

Influence of Carbon Nanotubes on Epoxy Resin Cure Reaction Using Different Techniques: A Comprehensive Review

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The results regarding the effect of carbon nanotubes (CNTs) on the cure process of epoxy resin are widespread and contradictory. Therefore, this article aims to review the key studies on the effect of carbon nanotubes related to the curing process of epoxy resin, separating them according to analysis technique. Many articles have shown that nanocomposite homogeneity and medium viscosity have great influence on the cure process. Some of them have shown that heterogeneity and high viscosity slow down the epoxy resin cure, reducing the cure reaction heat. Furthermore, the presence of chemical groups such as amine and hydroxyl can catalyze this reaction, especially in the case of homogeneous composites. This review describes briefly and straightforwardly the value of using several techniques for studying and monitoring the nanocomposite cure, among them: DSC, rheometry, DMA, Raman, FT-IR, and luminescence spectroscopy. That importance is remarkably noticeable for studying a particular temporal reaction step, where a particular technique is more suitable than another. In this sense, one could say that luminescence spectroscopy is appropriate for studying the ending step of the cure reaction. Moreover, a great amount of information is also provided for supporting further research. POLYM. ENG. SCI., 00:000-000, 2013. © 2013 Society of Plastics Engineers

INTRODUCTION

Carbon Nanotubes

Carbon nanotubes were discovered in 1991 by Sumio Iijima. Further analysis showed that carbon nanotubes are formed of rolled up graphene sheets in the cylinder form, where carbon atoms are covalently bonded as sp^2 hybrid orbitals. Carbon nanotube diameters can be less than 1 nm up to tens of nanometers and lengths ranging from

some microns to millimeter fractions. Carbon nanotubes formed by a single layer are called Single Walled Carbon Nanotubes (SWCNT) and those formed by concentric layers are called Multi Walled Carbon Nanotubes (MWCNT) [1, 2]. Figure 1 illustrates these two types of carbon nanotubes.

Carbon nanotubes have extraordinary mechanical, electrical, and thermal properties. They are extremely resistant materials, where the Young modulus is around 1 TPa and the maximum tensile strength can reach 300 GPa. The CNT's maximum tensile strength is about 100 times greater than that of steel's. Carbon nanotubes can also support a strong deflection force and return to their original shape. Their electrical behavior is similar to conductors or semiconductors and these properties depend on their spatial orientation and crystal lattice. Their unique electrical and mechanical properties make them a very interesting material for micro and nanotechnological devices, such as: nanocomposites, storage and energy conversion devices, hydrogen storage support, nanowires, nanotransistors, relays for field emission, new reinforced light alloy, functionalized materials and surfaces, sensors and biosensors, probes and interconnectors [2–5].

Epoxy Resin

Epoxy resin is a high performance thermoset material which contains at least two terminal epoxy groups. This resin is widely used in various industrial applications, especially in the electronics, automotive and aerospace industries [6]. Applications include protective coatings, adhesives, equipment for chemical industry, structural composites, electrical laminates and electronic packaging [7].

The most widely used epoxy resin is based on diglycidyl ether of bisphenol A (DGEBA) and its basic structure is shown in Fig. 2. DGEBA is obtained from the reaction between epichlorohydrin and bisphenol-A [8].

Epoxy resin is widely known due to its excellent mechanical and chemical properties, such as high tensile and compression strength and good chemical resistance to

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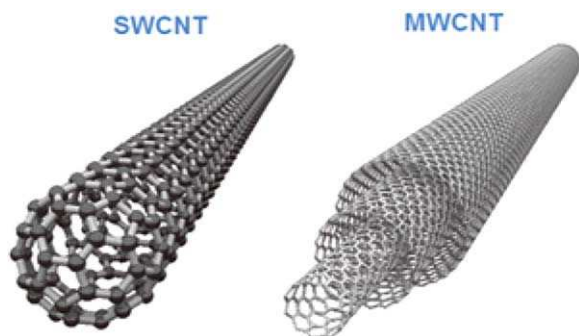


FIG. 1. Single-walled carbon nanotube (SWCNT) and multiwalled carbon nanotube (MWCNT) [3]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solvents [9]. The mechanical and chemical properties of epoxy resin are the result of cross-linking reactions related to the curing process. This reaction turns a low molecular weight resin into an infinite molar mass polymer, i.e. a three-dimensionally structured network that is composed of alternated segments of resin and curing agent [10]. Various curing agents (or hardener) can be used and they are compounded by amines (aliphatic and aromatic), anhydrides and isocyanates [6]. However, the cured resin properties depend on the resin structure and curing agent, which are related to the cure reaction extension, time and temperature [7, 11]. The hardener agent frequently determines the sort of curing reactions, where each hardener shows unique cure kinetics, processing cycle (viscosity vs. time) and gel point. Therefore, the hardener type will affect all properties of the cured material [7]. Therefore, the pairing of epoxy resin and hardener determines the glass transition temperature, elastic modulus, and mechanical strength. Table 1 shows the mechanical properties of a typical epoxy resin after curing [7].

Epoxy Resin Nanocomposites Reinforced with Carbon Nanotubes

In recent years, carbon nanotubes (CNTs) have been used in different types of polymer matrices, especially epoxy resins [9]. These nanocomposites have a number of interesting features and have been used by several industrial segments, such as the aerospace and electronics industries [12, 13].

