

A Concise Account on the Properties of CNT-Reinforced Epoxy Composites based on some Select References

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ABSTRACT

Recently it has been reported in the technical literature that carbon nanotubes (CNTs) have distinct effects on thermal, mechanical and electric properties of epoxy resins. Compared to single-walled nanotubes (SWCNT), multi-walled nanotubes (MWCNT) apparently show greater improvements. The maximum aspect ratio (L/D) of CNT is reportedly as high as 138,000,000. In addition, the carbon nanotubes when treated with surface modifier to generate functional groups on their surface can afford to provide better improvement of the properties of the epoxy based CNT-particulate composite system. There are a number of factors that can influence the properties of epoxy-CNT systems. This paper examined the technical contents from selective references and made an attempt to highlight the general understanding of the properties and performance of epoxy – CNT particulate composite systems.

Keywords: Carbon nanotubes, mechanical properties, aspect ratio, agglomeration

1. INTRODUCTION

A composite material generally comprises a combination of two or more identifiable components existing in a product to deliver desired properties such as mechanical strength, adhesive property, spatial stability and the like^{1,2}. On the other hand, nanocomposite in a broader sense, is considered as a system comprising two or more constituent materials in which each constituent material not only has significantly different physical or chemical properties but they also remain distinctly separated in the system where at least one of them must remain in its nanoscopic level^{3,4}.

Earlier, researchers studied reinforcement of various micron-size particulate phases such as rubber⁵, micro- Al_2O_3 fibre and micro- ZrO_2 powder to improve the properties of epoxy resins⁶. It is undeniable that nano-particles could generate increasingly greater importance in science and engineering compared to micro particles. Among different kinds of nano-particles, carbon nanotubes (CNTs) are a novel kind of additive which has a huge potential in reinforcing epoxy resins. Over the past decade, CNTs and CNT reinforced composites have developed rapidly - not only for laboratory work, but also in large-scale industrial product and commercial applications⁷. It is worth mentioning that the global retail price of carbon fibre has increased dramatically with the increasing requirement in aircraft industry and architecture⁸. So it is possible that CNTs as a small quantity added filler can rapidly reinforce the epoxy matrices for making particulate composites with superior mechanical, thermal as well as electrical properties in an attractive manner.

2. MATERIALS AND METHODS

2.1 Resin and Conventional Particulate Reinforcement

Diglycidyl ether of bisphenol-A (DGEBA) has been in large-scale production for several decades and is readily available in the market. Hence most of the research with epoxy is based on this type of resin for various purposes⁹.

3. CARBON NANOTUBES

CNTs are allotropic forms of carbon containing a cylindrical structure. The most significant parameter for CNTs being the L/D ratio (length to diameter ratio) what is also known as aspect ratio which can be achieved to as high as 132,000,000/1¹⁰; and interestingly it is worthy to note that this is also the highest L/D value among other materials. CNTs possess outstanding mechanical properties as understood from the report of modulus of around 1 TPa¹¹ and tensile strength in the range of 11 GPa - 63 GPa¹² which make them to act as reinforce in epoxy matrix based nanocomposites provided the dispersion of CNTs can be done properly. Owing to their excellent influence on the mechanical, electrical and thermo properties, CNTs find applications as additives to several materials to reinforce their properties¹³. Coto¹⁴, *et al.* reported that the length of the models of CNTs is a key factor that influences the interfacial shear strength (IFSS) values; and that the shear modulus of the epoxy matrix in the vicinity of the SWCNT is higher than the value for the bulk by a factor of 10. However, a decreasing trend was observed on the IFSS when the radius increased. As reported in the range 0.47 nm

- 1.644 nm the decrease of IFSS is ca. 24%. The chirality of the SWCNTs has a small effect on the IFSS with armchair SWCNTs showing a bit higher trends than in the case of zigzag nanotubes¹⁴.

