EFFECT OF GRAPHENE FILLER OXIDATION ON THE THERMAL DESTRUCTION OF EPOXY-GRAPHENE COMPOSITES

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The participation of the electronic subsystem of graphene nanoparticles in heat transfer on the interfaphase surface with epoxy polymer, its participation in the thermodestruction processes of epoxy matrix and the concentration interval of the subsystem's influence on the thermal destruction of the polymer matrix are investigated. For such purpose, epoxy resin composites with oxidized and non-oxidized graphene nanoparticles have been used. The particles were obtained by electrochemical method and those are characterized by the same dispersion and analogical of defect spectra. The particles have the same crystal structure, however in composites with oxidized graphene, the participation of the electronic subsystem in thermophysical processes on the interfacial surface is blocked by the atomic layer of adsorbed oxygen.

Composites of epoxy resin filled with the same particles of nonoxidized and oxidized nanoparticles in the filler content 0.0, 1.0, 2.0, and 5.0 wt%. The multilayered graphene particles were studied by X-ray diffraction analysis (XRD) and Raman spectroscopy (RS) methods. It was shown that the graphene particles are the 2D dimensional structures with about of 100 layers. Desorption curves of epoxy and its composites have been obtained using a programmable thermal desorption mass-spectroscopic (TDMS) technique for fragments with $15 \le m/z \le 108$ and temperature interval $35 - 800\ ^oC$.

The activation energy of desorption was determined from the Wigner-Polanyi equation as $35 - 150$ kJ/mol, temperature and mass dependences of the quantity of desorbed atomic fragments have been calculated.

It were established the graphene electron subsystem takes part in polymer structure thermodestruction for epoxy composites with nonoxidized graphene enhancing their heat resistance at graphene content $C \le 1$ wt%. With increasing filler content, the thermodestruction behavior in pristine epoxy and its composites with nonoxidized and oxidized graphene is analogical. The thermodestruction characterizes by the stepwise variations in the desorption intensity of atomic fragments. The electron subsystem of graphene particles does not participate in the heat resistance variations.

Keywords: *epoxy composite, unoxidized and oxidized graphene, thermal stability, fragment of destruction.*

Introduction

Polymer composites with graphene distinguish the possibility of producing materials combining excellent mechanical parameters with high electrical and thermal conductivity [1–5]. The enhancement of kinetic parameters and the extent of functionality will make the graphene composites by the most needed functional materials in many spheres of modern applications. In particularly, the widening of the operating temperature range, limited by the insufficient thermal

stability of the most polymer matrixes, is the scientific and technical problems of modern material science.

The heat resistance of polymer graphene composites can be enhanced due to the fastening of atoms of polymer chains with active surface sites of unoxidized graphene and the polymer structure stabilization [6]. Besides, the surface modification of graphene particles with active functional groups also leads to an enhancement in the composite heat resistance [7]. For the both cases, the stabilization of polymer structure results increasing thermal stability in graphene composites, while the heat transfer on the interface in the composites is different. In the first case, the heat transport realizes from the polymer chains into the graphene where it redistributes among phonon and electron subsystems. In the second case, the heat from polymer chains through atomic functional groups transfers into graphene and then divides between the both subsystems. Thus, in the first case the electron subsystem removes the heat partition on the interface from polymer chains. In another case, the heat removal occurs from functional groups at the interface. It is obviously, that the effect of heat transfer to the electron subsystem in the thermal stability of graphene composites is different.

Note, the heat resistance of composites depends on the many factors. In particular, it depends on the polymer structure and the polymerization degree of polymer matrix, the size and shape, and the defectiveness of graphene particles. Therefore, the goal of present study is to investigate the influence of graphene electron subsystem on the thermal stability of polymer composites with unoxidized and modified graphene using the same graphene particles and matrix, and the preparation conditions of composites. The surface modification of graphene particles was fulfilled using the surface oxidation. It was supposed, that the adsorbed atomic oxygen layer blocks the direct heat transfer from polymer chains to the graphene electron subsystem. Epoxy polymer was used as a composite matrix.

