The effect of carbon nanotubes on the curing processes of epoxy-amine compositions

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Abstract. The effects of the concentration and functionalization of carbon nanotubes on the degree of conversion of epoxy groups in epoxy-amine compositions based on ED-20 epoxy oligomer and the PEPA curing agent are studied. It has been shown that increasing the concentration of functionalized carbon nanotubes (CNT) from 0 to 0.5 % increases the degree of conversion of the epoxy groups during curing at a room temperature. Further increase in concentration CNT of up to 1 % does not effect on the reaction kinetics. For native CNT not established such a relationship. Explains such a pronounced effect on the f-CNT aminolysis reaction kinetics and ultimate degree of conversion of epoxy groups, apparently, the catalytic effect of oxygen-containing groups (hydroxyl, carboxyl, and others) grafted to the surface of CNTs and their direct involvement in the reaction. By optical microscopy showed that the size of the agglomerates of nanotubes were substantially higher in the native systems than in the system with the functionalized nanotubes. These results may be important for the development of creation of epoxy composites modified by nanoparticles.

Keywords: epoxy oligomers, epoxy-amine compositions, carbon nanotubes, ir-spectroscopy method.

1 Introduction
Epoxy resins are widely used in the production of structural and functional composite materials for various purposes, adhesives, sealants [1-6]. In this regard, the problem of increasing their physical, mechanical and operational characteristics is extremely urgent. One of the directions in which this problem can be solved is the modification of epoxy matrix by carbon nanotubes (CNTs) [7-12]. The effective influence of CNTs on the polymer matrix and the full disclosure of their potential properties can be achieved only if they are evenly distributed in the polymer matrix and the maximum polymer-CNT bond strength is ensured. For this, various methods of modifying the outer surface of nanotubes are used [13-18]. In this case, the effect of modified CNTs on the kinetics of curing of epoxy oligomers and on the degree of conversion of functional groups in the resulting composites is significant. Thus, this study is dedicated to the solution of this problem.

2 Methods
The effect of native (untreated) and functionalized multilayer carbon nanotubes (f-CNTs) on the kinetics of formation and the final degree of conversion of epoxy groups in a compositions based on the ED-20 epoxy oligomer cured by the polyethylene polyamine (PEPA) has been studied by IR spectroscopy method. Three types of nanotubes were used in the study: native nanotubes obtained on the laboratory plasmatron described in [19] (CNT-1), industrial native multilayer nanotubes of the Taunit brand (manufactured by NanoTechCenter LLC, Tambov City, Russia) (CNT-2) and functionalized multilayer nanotubes produced by the French corporation Arkema under the brand name «Graphistrength CS1-25» (CNT-3).

We studied the kinetics of the curing reaction of compositions containing from 0 to 1 wt % CNTs in the medium of an ED-20 epoxy oligomer, cured with a stoichiometric amount of PEPA, for 24 hours at room temperature, after which the samples were cured in an oven at 100o C for 4 hours. For preparing specimens based on CNT-1 and CNT-2, dry nanotubes were pre-grounded manually in an
agate mortar until the lumps were completely eliminated, after which the required amount of CNT was added into ED-20 in a water bath at 80°C for 6 hours with permanent stirring. For preparing samples based on CNT-3, the mass of granules, recalculated for the required amount of CNTs, was added into ED-20 and kept in the oven at 80°C for 12 hours. During this time, there was a complete swelling and partial dissolution of the granules in epoxy resin. After that, the composition was also mixed in a water bath at 80°C for 6 hours. A stoichiometric amount of PEPA was the composition cooled to room temperature immediately before recording the IR spectra.