Typically, multi-walled CNTs display a greater improvement on epoxy resin than single-walled CNTs. Furthermore, the surface modified CNTs contain functional groups on the surface, which can help dispersing and bonding to the polymer matrix, thus the additive/matrix system can achieve improved interaction to ensure better distribution of additives at nano scale level¹⁵ as observed when MWCNT weight percentage of 0%, 1%, 2% and 3% added into Araldite-420 (DGEBA epoxy composite) and Sikadur-30 (epoxy composite) system¹⁶. The results on strength and elastic modulus are shown in Table 1. According to the data, for Araldite-420, a rather small increase in modulus and strength was achieved at around 1 to 2 % CNT. For Sikadur-30, the modulus achieved a very good improvement to the tune of 33 % increase at 1 % addition of CNT, whilst tensile strength was hardly affected. Such low influence on tensile properties implicates the longitudinal fibre like characteristics of CNT.

Table 1. Multi-walled CNTs reinforce epoxy resin¹⁶

Epoxy based nanocomposite	MWCNTs (wt %)	Strength (MPa)	Elastic modulus (GPa)
Araldite-420	0	26.7	1.87
	1	27.9	2.13
	2	30.9	2.1
	3	27.2	1.92
Sikadur-30	0	22.8	9.29
	1	23.5	12.37
	2	17.7	10.84

3.1 Effect of Surface Coating on CNTs

Wei-Jen Chen¹⁴ et al. used vinyltriethoxysilane modified CNTs and unmodified CNT, and studied the resulting mechanical properties of composites at room temperature and also at elevated temperature 85 °C under 85% relative humidity (RH)¹⁶. Fig. 1 indicates that the optimal content of CNT-filler was 0.75 phr (parts per hundreds of resin). At room temperature, the maximum tensile strength and flexural strength of epoxy resin were almost unaffected with unmodified CNTs whereas with modified CNTs they increased by 11% and 21% respectively. According to Fig. 2, under 85 °C having 85% relative humidity (RH) condition, the tensile strength of pure epoxy resin, unmodified and modified epoxy/CNT particulate composites decreased by 24 %, 22% and 30% respectively. Although the modified CNT/epoxy system has showed a comparatively larger decrease in properties as a function of increasing temperature, it is still obvious that this system had better mechanical properties. It is worth noting that 85 °C is close to the glass transition temperature (T_g) of cured DGEBA epoxy resins used in structural applications. In a subsequent study, the team¹⁷ reported another study, with the use of titanium (IV) n-butoxide as a modifier, where it was observed

an obvious difference between modified-CNTs and unmodified-CNTs. According to Figs. 3 and 4, comparing the test results of unmodified and modified CNT-added nanocomposites, it is clear that the tensile and flexural strengths of modified CNT/epoxy system are better than that of unmodified CNT/epoxy system at room temperature as well as at elevated temperatures 85 °C and 175 °C. On the other hand, the electrical conductivity of epoxy resin (Fig. 3) is nearly doubled on addition of CNTs, and the modified CNTs still had more positive effect on that.

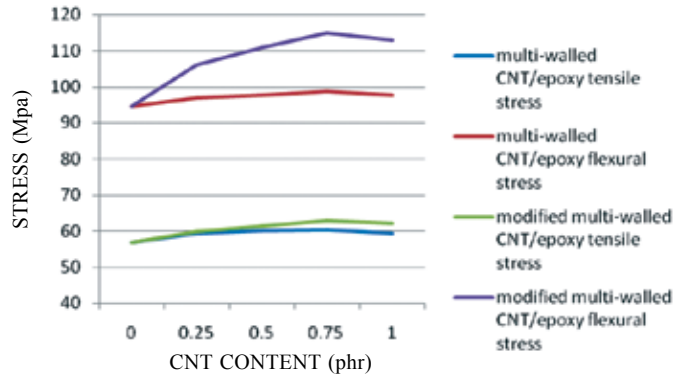


Figure 1. Tensile and flexural strength of epoxy resin reinforced by CNTs at room temperature¹³.

