Synthesis and Use of Polyoxychloropropylen-Epoxymethacrylate Oligoesters as Active Modifier of Epoxy Diane Resin Ed-20

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Abstract— *The synthesis of polyoxychloropropylenepoxymethacrylate oligoesters by esterification of polyoxychloropropylenetriepoxide by methacrylic acid has been carried out. It has been established that by varying the conditions of carrying out of the reaction, one can prepare, mainly, the mono-, di- and trimethacrylic oligoesters. On the basis of epoxy diane ED-20 and synthesized polyoxychloropropylenepoxymethacrylate oligoesters as modifiers there have been prepared the self-extinction compositions, which after curing by N, N^1–diaminodiphenylsulfone possess higher physical-mechanical, adhesion and heat-physical properties.*

Keywords— polyoxychloropropylenetriepoxide, ED-20, diaminodiphenylsulfone, methacrylic acid, epoxymethacrylate, methacrylate oligoesters, self-extinction compositions.

I. INTRODUCTION

The epoxymethacrylates prepared by esterification of epoxy-containing oligomers by methacrylic acid find wide application as the photo- and radiation-sensitive components and also as the modifiers of epoxide resins [1, 2]. Their use as the low-viscous plasticizers and reactive modifiers allows preparing the polymer materials with low residual tension, higher elasticity, high adhesion and impact strength. Most often, the composition containing oligoestermethacrylates as a modifier at structuring are chemically not connected with molecules of epoxy resin [3]. This leads to deterioration of some indices of the prepared polymer materials and first of all – to decrease of stability in the conditions of long exploitation. From this point of view the epoxymethacrylate oligoesters synthesized by esterification of polyoxychloropropylentriepoxide (1) by methacrylic acid are of interest. An availability of chlorine atom in composition of these compounds allows their use as antipyrenes and an availability of epoxide groups along with methacrylate fragments leads to the chemical binding with modifying epoxide resin during curing of the prepared mixture with curing agents of amine type.

II. EXPERIMENTAL

Polyoxychloropropylenetriglycidyl ester (I) has been synthesized on methodology given in [4, 5].

2.1 Interaction of polyoxychloropropylenetriglycidyl ester with methacrylic acid

a**)** 0,05 mol of polyoxychloropropylenetriglycidyl ester, 0.15 mol % of pyridine (from total quantity of reagents), 50 ml of toluene were placed in three-necked flask equipped with mechanical mixer, thermometer, reflux condenser and dropping funnel and were added on dropwise 0.0125 mol of freshly distilled methacrylic acid dissolved in 20 mi of toluene. The reaction temperature spontaneously raised to 313 K. Then for 3,5 h the reaction temperature was raised to 343 K. After completion the reaction mass was washed with water to neutral medium and extracted by toluene. After drying over Na_2SO_4 distillation of solvent the prepared product was separated by column chromatography (Al_2O_3, solvent – hexane-ethylacetate 40:1). Two fractions have been isolated, the first fraction – 5.7 g (83.8%), n_D^{20} =1.4790. Found, % : C 47.65, H 6.14, Cl 16.69, $C_{25}H_{41}O_{11}Cl_3$(II). Calculated, % C 48.09, H 6.57, Cl 17.07. The second fraction: 0.81 g (11.9%), n_D^{20} = 1.4730. Found, % : C 48.72, H 6.91, Cl 14.75. $C_{29}H_{47}O_{13}Cl_3$ (III). Calculated, % C 49.04, H 6.62,Cl 15.01.

b**)** Similarly to method (a) 0.05 of polyoxychloropropylenetriglycidyl ester, 0.025 mol of methacrylic acid, 30 ml of toluene and 0.0125 mol. % (from total quantity of reagents) of pyridine was heated at 365 K for 5h. On completion of the reaction the products were separated by column chromatography. Two fractions have been isolated: the first of them is completely identical to product III prepared on method (a), a yield is 15.4 g (86.8%), n_D^{20} =1.4790. Found, %: C 48.61, H 6.17, Cl 14.70, $C_{29}H_{47}O_{13}Cl_3$ (III). Calculated, % C 49.04, H 6.62, Cl 15.01. The second fraction: 3.6 g (8.9%), n_D^{20} =1.4685. Found, % : C 49.34, H 6.26, Cl 12.87. $C_{33}H_{53}O_{15}Cl_3$ (IV). Calculated, % C 49.78, H 6.66, Cl 13.38.