IR spectra were recorded by the Fourier IR spectrophotometer (Perkin-Elmer, Model Spectrum 65) using the Miracle ATR attachment (ZnSe crystal) in the area 4000-650 cm⁻¹ under standard recording conditions. Liquid compositions (before hardening) were applied directly to the ATR element. The cured samples in the form of tablets with a diameter of 2 cm and a thickness of about 2 mm were pressed against the crystal with a special clamp included in the set of the attachment. To prepare solid specimens, a liquid composition including an oligomer, CNTs, and a curing agent was molded into a special form of fluoroplastic and then cured according to the above regime. Since the adhesion of the epoxy polymer to the fluoroplastic is practically absent, the specimens were easily removed from the molds after curing. The same specimens were also used for microscopic studies. Kinetic measurements were carried out according to the procedure [20]. The fraction of unreacted epoxy groups was determined by normalizing the integral intensity (area) of the band of 915 cm⁻¹ of the epoxy ring [21] at time t to the intensity of the same band at time t₀. The time of the first measurement (approximately 5 min after the introduction PEPA into the mixture of ED-20 with CNTs) was taken as t₀. To control the optical contact of the sample with the crystal, on which the quality of the ATR spectrum depends strongly, we used the “internal standard” band — a characteristic doublet of 1606–1581 cm⁻¹ of benzene rings of the epoxy oligomer [22]. This band had equal intensity in all measured spectra. The mathematical processing of the spectra was carried out using the supplied software. After registration, an ATR correction was automatically carried out and the spectrum was transferred to the optical density scale. The integrated intensity (area) of the absorption band of the epoxy groups of 915 cm⁻¹ was calculated within the boundaries of 890–926 cm⁻¹ for all measured spectra.

To assess the degree of CNT agglomeration in the compositions, microscopic studies of extremely cured samples were carried out on a Biomed-4 optical microscope equipped with a DCM-510 digital attachment with a resolution of 5 Mpx for micrographs.

3 Results and Discussion
The kinetics of the curing of epoxy-amine compositions containing CNTs, including those using the IR spectroscopy method in the middle and near area, was previously studied in a number of papers [22-26]. However, most of these studies were largely limited to model systems based on DGEBA and low molecular weight di- or monoamines. In our study, we used industrial products: the epoxy oligomer ED-20 and the PEPA curing agent, which are widely used in practice.
Figure 1. IR spectra of a system containing 0.2 wt% CNT-3: before curing (1); after curing for 4 hours (2); 1 day (3); after curing at 100° C for 4 hours. (4).

Qualitative and quantitative changes in the IR spectra during curing of a composition containing 0.2 wt% CNT-3 are shown in Figure1 and Figure 2. As you can see, during the day of curing at room temperature there is a very significant decrease in the intensity of the band 915 cm\(^{-1}\), and after curing at 100° C it almost completely disappear in the spectrum. At the same time, for a composition not containing nanotubes, the degree of conversion of epoxy groups did not exceed 60%. According to the graphs (Figure 2B), it is seen that an increasing in the concentration of CNT-3 from 0 to 0.5 % leads to a monotonic increase in the degree of conversion of epoxy groups. It remains high (at least 90 % after 24 hours at room temperature for all systems with CNT-3 and almost 100 % for thermoset samples).
Figure 2. Temporal dependences of the conversion of epoxy groups in a system containing: 1 – 0.2 % of CNT-3, 2 – 0.2 % of CNT-2 and 3 – 0.2 % of CNT-1 (A); 1 – 0 %, 2 – 0.2 % of CNT-3, 3 – 0.5 % of CNT-3 and 4 – 1 % of CNT-3 (B).

However, the obtained result was a characteristic only for samples with functionalized CNT-3. When dry native CNT-1 and CNT-2 were introduced into the systems, the conversion curves practically coincided with each other and with the curve for a system without CNTs (Figure 2A, graphs 2, 3 and Figure 2B, graph 1). The conversion of functional groups in extremely cured samples was not complete and amounted to about 64 % for systems with CNT-1 and 75 % for systems with CNT-2. This indicated that native nanotubes did not significantly affect the kinetics of the curing reaction at room temperature, and even in some cases prevent the complete opening of epoxy groups in thermoset samples. There are researches [27-29], where the effect of CNTs on the speed and final conversion of epoxy groups during curing of epoxy resins was discovered. In particular, it was shown in [27] by the DSC method that upon curing of epoxy resins in the presence of 0–5 % multilayer functionalized CNTs, the conversion corresponding to the maximum rate increased with an increase in the concentration of CNTs, i.e. with an increase in the total surface area of the modifier. A similar result was obtained in [28], where the effect of small additions of f-CNTs on the properties of an epoxy polymer cured by diaminodiphenylsulfone was studied.

