

# Structurization and Moisture Absorption Features of Epoxy Nanocomposites with Carbon Nanotubes

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**Abstract**—Epoxy compositions cured in various temperature–time modes are studied by thermal analysis methods before and after modification by functionalized carbon nanotubes (FCNT). In the conditions where a formed network is not uniform and, thus, is characterized by a wide variety of different structural elements with different segmental mobility, the modification of epoxy resins leads to networks with less defects. In this case, the moisture sorption of the modified samples is lower as compared to the unmodified matrix. In the case where the selected temperature–time mode provides less defective networks in the starting sample, the moisture absorption of the modified sample is higher as compared to the unmodified one. It is shown that the mechanism of plasticizing of the FCN modified binders at moisture saturation depends on the mode of curing, differs from that of the unmodified samples, and requires further investigation.

**Keywords:** carbon nanotubes, aging, epoxy nanocomposite, thermal properties

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## INTRODUCTION

Carbon nanotubes (CNT) demonstrate a unique combination of physical, mechanical, electrical, and heat-conducting properties. The theoretical and experimental studies show that the values of the elastic modulus and the strength of CNT are about 1 TPa and 150 GPa, respectively [1, 2]. Depending on their atomic structure, CNT can show either metal ( $10^5$ – $10^6$  S/m) or semiconductor (10 S/m) conductivity [3]. According to the theoretical evaluations, the thermal conductivity of CNT is 2500–6000 W/(m K) [4, 5].

In addition, CNT have a low bulk density of 1.3–1.4 g/cm<sup>3</sup>, the specific surface of up to 1000 m<sup>2</sup>/g, and a high aspect ratio (nanotube length to diameter ratio) (more than 1000). Such a combination, in theory, makes CNT an ideal filler for the synthesis of composites combining high physical, mechanical, and functional properties (electrical and thermal conductivity, shielding, and absorption of radio-frequency electromagnetic waves), which can be applied in construction [6].

However, to provide the safe operation of polymeric composite materials (PCM), strict requirements on the reliability of structural materials are imposed. Currently, it is established that the technical state of products is the most significantly influenced not by mechanical wear of elements but by corrosion

and aging processes of structural materials under the combined action of atmospheric factors. Because of the absence of reliable information on the operating characteristics of PCM, high values of the factors of safety are used in design work, which decreases the efficiency of PCM use. The combined action of atmospheric factors leads to destructive processes which are localized in disordered regions of the polymeric matrix, namely, at the matrix–filler boundary, and cause an increase in the structural inhomogeneity [7].

The change in the strength parameters is determined by the chemical composition of the binder, the nature of fillers and coupling agents, the technological modes of the production, etc. At later stages of aging, the destructive processes become predominant, which leads to the decrease in the deformation and strength parameters. The change in the strength characteristics of composites appears at all stages of aging even in case where the influence of moisture is reversible. The decrease in the strength characteristics is especially pronounced (for certain materials higher than 50% of the starting values) at working temperatures, which is related to a significant decrease in the glass transition temperature of the polymeric matrix [8].

In [9], the regularities of change in the strength properties in PCM based on various fillers and epoxy

binders with the operating temperatures of 80 to 150°C are considered. The analysis of the results shows that the change in their properties at aging depends, first of all, on the chemical composition of binders, the stability of the polymer–filler boundary layer, and the degree of the exposure to aging of enhancing fillers. The moisture absorbed by the materials causes the weakening of the intermolecular interaction in the polymeric matrix (plasticizing effect), which contributes to the increase in the molecular mobility and, thus, leads to the decrease in the strength properties of a material. Simultaneously, the glass transition region shifts to the range of lower temperatures. Owing to the diffusion of the sorbed atmospheric moisture, the plasticizing effect of the polymeric matrix, and poor adhesion at the matrix–filler boundary, the deformation and strength properties decrease by up to 30% or more, and the glass transition temperature of the binders decreases by 25°C or more.

Despite the importance of studying the regularities of moisture absorption and the change in the properties of cured CNT-modified binders (epoxy nanocomposites) used for the development of structural functional materials, there are few works devoted to this topic yet [10].

The aim of this work is to study the effect of the curing modes on the moisture absorption of CNT-modified epoxy nanocomposites.

## EXPERIMENTAL

To perform a quantitative evaluation of the degree of functionalization of CNT by carboxylic groups, potentiometric studies by reverse acid–base titration were carried out using a TirolinEasy automatic titrator.