Samples and experimental methods

The commercially available CHS-EPOXY 520 (Czech Republic) DGEBA-epoxy resin, with epoxy group content 5.21–5.50 mol/kg. Epoxy Equivalent Weight 182–192 g/mol was used as the pure resin. The Polyethylene-polyamine (PEPA) was used as a curing agent. The structural formulas of the epoxy resin and hardeners can be found elsewhere [8].

Multilayered graphene particles have been obtained from thermal-expanded graphite flakes Ukrainian production by using the electrochemical technique described by Xia et al [9].

The so-prepared low-dimension particles to be multilayered graphene nanoplatelets of about 5×5 μm in-plane dimensions and 50 nm in thickness. The both surfaces of graphene particles have complicated morphology. On the basal surface, there are the edge defects, surface curvatures, waviness and mesovoids. The lateral surface contains about hundred graphene layers and characterizes with disordered structure and roughness.

The specific surface value $S_f \approx 740$ m^2/g have been determined for multilayered graphene nanoplatelets by measuring an amount of physically adsorbed nitrogen from adsorption–desorption isotherms according to the standard Brunauer, Emmett, and Teller (BET) method [10].

The X-ray diffraction analysis shows that the multilayered nanoplatelets contain graphene sheets (Fig. 1).

The X-ray diffraction analysis shows that the multilayered nanoplatelets contain 2D graphene sheets (Fig. 2). Raman spectra of nonoxidized multilayer graphene particles indicate that graphene particles constructed with loosely bound graphene flakes (Fig. 2). Raman spectra were recorded using the"DFS-52" double monochromator, CCD camera of Andor company and microscope. The emission of solid-state laser with wavelength of 457 nm was applied to excite Raman spectra. The reflection geometry applying the same lens to register the exciting and scattered radiations was used in the experimental setup. Obtained graphene Raman spectra

evince the 2D dimension of graphene flakes. Graphene Raman spectra characterize by a presence G (~1582 см$^{-1}$) band related to exhibition of tensile vibrations for all sp^2 hybridized atomic pairs of carbon atoms located in the benzene rings and as well as the D (~1350 см$^{-1}$) band indicating defect presence within graphene layers. In addition, in the Raman spectra the G (~1582 см$^{-1}$) band whose intensity exceeds that for D band is recorded. The latter is distinctive peculiarity of graphene spectra [11-13]. Note, the Raman spectra of one layer graphene particles (Fig. 2, spectrum 3) and multilayered graphene particles are identical. Thus, X-ray and Raman spectroscopies show the structural identity among one and multilayered graphene particles.
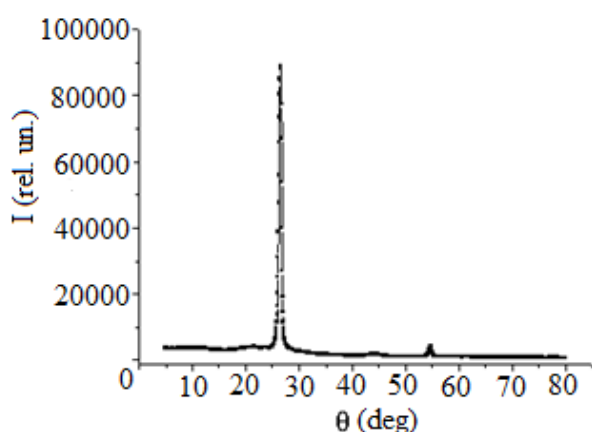

Fig. 1. X-ray diffraction analysis of graphene particles
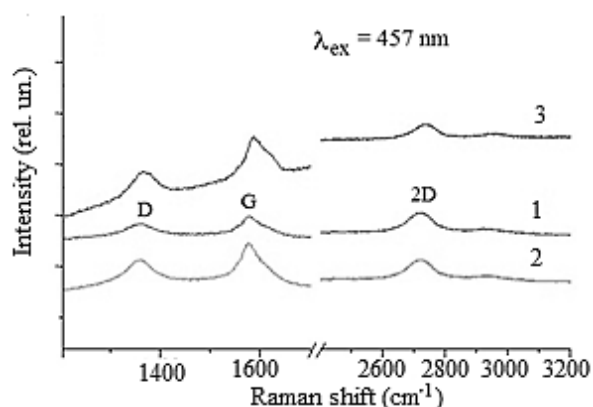

