity. Significant improvements were found in the ultimate stress (+1%) and fracture toughness (+19%) of cup horn sonication samples (CS). It should be noted that this significant percent improvement in K_{IC} is accompanied by a decrease in the fracture toughness of the neat epoxy due to processing (1.29 MPa$\sqrt{m}$). PS, on the other hand, causes a slight decrease (−2%) in fracture toughness relative to its control sample, possibly indicating CNT damage by the localized sonication energy.

Table 4 gives a summary of the important K_{IC} values from sections 3.1 to 3.3 while dispersing CNTs into the hardener first. The largest improvement was from HBS, although these improvements were not beyond the error bars due to high scatter in this data. The only significant improvement in K_{IC} relative to the error bars is with CS; however, this sample also has the lowest neat K_{IC} value. Practically speaking, this improvement is not significant relative to the same neat epoxy without significant processing.

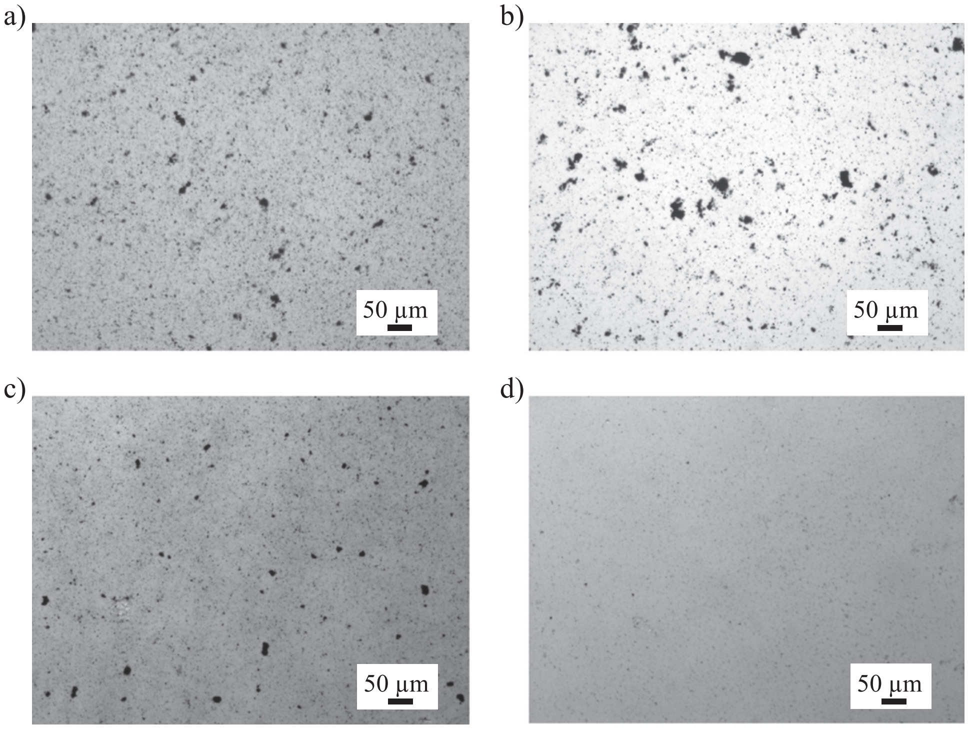

Figure 17. Optical microscopy of uncured 0.2 wt% unfunctionalized CNTs dispersed into both hardener and resin: (a) Baytubes with homogenization and less bath sonication than the optimized methods, (b) CNTs from NAMs with homogenization and less bath sonication than the optimized methods, (c) cup horn sonication (CS), and (d) probe tip sonication (PS). All images contain Baytubes except in (b).

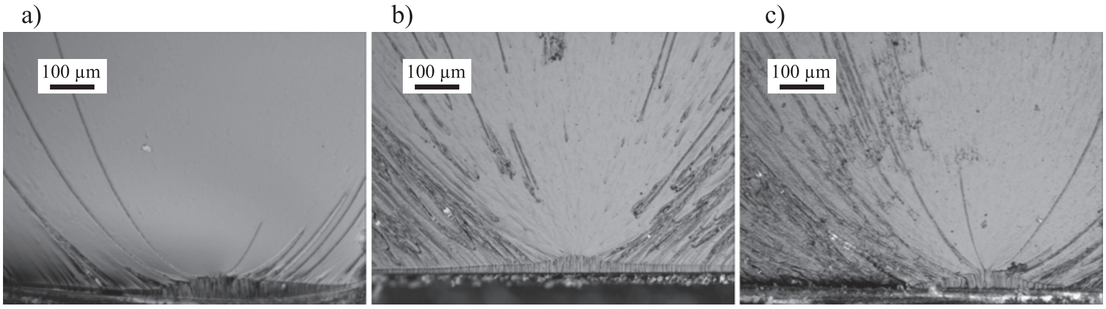

Figure 18. Optical micrographs of fracture surfaces of (a) neat epoxy, (b) 0.2 wt% NAMs, and (c) 0.2 wt% Baytubes. Baytubes show the highest surface roughness, while the neat epoxy has the lowest.

3.3.3. Optical microscopy

Figure 17 shows the dispersion state of the four different samples presented in this section. All samples contain Baytubes except for figure 17(b), which has unfunctionalized CNTs from NAMs. These uncured samples contain 0.2 wt% CNTs, Epikure W, and Epon 862. Agglomerates are largest in figure 17(b) with CNTs from NAMs and smallest in figure 17(d) with PS. All employed processing methods were not sufficient to optically disperse CNT agglomerates according to these images. The smallest agglomerates shown in figure 17(d) (which exhibited decreased toughness) may suggest that more aggressive PS could damage the CNTs.

