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THERMAL DESTRUCTION AND THERMOPHYSICAL PROPERTIES OF POLYMER COMPOSITES BASED ON POLYESTER RESIN WITH DIFFERENT CONTENT OF CARBON NANOTUBES

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The purpose of this study was to determine the effect of carbon nanotubes (CNTs) on the thermal decomposition and thermo-oxidative destruction of nanocomposites based on polyester resin with a content of 0.1, 0.3 and 0.5 % by weight of CNT as characteristics of their heat resistance. Determination of thermal decomposition products, activation energy of their desorption, total amount of volatile decomposition products of composites was determined by the method of thermoprogrammed desorption mass spectrometry (TPDMS). Using derivatography methods (Q 1500D), patterns of thermo-oxidative destruction of polymer composites were investigated. It is shown that the addition of 0.1 wt. % CNT in the resin shifts the temperatures of the maximum thermograms (T_m) to higher values, increases the activation energy of desorption of all fragments of destruction products in the range m/z 18–104, compared to the original resin, i.e. this indicates an increase in the thermal stability of this composite. Increasing the CNT content to 0.3, 0.5 % by weight shifts T_m towards lower values, significantly reduces the activation energy of desorption for almost all polymer fragments. If at a content of 0.1 wt. %, CNTs in the polymer matrix are structurally “ordered” according to possible mechanisms, then an increase in the content of CNTs, on the contrary, leads to a reversible effect, due to the relatively large content of CNTs, their insufficient deagglomeration and uneven distribution.

Thermo-oxidative degradation of unfilled resin has two characteristic minima at $T = 383$ °C and 439 °C (endothermic reactions of thermo-oxidative decomposition). The addition of CNTs in the amount of 0.1, 0.3, 0.5 wt. % shifts the temperatures towards higher values. Samples melt up to 385 °C followed by combustion with maximum temperatures at 443 and 534 °C. Probably, the presence of the second peak (534 °C) indicates the possibility of the formation of a certain percentage of a more ordered phase in the polymer. Thermooxidative decomposition of composites is characterized by an increase in the initial temperatures of phase transitions. This is probably due to the presence of a carbon nanofiller in the polymer matrix, which increases the heat capacity and thermal conductivity of the composite, possibly initiating crosslinking centers of free (unbound) polymer chains, which, in turn, causes a decrease in kinetic mobility in the polymer.

Keywords: thermophysical properties, activation energy, nanocomposite, thermal degradation, carbon nanotubes, polyester resin, polymer structure, thermal oxidation degradation

INTRODUCTION

The development of modern nanotechnology allows for the creation of new materials and the improvement of existing ones that will surpass the existing ones in terms of their physical and mechanical characteristics and heat resistance. Polymeric nanocomposites based on synthetic resins are promising. The study of thermophysical

properties, namely thermal stability and thermal decomposition processes of polymer nanocomposites, is important not only for determining their consumer characteristics, but also allows us to expand our understanding of the structural transformations of the polymer matrix reinforced with a nanoscale filler, as evidenced by a significant number of works in this area, for

example [1–21]. In particular, in [1–3], the authors proposed a mechanism for the pyrolysis of epoxy resin, which is similar in structure to polyester resin and includes three key stages: the breakdown of N-C and NC-COH bonds, phenolic O-C bonds, and adjacent C-C carbon bonds. Widespread polyester composites filled with carbon materials (carbon nanotubes, graphene nanoplates, carbon fibers, *etc.*) attract special attention. The properties of unsaturated polyester resin significantly depend on the type of filler and functional groups on their surface [4–10]. Carbon nanotubes (CNTs) have many potential applications and are ideal fillers for polymer composite materials [11–21]. It is known that CNTs have relatively high thermal stability [22–24] and can be modified by functionalizing their surface [25]. In addition, due to the uniquely large aspect ratio (length-to-diameter ratio $\eta \sim 10^3$), the flow threshold ($\phi_{th} \sim 1/\eta$), *i.e.*, the content of CNTs at which a continuous network of CNTs is formed in the matrix, is $\sim 10^{-3}$ [14, 19, 26, 27].

To determine the thermal characteristics of nanocomposites, one of the methods is thermally programmed desorption mass spectrometry [28–31]. In particular, in [32], the authors determined the effect of 0.3 wt. % CNTs on the thermal stability and mechanical parameters of polyester resin-based composites. A significant effect of the filler on the strength characteristics and a slight effect on thermal decomposition were noted. The data on the effect of CNTs on mechanical properties are consistent with the composites studied by us [33] and the authors of [34–36]. Work [37] investigated the effect of the diameter and content of CNTs on the effective thermal conductivity of polyester resin composites. The experimental data obtained in [38] describe a theoretical model of the thermal conductivity of polymer composites based on polyester resin filled with CNTs, which takes into account the dimensional effects of nanotubes. In [39, 40], the effect of CNTs on the thermal properties of polyester composites was studied, taking into account the type and content of CNTs: 0.10, 0.15, 0.20 % by weight. The specific heat capacity and linear thermal expansion coefficient were measured and compared for all nanocomposite samples. The nanocomposites (except for the polyester composite with 0.1 wt. % CNTs) showed an increase in the specific heat capacity compared to pure polyester.

