

## Effect of modification of carbon nanotubes by 3-aminopropyltriethoxysilane on the properties of silicone nanocomposites

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**Abstract:** The modification of the silicone compound with carbon nanotubes (CNTs) resulted in composites with improved physical properties and thermal stability. The carbon nanotubes were functionalized with 3-aminopropyltriethoxysilane for a more uniform distribution in the matrix. Initial and pre-oxidized CNTs containing different amounts of carboxyl groups were subjected to silanization. From 0.5 to 3 wt. % of the initial or functionalized CNTs were injected into Silagerm 2111 silicone compound. The obtained samples were characterized by FTIR and Raman spectroscopy and TG/DSC analysis. The silicon content in the silanized CNTs was determined by X-ray fluorescence spectroscopy. It was shown that the pre-oxidation of CNTs slightly affects the silicon content in the silanized nanotubes, which is up to  $(7.69 \pm 0.92)$  wt. %. According to Raman mapping of the surface of silicone composites, the silanized CNTs are more uniformly distributed in the surface layer of the material than the original nanotubes. This effect has a positive effect on the physical-mechanical properties of the composites. CNTs functionalized by 3-aminopropyltriethoxysilane are 1.5 times more effective in increasing the electrical conductivity than the original CNTs. The resulting composites retain their mechanical characteristics after thermal exposure and can be operated over a wider temperature range than the original silicone compound.

**Keywords:** nanomaterials; carbon nanotubes; nanocomposites; polymers; silicone; functionalization.

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## Влияние модифицирования углеродных нанотрубок 3-аминопропилтриэтоксисиланом на свойства силиконовых нанокомпозитов

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**Аннотация:** В результате модифицирования силиконового компаунда углеродными нанотрубками (УНТ) получены композиты с улучшенными физическими свойствами и термической стабильностью. Для более равномерного распределения в матрице углеродные нанотрубки подвергались функционализации 3-аминопропилтриэтоксисиланом. Силанизации подвергались исходные и предварительно окисленные УНТ, содержащие различное количество карбоксильных групп. От 0,5 до 3 масс. % исходных или функционализированных УНТ вводили в силиконовый компаунд марки «Силагерм 2111». Полученные образцы охарактеризованы методами ИК-Фурье и КР-спектроскопии, ТГ/ДСК-анализа. Содержание кремния в силанизированных УНТ определялось методом рентгенофлуоресцентной спектроскопии. Показано, что предварительное окисление УНТ незначительно влияет на содержание кремния в силанизированных нанотрубках, которое составляет до  $(7,69 \pm 0,92)$  масс. %. По данным рамановского картирования поверхности силиконовых композитов, силанизированные УНТ распределяются в поверхностном слое материала более равномерно, чем исходные нанотрубки. Функционализация способствует более равномерному распределению УНТ

в поверхностном слое материала. Данный эффект положительно сказывается на физико-механических свойствах композитов. Функционализированные 3-аминопропилтриэтоксисилом УНТ в 1,5 раза более эффективно увеличивают электропроводность, чем исходные УНТ. Полученные композиты сохраняют механические характеристики после термического воздействия и могут эксплуатироваться в более широком интервале температур, чем исходный силиконовый компаунд.

**Ключевые слова:** наноматериалы; углеродные нанотрубки; нанокомпозиты; полимеры; силикон; функционализация.

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## 1. Introduction

One-dimensional carbon nanostructures are often used as fillers that impart strength [1], thermal stability [2, 3], thermal conductivity [4] and electrical conductivity [5] of polymer composites, which can subsequently be used in various fields of technology. The advantages of carbon nanotubes (CNTs) and nanofibers as a modifying additive are, in addition to outstanding characteristics, a low specific gravity [6], due to which structures made with their use are very light.

The regularities of the formation of polymer nanocomposites based on CNTs have been studied in [7, 8]. It is noted that the strength properties of composites largely depend on the quality of the fiber-matrix interface, which determines the efficiency of stress transfer between carbon nanotubes and the polymer matrix [9, 10], and also that the nonpolar and smooth surface of CNT graphene layers often cannot provide the required interfacial interactions with the polymer matrix [11]. In addition, CNTs, like other nanomaterials, are prone to aggregation in various media, which significantly reduces the efficiency of their use in composites [12].

Functionalization of the nanotube surface is most often used to enhance the interaction of CNTs with polymer matrices and facilitate the dispersion of nanotubes in the bulk of the material. In the works of scientists, numerous methods are presented for grafting functional groups to the surface of CNTs, for example, by means of plasma treatment [13], electrochemical methods, liquid-phase oxidation [14–17], and treatment in vapors of various substances [18]. In [19], the regularities of covalent functionalization of CNTs by oxygen-containing groups are presented and the behavior of oxidized nanotubes when combined with polysulfone and polyaniline is shown. The authors noted that oxidized CNTs are capable of electrostatic interaction with polymer macromolecules, which changes the structure of the polymer layer adjacent to the nanotube surface.