Figure 18 shows optical micrographs of fracture surfaces of samples corresponding to figures 17(a) and (b) in the region immediately adjacent to the initial crack front. Despite the apparent differences in fracture surface roughness, there was no significant increase in fracture toughness (K_{IC}) by adding either type of unfunctionalized CNTs. Baytubes (figure 18(c)) show the highest surface roughness, while neat epoxy (figure 18(a)) has the lowest. All three fracture surfaces are very rough close to the initial notch, but surface roughness is visibly different in the post-initiation region and could be an indication of higher post-initiation fracture toughness due to the presence of CNTs.

3.4. Dispersing CNTs into the resin first

3.4.1. Methods

After having limited or no improvement in mechanical properties by dispersing unfunctionalized CNTs into the hardener first, NH_2-functionalized MWCNTs (Nanocyl 3152) were dispersed into the resin first. The functional groups on the CNTs interact with the resin, leading to much better initial dispersion by HS than when unfunctionalized CNTs were dispersed into the hardener first. Also by dispersing CNTs into the resin first, the original dispersion was diluted far less when adding the second part of the epoxy system, since the stoichiometric ratio of resin:hardener was 100:26.5 by weight for Epon 862 and Epikure W.

Many samples were processed using calendering (Exakt Model 80E), the popular industrial technique for dispersing CNTs in polymer systems. Resin and NH_2-CNTs are fed between three opposing rollers rotating at angular velocity ratio of 1:3:9, with the fastest roller rotating at 200 rpm. The two gap sizes of the calender can be set independently from 5 to 100 μm, and various combinations of these gap sizes were investigated. Because calendering is a high shear technique, it works better with higher viscosity material. The masterbatch technique is frequently used [21, 22, 28] in order to raise the viscosity during dispersion by first adding a small amount of resin to the CNTs, and then later diluting the CNT/resin mixture to the desired final wt% by adding additional resin.

Samples processed using 'calendering with a masterbatch' (CM) approach were first hand-stirred using 1.0 wt% NH_2-CNTs in the resin (where 1.0 wt% is calculated to include the hardener—that is ~1.3 wt% NH_2-CNTs in the resin.) The first pass of the masterbatch through the calender was with 90 and 30 μm gap settings. The second and third passes had 30 and 10 μm gap settings. Then resin was added to dilute the mixture to the final loading of 0.1, 0.2, or 0.3 wt% NH_2-CNTs (note that these weight percentages account for the hardener, which has not yet been added), and a fourth pass was made at 30 and 10 μm gap settings. Finally the hardener was hand-stirred and then mechanically stirred for 10 min at 2000 rpm.

The 'calendering methodology' (C) involves HS the full amount of resin and NH_2-CNTs (0.3 wt% including hardener) together and then passing the mixture through the calender three times (no masterbatch). Note that 0.3 wt% was chosen for this and many of the following methodologies based on the CM results, as well as the high viscosity observed in nanocomposites with more than 0.3 wt% NH_2-CNTs using the masterbatch (CM) method. On the first pass, both gaps are set to 30 μm; on the second pass, both gaps are set to 20 μm; and on the third pass, both gaps are set to 10 μm. Hardener was hand-stirred and then mechanically stirred at 2000 rpm for 10 min.

A third methodology involving calendering included probe tip sonication (PTC). 0.3 wt% NH_2-CNTs were hand-stirred into the resin and then probe tip sonicated using 25% amplitude (~190 W) at 20 s 'on' 20 s 'off' cycling for 30 min of 'on time'. Then the sample was passed through the calender three times, with both gaps set to 20 μm on the first pass, 10 μm on the second pass, and 5 μm on the third pass. Finally the hardener was hand-stirred and then mechanically stirred for 10 min at 2000 rpm.

A fourth methodology involving calendering also included speedmixing (CMS) in an effort to better distribute the well-dispersed masterbatch material into the additional resin. Both unfunctionalized Baytubes (initially 2.7 wt% in resin) and NH_2-CNTs (initially 1.3 wt% in resin) were initially processed much like the CM method. The first pass of the masterbatch through the calender was with 90 and 30 μm gap settings. The second pass had 30 and 10 μm gap settings. The third and fourth passes had 30 and 5 μm gap settings. Then additional resin was hand-stirred to dilute the mixture to 1.3 wt% Baytubes and 0.4 wt% NH_2-CNTs. Unlike the CM methodology, a FlakTek DAC 150 FVZ-K SpeedMixer was used to further disperse the masterbatch into the additional resin with three cycles of 5 min each at 3000 rpm. The hardener was then hand-stirred and speedmixed for three additional cycles, such that the final specimens were 1 wt% Baytubes and 0.3 wt% NH_2-CNTs. Note that the viscosity was actually higher for 0.3 wt% NH_2-CNTs than 1 wt% Baytubes.

Additional samples were processed similarly to those that gave the highest improvement (+27%) in K_{IC} when unfunctionalized CNTs were dispersed into the hardener first. NH_2-CNTs were first homogenized with resin for 5 min at 25 000 rpm. Then the sample was simultaneously mechanically stirred at 1000 rpm and bath sonicated at 37 kHz using an Elma Ultrasonics E60H bath sonicator for 30 min at 80 °C. Hardener was added such that the final weight percent of CNTs was 0.3 wt%, and then the mixture was mechanically stirred at room temperature for 10 min at 2000 rpm.

3.4.2. Results

Figure 19 shows the fracture toughness results when CM for 0.1–0.3 wt% NH_2-CNTs. In all of these cases, samples were homogenized for 5 min prior to calendering. Evidently, no improvements in measured K_{IC} values were observed.

