

## **Enhancement on mechanical strength of adhesively-bonded composite lap joints at cryogenic environment using coiled carbon nanotubes**

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### **Abstract**

The hardness, tensile and lap joint shear behaviors of pure epoxy, straight multi-walled carbon nanotube (MWNT)/epoxy and coiled multi-walled carbon nanotube (CCNT)/epoxy adhesives conditioned at room temperature (RT) and cryogenic temperature (CT) were investigated in the present study. Experimental results showed that all adhesives had greater Vickers hardness values, Young's moduli and tensile strengths at CT. The performance of

CCNT/epoxy adhesive at CT was outstanding due to the enhancement of mechanical interlocking effect between CCNTs and epoxy at low temperature. This effect led to a greater Vickers hardness value, Young's modulus and lap joint shear strength of this adhesive at CT when compared with MWNT/epoxy type. The result from finite element analysis (FEA) also proved that the contraction of matrix at CT induced additional clamping force onto the surface of nanotubes. Due to the larger surface area of CCNTs, a relatively stronger bonding strength was achieved, and thus, CCNT/epoxy adhesive had better mechanical properties at low temperature condition.

**Keywords:** A. Nano-structures, Polymer-matrix composites (PMCs); B. Adhesion, Mechanical properties

## **1. Introduction**

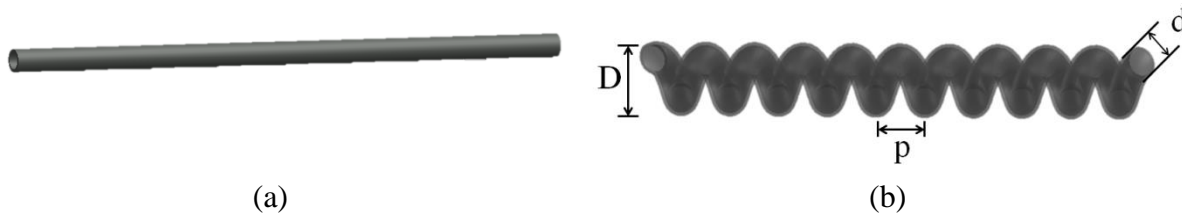
In recent years, the use of fiber reinforced polymer (FRP) composites in the aerospace engineering industry has been growing rapidly. To assemble these FRP structures, mechanical bonding methods such as fastening by bolts and nuts are currently used. However, there are many drawbacks for these methods. The metallic bolt and nuts are relatively heavy which contribute to the large amount of fuel use for modern aircraft. The undercuts for fasteners also lead to failure of composites since stress concentration will be developed around fastening joints. To solve these problems, the adhesive bonding method was suggested for FRP composite structures [1]. This method not only reduces the weight of aerospace structures, but also avoids the development of stress concentration and eliminates air gaps at the bonding area.

In fact, aerospace structures often encounter extremely low temperature conditions during their service. For example, spacecraft are servicing in the low earth orbit at a temperature down to  $-170^{\circ}\text{C}$  [2]. FRP composites with adhesive bonding are also used in cryogenic fuel tanks which carry extremely low temperature fuels ( $-150^{\circ}\text{C}$  or even lower) [3]. The mechanical behaviors of FRP composites at temperatures down to  $-60^{\circ}\text{C}$  were studied by many researchers [4-6], but studies on cryogenic conditions ( $-150^{\circ}\text{C}$  or lower) are still very limited. Epoxies are the most commonly-used adhesive for bonding FRP composites but they become brittle with low strength and fracture toughness at cryogenic conditions. Therefore, it is vital to enhance the mechanical behavior of epoxy adhesive for such circumstances.

In order to improve the mechanical strength of adhesively bonded lap joints at room temperature, researchers added nanofillers such as carbon nanotubes (CNTs) and nanoclay to an epoxy adhesive to form a new type of nanocomposite [7-9]. This method has been believed to effectively enhance the strength of the nanocomposite at extremely low temperature environments due to the mismatch of their coefficient of thermal expansion [10]. Owing to the high aspect ratio and extra-ordinary mechanical properties of straight multi-walled carbon nanotubes (MWNTs), adding them into epoxies as nano-reinforcement can enhance their mechanical properties. However, since the interfacial bonding strength between MWNTs and polymer is weak, the enhancement was not always very significant [11-13].

