Development and research of epoxy polymer with improved thermophysical characteristics

P.O. Maruschak[1], M.V. Kindrachuk[2], I.A. Sieliverstov[3], V.D. Sharanov[4], D.O. Danylenko[4], M.V. Storozhenko[4], L.O. Sapronova[4], Y.M. Shulga[4], O.V. Sharanov[4], V.M. Yatsyuk[5]

[1]Ternopol Ivan Pul'uj National Technical University, 56 Ruska Ave., Ternopil, 46001, Ukraine
[2]National Aviation University Kosmonavta Komarova 1, Kyiv, Ukraine, 03058, Ukraine
[3]Kherson National Technical University, 24 Beryslavs'ke Hwy., Kherson, 73008, Ukraine
[4]Kherson State Maritime Academy, 20 Ushakov Ave., Kherson, 73009, Ukraine
[5]Ternopil Research Forensic Center of MIA of Ukraine, Stepana Budnoho, 48 str., 46001 Ternopil, Ukraine

Technological methods for modifying the DER-331 epoxy oligomer have been developed to improve the thermophysical properties of composite materials and protective coatings based on them. The chemical structure of the phthalic anhydride modifier (PA modifier) was investigated by gas chromatography with mass selective detection. This allowed us to reveal the molecular compatibility of the components and, accordingly, their interaction. Based on the research findings, the optimal content of the phthalic anhydride modifier in the reactoplastic matrix with the improved thermophysical properties was determined, which is $q = 0.10...0.25$ pts. wt. per 100 pts. wt. of the DER-331 oligomer and 10 pts. wt. of the triethylenetetramine (TETA) cold hardener. The modified composites have the following characteristics: Martens heat resistance is $T = 360...362$ K; thermal coefficient of linear expansion is $\alpha = (2.33...2.49) \times 10^{-5}$ К$^{-1}$ in the $\Delta T = 303...323$ К temperature range; the glass-transition temperature is $T_c = 344...345$ К; shrinkage is 0.35%. The optical microscopy method was used to obtain a uniform, linearly oriented composite structure with the optimal modifier content of $q = 0.10...0.25$ pts. wt., which enhances the thermo-physical properties of materials.

Keywords: transport parts; epoxy resin; thermostability; properties; fracture; materials

Розробка та дослідження епоксидного полімеру з покращеними теплофізичними характеристиками. *П.О. Марущак, М.В.Кіндрачук, І.А. Селіверстов, В.Д. Шаранов, Д.О. Даниленко, М.В. Сторошенко, Л.О. Сапронова, Ю.М. Шульга, О.В. Шаранов, В.М. Яцюк*

У роботі наведено особливості модифікації епоксидного олігомеру DER – 331 для поліпшення теплофізичних характеристик композитних матеріалів і захисних покриттів на їх основі функціонального призначення. Методом газової хроматографії з масселективним детектуванням досліджено хімічну структуру модифікатора фталевого ангідриду, що дозволило виявити молекулярну сумісність компонентів, а отже, їх взаємодію. За результатами експериментальних досліджень встановлено оптимальний вміст модифікатора фталевого ангідриду у реактопластичній матриці з поліпшеними теплофізичними властивостями, який становить $q = 0,10...0,25$ мас.ч. на 100 мас.ч. олігомеру DER – 331 і 10 мас.ч. твердника

холодного тверднення триетилентетраміну ТЕТА. При цьому модифіковані композити характеризуються наступними властивостями: теплостійкість за Мартенсом становить – $T = 360...362$ К; термічний коефіцієнт лінійного розширення за діапазону температур ($\Delta T = 303...323$ К) – $a = (2,33...2,49) \times 10\text{-}5$ К$^{-1}$; температура склування $T_c = 344...345$ К; усадка – 0,35 %. Методом оптичної мікроскопії встановлено однорідну лінійно-орієнтовану структуру композитів з оптимальним вмістом модифікатора $q = 0,10...0,25$ мас.ч., що забезпечує поліпшення теплофізичних властивостей матеріалів.

