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EPOXY POLYMERS BASED ON DIGLYCIDYL ETHERS WITH CYCLIC GROUPS

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ABSTRACT

Glycidyl ethers of polycyclic bisphenols of norbornan type and their phenyl substituted derivatives were obtained and studied. They were solidified by diaminodiphenylsulphon and methyltetrahydrophthalic anhydride. The data of the termogravimetric analysis of the obtained polymers showed that they are characterizes by high thermal – and heat stability.

The properties of polymers depend on the structure of the hardener and its chemical nature as well. The properties of polymers were sharply changed when glycidyl derivatives of bisphenols were cured by hardeners of different chemical structure. The presence of cyclic structures in the hardener molecule causes considerable increase of their thermal stability. Polymers on the basis of chlorine substituted glycidyl ethers of polycyclic bisphenols are characterized by incombustibility.

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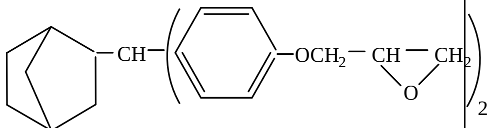
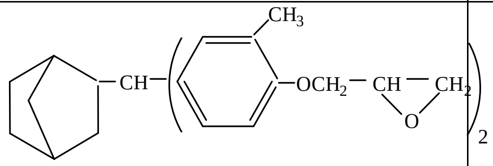
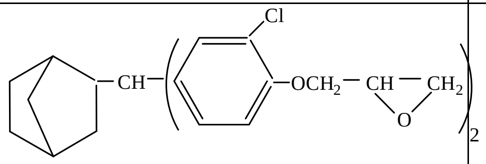
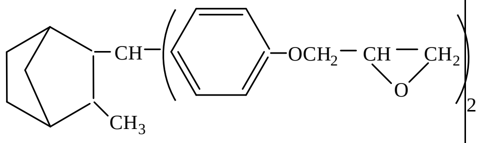
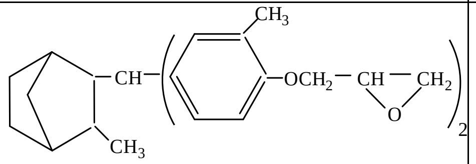
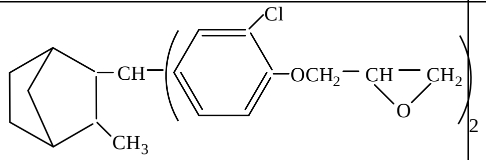
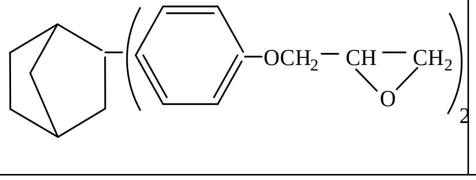
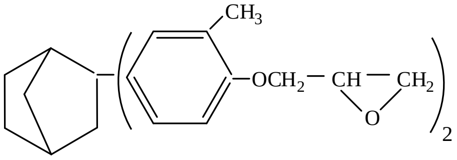
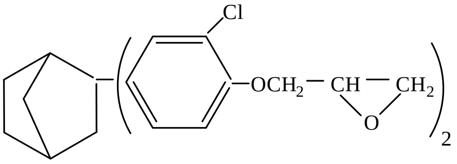
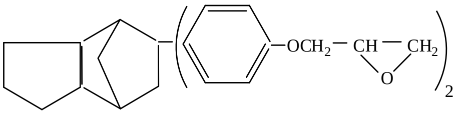
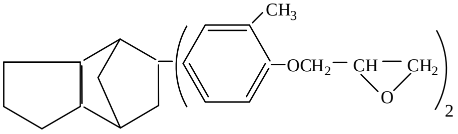
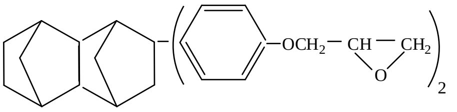
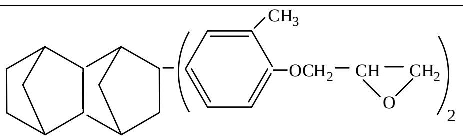
The works (1-6) describe epoxy polymers based on diglycidyl ethers of various bisphenols. Continuing researches in the field of this interesting, practically important class of polymers we considered interesting to synthesize polymers with increased thermal properties. Their presence in diol component of cyclic groups of aromatic as well as alicyclic nature largely determines the properties of structured polymer, contributing to the increase of thermal parameters of polymers. Components containing various cyclic groups were used as hardeners. Table 1 given below offers structural formulas of diglycidyl ethers of various bisphenols. The impact of structure of cyclic groups, as well as bisphenol groups substituted in phenyl nuclei on the properties of polymers were studied. Since the thermal and heat resistance of polymers, in addition of chemical structure of bisphenols depend also on the structure of the used hardener, to improve thermal parameters of polymers, both heat resistance and thermal resistance we used hardeners of various chemical nature. In the synthesized by us diglycidyl ethers, six of them were used for the first time. According to the external view, they are transparent products of the light yellow color, are well soluble in aromatic hydrocarbons, alcohols, ketones and other organic solvents. Diglycidyl ethers were cured with amine and anhydride hardeners. Methyltetrahydrophthaleic anhydride and 4,4^1-diamino diphenylesulfone were used as hardeners.