Fig. 2. Raman spectra of multilayer graphene particles are recorded with spectrometer slit width 70 (1) and 200 μm (2). Spectrum of one-layer graphene (3) was taken from [11]

Epoxy composites with non-oxidized graphene nanoplatelets have been prepared by pouring a suspension of particles in ethanol into an uncured resin, to avoid an oxidation of graphene in air. The filler-mass-loading C in the nanocomposites was 1, 2, and 5 wt% for thermophysical studies. As-prepared liquid composites were manually mixed until homogeneous suspensions were obtained and their further polymerization occurred at a room temperature during 72 hours with following heat treatment at ~ 60 °C for 1.5 hours. As a curing agent, 16% by weight of polyethylene polyamine was used.

The oxidization of graphene particles have been performed using Hammer method with subsequent purification from admixtures and in accordance with [14]. Epoxy composited with non-oxidized and oxidized graphene were obtained using analogical preparation method. The graphene content in epoxy matrix was of 1, 2, and 5 % wt.

An influence of graphene filler on the resin thermal stability have been determined using a programmable thermal desorption technique combined with a mass-spectroscopic detection via the single-pole mass-analyzer MX 7304A. Mass spectrometric analysis of positive charged atomic products was performed in the range 10–200 m/z (m is the mass, z is charge of the

fragment), within a temperature range of 25–800 ºC, at a pressure 0.1 Pa, and the heating rate 8 ºC/min [15].

Results and discussion
Thermodestruction data

The typical of desorption curves characterizing thermal destruction of epoxy chains in the composites with unoxidized and oxidized graphene is shown in Fig. 3.

Figure depicts that the behavior of thermal stability for both composites is significantly different. Thermal stability of composites with unoxidized graphene reveals a sharp increase, by more than 11 times, at low filling $C \leq 1.0\%$ and the weak nonmonotonic variations in the desorption intensity with rising graphene content (Fig. 3 *a*). Thermal destruction of composites with oxidized graphene shows a weak increase in the thermal stability of about 1.13 times at low filler content and a gradual reduction in the desorption intensity of volatile products with increasing filling (Fig. 3 *b*).
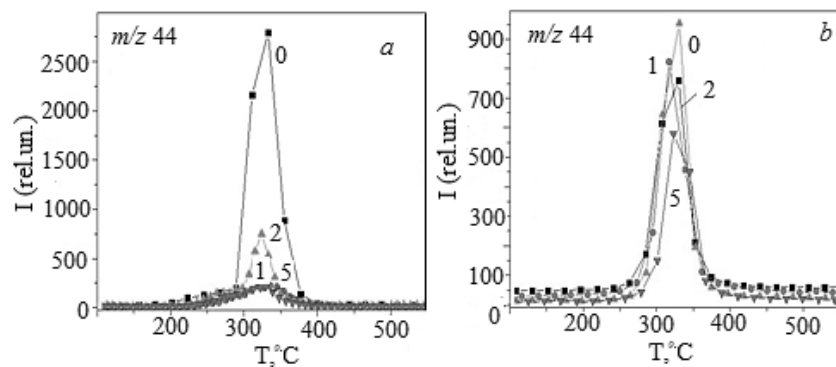

Fig. 3. Desorption curves of atomic fragments with *m/z* 44 (-COO-) for destruction of neat resin (0) and its composites with 1.0 (1), 2.0 (2) and 5.0 (5) % of unoxidized (a) and oxidized (b) graphene particles