The addition of carbon nanotubes in low levels to a polymeric matrix (used as a reinforced phase) has become

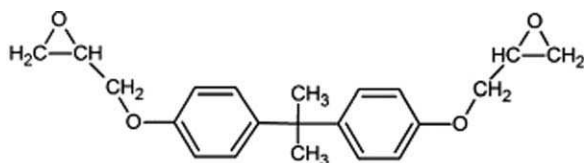


FIG. 2. Chemical structure of epoxy resin based on diglycidyl ether of bisphenol-A (DGEBA). Adapted from Ref. [8], with permission from Elsevier.

TABLE 1. Mechanical properties of a typical cured epoxy resin [7].

Mechanical property	Value
Tensile strength	40 a 90 MPa
Elastic modulus	2.5 a 6.0 GPa
Strain at break	1 a 6%
Compressive strength	100 a 220 MPa

an extremely attractive technique for enhancing the mechanical, electrical, and thermal properties of polymer matrix composite materials [14]. Nonetheless, these polymer properties are dependent on some CNT features and synthesis procedures. The former can be exemplified by the diameter, length and aspect ratio of CNTs and the latter by the technique used to produce CNTs, the purification process and impurity presence, etc. [15].

An effective reinforcement effect in CNT/polymer nanocomposites can be obtained by taking into account two aspects: the interfacial adhesion force between CNTs and epoxy matrix and the dispersion homogeneity of CNTs in the matrix.

The interfacial shear stress between CNTs and polymer in nanocomposites is known as a critical parameter that controls the stress transfer efficiency [16]. The shear stress depends on the interfacial adhesion between the two sides of the interface, which in its turn depends on the chemical affinity between the reinforcement and matrix. A higher interfacial shear stress decreases the tension between the matrix and the reinforcement, transferring effectively the stress from the polymer to the reinforcement. Therefore, the result of a good interfacial adhesion is a better balance of stiffness and toughness in the nanocomposite structure [17].

The adhesion at the interface of CNT/polymer depends on the interaction between the two phases. Wong et al. studied the adhesion between CNT and polymer in nanocomposites and suggested that in some cases CNTs are covalently bonded to the polymer matrix [16].

Bower et al. studied the fracture surface of the CNT/polyhydroxyaminoether nanocomposite by transmission electron microscopy (TEM) and they observed that the majority of CNTs were strongly bonded to polymer. In some cases, the entire surface of the nanotube was covered by a polymer layer [18].

Jia et al. used an in situ polymerization technique to obtain nanocomposites where CNTs were used as reinforcement and poly(methylmethacrylate) (PMMA) as the matrix. The infrared spectroscopy characterization showed the presence of a chemical bonding between CNTs and the matrix, which should be responsible for the strong interfacial adhesion between CNT/poly(methyl methacrylate) [19]. In this study, they used azobisisobutyronitrile (AIBN) as initiator, which was suggested to be able to open the π bonds of CNTs and consequently making the bonding between PMMA and CNTs very strong. However, the strong adhesion was only observed when the

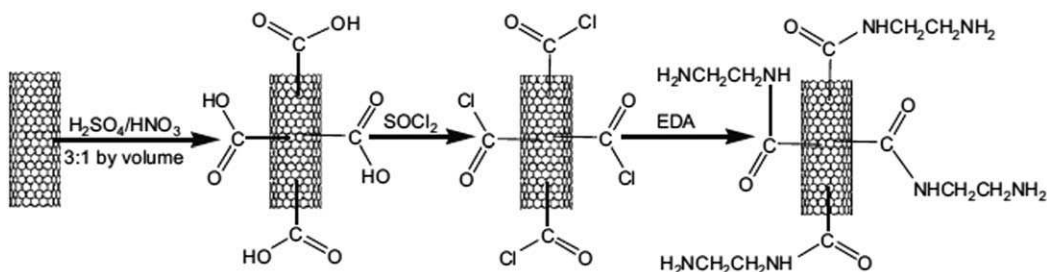


FIG. 3. Chemical routes for preparing functionalized CNTs [34].

nanotubes were pretreated in a ball mill with nitric acid. This effect was attributed to CNT shortening and due to the easier dispersion of CNTs in the matrix [19]. Generally, however, the interfacial interaction force between carbon nanotubes and epoxy resin is very poor, limiting the application of this type of composite [20]. In order to increase this interaction force, carbon nanotubes have been functionalized with chemical groups.

Composite homogeneity is another important parameter for an effective CNT reinforcement effect besides the interface adhesion. Carbon nanotubes tend to form agglomerates in the polymer matrix, making the mechanical properties of the composite worse than that of neat epoxy resin. Therefore, CNT homogeneous dispersion in the polymer matrix is an important feature to obtain the full capacity of a reinforced nanocomposite.

Physical and chemical methods can be used for an effective dispersion of CNTs. Examples of chemical methods are: surfactants and solvents, monomer in situ polymerization together with CNT and chemical functionalization. Among the physical methods are: mixture under high shear rate, ultrasonic probe and milling [21, 22].

Epoxy Resin Nanocomposites Reinforced with Functionalized Carbon Nanotubes

Carbon nanotubes are extremely difficult to disperse in the polymer matrix due to Van der Waals forces, and thus, typically, they form clusters. Moreover, their interactions with epoxy resin are usually poor since there is virtually no chemical group attached to their walls. The major challenge in the development of a high performance polymer/CNT composite is to achieve good dispersion and strong interfacial interactions between CNT/polymer.

