

N.V. Sigareva, B.M. Gorelov, O.V. Mistchanchuk, D.L. Starokadomsky

## THERMAL AND MECHANICAL PROPERTIES OF NONOXIDIZED GRAPHENE – EPOXY COMPOSITES AT LOW GRAPHENE LOADING

Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine  
17 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: microft2@ukr.net

*Thermophysical and mechanical properties of epoxy resin compositions with nonoxidized graphene particles have been investigated. The particles were obtained using the electrochemical method and they had a block structure with a thickness of about 50 nm. The particle concentrations in the composites were  $C = 1.0, 2.0$  and  $5.0\%$  for thermophysical studies and  $0.1, 0.2, 0.5$  and  $1.0\%$  for mechanical measurements.*

*Thermophysical measurements of the composite destruction were performed by method of thermo-programmable desorption with mass spectrometric recording of volatile products in the temperature range  $40-800^\circ\text{C}$ . The main effect of the introduction of unoxidized graphene particles is a sharp increase in the thermal stability of the composite and a decrease in the amount of the released volatile products  $Q_i$  in the low graphene loading at  $C \leq 1\%$ . With increasing loading, the value of  $Q_i$  nonmonotonously reduces with a maximum at  $C = 2.0\%$ .*

*Concentration dependences of the amount of the released volatile products and the activation energy of thermodesorption for volatile products were determined. The thermodesorption activation energy  $E_a$  for atomic fragments, which was determined from the Wigner-Polanyi equation, reduced. The  $E_a$  slightly and nonmonotonously increases with a maximum at  $C = 2\%$ . It has been shown that the run of the  $E_a(C)$  dependence correlates with the  $Q_i(C)$  behavior.*

*Models describing growth of thermal stability and variations of mechanical parameters are proposed. Compressive strength and elastic modulus have been measured in the low concentration range at  $C \leq 1\%$ . It has been found that the parameters nonmonotonously vary with maximum at  $C = 0.01\%$ . The absence of correlation between the behavior of mechanical parameters and the thermal stability of graphene composites is related with various reasons. Behavior of mechanical parameters is caused by variation in elastic and conformational deformations of polymer chains upon loading graphene filler in the polymer. The growth in thermal stability may be attributed to partial removal of heat flux energy at the interface in the electronic subsystem of graphene particles with subsequent lowering vibrational energy of atoms at the interface.*

**Keywords:** epoxy composite, nonoxidized graphene, thermal stability, mechanical parameters

### INTRODUCTION

Modern investment technologies demand improved functional properties for advanced materials. Among such materials, the polymer composites are still a rapidly growing area of multidisciplinary research interest owing to possibility of enhancement their properties by incorporation of nanosized fillers in polymer matrices [1–3].

In particular, the nanostructured graphene polymer composites are the objects for a wide scientific research because they allow expanding and improving the physical and chemical properties of composites due to the inclusion of various nanofillers in polymer matrices, as well as their wide industrial applications owing to the fact that they can be chemically and physically tailored to fulfil specific requirements for

modern materials. Non-oxidized, oxidized, and functionalized particles of single layer, double layer and multi-layered graphenes are used as graphene fillers [4–10].

Original graphene is a single-atom-thick sheet of  $sp^2$ -hybridized carbon atoms tightly packed in a two-dimensional honeycomb lattice with a carbon-carbon distance of  $0.142\text{ nm}$  [11]. The theoretical value of its room temperature thermal conductivity coefficient is about  $5000\text{ W}/(\text{m}\cdot\text{K})$  [12], that is higher than that of carbon nanotubes ( $3000-3500\text{ W}/(\text{m}\cdot\text{K})$ ) [13]. Recent experimental work on a large graphene membrane has shown its thermal conductivity to be  $\sim 600\text{ W}/(\text{m}\cdot\text{K})$  that is several times higher than that of copper [14]. Such an extraordinary thermal conductivity is due to the strong  $sp^2$ -carbon bonds in the graphene lattice which

allow phonons to travel easily through the graphene network without any significant scattering while the contribution of electrons to it is negligible [15].

Mechanical properties of graphene-based polymer nanocomposites are in a scope of various researches. Since graphene particles have a high mechanical strength and low weight, it has been assumed that the loading of polymer matrices with graphene particles increases the mechanical strength of polymer composites and simultaneously reduces their weight. There are many attempts to declare a dramatic growth in mechanical and thermal properties of polymers after the introduction of graphenes [16–19]. However, the measured strength values for polymer composites are ambiguous. Obtained parameter values depend on the structural and size differences of graphene particles used in the experiments.

Mechanical parameters of composites depend on many properties of filler and matrix, such as graphene type, aspect ratio and shape, surface morphology, dispersion, filler orientation, loading level and reactivity of an interface between graphene and polymer matrix [20–24]. Besides, in polymeric composites with one and double layer graphene the chaotic orientation of particles may impede the growth of mechanical parameters in composites. Indeed, measurements of the compressive strength for polymer composites with weakly ordered graphene particles in the polymer matrix shows a growth of mechanical parameters in the concentration range  $C > 1\%$  [21–22]. It should be noted that the effect of interfacial interaction on the polymer structure in the composites with different matrices can significantly influence on their mechanical parameters.