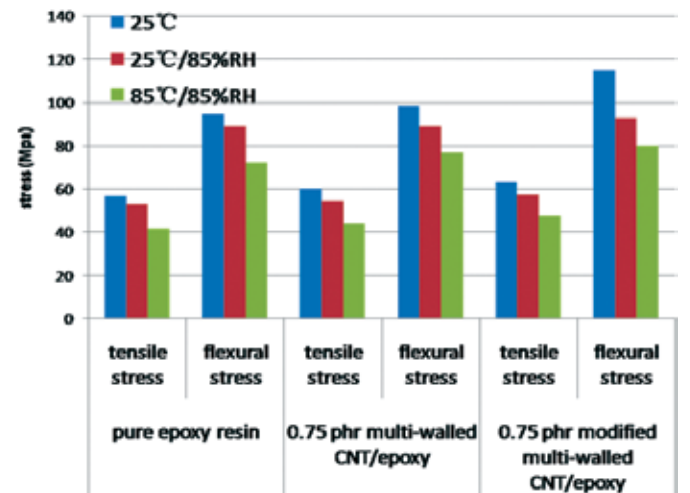


Figure 2. Tensile and flexural strength of epoxy resin reinforced by CNTs affected by temperature and humidity¹³.

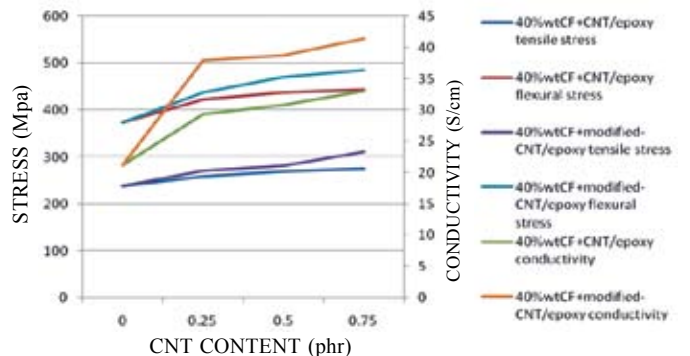


Figure 3. Mechanical properties and electrical conductivity of epoxy resin reinforced by CNTs¹³.

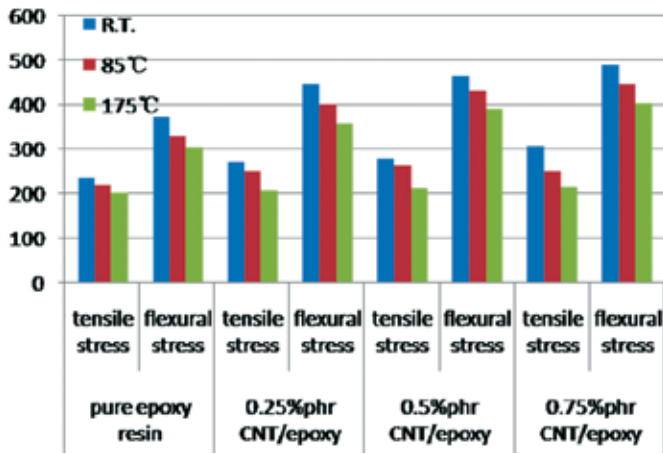


Figure 4. Tensile and flexural strength of epoxy resin reinforced by CNTs under different temperature¹³.

Nadler¹⁸, *et al.* used Disperbyk 2070 (a commercial additive), DY070 (a proton transfer catalyst), PVB (polyvinyl butyral) and OH⁻ treated CNTs for reinforcement in epoxy resin. According to Fig. 5, the original CNTs showed a negative effect on the elastic properties of epoxy resin. Secondly, the extent of CNTs in epoxy resin did not show a linear relationship to property improvement. In some cases, the system with 1.0 wt% of CNTs displayed worse properties than the composites with 0.5 wt% of CNTs which may be attributed to the problem of agglomeration of CNTs. Finally, in their research, the epoxy resin treated by DY070 (a proton transfer catalyst) and added with 0.5 wt% of PVB (polyvinyl butyral)-CNTs displayed highest elastic properties. The elastic modulus and flexural strength were each increased by about 30 %.