1. Introduction

In state-of-the-art industries, polymer matrices are commonly used to obtain composite materials or coatings based on them. In addition to the complex properties of composite materials, we can benefit from their manufacturability and simplicity of application [1-7]. Moreover, the relevant base of raw materials is available on the territory of Ukraine. Along with thermosetting binders (phenol-formaldehyde, polyester, carbamide, ether, copper, organosilicon ones), which are effectively used to create polymer materials for the transport sector, epoxy binders show a good potential. Such binders can be used to obtain coatings [8-11] or functional products [12-14] resistant to various thermal and mechanical effects. To improve the properties of polymer materials, we introduce modifiers, plasticizers and fillers into the binder to improve the structure formation processes during polymerization. This, in turn, enhances the material properties and provides savings by extending the service time of such materials between repairs.

Composite materials based on thermoset matrices adapt to any geometric shape and can be installed on any structure. Apart from being used to obtain functional coatings, new parts and mechanisms, they are suitable for the restoration of the existing ones [15-18]. A number of studies [16] focused on determining the adhesive properties of the polymer matrix based on the DER-331 epoxy binder suggest that the unmodified matrix is characterized by good adhesive properties that are 3.2 to 3.6 times higher than those of its counterpart (GEN-150) [16, 19], which is used to restore the wheel fit of the compressor part of marine turbocompressors. Moreover, the active modifier used will enhance both the adhesive and thermophysical properties, which, in turn, will expand the application area of the new modified composites.

This research is aimed at determining the optimal effect of the content of the modifier 2-Benzofuran-1,3-dione on the thermophysical properties and structure of the epoxy matrix.

2. Materials and methods

The DER-331 epoxy binder (CAS No. 25085-99-8) manufactured by Dow Chemical Comp (Germany) was used to obtain polymer materials. The triethylenetetramine (TETA) cold hardener (CAS No. 112-24-3) with a content of $q = 10$ pts. wt. (specified per 100 pts. wt. of DER-331 epoxy resin) was used to crosslink the epoxy binder. The structural formulas of the components are shown in Fig. 1 and Fig. 2, respectively.

To improve the structure and properties of the composites, the 2-Benzofuran-1,3-dione – phthalic anhydride modifier (CAS No. 112-24-3) was used, which was introduced into the binder at a content of $q = 0.10...3.00$ pts. wt. (hereinafter in this text, pts. wt. stands for 100 pts. wt. of the DER-331 epoxy oligomer).

The modified epoxy matrix was obtained in the following order:

- preliminary preparation and dosage of ingredients;

- heating the DER-331 epoxy resin to a temperature of $T = 373 \pm 2$ K and holding it for a specified period of time ($\tau = 20 \pm 0.1$ min);

- mechanical combination of ingredients (epoxy binder + modifier) for $\tau = 1.5 \pm 0.1$ min;
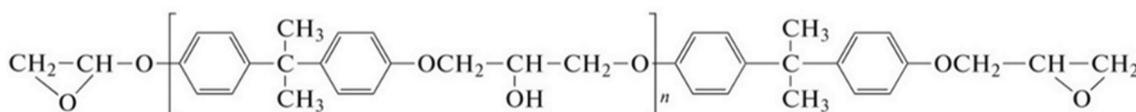

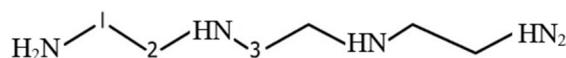Fig. 1. General structural formula of the DER-331 epoxy oligomer.

Fig, 2. Fragment of the TETA structural formula.

- sonicating the composition for $\tau = 1.5 \pm 0.1$ min;

- cooling the composition to room temperature $T = 273 \pm 2$ K for $\tau = 60 \pm 5$ min;

- introducing the TETA hardener and mixing the composition for $\tau = 5 \pm 0.1$ min;

- applying the composition either mechanically or by pneumatic spraying.

The materials were hardened under the experimental conditions:

- making specimens and holding them for $t = 12.0 \pm 0.1$ h at a temperature of $T = 293 \pm 2$ K;

- heating the specimens at a rate of $v = 3$ K/min to a temperature of $T = 393 \pm 2$ K;

- holding the specimens at this temperature for $t = 120 \pm 5$ min;

- cooling the specimens slowly to a temperature of $T = 293 \pm 2$ K.

To ensure the stability of the structural processes occurring in the matrix, the specimens were held for a time $t = 24$ h in air at a temperature of $T = 293 \pm 2$ K, after which the experimental tests were performed.

As part of this research, we investigated the structure of the modifier (by the method of gas chromatography with mass-selective detection), the thermal coefficient of linear expansion, Martens heat resistance, shrinkage, the glass-transition temperature, and the structure of composites (by the method of optical microscopy).

