UDC 541.64

DEFORMATION PROPERTIES OF COMPOSITE MATERIALS ON THE BASIS OF UNSATURATED POLYESTERS AND EPOXY RESIN**Yu.N.Gahramanly, A.M.Mustafayev*, I.A.Guseynov*, R.I.Ismaylova*, B.N.Babanly, N.T.Kakhramanov****Azerbaijan State Oil and Industry University***Institute of Polymer Materials of the Azerbaijan National Academy of Science**najaf1946@rambler.ru*

Received 22.10.2019

Accepted 17.04.2002

The synthesis of the unsaturated polyester method by the interaction of bicycloheptene dicarboxylic anhydride with glycerin and methacrylic acid and the properties of the obtained product are shown, the results of a study of the influence of various formulation of compositions based on epoxy and polyester resins on the physicommechanical properties and thermomechanical curves of the dependence of deformation on temperature are presented. The paper presents the results of a study of the influence of various formulation of compositions based on epoxy and polyester resin on the physicommechanical properties and thermomechanical curves of the dependence of deformation on temperature. It is shown that compositions with 20 wt. % content of a polyester resin have comparatively better properties.

Keywords: polyester resin, epoxy resin, thermomechanical properties, ultimate tensile stress, elongation at break, heat resistance.

*doi***Introduction**

The literature provides a large number of studies on the modification of the structure of epoxy resin ED-20 by loading various modifiers into its composition [1]. The main objective of research, as a rule, is dedicated to the problem of strengthening composite materials, which are widely used in aviation, military, space, military-space technology, shipbuilding, automobile production, building industry etc. Certainly, such a wide range of applications for resin-based potting and impregnating compounds is due to the specific features of their structure and properties. However, regardless of the application areas of the potting compounds, the problem of their strength and heat resistance has always been on the agenda. This circumstance is explained by the fact that precisely these indicators today determine the quality of the material. Obviously, in order to achieve the goal left, it becomes necessary to conduct a series of studies on the development of new composite materials based on epoxy binders of anhydride curing. It is this feature of composite materials that allows them to be used as potting and impregnating compounds in the production of various structural products.

In this regard, the goal of this work was the development of composite materials based on epoxy resin with improved deformation characteristics.

Experimental part

An ED-20 epoxy resin and a synthesized by us polyester resin were used as an object of study.

1. Synthesis of α,ω -dimethacrylate-(1.3)-(bis-glycerin)-2-bicyclo[2.2.1]hept-5-ene-2.3-dicarboxylate

In a reaction flask equipped with a mechanical stirrer, a thermometer, a nitrogen capillary, a Dean-Stark nozzle with a reflux condenser, a mixture of 164 g (1 mol) of anhydride and 184 g (2 mol) of glycerin, 392 g (4 mol) of methacrylic acid and 5 g of *para*-toluenesulfonic acid, 4 g hydroquinone, 500 ml of toluene is heated at 150–160°C, stirring for 4–5 hours until the reaction water is completely stopped.

At the end of the synthesis, the reaction mass, cooled to room temperature, is washed with a 10% aqueous solution of sodium chloride containing 5% sodium carbonate and finally washed with a 5% solution of sodium chloride.

The neutral toluene solution of the oligoester is dried with anhydrous sodium sulfate,

Table 1. Properties of unsaturated polyester (I)

Molecular weight by cryoscopic method in benzene	Acid number, mg KOH/g	Ether number, mg KOH/g		Bromine number g Br /100g		OH, %		Kinematic viscosity at 30°C in 40% styrene
		Found	Calculated	Found	Calculated	Found	Calculated	
1100 ± 20	40 ± 10	645	585	35	30	10	7	45 cSt при 20°C

after which the solvent is distilled off in vacuo at a temperature of a water bath of 50–60°C. The yield of ether is 80–83% of theoretical.

Average molecular weight of the resulting oligoester is determined by the cryoscopic method.

The physico-chemical properties of unsaturated polyesters (USPE) are shown in Table 1.

2. Compositions for studying their physico-mechanical characteristics were prepared at various ratios of USPE to epoxy resin (10, 20 and 30 parts by weight) polyethylenepolyamine (PEPA) was used as a curing agent

Samples in the form of spatulas were obtained according to the following procedure. USPE was added to the resin heated to 80°C with stirring in small portions. After that, the required amount of PEPA was added to the mixture. The mixture was poured into molds and cured for 24 hours at room temperature, then cured for 6 hours at 80°C, 4 hours at 120°C, 3 hours at 150°C.