Figure 20(a) shows fracture toughness results for several different methodologies using 0.3 wt% NH_2-CNTs. Figure 20(b) gives the fracture toughness results when CM without homogenization using 0.3–0.7 wt% NH_2-CNTs. Note that 0.3 wt% CM appears in both figures 20(a) and (b). As shown in figure 20(a), HBS gave a +4% (insignificant) improvement, calendering (C) without homogenization gave a +2% (insignificant) improvement, CM without homogenization resulted in a +10% (insignificant) improvement, and probe tip

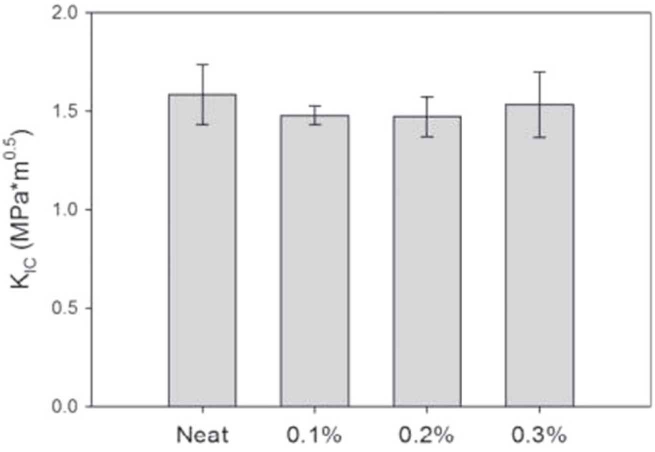

Figure 19. Fracture toughness of different wt% NH_2-CNTs dispersed first into resin using homogenization and calendering with a masterbatch (CM).

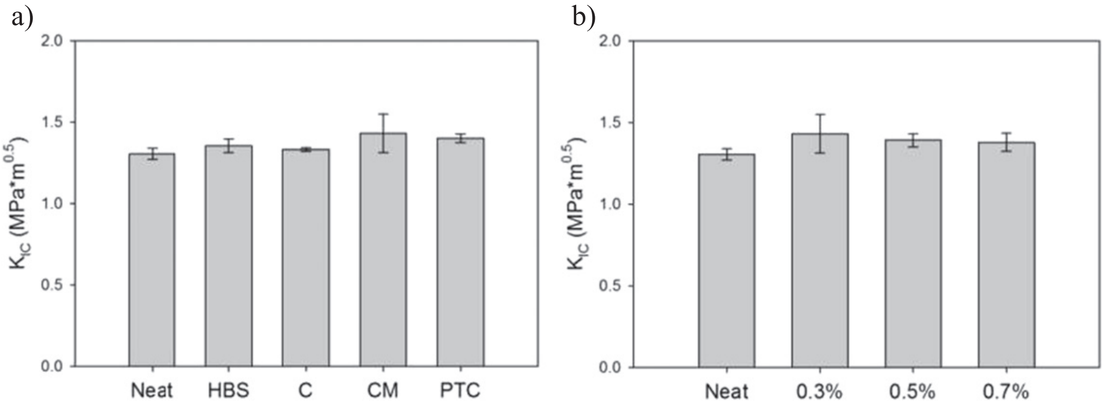

Figure 20. Fracture toughness of NH_2-CNTs dispersed first into resin using (a) several different methodologies all at 0.3 wt% (HBS = homogenization and bath sonication, C = calendering, CM = calendering with a materbatch, and PTC = probe tip sonication and calendering), and (b) using calendering with a masterbatch (no homogenization) at three different weight percentages. All methodologies gave small improvements in K_{IC}.

sonication and calendering (PTC) without homogenization gave a +7% (insignificant) improvement in fracture toughness. On the other hand, as shown in figures 20(b), 0.5 wt% CNTs gave a +7% (signifcant) improvement and 0.7 wt% gave a +6% (insignificant) improvement in K_{IC}; however, these two mixtures were far too viscous to be useful to process any three-phase fiber reinforced composite such as carbon fiber/CNT/epoxy composites.

Figure 21 shows fracture toughness for specimens dispersed by CMS. 0.3 wt% NH_2-CNTs had no effect on K_{IC}, while 1 wt% Baytubes caused a small but significant (+10%) improvement in K_{IC}.

Table 5 gives a summary of the important K_{IC} values from this section while dispersing CNTs into the resin first. Despite improvements in dispersion beyond those achieved when dispersing CNTs into the hardener first (see section 3.4.3), improvements in K_{IC} are less than those presented in table 4. Note also that the notch sharpening technique here differs from table 4, likely causing the discrepancy in Neat K_{IC} values between the two tables.

3.4.3. Microscopy

Figure 22 illustrates the difference between dilution effects of dispersing into the hardener first compared to dispersing into the resin first. Initial dispersion in figure 22(a) (hardener and unfunctionalized CNTs) is seemingly good; however, once the resin is added to the mixture in figure 22(b), the well-dispersed network of CNTs and hardener appear to be broken into many small, isolated patches. On the contrary, excellent dispersion was obtained by dispersing the NH_2-CNTs into the resin first and then adding hardener into the mixture (figure 22(c)).

Figure 23 shows optical microscopy of specimens produced by CMS using two different types of CNTs and dispersing into the resin first. Figure 23(a) closely resembles figure 22(c), both of which involve calendering NH2-CNTs with a masterbatch technique. Figure 23(b) shows improved dispersion by using unfunctionalized Baytubes. These CNTs can be processed at a much higher wt% while remaining relatively inviscous.

