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Study of thermal effects in polymer coatings with increasing temperature

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The change of linear deformations of the developed epoxy composites under the influence of a thermal field is investigated. It is established that nanocomposites are characterized by different rates of relaxation processes, which makes it possible to choose nanocomposites or coatings based on them with the required thermal coefficient of linear expansion for protection of parts of transport equipment, in particular, ship equipment against external influences. It was found that the optimal content of nanodispersed fullerene-carbon black mixture in the reaction plastic matrix is q = 0.050 pph per 100 pph of epoxy oligomer ED-20 and 10 pph of polyethylenepolyamine (PEPA) hardener. The obtained epoxy composites have the following characteristics: thermal coefficient of linear expansion is $-\alpha = (5.61\ldots5.79) \times 10^{-5}$ K^{-1} in the temperature range $\Delta T = 303\ldots323$ K; the glass-transition temperature is $T_c = 338\ldots343$ K; shrinkage up to 1%. Using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) methods, the operating temperature range of the developed composite materials without changing their properties was determined to be 273-555 K.

Keywords: nanodispersed fullerene-carbon black mixture, polymer coating, thermal coefficient of linear expansion, glass transition temperature, thermogravimetric analysis, differential thermal analysis.

Дослідження теплових ефектів у полімерних покриттях при зростанні температури. *О.О. Сапронов, П.О. Марущак, В.Л. Демченко, Р.Т. Біщак, В.Д. Шаранов, Д.О. Даниленко, А.В. Сапронова, В.В. Соценко, П.О. Воробйов, А.О. Сокол, К.Ю. Юренін, В.Л. Алексенкоьт*

Досліджено зміну лінійних деформацій розроблених епоксидних композитів під впливом теплового поля. Встановлено, що нанокомпозити характеризуються різною швидкістю проходження релаксаційних процесів. Це дає можливість підібрати нанокомпозити чи покриття на їх основі з необхідним значенням термічного коефіцієнту лінійного розширення для захисту деталей транспортної техніки, зокрема і суднового обладнання, від впливу зовнішніх факторів. На основі комплексних досліджень встановлено, що оптимальний вміст нанодисперсної фулерено-сажової суміші у реактопластичній матриці становить

q = 0,025…0,050 мас.ч. на 100 мас.ч. епоксидного олігомеру ЕД-20 і 10 мас.ч. твердника поліетиленполіаміну (ПЕПА). Такі епоксидні композити характеризуються наступними властивостями: термічний коефіцієнт лінійного розширення в діапазоні температур ΔT = 303…323 К становить – α = (5,61…5,79) × 10^{-5} $К^{-1}$; температура склування T_c = 338… 343 К; усадка до 1 %. Методами термогравіметричного (ТГА) та диференціально-термічного аналізу (ДТА) визначено діапазон робочих температур, при яких можлива експлуатація розроблених композиційних матеріалів без зміни їх властивостей – 273-555 К.

1. Introduction

Polymer coatings, especially epoxy-based ones, protect the surfaces of water transport because they contain hydroxyl, ether and epoxy groups [1-5]. These groups are polar structures that facilitate the diffusion process due to their compatibility with metal oxides [6-9]. The introduction of nano-dispersed fillers into the epoxy matrix allows for overcoming the main limitations of the functional capabilities of traditional polymeric materials, such as insufficient mechanical strength and low heat resistance [10-14]. Due to their unique properties, such as specific surface area and surface activity, nanoparticles can significantly improve the characteristics of polymer coatings. It was shown in [15-19] that the physicochemical nature, specific surface area, and filler content affect both the kinetics of hardening of the compositions and the thermodynamic characteristics of the process. At the same time, the presence of a significant number of adsorbed water molecules on the surface of nanoparticles negatively affects the adhesion of epoxy compositions. It prevents the formation of chemical and physical bonds between the filler surface and the polymer, reducing the physical, mechanical, and thermophysical properties of coatings. In addition, nanofillers are usually prone to aggregation due to significant van der Waals forces. However, the rational introduction of active nano-additives using physical and chemical methods (for uniform distribution of particles in the polymer volume) makes it possible to modify the structure of the polymer and increase resistance to mechanical and chemical influences. Polymeric materials can withstand higher temperatures without significant changes in their characteristics. Thus, in the works of the authors [20-23] it was shown that the introduction of fullerenes into the epoxy binder affects the thermo-oxidative destruction of the polymer. Therefore, nanofillers are essential for developing new-generation epoxy composites that can be used in various technical and industrial fields. However, despite the dynamics of increasing the mechanical characteristics of composites filled with carbon nano-additives [10, 13, 23-26], more and more attention is being paid to the use of cheaper nanoparticles.