For the heating and cooling curves, nanocomposites with CNTs showed higher values of specific heat capacity with a maximum of 0.15 wt. %. On the heating and cooling curves, the increase in specific heat capacity was 76 and 51 %, respectively, compared to pure polyester.

It should be noted that the dependence of the strength characteristics of nanocomposites on the content of nanotubes is not monotonic [41, 42]. The theoretical analysis carried out in various models, for example [16–17, 43–46], shows that such a change in properties is due to the characteristics of different phases formed at the interface between the nanofiller and bulk polymer. Molecular dynamics simulations [16] demonstrate the formation of an ordered layer of polymer matrix around the CNTs. This layer, known as the interfacial, plays a central role in the overall mechanical response of the composite. It is believed that due to poor load transfer from the matrix to the CNT, the strengthening effect associated with the CNT is negligible. Consequently, the presence of an interfacial surface is recognized as the only reason for improving the performance of the composite.

It should also be noted that the presence of defects in CNTs can also affect the degree of chemical interaction between the filler and the polymer. When CNTs are added to a resin, it is possible that the effectiveness of interaction with polymer chains depends on the number of defects in the nanotube structure, the state of the surface after its modification, and their optimal content in the composite [25].

Thus, from the literature review, it can be concluded that the addition of CNTs, both native and functionalized, increases the level of characteristics of nanocomposites.

MATERIALS AND METHODS

A commercial unsaturated polyester resin of the Estromal brand was used as a polymer matrix. This is an orthophthalic resin based on recycled PET (LERG S.A., Poland). As a filler, multilayer CNTs were used, which were synthesized by catalytic chemical vapor deposition (CCVD) in the fluidized bed mode, which was created by rotating the reactor [47]. A three-component oxide with a metal ratio of $\text{Al}_2\text{FeMo}_{0.21}$ was used as a catalyst. The source of carbon was propylene obtained in the process of propanol dehydration. The synthesized CNTs have a specific surface area of $\sim 240 \text{ m}^2/\text{g}$. The average diameter of the

CNTs was 10–40 nm according to [48]. The filler content in the polymer composites was 0.1, 0.3, and 0.5 wt. %.

Preparation of composites and curing conditions. CNTs were added to the liquid resin, after which the samples were placed in a flask, heated to 55 °C for 2 h and vacuumed until homogeneous solutions were obtained. As hardeners, 1.1 wt. % Luperox and 0.25–4 % cobalt solution were used as reaction accelerators. It should be noted that the effect of a uniform distribution of filler nanoparticles in the polymer matrix significantly depends on their size, the interaction of the polymer phase on the particle surface, and the interaction between the filler particles themselves and macromolecule segments that form the spatial molecular network of the polymer. Therefore, a preliminary ultrasonic dispersion of carbon nanotubes in hexane solution was performed to better distribute the nanoparticles in the matrix and to avoid their aggregation in the composite. The resin and its composites were polymerized at room temperature and then at ~ 55 °C for 18 hours.

Thermally programmed desorption mass spectrometry (TPDMS). The composition of volatile products of thermal degradation of composites was determined by the data of mass spectrometric registration of degradation products obtained on a mass spectrometer MX 7304A (Ukraine, Sumy) with a programmable temperature change in the range of 25–800 °C. The temperature measurement accuracy was ± 0.05 °C. The mass spectra of the decay products of the samples were recorded and analyzed using an automated computer-based data recording and processing system. The mass spectra were recorded in the range of m/z 15–200 a.m.u. According to the mass spectrometric analysis, desorption curves were obtained, which were used to determine the thermal decomposition of resin composites with CNTs.

The thermal properties of the polymer composites were studied using a Q-1500D derivatograph (MOM, Hungary) equipped with a computerized measurement recording system. Samples (50 mg) were heated in a ceramic crucible at a rate of 10 °C/min in an air atmosphere using aluminum oxide as a reference substance. Measurements were performed at a temperature of RT – 1000 °C.

Methods for calculating the activation energy of desorption. The activation energy E_d of

thermal destruction of composites was determined by the Wigner-Polanyi and Redhead formulas. The activation energy of desorption in different temperature ranges was calculated by the generalized Redhead formula [49]: $\ln(T_m^2/\beta) = [E_d/(R \cdot T_m)]$, $\rightarrow E_d = R \cdot T_m \ln(T_m^2/\beta)$, where T_m is the temperature of the maximum curve, R is the gas constant, and β is the heating rate. Wigner-Polanyi formula [50, 51]: $E_d = \ln(\Theta_1/\Theta_2) \cdot R \cdot (T_1 \cdot T_2)/(T_2 - T_1)$, where T_1 and T_2 are the temperature values in the middle of the maximum intensity of the desorption spectrum (from TPD MS data), R is the universal gas constant, $R = 8.314$ J/(mol·K), Θ_1 and Θ_2 are the areas under the curve corresponding to the relative amount of volatile products from T_1 and T_2 , respectively.