CNT functionalization is an effective way to prevent their aggregation [23]. The chemical functionalization of CNTs can also increase the interfacial interaction between CNTs and the matrix, which causes an increase in composite mechanical properties [24]. This enhancement is related to chemical bonds (covalent or not) that are formed between the functional groups of the CNT surface and the polymeric matrix [25, 26]. Two of the most common CNT functionalization types are performed in an acid or amino medium.

Mixture of H_2SO_4 and HNO_3 (3:1 v/v) is often used for acid functionalization. CNTs are mixed with this acid solution using ultrasound (typically bath sonication). The ultrasound time can be less than an hour up to 24 h and the functionalization degree increases when bath time also increases. Nevertheless, a long bath time can also create defects on CNT walls, which can result in a worsening of composite mechanical properties. Prolonged acid treatment can also generate a total degradation of a certain amount of CNTs, resulting in a decrease in the initial CNT amount [27].

Amino functionalization occurs, generally, in three stages. Initially, CNTs are functionalized with acid groups (step 1) and then they react with thionyl chloride, $SOCl_2$ (step 2). Finally, CNTs react with substances containing amino groups (step 3). $SOCl_2$ is used as an intermediate to facilitate the reaction between the carboxylic groups (generated on CNT walls by acid treatment) and amino groups, since acid halides are more reactive than carboxylic groups. The total reaction time varies from 2 to 5 days. Ethylenediamine (EDA) is a reagent that contains amino groups and is widely used as a functionalizing agent. The functionalization of acid-treated CNT with amino groups is also possible to occur without using the intermediate $SOCl_2$ [28–32]. In this case, an activator or coupling reagent is used together with the amino reagent to facilitate the reaction between the carboxylic groups linked to CNTs and amino groups (via amide formation). N-HATU (O-(7-azabenzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate) and DCC (N,N'-dicyclohexylcarbodiimide) are some examples of coupling agents. Using these coupling agents, the total time for the reaction is reduced to a few hours [28–32]. Nevertheless, Cividanes et al. [33] recently showed a methodology for preparing functionalized CNTs directly with EDA, without using any coupling agents or intermediates. The chemical route procedure for functionalizing CNT through acid and amino treatments is described in Fig. 3.

Some studies [25, 34–38] have shown that the mechanical properties of epoxy/CNT nanocomposites prepared with functionalized CNTs are better than those prepared with nonfunctionalized ones. Amino-treated CNTs generally provide greater reinforcement effect than acid-treated CNTs. Shen et al. [25] stated that amino-treated CNTs can easily integrate the epoxy matrix via covalent

bonding between amino groups on the CNT surface and the epoxy matrix. This would explain the further strengthening of amino-treated CNTs when compared with acid-treated ones.

O'Reilly [38] showed, using images from scanning electron microscopy, that nonfunctionalized CNTs are not well distributed in the epoxy matrix and that the adhesion force between the epoxy matrix and CNTs is weak. However, nanocomposites prepared with acid-functionalized CNTs showed a good homogeneity and a poor adhesion between the epoxy matrix and CNTs. Nonetheless, nanocomposites prepared with amino-treated CNTs that had previously been treated with acid showed both excellent homogeneity and strong adhesion force. They [38] suggested that extra amino groups present on the CNT wall can also participate in cure reaction, resulting in a higher adhesion force between CNT/matrix.

Meng et al. [34] prepared nanocomposites with polyamide and acid-treated CNTs and observed an increment in the mechanical properties due to CNT interactions with the polar matrix. However, they also observed a worse CNT dispersion in the matrix associated with the presence of hydrogen bonding (acid-treated CNT). The subsequent functionalization of acid-modified CNTs with a diamine weakened the CNT-CNT interactions, easing their dispersion in the polymer matrix and strengthening the interfacial adhesion force between CNTs and the polyamide matrix.

INFLUENCE OF CNTS ON THE CURING PROCESS OF EPOXY RESIN

The incorporation of carbon nanotubes influences the curing process of epoxy resin and an understanding of the cure reaction of CNT/epoxy composite is very important for the design, analysis and optimization of manufacturing materials. Therefore, for highly demanding manufactories, it is necessary to understand the nature of the curing process, once the final properties of the nanocomposite depend significantly on the curing conditions [1, 39, 40].

Most works in the literature related to CNT/epoxy composites are centered on the final properties of the material, and few of them are focused on processing. Nowadays, however, the trend is towards processing, making the products available at a lower cost. In order to achieve this goal it is necessary to study the curing of these composites.

The effect of different types of carbon nanotubes on the curing process of epoxy resin was shown in many articles, but the results are often conflicting due to the large number of variables that can influence the cure of this composite. For example, some authors found out different effects on the cure reaction using the same type of functionalizing reaction. However, besides the groups linked to the CNT walls, other parameters can influence the curing reaction. Some of these parameters are the differences in the aspect ratio and orientation of CNTs, as

well as the amount and type of impurities present in CNTs. Thus, these differences can lead to changes in the homogeneity of the composites, changes in the CNT-epoxy interaction or in the cure kinetics of epoxy resin.

Different techniques can be used to monitor the cure of these composites. The most widely used technique is the differential scanning calorimetry (DSC). However, there are other techniques for monitoring the cure reaction that provide important and complementary data to those provided by DSC analysis, which have been less explored. Consequently, this article aims to bring together key studies already conducted on the effect of carbon nanotubes on the curing process of epoxy resin, separating them according to analysis technique. Thereafter, this article will seek a better understanding of how different types of carbon nanotubes may or may not interact with epoxy resin, how this may influence the cure of the epoxy resin and how each technique may help to characterize these studies.

