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How carbon nanotubes affect the cure kinetics and glass transition temperature of their epoxy composites? – A review

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Abstract. Motivated by the widespread and contradictory results regarding the glass transition temperature of carbon nanotube (CNT)/epoxy composites, we reviewed and analyzed the literature results dealing with the effect of unmodified multiwall carbon nanotubes (MWNT) on the cure behaviour of an epoxy resin (as a possible source of this discrepancy). The aim of this work was to clarify the effective role of unmodified multiwall carbon nanotubes on the cure kinetics and glass transition temperature (T_g) of their epoxy composites. It was found that various authors reported an acceleration effect of CNT. The cure reaction was promoted in its early stage which may be due to the catalyst particles present in the CNT raw material. While SWNT may lead to a decrease of T_g due to their bundling tendency, results reported for MWNT suggested an increased or unchanged T_g of the composites. The present status of the literature does not allow to isolate the effect of MWNT on the T_g due to the lack of a study providing essential information such as CNT purity, glass transition temperature along with the corresponding cure degree.

Keywords: nanocomposites, carbon nanotubes, cure kinetics, glass transition temperature

1. Introduction

The use of carbon nanotubes (CNT) as nanofillers in polymer matrices is one of their most promising applications, especially regarding epoxy resin. Multiple enhanced properties at low loadings are the major advantage of CNT over other fillers. Thanks to its good mechanical properties, chemical resistance and thermal stability, epoxy resin is a widely used polymer as adhesive, coating or as matrix in structural composites. The choice of a given application for epoxy is often based on the glass transition temperature, noted as T_g . This is the temperature at which the mechanical properties of a polymer drop and corresponds to a second-order phase transition at which the polymer goes from a

glassy to a rubbery behaviour as the temperature increases. The T_g is closely linked to the thermo-mechanical stability, it is thus the property that dictates the potential application of a given epoxy resin as a function of the service temperature range envisioned. In the case of epoxy resin, the T_g is a function of the molecular architecture and depends on different parameter such as the functionality of the epoxy and of the hardener, the conversion degree, the curing cycle, etc. Due to the close relation between cure behaviour, glass transition temperature, mechanical properties and potential application of an epoxy resin, it is primordial to study the effect of CNT on the cure behaviour of the epoxy resin matrix.

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2. Cure kinetics

In the literature, different works were dedicated to the determination of the effect of CNT on the cure kinetics of an epoxy resin. Puglia *et al.* [1] claimed an acceleration effect of single wall carbon nanotubes (SWNT) on the cure reaction of the DGEBA/DETA epoxy system studied with dynamic and isothermal DSC. In that work, the decrease of the peak temperature (that is the temperature at the heat flow peak) in dynamic scans and the decrease of the time at heat flow peak in isothermal scans were taken as the proof of the acceleration in the early stage of the cure process. The presence of amine functional groups ($-NH_2$) on the surface of the SWNT that may react with the epoxy ring was the origin of the modification of the cure behaviour as shown in a paper from the same group presenting additional data on the same samples [2]. Xie *et al.* [3] also reported an acceleration effect in the case of multiwall carbon nanotubes (MWNT) for the TGDDM/DDS epoxy system using isothermal DSC. The higher initial reaction rate of the composites compared to the unfilled resin, the decrease of the time at maximum reaction rate and of the activation energy with increasing MWNT content were the indication of the acceleration effect. Evidence of the presence of hydroxyl groups ($-OH$) on the surface of the MWNT by FTIR spectroscopy which have a catalytic effect on epoxy ring opening was in that case the source of the modified cure. The last stage of the cure remained unaffected by MWNT. The same group reported [4] on the effect of carbon nanofibres (CNF) on the cure behaviour of the same epoxy system. They found a very small acceleration effect of CNF in the early stage of the reaction suggested by the decrease of the activation energy with an increase of the CNF content. On the other hand, the CNF hinders the reaction after that step. Tao *et al.* [5] studied the effect of SWNT in the DGEBA/DETDA epoxy system and observed a decrease of the onset temperature in dynamic scans and a decrease of the time at maximum reaction in isothermal scans. Contrary to previous studies, they found that the peak temperature remained unaffected by the presence of SWNT. The origin of the acceleration effect cannot be clearly determined in their work due to the absence of surface characterization of the SWNT material. The high percentage of catalyst particles in the SWNT raw material may