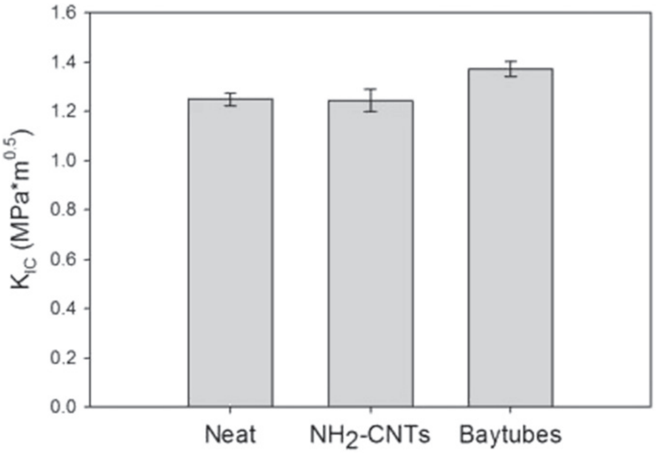

Figure 21. Fracture toughness of 0.3 wt% NH$_2$-CNTs and 1 wt% Baytubes dispersed by calendering and speedmixing (CMS). Baytubes gave a small but significant improvement in K_{IC}.

Table 5. Summary of important K_{IC} results when dispersing CNTs into the resin first.

Dispersion technique	CNT type	Neat K_{IC} (MPa$\sqrt{m}$)	CNT K_{IC} (MPa$\sqrt{m}$)	+% K_{IC}
HBS	0.3 wt% NH$_2$-CNTs	1.31 ± 0.03	1.36 ± 0.04	4
C	0.3 wt% NH$_2$-CNTs	1.31 ± 0.03	1.33 ± 0.01	2
CM	0.3 wt% NH$_2$-CNTs	1.31 ± 0.03	1.43 ± 0.12	10
PTC	0.3 wt% NH$_2$-CNTs	1.31 ± 0.03	1.40 ± 0.03	7
CMS[a]	0.3 wt% NH$_2$-CNTs	1.25 ± 0.03	1.24 ± 0.05	−1
CMS[a]	1.0 wt% Baytubes	1.25 ± 0.03	1.37 ± 0.03	10

[a] CMS batches were prepared with older hardener that had oxidized, likely leading to the reduced Neat K_{IC} value.

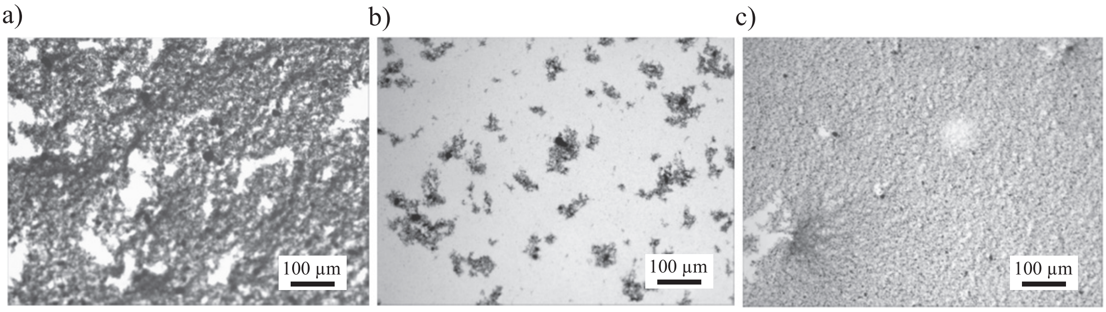

Figure 22. Optical micrographs of uncured CNT dispersions: (a) 0.25 wt% Baytubes dispersed in the hardener using homogenization and bath sonication, (b) resin added to (a), and (c) 0.5 wt% NH$_2$-CNTs dispersed into the resin first using calendering with a masterbatch (CM) after the addition of hardener. The final dispersion state in (c) is far superior to the final dispersion state in (b).

Figure 24 shows optical micrographs of fracture surfaces of samples containing CNTs dispersed using calendering in the region immediately adjacent to the initial crack front. Baytubes dispersed by CMS show the most surface roughness features; however, neat epoxy has the deepest features. It appears that the toughening mechanisms of the epoxy and the CNTs are competing with each other, possibly explaining the modest (+10%) improvements in K_{IC} with well dispersed Baytubes in figure 24(d).

3.5. Altering the stoichiometry

3.5.1. Methods

After dispersing CNTs into the resin first, achieving excellent dispersion, and yet failing to achieve significant improvements in fracture toughness, a new variable was considered. Ashrafi *et al* [2] initially achieved insignificant (+20%) improvement in K_{IC} at the manufacturer-recommended stoichiometry (1:0.8 molar ratio)

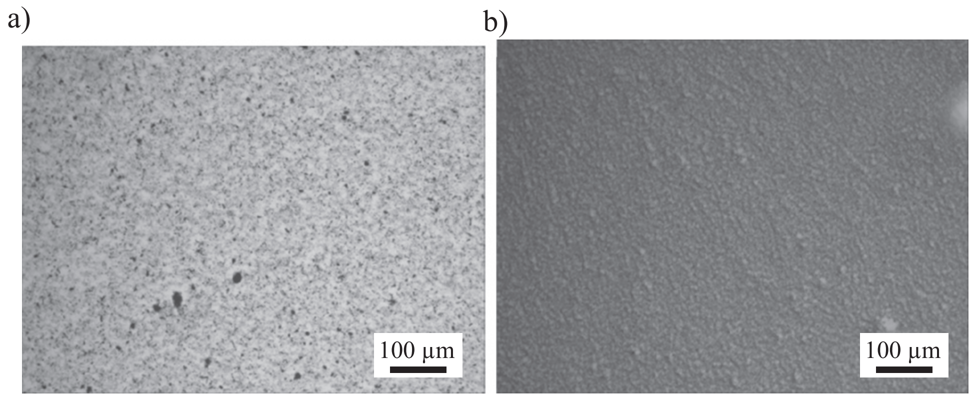

Figure 23. Optical micrographs of uncured CNTs, resin and hardener: (a) 0.3 wt% NH2-CNTs and (b) 1 wt% Baytubes. Both samples were dispersed using calendering and speedmixing (CMS). The dispersion state in (b) is superior to the dispersion state in (a).

