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SYNTHESIS MECHANISM AND PROPERTIES OF EPOXY RESINS MODIFIED WITH ADIPIC ACID

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Abstract. The mechanism of diepoxide and adipic acid (AA) reaction in the presence of benzyltriethylammonium chloride and 1,4-diazobicyclo[2,2,2] octane has been proposed. The thermal stability of the oligoester obtained *via* chemical modification of the dioxydiphenylpropane diglycidyl ether with AA and epoxy-oligoesteric mixtures with its participation has been studied. The viscoelastic properties of films based on epoxy-oligoesteric mixtures containing Epidian-5 epoxy resin, TGM-3 oligoesteracrylate, AA modified Epidian-5 and polyethylpolyamine have been determined.

Keywords: epoxy resin, adipic acid, catalyst, reaction mechanism, thermal stability, viscoelastic properties.

1. Introduction

The development of modern material science today is difficult to imagine without creating new materials. When creating new polymer materials, there are two possible approaches. The first one is a method, according to which the high-molecular compounds with desired properties are produced by combining monomers of various nature [1]. In accordance with the second approach, oligomers with functional groups in their structure are synthesized [2]. This makes it possible to use such compounds as binding agents between polymers of different nature to form a product with three-dimensional network [3]. The main requirement for such functional oligomers is the low molecular weight, the ability to be combined with the mixture components, and the presence of functional groups capable to react with the polymer reactive groups in the polymeric mixture.

Modern chemical industry produces a sufficiently large range of oligomers, which are used independently, and may be a binder for the creation of various polymeric products. Epoxy oligomers are of special attention; products based on them are characterized by high adhesion strength, good physico-mechanical characteristics and resistance to aggressive environments [4, 5]. Moreover, epoxy oligomers are able to combine with most polymers, allowing to vary the properties of polymer products; the presence of epoxy groups in their structure makes it possible to modify them by low- and high-molecular compounds [6]. Modification of epoxy oligomers improves their properties and expands the areas of their practical application. Alcohols [5, 7], phenols [5, 8], acids [5, 9, 10], acid anhydrides [11] and others [12, 13]) are among low-molecular compounds for epoxy oligomers modification.

When epoxides are modified with dibasic acids of aliphatic and aromatic types, the products with free epoxy and carboxy groups are obtained [14-16]. The structure of the synthesized oligomers is confirmed by a spectral analysis [17], and they may be used as binders to produce products based on epoxy-oligoesteric mixtures [15]. The catalysts proposed for the reaction between epoxide oligomer and dibasic acid are benzyltriethylammonium chloride (BTEACh), 1,4-diazobicyclo[2,2,2]octane (DABCO), *N*,*N*-dimethylaminopyridine (DMAP), 18-Crown-6, potassium hydroxide (KOH), triethylamine (TEA), zinc chloride ($ZnCl_2$) and a catalytic system consisting of 18-Crown-6 + $ZnCl_2$ [14, 16]. But the reaction mechanism is not described.

So, the aims of the present work are to propose the reaction mechanism of the diane epoxy oligomer with dibasic acid, to study the thermal stability of modified products and to investigate the thermal stability and viscoelastic properties of epoxy-oligomeric mixtures prepared on the basis of the modified products.

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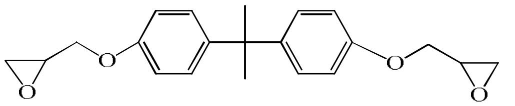
2. Experimental

2.1. Materials

The materials used for the experiments were:

Dioxydiphenylpropane diglycidyl ether (DPPDE) of the formula



with the epoxy groups content (e.n.) of 24.0 %.

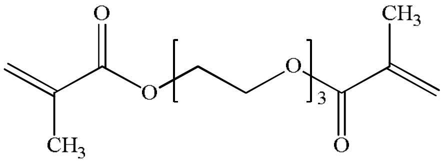
Epoxy resin Epidian-5 (Sarzyna-Ciech, Poland), with a molecular weight M_n of 430 g/mol and e.n. of 20.0 %.

