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INFLUENCE OF MODIFIED EPOXY RESIN ON PHYSICAL AND MECHANICAL PROPERTIES OF EPOXY COMPOSITE

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The main physical-mechanical and thermophysical characteristics of composite materials based on epoxy resin ED-20 and peroxide resin ED-20P (modified with tert-butyl hydroperoxide ED-20 of a molecular weight 480) in the ratio of 30 mass parts of ED-20P to 70 mass parts of ED-20 and unsaturated oligoester TGM-3 were researched. Butyl methacrylate was used as the active diluent of epoxy-oligoester mixtures. The polyethylene polyamine was used as hardener in a steochemical ratio. For the comparison we studied compositions which did not contain ED-20P resin. The advantage of compositions included ED-20P modified resin has been shown.

Key words: epoxy resin, composition, physicochemistry, modulus of elasticity, toughness, destructive stress

Introduction

Currently, there are many composite materials based on epoxy resins being created and manufactured by industry. Composite materials based on epoxy resin are characterized of high adhesion to organic and mineral fillers, low shrinkage during the curing, specified electrical insulating properties, chemical resistance, high strength and low tensile strength. under the load. The above mentioned allows successfully use epoxy-containing composite materials in construction, chemical industry, mechanical engineering and other industries. The example of epoxy composites foreseens the dermining of scientific and technological approaches to the formation of polymer-matrix composite systems of different degrees of filling with specified properties and mechanisms to regulate of such systems. Epoxy-containing composite materials application is aimed at adjusting the working properties of systems through the science-based introduction of structurally active modifiers and fillers. [1–4].

However, the task of finding an effective compositions whivh improve the physical and mechanical properties of epoxy polymers without reducing their inherent high cohesive strength, chemical resistance and adhesion to many metallic and polymer materials remains relevant. As known [5,6], the best physical and mechanical properties demonstratep the wares in which all the components are interrelated into a single three-dimensional structure polymer. It can be achieved by the combining of epoxy resins with other modifying compounds. The physicochemistry of gradient processes in polymers is closely related to the development of new epoxy-composite materials and heterogeneous systems for industry то be characterized by high working properties.

The study of polymer macromolecules behavior during the polymerization and operation of epoxy compound is one of the important tasks of physicochemistry of polymers, whereas the regulation of these processes provides a scientifically grounded prediction of the composite systems characteristics. Understanding the complex of physico-mechanical and thermophysical properties of polymers is bounded with analysis of such an important issue as the characteristics of thermal motion of matrix macromolecules, strength and crosslinking density of individual groups and radicals in the polymer chain.

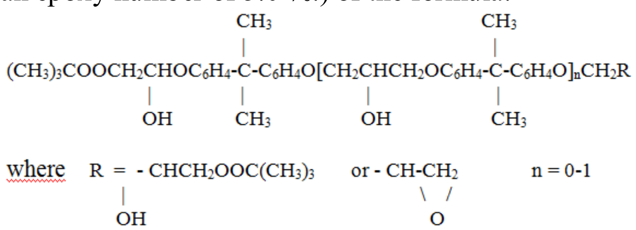
Research purpose

The formation of spatially crosslinked films based on epoxy oligomers can be occured both during the heating and at the room temperature. However, in order for the coatings to be resistant to aggressive environments and have improved physical and mechanical properties, it is necessary to apply the multicomponent systems. Applying of modified epoxy resin containing labile peroxide groups in combination with an industrial epoxy resin and oligoesteracrylate (last acrylate groups are capable of three-dimensional polymerization), the multicomponentity can be avoided. Consequently, the aim of given studies was to develop a small-component epoxy-oligoester composition with a crosslinked structure and research an influence of modified epoxy resin on improvement of thermal, physical and mechanical properties.

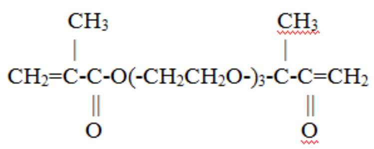
Research in mentioned direction allows to extend the possibilities of regulation of filled reactoplasts properties and to obtain new materials of the predetermined properties in a wide range of operating modes. One of the decisive factors in the reliability and durability of epoxy compounds is the strength cohesive of heterogeneous systems.