Table 1. Characteristics of glycidyl ethers

	Structure of glycidyl ether	Softening temperature, °C	concentration of epoxy groups, %		Molecular mass	
			computed	found	theoretical	determined by ebulioscopy
1	2	3	4	5	6	7
1		61	21.23	19.00	405	424
2		69	20.04	18.86	429	406
3		57	18.14	17.41	474	502
4		71	20.62	20.02	419	422
5		75	19.23	18.6	449	505
6		50	17.58	17.01	448	560
7		55	21.9	17.0	392	480

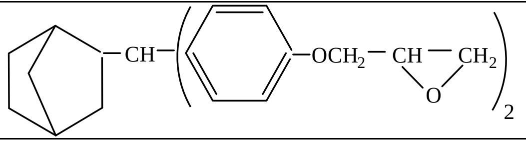
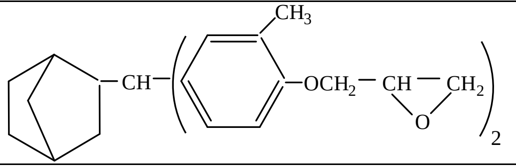
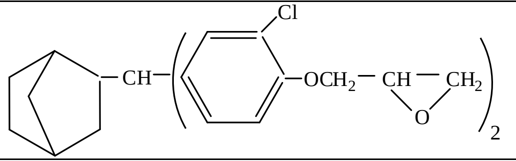
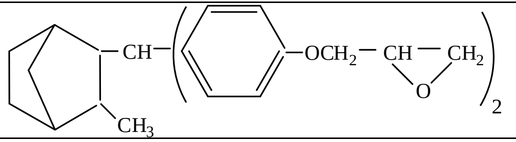
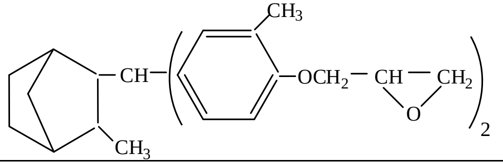
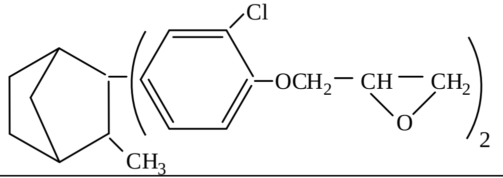
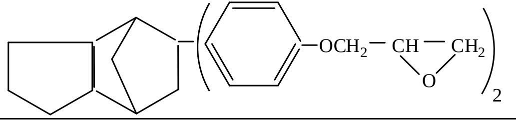
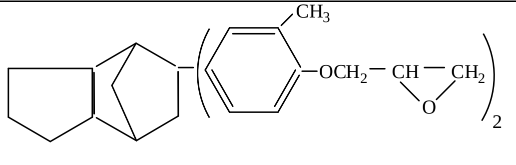
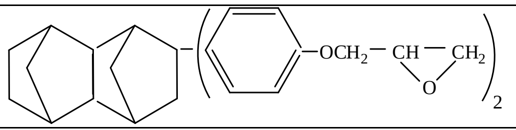
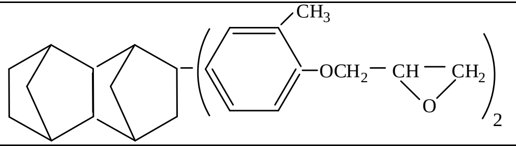
Continuation of table 1.