The loading effect of multilayered graphene particles on mechanical parameters of polymer composites is less studied particularly in the interval  $C \leq 1\%$  [8, 19, 25]. Multilayer graphene particles may have the basal surfaces with large sizes and the lateral surfaces arranged by hundred graphene flakes. In polymer composites filled with large-dimension particles having size of basal surfaces more than  $50\ \mu\text{m}$  [26], the contacts among graphene particles, their arrangement and concentration in polymer matrix essentially influence to mechanical and thermal composite parameters. Therefore experimentally

measured values of mechanical and thermal parameters depend on structural and size variations of multilayer graphene particles used in the experiments [17, 26–29]. Their interference originates the ambiguity in experimental results. In the higher concentration region upon  $C \geq 1\%$ , the mechanical strength of polymer composites with nonoxidized and oxidized graphene nanoplatelets having size of basal surface less than  $50\ \mu\text{m}$  depends slightly on the particle content [26]. In the graphene composites with low-sized particles for the concentration range  $C \leq 1\%$ , where the interface interaction has an essential effect on the physical properties of composites, the factors affecting behavior of mechanical parameters of polymer composites remain insufficiently studied.

It should be noted that in the polymer composites with three-dimensional particles of exfoliate graphite, it were obtained higher value of elastic modulus and less magnitude of the thermal expansion coefficient as compared to their values in the polymer composites with multilayer graphene particles [30, 31].

Multilayer graphene particles along with high mechanical strength possessing high reactivity of the base surface and nanoscale lateral surface are promising for application as fillers in polymer composites to improve their thermal stability [28, 29, 32, 33]. As a rule, introduction of multilayer graphene increases the heat resistance of polymer composites. Besides, the graphene particles may change the thermal destruction mechanism of polymer chains. In particular, the authors [33] note the appearance of additional polymer thermo-oxidative destruction and the transformation of two-stage matrix decomposition into one-stage process after loading with graphene particles.

The atomic composition of volatile products during the thermal destruction of epoxy composites at low content of multilayer graphene particles was determined using thermal desorption mass spectrometry. It has been found that the loading polymer with graphenes does not affect the atomic composition of destruction products, but it changes the desorption intensity of atomic fragments and the amount of released products [34].

In summary, the effect of interfacial interaction between atoms of graphene surface sites and macromolecule on the thermal stability

and mechanical strength of the polymer structure in related composites at low content of graphene filler is insufficiently investigated. Therefore, the goal of present work is to study the effect of low concentration of multilayer graphene particles on the thermal stability and mechanical strength of polymer composites. An epoxy resin, which is the most applied polymer component in functional materials, 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 neat resin. The Polyethylene-polyamine (PEPA) was used as a curing agent. PEPA is a mix of amines with a various molecular mass, its general structural formula is  $H_2N-[-CH_2CH_2NH-]_nH$ , where  $n = 3$  corresponds to triethylenetetramine,  $n = 4$  – to tetraethylenepentamine, and  $n = 5$  to pentaethylenehexamine. It is widely used as a hardener of epoxy resins due to its explosion-proof and hard ignitable properties. The structural formula of the resin can be found elsewhere [35].

Multilayered graphene particles have been prepared from thermal-expanded graphite flakes of Ukrainian production by using the electrochemical technique described by Xia *et al* [36].

The electronographic study showed the so-prepared low-dimension particles to be really multilayered graphene nanoplatelets of about  $5 \times 5 \mu m$  in-plane dimensions and 50 nm in thickness (Fig. 1). The X-ray diffraction analysis has shown that the multilayered nanoplatelets contain graphene sheets (Fig. 2).

The specific surface value of  $S_f \approx 740 m^2/g$  has been determined for bare multilayered graphene nanoplatelets by measuring an amount of physically adsorbed gaseous nitrogen from adsorption–desorption isotherms according to the standard Brunauer, Emmett, and Teller (BET) method [37].

Epoxy composites with non-oxidized graphene nanoplatelets have been prepared by pouring a suspension of particles in alcohol 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 % for thermophysical studies and 0.1, 0.2, 0.5 and 1.0 % for mechanical measurements. As-prepared liquid composites were manually mixed until homogeneous suspensions were obtained, and their further polymerization occurred at a room temperature during 72 h with following heat treatment at  $\sim 60^\circ C$  for 1.5 h. As a curing agent, 16 % by weight of polyethylene polyamine was used.

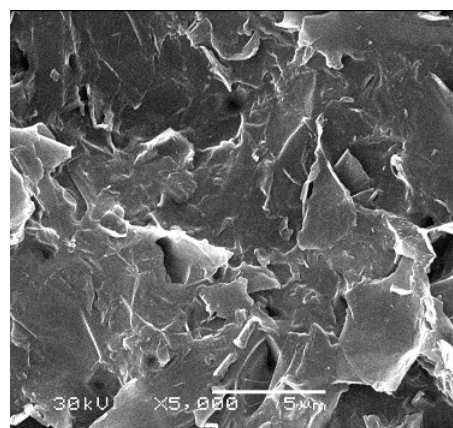


Fig. 1. Electronic photograph of graphene particles

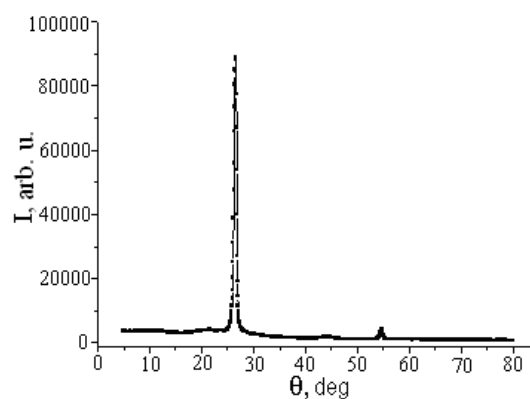


Fig. 2. X-ray diffraction analysis of graphene particles

An influence of graphene filler on thermal stability of the resin have been determined using a programmable thermal desorption technique combined with a mass-spectroscopic detection via a 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 the temperature range of 25–800  $^\circ C$ , at the pressure of 0.1 Pa, and the heating rate of 8  $^\circ C/min$ . The measurement details can be found elsewhere [34].