be a plausible source of the early cure initiation. In these investigations [1–5], it is believed that the modification of the cure behaviour in its early stage can be attributed to surface functional groups on CNT or catalyst particles. Wu *et al.* [6] studied the effect of three different carbon fillers (carbon fiber, carbon nanofiber and carbon black) on the cure reaction of the DGEBA/TETA epoxy system. They reported an increase of the total heat of reaction and a decrease of the temperature at the heat flow peak for all fillers. By comparing the effect of different pre-treatments of the carbon fibers, they explained the increase in the total heat of reaction as a result of the presence of surface functional groups on the fillers. The authors found that the acceleration effect, that is the decrease of the peak temperature, was closely related to the specific surface area (SSA) of the filler, in view of the proportionality between the SSA and the peak temperature drop (the higher the SSA, the higher the temperature drop). It should be noted that in that work, the fillers were manually dispersed in the resin and the filler content was high (around 20 wt%). The authors did not give indication on the dispersion state of the fillers. Their samples may not have been homogeneous at the micro-scale and should have mainly contained aggregates of the filler, especially in the case of CNF which are highly entangled and stick to each other by van der Waals interactions. Bae *et al.* [7] investigated the effect of CNT and carbon black (CB) on the cure reaction of liquid crystalline epoxy (DGE-DHAMS/sulfanilamide). In contradiction with all other studies, these authors reported a retardation effect of CNT, indicated by the slight increase of the temperature at maximum reaction. In their study, the presence of CNT did not have a significant effect on the total heat of reaction (except the expected decrease due to the lower weight fraction of epoxy in the composite) nor on the activation energy compared to unfilled epoxy. The authors noted that ΔH_0 was higher with CNT than with CB. The oxidation treatment decreased the activation energy in both cases.

3. Glass transition temperature

Regarding the T_g , the data of Puglia *et al.* [1] revealed higher curing degree of the composites compared to unfilled resin which may correspond

to a higher T_g . The T_g was not measured in their work. Similarly, Xie *et al.* [3] did not measure the T_g of their samples but their data revealed a higher curing degree of the composites for curing temperatures below 200°C. For higher curing temperatures, the curing degree of the epoxy was higher. The same group [4] found that CNF did not have any effect on the final curing degree. Tao *et al.* [5] measured the T_g of their samples after 2, 5 and 24 hours of isothermal curing and found that the T_g of the composites was always lower than the unfilled epoxy. They attributed this to the lower curing degree of the composites as indicated by their lower isothermal heat of reaction but the curing degree was not explicitly calculated.

The literature dedicated to CNT/epoxy composites is extremely prolific. Given the importance of the glass transition temperature in view of its link with mechanical properties, it is amazing to see that even the last publications on the subject still do not always provide this information. In the case of mechanical properties, for comparison purpose, it is primordial to have the T_g provided along with the curing degree of the samples. Most of the studies only claimed complete cure of the samples without further investigation. An analysis of the results from the literature dedicated to unmodified CNT in epoxy should lead to valuable conclusions. Any variations in the T_g may be explained by some size effect or physical interactions with polymer chains close to CNT surface, the unmodified nature of the filler should eliminate the need of explanations involving chemical effects. We thus compiled and analyzed data values of glass transition temperature of CNT/epoxy composites from different articles. The CNT used in these works were unmodified