The IR spectra of the CNT were studied using an Infracuum FT-801 IR spectrometer in the wavelength range from 4000 to 550  $\text{cm}^{-1}$  with the resolution of 4  $\text{cm}^{-1}$ . To study the CNT morphology, the images obtained by scanning electron microscopy (SEM) using a two-beam Neon 40 CarlZeiss scanning electron microscope were analyzed.

The moisture sorption by the unmodified and modified samples in conditions of a humid heat impace was determined by a periodic weighing using a GR-300 laboratory balance after their exposure in a Climats EX 5413-HE climatic chamber. The conditions of the exposure were as follows: the temperature of 60°C, the relative humidity of 85%, and the time of testing determined by the time of reaching the equilibrium moisture absorption.

The relaxation transitions in the samples were studied by the method of differential scanning calorimetry (DSC) using a DSC 204 F1 Phoenix® instrument (NETZSCH). The heating rate was 20 K/min. The measurements were carried out in an argon medium blown through the measuring cell at the rate of 50 mL/min. Samples with the mass of 17–20 mg were cut with a scalpel to preserve their thermal prehistory.

To determine the linear temperature expansion coefficient (LTEC), a TMA 202 instrument (NETZSCH) for the thermomechanical analysis was used. The heating rate was 5 K/min. The measurements were carried out in a helium medium blown through the measuring cell at the rate of 70 mL/min using samples with the length of 18–20 mm.

To prepare the epoxy nanocomposites, the CNT functionalized by carboxylic groups (FCNT) were selected. The starting CNT (Taunit-M) were synthesized by CVD (chemical vapor deposition) pyrolysis using a Fe/Co catalyst. According the SEM data, the starting product contains mainly cylindrical nanotubes composed of 6–10 layers of carbon atoms with the average outer diameter of 8–15 nm and the inner diameter of 4–8 nm. The length of the carbon nanotubes is about 2  $\mu\text{m}$ , the specific surface is 300  $\text{m}^2/\text{g}$ , and the volume density of the powder is 15–30  $\text{g}/\text{dm}^3$ .

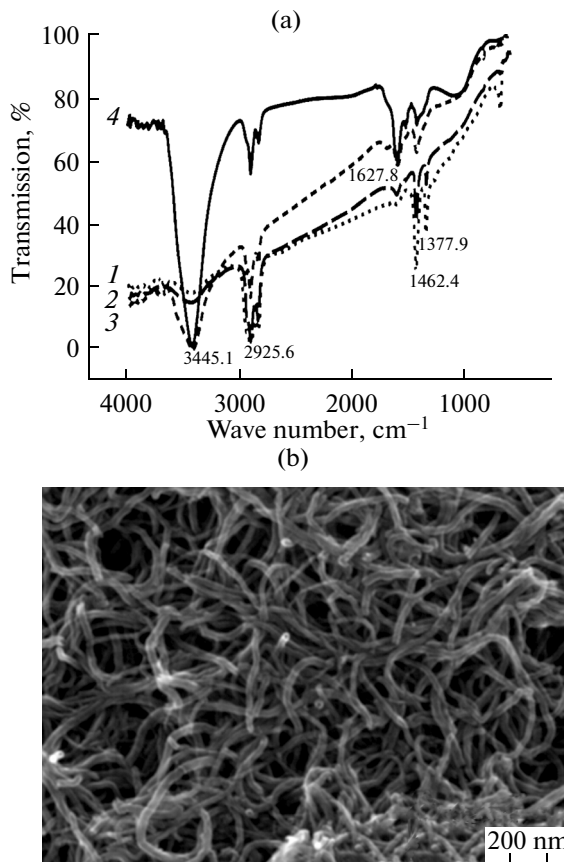
The functionalization of the surface of Taunit-M nanotubes surface by carboxylic groups was carried out by oxidation in concentrated nitric acid. Per 1 g of CNT, 50 mL of concentrated nitric acid (65%) was taken. The process was carried out in a reflux at the temperature of 110°C for 10 h. After the treatment, the functionalized CNT were isolated from the excess of acid by sedimentation and centrifugation, the precipitate was washed with distilled water in a filter until neutral pH. Then, it was washed with acetone several times until a thixotropic product was obtained. The content of the oxidized CNT in the obtained “paste” was 8.5–10.0 wt %. A similar technique was used in [11, 12] for the synthesis of the “paste.”