Abrupt variations of the total release of desorbed atomic fragments Q_i of composites with nonoxidized and oxidized graphene at low filling occurs in temperature range 300 – 400 ºC (Fig. 4). Loading with the low content of nonoxidized graphene particles essentially enhances the heat resistance of polymer matrix. Successive growth of graphene content upon $1 < C \leq 5\%$ renders practically the same action on the thermal destruction of composites with nonoxidized and oxidized graphene. Thus, the maximal effect on the thermal stability reveals at low content $C \leq 1\%$ of unoxidized graphene. In composites with oxidized graphene, the changing of filler content weakly influences their thermal stability. Note that the loading effect with unoxidized graphene particles at $1 \leq C \leq 5$ wt% and oxidized those at $0 < C \leq 1.0$ wt% is practically the same (Fig. 4). The latter indicates that the interface structure, and the reactivity, the surface layer disordering in graphene particles and the surface distortions of graphene energy bands in such composites is similar.

Note, the total amount of desorbed destruction products Q_i in the investigated temperature range was determined from the following expression:

$$Q_i(T) = \qquad\qquad (1)$$

where $I_i(T)$ is the temperature dependence of thermal desorption intensity of *i*-th product, and T_1 and T_2 are the temperature limits of integration.
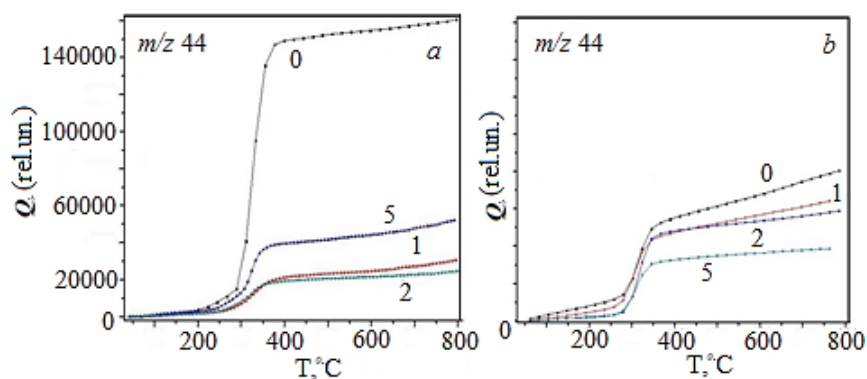
Fig. 4. Temperature dependences of the amount of desorbed atomic fragments with *m/z* 44 for destruction of pure resin (0) and its composites with 1.0 (1), 2.0 (2) and 5.0 (5) wt% of unoxidized (*a*) and oxidized (*b*) graphene particles

Sharp reduction in the thermodesorption intensity of polymer structure can be attributed to increasing destruction activation energy of polymer chains due to enhancing interatomic interaction in the composite matrix upon chemical bonding of atoms of polymer chains and cross-links with graphene surface sites. However, in the composites with nonoxidized and oxidized graphene the calculations of destruction activation energy E_d for atomic fragments with $17 \leq m/z \leq 108$, using the Polanyi – Wigner formula [16]:

$$E_d = \ln (\Theta_1/\Theta_2)RT_1T_2/(T_1 - T_2), \qquad (2)$$

where T_1 and T_2 are the temperature range of desorption peak width in the half-height, Θ_1 and Θ_2 are the areas under desorption curves corresponding to the amount of remaining substance after reaching T_1 and T_2 temperatures, gives the E_d values in the same range 55–150 kJ/mol.

Thus, the matrix's heat resistance behavior upon loading with graphene particles does not depend on the polymer structure rearrangement and the interatomic interaction in epoxy composites. The variations in the heat resistance behavior of polymer matrix in graphene composites can be attributed to the different structure of interphase border and heat processes at the interface. The destruction features of atomic fragments of polymer structure reveal in concentration dependences of the amount of desorbed destruction fragments (Fig. 5).