MWNT [8–16] or unmodified SWNT [5, 17–22]. The data relative to preparation method of the composites, glass transition temperature and its measurement method are summarized in Table 1. The relative difference of T_g between CNT filled epoxy and the unfilled epoxy as a function of the T_g of the unfilled resin or the weight fraction of CNT is plotted respectively in Figure 1a and 1b. In the graphs, the case of SWNT as filler was differentiated from that of MWNT due to the tendency of SWNT to form close-packed bundles with triangular arrangement in the section. It can be noticed that most of the data for SWNT showed a decrease of T_g compared to the unfilled resin which may be a consequence of this bundling tendency. Moniruzzaman *et al.* [21] developed a dispersion method allowing to debundle SWNT and found that T_g was unaffected by the presence of SWNT. The data for MWNT was more scattered and no clear trend appeared. The difficulty in analyzing these data resided primarily in the fact that the final cure degree was not provided. Liao *et al.* [22] showed that the use of solvent or surfactant in the fabrication process can lead to a large decrease of the T_g . Even after a relatively long process of evaporation (one hour heating + 4 hours degassing), Lau *et al.* [23] reported that remaining residual traces of the solvent (acetone, ethanol and DMF) used in the dispersion process of SWNT in the epoxy resin led to a decrease of the mechanical properties of the SWNT/epoxy composites. They noticed that these detrimental effects increased with the boiling point of the solvent. We plotted again the data for MWNT and made the distinction between experiments in which solvent was used or not in the dispersion process of MWNT in the resin (Figure 2a

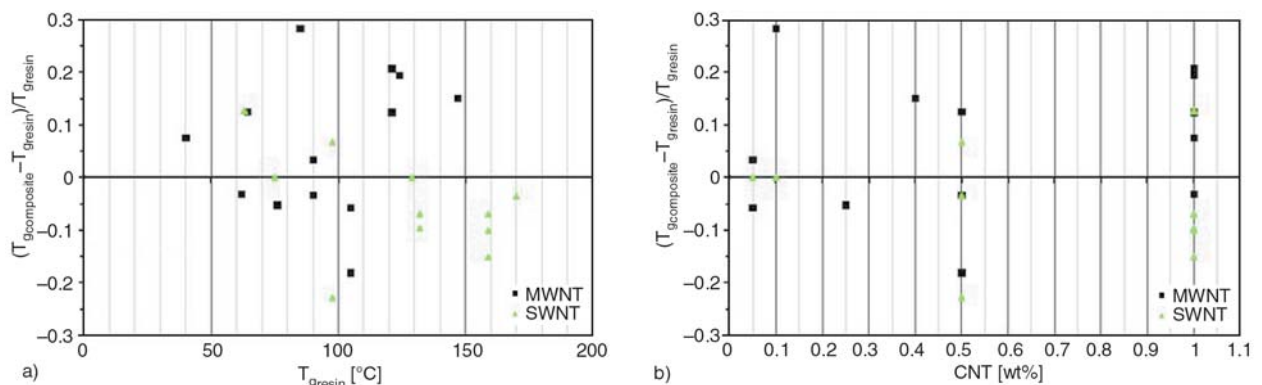


Figure 1. Relative difference of T_g of CNT composites compared to unfilled resin as a function of a) T_g of the unfilled resin b) CNT weight percentage (data taken from the literature)

Table 1. Compilation of data from the literature on CNT/epoxy composites (preparation method and glass transition temperature and measurement method, CNT type and aspect ratio when available)

