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Property enhancement of polymer-based composites at cryogenic environment by using tailored carbon nanotubes

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ABSTRACT

At high attitude, all polymer-based materials would suffer from degradation at very low temperature in the range between 220 and 77 K (commonly called "at cryogenic environment") and low atmospheric pressure. Within this temperature range, polymer-based composites behave very brittle and many micro-cracks are formed due to differential thermal coefficients of expansion (CTEs) between polymer matrix and high strength reinforcements. An anti-cracking mechanism in the composites is necessary and can be tailored by using nano-particles. Many studies have addressed that the use of single-walled (SWNTs) and multi-walled carbon (MWNTs) nanotubes could enhance the mechanical properties of polymer-based composites. However, interfacial bonding properties are always an issue as it would affect the efficiency and effectiveness of stress transfer in the composites. This paper addresses the viability of using coiled carbon nanotubes (CCNTs) and randomly-oriented nanoclay-supported nanotubes (NSCNTs) to enhance the mechanical properties of epoxy resin at the cryogenic environment.

1. Introduction

In the outer space, composite structures are always subject to cyclic thermal stress in which one surface of the structures facing to the Sun experiences temperature over 393 K while an opposite side is 173 K. Besides, the structures may also suffer from damages due to meteoroid attack, in which many tiny particles left over from the formation of the solar system and they are travelling at very high speed to cause serious impact and abrasion onto the structures. In the new Ares V Cargo Launch Vehicle (for the Mar's mission) designed by National Aeronautics and Space Administration (NASA), the core fuel storage tank will be made by using polymer-based composites and many materials science and engineering research have been conducted to better understand the behavior of these materials at cryogenic condition [1]. In view of all aforementioned problems, composites used at the high attitude (at the level above the Troposphere) should be able to maintain high strength at low temperature environment. Epoxy-based composites are very popular for making advanced composites due to their high strength and chemically-inert properties, making them excellent to be used as aircraft and aerospace structural materials. However, epoxy normally behaves very brittle and therefore, loss of its toughness and impact performance at low temperature. Besides, due to their low energy dissipatability at low temperature, any impact imposed onto its structures would cause delamination and debond at an interface between reinforced fibre and matrix [2].

Carbon nanotubes (CNTs) have been proved as very promising tiny reinforcements to improve the mechanical properties of polymer-based materials due to their ultra-high mechanical strength and aspect ratio. However, for bare CNTs without being chemically reacted with surface's functional groups, bonding is always an issue to allow stress transfer from the polymer matrix to the CNTs. Debonding followed by bare CNT pull-outs were observed by many research groups worldwide. Lu et al. [3,4] have developed coiled CNTs (CCNTs) and also nanoclay-supported nanotubes (NSCNT) (Figs. 1 and 2) and observed that the bonding properties of composites serving at room temperature (RT) were improved due to their unique surface morphologies.

2. Experimental study and discussion

As aforementioned, epoxy-based composites always suffer from failure due to the brittleness and low energy dissipation ability at the cryogenic environment when the composites are subject to dynamic loadings or foreign object impacts. By using straight CNTs somehow may not be appropriated due to their ultra-high strength

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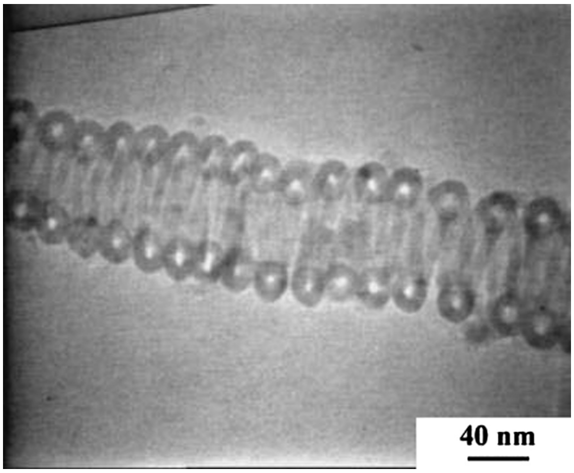

Fig. 1. SEM image of CCNT.

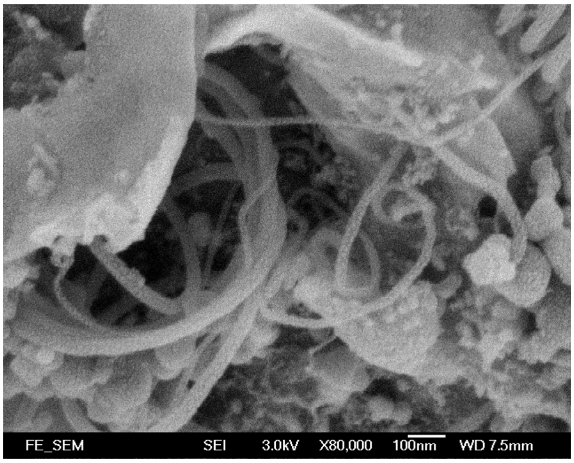

Fig. 2. SEM image of NSCNT.

and poor bonding characteristics between the CNT and matrix. Many studies have shown that pullout of nanotubes happened in polymer-based composites due to poor bonding at the interface. For multi-walled nanotubes (MWNTs), more severe as slipping between inter-walls of the nanotubes exists, which substantially lowers their mechanical strength due to the decrease of effective cross sectional area. To compare the result obtained from MWNT, CCNT and NSCNT reinforced epoxy composites, Table 1 shows that the properties of the composites are enhanced with the use of 2 wt% of CCNTs and NSCNTs as reinforcement at room temperature condition as compared with the one reinforced by 2 wt% MWNTs.