To tackle the aforementioned problem, coiled multi-walled carbon nanotubes (CCNTs) was proposed to be nano-reinforcements for nanocomposites [14]. CCNTs are carbon

nanotubes with a helical configuration, like springs. The strength enhancement effectiveness of nanocomposites is governed by the diameter of CCNT ( $d$ ), the diameter of coil ( $D$ ) and coil pitch ( $p$ ). Figure 1(a) and (b) illustrate the difference between a straight CNT and a CCNT. Previous studies have provided strong evidences that CCNTs can enhance the interfacial bonding properties and thus the mechanical properties of polymer-based composites. CCNT/epoxy composites were found to have a more compact interface than straight single-walled carbon nanotube (SWNT)/epoxy and straight multi-walled carbon nanotube (MWNT)/epoxy composites due to the existence of mechanical interlocking between the CCNT and surrounding matrix [14, 15]. The present study aims at investigating the hardness and tensile behavior of CCNT/epoxy nanocomposites and also the lap joint shear strength of this nanocomposite adhesive at cryogenic condition by comparing them with pure epoxy and MWNT/epoxy adhesives, to explore the feasibility of using CCNT/epoxy adhesive for aerospace engineering applications.

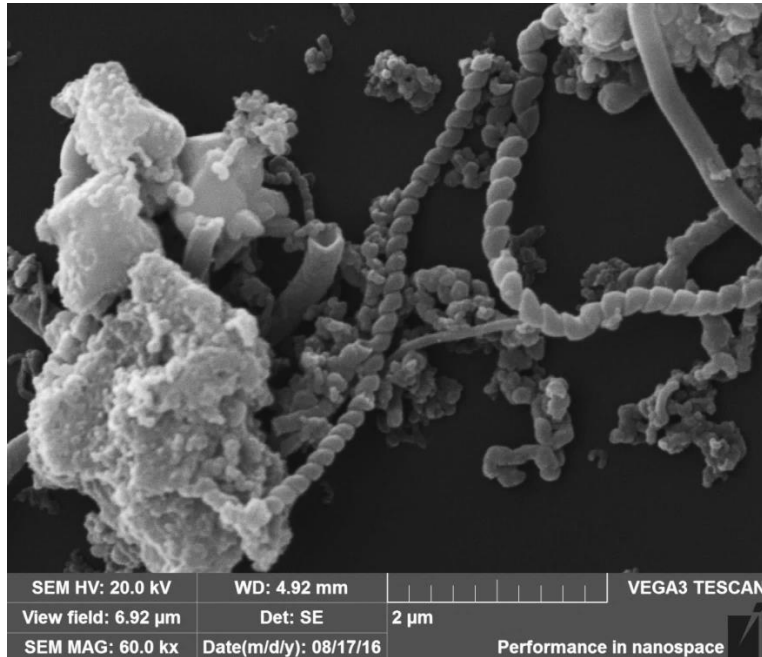


**Fig. 1.** Schematic diagrams of (a) a straight carbon nanotube and (b) a coiled carbon nanotube (CCNT)

## 2. Experimental

### 2.1 The nano-fillers

MWNTs used in the current study were purchased from Shenzhen Nanotech Port Co. Ltd. The outer diameter was 10-20nm while the length was around 5 $\mu$ m. CCNTs were produced by catalytic chemical vapor deposition (CCVD) in Shanghai Maritime University. Scanning electron microscopy (SEM), Tescan Vega3, was used to examine the CCNTs to study their geometry. Figure 2 shows an SEM image of CCNTs. The coil diameter (D) and coil pitch (p) are both around 200nm. The length of each CCNT is around 5 $\mu$ m which is similar to that of the MWNTs used in this study.