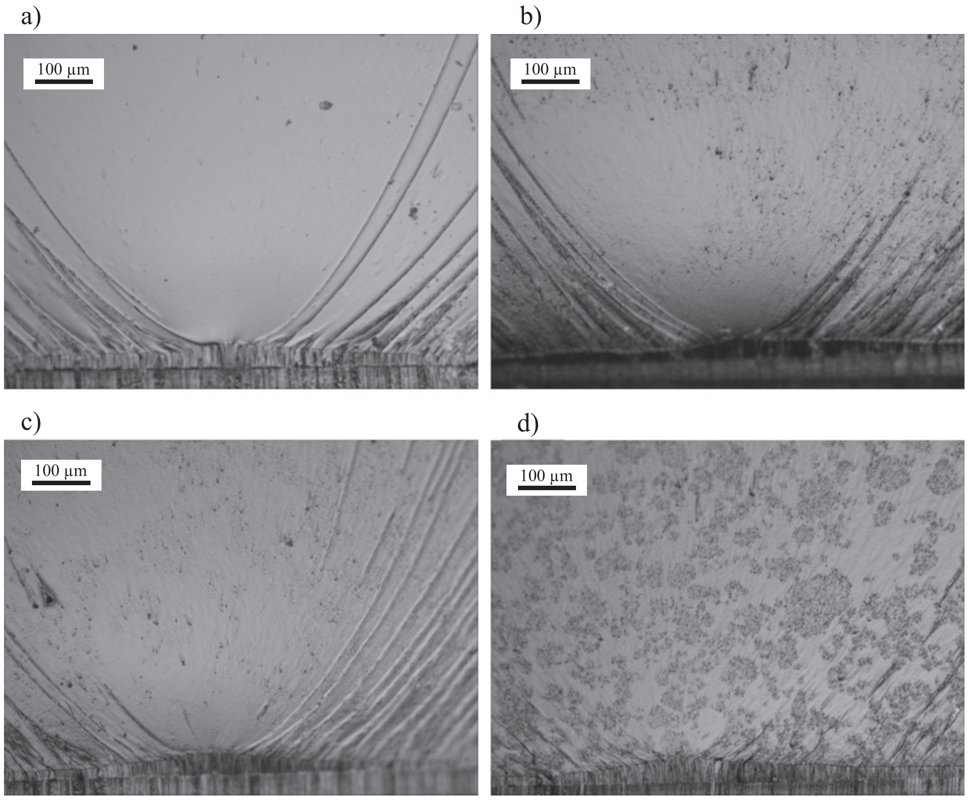

Figure 24. Optical micrographs of fracture surfaces of (a) neat epoxy, (b) 0.3 wt% NH_2-CNTs calendering with a masterbatch, (c) 0.3 wt% % NH_2-CNTs calendering with a masterbatch and speedmixing, and (d) 1 wt% Baytubes calendering with a masterbatch and speedmixing.

with 0.2 wt% functionalized CNTs (and a −28% decrease in K_{IC} with 0.2 wt% unfunctionalized CNTs); however, by adding 25% more hardener than the manufacturer-recommended stoichiometry (1:1 molar ratio), along with functionalized CNTs, they found significant improvements in K_{IC} (+38%), ultimate stress (34%), and ultimate strain (56%) (see tables 2 and 3).

In order to study the effects of varying the stoichiometry, samples were made with and without 0.2 wt% NH_2-CNTs (Nanocyl 3152) with an additional +5%, +10%, and +25% hardener (Epikure W) beyond the manufacturer-recommended 1:1 molar ratio of resin:hardener. In all these trials, CNTs were dispersed using calendering, with the first pass at 90 and 30 μm gap settings, the second pass at 30 and 10 μm gap settings, and then three more passes at 30 and 5 μm gap settings. The varied amounts of Epikure W were hand-stirred and then mechanically stirred for 10 min. Unlike previous samples of Epon 862 and Epikure W, these were cured for 3.5 h at 140 °C after degassing for 30 min at 80 °C. Note that this new curing schedule was chosen based on the