The degree of curing of the samples 97–98% was determined by extraction in the soxhlet apparatus with acetone.

The resulting samples are dark brown in color, transparent, odorless, with a shiny surface. The samples were tested on an FMPW-500 pendulum tensile testing machine with a lower clamp speed of 30 mm/min. The arithmetic average of five measurements was taken as the test results.

On the basis of the C₅ fraction obtained during the pyrolysis, dibasic dicarboxylic acid anhydrides were synthesized according to the scheme:

The unsaturated polyester was synthesized by reacting bicycloheptenedicarboxylic anhydride with glycerin and methacrylic acid:

Based on the C₅ fraction obtained during the pyrolysis, dibasic dicarboxylic acid anhydrides, by-products – glycerin and maleic anhydride were synthesized.

Based on these products, unsaturated polyesters were prepared, which at various ratios, were loading into the composition based on ED-20. The use of PEPA made it possible to obtain 3 cured compositions, the formulation of which is given below:

Composition – 1

ED-20 – 45g (90 wt. %)

Unsaturated polyester – 5g (10 wt. %)

PEPA – 4.5g (10 wt. % in ratio to epoxy resin)

The degree of cure of the epoxy composition – 98%.

Composition – 2

ED-20 – 45g (80 wt. %)

Unsaturated polyester – 10g (20 wt. %)

PEPA – 4.0g (10 wt. % in ratio to epoxy resin)

The degree of cure of the epoxy composition – 98%.

Composition – 3

ED-20 – 35g (70 wt. %)

Unsaturated polyester – 15g (30 wt. %)

PEPA – 3.5g (10 wt. % in ratio to epoxy resin)

The degree of cure of the epoxy composition – 98%.

Thermomechanical characteristics of this compositions were studied on a Kanavts instrument in a wide temperature range. Deformation was measured at successively varying temperatures (T). At constructing the thermomechanical curve of the polymer $\Delta = f(T)$, it is very important to cover, if possible, the entire temperature range of the polymer's existence – glassy (crystalline), highly elastic and viscous flow conditions. Thermomechanical curves reflect all possible physical, physico-chemical and chemical changes that occur in the sample in the process of changing the temperature of the experiment and, thus, provide reliable information about the temperature transitions that are significant for polymer processing.

Heat resistance was determined by the Vicat method.

Physicomechanical characteristics were determined by standard methods: ultimate tensile

stress (σ_s) and elongation at break (ϵ) were determined in accordance with GOST 11262-80.

Results and discussion

The composition and ratio of the components included in the main chain of the unsaturated polyester, their mutual compatibility, the degree of polycondensation, polydispersity, the nature of the end groups, the distribution of the structural units of the polymer chain, the composition of the unsaturated units – all together have a significant impact on the properties of the cured resins. In order to get a clear idea of the processes occurring in the ED-20-based polymer composition, it seemed interesting to first consider the regularities of changes in their thermo-deformation characteristics determined by the thermomechanical analysis method. Figure 1 shows the thermomechanical curves of the temperature dependence of deformation for 3 compositions differing in the content of unsaturated polyester. As can be seen from this figure, an increase in the concentration of unsaturated polyester in the composition is accompanied by a significant change in the thermomechanical curves. When the unsaturated polyester content in the composition is within 10 mass. %, noticeable changes in deformation from -48 to $+9$ μm are observed (Figure 1, curve 1). Moreover, an increase in the experimental temperature from 20 to 50°C is accompanied by an increase in the volume of the sample in the range up to 5 μm . At temperatures above 50°C , the process of softening of the sample begins, accompanied by an increase in deformation to 9 μm at 70°C . Then a further increase in temperature again leads to the reverse process, accompanied by a decrease in deformation and the transition of the composition into a solid glassy state. This state is characterized by the occurrence of intense crosslinking, as a result of which an increase in the volume of the sample is observed.

As can be seen from Figure, curve 2, when the content of unsaturated polyester in the composition of ED-20 is within 20 mass. %, an increase in the test temperature to 70°C is accompanied by an increase in deformation to 16

μm due to softening of the sample. A further increase in temperature (over 70°C) promotes the occurrence of intense crosslinking, which contributes to an increase in the volume of the sample.

The effect of the concentration of the polyester resin in the composition of ED-20 on the thermomechanical curves of composite materials: composition 1, composition 2, composition 3.