Adipic acid (AA) (purchased from Dupont, USA).

Catalysts benzyltriethylammonium chloride (BTEACh) and 1,4-diazobicyclo[2,2,2]octane (DABCO) purchased from Sigma Aldrich, USA.

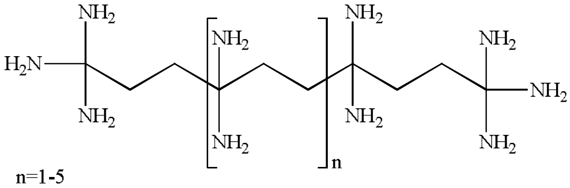
Isopropyl alcohol of chemically pure grade (as a solvent).

TGM-3 oligoesteracrylate of the formula



with M_n 280 g/mol (without additional purification).

Polyethylenepolyamine (PEPA) of the formula



(without additional purification).

2.2. Study of Kinetics

The kinetics of the reaction between DPPDE and AA was studied in a three-necked reactor equipped with a mechanical stirrer, thermometer and backflow condenser using the BTEACh or DABCO catalyst. The reactor was loaded with DPPDE and AA in a solution of isopropyl alcohol. The reaction mixture was heated to a predetermined temperature and a catalyst was added. Samples of 1 ml were taken from the reaction medium and the concentration of carboxyl groups (mol/l) was determined in them according to the formula (1)

$$\left[C_{carb.gr.}\right]=\frac{V_t \cdot N \cdot K}{V_s} \qquad (1)$$

where V_t is the quantity of KOH 0.1N solution spent on titration of acid groups in the sample, ml; V_s is the volume of the sample equal to 1.0 ml; N is a normality of alkaline solution, 0.1N; K is a correction factor of 0.1N solution.

The obtained results were used to plot graphic dependencies, from which the effective rate constants of the reactions between DPPDE and AA were determined.

2.3. Synthesis of Oligoesters

Synthesis of epoxy resins modified with adipic acid (oligoesters) was carried out in a three-necked reactor equipped with a mechanical stirrer, backflow condenser, drop funnel and thermometer. The reactor was loaded with a toluene solution of the epoxy component and BTEACh, dissolved in H_2O. The mixture was heated to 343 K under constant stirring and thermostatically kept for 2.5 h. At the same time the adipic acid dissolved in isopropyl alcohol was dropped from the drop funnel. After the addition of AA, the reaction mass was kept for 0.5–1.0 h under stirring at the above mentioned temperature. After completion of the process, the resulting mixture was cooled to room temperature and transferred to a separating funnel. Benzene was added for clear separation. The lower layer with the catalyst aqueous solution was poured out and the top layer was washed with water. The organic layer was vaccumized at 323 K till the mass became constant. In the synthesized oligoester the molecular weight and the content of epoxy and carboxy groups were determined.

Oligoester I was synthesized using 90 g of DPPDE dissolved in 300 ml of toluene, 17.1 g of BTEACh dissolved in 15 ml of H_2O and 36.6 g of AA dissolved in 300 ml of isopropyl alcohol. 107.7 g of the resulted product were obtained. Found: M_n 450 g/mol, content of carboxy and epoxy groups 8.8 and 8.1 %, respectively.

Oligoester II was synthesized using 90 g of Epidian-5 epoxy resin dissolved in 300 ml of toluene, 14.4 g of BTEACh, dissolved in 15 ml of H_2O, and 30.8 g of AA dissolved in 230 ml of isopropyl alcohol. 112.0 g of the resulted product were obtained. Found: M_n 570 g/mol, content of carboxy and epoxy groups 7.9 and 7.8 %, respectively.

