

Research Article

Development of Epoxy-Polyester Composite with Improved Thermophysical Properties for Restoration of Details of Sea and River Transport

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The results of the experimental investigations of the optimization of the content of the polyester resin in the epoxy binder are shown in the work. It was determined that composite with concentration of the polyester ($q = 10$ mas.fr.) was characterized by the maximal values of the thermophysical properties. The Martens thermal resistance temperature, the linear shrinkage, the thermal coefficient of linear expansion, and the glass transition temperature of the epoxy-polyester matrix were investigated. It was found that introducing the polyester resin into the epoxy oligomer in quantity of $q = 10$ mas.fr. leads to improving the Martens thermal resistance of the material to the $T = 352$ K and decreasing the linear shrinkage to the $\Delta l = 0.06\%$. The nonlinear dependence of the TCLE on the temperature was confirmed, and the tendency of changes in their values, depending on the content of polyester resin, was defined. The dilatometric curves were analyzed, and the glass transition temperature of developed epoxy-polyester matrix was determined at the level $T_c = 318$ K.

1. Introduction

It is necessary to use polymer materials in the construction, repair, and restoration of individual parts and mechanisms at the present stage of the development of the transport technology industry [1, 2]. In this direction, one of the rational solutions is the use of polymer composites. Therefore, the question of the creation of the polymeric composite materials (CM) with improved properties is actual today [3]. In particular, the advantages of CM over other materials (impermeability to water, chemical resistance, and high processability) allow them to be used in many industries. A special place is occupied by shipbuilding: polymers are used in the form of final products and as a restoring material of ship systems and devices. The details of the air ducts of the ship's ventilation and air-conditioning system, the technological isolation of the pipes of the ship systems, the ship pipelines of the power plants, the deadwood bearings, etc., are the examples. Simultaneously, with the development of technologies, the requirements to the

properties of polymers are increasing. If it is necessary to prepare a composite with a new complex of properties, it is expedient to obtain a mixture of polymers [4, 5]. Therefore, a compound of two binders with different nature in the one CM is interesting. This approach allows, even at low concentrations, to obtain a material that is characterized by increased performance characteristics [6]. At the same time, the importance in the manufacture and operation of a polymer product or protective coating has predictions of indicators of thermophysical properties. For the significant difference in thermal expansion leads to the formation of significant residual stresses, which are the cause of stratification and destruction of products and failure of parts and mechanisms as a result. Thus, the development of composite material with combination of polyester resin in epoxy binder with improved and specified parameters of thermophysical properties is an actual task of modern industry.

The authors had shown the results of investigation of thermophysical properties of epoxy composites in the works [7–10]. The kinetics of the glass transition process, thermal

expansion, and shrinkage were described and the thermal resistance (Martens) of materials was investigated. The main physical and chemical phenomena and processes in the epoxy binder at the polymerization that have a significant impact on the values of thermophysical properties of composites were defined. The results of experimental investigations of epoxy-polyester matrix were described in the works [11, 12]. The adhesion and physicomechanical properties of polymer materials were investigated by authors: P. Stukhlyak (Ukraine), Yu. Sokolova, D. Zharin (Russia), M. Mikhailov, A. Karpov, Yu. Pleskachevsky (Republic of Belarus), Y. Jahani, M. Ehsani (Iran), B. Mottershead, and S. J. Eichhorn (Great Britain) [13–17]. However, the thermophysical properties of developed polymer composites are not enough investigated. As it is known, the values of thermophysical properties significantly affect the performance characteristics of the product based on the polymer material. Therefore, the analysis of dynamics of thermophysical processes in the materials is an important stage of the creation of polymer products.

The purpose of this work was to develop the epoxy-polyester matrix with improved thermophysical properties for restoration of details of sea and river transport.