Materials and methods of research

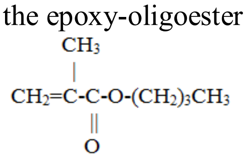
By the authors it have been studied the physical and mechanical properties of composite materials based on ED-20 brand industrial resin with a molecular weight of 390, an epoxy number of 20.1 % as well as peroxide resin ED-20P (modified with tert-butyl hydroperoxide ED-20 with a molecular weight of 480 active oxygen 2 , 1 % and an epoxy number of 5.0 %.) of the formula:



in the ratio of 30 mass parts ED-20P to 70 mass parts of ED-20 [7] and TGM-3 unsaturated oligoester with Mn = 280 of the formula:



Butyl methacrylate (BMA) was used as an active diluent of the epoxy-oligoester mixtures.



Polyethylene polyamine was applied as a hardener. The formula is:

H_2N-$(CH_2$-CH_2-$NH)_n$-H where n= 3,4,5

in a steochemical ratio. For the comparison, it has been studied a compositions which do not contain ED-20P resin. (table 1). The compositions were prepared by mixing the components at room temperature or during the heating to 313K for 15–20 minutes with further adding to homogeneous mixtures of PEPA hardener. [8–10].

The destructive tension (σ_{dt}) and elasticity modulus (E) of the composites at the bending were determined according to DSTU 2824-94 and 2825-94. The destructive tension at compression (σ_c) was determined according to DSTU 2444-94. Impact strength (α) was researched via pendulum copra according to DSTU EN 10045-1:2006. At the known lifting angle the scale of measuring device fixes the working angle of the pendulum after the sample destruction. The dimensions of sample were 60x10x8 mm.

Table 1

The content of epoxy-oligoester compositions

Component	Composition content, mass parts	
	I	II
ED-20	100	70
ED-20P	-	30
TGM-3	4	4
BMA	6	6

Note: the content of PEPA in all compositions was 14 mass parts.

The console method was applied to determine the internal stresses. The coating have been formed on a steel base of 0.3 mm thick. In order to stabilize the structural processes, after staying for 2 hours at 293 ± 2K and two-hour heat treatment at T = 393 ± 2K the samples were holded for 48 hours in air.

Dynamic mechanical characteristics: shear modulus (G '), loss modulus (G ”) and mechanical loss angle tangent (tg δ) were determined using a torsion pendulum formed as a bundle of fibers (basalt or glass) impregnated with the researched composite [11] .

The thermal coefficient of linear extension (TCLE) was determined by the change in the length of the sample with a change in temperature under stationary conditions according to the (ASTM D696-16). The length of the studied samples was 50 ± 5 mm. The number of the samples for each batch was chosen at least three. Absolute elongation was determined as the difference between samples elongation and quartz tips elongation.. Heat resistance (according to Martens) of polymer-composite materials was determined according to GOST 21341-2014. The thermal conductivity determination (λ) of composites was carried out applying the thermal conductivity meter IT-λ-400, which implements the method of dynamic calorimeter. [12,13]

Research results and discussion.

When studying the physical and mechanical properties of polymer composites, it was found that the composition which contains ED-20P resin possess better properties than without ED-20P (Table2).

Table 2

Comparative characteristics of physical and mechanical properties in researched composites

Composite	I	II
Destructive tension at bending σ_b, МПа	45,7	74,4
Modulus of elasticity at bending, *E*, GPa	1,8	2,08
destructive tension at compression, σ_c, MPa	175	494
Toughness, α, kJ / m2	9,87	12,6
Internal tensions, σ_{in}, MPa	3,8	5,7

The obtained data allow us to affirm that the the molecular mobility limitation of ED-20 molecules in the polymerization process causes an increase in the rigidity of its structural links ensuring the formation of a material with insufficiently high indicators of physical and mechanical properties.

When ED-20P peroxide resin is added into epoxy matrix an intensive interaction of the composition ingredients is taking place. It allows to obtain a composite of higher crosslinking density compared to ordinary resin, while the internal stresses of these systems increase to 5.7 MPa. Relaxation of internal stresses in time, due to the rearrangement of radicals and links of epoxy composites macromolecules allows to increase the modulus of elasticity in bending and toughness of filled materials by 15 % and 23 % accordingly.

Additives of the studied ED-20P epoxy resin also affected the dynamic mechanical properties of epoxy compositions which were determined during the curing of composites (Fig. 1).