2.4. Preparation of Epoxy-Oligoesteric Films

Epoxy-oligoesteric films were prepared by applying a mixture over the standard glass plates. The mixture was prepared as a result of all components mechanical mixing with PEPA hardener. Films were formed stepwise: at first at room temperature for 24 h, and then at 423 K for 75 min.

2.5. Thermal Stability

Thermal stability was studied using Thermogravimetric Analyzer TGA-7 in an atmosphere of nitrogen or air with O_2 content of 8 %. The samples were heated to 973–1173 K for 45 min [18].

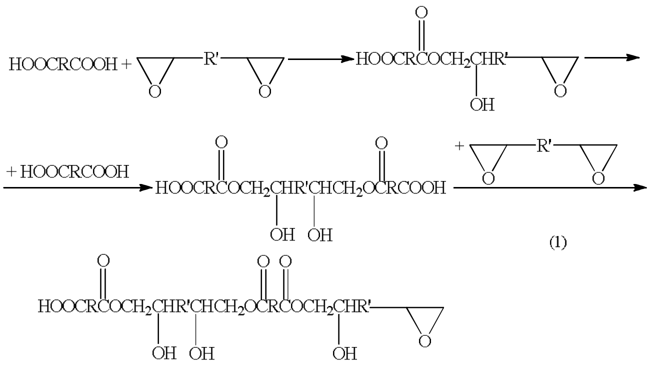
2.6. Viscoelastic Properties

The viscoelastic properties were determined using CSM Instrument Micro Combi Tester at room temperature. Film thickness was 3 mm.

3. Results and Discussion

3.1. The Mechanism of Reaction between the Epoxy Compound and AA

Bashta *et al.* [16] described some kinetic regularities of the epoxy oligomer reaction with dibasic carboxylic acids. It was established [16] that both BTEACh and DABCO may be the catalysts for this reaction. On the other hand, Paken [5] showed that acids themselves can act as a catalyst. So, the reaction between epoxy oligomer and dicarboxylic acid may proceed according to Scheme 1:



where R is the structural fragment of adipic acid; R' is a structural fragment of epoxy oligomer

Scheme 1

It was shown [16] that the reaction does not proceed with 5 mol % of BTEACh per g-eq. of AA carboxyl group at 353 K for 75 min. The increase in the catalyst amount to 10 mol % provides the reaction occurrence with an effective rate constant of $0.48 \pm 0.13 \cdot 10^{-4}$ l/mol·s. The amount of 30 mol % of BETAC provides the reaction rate sufficient for the chemical modification of epoxides with the dibasic acid. But Bashta *et al.* [16] used BTEACh as a catalyst in a pure form. Therefore, it was necessary to determine the effect of water on the reaction proceeded according to Scheme 1. For this, the reaction was studied using BTEACh in the form of 20, 40 60% aqueous solution (Fig. 1, Table 1) in the amount of 30 mol % per g-eq. of AA carboxy group.

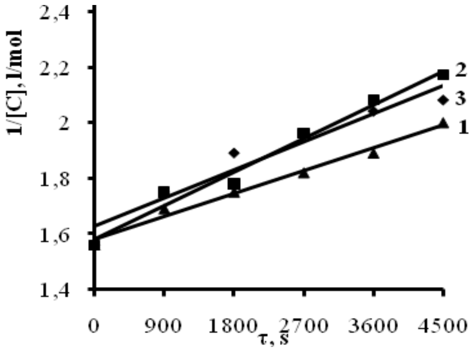


Fig. 1. Kinetic anamorphoses in coordinates $1/[C_{carb.gr.}]$-τ for the reaction of DPPDE with AA at 343 K in isopropyl alcohol medium in the presence of 20% (1), 40% (2) and 60 % (3) aqueous solution of BTEACh catalyst in the amount of 30 mol % per 1 g-eq. of AA carboxy group. The content of AA is 1 mol per 1 g-eq. of DPPDE epoxy group