1	2	3	4	5	6	7
8		75	20.4	17.5	420	505
9		45	18.6	18.1	561	420
10		65	19.9	15.1	432	612
11		65	18.6	17.4	460	472
12		83	18.7	14.0	458	508
13		75	17.9	15.3	486	530

When curing with anhydride, 0.85 mol of anhydride was taken per mol of glycidyl ether. When cured with a diamine 10-15 weight percent of the diamine was taken. Introduction of an accelerator, when we used anhydride (0.1 mass part of triethylamine per 10 weight parts of glycidyl ether) significantly accelerates the curing process and improves the properties of the obtained products.

Glycidyl ether heated to its softening temperature is placed in polymerization glass and a hardener is added. The mixture is thoroughly mixed until a homogeneous mass is formed and it is placed in heating cabinet. Curing is carried out at the following temperature regime: 120° - 2 hours, 140° – 2 hours, 160° – 2 hours, 180° – 2 hours, 200°C – 10 hours. The degree of curing is determined according to the content of the polymer after its extraction with acetone. The properties of the obtained polymers are given in Table 2. Figure 1-2 shows thermo mechanical curves and thermograms of some polymers. Thermo- mechanical and thermo-gravimetric analysis of polymers showed that epoxy polymers based on bisphenol diglycidyl ethers with cyclic groups are characterized by high thermal and heat resistance of the cured polymers. The structure of the cyclic group exerts no significant influence on the thermal and heat resistance of the cured polymers. However, the presence of substituting agents in ortho-position at the phenyl hydroxide in bisphenol affects these parameters. They are somewhat lower for polymers obtained on the base of alkyl- and halogen-substituted bisphenols.

Table 2. Properties of structured polymers based on bisphenol glycidyl ethers and their alkyl- and halogen –substituted derivatives *).

	Structure of glycidyl ether	Deformation by 10%		Temperature of weight reduction by 10%, °C**)	
		A	B	A	B
1		145	155	275	270
2		140	152	260	240
3		138	140	266	260
4		145	152	253	260
5		155	160	280	310
6		200	210	290	280
7		170	195	260	260
8		225	200	300	330
9		160	195	290	300
10		175	190	300	310

*) Hardener A – methyltetrahydrophthalic anhydride, B – diaminodiphenyl sulphon diaminodiphenylsulphon

**) The mass reduction temperature was determined from the thermogravimetric curve at a temperature rise rate of 465°C.min.

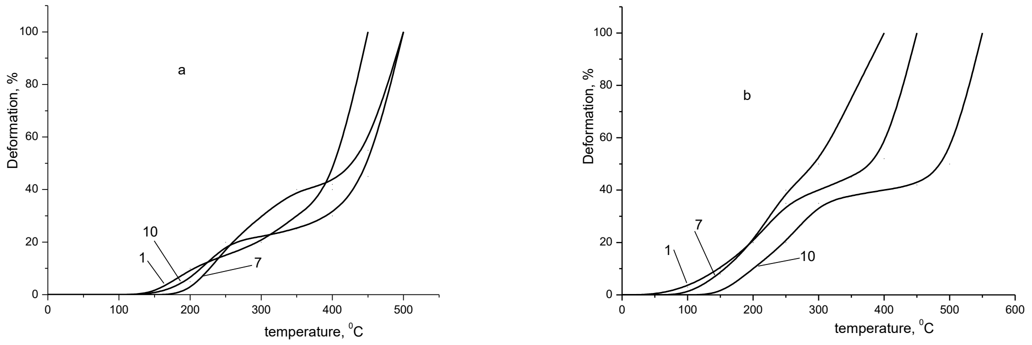


Fig.1. Thermomechanical curves of epoxy polymers: a) hardener – diaminodiphenylsulphon, b) hardener –methyltetrahydrophthalate anhydride (the numbers on the curve correspond to the polymers in Table 2)

Polymers cured with 4,4^1-diaminodiphenolsulphon, depending on the nature of the group substituted in the phenyl nucleus, are characterized by different heat resistance. So, if the polymer based on substituted bisphenol-4,4^1 –(hexahydro-4,7-methyleneinden-5-ylidene) of diphenol decreases in weight by 10% at 400 °C, the presence at a methyl group in the ortho-position to the phenolic hydroxyl of bisphenol, or presence of chlorine atoms, reduces the temperature of weight reduction by 10%, respectively, up to 325-315 °C.