To study the performance of these composites at space environment, CCNTs and NSCNT were therefore used to mix with the epoxy to study their mechanical performance at low temperature (∼93 K). All composite samples were tested immediately after they had been submerged into liquid nitrogen for 15 min. The samples were made in the diameter of 25 mm and 10 mm thick. The fabrication process was followed by the instruction as addressed in [5]. For both CCNT/epoxy and NSCNT/epoxy samples, CCNT and NSCNT were added from 0 up to 3 wt%. Hardness and Young's modulus of CCNT/epoxy samples were measured while only hardness test was conducted for NSCNT/epoxy samples.

Table 1
Comparison of the properties of epoxy reinforced by 2 wt% of MWNTs, CCNTs and NCNTs.

	MWNTs	CCNTs	NCNTs
Micro-hardness	0.26	0.31	0.32
Young's modulus	5	5.9	6.2

Table 2
Mechanical properties of CCNT reinforced epoxy composites at room temperature and 77 K.

Wt% of CCNT	Vicker's hardness			Young's modulus		
	RT	77 K	% increase	RT	77 K	% increase
0	0.23	0.31	35	5.0	7.1	42
1	0.28	0.36	28	5.3	7.5	41
2	0.31	0.38	23	5.9	7.9	34
3	0.35	0.41	17	7	8.9	27

In Table 2, it is found that both Vicker's hardness and Young's modulus of CCNT/epoxy samples increase with increasing the CCNT content at both RT and 77 K environments. The increase of strength has no surprise as the geometry of the CCNTs could enhance the strength and resilience of CCNT/epoxy samples. Spring-like CCNT can induce mechanical interlocking in the samples. Besides, this pattern can also increase the energy absorbability of the samples at both static and dynamic loading conditions. According to the Spring's theory, the energy absorption (E) of a spring subject to a compressive load is equal to the half of spring constant of CCNT (k) times the square of the amount of compression (x) ($E = ½kx^2$). As compared with the straight CNT, CCNT obviously has a relatively low mechanical strength along its coil's direction (i.e. coil's longitudinal axis). However, its coiled geometry can secure the bonding between CCNT and surrounding matrix so as enhance the stiffness and hardness of its composites. From the hardness reading, it also shows that the wear properties can also be improved through the use of CCNT as reinforcement in the epoxy. As a low temperature condition, epoxy experiences thermal contraction which induces high compressive strength toward the surface of CCNT. Thus, high clamping strength is resulted and thereby, better mechanical strength of CCNT/epoxy composites can be achieved.

In Table 3, the NSCNT provides similar property enhancement in the epoxy at both RT and 77 K environments. By growing CNT between clay layers can ensure an exfoliated nanoclay structure

Table 3
Hardness of NSCNT reinforced epoxy composites at room temperature and 77 K.

Wt% of NCNTs	Vicker's hardness		
	RT	77 K	% increase
0	0.23	0.31	34
0.5	0.25	0.38	53
1	0.26	0.41	54
2	0.32	0.39	23
3	0.31	0.48	52

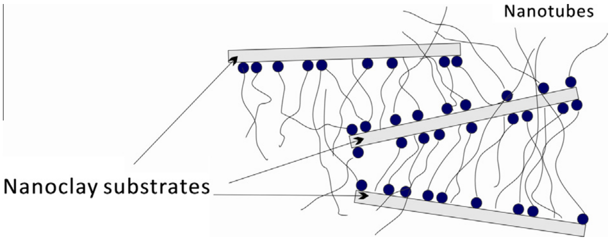

Fig. 3. Schematic of NSCNT (patent: CN 100432009C).

is achieved (Fig. 3). The grown CNTs can also be used as reinforcements for epoxy resin. As NSCNT is a structure combining both exfoliated nanoclay linked by CNTs, agglomeration of NSCNTs would not normally happen which provides the resultant composites with good dispersion properties, and thereby high mechanical strength. As cryogenic environment, although the hardness of a pristine epoxy sample is enhanced, the use of NSCNT can maintain better strength and keep the hardness 30% more as compared with the samples measured at RT condition. This result was firstly governed by the contraction of epoxy which additionally generated strong clamping forces to the NSCNTs, and thus enhanced the bonding strength between NSCNT and epoxy matrix. The uniform dispersion properties of NSCNTs also provided homogenous mechanical strength of the whole NSCNT/epoxy samples. Theoretically, these nano-reinforcements not only enhance the mechanical properties of polymer-based composites, but also minimize their crack-formation.

3. Conclusion

As a conclusion, the CCNTs and NSCNTs can enhance the strength of polymer-based composites due to their tailored geometrical patterns. Although few research works have reported that the use of straight-type of CNTs can enhance the strength of polymers, agglomeration is still an issue when their content exceeds 2 wt%. Compared with straight-type of CNTs, CCNT and NSCNT can compensate many problems arising from poor interfacial bonding properties, brittleness of polymers and agglomeration of CNTs.

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