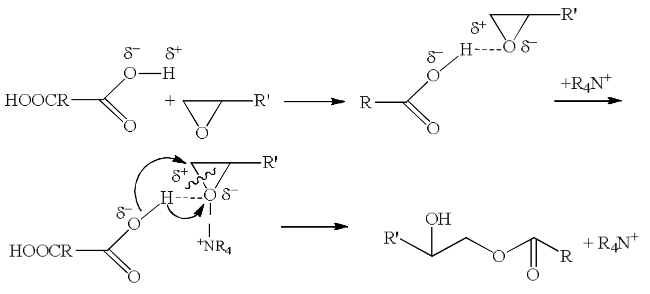
Table 1

Effective rate constants of the reaction between DPPDE and AA

BTEACh concentration in water, %	$K_{ef} \cdot 10^4$, l/(mol·s)	Correlation coefficient, R^2
20	0.90 ± 0.16	0.9859
40	1.10 ± 0.16	0.9795
60	1.00 ± 0.17	0.9353

Notes: reaction temperature 343 K, reaction medium is isopropyl alcohol, BTEACh - amount of 30 mol % per 1 g-eq. of AA carboxy group

Calculated on the basis of Fig. 1, the effective reaction rate constants (Table 1) indicate that water practically does not affect the occurrence of such reaction. Thus, it can be assumed that in the isopropyl alcohol medium, the reaction between dibasic carboxylic acid and the epoxide occurs *via* the formation of the complex (Scheme 2):



Scheme 2

In accordance with the proposed scheme, the reaction of epoxy with AA in the presence of BTEACh as a catalyst takes place in two stages. At the first stage a complex is formed with the participation of epoxy and acid. This stage proceeds fast enough. At the second stage, which is much slower, the formed complex transforms into a reaction product involving the catalyst, which is further recovered in its pure form. According to Scheme 2, the $^+NR_4$ ion catalyzes the reaction of epoxide with acid due to the formation of an equilibrium complex [acid-epoxide-catalyst]. The most probable is the formation of the final product due to the electrophilic cation $^+NR_4$ attack on epoxide by oxygen atom, which has a high electron density.

On the other hand, analyzing the results presented in [16], we find that apart from BTEACh, the catalyst for such a reaction may also be DABCO, but its amount cannot exceed 20 mol % per g-eq. of AA carboxy group. The increase in DABCO amount to 30 mol % and higher leads to the polymerization of the reaction products and their precipitation from the reaction medium. In this connection, it was assumed that DABCO, on the one hand, proves itself as a reaction catalyst (Scheme 1), and, on the other hand, serves as a catalyst for the polymerization reaction of epoxide with epoxy groups. In order to verify the possibility of a polymerization reaction proceeding in the presence of such catalyst, we studied the reaction involving DPPDE and DABCO in the absence of acid (Fig. 2).

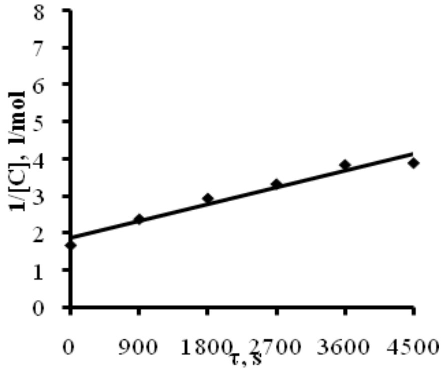
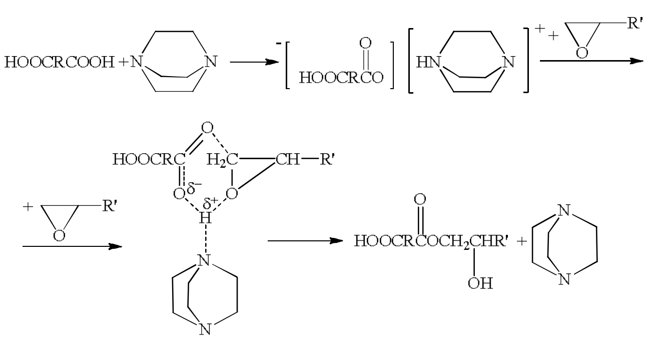