The aim of this study is to determine the optimal content of a nanodispersed fullerene-carbon black mixture to improve the thermal properties and structure of epoxy coatings.

2. Experimental

Epoxy resin ED-20 (ISO 18280:2010, Technobudresurs, Kyiv, Ukraine) was selected as the main component of the binder for the formation of the epoxy composite materials (CM). Epoxy resin is characterized by high adhesive and cohesive strength, low shrinkage, and processability when applied on the surfaces of complex profiles.

The curing agent is polyethylene polyamine (PEPA) (Technical Regulations TU 6-05-241-202-78, Technobudresurs, Kyiv, Ukraine) was used for cross-linking of epoxy composites.

Nanodispersed fullerene-carbon black mixture (NFCM) (Yong Feng Chemicals, Hefei, China) was used as an active additive for experimental studies. NFSS is a nanocarbon material obtained during the synthesis of fullerenes using the laser evaporation technology of graphite. Separation of NFSS from fullerenes was carried out using non-polar organic solvents and their subsequent removal. The size of NFSS is 30-40 nm, the specific surface area is 150-200 m^2/g, and the fullerene content is no more than 0.1%.

The technology of coating formation was carried out in a sequence specified in works [27-29].

The following properties of polymers were investigated in the work: coefficient of linear thermal expansion, glass transition temperature, shrinkage, and heat resistance.

The thermal coefficient of linear expansion (TCLE) was calculated from the dependence of relative strain on temperature. The relative strain was determined from the change in the length of the specimen with increasing temperature under steady-state conditions (ISO 11359-2). The dimensions of the specimens were 65 × 12 × 12 mm, the non-parallelism of the polished ends was no more than 0.02 mm.

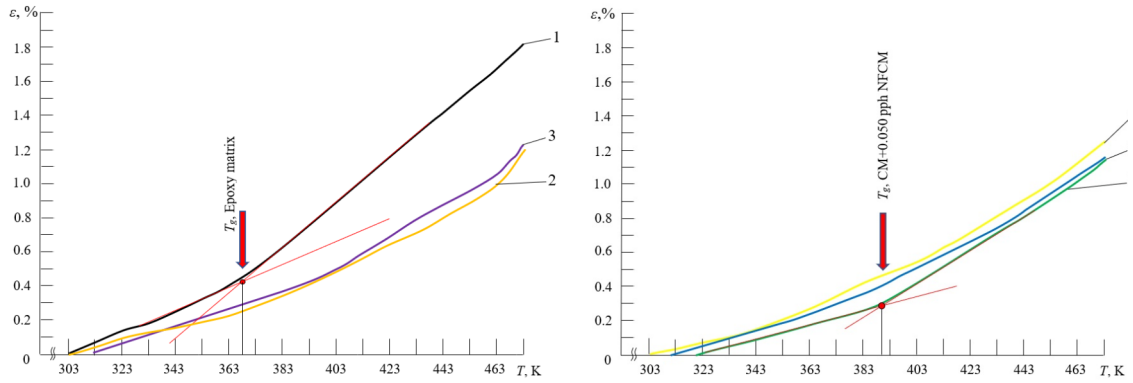

Fig. 1 a. Dilatometric curves of epoxy matrix and CM: 1 – epoxy matrix; 2 – 0.010 wt.% NFCM; 3 – 0.025 wt.% NFCM.b. Dilatometric curves CM: 1 – 0.050 wt.% NFCM; 2 – 0.075 wt.% NFCM; 3 – 0.100 wt.% NFCM.