2. Materials and Methods

For the formation of the matrix for CM with increased thermophysical properties, the following components were used in the work:

- (a) Epoxy resin ED-20 (GOST 10587-84) ($q = 100$ mas. fr.).
- (b) Orthophthalic dicyclopentadiene (DCPD) unsaturated preaccelerated polyester resin ENYDYNE H 68372 TAE ($q = 10$ mas.fr.) (the content is indicated on 100 weight parts of epoxy resin), which has an inhibitor to prevent instant polymerization (gel time from $t = 20$ to 24 min). It should be noted that during the copolymerization reaction of the composition of unsaturated polyesters with non-limiting monomer compounds in the presence of initiators, a significant amount of heat is released; therefore, the reaction is exothermic.
- (c) The cold curing hardener polyethylene polyamine (PEPA) (TU 6-05-241-202-78) ($q = 10$ mas.fr.) (the content is indicated on 100 weight parts of epoxy resin).
- (d) The initiator for polyester resins Butanox-M50 ($q = 1.5$ mas.fr.) (the content is indicated on 100 weight parts of polyester resin), which is a peroxide of methyl ethyl ketone (MEKP) and contains a low amount of water and a minimum amount of polar compounds in comparison with ethylene glycol.

The matrix was formed at a cross-linking temperature of $T = 393 \pm 2$ K.

The following thermophysical properties of CM were investigated for determining the optimal ratio between the concentration of polyester resin (PR) and epoxy oligomer in

the binder: the Martens thermal resistance temperature, the thermal coefficient of linear expansion, the glass transition temperature, and the shrinkage. The content of the unsaturated polyester has been changed within the range from $q = 10$ to 120 mas.fr. per 100 mas.fr. of epoxy oligomer ED-20. The concentration of hardeners in the compositions and the cross-linking temperature has been defined according to the previous research results.

The Martens thermal resistance for CM was determined according to GOST 21341-75. The methodology of investigation consists in determining the temperature at which the specimen has been heated at a rate of $v = 3$ K/min under the influence of the constant bending load $F = 5 \pm 0.5$ MPa, as a result of which it is deformed on a predetermined amount ($h = 6$ mm).

The thermal coefficient of linear expansion (TCLE) of materials was calculated by the curve of the relative deformation from a temperature, approximating this dependence by the exponential function. The relative deformation was determined from the change in the specimen length with increasing the temperature under steady-state conditions (GOST 15173-70). Specimens for the research with the size of $65 \times 12 \times 12$ mm had nonparallelism of the polished ends of not more than 0.02 mm. The length of the specimen was measured with an accuracy of ± 0.01 mm. The heating rate was $v = 2$ K/min.

The structure of the CM was studied on a XJL-17AT metallographic microscope, which is equipped with a Levenhuk C310 NG (3.2 megapixels) camera. The image enlargement range varied from $\times 100$ to $\times 1600$ times. Directly in the work, the samples were examined with an increase of $\times 400$ times. For the processing of digital images, "Levenhuk ToupView" software was used.

The materials were solidified according to the following regimen: the formation of specimens and their holding over time $t = 12.0 \pm 0.1$ h at a temperature $T = 293 \pm 2$ K, heating at a speed of $v = 3$ K/min to a temperature $T = 393 \pm 2$ K, holding the specimens at a given temperature during the time $t = 2.0 \pm 0.05$ h, and slowly cooling to a temperature of $T = 293 \pm 2$ K. In order to stabilize the structural processes in the matrix, the specimens were kept during time $t = 24$ h in air at a temperature $T = 293 \pm 2$ K, followed by conducting experimental tests.

3. Results and Discussion

Thermal resistance (Martens) of CM was investigated on the first stage. As it is known, the thermal resistance is determined by the properties of the binder. The epoxy oligomer with addition of polyester unsaturated resin was used as a binder according to the methodology of investigation. The introduction of the polyester in quantity of $q = 10$ mas.fr. (the content is indicated on 100 weight parts of epoxy resin) leads to increasing the thermal resistance of composites from $T = 341$ K (matrix based on an epoxy binder) to $T = 352$ K (Figure 1). The monotonic decrease in the thermal resistance (Martens) of developed composite materials was determined with the increasing of the concentration of polyester from $q = 20$ to 120 mas.fr. (Figure 1, Table 1).