RESULTS AND DISCUSSION

To study the thermal properties of nanocomposites, the method of thermally programmed desorption mass spectrometry and derivatography methods was used. It is expected that the results obtained can provide useful information on the thermal destruction of composites to obtain materials with increased thermal stability. In our previous studies, it was found that the addition of carbon nanotubes to unsaturated polyester resin has a positive effect on the properties of the composite [33]. The purpose of this study was to determine the effect of CNTs on the thermal stability of polyester resin, i.e., on the thermal decomposition and thermo-oxidative destruction of nanocomposites: determination of decomposition products and desorption activation energy of thermal decomposition products and patterns of thermo-oxidative destruction of composites based on polyester resins depending on the content of CNTs.

Based on the results of the TPDMS data, the decomposition of composites, namely polymer chains, was studied and their main decomposition products, which are part of the structural links of unsaturated polyester resin, were determined according to [52]. It should be noted that the resin has a three-dimensional spatial structure, which has benzene rings with carbohydrate groups that act as transverse bridge bonds [53] between the main chains of the polymer and play a role in the resistance of the polymer properties to external factors (temperature, aggressive environment, mechanical loads).

The main decomposition products were determined by mass spectra in the range of $15 \leq m/z \leq 200$ for unfilled resin and resin with CNTs (Fig. 1 *a-d*). As can be seen from Fig. 1, the destruction of resin and composites produces volatile products with different m/z , which can be identified as 18 (H_2O), 28 (CO), 44 (CO_2), 78 (C_6H_6) (benzene ring), 91 ($\text{HC}_6\text{H}_6\text{C}$), 104 (styrene). The benzene ring and styrene act as bridge chains of the resin and are one of the main decomposition products of composites based on synthetic resins according to [4, 54]. Therefore, it is important to reduce the desorption of styrene under the influence of high temperatures, for

example, by their interaction with the functional groups of the filler. It should be noted that the mass spectra do not contain decay products with masses greater than 120 a.u., which probably indicates the thermal stability of significant sections of the polymer chains. When the heating temperature of the samples reaches ≥ 250 °C, the destruction of bridge cross-links between the polymer chains occurs, as evidenced by the formed fragments with masses $75 < m/z \leq 105$. At temperatures above 317 °C, a decomposition product with m/z 118 appears in the mass spectra, which probably characterizes the desorption of significant polymer chains.

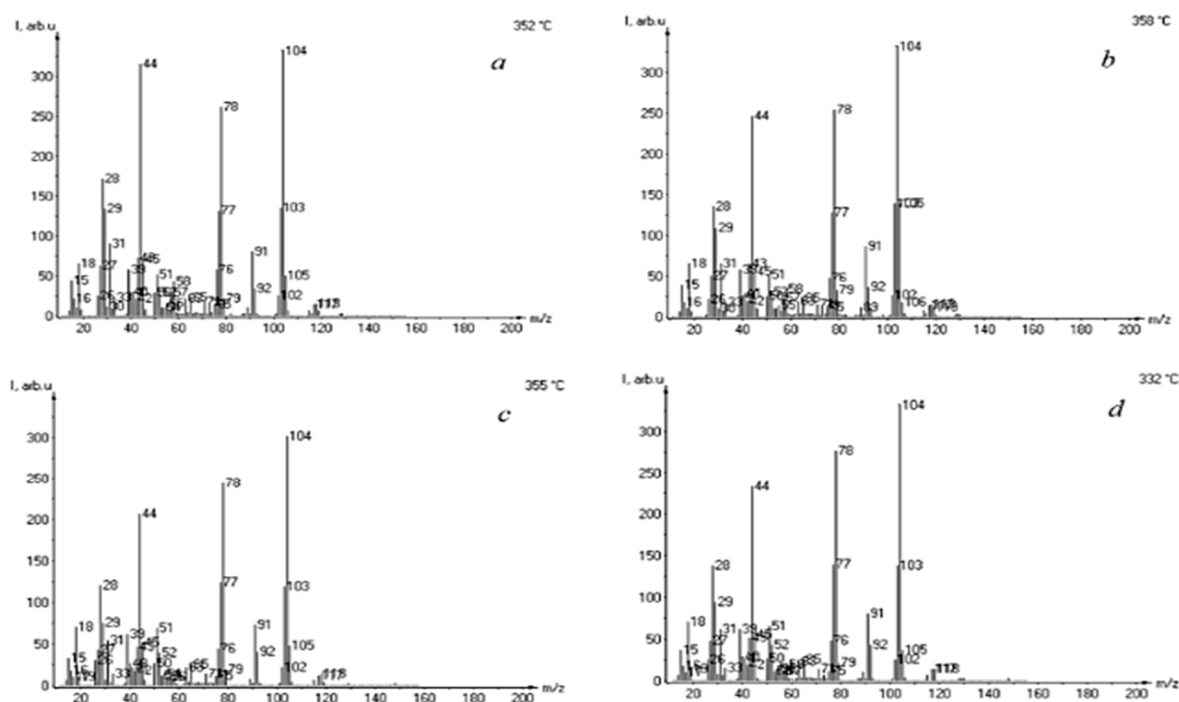


Fig. 1. Mass spectra of unfilled polyester resin (*a*) and its composites with CNTs at 0.1 (*b*), 0.3 (*c*), and 0.5 (*d*) wt. %