In various studies, to modify silicone matrices, CNTs were preliminarily combined with

molybdenum dioxide [20], carbon black [21, 22], graphene [23, 24], branched alumina [25], and titanium dioxide [26]. It was shown in [27] that the dispersibility of CNTs plays a decisive role in the thermal stability of CNT/silicone rubber composites. In addition, the material containing evenly distributed nanotubes retains elasticity after holding at 280 °C for 7 days. For deagglomeration of nanotubes, long-term ultrasonic treatment in combination with jet milling was used in the study.

In addition, oxidized CNTs [28] functionalized with polysiloxane [29], dopamine [30], and aminosilanes [31–33] were used in composites with silicone.

The latter type of modifier is much better studied in the preparation of epoxy composites. It was shown in [20] that CNTs functionalized with 3-aminopropyltrimethoxysilane improve the mechanical properties of the epoxy polymer to a greater extent than the original nanotubes.

In [7], preoxidized CNTs were modified with 3-aminopropyltriethoxysilane. It is shown that surface-modified CNTs caused an increase in the elastic modulus and tensile strength of nanocomposites by 18 and 15.8 %, respectively, better than oxidized CNTs.

The efficiency of aminosilanes is explained by their ability to participate in the curing of the epoxy matrix (by amino groups), which promotes the formation of covalent bonds between functionalized CNTs and the epoxy network and improves the properties of the material [22–25]. The efficiency of silanized CNTs in silicone composites is due to the closeness of the chemical nature of the matrix and functional groups on the surface of nanotubes.

This study aims to investigate the effect of CNTs functionalized with 3-aminopropyltriethoxysilane on the properties of the Silagerm-2111 silicone compound, as well as to establish the dependence of the effect of using silanized CNTs on the conditions of preliminary oxidation of nanotubes with nitric acid.

## **2. Materials and Methods**

### *2.1. Characteristics of starting materials and reagents*

In this paper, we used Taunit-M carbon nanotubes manufactured by LLC Nanotechcenter (Tambov) with a diameter of 10–30 nm and a length of more than 3  $\mu\text{m}$ , obtained by the CVD method from a propane-butane mixture at a Co/Mo/Mg catalyst./Al [34].

For the oxidation of CNTs, nitric acid of chemically pure grade was used. (Khimmed, Russia). For CNT silanization we used: 1) 3-aminopropyltriethoxysilane  $\text{C}_9\text{H}_{20}\text{O}_5\text{Si}$  (98 % purity) provided by Nanjing Genesis Chemical Auxiliaries Co., Ltd. (Nanjing, China); 2) glacial acetic acid (Component-Reaktiv LLC, Russia); 3) isopropyl alcohol of chemically pure grade (CJSC Laverna, Russia).

Silicone compound Silagerm 2111 (Technology-Plast Production Association, Russia) was used as a composite matrix.

### *2.2. CNTs functionalization method*

A portion of carbon nanotubes weighing 0.5 g was dispersed in 95 mL of a solution of dilute acetic acid with  $\text{pH} = 5.2$  for 10 min using an ultrasonic homogenizer. 3-aminopropyltriethoxysilane was added to the resulting suspension. The mass ratio of CNTs/3-aminopropyltriethoxysilane was 1:10. The resulting mixture was kept in a flask under reflux at 80  $^{\circ}\text{C}$  for 4 hours with constant stirring at a speed of 100 rpm. At the end of the process, the CNTs were washed with distilled water to neutral pH and then dried in a heating cabinet at 80  $^{\circ}\text{C}$ .

In a number of cases, CNTs preliminarily oxidized with nitric acid were subjected to silanization. To do this, CNTs were boiled in concentrated nitric acid (1 g of CNTs per 50 mL of acid) in a flask under reflux for 2, 5, and 10 hours, after which they were washed on a filter with distilled water to neutral pH. The resulting aqueous paste was dried in a Scientz-10N Freeze Dryer (Scientz, China).

### *2.3. Nanocomposite preparation method*

The original and silanized CNTs were introduced into the silicone compound so that the mass fraction of nanotubes in the composite was 0.5, 1, or 3%. The resulting mixture was stirred for 3 minutes at a stirrer speed of 250 rpm. Next, the suspension was subjected to evacuation. Vulcanization took place at room temperature for 24 hours.