Study of the Cure Reaction by DSC

Most articles in the literature study the cure reaction of CNT/epoxy resin composites by DSC. This technique starts with a freshly prepared sample and the cure reaction occurs in a crucible during the analysis, under different conditions of temperature and heating rate (isothermal and nonisothermal). DSC provides several pieces of information but the main ones are: cure enthalpy, temperature/time of each reaction step, and activation energy. If more than one cycle is performed, DSC also provides the glass transition temperature (T_g). Some DSC results of CNT/epoxy resin nanocomposites are reported in the following paragraphs.

Puglia et al. used DSC to investigate the incorporation effect of SWCNTs on the curing reaction of epoxy resin. They observed that SWCNT acts as a strong catalyst, where the shifting of the cure reaction peak was related to SWCNT contents. Both samples prepared with 5% (w/w) and 10% (w/w) of nanotubes shifted that peak to a lower temperature. The reaction temperature of the sample prepared with 10% was higher than that of the sample prepared with 5%, but as CNT content increased, the temperature difference was not proportional to CNT content. They concluded that this nonproportional effect was related to a saturation effect, which is typical of catalyst behavior. The thermal stability of composite and neat resin was examined by thermogravimetric analysis (TGA), showing a faster thermal degradation for composites. The authors attributed these effects to the high thermal conductivity of SWCNTs and high surface heat propagation [12].

The effect of different concentrations of carbon nanotubes in the epoxy resin cure was also examined by Tao et al. using the DSC technique. They prepared nanocomposites with only SWCNT and mixtures of SWCNT with CNT of double or triple walls. On this occasion, the

authors showed that nanotubes can initiate the resin cure at lower temperatures. However, the overall curing process was slower for nanocomposites, which was shown by a lower total reaction heat and a lower T_g . They also showed that the addition of carbon nanotube in the epoxy resin may induce the composite thermal degradation at lower temperatures [13].

Yang et al. [41] showed that CNT/epoxy composites prepared with nonfunctionalized MWCNTs have a delayed effect on the curing reaction of epoxy resin as compared to neat resin. That is, the curing process of these composites occurred at higher temperatures than neat resin. However, composites prepared with epoxy resin and amino-functionalized MWCNTs have an effect of accelerating the cure, i.e., the curing process occurred at lower temperatures. They attributed this effect to the presence of amino groups on the CNT surface that act as a catalyst of the cure reaction. The presence of amino groups decreases the activation energy of the curing reaction. They also observed that the CNT presence increases the thermal stability of the nanocomposites.

The effect of carboxyl and fluorine-functionalized MWCNTs on epoxy curing reaction was studied by Abdalla et al. using the DSC technique [42]. They showed that the presence of these groups on the SWCNT surface does not change the final cure degree and the glass transition temperature of the neat epoxy. The reaction with carboxyl groups showed the highest value of activation energy, while the reactions with fluorine groups and neat epoxy had the same values of activation energy. The cure enthalpy was lower for nanocomposites than for neat resin, but composites prepared with fluorine-CNT showed values more similar to neat resin. The cure mechanism of nanocomposites was explained in terms of homogeneity, since the authors observed a good dispersion of fluorine-CNTs in the epoxy matrix, whilst the carboxyl modified CNTs were not well dispersed.

Zhengping et al. studied the concentration effect of amino-functionalized MWCNTs on the curing behavior of epoxy resin using DSC. They observed that the nanocomposite activation energy was lower than the neat epoxy one. The cure enthalpy of the system epoxy/1% (w/w) of amino-MWCNT was higher than for neat resin, while the enthalpy of the system epoxy/nonfunctionalized MWCNTs was lower than that of neat resin. However, when the concentration was 2 wt% of MWCNTs, the cure enthalpy of the composite prepared with functionalized and nonfunctionalized MWCNTs was lower than neat resin [43]. The difference was explained by the increase in viscosity caused by the addition of CNTs, especially the nonfunctionalized ones and due to the homogeneity degree of the nanocomposite.

Qiu and Wang [44] studied the effect of CNT size and various functionalization types (with amine and epoxide groups) in the curing of epoxy/CNT composite. They showed, by DSC, that the total cure enthalpy is lower for all nanocomposites in relation to neat resin, which was

explained by the decrease in the epoxy monomer mobility. Shorter CNTs provoked remarkable effects, decreasing both the reaction enthalpy and the extent of conversion, because they elevated the size effect-induced interference. This size effect is related to the change of diffusivity of epoxy and curing agent molecules because shorter CNTs have the size in the same scale as epoxy resin molecules. The lowest effect, that is, the higher enthalpy, was observed for the CNT functionalized with the epoxide group, since this group participated in the curing reaction and was present in great concentration. All CNTs (functionalized or not) reduced the onset curing temperature, accelerating the epoxy cure reaction at the initial stage. The largest acceleration occurred when they used epoxide-functionalized CNTs. However, amino-CNTs increased the activation energy of the overall cure reaction, while epoxide-CNTs slightly decreased the activation energy (compared with neat epoxy).