To determine the course of thermal degradation of nanocomposites, we determined the intensity and temperatures of the maxima of thermograms of polymer chain degradation products, which is known to depend on the number of weakened/destroyed/formed chemical bonds in the composite. Fig. 2 shows the desorption curves characterizing the thermal decomposition of the native polyester resin (*a*) and its composites with CNTs at 0.1 (*b*), 0.3 (*c*), and 0.5 (*d*) wt. %.

As can be seen from Fig. 2, the desorption of products with $m/z > 18$ is characterized by a

single stage of thermal decomposition with a single temperature maximum (Table 1). The maximum amount of desorbed water ($m/z = 18$) is observed in the temperature range up to 100 and ~ 350 °C. The second temperature maximum is probably due to the destruction of the chemical bond between atoms in the polymer links. At a CNT content of 0.1 wt. % the maximum decomposition temperature increases by approximately 5–10 °C, *i.e.*, the thermal stability of the composite increases. This effect indicates a certain structural rearrangement of the polymer matrix, possibly with the formation of an

interfacial surface or greater interaction of the functional groups of the filler with the polymer chains (Table 1).

It should be noted that the T_m °C position shifts towards lower temperatures at 0.3 and

0.5 wt. % CNTs °C (Table 1), but the intensity of thermal degradation of decomposition products in composites with CNTs decreases over the entire filling interval (Fig. 3).

Table 1. Maximum desorption temperatures of thermal decomposition products of polyester resin (0) and composites with CNTs at 0.1 wt. %, 0.3 and 0.5 wt. %

<i>m/z</i>	composition	$T_m, ^\circ\text{C}$			
		0	0.1 %	0.3 %	0.5 %
18		345	348	325	330
28		345	351	330	309
44		348	354	332	311
78		369	374	337	331
91		370	362	338	337
104		356	362	337	334

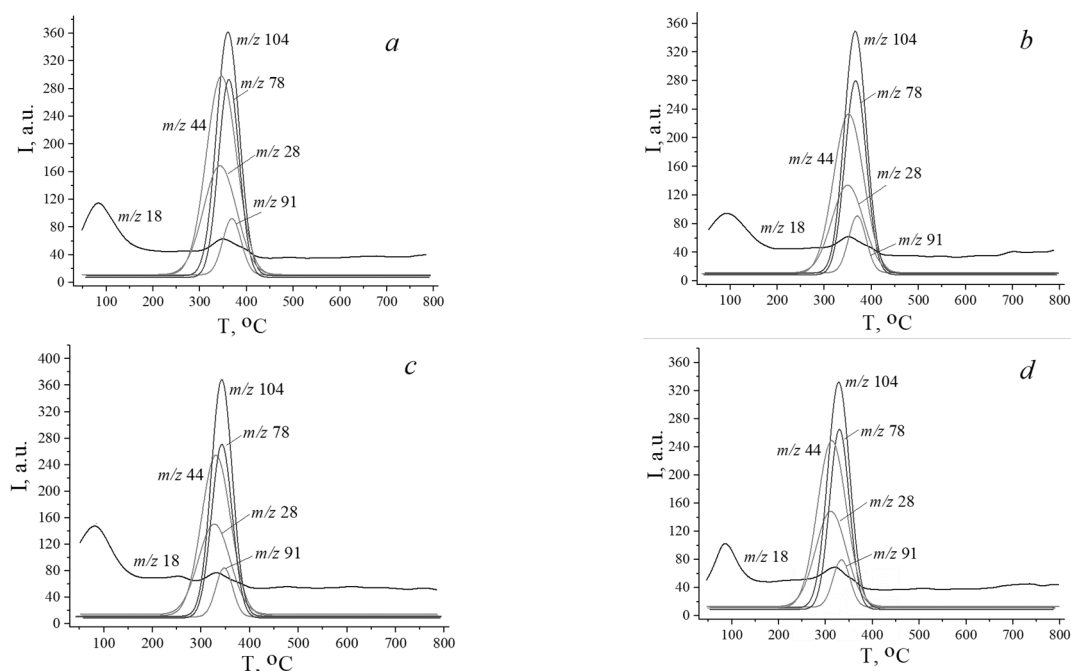


Fig. 2. Thermograms of decomposition products of unfilled polyester resin (a) and its composites with CNTs at 0.1 (b), 0.3 (c), and 0.5 (d) wt. %