Table 1. Thermal coefficient of linear expansion of polymer coatings in different test temperature ranges.

№	Content of a nanodispersed fullerene-carbon black mixture, q, wt.%	Glass transition temperature, T_g, K	Shrinkage, δ, %	Coefficient of linear thermal expansion, $\alpha \times 10^{-5}$, K^{-1}			
				Temperature ranges, ΔT, K			
				303-323	303-373	303-423	303-473
1	Epoxy matrix	327.0	0.31	5.73	6.41	8.63	1.06×10^{-4}
2	0.010	333	0.27	5.67	6.24	8.48	1.04×10^{-4}
3	0.025	338	0.27	5.61	6.11	8.32	1.04×10^{-4}
4	0.050	343	0.16	5.79	6.51	8.76	1.07×10^{-4}
5	0.075	336	0.16	5.80	6.62	8.90	1.08×10^{-4}
6	0.100	316	0.29	5.73	6.41	8.63	1.06×10^{-4}

Before the experiment, the length of the sample was measured with an accuracy of ±0.01 mm. The heating rate was v = 2 K/min.

When measuring the thermal coefficient of linear expansion of the polymer, the deviation from the nominal value was 4...6%.

The thermal stability of polymeric materials was studied by the methods of thermogravimetric (TGA) and differential thermal analysis (DTA) using the derivatograph "Thermoscan-2". When determining the exothermic effects during heating of the polymer coating, the rate of temperature increase was 10 degrees/min. The error in determining the temperature in this case is ±1 degree. The accuracy of determining the thermal effects was ~ 3 J/g. The accuracy of determining the change in sample weight is ~ 0.02 g.

3. Results and discussion

When repairing parts of transport equipment operated at different temperatures, the indicators of the thermal coefficient of linear expansion (TCLE) are essential. As the temperature rises, the amplitude of oscillations of atoms and molecules and their average displacement from the equilibrium position increase, which ensures a change in the dimensions of composite materials. High TCLE values often lead to the formation of residual stresses leading to the cracking and peeling of coatings, as well as to the possibility of significant thermoelastic stresses that destroy the composite material when the temperature rises. Therefore, the study of the temperature dependence of composites is relevant, which allows identifying and analyzing temperature transitions in the composite materials being developed.

Based on dilatometric curves (Fig. 1,a,b), the thermal coefficient of linear expansion ($\alpha \times 10^{-5}$, K^{-1}) and glass transition temperature (T_g) were calculated. The glass transition temperature value was previously analyzed (Fig. 1, Table 1). The glass transition temperature depends on the structure and polarity of the polymer, which affects both the flexibility of the chain and the energy of intermolecular interaction. It is established that the highest glass transition temperature T_g = 387-390 K is characteristic of CMs filled with NFCM with a content of q = 0.025...0.050 pph (Table 1). It is believed that the optimal content of nanoparticles ensures a

Table 2. Structural changes in polymers with the nanodispersed fullerene-carbon black mixture under the influence of temperature.

Nanodispersed fullerene-carbon black mixture, wt.%	T_0, K	T_5, K	T_{10}, K	T_{20}, K	T_f, K	ε_m, %
0.010	600	612	628	642	719	60
0.025	603	615	637	649	723	59
0.050	605	620	642	653	733	58
0.075	583	600	619	631	721	62
0.100	580	598	619	632	719	61

Note: T_0 – is the initial mass loss temperature (start of destruction); T_5, T_{10}, T_{20} – are the mass loss temperatures (5%, 10%, 20%); T_{fin} – is the final mass loss temperature (completion of destruction); ε_m – is the relative mass loss.

decrease in the flexibility and mobility of structural elements, due to the interfacial interaction of polymer components; this leads to an increase in the potential barrier of their rotation and, as a result, an increase in the glass transition temperature. Then, the introduction of q = 0.100 pph, NFCM provides a decrease in the glass transition temperature (Table 1), which is associated with the morphological features of the composite structure due to the agglomeration of nanoparticles.