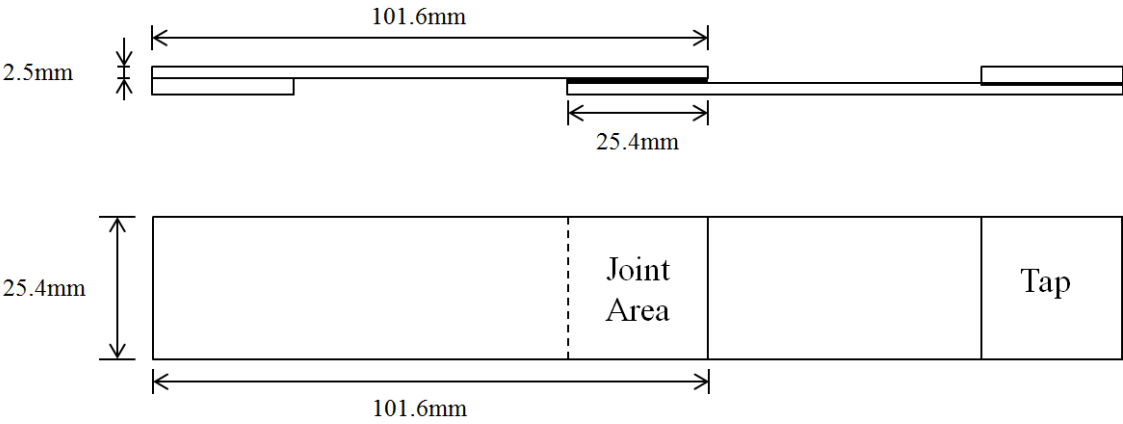
**Fig. 2.** SEM image of CCNTs

## 2.2 Sample preparation

The nanocomposite samples for Vickers hardness test and tensile test were prepared according to the method reported by Lau et al. [4]. Araldite GY251 Epoxy and HY956 Hardener were used as the matrix of all the samples in the current study. All samples contained 1% of carbon nanotubes by weight. They were molded into different shapes

according to the standard ASTM E384 (Vickers Hardness test) and ASTM D638 (type IV) (tensile property test). Pure epoxy samples were also prepared by the same route for comparison.

The samples for lap joint shear test were manufactured according to the standard ASTM D5868 and ASTM D1002. The adherent, woven glass fiber/epoxy composites, was prepared by hand lay-up. 8 layers of glass fiber were used and the composite thickness was 2.5mm. Composite taps were stack onto the adherent to ensure proper loading direction. The joint surfaces were roughened by sand paper, cleaned by ethanol and dried before applying adhesive. The adhesive, with and without nanofillers, was also prepared by the aforementioned method. After applying adhesive to the joint area, 500g weights were placed on top of each specimen to obtain an adhesive thickness of 1mm. All samples were cured at room temperature for 24 hours. Figure 3 shows a schematic diagram of a lap joint shear test sample.



**Fig. 3.** Schematic diagrams of a lap joint shear test sample

Before conducting the hardness, tensile and lap joint shear tests, the samples were conditioned at room temperature (RT, 295K) and cryogenic temperature (CT, 77K). CT

was achieved by immersing the samples into liquid nitrogen inside a liquid nitrogen dewar (Taylor Wharton 4LDB) for 20mins to ensure the temperature was uniform throughout. The samples were transferred to the testing machines and tested immediately after being taken out from the dewar. These pretreatment steps were similar to that reported by Guan et al. [16].