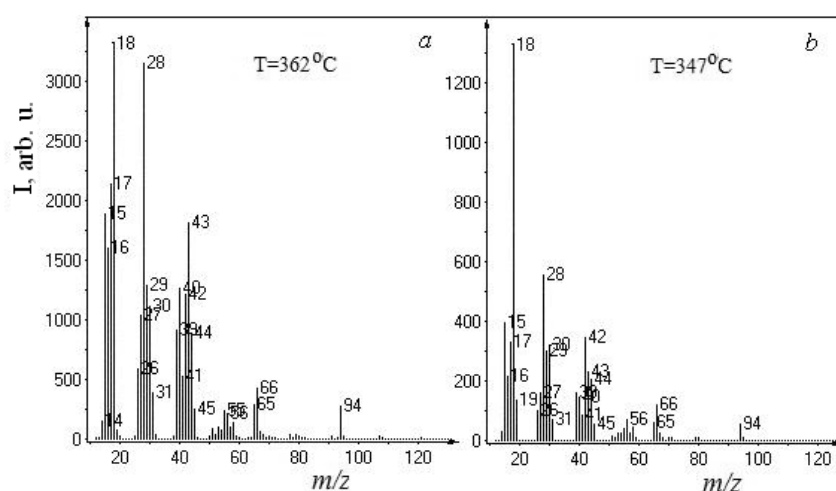
Mechanical parameters such as the compressive strength  $\sigma$  and the elastic modulus  $E$  have been measured using a “Luis Shopper” machine. Samples for research had the cylindrical shape with diameter and height about 10 mm. The values of  $\sigma$  and  $E$  parameters were determined as the average magnitude according to the results for mechanical loading of five samples.

## RESULTS AND DISCUSSION

**Thermodestruction data.** The mass spectra of atomic destruction fragments of the pure resin and its composite with 1% of multilayer graphene particles at temperatures corresponding to the maximum intensity of the mass-lines of the spectrum are shown in Fig. 3. It can be seen from Fig. 3 that the rather strong lines visible in the mass-spectrum of the neat resin and of its composites with graphene correspond to the

following  $m/z$ -moieties: 14–18, 28–31, 40–45, 56–59, 65–67, 94. The majority of lines observed in the spectra can easily be identified by looking on the epoxy’s structural formula [35]. Among these lines, hydroxyl-containing moieties of  $m/z = 17$  (OH), 43 ( $\text{CH}_2\text{COH}$ ), and 94 ( $\text{C}_6\text{H}_5\text{OH}$ ) originate from epoxy chains.

The introduction of graphene particles does not vary the number of mass-lines of desorbed atomic fragments of polymer structure. However, the interaction of polymer atoms with the graphene surface sites significantly affects the intensity of thermal decomposition of the polymer matrix and its thermal stability. The loading with multilayered graphene improves the thermal stability of composites. The latter is clearly manifested upon the content of graphene particles  $C = 1\%$ , when the mass-lines intensity drops in 3–7 times (Fig. 3).



**Fig. 3.** Mass-spectra of epoxy (a) and of its composite with 1% multilayered graphene particles (b)

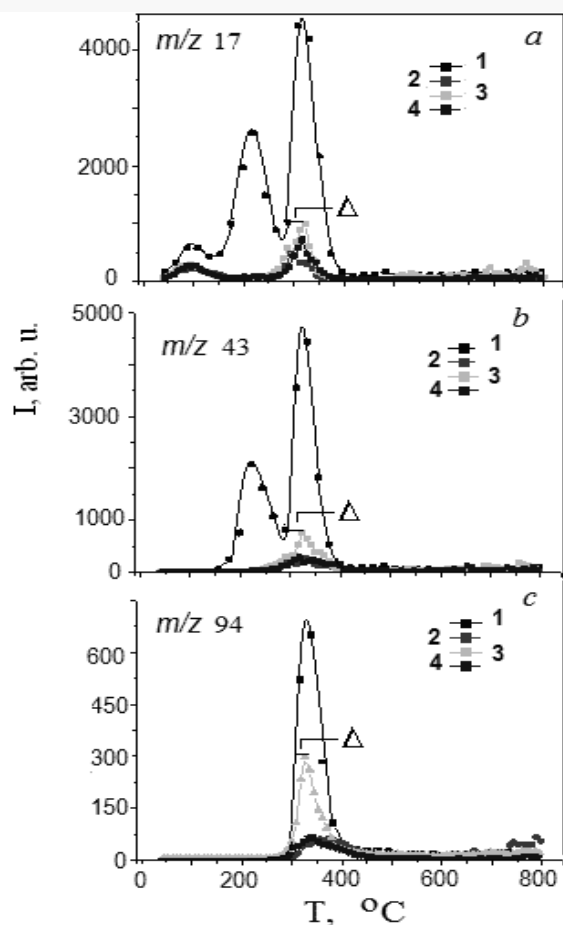
Interaction of graphene surface sites with macromolecule atomic groups significantly changes the epoxy polymer structure. Unbound moieties of polymer chains fasten on the active surface centers enhancing polymeric structure [38]. Unfixed atomic fragments reveal in the desorption curves at temperatures  $T \leq 250$  °C, where their desorption peaks are recorded for the unfilled epoxy polymer. The main contribution to the thermal stability improvement comes from the fastening process of atomic fragments with structures including hydroxyl groups, such as OH,  $\text{CH}_2\text{COH}$ , and  $\text{C}_6\text{H}_5\text{COH}$  (Fig. 4).