Also, based on the dilatometric curves (Fig. 1, a, b), it was established that with increasing temperature, the TCLE of nanocomposite materials increases curvilinearly, which is associated with relaxation processes during temperature transitions.

In the temperature range ΔT = 303-323 K, a decrease in the TCLR of the nanocomposite by 1.1 times ($\alpha = 5.73\times10^{-5}$ K^{-1}) was observed when introducing NFSS at a concentration of q = 0.010 pph (compared to the epoxy matrix). The lowest TCLR value $\alpha = 5.61\times10^{-5}$ K^{-1} was observed with the introduction of q = 0.050 pph of NFSS (Table 1). With increasing temperature (ΔT = 303-373 K), the TCLR changed insignificantly, and in the temperature range ΔT = 303-373 K, the lowest TCLR value $\alpha = 6.11\times10^{-5}$ K^{-1} was observed when introducing q = 0.050 pph of NFSS. In this temperature range, relaxation of elastic strains occurs with partial destruction of adhesive bonds at the "polymer-nanoparticle" interface and a decrease in internal stresses with a sharp increase in TCLR.

In the temperature ranges ΔT = 303-423 K and ΔT = 303-473 K, rapid dynamics of TCLR changes was observed. Changes in the volume of the nanocomposite occur more quickly due to changes in the magnitude of the vibration amplitude of atoms and molecules. Thus, in the temperature ranges ΔT = 303-423 K and ΔT = 303-473 K, an increase in the TCLE of

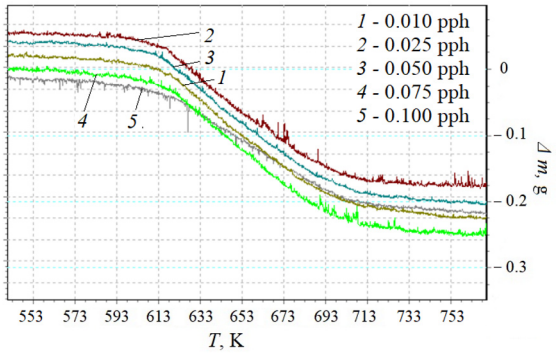

Fig. 2. Results of thermogravimetric analysis for polymers with the nanodispersed fullerene-carbon black mixture content (wt.%): 1) 0.010; 2) 0.025; 3) 0.050; 4) 0.075; 5) 0.100.

nanocomposites by 1.2-1.3 times was observed (compared to the previous temperature ranges).

When developing nanocomposites, protective coatings or adhesives based on them, it is necessary to take into account the operating temperatures at which the equipment is used. To determine the maximum operating temperatures for the developed materials, TGA and DTA analyses were performed. Based on the analysis of TGA curves (Fig. 2, Table 2), structural changes in filled polymers (in the temperature range of 580-733 K) were studied. At the initial stage of increasing temperature, various structural changes occur in polymers. They depend on the presence of a "sol fraction" and a "gel fraction" in the polymer volume, which directly characterizes their degree of crosslinking.

The initial temperature of mass loss of filled polymers was determined by the deviation of the curve from the straight horizontal segment. It has been established that destructive processes primarily occur in polymers with a higher content of NFCM (q = 0.075-0.100 pph). Moreover, the value of the relative mass loss of such polymers is the highest among those studied – ε_m = 61-62%, which confirms the proposed assumption. At the same time, the increased content of the nanofiller in the volume of the

Table 3. Structural change in polymers with the nanodispersed fullerene-carbon black mixture according to the results of DTA analysis.