### *2.3 Experiment set-up*

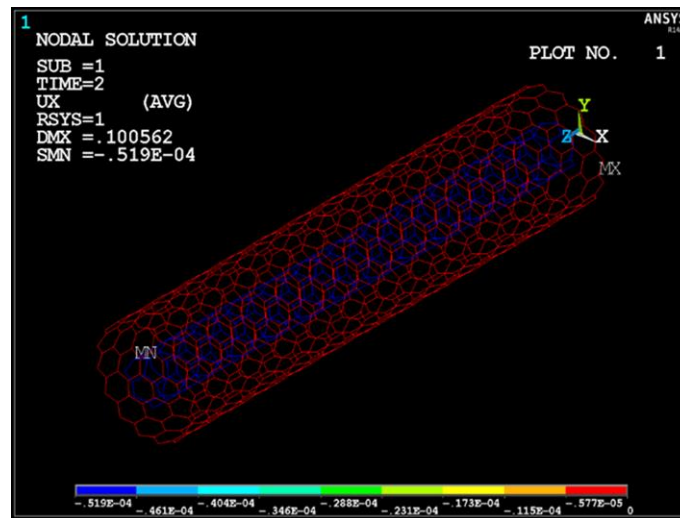
Vickers hardness test was performed by a Vickers hardness tester (Future-tech FM series). In each indentation, a 100gf test force was applied for 15s. 10 indentations were made for each sample to obtain reliable readings. Tensile property test was conducted by MTS Alliance RT/50 with an extensometer (MTS 634.12F-21). This extensometer was especially for cryogenic condition with a service temperature range of -265°C to 65°C. The crosshead speed was set to 2mm/min. Five samples were tested for each group. Lap joint shear test was also conducted by the same tensile test machine with the same crosshead speed. Fives samples were also tested for each group.

## **3 Results and discussion**

### *3.1 Vickers hardness test*

The Vickers hardness test results are shown in Table 1. All samples have greater Vickers hardness readings at CT environment as materials became stiffer. Adding MWNTs and CCNTs to epoxy as nanofillers is found to slightly improve (approximately 4%) the hardness reading at RT as compared with epoxy samples. Yet, in CT, CCNTs performs exceptionally better with a percentage increase in hardness by 36.9%. This indicates that there was a strong interfacial bonding between CCNT and epoxy because of the existence

of mechanical interlocking. The bonding was even better at low temperatures when both CCNTs and epoxy experienced negative thermal expansion. Since the coefficient of thermal expansion (CTE) of epoxy is much greater than that of CCNTs, it tightens the carbon nanotubes at low temperatures by applying an extra clamping force onto the surface of CCNTs. Due to the helical configuration of CCNTs, this clamping force will be more effective in CCNT/epoxy composite than in MWNT/epoxy composite and eventually leads to effective stress transfer from epoxy to CCNTs at CT. In Figure 4, finite element analysis (FEA) shows a negative radial displacement of a MWNT at CT, which further demonstrates the existence of compression on the outmost layer of the nanotubes [17].



**Fig. 4.** Negative radial displacement is shown in FEA for MWNT at CT.

**Table 1** Vickers hardness reading

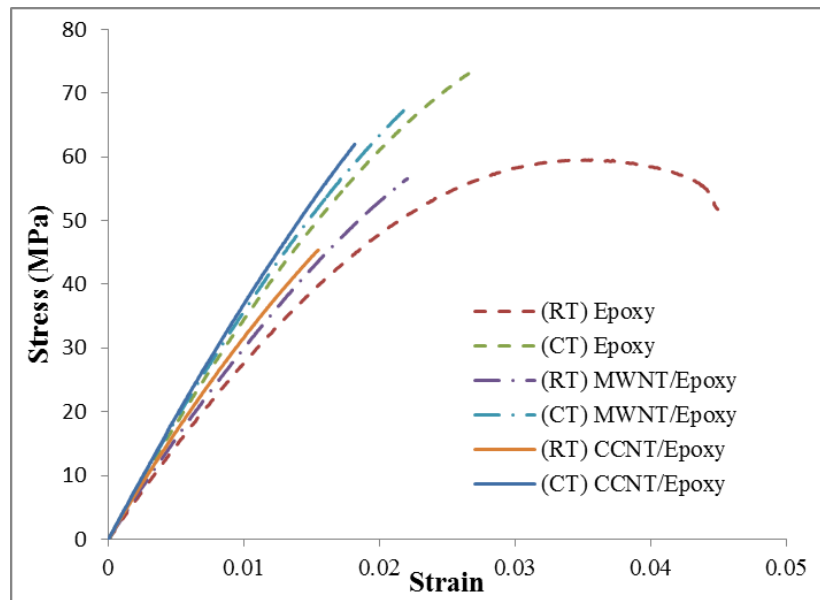
Sample		Mean Vickers no. (HV)	Percentage of improvement*
Room Temperature (295K)	Epoxy	15.7±0.2	0
	MWNT/epoxy	16.3±0.3	3.82
	CCNT/epoxy	16.4±0.1	4.46
Cryogenic Temperature (77K)	Epoxy	19.5±0.5	24.2
	MWNT/epoxy	20.2±0.2	28.7
	CCNT/epoxy	21.5±0.6	36.9