The qualitative composition of functional groups on the CNT surface was determined by the IR spectroscopy methods (Fig. 1a) by the absorption peaks in the band of 1627.8  $\text{cm}^{-1}$  referring to the C=O bond oscillations in carboxylic groups. The titrimetric analysis showed that the concentration of COOH groups after treatment of the nanotubes in nitric acid for 10 h was 0.6 mmol/g (by mass of nanotubes). The microstructure of the obtained CNT is shown in Fig. 1b.

The FCNT “paste” was mixed with ED-20 epoxy resin using a ULTRA-TURRAX T10 disperser (IKA) at the rate of 3000 rpm until a uniform dispersion was obtained. The rest of the acetone was eliminated by degassing at the temperature of 80°C for 40 min until the release of acetone stopped.

Then, a 4,4'-diaminodiphenylsulfone hardener was added to the dispersion in the stoichiometric ratio. The hardener was mixed with the dispersion using a laboratory stirrer at the temperature of 120°C for 20 min. The final FCNT concentration was 0.5 wt % of the mass of the resin and the hardener.

The ready composition were poured into aluminum foil molds and cured. The curing of the samples was carried out in three modes as follows: curing mode 1 was 140°C for 30 min and 180°C for 240 min; curing mode 2 was 140°C for 60 min and 180°C for 240 min;



**Fig. 1.** (a) Dependence of the IR spectrum of the Taunit-M CNT on the time of boiling in nitric acid: (1) starting sample, (2) 2-h oxidation, (3) 5-h oxidation, (4) 10-h oxidation; (b) SEM microphotographs of the Taunit-M CNT oxidized by boiling in nitric acid for 10 h:

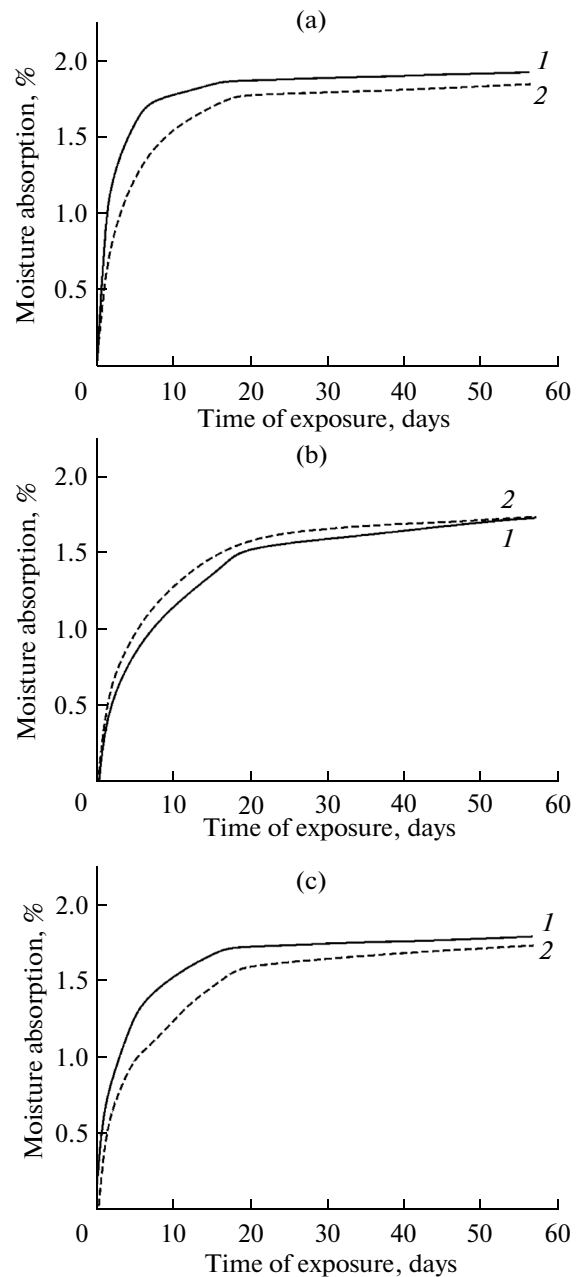
and curing mode 3 was 140°C for 90 min and 180°C for 240 min.

To perform the humid heat tests, rectangular samples with dimensions of 6 × 6 × 20 mm were sawed out of the cured materials.

## RESULTS AND DISCUSSION

In Figs. 2a–2c, the dependence of the moisture sorption of the unmodified and modified FCNT samples cured in various temperature–time modes are shown. The saturation of the materials with moisture was carried out until the equilibrium state over a period of 60 days.