Desorption peaks of unbound fragments with OH groups do not reveal in the desorption

curves after loading graphene nanoparticles into epoxy polymer (Fig. 4 a, b, c curves 1). Simultaneously with a sharp reduction in the desorption intensity of unfixed fragments, the thermodestruction intensity of formed polymer chains and cross-links, which occurs in the temperature range of 250–450 °C, significantly decreases (Fig. 4, curves 2, 3 and 4). Such reduction is a consequence of the stabilization effect of polymeric structure [38].

Thus, the side OH-fragments of polymer chains, on the one hand, catalyze the chain destruction process, and, on the other hand, take part in the fastening process of polymer chains

and cross-links with the active surface sites of multilayered graphene.

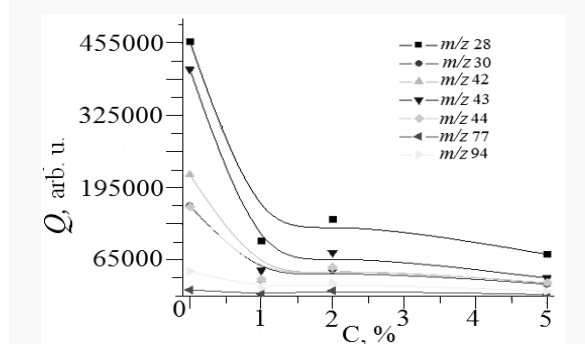


**Fig. 4.** Temperature dependences of the desorption intensity of volatile fragments with  $m/z$  17 (a), 43 (b), and 94 (c) at thermal destruction for neat epoxy (1) and its composites with 1 (2), 2 (3) and 5 % (4) multilayer graphene particles

The fastening process of unbound polymer structure fragments is apparently saturated upon graphene concentration  $C \leq 1\%$ , since the low temperature destruction of unfastened fragments is not revealed in the desorption curves obtained at thermal decomposition of graphene composites with higher filler concentrations (Fig. 4). The loading with higher graphene concentration yields a slight effect on the desorption intensity of stabilized polymeric structure. There is a slight nonmonotonous growth in the destruction intensity with a maximum at the graphene content  $C = 2\%$  (Fig. 4, curves 2, 3 and 4). Hence, in graphene composites the stabilization process of polymeric structure consisting in fastening unbound

moieties of chains and cross-links with graphene surface sites prevails in the concentration range  $C \leq 1\%$ . The binding of atomic groups of formed polymer chains and cross-links with active surface sites of graphene particles apparently dominates at higher filler concentrations.

Nonmonotonous growth in the thermal destruction intensity with rising graphene content may evidence the nonmonotonous transformation of polymeric structure due to the random fastening nature of epoxy polymer atoms with graphene surface sites. Development and evolution of random fastening of polymer chains in the interface region enhance the disorder of polymer structure in the composites. Disorder level of polymeric structure nonmonotonously varies with increasing graphene concentration and its behavior reveals in relevant variation of thermal stability of polymeric matrix. Besides, the disorder variations of polymer structure with arising graphene content are accompanied by nonmonotonous behavior in the concentration dependence of destruction activation energy of polymer structure.



**Fig. 5.** Concentration dependences of the amount of released volatile products with  $m/z$  28, 30, 42, 43, 44, 77, and 94

The concentration dependences of an amount of thermodesorbed atomic fragments for polymeric structure are shown in Fig. 5. The total amount of desorbed destruction products  $Q_i$  in the investigated temperature range was determined from the following expression:

$$Q_i(T) = \int_{T_1}^{T_2} I_i(T) dT \quad (1)$$

where  $T_1 = 250\text{ }^\circ\text{C}$  and  $T_2 = 550\text{ }^\circ\text{C}$  are the temperature interval of the desorption peak for the  $i$  thermodesorption fragment of the polymer matrix. Fig. 5 shows that the amount of desorbed polymeric degradation products sharply reduces

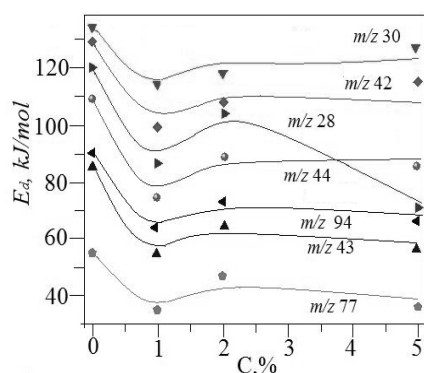
upon the filler content is  $C \leq 1.0\%$ . The  $Q_i(C)$  nonmonotonously diminishes with a slight maximum at  $C = 2\%$  upon increasing graphene concentration. Sharp reduction in the thermodesorption intensity of epoxy polymer structure can be related to rising destruction activation energy of polymer chains due to enhancing interatomic interactions in the composite matrix throughout chemical bonding of atomic fragments of polymer chains and cross-links with graphene surface sites.