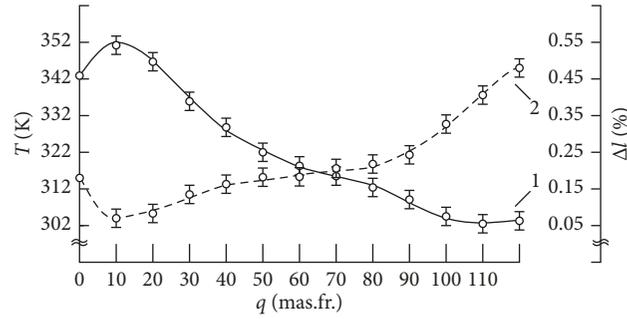


FIGURE 1: The dependence of thermophysical properties of matrix on the content of polyester resin. 1: thermal resistance (Martens), T ; 2: linear shrinkage, Δl .

TABLE 1: Thermophysical properties of CM with different contents of the polyester resin.

No	Content of the polyester resin, q , mas.fr.	Thermal resistance, T , K	Glass transition temperature, T_g , K	Glass transition area, ΔT , K	Shrinkage, Δl , %
1	—	341	311	306–343	0.31
2	10	352	318	310–355	0.06
3	20	347	312	309–342	0.10
4	40	328	309	305–333	0.16
5	60	318	317	311–323	0.21
6	80	313	315	307–333	0.24
7	100	304	317	303–323	0.32
8	120	302	304	303–317	0.48

The results can be explained on the basis of the thermodynamics of polymer mixture [18]. According to the theoretical positions, the mutual solubility of most polymer pairs over a wide range of temperatures is a tenth or even a hundredth of a percent. A slight difference in the chemical structure or polarity of the two polymers results in their low mutual solubility. That is, the two polymers form a biphasic mixture. The polyester resin at a slight content is in a discrete phase in the epoxy binder. With a further increase in the concentration of the ENYDYNE H 68372 TAE (from $q = 20$ to 120 mas.fr.), a continuous polyester phase is clearly formed. In this case, thermophysical properties of CM are deteriorating which, in our opinion, is due to the excess content of the polyester resin in the binder.

For qualitative confirmation of the results of the experiment, microstructure of the fracture surface of the specimen was studied using an optical microscope. The typical forms of the surfaces of the studied specimens are shown in Figure 2. It was found that the structure of the material surface at the concentration of polyester $q = 10$ mas.fr. was characterized by a homogeneous structure. There are no visible defects in the cross-linking of the two polymers (Figure 2(b)). With an increase of the content of the polyester binder ($q = 60$ mas.fr.), the appearance of defects in the cross-linking of the matrix was observed (Figure 2(c)). This may be due to the excessive amount of the chemical bonds of the polyether component of the matrix that do not interact with the epoxy binder during polymerization and the formation of temperature stresses. With an increase of the concentration to $q = 120$ mas.fr., a similar propagation of defects on the fracture fractogram of the composite material was observed (Figure 2(d)).

Similarly, the functional dependence of linear shrinkage on the concentration of the polyester resin in the epoxy binder was observed. The shrinkage of the matrix based on the epoxy binder was $\Delta l = 0.31\%$. It was found that the minimal shrinkage ($\Delta l = 0.06\%$) has CM which contain ENYDYNE H 68372 TAE in quantity of $q = 10$ mas.fr. Further increasing of concentration of polyester resin leads to the increasing of linear shrinkage from $\Delta l = 0.10$ to 0.48% (Figure 1, Table 1). According to the relaxation theory of glass transition, the mobility of kinetic units of polymer with the increasing of the temperature increases as a result of increasing of intensity of thermal motion, and also due to the destruction of the bonds between them in the case of fluctuation collisions [19].