### *2.4. Characterization of CNTs samples and composites based on them*

The degree of functionalization of oxidized CNTs with carboxyl, lactone, and phenol groups was determined titrimetrically according to the Boehm method [35].

The silicon concentration in functionalized CNTs was determined by energy dispersive X-ray fluorescence analysis on an ARL QUANTX spectrometer (Thermo Fisher Scientific, Switzerland).

The IR spectra of carbon nanotubes were recorded in the range from 500 to 4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  on an FT/IR 6700 spectrometer (Jasco, Japan) equipped with an ATR attachment with a zinc selenide prism.

The Raman spectra of the samples with a resolution of 5  $\text{cm}^{-1}$  were obtained at an exciting laser wavelength of 532 nm on a DXR Raman Microscope (Thermo Scientific, USA). Raman maps of silicone nanocomposites with a step of  $10 \times 10 \mu\text{m}$  were recorded on the same device. The OMNIC<sup>TM</sup> Atlas software was used to analyze Raman spectroscopy and Raman mapping data.

The TG and DSC curves of the samples in air and argon were obtained on an STA 449 F3 Jupiter synchronous thermal analysis instrument (NETZSCH-Feinmahltechnik GmbH – Selb, Germany). The temperature program included holding at 30  $^{\circ}\text{C}$  for 10 minutes and heating from 30 to 900  $^{\circ}\text{C}$  at a rate of 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$ .

The electrical resistance of silicone nanocomposites was measured using an E6-13A teraohmmeter (Punane RET, Estonia). Raman spectra were obtained on a DXR Raman Microscope (Thermo Fisher Scientific, USA) with an excitation laser wavelength of 532 nm.

## **3. Results and Discussion**

### *3.1. Finding the parameters of oxidized and silanized CNTs*

According to the data of titrimetric analysis (Table 1), the composition of CNTs oxidized at various durations of treatment in  $\text{HNO}_3$  differs insignificantly. CNTs after 2 hours of treatment contain the maximum amount of phenolic groups, and CNTs after 10 hours of treatment are characterized by a higher content of carboxyl groups. The patterns of changes in the chemical composition of functional groups upon oxidation in  $\text{HNO}_3$  generally correspond to the data presented in [36].

**Table 1.** The content of acidic groups in oxidized CNTs

Duration of oxidation, h	Content of functional groups, mmol·g <sup>-1</sup>		
	phenolic	lactone	–COOH
2	0.3	0.3	0.5
5	0.2	0.4	0.5
10	0.2	0.4	0.6

According to [37], phenolic groups play the greatest role in the functionalization of oxidized CNTs with aminosilanes. It is in their place that Si–O–C bonds are formed. It is also possible to form hydrogen bonds between the C=O groups and the hydrolyzed silane.

According to the data of energy dispersive X-ray fluorescence analysis (Table 2), the content of silicon in samples of silanized CNTs differs insignificantly. However, oxidized CNTs interact with 3-aminopropyltriethoxysilane somewhat more efficiently than the original ones. The CNTs subjected to silanization after 2-h oxidation of CNTs with nitric acid are characterized by the highest Si content. Recall that these CNTs contained more OH groups than other types of oxidized CNTs.

Figure 1 shows typical IR spectra of the original, oxidized, and silanized CNTs. The original CNTs contain alkyl groups, which correspond to bands at 2920 and 2850 cm<sup>-1</sup> [38]. The broad band at about 3450 cm<sup>-1</sup> refers to the stretching vibrations of the O–H bonds of water molecules [39], which can be sorbed on the CNT surface. According to [40], the peaks near 1618 and 1385 cm<sup>-1</sup> are due to vibrations of the C=C and C–H bonds.

During oxidation, due to an increase in the hydrophilicity of the CNT surface, the intensity of the band at 3450 cm<sup>-1</sup> increases. In addition, a low-intensity peak appears at 1740 cm<sup>-1</sup> due to vibrations

of C=O bonds in carboxyl groups, the number of which was previously analyzed based on titration data. According to [41], the peak at 1136 cm<sup>-1</sup> in the spectrum of oxidized and silanized CNTs is due to vibrations of C–O bonds.

In the IR spectrum of CNTs treated with 3-aminopropyltriethoxysilane without preliminary oxidation, the band at 1385 cm<sup>-1</sup> takes the form of a narrow peak, which, according to [40], can be explained by vibrations of C–H bonds in the alkyl groups of the modifying reagent. In addition, a group of peaks is found in the region of 880–1262 cm<sup>-1</sup>, which, according to [42], are characteristic of silanized CNTs. A more detailed explanation is given in [43], where it is shown that the peaks at 880, 950, and 1262 cm<sup>-1</sup> are caused by vibrations of the Si–OH, Si–O–Si, Si–O–C, and Si–CH<sub>3</sub> bonds. It should be noted that there is no peak at 1385 cm<sup>-1</sup> in the spectra of CNTs silanized after preliminary oxidation, which may indicate a different nature of the interaction of 3-aminopropyltriethoxysilane with the surface of oxidized CNTs.