\* Percentage change as compared to (RT) Epoxy

### *3.2 Tensile property test*

Tensile stress-strain curves are plotted for each sample group as shown in Figure 5. The calculated means of the Young's Modulus and tensile strength are tabulated in Table 2. The Young's Modulus and tensile strength of all samples at CT are greater as a result of the increase in stiffness. At both RT and CT conditions, CCNT/epoxy composites show the greatest Young's Modulus but smallest tensile strength. The substantial increase in Young's modulus, 14.7% in RT and 37.6% at CT with respect to epoxy at RT, indicates that the interfacial bonding in CCNT/epoxy was better than that in MWNT/epoxy owing to the existence of clamping force induced as mentioned above. Nevertheless, the tensile strength of epoxy was greatly reduced when CCNTs were added. To understand the cause, the fracture surfaces of MWNT/epoxy and CCNT/epoxy samples conditioned at CT (Figure 6(a) and (b)) were examined by a scanning electron microscope (SEM, Jeol 6490). Numerous protruded MWNTs on the fracture surface show that MWNTs were pulled out during the tensile property test. No CCNT pullout is observed on the fracture surface of CCNT/epoxy composites but fractured CCNTs are seen. Due to the improved interfacial bonding, CCNTs could not be pulled out easily. They experienced shear fracture within the coils instead. In fact, CCNTs are carbon nanotubes with natural topological defects. These defects increase the stress concentration in CCNTs and thus, reduce their strength [18].

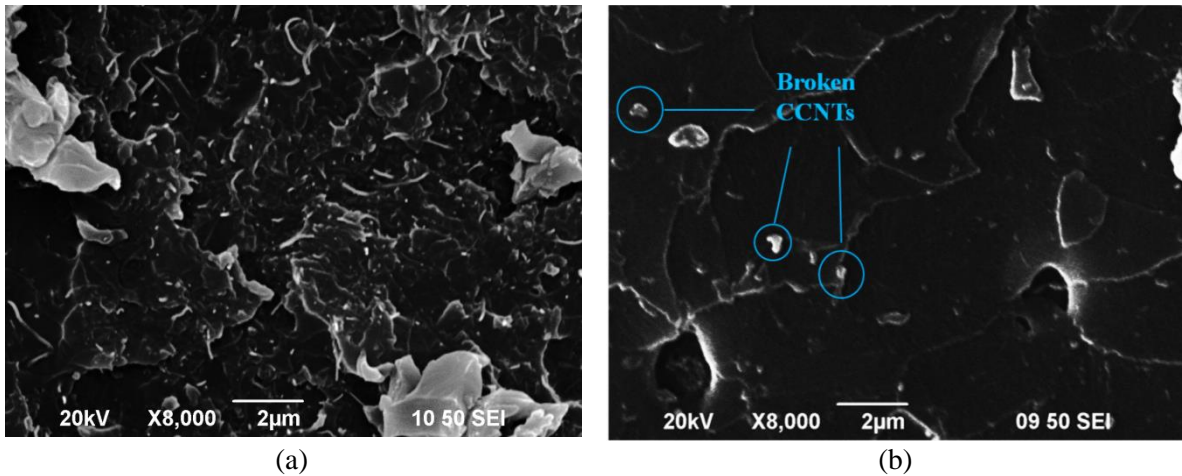


**Fig. 5.** Tensile stress-strain curves of epoxy, MWNT/epoxy, CCNT/epoxy samples at both RT and CT

**Table 2** Results extracted from the tensile property test

Sample	Young's modulus (GPa)		Tensile strength (MPa)	
	Mean	Percentage change*	Mean	Percentage change*
(RT) Epoxy	2.79±0.08	0	61.0±2.3	0
(RT) MWNT/Epoxy	3.02±0.20	8.24	56.7±1.9	-7.05
(RT) CCNT/Epoxy	3.20±0.14	14.7	44.3±4.4	-27.4
(CT) Epoxy	3.42±0.18	22.6	72.3±3.1	18.5
(CT) MWNT/Epoxy	3.71±0.11	33.0	67.1±2.6	10.0
(CT) CCNT/Epoxy	3.84±0.14	37.6	61.0±2.3	0