Reference	CNT dispersion process	T _g Measure method	wt% CNT	CNT type	CNT aspect ratio (length/diameter)	T _{g, resin} [°C]	ΔT = T _{g, composite} – T _{g, resin} [°C]
Tao <i>et al.</i> [5]	Grinding/acetone	DSC	1.0	Short SWNT	417	159.0	–24.0
				HiPCO SWNT	–		–11.0
				SWNT/DWNT	–		–16.0
Zhou <i>et al.</i> [8]	USP	DMA	0.4	MWNT	150	147.0	22.0
Ganguli <i>et al.</i> [9]	Shear mixing/USP	DMA	1.0	MWNT	625	124.0	24.0
Ganguli <i>et al.</i> [10]	High speed mixing	DMA	0.1	MWNT	125	85.0	24.0
Shen <i>et al.</i> [11]	High speed stirring/USP	DSC	1.0	MWNT	1750	62.0	–2.0
				MWNT-CONH	–		–19.0
Tseng <i>et al.</i> [12]	Shear mixing/USP	DSC	1.0	MWNT	–	40.0	3.0
				Plasma maleic anhydride-grafted MWNT	–		10.0
Gojny <i>et al.</i> [13]	USP	DMA	0.5	MWNT	3333	64.5	8.0
				MWNT-NH ₂	3333		14.0
Shen <i>et al.</i> [14]	High speed stirring/USP	DSC	0.25	MWNT	1750	76.0	–4.0
				Diaminodiphenyl methane-MWNT	–		–8.0
				Diaminodicyclohexyl methane-MWNT	–		7.0
Hernandez-Perez <i>et al.</i> [15]	USP/ethanol/stirring	DMA	1.0	MWNT	50	121.0	15.0
				MWNT	857		25.0
Fidelus <i>et al.</i> [16]	Tip/Bath USP/THF	DMA	0.5	MWNT	85	90.0	1.0
	Tip/Bath USP/surfactant	DMA	0.5	SWNT	1000		2.0
	Tip/Bath USP/THF	DMA	0.5	MWNT	85	105.0	–15.0
	Tip/Bath USP/surfactant	DMA	0.5	SWNT	1000		–2.0
Gong <i>et al.</i> [17]	Stirring	DMA	1.0	MWNT	–	63.0	9.0
	Stirring/acetone/surfactant						25.0
Wang <i>et al.</i> [18]	USP/acetone	DMA	0.5	SWNT	–	170.0	–6.0
				SWNT-NH ₂	–		–11.0
Wang <i>et al.</i> [19]	USP/acetone	TMA	1.0	SWNT	500	132.0	–12.7
				Chopped SWNT	–		–9.1
				Oxidized SWNT	–		–2.4
				Gum Arabic wrapped SWNT	–		–21.4
Valentini <i>et al.</i> [20]	USP	DMA	0.1	SWNT	357	75.0	0.0
				Butylamine-SWNT	–		10.0
Moniruzzaman <i>et al.</i> [21]	USP/DMF/high shear mixer	DSC	0.05	SWNT	–	129.0	0.0
Liao <i>et al.</i> [22]	Surfactant/acetone/manual stirring	DMA	0.5	SWNT	–	97.6	–23.6
	Bath/tip USP						6.6
	Tip USP/acetone						–22.2
	Bath USP/surfactant						–22.2
	Tip USP/surfactant						–13.4
	Bath/tip USP/surfactant/acetone						–7.5

(USP: Ultra Sonic Processing)

and 2b). These plots led us to the conjecture that the use of unmodified MWNT as fillers in epoxy may increase or not change the glass transition temperature.

The curing agent type and concentration plays an important role on the final T_g of the resin. Curing

agent with high functionality provide high T_g . The T_g can also be modified by the curing agent/resin ratio, using a ratio in little excess of the stoichiometry gives higher T_g . The cure behaviour of an epoxy resin can be divided into two stages, a first one in which the reaction is chemically controlled and a

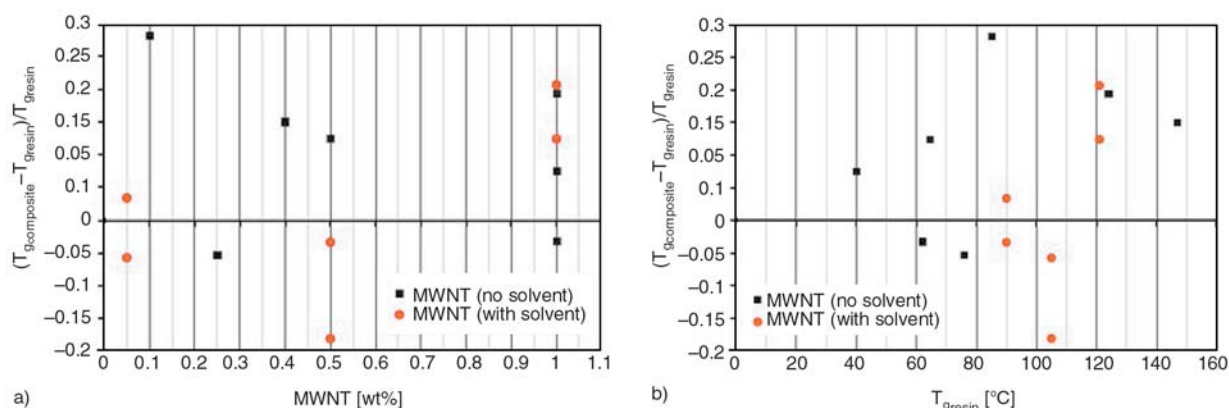


Figure 2. Relative difference of T_g of unmodified MWNT composites compared to unfilled resin as a function of a) CNT weight percentage, b) T_g of the unfilled resin (data taken from the literature)