**Destruction activation energy.** The thermo-desorption activation energy  $E_d$  for atomic fragments was determined from the Polanyi – Wigner formula [39]:

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

where  $T_1$  and  $T_2$  are the temperature range of the desorption peak width in the half-height,  $\Theta_1$ ,  $\Theta_2$  are the areas under desorption curves which correspond to the amount of remaining substance after reaching  $T_1$  and  $T_2$  temperatures.

Calculations of the activation energy for neat epoxy polymer give  $E_d$  values in the range 55–132 kJ/mol. The  $E_d$  concentration dependence is presented in Fig. 6. It can be seen from the Fig. 6 that the activation energy of all the volatile fragments significantly reduces upon loading with 1% graphene nanoplatelets. With growth in the filler content, the  $E_d$  slightly and non monotonously increases with a maximum at  $C = 2\%$  to values not exceeding the  $E_d$  magnitude for the unfilled polymer over the entire  $C$  interval.



**Fig. 6.** Concentration dependences of the desorption activation energy for volatile products with  $m/z$  28, 30, 42, 43, 44, 77, and 94

The run of the  $E_d(C)$  dependence correlates with the  $Q_i(C)$  behavior (Figs. 5 and 6). However, the reduction in the desorption

activation energy does not correlate with a sharp increase in the thermal stability of composites and a relevant diminishing in the destruction intensity of the polymer matrix. The  $E_d(C)$  behavior evidences the formation of polymer structure regions with a reduced activation energy in the composite matrix during polymer structure stabilization process. Disordered polymer structure is produced during stochastic process of chemical binding of polymer atoms with graphene active sites arranged within the composite matrix in disordered manner due to a complicate morphology of basic and lateral surfaces of multilayer graphene particles. The complicate morphology of the base surface of graphene particles, namely, curvature, pores, edge defects of graphene planes is shown in Fig. 1. Besides, the active sites on the both graphene surfaces locate in disordered manner and their concentration on both surfaces is different. The disordering in the polymer structure arises with increasing graphene content. Simultaneously disordering of polymer chains leads to the lowering their destruction activation energy  $E_d$ .

Thus, the random interaction nature of surface sites with atoms of polymer chains, cross-links and unbound atomic moieties leads to a weakening in the composite structure and lowering destruction energy of polymer chains.

**Heat transport.** It is known [38], that the stabilization effect in the polymer structure leads to a growth of the heat resistance in graphene composites. Besides, an additional mechanism raising heat resistance may be realized in graphene composites. Such a mechanism can be related with a participate of graphene electron subsystem in heat transport. In that case the phonon heat flux propagating in polymer chains to graphene particles redistributes between the phonon and electron subsystems of graphene particles at the interface. The graphene phonon subsystem, as a result of heat removal by the conductive electrons, has a lower temperature at the interface than that of the polymer phonon subsystem. In other words, at the heat propagation along polymer chains fastened to graphene atoms at the interface, a local diminishing in the energy of vibration of surface atoms occurs. Such a process reveals as the local weakening of destruction for atomic groups of polymer chains bonded with surface sites.

Phenomenological model of local thermal processes at the interface is as follows. The transport of heat  $q$  entering into the unfilled polymer from an external source is carried out by propagating of the phonon flux  $q_{ph}^{ep}$  through the polymer chains and cross-links into the epoxy polymer bulk. Neglecting heat dissipation on the surface, defects and phonons, we can write:

$$q = q_{ph}^{ep}. \quad (3)$$

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

$$q_{ph}^{ep} = -\kappa_{ph} \nabla T_{ph}, \quad (4)$$

where  $\kappa_{ph}$  is the thermal conductivity coefficient of the epoxy polymer chains,  $\nabla T_{ph}$  is temperature gradient in the polymer chain. The heat transfer from local phonons to the electronic and phonon subsystems of graphene particles realizes 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 interface boundary for temperature  $T$ , heat transfer from the polymer to the graphene particle can be described by expression

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

where  $\Theta$  is the heat transfer efficiency at the interface,  $q_{ph}^{gr}$  and  $q_e^{gr}$  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 as a result of the electron-phonon interaction during relaxation time  $\tau_r$  at a distance from the interface

$$s = v\tau_r, \quad (6)$$

where  $v$  is the velocity of heated electrons. In the local approximation, on the interphase 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  $T_e^{gr}$  in graphene are the same

$$T = T_{ph}^{ep} = T_{ph}^{gr} + T_e^{gr}. \quad (7)$$

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

$$\Delta = T_e^{gr} = T_{ph}^{ep} - T_{ph}^{gr} \quad (8)$$

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.

Since atomic fragments of polymer chains fastened to surface sites have different masses, their frequency vibration modes differ for various atomic groups in the interface regions. In addition, at the interface the velocities  $u_i$  and impulses  $p_i$  of local phonons in polymer chains fastened to surface sites by various atomic groups are also different. Therefore the transferred momentum and energy values from the phonon subsystem of polymer chains to the graphene electronic and phonon subsystems as well as the value of the temperature jump  $\Delta$  depend on the masses of bound atoms at the interface. The heat transfer from polymer chain to graphene realizes through local surface site.