Nanodispersed fullerene-carbon black mixture, q, wt.%	Temperature Intervals of Exoeffects		Maximal temperature exoeffects, T_{max}, K
	T_i, K	T_{fin}, K	
0.010	470	670	540
0.025	484	670	546
0.050	473	670	555
0.075	473	674	540
0.100	472	674	538

Note: T_i – is the initial exoeffect temperature; T_{fin} – is the final exoeffect temperature

composition affects the rheological characteristics, in particular viscosity, which leads to morphological changes in the structure of the polymer during the polymerization process. Whereas the optimal content of the nanoadditive (q = 0.010-0.050 pph) ensures a shift in the initial temperature of mass loss to the region of higher temperatures by 20-25 K. This allows us to assert the inhibition of thermal destruction reactions, which is also associated with limited mobility of polymer segments network and the main chain of the filled polymer. That is, a small content of nanoadditives ensures ordering of the polymer structure, which indicates an increase in the gel fraction in the polymer volume (compared to CMs filled with a high content of NFCM). The relative mass loss of such polymers is ε_m = 58-60%.

To study thermal effects, differential thermal analysis was additionally carried out (Fig. 3). It has been established that the initial temperature of the exo-effect upon introducing NFCM at a content of q = 0.010-0.100 pph changes insignificantly, except for the CM filled with NFCM at a content of q = 0.025 pph (Table 3). From the TGA and DTA curves it follows that the onset of destructive processes occurs at a temperature of 580-605 K. Taking into account the above, as well as the lower initial temperature of the exo-effect (470–484 K) for filled polymers (before the onset of destructive processes), it can be argued that mobility and deformation of bonds occurs with increasing temperature, which is consistent with the works [23, 27, 30].

Additionally, the peak of the exo-effect T_{max} = 555 K was established for composite materials filled with NFCM at a content of q = 0.050 pph. It should be noted that at T_{max} = 555 K no mass loss of the material under study was observed (Fig. 2). Whereas a comparative analysis of the final temperature

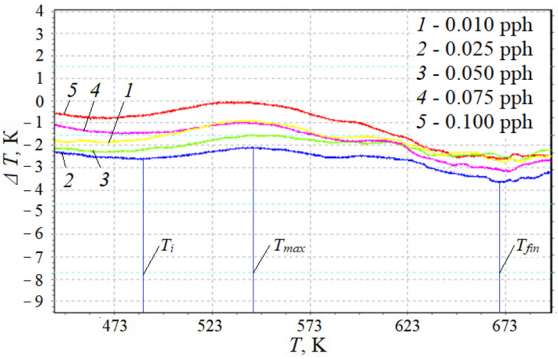

Fig. 3. Results of differential thermal analysis for polymers with the nanodispersed fullerene-carbon black mixture content (wt.%): 1) 0.010; 2) 0.025; 3) 0.050; 4) 0.075; 5) 0.100.

of the exo-effect (T_{fin}) (Fig. 3) and thermogravimetric analysis curves (Fig. 2) allows us to state the destruction of a significant number of chemical bonds.

Consequently, based on a comprehensive assessment of the thermophysical characteristics and structure of the developed polymer materials, it has been established that the most thermostable polymer material contains a nanodispersed fullerene-soot mixture with a content of q = 0.025-0.050 pph. It is advisable to use the developed materials up to the peak of the exoeffect, that is, up to the temperature T_{max} = 555 K.

4. Conclusions

On the basis of complex experimental investigations into the thermophysical characteristics (using modern research methods), the efficiency of using a nanodispersed mixture of fullerene-technical carbon in the manufacture of polymeric materials intended for the protection and repair of transport parts has been proven.

In particular, the dynamics of changes in the thermal coefficient of linear expansion in temperature ranges associated with the rate

of relaxation processes was established. The calculated values of the thermal coefficient of linear expansion vary from $\alpha = 5{,}61 \times 10^{-5}$ K^{-1} in the temperature range $\Delta T = 303\text{-}323$ K to $\alpha = 1{,}08 \times 10^{-4}$ K^{-1} in the temperature range $\Delta T = 303\text{-}473$ K. By manipulating the composition it is possible to select nanocomposites or coatings based on them with the required value of TCLE for protection and repairing parts of transport equipment.

Based on a set of experimental studies using the method of differential thermal analysis (DTA) and thermogravimetric analysis (TGA), it can be stated that the operating temperature of the developed nanocomposites, protective coatings, or adhesives based on them should not exceed $T = 555$ K.

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