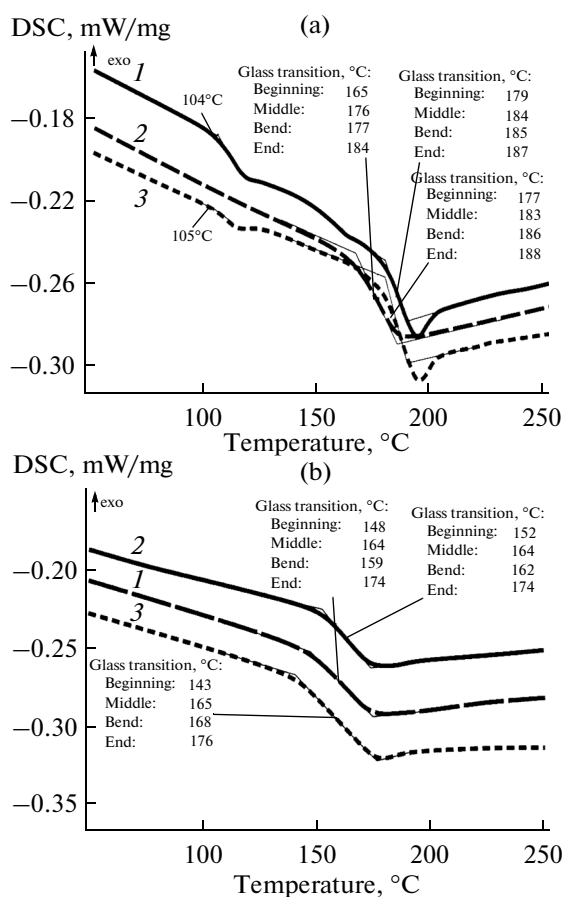
As seen from the results presented, the FCNT modification of epoxy resin influences the moisture sorption rate at the initial stage of saturation of the samples with moisture. At curing of the samples in modes 1 and 3, the modification leads to the decrease in the sorption rate, while in mode 2, the sorption dependences of the unmodified and modified samples almost coincide.



**Fig. 2.** Dependence of the moisture absorption on the time of exposure in the chamber in curing modes (a) 1, (b) 2, and (c) 3. Samples: (1) unmodified, (2) modified.

In Fig. 3, the DSC curves of the unmodified (a) and modified (b) samples cured in different modes are shown.

It is seen that the value of the temperature range  $\Delta T$  where the glass transition occurs ( $\Delta T = T_f - T_i$ , where  $T_f$  and  $T_i$  are the temperatures of the end and the beginning of the glass transition process, the point of the first bend of the DSC curve) depends on the curing mode. For the samples of the unmodified binder cured in modes 1 and 3, the  $\Delta T$  values almost coincide and they are 83°C, while for the sample cured at the mode 2,



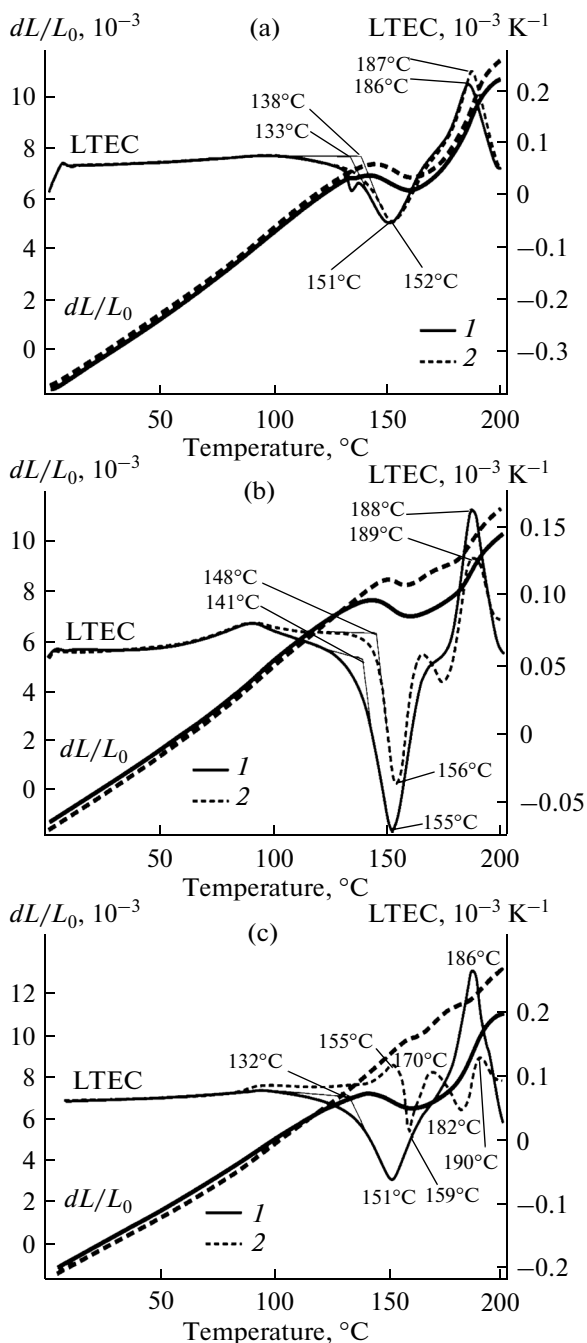
**Fig. 3.** DSC curves of the samples cured in various modes: (a) unmodified binder, (b) FCNT modified binder. The numbers of the curves correspond to the numbers of the curing modes.