Fig. 2. Kinetic anamorphoses in coordinates $1/[C_{carb.gr.}]$-τ for the reaction of DPPDE with DABCO at 343 K in isopropyl alcohol medium. The amount of DABCO is 20 mol % per 1 g-eq. of DPPDE epoxy group

It is observed (Fig. 2) that the concentration of epoxy groups decreases already at 323 K, which may indicate their exhaustion as a result of polymerization. However, the results given in [16] show that with a small amount of DABCO (up to 20 mol %) there is a decrease in the concentration of carboxy groups in the reaction medium. Therefore, it can be concluded that such a catalyst can catalyze the reaction of epoxide with acid according to the following mechanism:



Scheme 3

In accordance with Scheme 3, the acid and DABCO form salt, which further forms an intermediate six-member transition complex in the presence of an epoxide. During complex decomposition a catalyst is released and the resulted product is formed. In addition, DABCO (as a basic type catalyst) causes polymerization of the epoxide by epoxy groups. So, with a sufficiently large amount of the catalyst (30 mol % and more), two parallel reactions can occur, *i.e.*, the actual formation of the oligoesters and polymerization of the epoxide with the formation of a high-molecular compound, which is insoluble in isopropyl alcohol, and therefore precipitates from the reaction medium.

3.2. Thermal Stability

3.2.1. Thermal stability of oligoesters

Thermal stability of the synthesized oligoesters was studied to evaluate their possible use in various polymer mixtures. Oligoester **I** was used for the study. The procedure is described in Subsection 2.5. The result is shown in Fig. 3.

The product begins to decompose slowly only at 433 K. The rapid change in a mass loss takes place in the temperature range of 633–773 K and achieves 78 % at 773 K. Then there is a slight loss of mass and at 950 K it reaches 88 %. This allows to predicate that oligoester **I** is a sufficiently stable product up to 633 K.

3.2.2. Thermal stability of the films

The literature data [15, 19] describe the possibility of using oligomers with functional groups based on epoxy resins as active additives during products formation. Such products are used as protective coatings for various solid materials, in particular metal, glass, *etc.*, and are resistant to atmospheric and environmental conditions. But in some cases, such coatings are exposed to high temperatures and it is important to know their thermal stability.

Thermal stability of the films based on the synthesized oligoesters was studied according to the method described in Subsection 2.5. Mixtures containing Epidian-5 epoxy resin, oligoester I and TGM-3 oligoesteracrylate were prepared. Polyethylenepolyamine (PEPA) served as a hardening agent. The composition of epoxy-oligoesteric mixtures is given in Table 2.

Films were formed according to the procedure described in Subsection 2.4. The results are represented in Fig. 4 and their interpretation – in Table 3.

Table 3 shows that all investigated films are characterized by practically the same beginning of mass loss. At the same time, films containing synthesized oligoester I have a slightly higher end of the first stage of mass loss. The addition of TGM-3 oligoesteracrylate in the case of using Epidian-5 alone leads to the increase in the decomposition temperature of such films (mixture II), and in the case of oligoester I presence – to the decrease in the mass loss temperature at the first stage (mixture IV). The complete decomposition of the films takes place at the temperature of 873 K and above.