For a polymer based on non-substituted bisphenol, a decrease in weight by 40% is observed at 435 ^{o} C. While polymers based on methyl and chlorine-substituted bisphenols suffer reduction in weight at 390 and 360 °C.

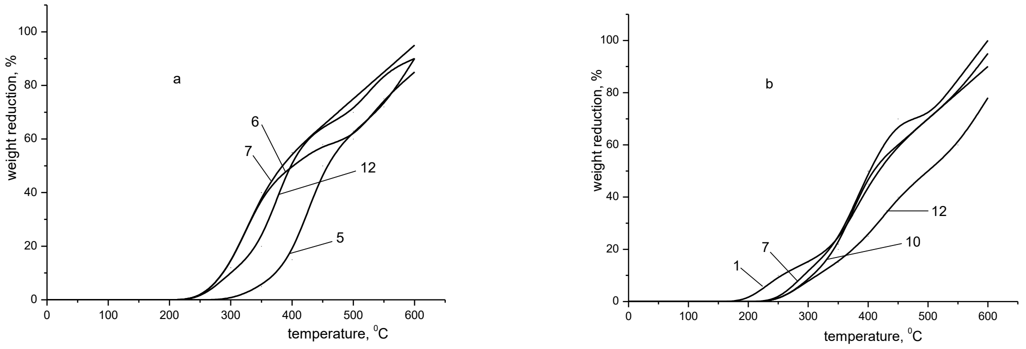


Fig.2. Thermogravimetric curves of epoxy polymers: a) hardener – diaminodiphenylsulphon, b) hardener – methyltetrahydrophthalic anhydride (numbers in curves correspond to polymers of Table 2).

Heat resistance of polymers depends also on chemical nature of the hardener. Polymers cured with diaminodiphenylsulphon are characterized with high thermal resistance than polymers cured with methyltetrahydrophthalic anhydride. Thus, temperature of weight reduction by 10% for a polymer based on bisphenol with indan group that is cured with 4,4 $^{1-}$diaminodiphenyl sulphon equals to 425°C, while for a polymer cured with methyltetrahydrophthalic anhydride it equals to 340°C.

The heat resistance of polymers is also influenced by the structure of the hardener. Thus, when curing diglycidyl derivatives of bisphenols with anhydryl-type hardeners, depending on their chemical structure, the thermal resistance of polymers is significantly different. The presence of cyclic structures in curing agent molecule noticeably increases their thermal resistance compared to the case when the curing agent has an aliphatic structure. So, if a polymer based on bisphenol with an indan group in the molecule, cured with maleic anhydride, suffers decrease in mass by 40% at 380°C, the same polymer cured with methyltetrahydrophthalic anhydride decreases in mass by the same amount already at 460°C, that is, at 80°C higher. A similar trend is observed in the cases of other bisphenols.

Above 600°C all polymers decompose without the formation of coke residue, which is generally typical for other types of polymers based on bisphenols with groups of the norbornane type

As seen from Fig.1 a and b, cured epoxy polymers based on bisphenols with norbornane type groups have a rather high heat resistance compared to conventional epoxy polymers based on dian and other bisphenols. Thus the glass transition temperature (deformation by 5%) of an epoxy polymer cured with an amine-type hardener is 235°C (Fig,1a, curve 10), while the glass transition temperature of epoxy polymers based on dioxydiphenyl propane, dioxydiphenyldimethyl methane, phenolphthalein and other bisphenols cured by the same hardener is much lower (80, 103, 100 and 120°C, respectively).

The volume of the cyclic grouping does not significantly affect the glass transition temperature. However, the presence of groups substituted in the phenolic nucleus of bisphenols has an effect. They lower the glass transition temperature of polymers. So, if epoxide polymer based on bisphenol with an indan group, cured with diaminodiphenyl sulphon, is deformed by 10% at 235°C, methyl and chlorine substituted bisphenols of the same bisphenol are deformed by the same amount already at 225 and 190°C, respectively. A similar dependence is observed in the case of other bisphenols (Table 2). Replacing the amine hardener with anhydride does not violate this relationship (Fig. 1b, Table 2).

Polymers based on chlorine-substituted oligomers are characterized by non-inflammability.

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