the temperature range of the glass transition is only 19°C.

The FCNT modification of the binder leads to the decrease in the temperature range of glass transition in modes 1 and 3 down to 27 and 33°C, respectively. For curing mode 2, the  $\Delta T$  value is 22°C. For this mode, the modification of the binder by carboxylated FCNT leads to the decrease in temperature  $T_i$  by 14°C.

In Figs. 4a–4c, the temperature dependences of the elongation and the linear temperature expansion coefficient (LTEC) of the samples of the unmodified and FCNT modified binders immediately after moisture saturation for 11 days cured in modes 1–3 are shown.

For the unmodified samples cured in various modes, at the increase in the temperature, the LTEC value, after an insignificant increase, sharply decreases, passes through a minimum, then sharply increases, passes through the second peak, and then decreases again. The transition from the minimum to the maximum has a step-by-step character. For the samples cured in modes 1, 2, and 3, the temperatures of the first temperature transition are 133, 141, and



**Fig. 4.** Linear temperature expansion coefficient and elongation of the binder samples: (1) ED20/DADFS, (2) ED20/DADFS/FUNT, cured in modes (a) 1, (b) 2, and (c) 3, after moisture saturation for 11 days.

132°C, respectively, and the temperatures of the second peak are 186, 188, and 186°C, respectively.

It is noteworthy that, for the unmodified and modified samples that were not exposed to the impact of moisture, the temperature dependence of the LTEC value passes through only one bend (Fig. 5).

For the FCNT modified samples, the temperature dependence of the LTEC becomes more complex

(Fig. 5b). For the sample cured in mode 1, the temperature dependence of the LTEC was identical to the modified one, while for the samples cured in modes 2 and 3, there is one more minimum instead of the plateau. The same is the dynamics of the temperatures of the first transition (138, 148, and 155°C, respectively) and of the second peak (187, 188, and 182°C, respectively) for the modified samples cured in modes 1, 2, and 3.

## DISCUSSION OF RESULTS

It is natural to assume that the moisture absorption rate at the initial stage of the moisture saturation of the cured samples is determined by the quantity of structural defects in the network of transverse chemical bonds in the epoxy matrix. Then, the analysis of the moisture absorption curves for the unmodified samples allows us to conclude that curing in modes 1 and 3 leads to the formation of networks with a higher quantity of defects as compared to curing in mode 2.