The structure of the modifier was determined by gas chromatography with mass selective detection. The study was conducted on the GC/MS Agilent Technologies 6890 N setup with an embedded HP 19091S-433 (NR-5MS) quartz capillary column with the following specifications: the capillary length – 30 m; the inner diameter – 0.25 mm; the film thickness – 0.25 μm. The weight of the test substance diluted in methanol was 0.0124 g. Helium was used as the carrier gas. Temperature conditions were as follows: $T_{init.} = 100°$ C, holding time – 2 min, heating rate – 15 °C/min., $T_{final} = 280$ °C.

The structure (topology) of materials was studied on a XJL-17AT metallographic microscope equipped with a Levenhuk C310 NG camera (3.2 Mega pixels). The image magnification range was from ×100 to ×1600. The Levenhuk ToupView software was used to process digital images.

The Martens heat resistance of the matrix was determined according to ISO 75-2. The research technique consisted in determining the temperature, to which the test specimen was
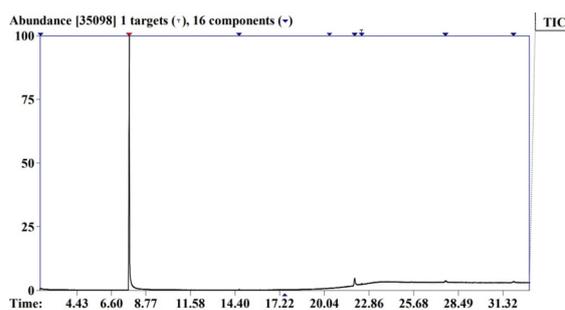

Fig. 3. Chromatogram of the modifier studied.

heated at a rate of $v = 3$ K/min under the action of a constant bending load $F = 5 \pm 0.5$ MPa, leading to deformation of the test specimen by a given value ($h = 6$ mm).

The thermal coefficient of linear expansion of the sample (TCLE) was calculated from the curve of relative deformation versus temperature. Then this dependence was approximated with an exponential function. Relative strain was determined by the change in length with increasing temperature under steady-state conditions. (ISO 11359-2). Specimen dimensions were $65 \times 12 \times 12$ mm, the non-parallelism of the polished ends was not more than 0.02 mm. Before the experiment, the specimen length was measured with an accuracy of ±0.01 mm. The heating rate was $v = 2$ K/min. When studying thermophysical properties (Martens heat resistance, TCLE), the value deviation from the nominal value was 4...6%.

3. Results and discussion

At the initial stage, we studied the PA structure by the method of gas chromatography with mass selective detection in order to determine the compatibility of the modifier with the DER-331 epoxy oligomer. This made it possible to define the molecular weight of the modifier and the degree of interaction of the structural elements of the epoxy composition.

The signal retention time $t_R = 7.734$ min was determined from the chromatogram of a sample of the modifier (Fig. 3).