c) 0.15 mol of methacrylic acid was added to solution of 0.05 mol of polyoxychloropropylenetriglycidyl ester in 50 ml of toluene, 0.0125 mol % (from total quantity of reagents) of pyridine and was heated at 365 K for 5 h. On completion of the reaction products were separated by column chromatography. The isolated product (37.5 g, 94.2%) on physical-mechanical indices coincides completely with compound IV prepared on methodology (b).

d) The compositions were made by intensive mixing the calculated quantities of ED-20 and modifier to complete homogeneity on water bath (363-373 K) and then the curing agent (DADPhS) was introduced to the system. After complete dissolution of components, the composition was degased under vacuum and poured in fluoroplastic forms necessary for preparation of the samples in accordance with intended tests. The compositions after keeping at room temperature for 24 h was subjected to thermocuring. Curing mode: at 393 K – 3 h, at 423 K – 3 h, at 483 K – 5 h. A degree of curing of the compositions was estimated by extraction of their crushed samples by acetone in Soxhlet apparatus for 8-10 h. In the tested samples a degree of curing was no less 96-98%. In the identical conditions there have been made the compositions ED-20 / DADPhS for comparison.

The test of the samples was carried out on tensile testing machine of pendulum type FMPW-500 with movement rate of the lower clamp 30 mm/min. The average-arithmetical values of five measurements have been taken as the results of the tests.

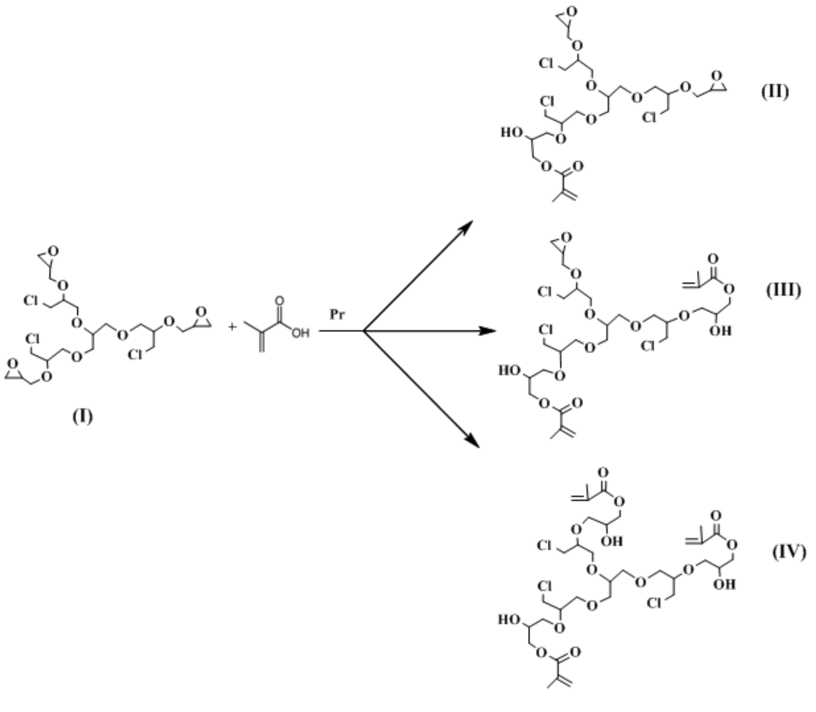
e**)** The curing reaction of composition has been studied by a method of thermal analysis on derivatograph of system “Paulik-Paulik-Erdei”. Weighting of the studied sample – 200 mg, sensitivity of the channels TGA-200 and sensitivity of galvanometer DTA-250 μν and DTG-1 μν, temperature rise rate – 5 deg./min. in air current.

