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## STRUCTURING OF EPOXY-OLIGOESTER COMPOSITIONS IN THE PRESENCE OF PEROXIDATED EPOXY RESIN

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The method of obtaining of epoxy-oligoester compositions based on ED-20 dyano epoxy resin in the presence of modified ED-20P epoxy resin was developed. The influence of amount of epoxy components and unsaturated MGPh-9 oligoester on structuring process of epoxy-oligoester blends was studied. The heating of such blends causes complete decomposition of labile peroxide groups and also subsequent polymerization of unsaturated oligoesters which, in the presence of ED-20P resin is included to the crosslinked structure of blend providing the derivation of epoxy-oligoesters with improved physical, mechanical and chemical properties.

**Key words:** epoxy resin, composition, structuring, gel fraction, hardness, film.

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## СТРУКТУРУВАННЯ ЕПОКСИОЛІГОЕСТЕРНИХ КОМПОЗИЦІЙ У ПРИСУТНОСТІ ПЕРОКСИДОВАНОЇ ЕПОКСИДНОЇ СМОЛИ

Розроблено методику одержання епоксидолігоестерних композицій на основі діанової епоксидної смоли ЕД-20 в присутності модифікованої епоксидної смоли ЕД-20П. Вивчено вплив кількості епоксидних компонентів і ненасиченого олігоестеру МГФ-9 на процес структурування епоксидолігоестерних сумішей. Нагрівання таких сумішей спричиняє повний розклад лабільних пероксидних груп і подальшу полімеризацію ненасиченого олігоестеру, який, в присутності смоли ЕД-20П, входить у зшити структуру суміші, що і надає змогу отримувати епоксидолігоестерні плівки з покращеними фізико-механічними і хімічними властивостями.

**Ключові слова:** епоксидна смола, композиція, структурування, гель-фракція, твердість, плівка.

### Introduction

The linking of epoxy resins with oligoester is carried out on the one hand to reduce the cost of epoxy-based materials, and on the other to improve their properties [1, 2].

In most cases, oligoesters serve as plasticizers of epoxy compositions and therefore are not chemically bonded with polymer grid in epoxy polymer. The resins of a different molecular mass [3, 4, 5] are being used as oligoester resins, as well as products of condensation of saturated and unsaturated dibasic acids or their anhydrides with glycols. However, such plasticization of epoxy compositions, despite the fact that it allows

reducing the fragility of products, in general, does not improve their working properties. It caused by the fact that the oligoester, which is not chemically bounded to the molecules of epoxy resin, during the exploitation of the polymer material “perspires” and thus leads to deterioration of its properties.

In this regard, the efforts of many scientists are aimed at the development of methods that would allow polyester resin chemically being included to the structure of the crosslinked epoxy polymer [6, 7]. To achieve above mentioned goal the composition containing epoxy resin ED-20, oligoester resin MGPh-9, peroxide benzoyl,

dimethylaniline and maleic anhydride or blends of maleic and chlorinated derivatives was studied. In this case, the anhydrides of the acid react with an epoxy resin to form, instead of epoxy groups, the fragments of unsaturated anhydride. Further in the presence of benzoyl peroxide, which, during the heating to 353 K forms free radicals the process of three-dimensional polymerisation of MGPh-9 resin and modified with anhydride epoxy resin is observed. Such epoxy-oligoester compositions are applied in the production of plastic glass.

In other works the resins such as THF, HE and AF are studied as unsaturated oligoesters components. Epoxy components were industrial products marked ED-20 and ED-16. In order to dilute the epoxy-oligoester system it is proposed to use styrene.

Another approach to the creation of chemically bounded epoxy-oligoesters compositions is described in [8, 9]. Accordingly to this, the epoxy resins is being modified by unsaturated carboxylic acids. As modifiers the acrylic, methacrylic and croton acids are being applied. The obtained products contain unsaturated double bonds that are able to combine with oligoester. During injecting into such system the initiators of radical polymerization (when heated) the transition of such composition into an insoluble state is being occurred. In order to reduce viscosity of the system the monomers such as styrene and vinyl acetate are injected in epoxy-oligoester composition. Such an approach to the creation of an epoxy-oligoester blends allow to reduce the number of components of the system.