Since individual compounds may have similar properties and the same retention time, mass spectral analysis was performed to obtain more detailed information about the test substance (modifier). Since modifier fragments are characterized by charged ions of a certain mass, and the signal retention time was $t_R = 7.734$ min, we looked for the m/z ratio, namely the mass of the ion (m) to its charge (z).
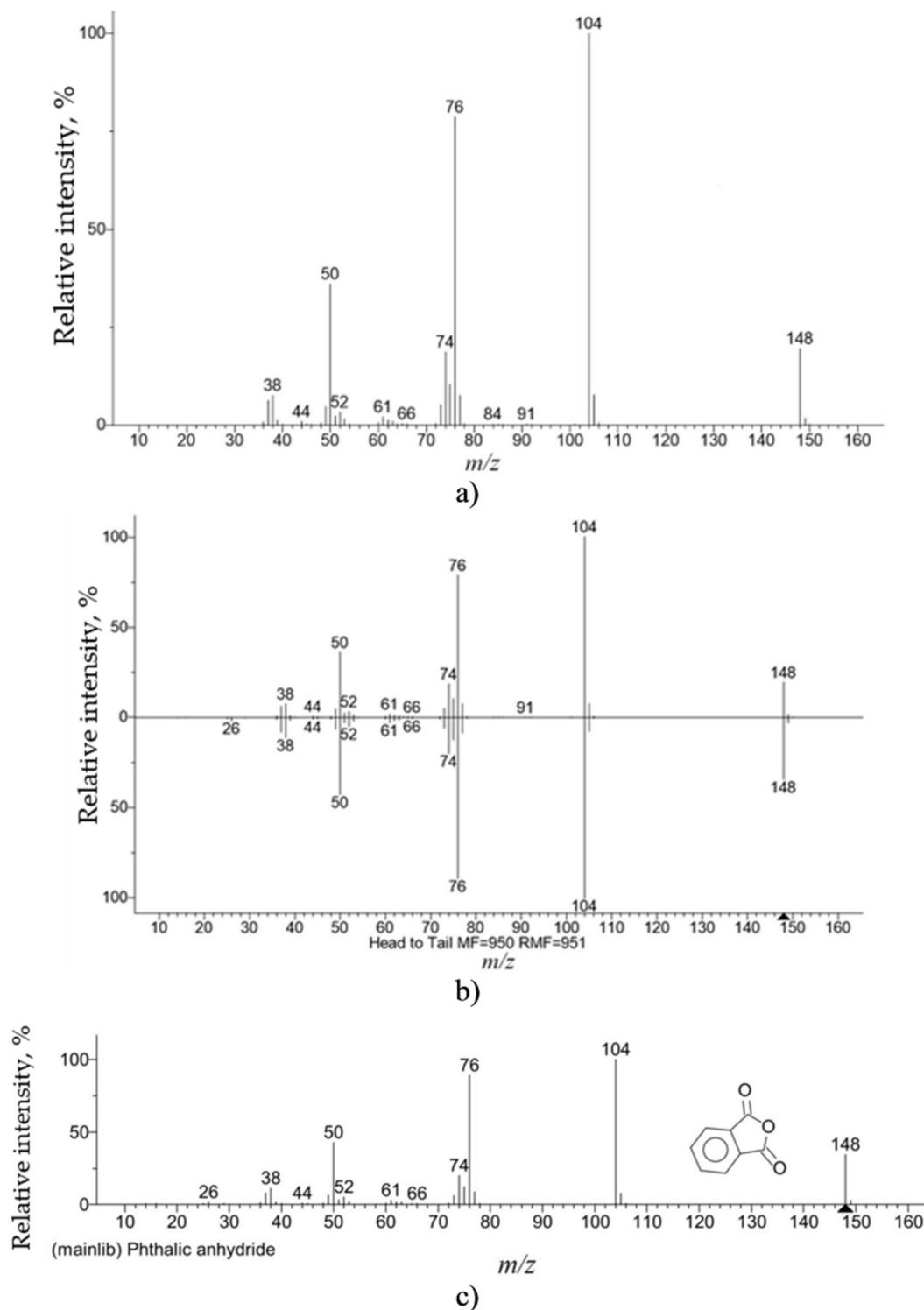
Fig. 4. Mass spectra of 2-Benzofuran-1.3-dione modifier samples with signal retention time $t_R = 7.734$ min: a), b) characteristic signals of the modifier molecules in the full scan range; c) chemical structure of the modifier according to the electronic library of known substances.

The obtained values correspond to the molecular weight of the modifier fragment.

In addition, we analyzed the set of characteristic signals. This made it possible to iden-

tify ten major peaks (Fig. 4), each of which corresponds to a specific molecular cation formed during ionization of the modifier sample. Figure 5 a, b shows the base peak located near
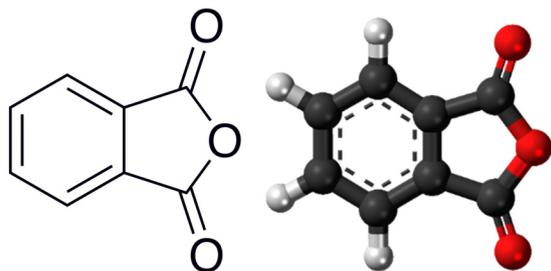
Fig. 5. Structural formula of the 2-Benzofuran-1.3-dione modifier ($C_8H_4O_3$).

the middle of the spectrum. It corresponds to $m/z = 104$ amu (atomic mass unit). However, the most intense distant peak with $m/z = 148$ amu was observed at the extreme right of the spectrum. Based on this, we can assume that this is a molecular peak, that is, the heaviest molecule that passed through the mass spectrometer to the detector.

Comparing the obtained spectra with an electronic library of known substances, we established that the test sample of the modifier is an organic compound - phthalic anhydride, which has the structural formula: $C_8H_4O_3$ (Fig. 4, c, Fig. 5).