f) The thermooxidative destruction of the cured epoxide compositions was also studied by derivatographic method on derivatograph of system “Paulik-Paulik-Erdei” at dynamic regime in air current. Temperature rise rate – 5 deg./min. The sensitivity of the channels TGA-200 μν, galvanometer DTA-250 μν and DT-1 μν. Weighting of the samples – 200 mg. The heat-resistance of the cured samples was determined on Vicat device, load – 5 kg.

g) The IR-spectra of substances in vaseline oil were taken on spectrometer “UR-20”. The NMR^{1}H-spectra were registered on spectrometer “Bruker-300” (300MHz) for solutions in deuterated acetone. Internal standard – HMDS.

III. RESULTS AND DISCUSSION

This work has been devoted to the preparation and investigation of modifying influences of properties of epoxymethacrylate oligoesters on the basis of polyoxychloropropylenetriepoxide compound (I) synthesized on method described in [4-7]. The esterification of polyoxychloropropylenetriepoxide oligoester by methacrylic acid was carried out in a medium of toluene in the presence of pyridine (0,15 mol. % from total quantity of reagents).



The reaction course was controlled on consumption of methacrylic acid by a method of acid-base titration (0,1 n. aqueous solution KOH, indicator – bromthymol blue). The results of the carried out experiments showed that a degree of conversion and ratio of the prepared reaction products depend on molar ratio of the initial reagents, temperature and reaction duration. For quantitative estimation and isolation as individual view of the reaction products with the aim of their identification and subsequent analysis it was used the column chromatography on aluminum oxide with use of hexane-ethyleacetate as eluent of mixture (40:1). Under optimal conditions the yields of corresponding epoxymethacrylates are 85-93%.

The structure of the synthesized compounds has been confirmed by the methods of IR- and PMR-spectroscopy. In the IR-spectra of the compounds II-IV there are absorption bands at 1620 cm^{-1}, stipulated by valence vibration of double bond. The absorption bands at 1180 and 724-748 cm^{-1}evidence about availability of C-O-C and C-Cl- bonds, and the band at 1715 cm^{-1} is characteristic for valence vibrations of carbonyl group in ester fragments. The weak bands at 915 cm^{-1} in the IR-spectra of the compounds II, III correspond to vibrations of epoxide ring. An availability of the wide absorption band about 3460 cm^{-1} confirms an appearance of the secondary hydroxyl groups in the compounds II-IV [8].

In the PMR-spectra of the synthesized compounds along with signals of protons of the initial compound (I) there are the signals of methyl group (1.75 ppm), multiplet of protons in double bond (5.2 ppm), the signals of protons of methylene group in ester fragment (4.16 ppm). A group of the signals of small intensity in the field of 2.64-2.73 ppm refers to the signals of residual epoxide groups in the compounds II, III [9].

The synthesized polyoxychloropropylenepoxymethacrylates (II-IV) were used as modifier of the epoxide composition on the basis of ED-20. N, N^1– diaminodiphenylsulfone (DADPhS) was used as a curing agent. It was known that for development of the qualitative epoxide compound it is necessary to choose the optimal quantity of curing agent, modifying addition and to find the optimal regime of curing. The optimal quantity of the compounds (II-IV) used as modifier have been determined experimentally and controlled by mass loss on curves TGA and DTA. The curing reaction proceeds in the field of 353-473K, about which an exopeak of curing on DTA curve evidences.

The obtained results evidence that on DTA curves there are appeared two exopeaks in the temperature interval 393-488 K (Fig.1).