Fig. 3 shows the TPD spectra of decomposition products of the resin and its composites depending on the content of CNTs. Thermal decomposition of resin and composites with CNTs according to the desorption spectra occurs in the temperature range of 200–450 °C, which is typical for polyester resin [54]. Fig. 3 shows that the desorption of water from *m/z* 18 composites with CNTs at 0.1 and 0.5 wt. % occurs in two stages and has two temperature maxima in the intervals $50 \leq T \leq 110$ °C and $300 \leq T \leq 400$ °C. At a content of 0.3 wt. % of

CNTs, an intermediate peak in the range $230 \leq T \leq 260$ °C and an increase in the intensity of thermal destruction are observed. At the same time, the temperature of the second maximum for the composite with 0.1 wt. % coincides with the temperature of the maximum of the original resin, and at the content of 0.3 and 0.5 wt. % shifts in the area of lower temperatures, the more the content of CNTs is higher.

Practically for all mass fragments for a composite with a content of 0.1 % by mass the temperature of the CNT desorption maximum

increases compared to the original resin, while for composites with a content of 0.3 and 0.5 wt. % are decreasing. Moreover, this decrease is greater for the system with a higher content of CNTs. At

the same time, the decomposition temperature interval practically does not change. The intensity of thermodegradation slightly decreases with the filling of CNTs.

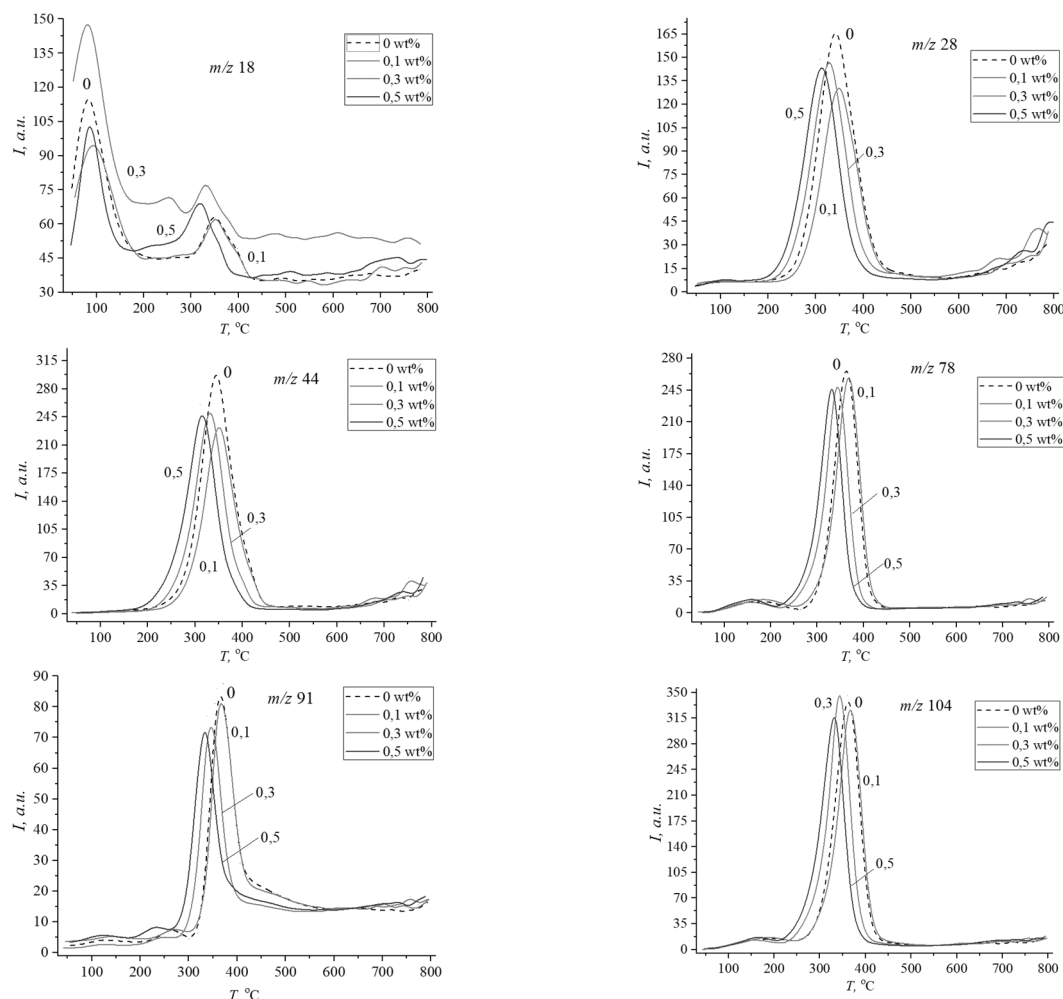


Fig. 3. Thermograms of decomposition products with m/z 18 (H_2O), 28 (CO), 44 (CO_2), 78 (C_6H_6) (benzene ring), 91 ($\text{HC}_6\text{H}_6\text{C}$), 104 (styrene) ($\text{C}_6\text{H}_5\text{C}=\text{CH}_2$) of resin and its composites with CNTs at 0.1, 0.3, and 0.5 wt. %

To determine the kinetic parameters of the thermal degradation of polyester resin and composites with CNTs, the activation energy of degradation was calculated from the thermograms of TPD MS (Figs. 2 and 3) and derivatographic study curves (Fig. 6).