The  $\Delta$  value and its dependence on the mass of thermodeconstructed atomic fragments can be estimated from the desorption curves of fragments with  $m/z$  17, 43 and 94 for neat epoxy resin and its composite with 2 % graphene nanoplates. The value of the temperature jump  $\Delta_i$  for  $i$  destruction fragment can be determined as a temperature interval in the region  $T \leq T_m$ , here  $T_m$  is the maximum temperature of desorption peak for atomic destruction fragments of epoxy composite with 2 % graphene. The  $\Delta$  value is a difference between the temperatures in desorption curves for atomic fragments with the same  $m/z$  values for the neat polymer  $T_i$  and its composite with 2 % particles  $T_c$  when the desorption intensity values of both curves are

equal to maximal magnitude of intensity for the composite's desorption peak  $I_c(T_m)$  (Fig. 4). The  $\Delta_i$  interval corresponds to reduction in destruction temperature  $T_i$  of  $m/z$  atomic fragment for unfilled polymer structure after introduction of graphene particles in polymer when the desorption intensities of  $m/z$  fragments for neat polymer  $I_i$  and its composite  $I_c$  is the same. The value of  $\Delta_i$  is as follows:

$$\Delta_i = T_i(I_c) - T_c(I_c). \quad (9)$$

Estimations give the values  $\Delta \approx 34, 28.5,$  and  $17^\circ\text{C}$  for fragments with  $m/z$  17, 43, and 94 respectively (Fig. 4). Thus, when mass of fastened atomic fragments increases,  $\Delta$  and the amount of transferred heat to the graphene electronic subsystem reduce.

Thus, the loading with graphene particles gives rise to the growth in the epoxy-polymer thermal stability at concentration range  $C \leq 1\%$  and the thermal stability nonmonotonously slightly reduces with rising graphene content. Along with improving polymer structure, the loading with graphene in the polymer leads to reduction of activation energy for the polymer destruction. In addition, at the interface the distribution of heat phonon flux from polymer chains among electronic and phononic heat carriers in graphene particles gives the reduction of temperature for phonon flux in the thin surface graphene layer with thickness no more than  $s$  value.

**Mechanical parameters.** Concentration dependences of the compressive strength and the Young's modulus for graphene composites characterize by the similar nonmonotonous behavior with increasing graphene content. The  $\sigma$  and  $E$  values raise in the extremely low loading interval at  $C \leq 0.01\%$ , and in the content range  $0.01 < C \leq 1\%$  the  $\sigma$  and  $E$  smoothly diminish with arising  $C$  (Fig. 7).

The loading curves of the neat resin and its graphene composites are shown in Fig. 8. The curves are characterized by two loading intervals having different physical nature of deformation. In the deformation range of  $\varepsilon < 3$ , where strain linearly increases with growing stress, the deformation is elastic. The conformational plastic deformation occurs at  $\varepsilon > 2.5$ , when  $\varepsilon(P)$  is practically unchanged. During conformational deformation the irreversible configuration changes realize in the polymer chain structure. Structural deformation of polymer chains are

accompanied by relevant altering in the free volume of composites. Conformational deformation reveals in the neat polymer (Fig. 8 a). The loading of polymer with graphene leads to the nonmonotonous change in the volume of configurational deformations. At an extremely low content of graphene particles upon  $C \leq 0.01\%$ , the plastic deformation value  $\Delta\varepsilon = \varepsilon_0 - \varepsilon_c$ , here  $\varepsilon_0$  and  $\varepsilon_c$  are the strain values for the onset and ending of plastic deformation, and the relevant volume of configurational deformation in the polymeric chains increases (Fig. 8 b). However, in the concentration interval  $0.01 < C \leq 1.0$ ,  $\Delta\varepsilon(C)$  and the plastic deformation volume of polymeric structure gradually decrease with increasing filling (Fig. 8 c, d, e).

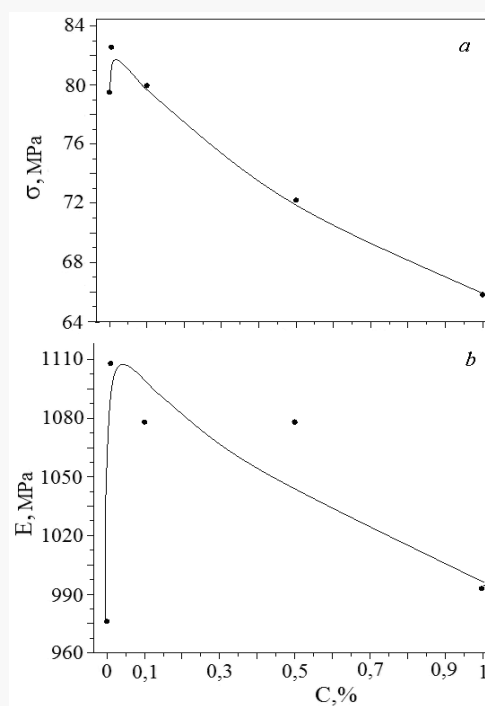


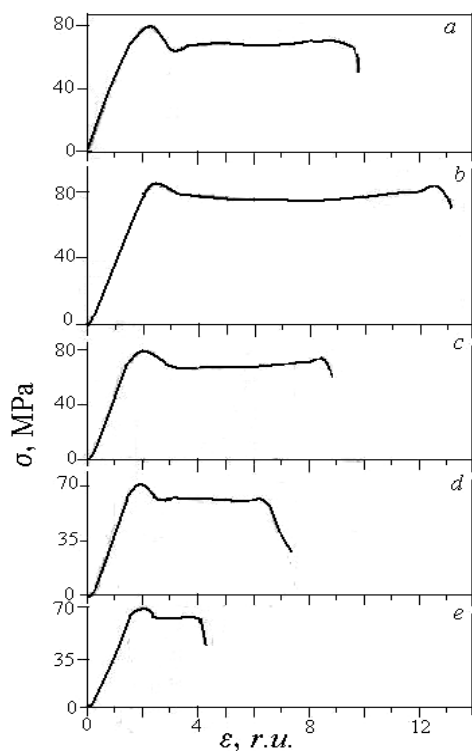
Fig. 7. Dependences of compressive strength (a) and elastic modulus (b) on the graphene content