Xie et al. [45] studied the effect of MWCNT (1 and 5 wt%) on cure of epoxy resin by DSC. They observed that CNT behaves as an autocatalyst and that MWCNT/epoxy nanocomposites showed the highest initial reaction rates, the lowest time to reach the maximum rate and the lowest activation energy values in the initial reaction stage (in relation to neat epoxy). However, the CNT presence no longer influenced the last stage of the cure reaction. The catalytic effect of CNTs was explained by the presence of OH groups on the MWCNT surface, which exerts catalytic effects for epoxide ring opening. Table 2 summarizes the main information of each work cited above, and some additional information.

The works cited above and Table 2 shows some controversy in the results of CNT influence on the cure process of epoxy resin. Each author attributes their own explanation about this controversial behavior, which can be: an increase or decrease in the steric hindrance effect; an increase in thermal conductivity due to excellent CNT thermal conductivity; an increase or decrease in viscosity; a catalytic effect due to the chemical groups of the CNT walls etc. However, despite this controversy, CNT dispersion homogeneity into epoxy resin and viscosity of the medium seem to be the most responsible for the anomalous behavior of this class of nanocomposites. For example, the effect of non-functionalized CNTs can lead to a faster cure, but sometimes to a slower one as well. This contradictory effect is due to a great number of variables that can influence the curing reaction, e.g. length and diameter of the CNT, purity, type and quantity of chemical groups attached to their walls, CNT amount, dispersion method etc. Thus, composites prepared with the same CNT type can lead to different dispersion degrees of CNTs in epoxy resin and different viscosity values, which in their turn determine the kinetics and thermodynamics of the cure reaction. For example, amine-functionalized CNTs can catalyze the curing reaction, but if they are added in large amounts they will greatly increase the viscosity of the

TABLE 2. Thermodynamic and kinetic parameters of epoxy cure reaction.

Ref.	CNT type	wt% CNT	Dispersion	Enthalpy (ΔH)	Activation energy (E)	Explanation
[12]	A	5, 10	Regular	$\Delta H^A < \Delta H^J$	—	Thermal conductivity
[13]	B	1	Regular	$\Delta H^B < \Delta H^J$	—	—
[41]	C	0.5	—	—	$E^C > E^J > E^D$	Steric hindrance of MWNTs
[41]	D	0.5	High	—	—	Amine: act as curing agent
[42]	E	1	Low	$\Delta H^E < \Delta H^F < \Delta H^J$	$E^E > E^J \sim E^F$	Heterogeneous dispersion: hinder mobility
[42]	F	1	High	—	—	Good dispersion
[43]	D	1	High	$\Delta H^D > \Delta H^J$	$E^D < E^J$	Good dispersion
[43]	C	1	Low	$\Delta H^C < \Delta H^J$	$E^C \sim E^J$	Heterogeneous dispersion
[43]	D	2	High	$\Delta H^D < \Delta H^J$	$E^D < E^J$	High viscosity
[43]	C	2	Low	$\Delta H^C < \Delta H^J$	$E^C \sim E^J$	High viscosity
[44]	A, G, H, I	—	—	$\Delta H^H < \Delta H^G < \Delta H^A < \Delta H^I < \Delta H^J$	$E^I < E^J < E^G < E^A < E^H$	Hinder mobility, CNT groups: participate in cure

A = SWNT; B = mixture of SWNT, double-walled carbon nanotube, triple walled carbon nanotube; C = MWNT; D = MWNT functionalized with amine group; E = MWNT functionalized with carboxyl group; F = MWNT functionalized with fluorine group; G = SWNT functionalized with amine group; H = cut-SWNT; I = SWNT functionalized with epoxide group; J = neat epoxy).

noncured resin, hindering the cure reaction. Moreover, dispersion homogeneity seems to be a decisive factor which will determine the curing reaction of the epoxy/CNT composites. One can say that heterogeneous CNT dispersion slows down the rate of epoxy resin cure and reduces the heat curing reaction [42, 43]. Therefore, in order to clarify the effect of CNTs on the curing reaction of epoxy resin, information related to CNT dispersion homogeneity must be supplied, such as the aspect ratio of CNTs, the amount added, the purification and dispersion method, as well as fracture surface micrographs and viscometry.

Furthermore, CNTs are often cited as acting as catalysts for the epoxy resin cure at early steps and for their minimal influence at the final stage. The catalyst action of CNT is often attributed to CNT thermal conductivity (especially when they are added in large amounts), and to the presence of functional chemical groups, such as amine, hydroxyl or fluorine. These amine groups act as curing agent since they have a similar chemical structure to hardener, and the hydroxyl group can catalyze the ring opening of epoxy. Fluorinated CNT may react with the amine curing agents, so they can essentially act as a curing agent and react with other epoxy groups [42]. Some authors also suggested that the metallic residue from the manufacturing process that is still in the CNT interior could also act as a hydrogen donor and catalyze the cure reaction, especially at the early stages [46]. However, the extension degree of total cure is often similar to or lesser than that of neat resin. The lowest extension degree of cure reaction is described by the increase in the viscosity caused by the CNT addition, which hinders the mobility of epoxy chains. Furthermore, the CNT addition into epoxy resin changes the optimized curing ratio between epoxy/hardener.

Figure 4 summarizes the possible effects of CNTs on the curing reaction of epoxy resin and the factors that may interfere on the reaction.

Study of the Cure Reaction by DMA

The dynamic mechanical analysis (DMA) is mainly used for obtaining the glass transition (T_g) of polymer samples. The glass transition value of a composite sample is often related to the cure extension of epoxy resin, as well as to the interfacial interaction of epoxy/CNT. Both the interface strength and the cure extent can reduce the mobility of epoxy resin chains in cured samples, increasing the glass transition temperature.