There is some difference in the IR spectra of CNT samples silanized before and after oxidation. In the case of pre-oxidized CNTs, the peak at 1384 cm<sup>-1</sup> is weak or absent, which can be explained by a change in the nature of the interaction between CNTs and aminosilane. In the case of unoxidized ones, a modifier layer is formed that does not form covalent bonds with the CNT surface. When oxidized CNTs are used, the OH groups of the hydrolyzed silane are involved in the formation of covalent and hydrogen bonds with the oxygen-containing groups of the nanotubes.

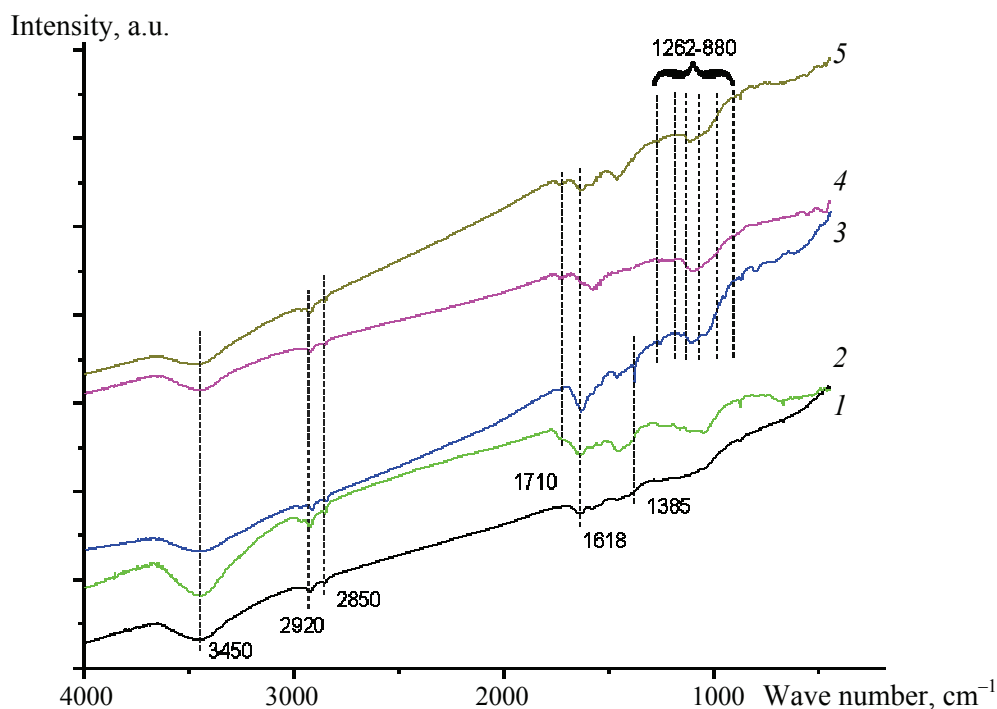
The Raman spectra (Fig. 2) of various types of CNTs used in the work show characteristic peaks G (~1570 cm<sup>-1</sup>), D (1350 cm<sup>-1</sup>), D + G (~2920 cm<sup>-1</sup>) and 2D (2700 cm<sup>-1</sup>). According to [44], the G peak dominates in the spectra of highly crystalline graphite, while the D peak is due to the presence of amorphous carbon. The integral intensity ratio D/G is usually used to characterize the number of defects in carbon materials [45]. Peaks 2D and D + G are overtones of the main peaks.

The results of processing the Raman spectra are presented in Table 3. Peak G in the Raman spectra of oxidized CNTs is shifted to higher wavenumbers compared to the same value for the original CNTs. In this case, the values of the D/G and 2D/G ratios for oxidized and silanized CNTs are practically the same as for the original CNTs. Consequently, functional groups are formed during oxidation at the site of defects in the original nanotubes, and new defects are formed to an extremely small extent.