Thus, the concentration dependence of the volume of conformational deformations indicates a nonmonotonous dependence of the free volume in the composite matrix on the graphene content in the content region  $C \leq 1.0\%$ .

The changes of conformational deformation volume upon loading polymer with graphene correlate with variations in the  $\sigma(C)$  and  $E(C)$  parameters (Fig. 9). Loading with graphene particles changes the polymeric structure chains,



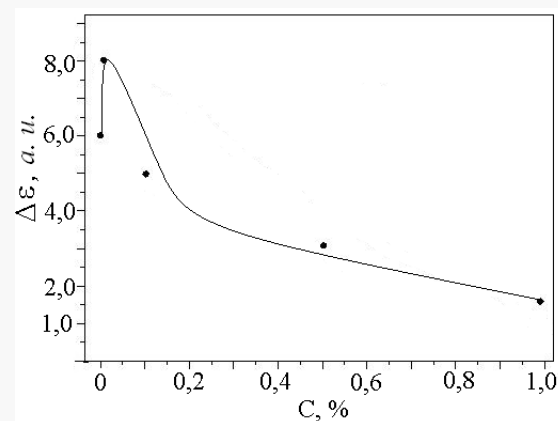
free volume of composites and their mechanical parameters in the similar way. Increasing free volume and  $\Delta\varepsilon(C)$  at  $C \leq 0.01\%$  lead to growth in the strength and elastic modulus of the composites. Reduction in the volume of configurational deformations in the range  $C > 0.01\%$  accompanies a diminish of both  $\sigma(C)$  and  $E(C)$  parameters. The growth of free volume and strength of composites upon  $C \leq 0.01\%$  can be attributed to fastening unbounded moieties of polymer chains with graphene surface sites. Fastening process reduces the faultiness of polymer chains and cross-links and leads to more perfect and strength polymeric structure. The latter reveals in the increasing free volume and mechanical parameters.



**Fig. 8.** Dependence of deformation on loading of samples of the neat resin (a) and its composites with 0.01 (b), 0.1 (c), 0.5 (d) and 1% (e) of graphene particles

In the concentration interval  $0.01 < C \leq 1.0\%$  the disorder in polymer structure caused by random process of fastening atoms of polymer chains with active surface sites of graphene particles dominates. Such fastening gives rise to enhancement of conformational strains in polymer chains and correlated lowering

of mechanical parameters in the composites. Besides, the polymer structure disordering with increasing graphene content at  $C > 0.01\%$  also results in reduction of activation energy of destruction for the polymer chains and cross-links.



**Fig. 9.** Concentration dependence of the configurational deformation

Thus, the interface atomic interaction of polymer chains with surface sites of graphene particles results in the stabilization of polymer structure due to fastening unbound moieties of polymeric chains and cross-links with surface sites at the extremely low graphene content. Stabilization in the polymer structure yields an increase in the free volume, the number of structure defects and mechanical parameters. The random character of the interface atomic interaction polymer chains and surface sites reveals in the growth of polymer structure disorder and reducing in the activation energy of polymer structure decomposition and mechanical parameters. The disorder process prevails with increasing content of graphene particles at  $C > 0.01\%$ .

It should be noted that the nonmonotonous reduction in the mechanical parameters does not correlate with the monotonic increase in the thermal stability of polymer structure in the concentration range  $0.01 < C \leq 1\%$ . The absence of correlation between the behavior of mechanical parameters and the thermal stability of graphene composites is related with various reasons. Behavior of mechanical parameters is caused by variation in elastic and conformational deformations of polymer chains upon loading graphene filler in the polymer. The growth in thermal stability may be attributed to partial removal of heat flux energy at the interface in

the electronic subsystem of graphene particles with subsequent lowering vibrational energy of atoms at the interface.

### CONCLUSIONS

The effect of low concentrations of multilayer graphene particles on the thermal stability, compressive strength and elastic modulus of epoxy composites has been studied.

The loading with graphene particles in concentration  $C \leq 5\%$  results in an essential increase in the thermal stability of composites and a reduction in the activation energy of destruction of polymer structure in the epoxy composites.

The influence of low concentration of graphene particles at  $C \leq 1\%$  on the compressive strength and the Young's modulus

have been investigated. It has been found that both mechanical parameters increase in the extremely low concentration interval upon  $C \leq 0.01\%$  and reduce with increasing graphene content.

The reduction in the activation energy of destruction in polymer structure and mechanical parameters is related to a rise of the disorder in polymer structure due to arbitrary atomic binding polymer chains with surface sites of graphene particles.

The growth in thermal stability is related to lowering vibrational energy of atoms of graphene surface sites due to partial removal of heat flux energy from polymer chains by the electronic subsystem of graphene particles at the interface.