Monitoring the epoxy resin cure reaction using DMA is very difficult since the sample is liquid before the curing process. Thus, DMA is often used to study cured samples, providing T_g values. T_g can also be determined by DSC analysis, but the DMA technique provides more accurate values than DSC.

Allaoui et al. [47] showed that composites prepared with nonfunctionalized SWCNT had lower T_g than neat epoxy due to the bundling tendency of SWCNT. However, the T_g was not affected by CNT addition when they were well dispersed in the matrix [47]. Therefore, the glass

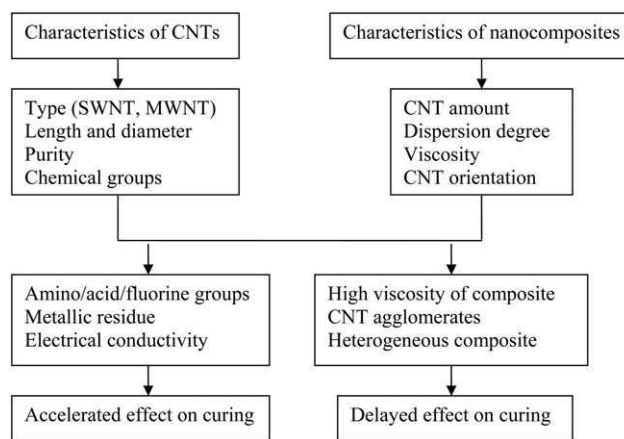


FIG. 4. Factors that may interfere on the curing reaction of CNT/epoxy nanocomposites.

transition temperature is greatly influenced by the homogeneity of the composite, as is the curing reaction.

Luo et al. [48] determined the T_g and storage modulus (G') of composites prepared with amino-functionalized CNT by DMA. They showed that composites with higher homogeneity and good adhesion between the resin and nanotubes had higher T_g and G' than neat epoxy. In particular, CNTs functionalized with phenylbiguanide had the highest values of T_g and storage modulus (G') [48]. Grikas et al. [49] studied how the time interval and amplitude pulse of the sonication step during CNT dispersion in epoxy resin have an influence on T_g and G' and their results were similar to Luo et al. Abdalla et al. [50] determined the following order of glass transition temperature for some functionalized CNT/epoxy composites: fluorinated CNT > carboxylated CNT > neat epoxy, which agrees with the order of chemical strength bonding between the functional group and epoxy resin.

Gude et al. [51] prepared neat epoxy and CNT/epoxy samples with different concentrations of curing agent and submitted them to DMA and flexural tests. The highest glass transition temperature was obtained by samples with stoichiometric composition of curing agent, while the epoxy-rich samples showed the highest glassy storage and flexural modulus. In addition, they concluded that the curing agent concentration is much more relevant than the CNT addition for the epoxy curing process, while CNT addition was more relevant in the epoxy-rich resin, increasing the elastic modulus and T_g . Therefore, the authors suggested that the amount of the curing agent is by far the most relevant parameter to be controlled in the epoxy resin synthesis. Nevertheless, considering synthesis with the same curing agent/epoxy resin ratio, the type, concentration, and mainly the dispersion degree of CNT into epoxy resin became very important parameters.

Study of the Cure Reaction by Rheology

The manufacturing process of polymer composites requires information such as viscosity and resin cure. The viscosity of composites depends not only on the cure degree, but also on the shear rate. The control of the rheological properties is very important for obtaining reproducible CNT/epoxy resin samples. However, despite the importance of this information, few works can be found in the literature related to the rheology of these composites. Unlike DMA testing, the rheometer provides insights into the initial step of cure reactions. For many authors, the beginning of the cure reaction is the step where the most important differences between the neat epoxy and the composites happen. Therefore, the initial steps of the cure of epoxy/CNT composites are very important to be analyzed and some results are summarized in the next paragraphs.

Fan and Advani [52] prepared samples with several dispersion degrees of nanotubes in epoxy resin using oscillatory experiments, and observed significant changes

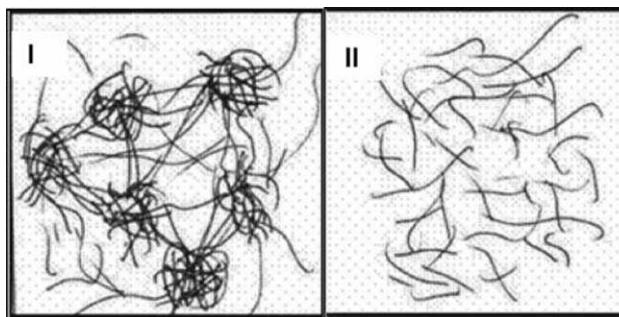


FIG. 5. Structure of two types of nanotubes: (I) with agglomerates, (II) without agglomerates [52].

in the CNT/epoxy rheological properties with the dispersion degree. Figure 5 shows two types of CNT dispersion which showed different rheology behaviors [52]. The authors showed that good CNT dispersion, high CNT aspect ratio and high CNT concentration in the matrix caused strong CNT networking, which was shown by the high values of storage modulus (G') and complex viscosity ($|\eta^*|$).