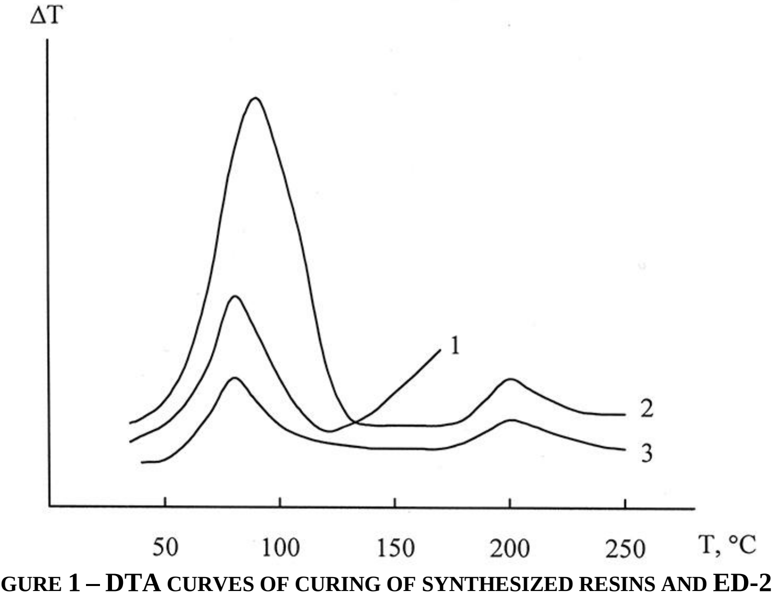


FIGURE 1 – DTA CURVES OF CURING OF SYNTHESIZED RESINS AND ED-20 WITH:
1 – ED-20 EPOXIDE RESIN;
2 – POLYOXYCHLOROPROPYLENEPOXYMETHACRYLATE OLIGOMER;
3 – POLYOXYCHLOROPROPYLENEPOXYMETHACRYLATE.

The obtained experimental data evidence that in the compositions cured at high temperatures the internal defects are formed. In this connection, for realization of curing process at relatively low temperatures an accelerator UP 606/2 2,4,6-tris (dimethylaminomethyl phenol) was introduced in reaction mixture. In these cases, two exopeaks on DTA curves in curing process of the compositions are also observed, and the first of them is displaced to more low temperature field.

It has been established that the observed exopeak at 363 K has been connected with curing with participation of epoxide groups, and the second exopeak at 473 K characterizes a conversion proceeding with participation of double bond of modifying oligomers (interaction with amine of group of curer or its fragment and thermal polymerization). Indeed, during carrying out of curing process of system ED-20 + triglycidyl ester of propantriol + curing agent on DTA curve an exopeak at 473 K is not observed and only one exopeak at 363 K is appeared.

The thermal stability of the prepared compositions was estimated on values of temperature corresponding to 10%, 20% and 50% mass loss of the samples and on activation energy value of decay calculated on TGA curve by a method of double logarithm. The obtained data are presented in Table 1.

TABLE 1
THERMAL CHARACTERISTIC OF CURED EPOXIDE COMPOSITIONS PREPARED WITH USE OF COMPOUNDS II AND III AS A MODIFIER

Composition, mass.p.	T_{10}	T_{20}	T_{50}	Polydecay period, T ½, min.	E of decay kJ/mol
ED-20-100 DADPhS-20 Modif.(II)-10	150	180	290	40	63.52
ED-20-100 DADPhS-20 Modif.(II)-20	180	210	330	48	69.87
ED-20-100 DADPhS-20 Modif.(II)-30	130	170	260	37	60.21
ED-20-100 DADPhS-20 Modif.(III)-10	180	200	300	35	95.8
ED-20-100 DADPhS-20 Modif.(III)-20	210	225	350	55	115.82
ED-20-100 DADPhS-20 Modif.(III)-30	120	180	280	40	65.4

As is seen from results presented in Table the optimal quantity of modifier is 20 mass p. per 100 mass p. of epoxy diane resin, at such ratio of components the best thermal stability of cured composition material is reached. It should be noted that the modification of epoxide resin by compound (III) leads to a formation of more thermostable materials, which has been apparently connected with availability of two epoxide groups in one molecule of the compound III and as a result with formation of more thick-cross-linked structure in the curing process.