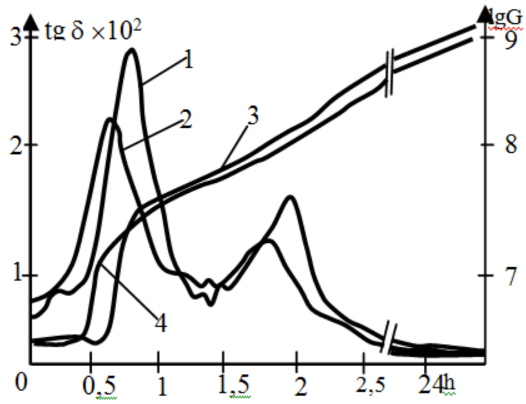


Fig. 1. The dependence of change in the angle tangent of mechanical losses (1, 2) and dynamic shear modulus logarithm (3, 4) of the composites based on ED-20 (1, 3) and ED-20 and ED-20P blend (2,4).

Adding of ED-20P caused the significant reduction of α-transition intensity which is associated with the glazing of the composite as well as its earlier appearing unlike to the composite without ED-20P. The possible reason for this effect may consist in as follows. During the epoxy polymer have been filling the angle tangent of mechanical losses decreases in proportion to the volume fraction of the filler and its surface activity relatively to the matrix.

Table 3

The comparative characteristics of thermo-physical properties of researched composites

Composite	TCLE, $\alpha \times 10^{-5}$, K^{-1}			Thermal conductivity coefficient, , λ,Вт/м×К			Heat resistance (according to Martens)
	Temperature, K						
	293	333	393	293	333	393	
I	1,02	2,57	4,14	0,45	0,37	0,36	84
II	1,82	4,77	5,57	0,48	0,42	0,38	62

Thus, if we consider ED-20P as a chemically active filler in relation to the matrix of ED-20, it is easy to explain the reduction of mechanical losses in epoxy polymers in the diapason of the α- transition while the adding of ED-20P modified resin.

Studies of polymer systems filled with peroxide resin allow to show the influence of nature of chemical bonds on the molecular mobility of heterogeneous systems as well as the influence of the own mobility of epoxy molecules on thermo-physical properties of composites. Dilatometer studies have shown (Table 3) that the adding of ED-20P into epoxy polymer also affects the value of TCLE.

A significant increase in TCLE and low heat resistance of the given systems has been determined. It explains by the relaxation spectrum extension in the filled systems through the increase of conformational batch of polymer chains which leads to the formation of "looseness" of packaging and significant mobility of molecular groups. Accordingly, the presence of chemically linked components of ED-20 with radicals of ED-20P molecules ensures the passage of intense relaxation processes as well as prevents the rigid polymer chains formation in comparison with ordinary ED-20 resin.

Conclusions

In this manner, the modification of epoxy matrix with ED-20P peroxide resin which in the polymerization process is chemically links to the macromolecules of the binder provides a significant increase in physical and chemical properties of the materials. As the temperature increases as a result of thermal relaxation processes associated with conformational movements of macromolecules groups in the direction of smaller stress gradients, a significant thermal expansion of the compound is being observed. At the same time, a more equilibrium state of the epoxy-compound is realized due to the compatibility of the polymer and modified ED-20P resin, that is an effective method of regulating the working properties of heterogeneous polymer systems.

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ВПЛИВ МОДИФІКОВАНОЇ ЕПОКСИДНОЇ СМОЛИ НА ФІЗИКО-МЕХАНІЧНІ ВЛАСТИВОСТІ ЕПОКСИДНОГО КОМПОЗИТУ

Досліджено основні фізико-механічні та теплофізичні характеристики композитних матеріалів на основі епоксидної смоли ЕД-20 і пероксидної смоли ЕД-20П (модифікована трет-бутил гідропероксидом ЕД-20 з молекулярною масою 480) у співвідношенні 30 мас.ч. ЕД-20П на 70 мас.ч. ЕД-20 і ненасиченого олігоестеру ТГМ-3. Як активний розбавлювач епокси-олігоестерних сумішей використовували бутилметакрилат. В якості твердника застосовували поліетиленполіамін в стеохімічному співвідношенні. Для порівняння вивчали композиції, які не містили смоли ЕД-20П. Показана перевага композицій в склад яких входить модифікована смола ЕД-20П.

Ключові слова: епоксидна смола, композиція, фізико-хімія, модуль пружності, ударна вязкість, руйнівне напруження