Johnson and Pitchumani [53] studied the curing process of epoxy/CNT composite using CNTs in different concentrations and aspect ratios by DSC and rheology techniques. Their results showed that the CNT presence did not change the cure mechanism and cure heat. However, the CNT addition decreased the activation energy of cure resin. In addition, they showed that the CNT presence increased the viscosity and introduced a distinct shear-thinning rheology, with the shear thinning effect being greater with the higher amount of CNT.

Abdalla et al. [50] studied uncured epoxy resin/CNT samples and observed that the rheological properties are affected by the covalent bonds of CNTs. Systems without CNT showed a Newtonian behavior, while the CNT presence led to a non-Newtonian behavior, mainly if the composite had been prepared with fluorinated nanotubes. Another study [42] showed that the presence of CNTs functionalized with carboxyl groups decreased considerably the gel time of epoxy resin in relation to neat resin and to fluorine-functionalized CNT [42]. Thus, hydroxyl groups act as catalysts for the early stages of cure reaction.

Terenzi et al. [54] showed by the rheometry technique that the cure reaction of epoxy resin composites and amino-functionalized CNTs was accelerated by the presence of amino group on CNTs. They showed the composite reached higher cure degree in shorter times, as well as the gel point occurring in less time when compared with neat epoxy.

Rheology is a simple technique that allows for studying the influence of carbon nanotubes in the cure of epoxy resin, but it also provides information concerning the homogeneity, viscosity, and chemical-physical interactions of a composite. Thus, it is a technique that has great potential to be applied in studying the effect of different

kinds of variables on the cure process of composites prepared with epoxy resin and carbon nanotubes. Moreover, this technique is important to the manufacturing process of these composites, since it allows the obtaining of viscosity values at different shear rates.

The previous results showed that composite homogeneity is a critical parameter in determining the rheological behavior of the samples. Besides that, the CNT catalytic effect on the initial stages of curing reaction was observed by rheology studies as well as by the DSC technique.

Study of Cure Reaction by Raman, Luminescence Spectroscopy, and FT-IR

Luminescence spectroscopy is a very sensitive technique which has been used to monitor the cure of epoxy resin and other composites, such as epoxy/carbon fiber and epoxy/glass fiber. This technique had not been applied to study the curing of epoxy/CNT, until the work performed by Cividanés et al. [33]. In this study [33], two unconventional techniques were applied to study the influence of CNTs, functionalized or not, in the cure of epoxy resin: Raman and luminescence spectroscopy. The cure process was monitored by Raman spectroscopy using the intensity of two bands of the Raman spectrum: 1610 cm^{-1} , characteristic of the stretching of aromatic ring C=C, and 3065 cm^{-1} , characteristic of epoxy ring stretching. On the other hand, luminescence spectroscopy was applied to monitor the cure by calculating the cure degree, using the Equation:

$$\alpha = \frac{I_t - I_i}{I_f - I_i} \quad (1)$$

where I_i means the intensity of the emission peak obtained from the studied sample after pre-cure at 80°C for 1 h; I_f means the intensity of the emission peak obtained using the studied sample after cure at 120°C for 1080 min; I_t is the intensity of the emission peak obtained using the studied sample after thermal treatment at 120°C for a given period of time (t).

The presence of CNTs, functionalized or not, increased the resin cure degree. The composites prepared with annealed CNT (purification to 1800°C , vacuum) and acid-treated CNT had considerably higher cure rates at the reaction beginning. Composites prepared with amino-functionalized nanotubes and neat epoxy resin had a lower cure rate. The difference in the cure rate was explained by means of the sample's homogeneity (greater in the composite prepared with amino-CNT) and the presence of chemical groups.

A problem observed when using Raman spectroscopy to measure the cure intensity of epoxy resin/CNT is the influence of background fluorescence in the Raman spectra. Depending on the type of epoxy resin and hardener used, this effect can change the intensity of the peaks

exactly in the region of interest, as in the aforementioned work [34].

An advantage of luminescence spectroscopy in relation to other techniques is its sensitivity to detect the curing reaction, particularly at its final stages. Therefore, this technique can be used to monitor the cure reaction after the gel point [55].

Vega et al. [56] used in situ Raman spectroscopy and electrical conductivity measurements to monitor the internal stresses arising from the curing process of composites epoxy/SWCNT. They did preliminary investigations to analyze how SWCNT Raman spectra changes with temperature. They showed that the G band position was dependent on temperature and on cure degree. However, the effect of adding 0.2% of SWCNT in epoxy was found to be negligible for the curing process.

Valentini et al. [57] used Raman spectroscopy not to monitor the cure, but to understand the interaction between CNTs and epoxy resin during the cure. They studied three types of composites: (a) fluorinated SWCNT (F-SWCNT); (b) F-SWCNT grafted with butylamine (BAM-SWCNT); (c) unfunctionalized SWCNT (u-SWCNT). They observed that BAM-SWCNT acts as a strong catalyst during the cure reaction because of cross-linking interactions between epoxy resin and BAM-SWCNTs, since BAM is the hardener of epoxy resin. Raman spectra of the epoxy/u-SWCNT composite did not show frequency shifts of typical bands of SWNTs, while F-SWCNTs showed an important chemical affinity with epoxy, resulting in a shifting of its Raman peaks. This peak shifting toward higher frequencies is due to the opening of CNT bundles which was produced by the cross-linked resin intercalation.