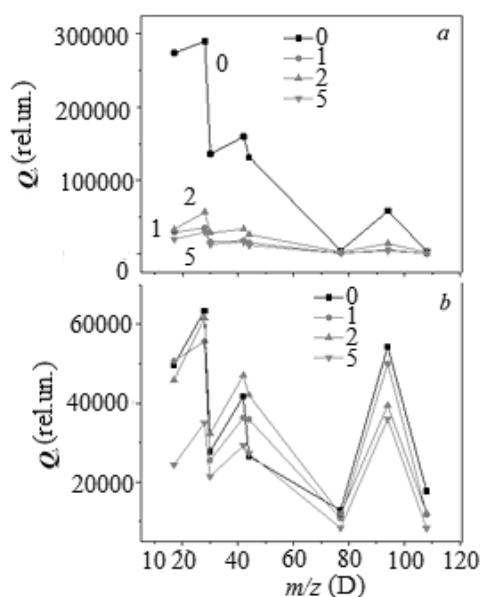

Fig. 5. Concentration dependences of total quantity of desorbed destruction products for epoxy resin (0) and its composites with 1 (1), 2 (2) and 5 % (5) nonoxidized (a) and oxidized graphene particles (b) in the range $17 \leq m/z \leq 108$

Fig. 5 shows the two features in the polymer structure destruction reveals in graphene composites. Firstly, the abrupt enhancement in the thermal stability of atomic fragments with 17 ≤ m/z <77 in composites with nonoxidized graphene at low filling $C ≤ 1\%$, and secondly, the analogical stepwise behavior of polymer structure destruction in composites with nonoxidized graphene at filling C >1 % and for the neat epoxy and its composites with oxidized graphene. The thermal stability enhancement of polymer structure in composites with nonoxidized graphene depends on the participation of graphene electron subsystem in the redistribution of heat fluxes at the interphase border. In this case, the electron subsystem removes the heat flux partition from the graphene phonon subsystem. In result of the heat removal, the vibrational energy of atoms fastened with graphene surface sites reduces and the heat resistance of atomic fragments bounded with surface atoms rises.

In the concentration range of graphene filling C >1 % during epoxy polymerization the chemical bounding of macromolecule atoms with graphene surface sites takes place. Since the fastening of polymer chains and cross-links is the stochastic process, the disordering structure of fixed atomic fragments arranges on the surface of graphene particles. The affect of disordered electrostatic potential of charged surface sites lead to the surface amorphization of graphene particles and distortion their electron bands. Formation of disordered electron states in the surface layer of graphene particles blocks the heat removal in the graphene electron subsystem at the interface. Therefore, in composites with unoxidized graphene at C >1 wt% the electron subsystem of particles does not participate in the heat transport due to disordering electron bands in the interface region.

The identity of polymer structure destruction in the pristine epoxy and its composites with oxidized graphene and nonoxidized graphene at C > 1 wt% evinces the electron subsystem of graphene particles does not participate in the thermal decomposition of epoxy composites. The variations of destruction intensity depend on the heat dissipation at the interface. Note, that the effect of surface oxidation is analogical to the influence of surface modification of graphene particles due to fastening of polymer chains and cross-links during epoxy condensation. The both types of surface modification leads to the blocking of graphene electron subsystem due to disordering electron bands in the surface layer of graphene particles.

The stepwise behavior of polymer structure destruction shows that in composites with nonoxidized graphene at filling C >1 wt% and in the neat epoxy and its composites with oxidized graphene the destruction intensity of atomic fragments with m/z 28 (–CO), 42 (–CH$_2$OC–) and 94 (C$_6$H$_5$OH –) exceeds that of fragment with m/z 17 (–OH), 30 (–CH$_2$O–), 77 (C$_6$H$_5$ –) and 108 (C$_6$H$_5$CH$_2$OH–) (Fig. 5). Step variations in the thermal stability of polymer structure atomic fragments may indicate the inhomogeneous temperature distribution in polymer chains during heat transport.