\* Percentage change as compared to (RT) Epoxy



**Fig. 6.** SEM images of the fracture surface of (a) MWNT/epoxy and (b) CCNT/epoxy samples conditioned at CT

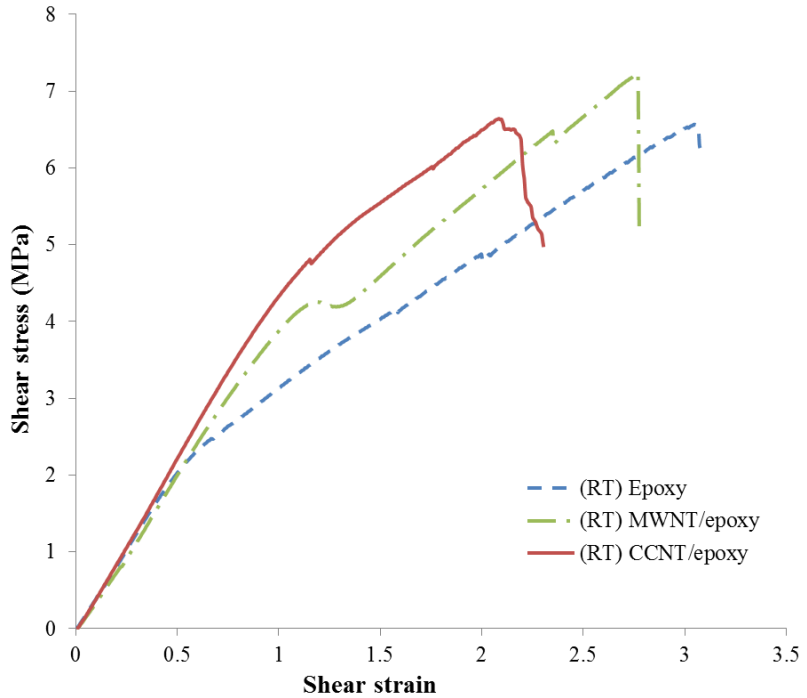
### 3.3 Lap joint shear test

Shear stress-strain curves are plotted to illustrate the lap joint shear test results. Figure 7 shows the curves of the three sample groups at RT while Figure 8 shows their curves at CT. The mean lap joint shear strengths are tabulated in Table 3 and the percentages of improvement, when comparing to pure epoxy in RT, are calculated. At RT, MWNT/epoxy samples have the greatest lap joint shear strength (7.32MPa) while pure epoxy and CCNT/epoxy samples have similar lap joint shear strength (around 6.8MPa). From the shear stress-strain slopes, it can be seen that after adding either MWNTs or CCNTs, the stiffness of epoxy significantly increases. Although the slope of CCNT/epoxy samples is the greatest, they do not show the greatest lap joint shear strength. This can be explained by the fact that the total number of carbon nanotubes in MWNT/epoxy composites was much greater than that in CCNT/epoxy composites for the same weight percentage (1%) [19]. The higher density of MWNTs in samples led to better reinforcement at RT. Matrix cracking and crack propagation were also resisted by the high density of