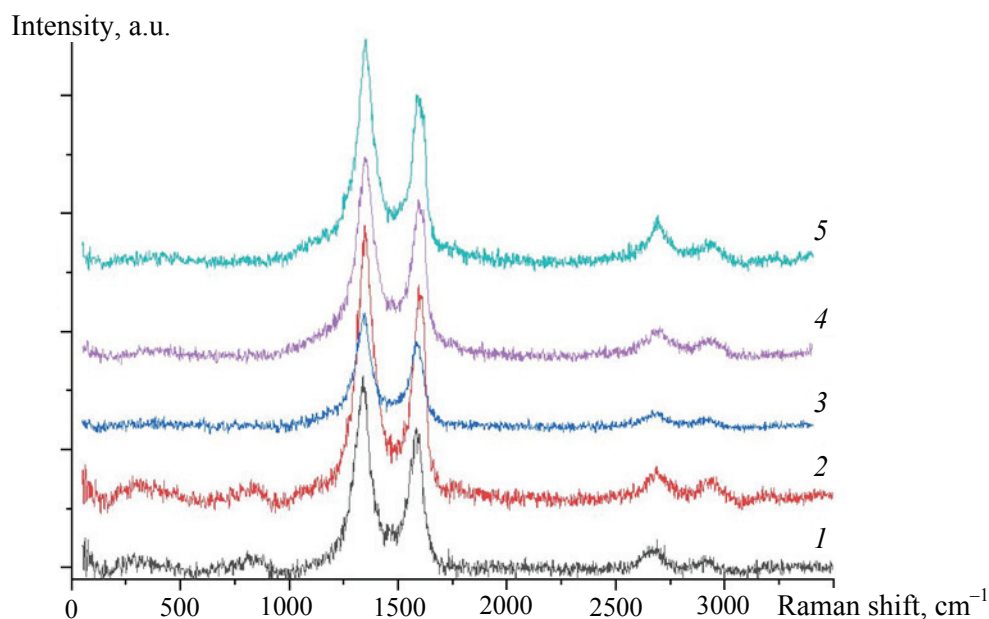
**Table 2.** Silicon content in samples of silanized CNTs according to energy dispersive X-ray fluorescence analysis

CNT pre-treatment conditions	Silicon content, wt. %
Without pretreatment	6.26 ± 0.75
2 hour oxidation	7.69 ± 0.92
5 hour oxidation	6.64 ± 0.80
10 hour oxidation	6.70 ± 0.80





**Fig. 1.** IR spectra of the original (1) oxidized with nitric acid for 2 hours (2), silanized without pre-oxidation (3) and after pre-oxidation for 2 (4) and 10 (5) hours



**Fig. 2.** Raman scattering spectra of CNTs: original (1); silanized without preliminary preparation (2); oxidized for 2 (3), and 10 (4) hours; silanized after preliminary oxidation for 5 (5) hours

In some cases, silanization contributes to an increase in the value of 2D/G due to the formation of a modifying layer of silanes or functional groups containing alkyl fragments.

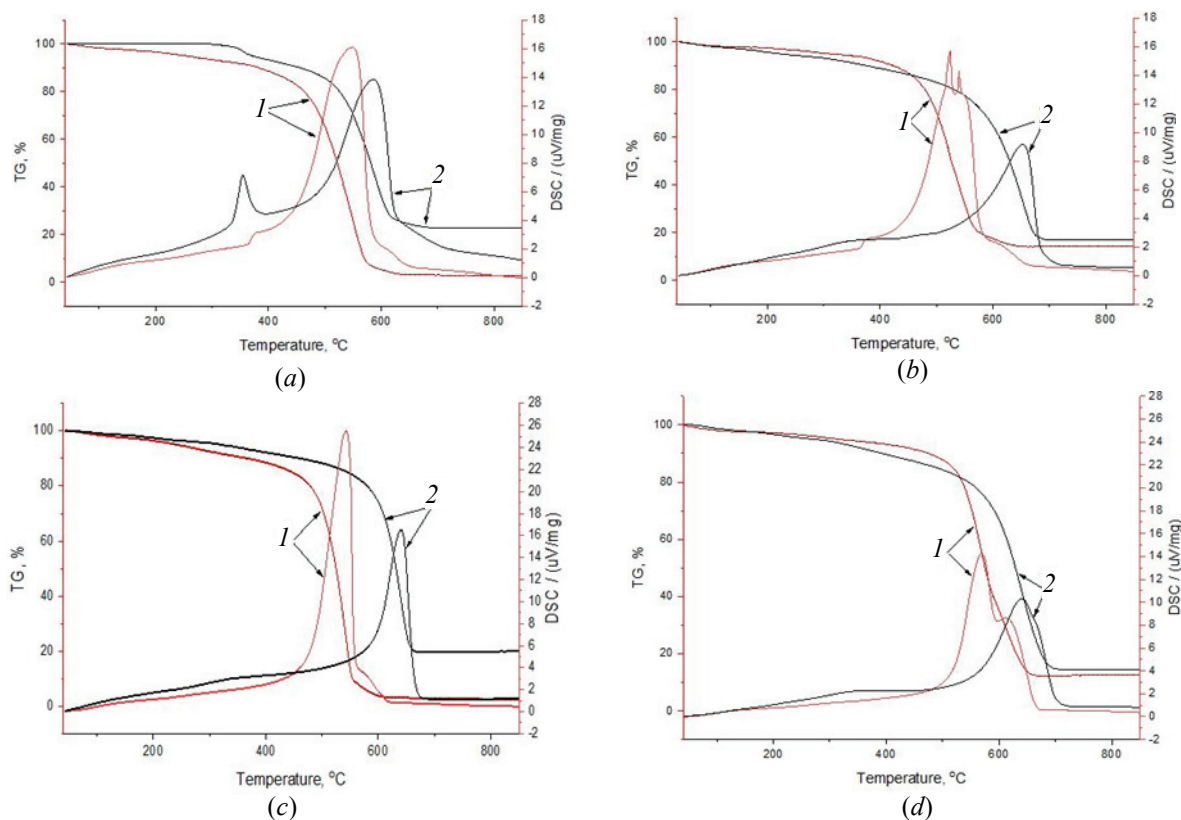
The data of TG/DSC analysis (Fig. 3) shows that the nature of the interaction between CNTs and 3-aminopropyltriethoxysilane and the behavior of the modified form upon thermal treatment depend on the