In Lviv Polytechnic National University, were carried out and currently carry out the works concerning the synthesis based on epoxy resins of peroxide derivatives [10]. The synthesized products contain finite peroxide groups, which during the heating are able to decompose with free radicals formation that can initiate the polymerization of unsaturated products. This allowed us to propose the application of modified hydroperoxide epoxy resins to create spatially cross-linked epoxy-oligoester compositions. The structuring of such compositions occurs at elevated temperatures (383–423 K) and gel fraction content in such blends depends on the ratio of the initial components. The next step for solving the problem of polymer grid formation based on epoxy and oligoester resins is the

research, in which into composition containing ED-20 epoxy resin, unsaturated polyester, and a polyethylenepolyamine additionally in an amount of 3 to 5 mass fraction the di-epoxy derivative of azo-compound (azoglycidylpentane) was injected. The structuring of such blend proceeds step by step. At the beginning, at the room temperature for 24 hours (in the presence of polyethylene-polyamine) a partial crosslinking of molecules of ED-20 epoxy resin and azoglycidylpentane is being occurred. The unsaturated polyester molecules, as well as the monomer molecules are not chemically bonded to the molecules of structured epoxy resins at this stage. However, the molecule of the crosslinked epoxide includes fragments of azglicidylpentane containing labile – N = N-groups. It is known from the literature sources that –N = N-groups are able to decompose at 343 K and higher with free radicals forming and the molecular nitrogen releasing. Therefore, at the second stage the partially crosslinked composition is being heated at 343 K for 0.5–1 hours. This leads the grafted co-polymerization of the monomer molecules and unsaturated resin to the molecules of epoxy product. Such epoxy-oligoester compositions exhibit good adhesion properties to metals and are recommended as protective coatings. Thus, on the basis of the literature analysis we can conclude that the issue of creation of epoxy-oligoester compositions is given a great attention. This is caused primarily due to cheaper epoxy resin materials, the approachability of oligoesters and the possibility to improve the working properties of epoxy-based materials.

### **Purpose of the research**

The formation of spatially-crosslinked films based on mentioned polymers can occurs both during heating and at room temperature. However, in order to ensure that the coatings are resistant to aggressive media, it is necessary to use multi-component systems containing maleic anhydride, styrene, hydroperoxide, accelerator of hydroperoxide decomposition, etc. [11, 12, 13]. In this regard, the purpose of presented research was to develop low-component epoxy-oligoesters compositions with a crosslinked structure in the presence of modified ED-20P epoxy resin and to create a coating of high anticorrosive properties on its basis.

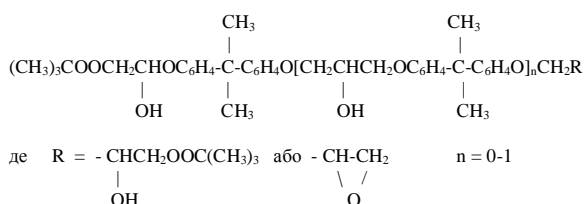
To achieve the above it was necessary:

– to develop the methods for the forming of epoxy-oligoesters compositions based on industrial ED-20 epoxy resin, ED-20P peroxide resin and MGPh-9 oligoesteracrylate at the room temperature and during heating;

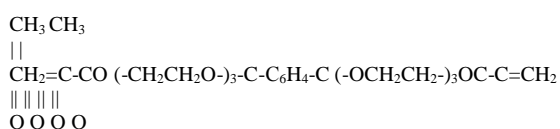
– to study the influence of various factors on gel fraction content, hardness and other characteristics in epoxy-oligoester compositions.

### Materials and methods of research

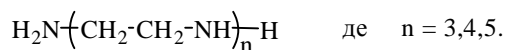
It is proposed to obtain spatially-crosslinked epoxy-oligoesters in the presence of modified with hydroperoxide tert-butyl epoxy resin (ED-20P resin) by the formula:



Modified ED-20P resin was obtained following the method of work [10]. Offered material is a viscous product of light brown color with a molecular weight of 480, an active oxygen of 2.1 % and an epoxy number of 5.0 %. As the initial epoxy resin the industrial resin marked ED-20 of 390 molecular weight and an epoxy number of 20.1 % was applied. The unsaturated oligoester component of the polymer blend was  $\alpha$ ,  $\omega$ -methacryl- (bis-triethylene glycol) phthalate (MGPh-9 oligoester) of the molecular weight 540 with the next formula:



The hardener of epoxy-oligoester blends was polyethylenepolyamine (PEPA), whose general formula is:



The compositions were prepared by mixing components at the room temperature or by heating up to 313 K for 15–20 min with the subsequent adding of PEPA hardener to a homogeneous blend. The blends were covered by pouring on standard glass or metal plates pre-degreased with acetone and were conducted the hardening for the compositions initially at room temperature for 24 hours and then heated to 373 K for 15–75 minutes.

Control over structural changes was carried out by determining the film hardness applying the M-3 device at the room temperature, as well as by determining the gel fraction of the grinded samples in the Soxhlet apparatus via acetone extraction for 10–12 hours. For comparison the compositions which did not contain ED-20P resins were studied.