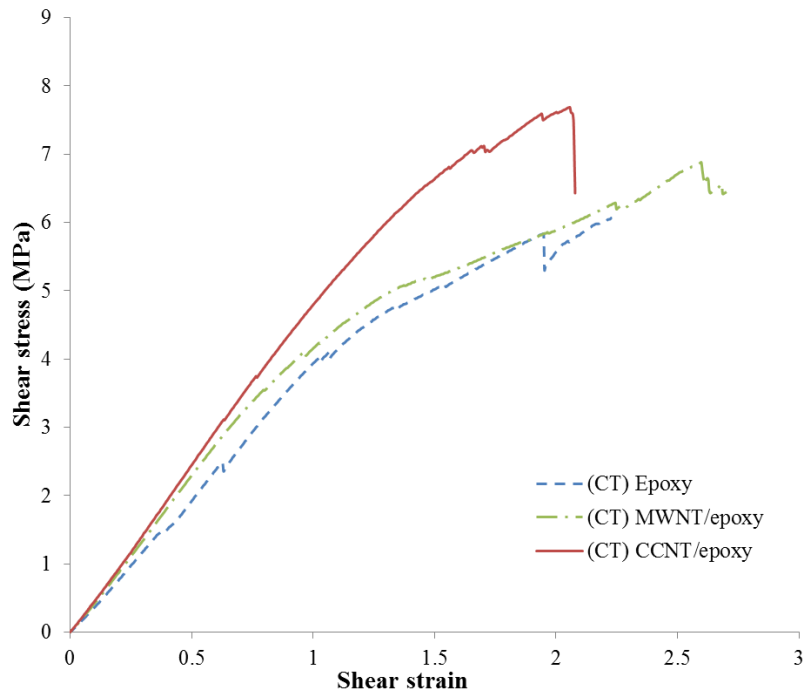
MWNTs. Therefore, MWNT/epoxy composites could withstand a greater load before failure. However, the interface between MWNT and epoxy was atomically smooth due to the perfect hexagonal structure of MWNTs. Stress transfer in MWNT/epoxy was less effective than that in CCNT/epoxy so the stiffness of CCNT/epoxy was slightly greater. Lap joint shear fracture surfaces of the three different samples are shown in Figure 9. Interfacial failure between glass fiber and adhesive is the dominant failure mode. The first layer of woven glass fiber is clearly visible from the fracture surfaces of each sample with very little adhesive remain on it. This indicates that the bonding between adherent and adhesive was poor at RT.

At CT, the performance of CCNT/epoxy composites was outstanding. They show the greatest lap joint shear strength as well as the greatest slope of shear stress-strain curves. That means CCNT/epoxy composites were the stiffest and the toughest among the three groups. It is interesting to see that only CCNT/epoxy samples show an increase in lap joint shear strength at CT (from 6.80MPa in RT to 7.48MPa at CT). On the contrary, the strength of epoxy is greatly reduced from 6.82MPa to 6.44MPa and MWNT/epoxy composite behaves similarly with a reduction in strength from 7.32MPa to 6.92MPa. As mentioned in the results of Vickers hardness and tensile property tests, the special helical configuration of CCNTs led to a much stronger cryogenic clamping force. The curved surface of CCNT allowed the clamping force to be acted in many different directions towards the tube so the reinforcement efficiency was significantly increased. Although the total number CCNTs was smaller than that of MWNTs, the effect of clamping force dominated at CT. The fracture surfaces of pure epoxy and MWNT/epoxy at CT (Figure 10(a)-(b)) are relatively clean. Yet, the fracture surface of CCNT/epoxy (Figure 10(c)) is distinctive. A lot of

CCNT/epoxy adhesive is found remaining on the woven glass fiber fabric which is an evident of the excellent interfacial bonding between adherent and adhesive. Hence, it can be concluded that CCNT/epoxy adhesive was the best candidate in cryogenic lap joint shear test.