## Теплові та механічні властивості композитів епоксидної смоли з неокисненим графеном за малого вмісту графену

Н.В. Сігарьова, Б.М. Горєлов, О.В. Місчанчук, Д.Л. Старокадомський

*Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України  
вул. Генерала Наумова, 17, Київ, 03164, Україна, microsoft2@ukr.net*

*Досліджено теплофізичні та механічні властивості композитів епоксидної смоли з неокисненими графеновими частинками. Частинки були отримані електрохімічним методом та мають структуру блоків завтовжки біля 50 нм. Концентрація частинок у композитах становила  $C = 1.0, 2.0$  і  $5.0\%$  для теплофізичних досліджень та  $0.01, 0.1, 0.5$  і  $1.0\%$  для механічних експериментів.*

*Теплофізичні виміри деструкції композитів виконані методом термопрограмованої десорбції з мас-спектрометричною реєстрацією летких продуктів в інтервалі температур  $40-800\text{ }^\circ\text{C}$ . Основним ефектом введення неокиснених графенових частинок є різке збільшення термічної стійкості композиту та зменшення кількості виділених продуктів деструкції  $Q_i$  при малому вмісті графену  $C \leq 1\%$ . Зі збільшенням концентрації наповнення, значення  $Q_i$  немонотонно зменшується та має максимум при  $C = 2.0\%$ .*

*Були визначені концентраційні залежності кількості виділених продуктів терморозкладання та їхньої енергії активації десорбції. Енергія активації десорбції  $E_d$  для атомних фрагментів, розрахована за формулою Вігнера – Поляні, зменшується. Значення  $E_d$  неістотно та немонотонно зростає та має максимум при концентрації графену  $C = 2\%$ . Показано, що залежність  $E_d(C)$  корелює зі зміною  $Q_i(C)$ .*

*Запропоновані моделі, які описують поведінку теплофізичних та механічних параметрів. Межа міцності на стискання та модулі пружності визначені для епоксикомпозитів з вмістом графену не більше  $1\%$ . Виявлено, що параметри немонотонно змінюються з максимумом при  $C = 0.01\%$ . Відсутність кореляції між поведінкою механічних параметрів і термічною стійкістю графенових композитів пов'язана з багатьма причинами. Зміна механічних параметрів зумовлена варіацією еластичних та конформаційних деформацій полімерних ланцюгів від вмісту графенового наповнювача в полімері. Зростання термостабільності зумовлено частковим перерозподілом теплового потоку на міжфазній поверхні електронною підсистемою графену з подальшим зниженням енергії коливань атомів на межі поділу фаз.*

**Ключові слова:** епоксидний композит, неокиснений графен, хімічна стійкість, механічні властивості

## Тепловые и механические свойства композитов эпоксидной смолы с неокисленным графеном при малом содержании графена

Н.В. Сигарёва, Б.М. Горелов, А.В. Мисчанчук, Д.Л. Старокадомский

Институт химии поверхности им. А.А. Чуйко Национальной академии наук Украины  
ул. Генерала Наумова, 17, Киев, 03164, Украина, microfi2@ukr.net

Исследованы теплофизические и механические свойства композитов эпоксидной смолы с неокисленными графеновыми частицами. Частицы синтезировали электрохимическим методом и имели блочную структуру толщиной примерно 50 нм. Содержание графена в композитах составляло  $C = 1.0, 2.0$  и  $5.0\%$  для теплофизических исследований и  $0.01, 0.1, 0.5, 1.0\%$  для механических экспериментов.

Теплофизические исследования десорбции композитов выполнены методом термопрограммированной десорбции с мас-спектрометрической регистрацией летучих продуктов в интервале температур  $40\text{--}800\text{ }^\circ\text{C}$ . Основным эффектом введения неокисленных графеновых частиц является резкое повышение термической стабильности композита и понижение количества десорбированных летучих продуктов  $Q_i$  при малом содержании графена, когда  $C \leq 1.0\%$ . С увеличением концентрации наполнителя, значение  $Q_i$  немонотонно уменьшается и имеет максимум при  $C = 2.0\%$ .

Были определены концентрационные зависимости количества выделенных продуктов термодесорбции и их энергии активации десорбции  $E_d$ . Энергия активации десорбции  $E_d$  для атомных фрагментов, полученная из расчетов по формуле Вигнера – Поляни, уменьшается. Значение  $E_d$  незначительно и немонотонно увеличивается, и имеет максимум при концентрации графена  $C = 2\%$ . Показано, что зависимость  $E_d(C)$  коррелирует с изменением  $Q_i(C)$ .

Предложены модели, описывающие поведение теплофизических и механических параметров. Предел прочности на сжатие и модули упругости определены для эпоксидных композитов с содержанием графена не более  $1\%$ . Обнаружено, что параметры немонотонно изменяются с максимумом при  $C = 0.01\%$ . Отсутствие корреляции между поведением механических параметров и термической стойкости графеновых композитов связано с многими причинами. Изменение механических параметров обусловлено вариацией эластичных и конформационных деформаций полимерных цепей от содержания графенового наполнителя в полимере. Увеличение термостабильности обусловлено частичным перераспределением теплового потока на межфазной поверхности электронной подсистемой графена с дальнейшим снижением энергии колебаний атомов на границе раздела фаз.

**Ключевые слова:** эпоксидный композит, неокисленный графен, химическая стойкость, механические свойства

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