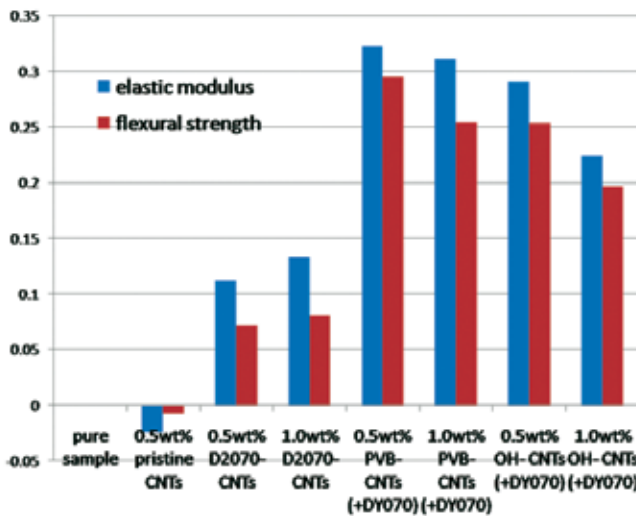


Figure 5. The elastic properties of epoxy resin reinforced by different CNTs¹⁸.

Kim¹⁹, *et al.* carried out a simulation of the mechanical properties of epoxy-CNT composites and reported the comparative view through experimental results vis-a-vis their simulation. According to their data, summarized in Fig 6, when the CNT content was lower than 1 wt%, the simulation came to a good agreement with the experimental result. However, the experimental results of the epoxy-CNT composite at higher CNT content were much lower than the simulation. At high

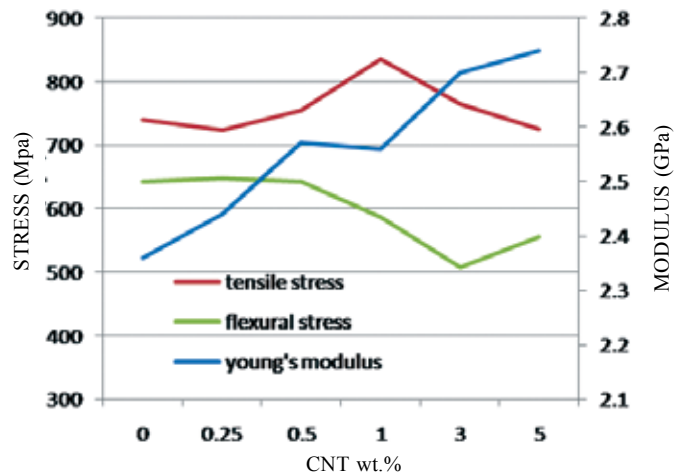


Figure 6. The experimental result of mechanical properties of epoxy-CNT composites¹⁹.

CNT content, the CNTs tend to aggregate which had a negative effect on the bonding sites between CNTs and epoxy matrix and finally generated the defects in the composite sample. The defects can affect the mechanical properties of the composites where the optimal content of CNT was 1wt% as reported in their study.

CNTs can furthermore enhance the thermal properties of epoxy resins. A research report by Balakrishnan and Saha²⁰ indicated a 16% increase in thermal conductivity at 0.4 wt% CNT. By studying the fracture surface, it was found that the CNT agglomeration increased with increasing CNT weight content.

4. COMPARISON BETWEEN CNTS AND OTHER NANO-FILLERS

Owing to their superior electrical properties, CNTs display an obvious reinforcement in electrical conductivity of epoxy resin compared to other nano-fillers. Li and Zhang²¹ studied CNTs reinforced epoxy resin and nano-SiO₂ reinforced epoxy resin. As seen in Fig. 7, the conductivity decreased with