**Fig. 7.** Shear stress-strain curves of epoxy, MWNT/epoxy and CCNT/epoxy at RT

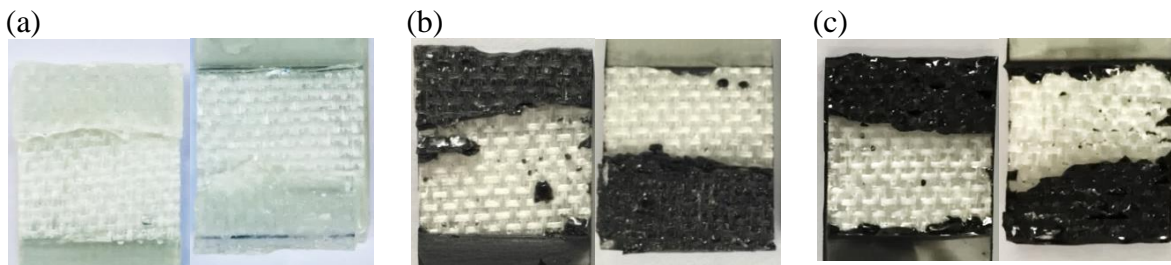


**Fig. 8.** Shear stress-strain curves of epoxy, MWNT/epoxy and CCNT/epoxy at CT

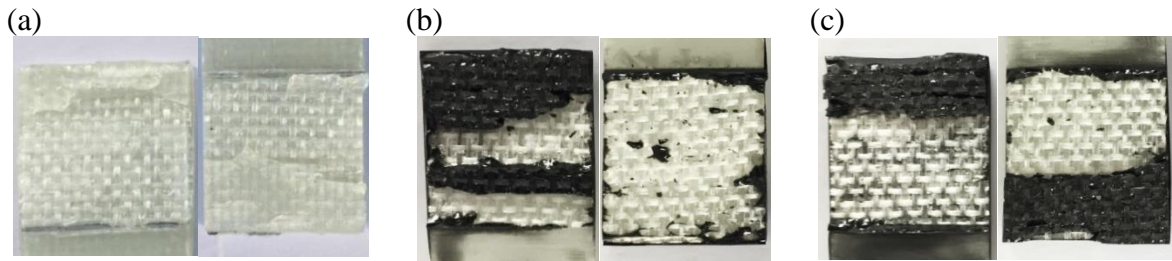
**Table 3** Lap joint shear strength

Sample		Mean lap joint shear strength (MPa)	Percentage of improvement*
Room Temperature (295K)	Epoxy	$6.82 \pm 0.38$	0
	MWNT/epoxy	$7.32 \pm 0.18$	+7.33
	CCNT/epoxy	$6.80 \pm 0.20$	-0.29
Cryogenic Temperature (77K)	Epoxy	$6.44 \pm 0.26$	-5.57
	MWNT/epoxy	$6.92 \pm 0.12$	+1.47
	CCNT/epoxy	$7.48 \pm 0.28$	+9.68

\* Percentage change as compared to (RT) Epoxy



**Fig. 9.** Fracture surfaces of (a) epoxy, (b) MWNT/epoxy and (c) CCNT/epoxy samples at RT



**Fig. 10.** Fracture surfaces of (a) epoxy, (b) MWNT/epoxy and (c) CCNT/epoxy samples at CT

#### 4 Conclusion

In the present study, hardness, tensile and lap joint shear tests were performed to investigate the mechanical behavior of three different types of adhesives, namely pure epoxy, MWNT/epoxy and CCNT/epoxy adhesives. Experimental results revealed that both MWNT/Epoxy and CCNT/Epoxy composites were stiffer at CT as the negative thermal expansion of polymer at low temperature induced a clamping force onto nanotubes. This phenomenon was also proved by finite element analysis (FEA). The performance of CCNT/epoxy adhesive was appealing, especially in the CT environment. They were much stiffer than MWNT/epoxy composite because of the helical configuration of CCNTs which led to a strong interfacial bonding between the CCNT and the epoxy. The lap joint shear strength of CCNT/epoxy adhesive was higher as compared with other types of adhesive. Images captured from the fracture surfaces showed that CCNT/epoxy adhesive had the best bonding with epoxy at CT. Although the tensile strength of CCNT/epoxy composites was relatively lower, CCNT/epoxy adhesive can still be claimed as the best candidate for composite lap joints. It is also worthwhile to note that although the same weight percentage of MWNTs and CCNTs were used in all samples, the number of CCNTs was less than

MWNTs due to the fact that the length of CCNT is much longer than that of a MWNT as a result of its helical configuration.

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