duration of the preliminary oxidation of CNTs. The behavior of the original CNTs (Fig. 3a, curves 1) is typical and was previously explained in detail in other papers [19].

Silanization in some cases contributes to an increase in the value of 2D/G due to the formation of a modifying layer of silanes or functional groups containing alkyl fragments.

**Table 3.** Results of processing of Raman spectra of original, oxidized and silanized CNTs

Sample	G Peak position, $\text{cm}^{-1}$	D/G	2D/G
Original CNTs	1584	0.85	1.69
CNTs oxidized for 2 hours	1599	0.84	1.68
CNTs oxidized for 5 hours	1592	0.85	1.69
CNTs oxidized for 10 hours	1610	0.84	1.67
CNTs silanized without pre-oxidation	1586	0.85	1.69
CNTs silanized after oxidation for 2 hours	1593	0.85	1.69
CNTs silanized after oxidation for 5 hours	1584	0.85	1.70
CNTs silanized after oxidation for 10 hours	1593	0.85	1.69

**Fig. 3.** TG and DSC-curves in air of original (a) and oxidized CNTs for 2 (b), 5 (c) and 10 (d) hours before (1) and after (2) silanization

The data of TG/DSC analysis (Fig. 3) show that the nature of the interaction between CNTs and 3-aminopropyltriethoxysilane and the behavior of the modified CNTs upon thermal treatment depend on the duration of the preliminary oxidation of CNTs. The behavior of the original CNTs (Fig. 3a, curves 1) is typical and was previously explained in detail in other studies [19].

The TG/DSC curves of the sample obtained by silanization of the original CNTs (Fig. 3a, curves 2)

contain 2 separate regions corresponding to the decomposition of CNTs and 3-aminopropyltriethoxysilane. The silanized CNTs are noticeably more thermally stable than the original ones; however, it can be assumed that in this case the modifier (3-aminopropyltriethoxysilane) does not form covalent bonds with the nanotube surface, but non-covalent modification takes place.

As a result of silanization of oxidized CNTs, we obtained materials whose intense thermal

decomposition begins 100–150 °C later than the corresponding nanotubes before modification (Fig. 3b–d). The change in the nature of the TG/DSC curves indicates a change in the nature of the interaction between CNTs and 3-aminopropyltriethoxysilane and the formation of chemical bonds between them. The best thermal stability is shown by the sample obtained by silanization of CNTs preliminarily oxidized for 5 hours.