At the next stage, the thermal coefficient of linear expansion of matrices and their glass transition temperature was investigated. The singularity of the thermal expansion of epoxy-polyester matrices was investigated in the following temperature ranges: (1) $\Delta T = 303\text{--}323$ K; (2) $\Delta T = 303\text{--}373$ K; (3) $\Delta T = 303\text{--}423$ K; and (4) $\Delta T = 303\text{--}473$ K (Figure 3). The following values of TCLE were obtained for the matrix: $\Delta T = 303\text{--}323$ K, $\alpha = 6.3 \times 10^{-5} \text{ K}^{-1}$; $\Delta T = 303\text{--}373$ K, $\alpha = 6.8 \times 10^{-5} \text{ K}^{-1}$; $\Delta T = 303\text{--}423$ K, $\alpha = 9.9 \times 10^{-5} \text{ K}^{-1}$; and $\Delta T = 303\text{--}473$ K, $\alpha = 10.9 \times 10^{-5} \text{ K}^{-1}$. It was found that at the first temperature range, the minimal TCLE has CM with the content of PR $q = 10$ mas.fr. Compared with the initial epoxy matrix, the TCLE decreased by $\Delta\alpha = 4.6 \times 10^{-5} \text{ K}^{-1}$ (Table 2). Analogical dynamics of TCLE values was observed also at the following temperature ranges at the same concentration of polyester resin: $\Delta T = 303\text{--}373$ K, $\alpha = 2.2 \times 10^{-5} \text{ K}^{-1}$; $\Delta T = 303\text{--}423$ K, $\alpha = 3.8 \times 10^{-5} \text{ K}^{-1}$; and $\Delta T = 303\text{--}473$ K, $\alpha = 8.9 \times 10^{-5} \text{ K}^{-1}$. The obtained data can characterize a matrix