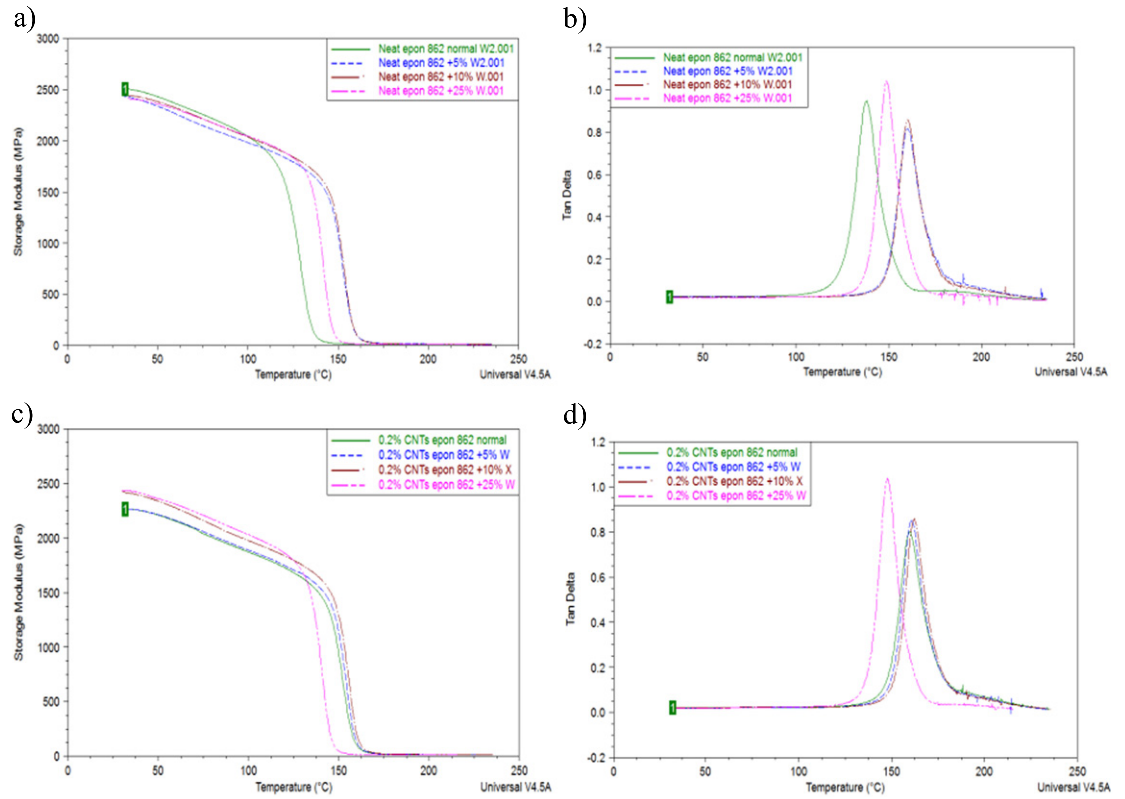

Figure 25. Effect of additional hardener (+5%, +10%, +25%) beyond the manufacturer-recommended (1:1 molar) ratio, with and without 0.2 wt% NH_2-CNTs on DMA parameters: (a) storage modulus of neat epoxy samples, (b) tan delta of neat epoxy samples, (c) storage modulus of CNT-modified epoxy samples, and (d) tan delta of CNT-modified epoxy samples.

cure kinetics of NH_2-CNTs in Epon 862 and Epikure W at the manufacturer-recommended ratio of resin: hardener.

3.5.2. Results

Figure 25 gives the results of DMA using three-point bending samples with the normal amount of hardener, as well as an additional +5%, +10%, and +25%. Figures 25(a) and (c) correspond to neat epoxy samples, while figures 25(b) and (d) correspond to CNT-modified samples with 0.2 wt% NH_2-CNTs dispersed by calendering. CNTs reduced the initial storage modulus of samples with the normal amount and +5% additional hardener, whereas little initial change was observed for the samples with +10% and +25% additional hardener. The glass transition occurred at a much higher temperature (~20 °C) for normal (1:1 molar ratio) epoxy with CNTs than the corresponding neat sample. Similar increases in the glass transition temperature occurred with additional +5% and +10% hardener *with or without adding CNTs*. No change was attributed to the addition of CNTs to any of the samples with additional (+5%, +10%, +25%) hardener. It appears that the amine groups on the CNTs participate in the epoxy reaction, especially for the manufacturer recommended stoichiometry.

Figure 26 gives the results of thermal and mechanical tests of epoxy when the amount of hardener was varied, with and without 0.2 wt% NH_2-CNTs. The glass transition temperature (T_g) (figure 26(a)) was determined to be the peak of the tan delta curve (figures 25(b) and (d)). The crosslink density (figure 26(b)) was determined using

$$\eta = \frac{E'}{3RT}, \quad T = T_g + 40\ ^{\circ}\mathrm{C}, \tag{3}$$

where η is the crosslink density, E' is the storage modulus evaluated at T, and R is the gas constant [29]. Because the primary reaction between the diamine hardener and the resin prepolymer is more reactive than the secondary amine reaction, additional hardener lowers the crosslink density. This decreased crosslink density has little effect on Young's modulus (figure 26(c)), ultimate stress (figure 26(d)), or ultimate strain (figure 26(e)), but it has an inverse relationship with the fracture toughness (figure 26(f)), with or without the presence of CNTs. Decreased crosslink density causes a decrease in brittleness and hence an increase in fracture toughness. While the mechanical improvements of adding additional hardener and CNTs simultaneously to neat epoxy of Ashrafi *et al* [2] were not realized, there is a decrease in the ultimate stress (figure 26(d)) and ultimate strain (figure 26(e))