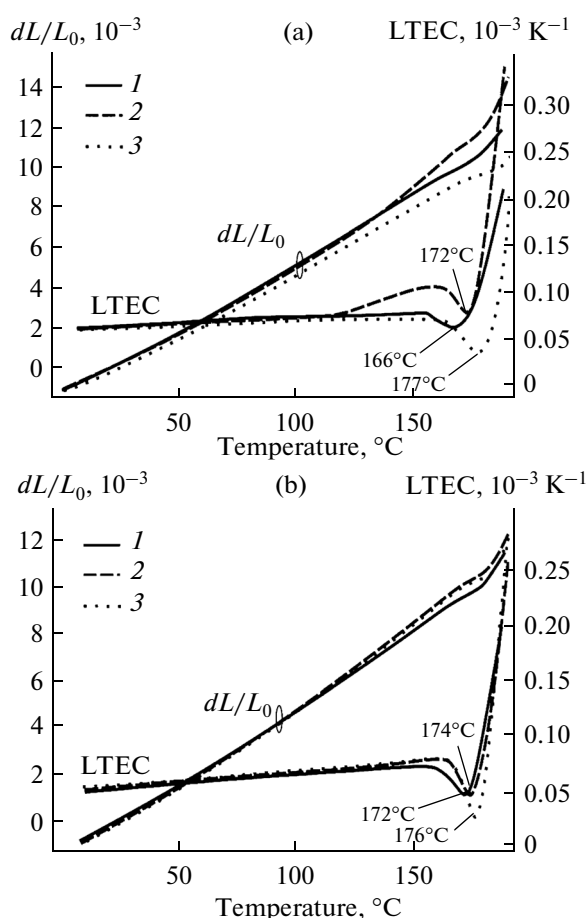
This is confirmed by a wider temperature range where glass transition occurs for the samples cured in modes 1 and 3. The defects occur as result of a nonoptimal temperature–time mode of curing. At curing in mode 1, an insufficient exposure at the low-temperature stage of curing leads to an early branching of the growing macromolecules and the formation of structural elements with different segmental mobility. At curing in mode 3, the transition to the high-temperature stage occurs after the gelling point (the gelling time in the studied composition is 80 min), which probably leads to the destruction of the network structure formed at the low-temperature stage of curing.

The network formed at curing in these modes is inhomogeneous and has numerous defects and “hanging” ends [13]. Thus, it is characterized by a wide spectrum of structural elements with different segmental mobility.

According to the results presented, the modification of epoxy binders by nanotubes functionalized by carboxylic groups leads to the decrease in the moisture absorption rate, which proves a lower quantity of defects in the network structure formed in the presence of FCNT.

In case of curing in the optimal mode (mode 2), the moisture saturation curve of the modified sample is somewhat higher as compared to the FCNT-free sample, which proves that FCNT contribute to the formation of a less dense network of transverse chemical bonds. This is also confirmed by the DSC results, which prove that the glass transition temperature of the modified sample is 11°C lower.

Probably, the appearance of the second peak in the temperature dependence of the LTEC of the unmodified samples saturated with moisture is related to partial evaporation of water in the process of the experiment. According to the thermogravimetric analysis data, in the heating conditions modeling the experi-



**Fig. 5.** Linear temperature expansion coefficient (LTEC) and elongation ( $dl/l_0$ ) of the binder samples: (a) ED20/DADFS, (b) ED20/DADFS/FUNT, cured in modes 1, 2, and 3.

ment for the determination of the LTEC, up to 80% of the adsorbed moisture is evaporated. In this case, the first transition on the LTEC temperature dependence curve can be identified as the glass transition of the “wet” part of the polymeric matrix. The glass transition temperature of the “wet” part of the samples cured in modes 1 and 3 almost coincide ( $\sim 133^\circ\text{C}$ ), while this temperature of the samples cured in mode 2 is significantly higher ( $\sim 141^\circ\text{C}$ ). This proves the assumption concerning a lower quantity of defects in the structure of this material.

As is seen from the given data, the FCNT modification of the epoxy binder samples leads to the shift of the temperature of the glass transition of the wet sample to higher temperatures as compared to the unmodified samples. In case of the modified samples cured in modes 1 and 3, the shift is 5 and 23°C and it can be explained by a higher content of moisture in them, while for the modified sample cured in mode 2, the value of the shift is 7°C. However, in this case, according to the moisture saturation data (Fig. 2b), the quantity of

moisture sorbed by the modified sample is somewhat higher than in case of the unmodified sample.

Probably, this fact, as well as the additional minimum in the region between the glass transition temperature of the “wet” and the “dry” part of the modified samples, indicates the difference of the plasticization of the unmodified and modified binders, which requires further investigation.

### CONCLUSIONS

The unmodified and FCNT-modified epoxy compositions cured in different temperature–time modes were studied by thermal analysis methods. In the conditions where the formed network is inhomogeneous, has a large number of cycles, and, thus, is characterized by a wide variety of structural elements with different segmental mobility, the modification of the epoxy binders leads to the formation of networks with less defects. In this case, the moisture absorption of the modified samples is lower as compared to the unmodified binders. In the case where the selected temperature–time mode provides less defective networks in the starting sample, the moisture absorption of the CNT modified sample is higher as compared to the unmodified one.

It was shown that the plasticization of the FCNT modified binders at the moisture saturation depends of the curing mode, differs from plasticization of the unmodified samples, and requires further investigation.

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