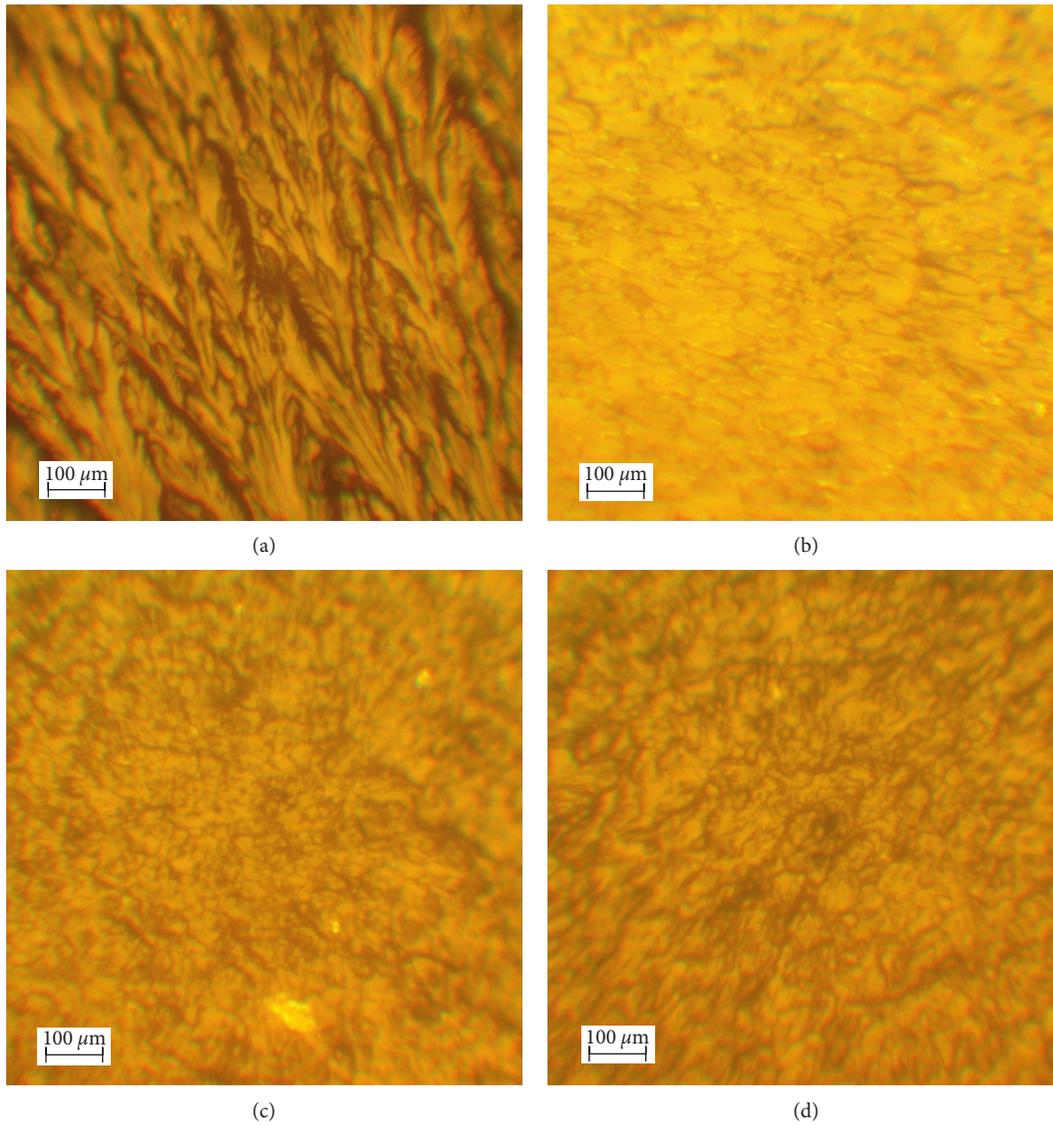


FIGURE 2: Microstructure of surfaces of the studied composite materials (with an increase of $\times 400$ times): (a) matrix, (b) 10 mas.fr., (c) 60 mas.fr., and (d) 120 mas.fr.

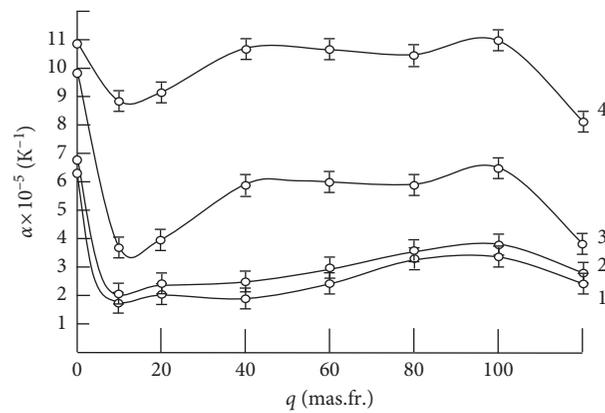


FIGURE 3: The dependence of thermal coefficient of linear expansion on the content of polyester resin at different temperature ranges. 1: $\Delta T = 303\text{--}323$ K; 2: $\Delta T = 303\text{--}373$ K; 3: $\Delta T = 303\text{--}423$ K; 4: $\Delta T = 303\text{--}473$ K.

TABLE 2: The values of TCLE depending on the content of PR at the different temperature ranges.

Content of PR, q , mas.fr.	Thermal coefficient of linear expansion, $\alpha \times 10^{-5}$, K^{-1}			
	Temperature test ranges, ΔT , K			
	303–323	303–373	303–423	303–473
—	6.3	6.8	9.9	10.9
10	1.7	2.2	3.8	8.9
20	2.0	2.4	4.0	9.1
40	1.9	2.5	5.9	10.7
60	2.4	2.9	6.0	10.6
80	3.4	3.5	5.9	10.5
100	3.5	3.8	6.5	11.0
120	2.5	2.8	3.8	8.1

with concentration of PR $q=10$ mas.fr. as a material with a higher cross-linking density, compared with epoxy [19]. With an increase of the concentration of polyester from $q=20$ to 100 mas.fr., an increase of the TCLE was observed at all temperature ranges of the study (Figure 3; Table 2). As a result of the studies, it was confirmed that the dependence of TCLE on temperature is nonlinear. When the polyester resin is introduced over $q=100$ mas.fr., the sharp falloff of TCLE was observed. In our opinion, this is a consequence of the destructive processes taking place in the composite: the destruction of spatial structures, the change in the nature and intensity of the intermolecular interaction, and the destruction of intermolecular bonds.