The values of the activation energy of destruction E_d as dependent on the content of CNTs are shown in Fig. 4 and the concentration dependences of E_d and the total amount of desorbed decomposition products Q depending on the mass m/z of thermal decomposition products (Fig. 5). Fig. 4 very tellingly shows that the introduction of 0.1 wt. % CNT increases the

activation energy of the degradation of the polymer composite, while increasing the content of CNT to 0.3, 0.5 wt. % significantly reduces this energy for practically all polymer fragments. This conclusion is consistent with the data in Fig. 5 *a*. As can be seen from Fig. 5 *b*, the relative amount of Q products for m/z 28 and 44 during the degradation of CNT-filled resin composites decreases with filling. However, for larger m/z , it practically does not change.

If at a content of 0.1 wt. % CNTs in the polymer matrix are structurally “ordered”, which probably corresponds to an increase in the degree of orderliness of the structure of composites in the

interphase region, including due to the formation of heat-resistant bonds between polymer chains and the filler, then increasing the content of CNTs, on the contrary, leads to a reversible effect, according to due to the relatively large content, insufficient deagglomeration and uneven distribution of CNT. As, for example, [26], where the most uniform distribution of CNTs was

observed in the polychlorotrifluoroethylene (PCTFE)–CNTs system (with a content of 0.5, 0.25 and 0.125 wt. %), achieved with a minimum content of CNTs during dispersion (0.125 wt. % CNTs), corresponds to the maximum value of electrical conductivity, the lowest percolation threshold, and correlates with the maximum bending strength.

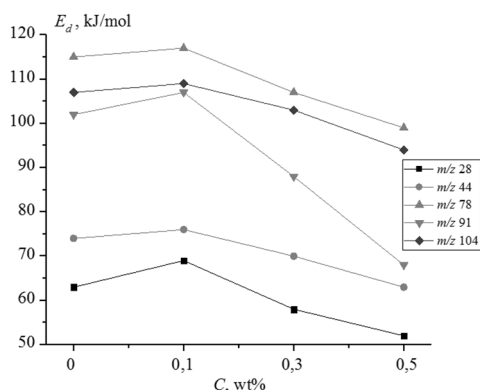


Fig. 4. Dependence of the activation energy of decomposition E_d of decay products calculated by the Polanyi-Wigner formula for polyester resin composites (0) on the content of CNTs at 0.1, 0.3, and 0.5 wt. %

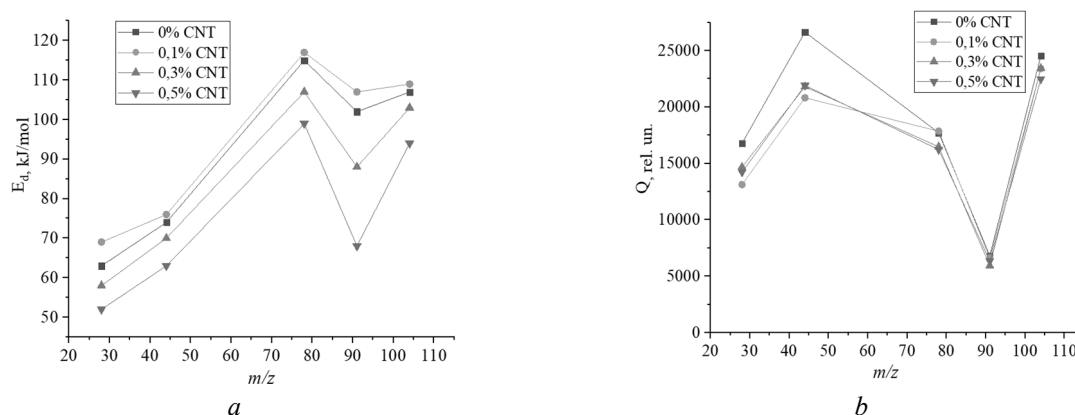


Fig. 5. Dependences of the activation energy of desorption products (a) and the total amount of volatile decomposition products (b) with different m/z depending on the content of CNTs