In Figure, curve 3 the thermomechanical curve of the dependence of deformation on temperature is presented for compositions with a 30 mass. % polyester content. According to the data shown in this figure, this dependence is fundamentally different from the thermomechanical curves of the previous two samples. The main difference is expressed in a slight deformation of the samples from the temperature and a shift in the softening temperature of the samples to high temperatures. So, for example, the first softening of the sample begins not at 50°C , but at 60°C . The curing process does not occur at 70°C , but at 82°C . And finally, the most important point and distinguishing feature of sample 3 is expressed in the fact that at

105°C the softening of the sample again occurs, accompanied by an increase in deformation.

There is reason to believe that at 30 mass. % of the polyester, such a wave-like course of the process of softening and crosslinking (curing) indicates complex and ambiguous physico-chemical processes taking place in this composition. In addition, there is reason to believe that the curing process of polyester and ED-20 in the composition can proceed in several stages, which is regulated by the viscosity of the mixture. Should take into account the fact that the chain length, as well as the chemical structure of the reagents used, to a certain extent predetermine the structure and properties of the cured polyester.

The ultimate tensile stress and elongation at break of the considered ED-20 compositions were investigated. As can be seen from table 2, all 3 compositions of ED-20 differ in the content of polyester. From a comparative analysis of the data presented in this table, it can be established that composition 2 has a comparatively better strength properties, in which the ultimate tensile stress is 17.0 MPa, the elongation at break is 15%, and the heat resistance is 160°C . In this case, the high heat resistance of the composition is determined, first of all, by that limiting concentration of polyester, at which a uniform redistribution of the crosslinking density is achieved over the entire volume of the sample, and the maximum speed and degree of crosslinking are also ensured.

Table 2. Physico-mechanical properties of composite materials based on ED-20 and polyester resin

Composition	Ultimate tensile stress, MPa	Elongation at break, %	Heat resistance, $^{\circ}\text{C}$
Composition 1	11.0	10	150
Composition 2	17.0	15	160
Composition 3	14.0	10	155

Similarly, the compressive strength of the samples was investigated. During the research, it was found that the compressive strength of the samples changes as follows: Composition 1 – 4.70 N/mm^2 , composition 2 – 26.27 N/mm^2 , composition 3 – 1.08 N/mm^2 . Comparative analysis of the data can establish the maximum value

of compressive strength has a composition with 20 mass. % content. There is reason to believe that in the composition at a polyester concentration of more than 20 mass. %, a certain part of it does not participate in the polycondensation reaction, which leads to a noticeable decrease in the compressive strength of the sample. All obtained experimental data are analytical, since 5 samples were used in the test.

Thus, based on the foregoing, it can be stated that the maximum effect of improving the properties of cured resins is achieved when the content of polyester in the composition ED-20 in the amount of 20 mass. %.

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DOYMAMIŞ POLİEFİRLƏR VƏ EPOKSİD QATRANI ƏSASINDA OLAN KOMPOZİSİYA MATERIALLARININ DEFORMASIYA XÜSUSİYYƏTLƏRİ

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Bitisklohepten dikarbon anhidridinin qliserin və metakril turşusu ilə qarşılıqlı təsirdən doymamış poliefirin sintezi üsulu və alınmış məhsulun xassələri verilmiş, epoksid qatranı və poliefir əsasında olan kompozisiyalarının müxtəlif tərkibinin fiziki-mexaniki xüsusiyyətlərə və deformasiyanın temperaturdan asılılıq əyrilərinə təsiri tədqiqatlarının nəticələri təqdim olunmuşdur. Tərkibində 20 kütlə % poliefir olan kompozisiyaların müqayisədə daha yaxşı xüsusiyyətlərə malik olduğu göstərilmişdir.

Açar sözlər: poliefir qatranı, epoksid qatranı, termomexaniki xüsusiyyətlər, dartılmada möhkəmlik həddi, nisbi uzanma, istiliyədavamlılıq.

ДЕФОРМАЦИОННЫЕ СВОЙСТВА КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ НА ОСНОВЕ НЕНАСЫЩЕННЫХ ПОЛИЭФИРОВ И ЭПОКСИДНОЙ СМОЛЫ

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В работе показано синтез метода ненасыщенного полиэфира взаимодействием бициклогептен дикарбонового ангидрида с глицерином и метакриловой кислотой и свойства полученного продукта, приведены результаты исследования влияния различных составов композиций на основе эпоксидной и полиэфирной смол на физико-механические свойства и термомеханические кривые зависимости деформации от температуры. Показано, что сравнительно лучшими свойствами обладают композиции с содержанием – 20 масс. %. полиэфирной смолы.

Ключевые слова: полиэфирная смола, эпоксидная смола, термомеханические свойства, разрушающее напряжение, относительное удлинение, теплостойкость.