As it is known, one of the important performance properties of CM is a glass transition temperature (T_g). The T_g determines the upper permissible range of operating temperatures and is the edge of the glassy and highly elastic states. The dilatometric curves which image the dependence of relative linear deformation of the specimens on the temperature were investigated. It was experimentally found that the glass transition temperature of the epoxy matrix is $T_g = 311$ K and the maximal value $T_g = 318$ K is designated for the composite with content of PR in quantity of $q=10$ mas.fr. (Figure 4). It was detected that the glass transition temperature shifts to low temperatures (Figure 4, Table 1) with the further increasing of concentration of polyester resin (from $q=20$ to $q=120$ mas.fr.). Evidently, the increasing of glass transition temperature is linearly related to the degree of cross-linking of the polymer matrix [20]. Therefore, it was considered that the increasing of the concentration of PR over $q=10$ mas.fr. decreases the number of physicochemical bonds in the spatial polymer network. It leads to decreasing of T_g and deterioration of thermophysical properties of CM. The results of the investigation of the glass transition temperature accord with values of the thermal resistance and TCLE. Also, it should be noted that it correlates with previous data of the investigation of adhesion and physicochemical properties of CM. This indicates the reliability of the obtained results of the study.

4. Conclusion

The thermophysical properties of epoxy matrix have been investigated at different concentrations of polyester resin. It

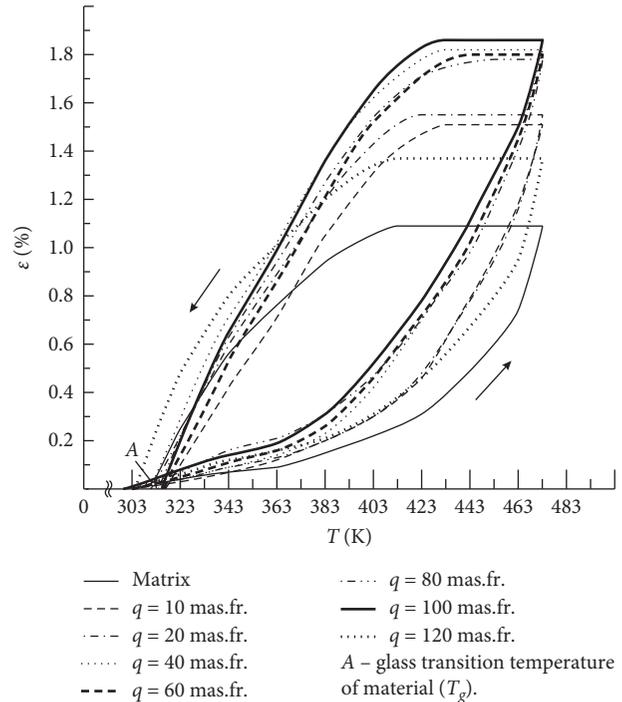


FIGURE 4: Dilatometric curves of the matrices at the different content of polyester resin.

was found that the epoxy matrix with the content of polyester resin ENYDYNE H 68372 TAE in quantity of $q=10$ mas.fr. is characterized by maximal values of the thermophysical properties. In addition, the following results were found:

- (1) The introduction of the polyester resin in the epoxy binder at a low concentration ($q=10$ mas.fr.) leads to increasing of the thermal resistance of the matrix from $T=$ to $T=352$ K and decreasing of the linear shrinkage of the composite from $\Delta l=0.31\%$ to $\Delta l=0.06\%$.
- (2) Value of indicators of thermal coefficient of linear expansion at all the studied temperature ranges decreases compared with the indicators of TCLE of epoxy matrix. Minimal values of the indicators of TCLE were obtained at concentration of polyester resin $q=10$ mas.fr. at the appropriate ranges: $\Delta T=303-323$ K, $\alpha=1.7 \times 10^{-5} K^{-1}$; $\Delta T=303-373$ K, $\alpha=2.2 \times 10^{-5} K^{-1}$; $\Delta T=303-423$ K, $\alpha=3.8 \times 10^{-5} K^{-1}$; $\Delta T=303-473$ K, $\alpha=8.9 \times 10^{-5} K^{-1}$.
- (3) Glass transition temperature T_g of the developed material increases from $T_g=311$ K to $T_g=318$ K. This is caused by increasing of the degree of cross-linking of the matrix.

The obtained results of investigation of thermophysical properties of composite materials correlate with data of investigation of the adhesion and physicochemical performance. This confirms the expedience of the use of polymer products based on the developed CM for the restoration of transport details.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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