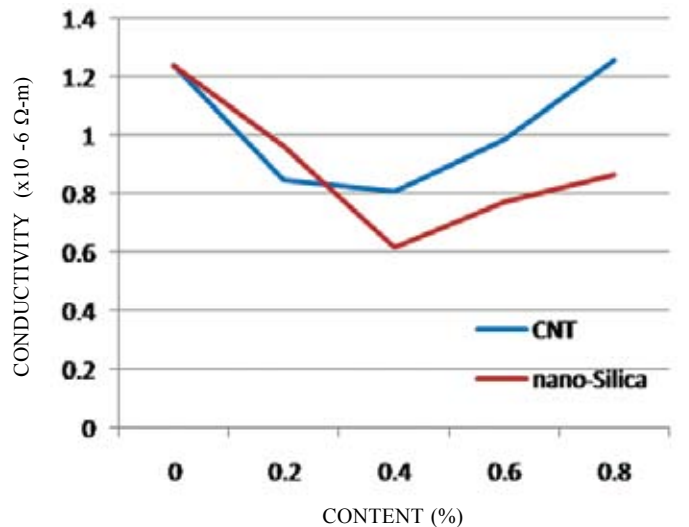


Figure 7. Conductivity of epoxy resin filled by CNTs and nano-SiO₂²¹.

the addition of nano-fillers until 0.4 wt%. After that, when the content of nano-filler exceeded 0.4 wt%, conductivity continued to increase and the CNTs reinforced epoxy resin showed a better conductivity than nano-SiO₂ filled epoxy resin.

CNTs display a greater reinforcement in conductivity than by carbon black²². The data in Fig. 8 indicates that epoxy resin containing carbon black show a lower conductivity than epoxies with CNTs.

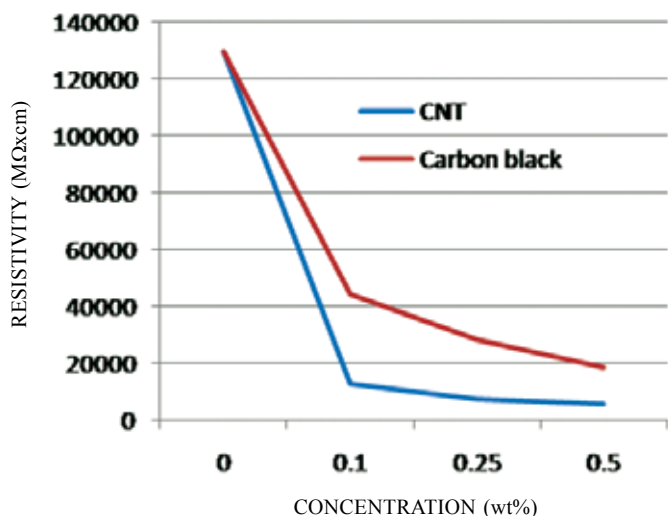


Figure 8. Conductivity of epoxy resin filled by CNTs and carbon black²².

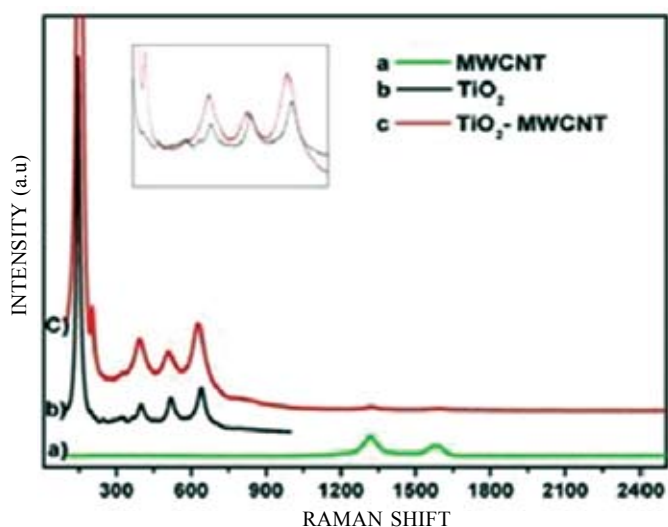


Figure 9. Raman spectrum²⁴ of (a) Multiwalled Carbon nanotubes, MWCNTs, (b) Titanium dioxide, TiO₂ (c) Multiwalled carbonnanotube) nanocomposites (TiO₂-MWCNT)²⁴.