According to the results of thermal analysis (DTA and TG/DTG, Fig. 6), it was determined that the thermal decomposition of the native resin and composites with CNTs begins at ~ 230 °C. The initial mass loss at $T \leq 100$ °C is due to residual water in the samples. It was determined that the percentage of water is about 3–4 %, which indicates the hydrophobicity of the resin. According to the DTA curves, the thermo-oxidative degradation has two characteristic maxima at 383 and 439 °C for the unfilled resin. The addition of CNTs in the amount of 0.1 wt. %

shifts the maxima towards higher temperatures. These two stages characterize endothermic thermal decomposition reactions. In the temperature range up to 385 °C, melting of the samples occurs, followed by burning of the sample with temperature maxima at 443 and 534 °C. Probably, the presence of the second peak indicates the possibility of the formation of a certain percentage of crystalline structures of the “interfacial surface” (crosslinking between chains) in the polymer. Such structures, in our opinion, are an ordered arrangement of polymer

chains due to interaction with CNTs. When $T \sim 500\text{ }^{\circ}\text{C}$ is reached, the solid crystalline phase of the composites transitions to the melt phase. Since the DTA shows a wide range of thermal oxidation (600–900 $^{\circ}\text{C}$), we can assume high thermal stability. According to the TGA curves, it was determined that thermal decomposition is characterized by an increase in the initial temperatures of phase transitions when filling the CNTs. This is probably due to the presence of a carbon nanofiller in the polymer matrix, which

increases the heat capacity and thermal conductivity of the composite, possibly initiating crosslinking centers of free (unbound) polymer chains, which, in turn, causes a decrease in kinetic mobility in the polymer.

Among other things, the presence of carbonyl groups and aliphatic chains in CNT composites helps to reduce chain flexibility and, as a result, increase thermal resistance to thermal oxidative degradation.

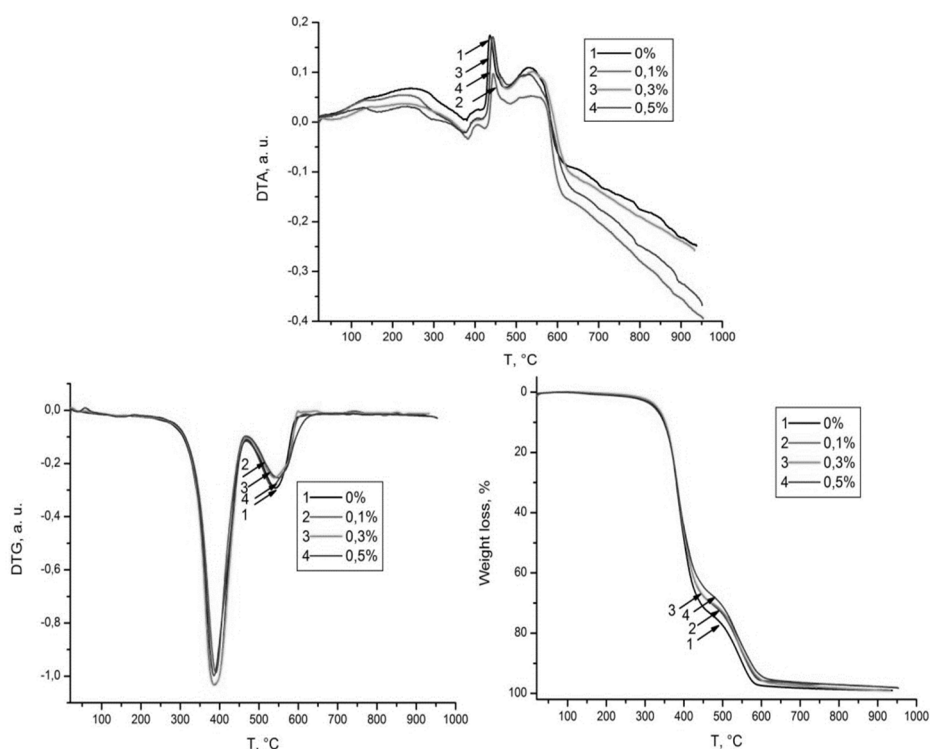


Fig. 6. Thermogravimetric analysis of polyester resin: DTA – differential thermal analysis, DTG – differential thermogravimetric analysis, TG – thermogravimetric analysis

Table 2. Activation energy of degradation calculated by the Redhead formula from differential thermal (DTA) analyses of unfilled resin and its composites with CNTs

Sample	E_{d1} , kJ/mol	E_{d1} , eV	E_{d2} , kJ/mol	E_{d2} , eV
UPR	88	0.91	102	1.05
UPR+0.1 % CNT	89.1	0.92	103.1	1.06
UPR+0.3 % CNT	89	0.92	103	1.06
UPR+0.5 % CNT	89	0.92	101.4	1.05

Thus, the addition of CNTs to unsaturated UPR increases the resistance of composites to thermal oxidative degradation due to the effect of

the filler on the homogeneity and ordering in the separation system at the polymer-carbon surface interface. These results are in good agreement

with the data for other polymers filled with CNTs, for example, [18, 46].

Using the generalized Redhead formula $E_d = R \cdot T_m \ln(T_m^2/\beta)$ [49], the activation energy of degradation was determined from the thermogravimetric analysis curves.

As can be seen from Table 2, during thermo-oxidative degradation, the introduction of CNTs in the amount of 0.1 and 0.3 wt. % leads to a slight increase in the activation energy to $E = 89.1\text{--}103.1$ kJ/mol.