second one in which diffusion dominates due to the phenomena of gelation and vitrification. In the early stage, the reaction is initiated by any hydrogen-bond donor molecules which can be moisture, impurities... The reaction is then accelerated by these molecules and the hydroxyl groups formed during the reaction. In the last stage, the viscosity of the mixture increase significantly and the reaction is diffusion-controlled. In the case of epoxy with MWNT, the presence of catalyst particles can initiate the reaction earlier compared to the unfilled resin. The introduction of MWNT in epoxy was found to increase significantly the viscosity of the mixture, up to one of order of magnitude with 1 wt% MWNT [24]. The improvement of the CNT dispersion state using a mechanical method led to an additional viscosity increase with factor 2. It is thus expected that the diffusion-controlled stage may be reached earlier in the case of the composites due to the higher viscosity level. The ‘advanced’ cure degree obtained in the early stage could be counterbalanced by the rapid decrease of the cure in the diffusion-controlled stage. Lower or comparable cure degrees of the composites compared to the resin are expected. Lower cure degree should lead to lower T_g . In view of their dimensions comparable to polymer chains, CNT could limit their mobility and provide higher T_g level. The lower cure degree could be counterbalanced by the restricted mobility of the polymer chains in the vicinity of the CNT. High aspect ratio and good dispersion state of CNT in the epoxy may promote the mobility reduction effect. The presence of CNT could also modify the structure of the final epoxy network which may present a gradient of cross-linking points around CNT. The use of an over-aged hardener [25] gave a

rubbery epoxy and remarkable improvement of mechanical and electrical properties with 1 wt% MWNT. These improvements could be attributed to the loose nature of the rubbery epoxy network which was modified by MWNT. MWNT may have a perturbation effect during the formation of the epoxy network (with more cross-linking points around CNT) allowing them to act as an effective reinforcement. A thermal treatment of epoxy close to its T_g allows to study the effect of physical aging which allows some rearrangement of the polymer chains. It was found that physical aging limits the strain range over which CNT effectively reinforce the epoxy matrix [26] suggesting possible formation of voids between polymer chains with reduced mobility at the vicinity of CNT and ‘free’ chains allowed to rearrange through physical aging and sufficiently far from CNT.

The case of functionalized CNT is more complex due to the presence of surface groups that can react with the resin or the hardener, variations of T_g are thus expected due to the modified chemical reaction. Miyagawa *et al.* [27] dispersed fluorinated SWNT in a DGBEF epoxy and observed a decrease of T_g that they explained by the non-stoichiometric balance of epoxy to hardener due to fluorine on the surface of SWNT. Even after adjusting the amount of the anhydride hardener, the T_g of the composites was always lower than that of the resin. They also observed a slight decrease of the T_g when vapour grown carbon fibers (VGCF) were used as fillers in epoxy. They attributed this effect to hydroxyl groups present on the surface of VGCF that can react with hardener. Valentini *et al.* [20] used butylamine-grafted SWNT in a DGEBA epoxy resin with butylamine as the hardener. They reported an

increase of the total heat of reaction, a higher final cure degree and a higher glass transition temperature of the functionalized SWNT-based composites compared to the unfilled epoxy. The surface groups reacted with the epoxy resin allowing these improvements.

4. Conclusions

In this study, the effect of unmodified MWNT on the cure kinetics and glass transition temperature of an epoxy resin was analyzed on the basis of the literature results. It was found that various authors reported an acceleration effect of CNT. The cure reaction was promoted in its early stage which may be due to the catalyst particles present in the CNT raw material. The effect of CNT on the T_g remains unclear. SWNT may lead to a decrease of T_g due to their bundling tendency. On the other hand, results reported for MWNT showed an increased or unchanged T_g of the composites. The use of solvent can lead to a decrease of T_g even after careful evaporation due to residual traces. The present status of the literature does not allow a clarification due to the lack of a study providing essential information such as purity (catalyst particles can affect cure reaction), glass transition temperature along with the corresponding cure degree (to isolate the true potential effect of CNT from curing variations).

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