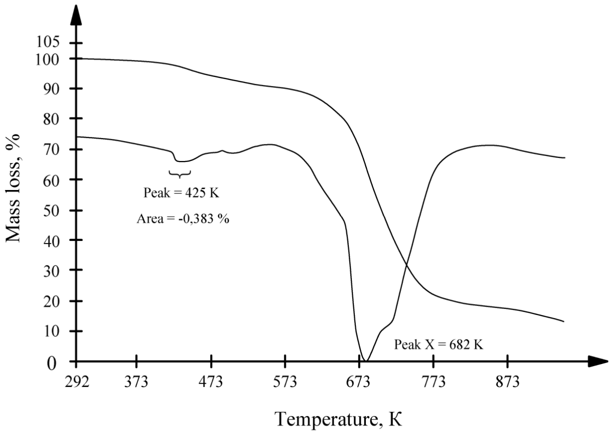
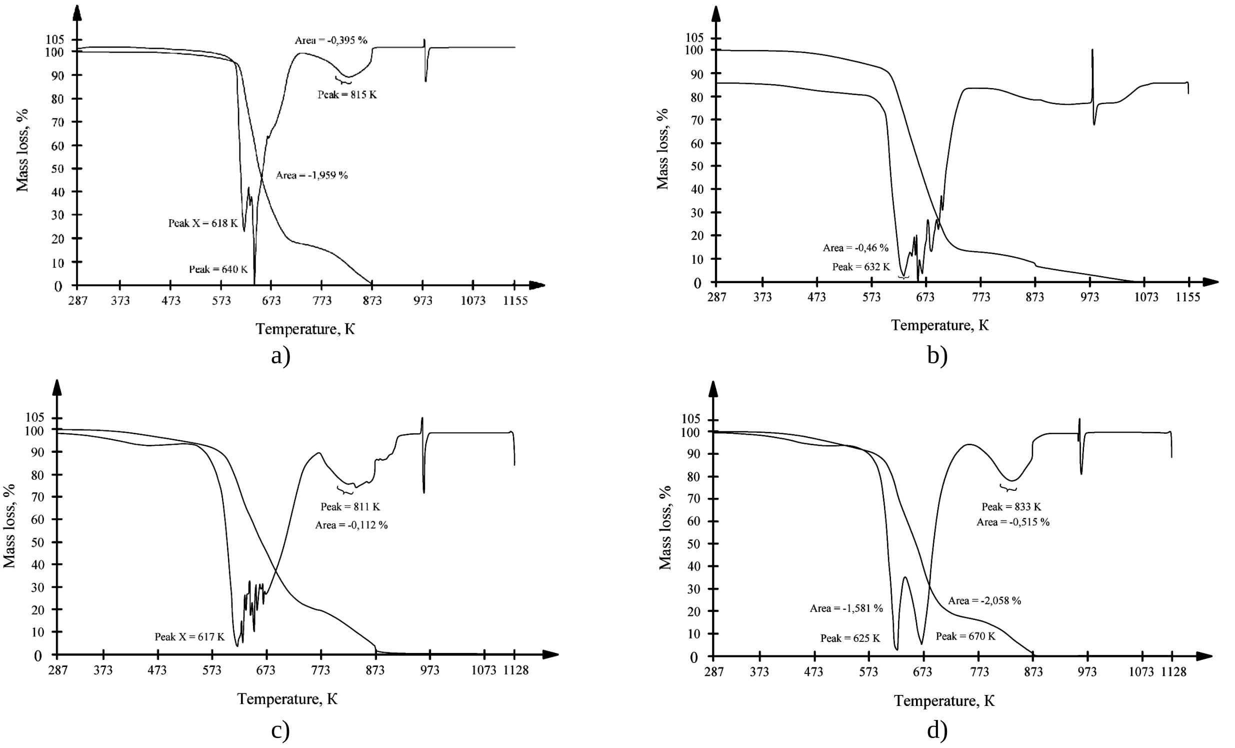


Fig. 3. TGA curves of oligoester I

Table 2

Composition of epoxy-oligoesteric mixtures

Component	Component amount, wt parts					
	I	II	III	IV	V	VI
Epidian-5	100	91	60	55	60	55
Oligoester I	–	–	40	36	–	–
Oligoester II	–	–	–	–	40	36
TGM-3	–	9	–	9	–	9
PEPA	14	14	10.6	9	10	9



a) b)