### 3.2. Investigation of the properties of silicone nanocomposites

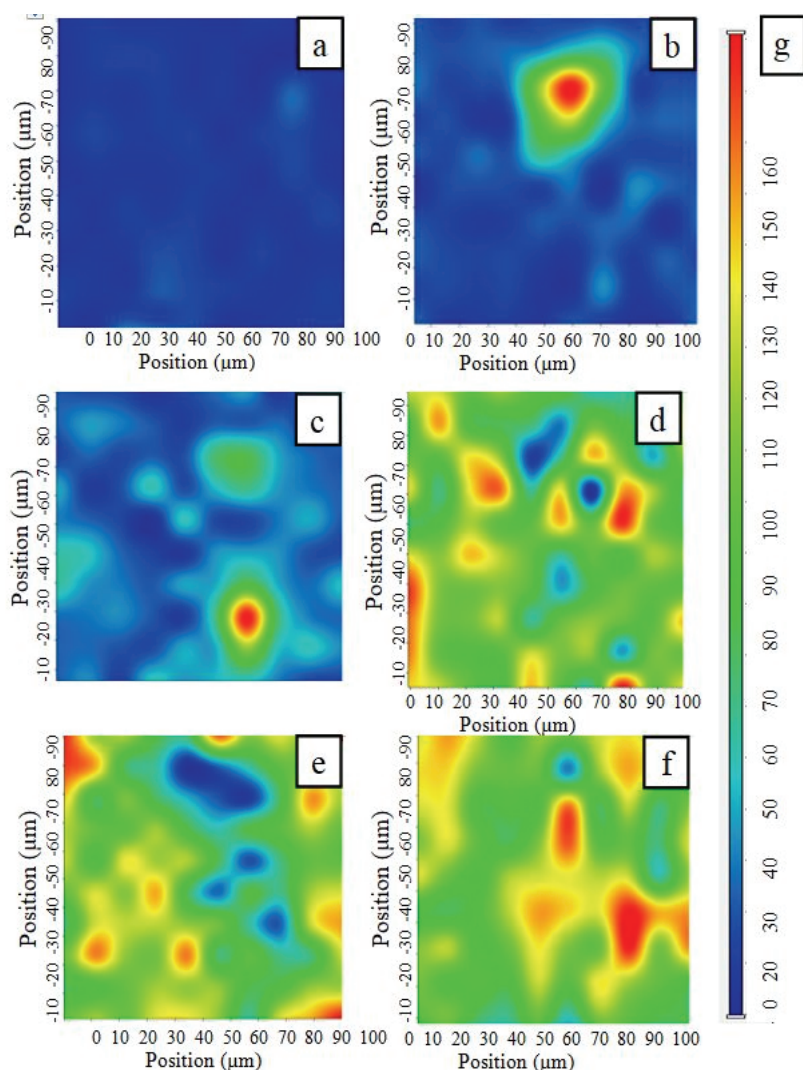
To find out the nature of the distribution of CNTs in the silicone matrix, Raman maps of nanocomposites were recorded (Fig. 4) and the intensity of the G-peak signal at different points of the surface was analyzed.

There is no G-peak signal on the Raman map of the surface of the nanocomposite obtained by adding

0.5 wt. % of the original CNTs to silicone (Fig. 4a). This indicates that the nanotubes are located in the bulk of the polymer matrix, at a considerable distance from the surface layer.

Regions up to  $20 \times 20 \mu\text{m}$  in size with a high intensity of the G-peak signal are found on the Raman map of the sample obtained by introducing the same amount of silanized CNTs into silicone (Fig. 4b). This indicates the tendency of this type of CNT to be localized in the surface layer of the composite.

A comparison of the Raman maps of samples containing 1 wt. % of the original (Fig. 4c) and silanized (Fig. 4d) CNTs shows that in the second case, the surface layer of the nanocomposite contains a larger amount of CNTs. As in the previous case, they form “islands” with transverse dimensions up to  $20 \mu\text{m}$ .



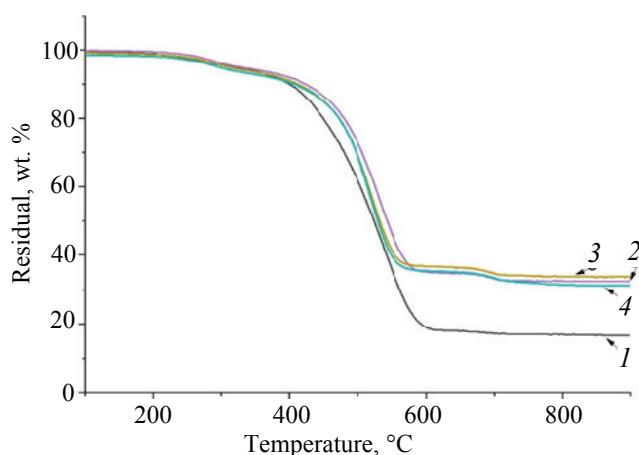
**Fig. 4.** Raman maps of the surface of silicone nanocomposites containing 0.5 (a, b), 1 (c, d) and 3 (e, f) original (a, c, e) and silanized (b, d, f) CNTs and the G-peak signal intensity scale (g)

When comparing the composition of the surface of composites containing 3 wt. % of original (Fig. 4e) and silanized (Fig. 4f) CNTs, it can be concluded that the area of areas without CNTs in the second case is noticeably smaller.