The dependence of some physical-mechanical indices of epoxide compounds modified (II-IV) is presented in Table 2.

As is seen from obtained data, the physical-mechanical properties of the cured epoxide compositions with participation of modifiers II-IV are essentially higher than such ones for compositions ED-20:curer. An increase of a quantity of modifier in all samples of the compositions to 30 mass p. although leads to essential increase of deformation properties, however the strength properties of the compositions reach maximum at content 20 mass p. of modifier. A heat-resistance of modified compositions is considerably higher than in unmodified ones, and an availability of chloromethyl groups gives self-extinction to compositions. The results of the experiments evidence about that the modifier containing both hydroxyl and methacrylic groups in its composition immediately influences on formation process of net structure of cured material. As the authors have shown [10], in the polycondensated processes at formation of three-dimensional net and availability of hydroxyl group not only increases a reactivity of oligomers but actively influences on process direction.

TABLE 2

PHYSICAL-MECHANICAL INDICES OF COMPOSITIONS ED-20/MODIFIER (II-III) OF THE VARIOUS COMPOSITION CURED BY DADPHS (ACCELERATOR – UP-606 / 2)

Ratio of ED-20: modifier: curing agent, mass.p.	Ultimate strength (MPa) at			Adhesion to steel, MPa	Relative elongation, %	Vicat heat-resistance, ^{0}C	Burning time of the sample after fire removal, sec.
	tension	flexure	com-pression				
Modifier (II)							
90:10:20	77	142	147	20	3.5	165	17
80:20:20	84	151	161	24	6.3	157	Damps
70:30:20	73	127	143	17	13.4	121	Damps
Modifier (III)							
90:10:20	80	149	156	21	3.4	175	21
80:20:20	90	161	165	26	6.5	163	Damps
70:30:20	78	141	144	17	13.7	125	Damps
Modifier (IV)							
90:10:20	84	154	159	20	3.7	163	21
80:20:20	91	165	164	26	6.5	154	Damps
70:30:20	79	135	147	19	13.8	120	Damps
ED-20: DADPhS 100:20	51±4	121+5	140	14	2.3	119	Burns

Among modifiers II-IV the compound III as a result of the most successful combination of epoxide, hydroxyl and methacrylic groups showed the best and stable results in the compositions with DADPhS.

The improvement of heat-physical, deformation and strength properties of the prepared compositions on the basis of ED-20 and modifying oligomers of II-IV has been connected with active participation of epoxide, hydroxyl and double bonds in formation of effective net structure. At the initial stage of curing the epoxide groups of modifier react actively (at 80-90°C on DTA curve an exopeak is appeared), and at the deep stages the double bonds of modifier molecule or their fragments in the composition of macromolecule undergo the reaction with amine group of curing agent or thermal polymerization. As a result more thick-cross-linked structures are formed and the cross-linked areas are basically formed from molecules of modifying oligomer and possess more high elasticity. An availability of such net structure stipulates an improvement of the above-mentioned exploitation indices of the developed composition materials.

Thus, the obtained results evidence about that the compounds II-IV used as modifier-antipyerene partcipate actively in the process of formation of set structure in the epoxide compositions, provide them high physical-mechanical, heat-physical and adhesion indices and give self-extinction to compositions.

IV. CONCLUSIONS

Polyoxychloropropylenepoxymethacrylate oligoesters by esterification of polyoxychloropropylenetriepoxide of methacrylic acid have been synthesized. It has been shown that by varying the conditions of carrying out of the reaction, one can prepare, mainly, the mono-, di- and trimethacrylic oligoesters.

On the basis of epoxy diane ED-20 and synthesized polyoxychloropropylenepoxymethacrylate oligoesters as modifiers there have been prepared the self-extinction compositions, which after curing by N, N^1–diaminodiphenylsulfone possess higher physical-mechanical, adhesion and heat-physical and thermal properties.

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