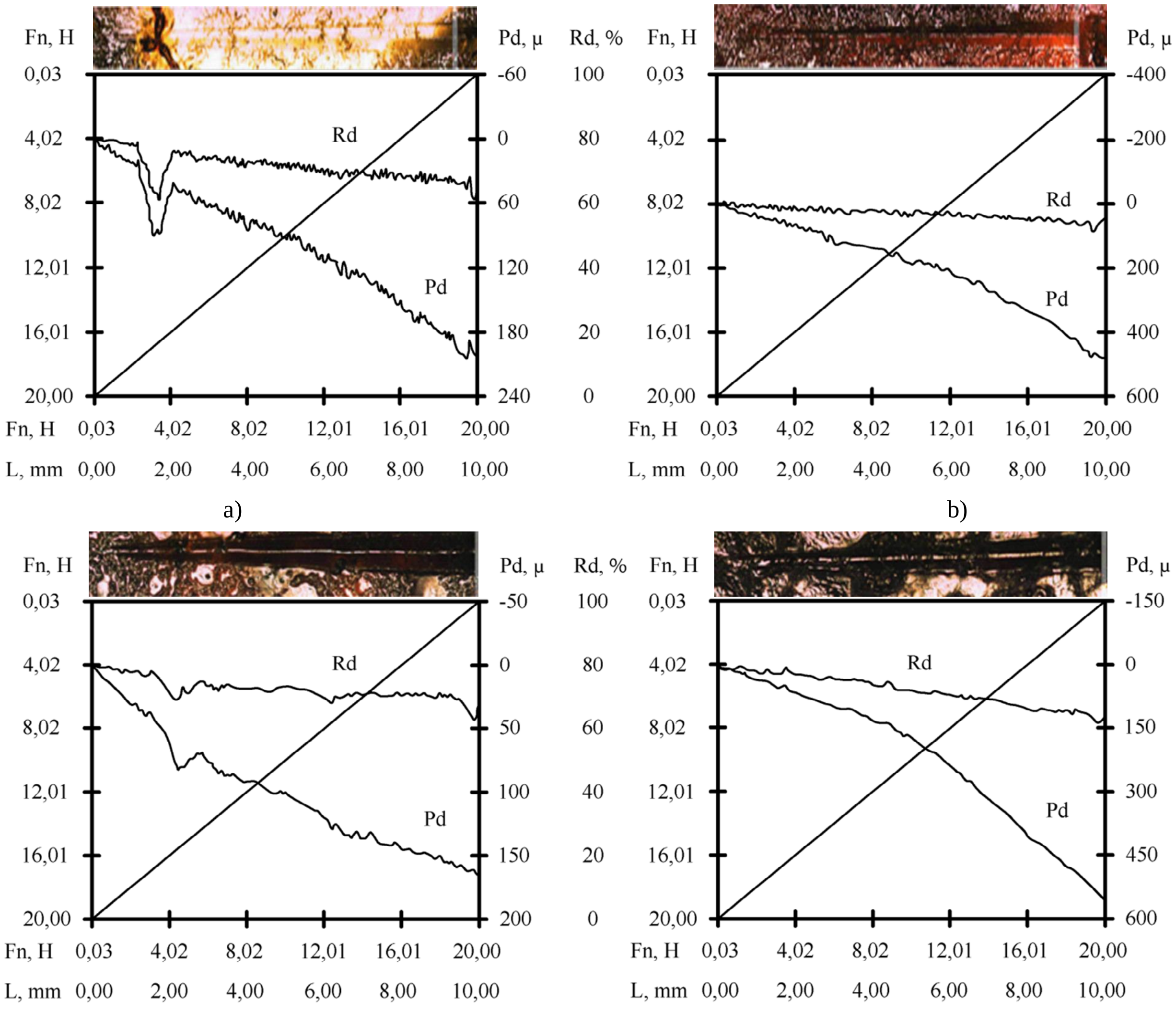
c) d)