Heat transport

Phenomenological model of local thermal processes at the interface with participation of graphene electron subsystem is following. The heat flux q entering into the unfilled polymer from an external source propagates as the phonon flux $q_{\mathrm{ph}}^{\mathrm{ep}}$ through the polymer chains and cross-links into the polymer bulk. Neglecting heat dissipation on the surface, defects and phonons, we can write:

$$q = q_{\mathrm{ph}}^{\mathrm{ep}}, \tag{3}$$

In epoxy composite, the heat transport realizes through polymer chains attached to surface active sites of graphene particles. Heat flux along each epoxy polymer chain to the interface is transported by propagating flux of local phonons $q_{\mathrm{ph}}^{\mathrm{ep}}$ in accordance with the Fourier equation

$$q_{\mathrm{ph}}^{\mathrm{ep}} = - \kappa_{\mathrm{ph}} \nabla T_{ph}, \tag{4}$$

where κ_{ph} is the thermal conductivity coefficient of epoxy polymer chains, ∇T_{ph} is temperature gradient in the polymer chain.

The heat transfer from local phonons to the electronic and phonon subsystems of graphene particles occurs at the interphase boundary in the places of fastening chain atomic fragments, having different atomic compositions, to the graphene surface sites in accordance with the laws of energy and momentum conservation. In the local approximation, at the interphase boundary for temperature T, heat transfer from the polymer to the graphene particle can be described by expression

$$q_{ph}{}^{ep} = \Theta(q_{ph}{}^{gr} + q_e{}^{gr}) \tag{5}$$

where Θ is the heat transfer efficiency at the interface, $q_{pi}{}^{g}$ and $q_{ei}{}^{g}$ are the phonon and electron heat fluxes in graphene particles. At high temperatures close to destruction temperatures of polymer chains, the heat transfer occurs in the anharmonic mode of phonon generation, when backscattering local phonons at the interface is unlikely and the transfer efficiency is high and probably about to unity $\Theta \approx 1$. The obtained heat by the graphene electronic subsystem does not return to the phonon subsystem of polymer due to absence of electron transport in the polymer. In graphene a heated electron gas dissipates the received heat into the phonon subsystem due to the electron-phonon interaction during relaxation time τ_r at a distance from the interface

$$s = v\tau_r \tag{6}$$

where v is the velocity of heated electrons. In the local approximation on the interface surface the temperature of the heat flux of local phonons in the polymer $T_{ph}{}^{ep}$ and the heat fluxes of phonons $T_{ph}{}^{gr}$ and electrons $T_{ph}{}^{gr}$ in a graphene are the same

$$T = T_{ph}{}^{ep} = T_{ph}{}^{gr} + T_e{}^{gr} \tag{7}$$

Hence, the temperature of the phonon flux in graphene $q_{ph}{}^{gr}$ at the interphase boundary abruptly decreases by the temperature value of heated electrons

$$\Delta = T_e{}^{gr} = T_{ph}{}^{ep} - T_{ph}{}^{gr} \tag{8}$$

Reduction in the temperature of the graphene phonon subsystem leads to a decrease in the energy of vibrations of surface site atoms by value $k\Delta$ (k is the Boltzmann constant). As a result, the destruction probability of polymeric atom groups fixed with surface sites decreases, and the decomposition intensity of the polymer structure located near the interface also reduces.

In composites with oxidized graphene at the border with adsorbed oxygen layer the phonon flux $q_{ph}{}^{ep}$ tests the boundary heat resistance (Kapitza resistance) and the temperature step ΔT_K.

Values of the boundary heat resistance and the temperature step depend on the bind character between oxygen sites and the polymer chain atoms. In the case when the binding does not change the acoustic parameters of polymer chains fastened with oxygen sites Kapitza resistance has a minimal value and the flux value $q_{ph}{}^{ep}$ through oxygen layer can be unchanged.

At the interphase border with graphene the heat resistance does not exhibits in the temperature range close to destruction temperatures since the thermal decomposition of atomic fragments in the pristine epoxy and its graphene composites is practically the same (Fig. 5 *b*). Within graphene particles the phonon flux passes through the amorphous layer where the energy of localized electrons can be increased in the result of heat loss. However, at the interphase border the heat removal by the localized electrons does not occurs. In the graphene bulk where the band structure is undisturbed the heating of band electrons occurs, however it does not effect at the destruction of polymer matrix.