FT-IR technique is often used to study epoxy/CNT composite curing for comparing the area of the epoxy ring peak before and after the curing process. Yang et al. [41] compared the peak area of an epoxy ring (peak at $\sim 913\text{ cm}^{-1}$) with a reference peak (at 1610 cm^{-1}) which is characteristic of a benzene ring and does not vary with the cure degree. They found that the final cure degree of the composites prepared with nonfunctionalized CNT and amino-CNT was basically the same ($\sim 98\%$). In another study [42], a very similar cure degree between neat resin (95%) and composites prepared from carboxylated and fluorinated MWCNTs (96%) were obtained.

Table 3 summarizes some information about the curing reaction of epoxy resin in presence of carbon nanotubes, describing the advantages and disadvantages of each technique.

The DSC technique is the most used because of its practicality and the large amount of information that can be obtained through it. Even so, a lot of information can be obtained from other techniques with advantages over DSC. For example, luminescence spectroscopy is a very sensitive technique for monitoring the cure reaction, making it possible to obtain data which are impossible from others. Moreover, luminescence spectroscopy is used

TABLE 3. Characteristics of different techniques used to study the curing of epoxy resin/CNT composites.

Technique	Information	Advantages	Disadvantages
DSC	Enthalpy, time/temperature of peak, E, T _g , cure degree.	Study all stages of the reaction.	Destructive
DMA	T _g , viscoelastic study after gel point.	T _g with greater accuracy.	Usually used only after gel point.
Rheometry	η^* under various shear rates, gel time, viscoelastic study before gel point.	Study of the initial reaction.	Usually used only before gel point, destructive test.
Luminescence	Cure degree, photophysical and photochemical study.	Greater sensitivity, especially in the final times, non destructive.	Usually used only after gel point
Raman	Cure degree.	Simplicity of the sampling requirements, non destructive.	Interference of fluorescence.
FT-IR	Cure degree.	Study of the initial and intermediate stages.	Low sensitivity for final cure stages.

E = activation energy, η^* = complex viscosity.

together with the FT-IR technique, since the latter is able to easily detect the initial cure reaction, while the former is highly sensitive to the final cure reaction.

Raman spectroscopy also allows monitoring of the cure reaction. However, this technique can be influenced by the fluorescence of epoxy resin and of hardener, which is a disadvantage of this technique.

These three techniques (Luminescence, FT-IR, and Raman) are capable of detecting the cure degree of the composite during the reaction. For this, it is necessary to cure the sample at different times/temperatures (t/T), and thus perform the analysis of each point t/T . Therefore, they are not as practical as DSC, which is a continuous analysis of the curing reaction. However, it is possible to couple an oven to the equipment to increase the practicality of the cure analysis with these techniques. That is, the samples are cured and tested at the same time in the same equipment. These three techniques also provide information about the chemical groups belonging to nanocomposites, thus further studies can be performed while studying the cure process. For example, study of the degradation of epoxy resin by FT-IR in tandem with studying the cure.

The rheometer and DMA techniques are also often used together, since the first one evaluates the viscoelastic properties of composite until the gel point and the second, after the gel point. The rheometer allows for obtaining information that is not obtained with any other technique considered, such as the variation of viscosity with shear rate and gel time, which is valuable information for processing and fabrication of composites. On the other hand, DMA is a much more sensitive technique than DSC for determining T_g of polymers.

CONCLUSIONS

The study of the cure reaction of epoxy resin and carbon nanotube composites often shows controversial results. This is so due to the large number of variables that can influence the curing reaction, variables that have

not been fully explored, and often are not mentioned in the works. For example, information such as type of CNT purification, type of impurities, diameter, length and aspect ratio of the nanotubes, the orientation of nanotubes in the matrix, etc.

Most authors indicate that the degree of CNT dispersion and viscosity are primarily responsible for the cure kinetics of CNT/epoxy nanocomposite. Heterogeneous composites and high viscosity, for example, have a greater effect on slowing the cure of the epoxy resin and reduce the cure heat of the reaction. Moreover, the presence of chemical groups such as amine and hydroxyl can catalyze the cure reaction, especially in the case of homogeneous composites.

Therefore, it is necessary to study systematically how the process variables can influence CNT homogeneity, and consequently, the curing reaction of composites. Furthermore, it is necessary to be resolute about publishing complete information concerning data related to homogeneity. For example, surface fracture micrographs are often not shown in the articles, despite its great importance. Besides that, monitoring the viscosity of the composite during the curing reaction is also very important, since it directly influences the cure of the material.

The curing reaction of the epoxy resin can be studied by several techniques. The DSC technique is the most widely used technique due to the quantity of information obtained through it, apart from its practicality. However, other techniques may be used with considerable advantages, depending on the type of the cure study or the type of epoxy resin. Among them, luminescence spectroscopy can investigate cure degree with high sensitivity at final cure stages, which is difficult to analyze using other techniques. However, analysis by a rheometer provides information about viscosity under different shear rates and gel time, which is not obtained through other techniques. Other techniques to monitor and study the cure of composites are DMA, Raman, and FT-IR.

Thus, for further elucidation of the effect of carbon nanotubes in the curing process of epoxy resin, some suggestions are summarized below:

- Systematic study of the variables that may influence the homogeneity and the curing of the composite.
- Study of variables that have not yet been explored, such as the purification and mixing method.
- Study of the viscosity of the composite during the curing reaction.
- Study of the first stages of the cure reaction, that are more influenced by CNT presence.
- Study of curing reaction by other techniques besides DSC and comparing the results.

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