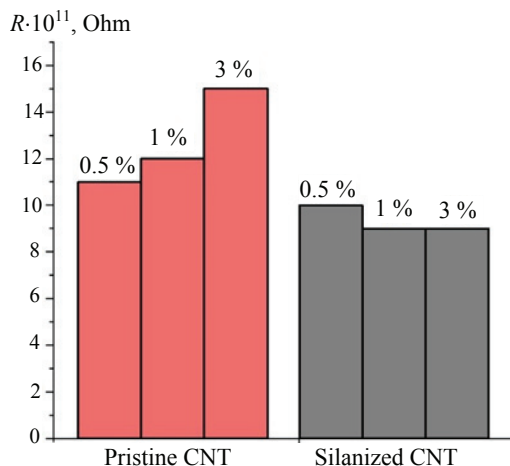
Thus, silanization contributes to a more uniform distribution of CNTs in the surface layer of silicone composites.

Figure 5 shows the TG curves of the original silicone and nanocomposites containing 0.5–3 wt. % silanized CNTs. It should be noted that the original Silagerm 2111 silicone compound is quite thermally stable. Up to 300 °C, its weight remains unchanged, and intensive destruction begins after 400 °C. The introduction of silanized CNTs practically does not change the behavior of the material in the temperature range up to 300 °C, but makes it somewhat more stable at temperatures above 400 °C. It should also be noted that the original silicone after holding at a temperature of 300 °C for 3–4 hours, according to visual observations, loses its elasticity, becomes brittle, and crumbles, while the appearance and mechanical characteristics of the nanocomposites remain unchanged. A similar effect was previously described in [46].

Also, by the TG curves, one can notice a significant difference in the residual mass of the composites and the original silicone. Given that the composites contain no more than 3 wt. % CNTs, the residual mass of these materials should not differ from the corresponding parameter of the unmodified material by almost 20 wt. %. It can be assumed that the introduction of silanized CNTs form chemical bonds with the silicone matrix, contributing to the formation of a material with a much higher thermal stability in an inert atmosphere.



**Fig. 5.** TG curves in argon of the original silicone (1) and nanocomposites containing 0.5 (2), 1 (3) and 3 (4) wt. % silanized CNTs



**Fig. 6.** Electrical resistance of nanocomposites containing original and silanized CNTs

Figure 6 shows data on the electrical resistance of the obtained nanocomposites. All obtained materials are dielectrics. According to [47], to achieve the percolation threshold and a noticeable increase in the electrical conductivity, more than 5 wt. % CNTs should be introduced into various polymer matrices. Possibly, in this case, too, a larger amount of conductive filler should have been introduced. We plan to obtain and study such nanocomposites in the future. However, a number of effects should also be noted here.

Thus, due to the significant agglomeration of the original CNTs in the silicone matrix, an increase in their concentration, contrary to expectations, leads not to a decrease, but to an increase in the electrical resistance of the material. Nanocomposites containing silanized CNTs, in general, have a lower resistance value than materials of a similar composition with original CNTs. With an increase in the concentration of silanized CNTs, there is a trend towards an increase in the electrically conductive properties of the nanocomposite due to the saturation of its surface layer with a conductive component. As a result, the electrical resistance of the nanocomposite containing 3 wt. % silanized CNTs is 1.5 times lower than that of the composite containing the same amount of original nanotubes.

#### 4. Conclusion

The functionalization of the original and preliminarily oxidized carbon nanotubes with concentrated nitric acid for various times with 3-aminopropyltriethoxysilane was carried out. It is shown that the content of silicon in functionalized samples weakly depends on the oxidation conditions; however, CNTs containing the



largest amount of phenolic groups are silanized more efficiently. The presence of silanol groups in the composition of modified CNTs is proved by IR spectroscopy data. According to TG/DSC analysis, 3-aminopropyltriethoxysilane is not chemically bonded to the surface of unoxidized CNTs, while covalent bonds are formed with oxidized nanotubes. Raman mapping of the surface of silicone nanocomposites made it possible to establish that silanization contributes to a more uniform distribution of CNTs in the surface layer of the material. Introduction 0.5–3.0 wt. % silanized CNTs with silicone compound Silagerm 2111 contributed to an increase in its thermal stability and retention of the mechanical properties of the binder after exposure at a temperature of 300 °C. The resulting nanocomposites were dielectrics; however, composites containing 3 wt. % silanized CNTs had a 1.5 times higher electrical conductivity compared to composites containing a similar amount of original CNTs. The studies performed have shown the promise of using silanized CNTs as part of silicone nanocomposites in order to expand the operating temperature range, maintain mechanical properties after thermal exposure, and increase electrical conductivity.

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### 7. Conflicts of Interest

The authors declare no conflict of interest.

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