The research results suggest that the molecular weight of the phthalic anhydride modifier is 148 amu, which is very close to that of the TETA hardener (146 amu) and the DER-331 epoxy oligomer (182...192 amu). It was believed that molecular compatibility would allow a controlled influence on the processes of structure formation, providing enhanced cross-linking of epoxy composites and, accordingly, the properties of modified epoxy composites.

Next, we investigated how the content of the phthalic anhydride modifier may affect the thermophysical characteristics of composite materials (Fig. 6). The Martens heat resistance of the unmodified epoxy composite was found to be $T = 359$ K. At the same time, the introduction of a modifier with a content of $q = 0.10...0.25$ pts. wt. provided a maximum increase in heat resistance to $T = 360...362$ K. Introduction of phthalic anhydride at a content of $q = 0.50$ pts. wt. gives heat resistance equal to unmodified epoxy matrix (Fig. 6). Increasing the modifier content to $q = 1.00...3.00$ pts. wt. leads to a monotonous decrease in Martens heat resistance to $T = 355...360$ K.

To analyze the behavior of the resulting composite in the temperature range $\Delta T = 303...473$ K, the thermal coefficient of linear expansion (TCLE) was studied. Using dilatometric curves
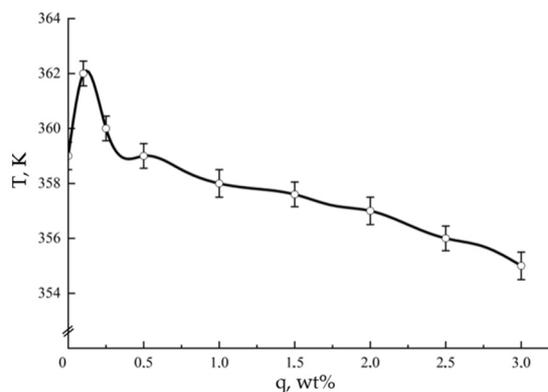

Fig. 6. Thermophysical properties of composites with different contents of the 2-Benzofuran-1.3-dione modifier.
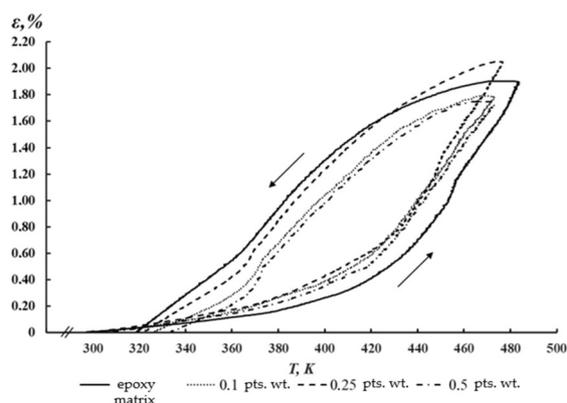

Fig. 7. Indicators of dilatometric curves of the epoxy matrix depending on the content of the 2-Benzofuran-1.3-dione modifier.
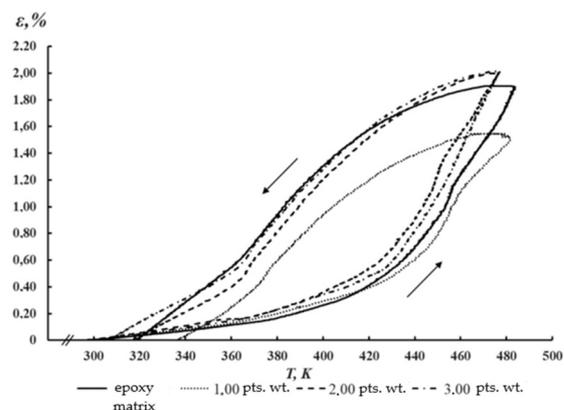

Fig. 8. Indicators of dilatometric curves of the epoxy matrix depending on the content of the 2-Benzofuran-1.3-dione modifier.