It was found that in the range of CNT concentrations from 0.01 to 0.5 wt %, an extreme dependence of the dynamic elastic modulus and glass transition temperature on the modifier concentration is detected. This pronounced effect of functionalized CNTs on curing processes in [7] is explained by the fact that, due to the presence of a large number of oxygen-containing groups
(hydroxyl, carboxyl, etc.) on the surface of f-CNTs, the curing reaction acquires a catalytic character, and its rate can be 3-4 times higher than non-catalytic [17]. Another additional factor affecting the reaction rate and the conversion of epoxy groups according to [22] may be the formation of a large number of H-bonds between the functional groups of the epoxy oligomer and the surface of the modifier. In contrast, untreated nanotubes are prone to agglomerates due to their high surface energy and possibly static charge. Native nanotubes can form only weak van Der Waals interactions with the epoxy oligomer and are not able to catalyze the reaction. Agglomerates of nanotubes can also cause steric hindrance to the aminolysis of epoxy groups at high cure temperatures. Functionalized CNTs have a significant amount of active groups on the surface (predominantly carboxylic) directly involved in the reaction with epoxy groups, which determines a higher depth of the reaction both at room temperature and during thermosetting of systems.

To assess the degree of agglomeration of functionalized and native nanotubes in composites, microscopic studies of samples were carried out. Samples with a CNT content of more than 0.3 wt % were practically opaque; therefore, the measurements were limited to systems containing 0, 0.1, and 0.2 wt % CNTs. Microphotographs with a 400x magnification of the unmodified composition and systems containing 0.1 % of each type of CNT are shown in Figure 3. For the unmodified composition shown in Figure 3a, microbubbles of air are visible in the photo (marked by arrows). For systems containing CNTs, the agglomerates of nanotubes are clearly distinguishable in the photo, and the size of agglomerates for native CNT-1 was large (Figure 3b), and for CNT-2 it was much larger (Figure 3c) than for functionalized CNT-3 (Figure 3d). Obviously, the functionalization of nanotubes positively affects the degree of their dispersion in the polymer matrix, which ultimately leads to a higher conversion of epoxy groups.

![Microphotographs of compositions containing 0 % (a); 0.1 % CNT-1 (b); 0.1 % CNT-2 (c); 0.1 % CNT-3 (d). Magnification 400x.](image)

**Figure 3.** Microphotographs of compositions containing 0 % (a); 0.1 % CNT-1 (b); 0.1 % CNT-2 (c); 0.1 % CNT-3 (d). Magnification 400x.

4 Conclusion

Thus, the study of the effect of the concentration and functionalization of carbon nanotubes on the degree of conversion of epoxy groups in epoxy-amine compositions based on ED-20 and PEPA was carried out. It was shown that an increase in the concentration of functionalized CNTs from 0 to 0.5 % leads to an increase in the degree of conversion of epoxy groups upon curing at room temperature. A
further increase in concentration to 1 % does not affect the kinetics of the reaction. For native CNTs, no such dependence has been detected. This pronounced effect of f-CNTs on the kinetics of the aminolysis reaction and the final degree of conversion of epoxy groups is explained, apparently, by the catalytic effect of oxygen-containing groups (hydroxyl, carboxyl, etc.) grafted to the surface of CNTs and their direct participation in the reaction. It was shown by optical microscopy that the sizes of agglomerates of nanotubes were significantly higher in systems with native ones than in systems with functionalized nanotubes. These results can be significant in the development of nanoparticle modified epoxy composites.

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