Note, at the interface due to the complicate morphology of graphene surface the phonon-phonon interaction is obviously enhanced. Intensive phonon interaction can lead to the local heating of filler surface and surface sites with fastened atomic fragments enhancing their thermal

decomposition [17]. In particular, in the composites with oxidized graphene the intensive thermal destruction of some atomic fragments exceeding that in the neat epoxy can be attributed to the enhanced phonon- phonon interaction.

Conclusions

The thermodestruction of epoxy resin and its composites with the same nanoparticles of nonoxidized and oxidized graphene have been investigated using a programmable thermal desorption mass-spectroscopic technique in the graphene content range $0 \leq C \leq 5$ wt% and temperature interval 35–800 ºC.

The thermodesorption curves for atomic fragments with $15 \leq m/z \leq 108$ were obtained. The activation energy of desorption, temperature and mass dependences of the quantity of desorbed atomic fragments have been calculated.

It were established the graphene electron subsystem takes part in polymer structure thermodestruction for epoxy composites with nonoxidized graphene enhancing their heat resistance at graphene content $C \leq 1\%$. With increasing filler content, the thermodestruction behavior in pristine epoxy and its composites with nonoxidized and oxidized graphene is analogical. The thermodestruction characterizes by the stepwise variations in the desorption intensity of atomic fragments. The electron subsystem of graphene particles does not participate in the heat resistance variations.

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ВПЛИВ ОКИСНЕННЯ ГРАФЕНУ НА ТЕРМІЧНУ ДЕСТРУКЦІЮ ЕПОКСИ-ГРАФЕНОВИХ КОМПОЗИТІВ

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У роботі досліджена участь електронної підсистеми графенових наночастинок в теплопереносі на міжфазній поверхні з епоксидним полімером, її участь у процесах термічної деструкції епоксидної матриці та концентраційний інтервал впливу підсистеми графену на терморуйнування полімерної матриці. Для цього використано композити епоксидної смоли з частинками окисненого на неокисненого графену, які отримані електрохімічним методом. Частинки характеризуються однаковою дисперсією та аналогічними спектрами дефектів. Частинки мають однакову кристалічну структуру, але відрізняються тим, що в композитах з окисненим графеном участь електронної підсистеми у теплофізичних процесах на міжфазній поверхні блокована атомарним шаром адсорбованого кисню.

Досліджено композити епоксидної смоли, наповнені однаковими наночастинками неокисненого і окисненого графену в інтервалі наповнень 0.0, 1.0, 2.0, і 5.0 мас%. Частинки багатошарового графену характеризувалися методами рентгентгено-структурного аналізу (РСА) і Рамінівської спектроскопії (СКР) як двомірні структури з числом шарів близько 100. Десорбційні криві епоксидної смоли і композитів отримано за результатами досліджень методом термопрограмованої десорбційної мас-спектроскопії (ТПДМС) фрагментів з $15 \leq m/z \leq 108$ в інтервалі температур 35−800 °C.

Визначено енергію активації деструкції атомних фрагментів 35−150 кДж/моль і отримано температурні і масові залежності десорбції атомних фрагментів.

Встановлено, що в композитах з неокисненим графеном при наповненні $C \leq 1$ мас% електронна підсистема частинок графену бере участь в термодеструкції, підвищуючи термостійкість композитів. При збільшенні наповнення поведінка термодеструкції в ненаповненій смолі і її композитах з неокисненим і окисненим графеном аналогічна і характеризується немонотонною зміною інтенсивності термічної деструкції атомних фрагментів. Проведено аналіз теплових процесів на міжфазній границі композитів епоксидної смоли з багатошаровим графеном.

Ключові слова: *епоксидний композит, неокиснений та окиснений графен, термічна стійкість, фрагмент деструкції.*