(strain versus temperature) (Fig. 7, 8), the glass transition temperature (T_{gt}) was determined and the thermal expansion coefficient of the composite was calculated in the considered temperature ranges. The glass-transition temperature (T_{gt}) characterizes the mobility of the independent kinetic elements (macromolecules and segments) of epoxy composites. The

Table 1. Thermal coefficient of linear expansion for composites modified with 2-Benzofuran-1.3-dione in different temperature ranges

Modifier content, q, pts. wt.	Thermal coefficient of linear expansion, $\alpha \times 10^{-5}$, К⁻¹				Glass transition temperature, T_c, К	Shrinkage, Δl, %
	Test temperature ranges, ΔT, К					
	303…323	303…373	303…423	303…473		
Epoxy Matrix	2.50	2.74	4.96	9.78	320	0.35
0.10	2.33	2.59	4.39	9.70	345	0.36
0.25	2.49	2.72	4.45	9.79	344	0.35
0.50	2.41	2.56	4.08	9.73	340	0.45
1.00	2.48	2.74	4.31	9.74	335	0.30
2.00	2.75	2.84	4.64	10.10	317	0.28
3.00	2.80	2.90	4.45	10.00	310	0.10

composites filled with a modifier at a content of q = 0.10...0.25 pts. wt. (Figs. 7, 8, Table 1) were found to have the highest glass-transition temperature (T_{gt}) = 344...345 K. Such composites have a lower mobility of the independent kinetic elements (due to the limited mobility of structural elements, including C-O bonds of the modifier present in the boundary layer), which is associated with a greater value of the potential rotation barrier, and, consequently, a higher glass-transition temperature.

Data on thermal expansion coefficient of modified composites are presented in Fig. 7, 8 and Table 1. An increase in the content of the modifier in the composite ensures a gradual increase in the thermal coefficient of linear expansion only up to a certain level, that is, up to the temperature range ΔT = 303...373 K. An extreme increase in the TCLE was observed in the temperature ranges ΔT = 303...423 K and ΔT = 303...473 K, which is associated with the rate of transition from the non-equilibrium to the equilibrium state of composite materials. The phthalic anhydride modifier at a content of q = 0.10 pts. wt. ensures the formation of composites with the lowest TCLE (among those studied) in the temperature range ΔT = 303...323 K (Table 1). Further introduction of the modifier (q = 0.25...3.00 pts. wt.) provides a linear increase in the TCLE for all studied composites. In the temperature range ΔT = 303...373 K, the TCLE increases by Δa = 0.26×10⁻⁵ К⁻¹ with a minimum modifier content (q = 0.10 pts. wt.). Accordingly, when introducing phthalic anhydride at a content of q = 0.25...3.00 pts. wt., a linear increase in TCLE is observed. A sharp increase in the TCLE (1.6 to 1.8 times) in the temperature range ΔT = 303...423 K (as compared to the previous temperature ranges) is associated with the proximity of the modified composite to the yield temperature character-istic of the viscous state. This is consistent with the results presented in [18, 20]. Similar relaxation processes were observed in the high-temperature range (ΔT = 303...473 K), where the lowest TCLE a = 9.70×10⁻⁵ К⁻¹ is inherent in composites with the modifier content of q = 0.10 pts. wt.

Shrinkage affects dimensional stability to produce a coating of controlled thickness and therefore a protective effect of equal stability. Therefore, we studied the effect of the phthalic anhydride modifier on the shrinkage of the composites. Table 1 shows the linear shrinkage of Δl = 0.35% for the unmodified composites. With the modifier content of q = 0.10...0.25 pts. wt., a slight increase in the linear shrinkage by the value of Δl = 0.01% was observed, which is typical of the unmodified epoxy composites. An increase in the modifier content to q = 0.50 pts. wt. leads to the maximum shrinkage, which is Δl = 0.45% (Table 1). At a content of q = 1.00...3.00 pts. wt., the modifier provides a decrease in the linear shrinkage to Δl = 0.30...0.10%. At the same time, the composite with the maximum modifier content (q = 3.00 pts. wt.) is characterized by the minimum shrinkage (Δl = 0.10%).