### Results and Discussion

The MGPh-9 oligoesteracrylate molecule contains finite acrylate groups that are able to react in three-dimensional polymerization. During the research the influence of MGPh-9 oligomer as well as an amount of ED-20 and ED-20P resins on the gel fraction content in the compositions and the hardness of the obtained films were studied. Composition content of the based on MGPh-9 is shown in Table.

Content of epoxy-oligoester compositions

Component	Component content, mass fractions							
	K1	K2	I	II	III	IV	V	VI
ED-20	100	100	85	70	50	70	70	70
ED-20P	–	–	15	30	50	30	30	30
MGPh-9	16	8	16	16	16	6	8	12

Note: PEPA content in all compositions made up 14 mass fractions.

The results of the research in Fig. 1 and Fig. 2 indicate that the content of the gel fraction in compositions and the hardness of obtained polymer films depends on amount of modified ED-20P resin, ED-20 industrial epoxy resin and MGF-9 oligoester as well as time and glass transition temperature.

At the polymerization of control compositions (comp. K1 and K2) at room temperature for 24 hours the gel fraction content of such blends does not exceed 82 % (Fig. 2a) and depends on MGF-9 oligomer amount in the composition.

An increase in MGPh-9 content from 8 % by mass fractions (comp. K2) up to 16 mass fractions (comp. K1) leads to a reduction of gel fraction to 79 % (Fig. 1, a). At the same time, such an increase in the content of oligoesteracrylate significantly affects the hardness of the films which decreases from 0.45 relative units (Fig. 2, b) to 0.15 rel. unit (Fig. 1, b). This indicates that the MGPh-9 oligomer does not link chemically to the molecules of the spatially-crosslinked with PEPA epoxy resin ED-20.

Studying the effect of ED-20P resin on the gel fraction content in polymer films structured at room temperature it was determined (Fig. 1, 2) that it does not exceed 84 % in the case of composition IV. The film hardness also increases and reaches a maximum value of 0.55 rel. unit for films based on composition VI. The obtained results show that in the compositions containing ED-20P peroxide resin at the room temperature there is additional cross- linking which occurs via radical processes. In such mixtures, due to the reduction of the total amount of epoxy groups the possibility of insoluble products formation by the presence of PEPA decreases.

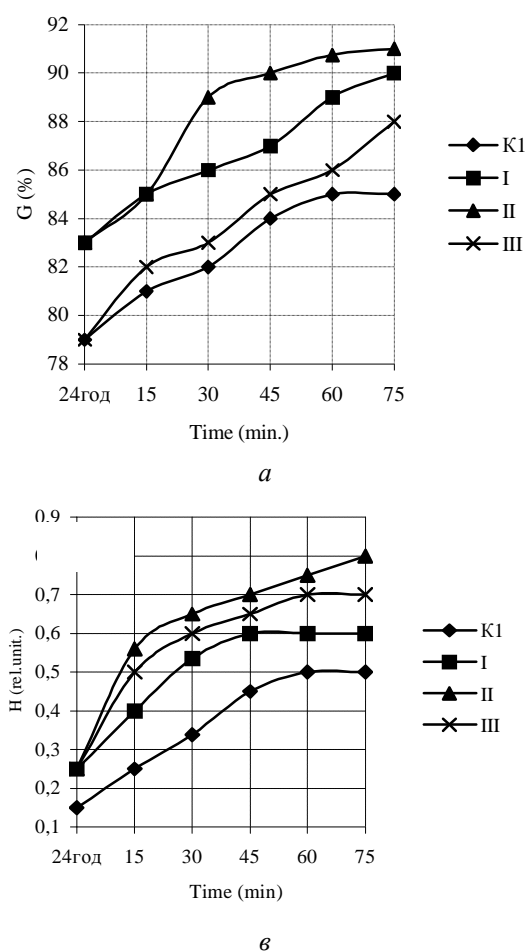


Fig. 1. Dependence of (a) gel fraction content and (b) film's hardness on the number of epoxy components and the time of structuring at 373 K

However, taking into account the presence of PEPA in the system whose molecule contains a tertiary nitrogen atom and which can be formed by interaction of hardener with epoxy groups so at the room temperature a decomposition of -O-O-bonds with partially free radicals formation is being occurred. A small amount of the formed free

radicals leads to polymerisation of the MGPh-9. This ultimately increases the content of the gel fraction and especially the hardness of the films since the molecules of oligoesteracrylate chemically bonds to the molecules of cross-linked epoxy resins.