SWCNT as a semiconductor but it can also be used to activate photo oxidative process like TiO₂. While adding SWCNTs into epoxy resin, the epoxy-CNT system can act as a photo-catalyst for both oxidative and reductive reactions²³. In their study, the epoxy film with SWCNT was prepared by UV inducing polymerization. The materials with 0.1 wt% and 0.3 wt% displayed similar catalyst efficiency and the photo catalyst performance was evaluated in absorbed state, aqueous

Table 2. Photo catalytic performance of the films with TiO₂ and SWCNT

Chemicals	Catalyst		K (h ⁻¹)
	Type	Content	
Methylene blue	TiO ₂	0.5g/L	2.52
	CNT	0.1wt%	1.50
		0.3wt%	1.50
Phenol	TiO ₂	0.5g/L	0.029
	CNT	0.1wt%	0.019
3,5-Dichlorophenol	CNT	0.1wt%	0.017

phase and gas phase. Table 2 shows the results of this novel catalyst compared with the traditional TiO₂ catalyst. The rate constant K indicates the catalyst efficiency of the materials - as K increases, the efficiency goes up.

TiO₂ was reportedly incorporated in functionalized MWCNT to prepare using hydrothermal route; and the nanocomposite product showed significant improvement in photocatalytic activity to degrade organic dye like methyl orange (MO)²⁴. Raman spectroscopic information supports the formation of anatase phase in such TiO₂/MWCNT nanocomposites.

Figure 10 indicates the influence of the reinforcement of epoxy by CNTs. For example, considering about tensile strength, we can see a blue bar on the left, which indicates the 100% tensile strength of pure epoxy; the bar on the right with green on the top and red at bottom indicates the tensile strength of CNTs-reinforced epoxy composites. The green region in the bar indicates the improvement of the composites compared with pure epoxy¹⁶⁻¹⁹. By adding CNTs, the tensile strength of the CNT/epoxy composite can achieve improvement from 3 to 30% (Fig. 10). The minimum improvement of the composite is about 3% (the bottom line of green area), and the maximum improvement is nearly 30% (the top line of green area). The same applies re flexural stress and elastic modulus; the green area means the reinforcement of the composite.

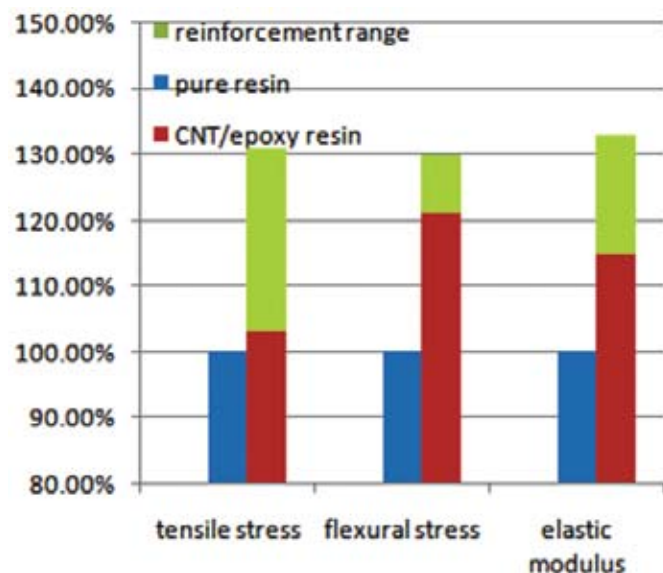


Figure 10. The expected improvement in mechanical properties of CNT/epoxy composites¹⁶⁻¹⁹.

5. CONCLUSIONS

- (a) The CNT has great effects on mechanical, electrical and thermal properties of epoxy composites. The highest concentration of CNT tried so far in epoxy is reportedly maximum to the tune of 2 % by wt.
- (b) Due to more active groups on the surface, surface modified CNTs generally display a greater reinforcement in mechanical properties for the particulate composite materials than the corresponding unmodified CNTs.
- (c) With the effect of CNTs, the elastic modulus of the composite can display an increment between 15% and 30% (Fig. 10).
- (d) By adding CNTs, the tensile strength of the CNT/epoxy composite can achieve improvement from 3% to 30% (Fig. 10).
- (e) Flexural stress of the composite of epoxy resin reinforced with CNTs can at least increase by approximately 21% and can reach near 30% in some cases (Fig. 10).
- (f) The electrical properties of epoxy resin are also influenced greatly with the addition of CNTs.

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