The results obtained on heat resistance suggest that the modifier introduced into the epoxy binder at the minimum content (q = 0.10...0.25 pts. wt.) provides a spatial polymer grid with the uniformly distributed internal stresses. This, in turn, leads to the formation of a linearly oriented structure (Fig. 9), which is quite stable under significant temperature fluctuations, which is a very important factor in the manufacture and operation of protective coatings.
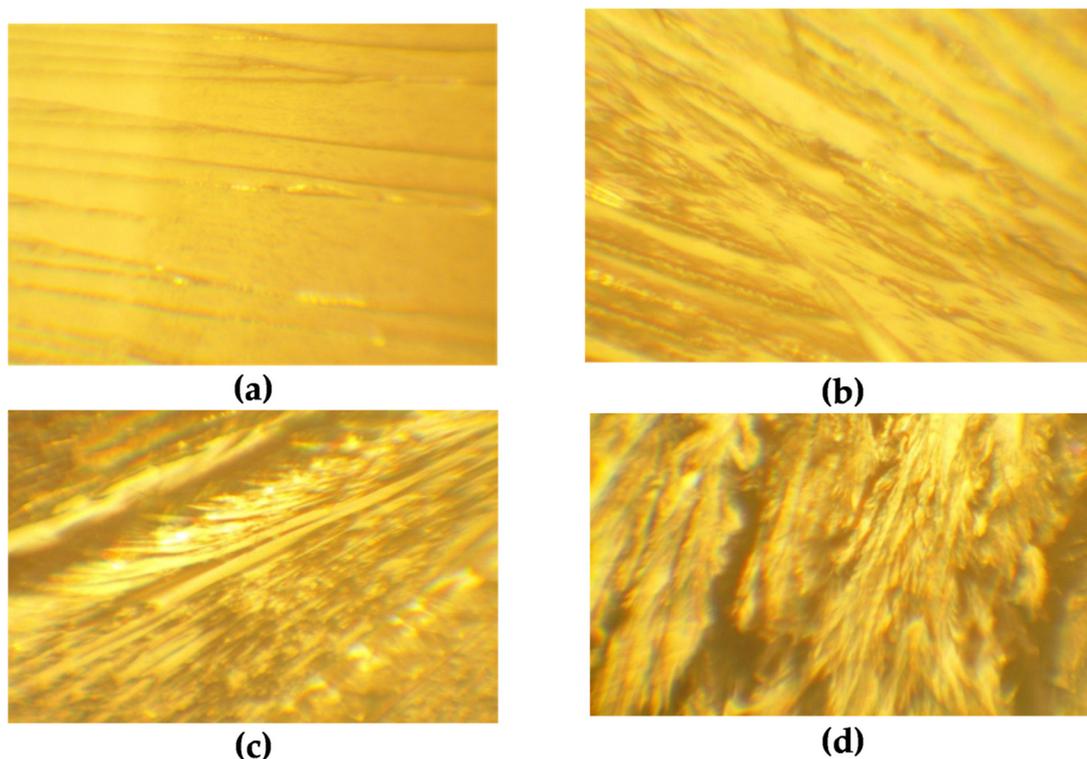
Fig. 9. Macrofracture of epoxy composites modified with 2-Benzofuran-1.3-dione, q, pts. wt.: a) 0.10; b) 0.25; c) 1.00; d) 3.00.

4. Conclusions

Based on complex experimental investigations into the thermophysical characteristics using modern research methods (gas chromatography with mass selective detection), the effectiveness of the phthalic anhydride modifier in the manufacture of polymer materials intended for the restoration of transport parts has been proven.

The molecular compatibility of the components of a composite material consisting of DER-331 epoxy oligomer, the triethylenetetramine hardener and the phthalic anhydride modifier was determined by gas chromatography with mass selective detection. A rational combination of the components ensures a high degree of crosslinking of modified composites, and, accordingly, high thermophysical properties.

It has been established that composites containing q = 0.10...0.25 pts. wt. phthalic anhydride modifier have better thermophysical properties. The Martens heat resistance was T = 360...362 K; the thermal coefficient of linear expansion in the ΔT = 303...323 K temperature range was a = (2.33...2.49) × 10^{-5} K^{-1}; the glass-transition temperature was T_{gt} = 344...345 K. The shrinkage of the resulting composite materials did not exceed 0.35%, which made it possible to obtain a coating of a controlled thickness, and, accordingly, with the protective effect of the same stability. The research results were confirmed by the optical microscopy method. In particular, the linearly oriented structure of the developed materials was formed by introducing a modifier in an amount of q = 0.10...0.25 pts. wt.

Comparison of the results obtained for Martens heat resistance (T = 355 K), linear increase in the thermal coefficient of linear expansion and minimal shrinkage ((Δl = 0.10%) indicates the plasticizing effect of the modifier at the maximum PA content q = 3.0 pts. wt. This creates conditions for further development and research of modified protective coatings with a damping effect for the body parts, in particular, of marine transport.

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