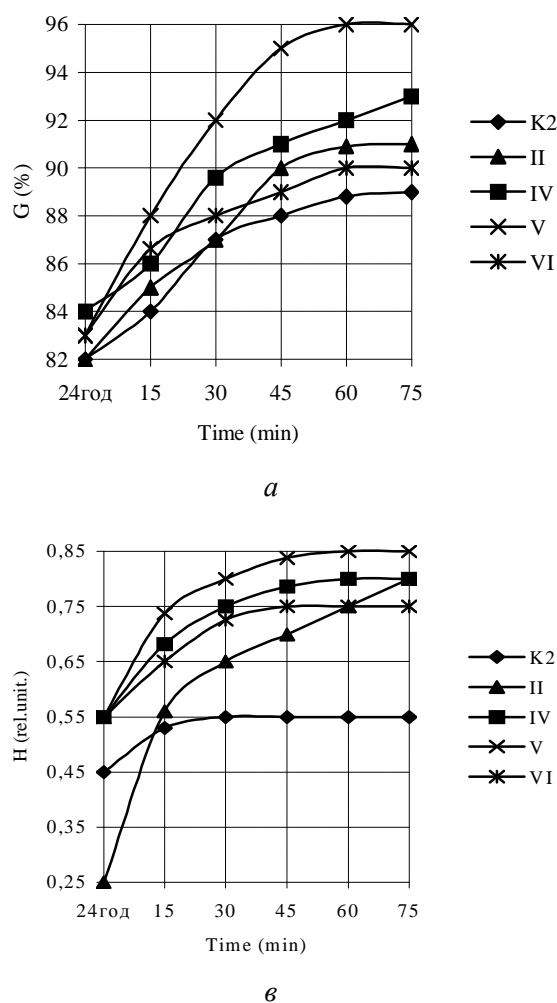


Fig. 2. Dependence of (a) gel fraction content and (b) film's hardness on the TGM-3 oligoester's amount and the time of structuring at 373 K

With temperature rise to 373 K there is an increase in decomposition rate of -O-O-bonds in ED-20P resin (Fig. 1, 2).

However, an increase in the amount of modified ED-20P resin up to 50 mass fractions leads to a decrease in both the gel fraction (Fig. 1, a) and the hardness of films (Fig. 1, b). Above mentioned can be explained by the fact that in such compositions, in combination with the reaction of three-dimensional polymerization of an unsaturated oligoesters initiated by free radicals (formed as a result of the decomposition of peroxide groups in ED-20P) the recombination of oligo-radicals is being

occurred. The recombination of radicals takes place due to viscosity of the system and their sufficiently large amount. This reaction leads to the formation of linear molecules that are soluble in organic solvents and during extraction are being transformed into a sol-fraction. At the same time, the reactions of  $\beta$ -decay may occur that also does not allow obtaining the films of spatially-crosslinked structure. The optimal composition at 373 K is the blend in which the ratio of ED-20P to ED-20 makes 30:70 % by weight. (comp. II). The hardness of films at 373 K during 75 minutes reaches 0.8 rel. unit (Fig. 1B).

Based on the conducted studies considering that ED-20P resin is more expensive than ED-20 one and taking into account obtained results the optimum amount of ED-20P product in epoxy oligoesters compositions is 30 mass fractions of ED-20P to 70 mass fractions of ED-20 resin (Comp. II). The obtained results were used to determine the effect of MGPh-9 oligomer amount on the gel fraction content and the polymer films hardness.

The amount of MGPh-9 in the compositions was 6, 8, 12 and 16 mass fractions (Table 1). The research have shown (Fig. 2) that at 373 K the decrease of content of unsaturated oligoether in the blend up to 8 mass fractions leads to an increase in gel fraction in the compositions and an increase in hardness of films based on epoxy-oligoesters compositions. Therefore, the optimum amount of MGPh-9 oligoester in structuring processes up to 373 K makes 8 mass fractions.

### Conclusions

Consequently, on the basis of the conducted research the influence of epoxy components number and unsaturated oligoester on the structuring process of epoxy-oligoesters blends was studied. The structuring process of such compositions at the room temperature occurs due to the interaction of epoxy groups of ED-20 and ED-20P resins with PEPA molecules. At the same time, in the presence of PEPA a partial decomposition of peroxide groups of ED-20P resin proceeds with the formation of free radicals which cause three-dimensional polymerisation of unsaturated oligoester's molecules. The heating of such blends promotes a complete decomposition of labile

peroxide groups and subsequent polymerization of an unsaturated oligoester which, in contrast to known compositions not containing ED-20P resin is included in the crosslinked structure of the blend which makes it possible to receive epoxy-oligoester films with improved physical, mechanical and chemical properties.

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