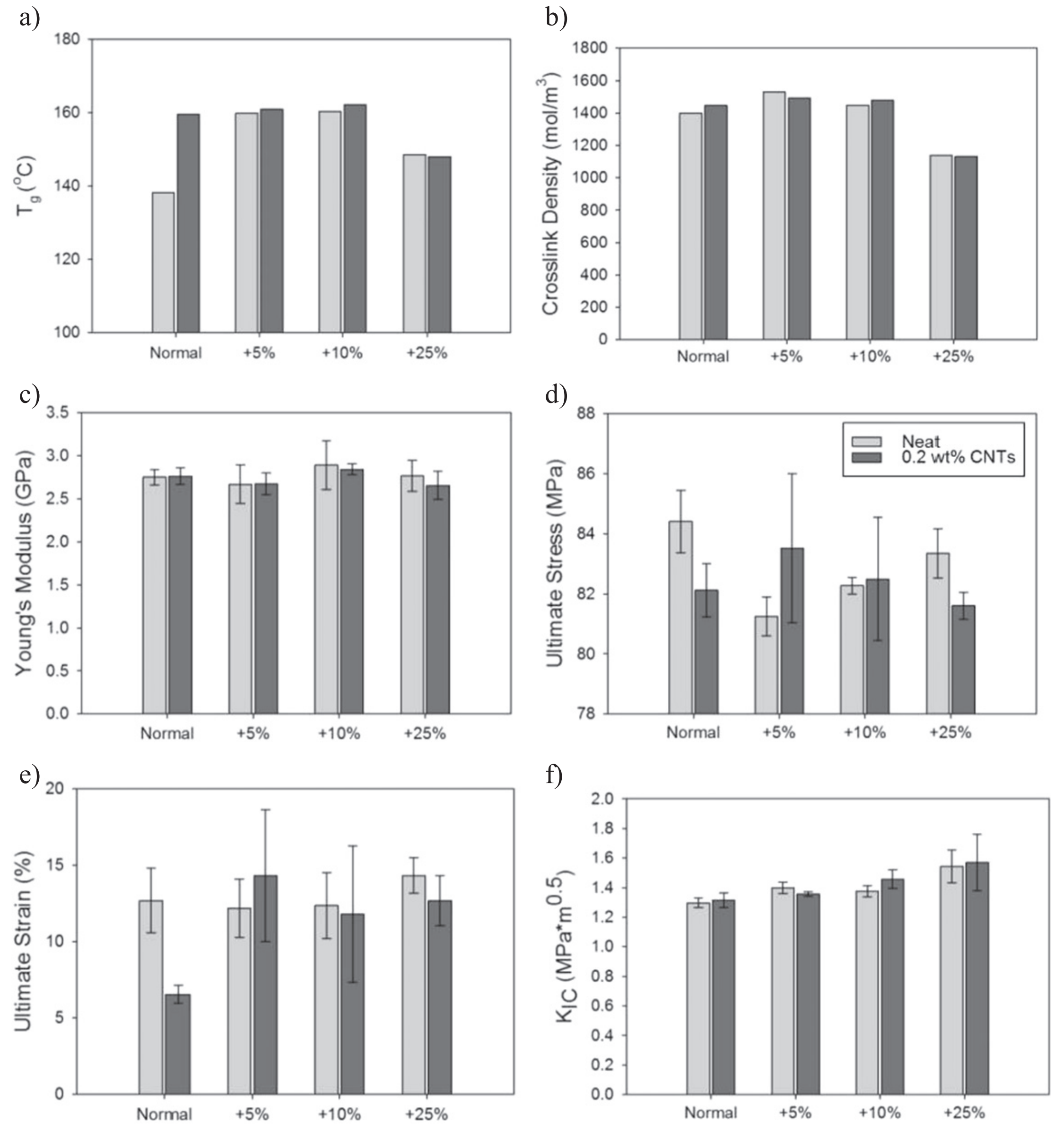

Figure 26. Effect of altering the stoichiometry with additional hardener (+5%, +10%, +25%) (beyond the manufacturer-recommended resin:hardener 1:1 molar ratio), with and without 0.2 wt% NH_2-CNTs, on (a) glass transition temperature (T_g), (b) crosslink density, (c) Young's modulus, (d) ultimate stress, (e) ultimate strain, and (f) fracture toughness (K_{IC}).

when CNTs are added without additional hardener. These properties are regained with a small amount (+5%) of extra hardener.

In addition to the processing conditions, a difference in stoichiometry or the presence of amine groups on functionalized CNTs can change the nature of the epoxy matrix significantly. When NH_2-CNTs are well-dispersed, they can have a similar effect on the entire matrix as adding extra amine-based hardener. When enough additional hardener (+25%) was added, a 19% improvement in K_{IC} was found *without CNTs*, most likely due to the decrease in crosslink density. It is therefore very important to compare CNT-modified samples with neat epoxy using the same processing conditions and the same chemical environments (when functionalized CNTs are used).

4. Discussion

Despite various attempts[5] to improve the mechanical properties of epoxy using CNTs through many different dispersion techniques detailed above, no significant improvements were observed large/significant enough to

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[5] Many other iterations of material preparation were also attempted but are not detailed here in favor of brevity.

Table 6. Details of multi-walled CNTs used and largest improvement in K_{IC}.

MWCNT	Functionalized?	OD (nm)	Length (μm)	+% K_{IC}
Baytubes C150P	No	15	1–>10	27
NAMs[a]	No	<8	20	14
Nanocyl 3152 (short thin)	NH_2	9	>1	10
Nanocyl 7000 (plasma)	NH_2	9.5	1.5	2

[a] NAMs = Nanostructured and Amorphous Materials, Inc.

Table 7. Different epoxy systems used and largest improvement in K_{IC} *of neat epoxy*.

Resin	Hardener	Lowest K_{IC} measured (MPa $\sqrt{m}$)	Highest K_{IC} measured (MPa $\sqrt{m}$)	+% K_{IC}
Epon 862	Epikure W	1.3	1.6	23
Epon 862	Epikure 3230	2.0	3.8	90
SC15 Part A	SC15 Part B	1.8	2.7	50
US Composites 635	Medium (speed)	1.8	2.7	50

justify the elaborate processing or the cost of CNTs (although the thermal and electrical properties were not examined thoroughly in this work). Four different types of CNTs were used; their descriptions and the largest improvements in K_{IC} found with each are listed in table 6. (Note that no results have been detailed above using Nanocyl 7000 for brevity.)

When control epoxy samples were not processed by the same dispersion techniques as their CNT-modified counterparts, improvements in mechanical properties were artificially inflated (figures 10 and 11). It is therefore possible that some mechanical property improvements reported in the literature are due to processing differences, rather than the presence of CNTs.