CONCLUSION

Composites based on unsaturated polyester resin reinforced with multi-walled carbon nanotubes with a content of 0.1, 0.3 and 0.5 wt. % were synthesized. The effect of CNTs content on the thermal decomposition of composites was investigated by the method of thermally programmed desorption mass spectrometry (TPDMS): the products of thermal decomposition, the maximum temperatures of the thermograms of polymer chain destruction products and the activation energy of their desorption were determined. The patterns of thermo-oxidative destruction of composites were determined by the methods of deriography.

It is shown that the addition of 0.1 wt. % into the resin shifts the temperatures of the maxima of the thermograms to higher values, increases the activation energy of thermal destruction for all fragments of destruction products in the range of m/z 18–104, compared to the original resin, that is, it indicates an increase in the thermal stability of this composite. While increasing the CNT content to 0.3, 0.5 wt. % shifts the temperatures

of the maxima of thermograms to lower values, significantly reduces such activation energy for practically all polymer fragments.

If at a content of 0.1 wt. % CNTs in the polymer matrix are structurally “ordered” according to possible mechanisms, then an increase in the content of CNTs, on the contrary, leads to a reversible effect, due to the relatively large content of CNTs, their insufficient deagglomeration and uneven distribution.

According to the results of thermal analysis (DTA and TG/DTG), thermal oxidative destruction in unfilled resin has two characteristic maxima at $T = 383$ and 439 °C. The addition of CNTs in the amount of 0.1, 0.3, 0.5 wt. % shifts the maxima towards higher temperatures. These two stages characterize endothermic reactions of thermooxidative decomposition. In the temperature range up to 385 °C, samples melt with subsequent combustion of the sample with maximum temperatures at 443 and 534 °C. Probably, the presence of the second peak (534 °C) indicates the possibility of the formation of a certain percentage of crystalline structures of the “interphase surface” (crosslinking between chains) in the polymer. According to the TGA curves, it has been found that thermo-oxidative decomposition is characterized by an increase in the initial temperatures of phase transitions when filling CNTs. This is probably due to the presence of a carbon nanofiller in the polymer matrix, which increases the heat capacity and thermal conductivity of the composite, possibly initiating crosslinking centers of free (unbound) polymer chains, which, in turn, causes a decrease in kinetic mobility in the polymer.

Термічна деструкція та теплофізичні властивості полімерних композитів на основі поліефірної смоли з різним вмістом вуглецевих нанотрубок

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Метою даного дослідження було визначення впливу вуглецевих нанотрубок (ВНТ) на термічне розкладання та термоокисну деструкцію нанокомпозитів на основі поліефірної смоли за вмісту 0.1, 0.3 і 0.5 мас. %. ВНТ, як характеристики їхньої термостійкості. Визначення продуктів термічного розкладання, їхньої енергії активації десорбції, сумарної кількості летких продуктів розпаду композитів визначалися методом термопрограмованої десорбційної мас-спектрометрії (TPDMS). Закономірності термоокисної деструкції полімерних композитів досліджували методами дериватографії (Q-1500D). Показано, що додавання 0.1 мас. % ВНТ в смолу зміщує температури максимумів термограм (T_m) в область більших значень, збільшує енергію активації термічної десорбції для всіх фрагментів продуктів деструкції в інтервалі m/z 18–104, в порівнянні з вихідною смолою, тобто свідчить про збільшення термічної стійкості цього композиту. Збільшення вмісту ВНТ до 0.3, 0.5 мас. % зміщує T_m до нижчих значень, помітно зменшує енергію активації десорбції для, практично, всіх фрагментів полімера.

Якщо за вмісту 0.1 мас. % ВНТ в полімерній матриці відбувається структурне «впорядкування» за можливими механізмами, то збільшення вмісту ВНТ, навпаки призводить до оборотного ефекту, за рахунок порівняно великого вмісту ВНТ, недостатньої їхньої деагломерації та нерівномірності розподілу.

Термоокиснювальна деструкція ненаповненої смоли має два характерних мінімуми при 383 і 439 °C (ендотермічні реакції термоокисного розкладання). Додавання ВНТ у кількості 0.1, 0.3, 0.5 мас. % зміщує температури в бік вищих значень. До 385 °C відбувається плавлення зразків з подальшим спалюванням з максимумами температури при 443 і 534 °C. Ймовірно, наявність другого піку (534 °C) вказує на можливість утворення в полімері певного відсотка більш упорядкованої фази. Термоокисне розкладання композитів характеризується підвищенням початкових температур фазових переходів. Ймовірно, це пов'язано з наявністю в полімерній матриці вуглецевого нанонаповнювача, який підвищує теплосмність і теплопровідність композиту, можливо, ініціює центри зшивання вільних (незв'язаних) полімерних ланцюгів, що, у свою чергу, викликає зниження кінетичної рухливості в полімері.

Ключові слова: термофізичні властивості, енергія активації, нанокомпозит, термодеструкція, вуглецеві нанотрубки; поліефірна смола; структура полімера, термоокисна деструкція

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