Fig. 4. TGA curves of the films based on epoxy-oligoesteric mixtures I (a), II (b), III (c) and IV (d). The mixture compositions are given in Table 2

Table 3

Thermal stability of the films

Mixture according to Table 2	Temperature, under which the mass loss is observed, K/mass loss amount, %			
	First stage		Second stage	
	beginning	end	beginning	end
I	603	713/80	713	873/100
II	603	733/85	733	1073/100
III	593	753/80	753	873/100
IV	593	743/83	743	873/100



a) b) c) d)

Fig. 5. Viscoelastic properties of polymer films based on epoxy-oligoesteric mixtures I (a), II (b), V (c) and VI (d)

3.3. The Viscoelastic Properties of Epoxy-Oligoesteric Films

To study the viscoelastic properties of the films, epoxy-oligoesteric mixtures I, II, V and VI (Table 2) were used. The films were formed according to the method described in section 2.6, and the results obtained are shown in Fig. 5.

The most homogeneous is a film based on mixture VI, containing oligoester II; this film is characterized by the best restorability (Fig. 5d). The films only with Epidian-5 (mixtures I and II) are non-uniform and their surface is rough. All of the films under investigation withstand a full load of 20 N. The film based on mixture I is characterized by a penetration of 200 µm. When introducing TGM-3 oligoesteracrylate (mixture II), the film becomes more elastic and the penetration value reaches 500 µm. The introduction of oligoester II into epoxy-oligoesteric mixture leads to the increase in the film hardness (Fig. 5c), as evidenced by the penetration value equal to 170 µm. The parallel introduction of oligoester II and TGM-3 into the mixture (mixture VI) significantly improves the viscoelastic properties of the coating. Penetration for this film is 590 µm.

The above results indicate that the introduction of the synthesized oligoester II into epoxy-oligoesteric mixture improves the viscoelastic properties of the films based on Epidian-5.

4. Conclusions

On the basis of the conducted researches and taking into account the literature data, a probable mechanism of chemical reaction between DPPDE and AA in the presence of BTEACh or DABKO was proposed. When using BTEACh as a catalyst, the most probable is the formation of the final product due to the electrophilic cation $^{+}NR_4$ attack on epoxide by oxygen atom. DABKO, as the catalyst, and adipic acid form salt, which further forms an intermediate six-member transition complex in the presence of an epoxide. During complex decomposition the catalyst is released and the resulted oligoester is formed.

By means of TGA analysis it was established that oligoester I is a sufficiently stable product up to the temperature of 433 K. Epidian-5 based films with oligoester I in their composition are completely decomposed at 873 K. Films containing oligoester II, in comparison with Epidian-5-based films without oligoester II, are characterized by better homogeneity and restorability; thier penetration was 590 µm.

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МЕХАНІЗМ РЕАКЦІЇ СИНТЕЗУ ТА ВЛАСТИВОСТІ ЕПОКСИДНИХ СМОЛ, МОДИФІКОВАНИХ АДИПІНОВОЮ КИСЛОТОЮ

Анотація. *Запропоновано механізми реакцій між ді-епоксидною сполукою та адипіновою кислотою (АА) в присутності бензилтриетиламоній хлориду та 1,4-діазобіцикло[2,2,2]октану. Вивчено термічну стабільність олігоестеру, отриманого внаслідок хімічного модифікування дигліцидилового етеру діоксидифенілпропану АА та епоксиолігоестерних сумішей за його участі. Визначено в'язкоеластичні властивості плівок на основі епокси-олігоестерних сумішей, які містять у своєму складі епоксидну смолу Epidian-5, олігоестеракрилат ТГМ-3 та поліетилполіамін.*

Ключові слова: *епоксидна смола, адипінова кислота, каталізатор, механізм реакції, термічна стабільність, в'язкоеластичні властивості.*