Depending on the dispersion technique, age of the resin and hardener, cure cycle, and notch sharpening technique, a wide variety of K_{IC} values (1.29–1.59 MPa $\sqrt{m}$) have been reported in this work for *neat* Epon 862 and Epikure W at the manufacturer-recommended resin:hardener ratio of 100:26.5 by weight. When holding all of these variables constant and increasing the amount of hardener (+5%, +10%, +25% more than the manufacturer-recommended ratio by weight), K_{IC} increased from 1.30–1.54 MPa $\sqrt{m}$ with insignificant changes in the tensile properties (figure 26). In other words, without sacrificing tensile properties, K_{IC} of Epon 862 and Epikure W can be improved significantly (+19%) by adding relatively inexpensive hardener *instead of CNTs*. This is consistent with the observations of Ashrafi *et al* [2], as well as Fernandez *et al* [30] and Gupta *et al* [31], who all measured increases in K_{IC} after adding additional hardener beyond the 1:1 molar ratio of resin: hardener. However, increasing the amount of hardener beyond the stoichiometric ratio may negatively affect material properties not measured in this work, as additional hardener has previously been shown to significantly decrease the dynamic mechanical properties after aging in water at 45 °C [32].

In order to study the effects of curing chemistry on the material properties, the authors examined crosslink density using DMA. The effects of amino-functionalized CNTs on neat epoxy were compared to the effects of additional hardener beyond the stoichiometric ratio on stoichiometric neat epoxy (figure 26). Whereas both amino-functionalized CNTs and additional hardener were shown to have significant effects on the mechanical properties (CNTs reduced the failure strain, whereas additional hardener increased fracture toughness), only additional hardener affected the crosslink density significantly. Future research should include further investigation of the effects of curing chemistry on the mechanical properties of epoxy with and without CNTs.

Similar to the enhancements in fracture toughness caused by additional hardener, the addition of homogenization to the methodology consistently increased K_{IC} of the neat epoxy. During homogenization of the hardener with CNTs, Epikure W was observed to oxidize, which also typically occurs as it ages. It is quite possible that this oxidation affected the polymerization chemistry in much the same way as additional hardener (figure 26).

Four different epoxy systems were used unsuccessfully to *significantly* improve the fracture toughness of neat epoxy with CNTs (although only results using Epon 862 and Epikure W have been presented for brevity); they are listed in table 7 along with the percent improvement in K_{IC} found *without CNTs* between the lowest and highest K_{IC} measured for each *neat* epoxy system. The differences in K_{IC} for the other three epoxy systems are attributed largely to differences in cure schedule (typically room temperature versus high temperature cure). It should be emphasized here that the combination of Epon 862 and Epikure W does not cure at room temperature.

Evidence in this work, as well as the works of Mirjalili *et al* [15] and Thostenson and Chou [23], suggests that it is possible for dispersion to be too complete for improvement in fracture toughness. Instead it may be that a certain agglomeration size and distribution is ideal for resisting crack initiation. Mirjalili *et al* [15] quantified dispersion using optical microscopy and saw the highest improvement in K_{IC} for a CNT area fraction (A_f) value around 0.5 using optical microscopy. Specimens with A_f values of 0.2 (poor dispersion) had decreased K_{IC} compared to neat epoxy, while specimens with A_f values greater than 0.9 (better dispersion) had negligible improvements in K_{IC}. Similarly, Thostenson and Chou [23] reported higher K_{IC} for more highly agglomerated samples and lower K_{IC} for samples with optimized dispersion. In the present work, optimized dispersion techniques (section 3.2) led to decreases in K_{IC} when dispersing into the hardener first. When dispersing into the resin first, calendering with a masterbatch with (CMS) and without (CM) speedmixing led to excellent dispersion but only 10% improvements in K_{IC}, provided that samples were not homogenized first. (Homogenization may actually improve the fracture toughness of neat samples more than the addition of well-dispersed CNTs.) Furthermore, the best overall improvements presented here (+27% in figure 15(d)) have relatively inferior dispersion (figure 17(a)) of CNTs.

Excluding the methodologies recreated by the current authors without finding significant improvements in K_{IC}, only four previous reports in table 1 (Alishashi *et al* [4], Ayatollahi *et al* [5], Gkikas *et al* [7], and Shtein *et al* [18]) have improved the fracture toughness of their CNT-modified epoxy nanocomposites beyond the values measured here for neat Epon 862 and Epikure W. This suggests that it is easier to improve the fracture toughness of an epoxy system with nanotubes if the initial neat K_{IC} is relatively low. Figure 24 may indicate that the toughening mechanism provided by well-dispersed CNTs (as demonstrated in many previous works with relatively brittle epoxy) actually competes with the toughening mechanism of the relatively tough epoxy system investigated in this work (Epon 862 and Epikure W). Ultimately, the practical application of modifying epoxy with CNTs may reside with a few researchers [4, 5, 7, 18] who have produced relatively tough epoxy nanocomposites, in all cases using PS of unfunctionalized MWCNTs.

5. Conclusion

A review of the literature indicates that the keys to enhancing the mechanical properties of epoxy with CNTs are the exceptional mechanical properties of the individual CNTs, the quality of the dispersion of the CNTs within the epoxy matrix, and good adhesion between the CNTs and epoxy matrix. Many researchers have reported statistically significant improvements in the fracture toughness of epoxy when adding CNTs. Others have struggled to demonstrate significant mechanical property enhancements, and have resorted to trying different types of CNTs (functionalized versus unfunctionalized), aligning the CNTs electrically, or varying the epoxy stoichiometry, in order to enhance the fracture toughness beyond that of neat epoxy. Multiple works indicate highest enhancement of fracture toughness when CNTs are not completely dispersed, and show a decrease in fracture toughness with further dispersion. In this work, CNTs have been shown to increase the mechanical properties of epoxy only slightly, and often not beyond the error bars, despite using many different types of CNTs, many different epoxy systems, and many different dispersion techniques. Similar improvements in the fracture toughness of *neat* epoxy have been found by changing the cure schedule, homogenizing (oxidizing) the hardener, and by adding additional hardener beyond the stoichiometric ratio, all without the addition of CNTs.

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