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**Thioether Glycidyl Resins. VIII.* Products of Condensation
of Bis(-mercaptoethyl)-formal with Epichlorohydrin as a Modifier
of Diglycidyl Ether of Bisphenol-A Resin**

Żywicze tioeteroglicydyłowe. VIII.* Produkt kondensacji bis(β -merkapto)etyloformalu
z epichlorohydryną jako modyfikator żywicy diglicydowej bisfenolu A

INTRODUCTION

Most epoxide resins cured by means of amine aliphatic and aromatic type curatives as well as acid anhydrides are characterized by very useful application properties. However, they are rigid and relatively brittle polymers with high resistance to bending, squeezing, stretching, high elastic modules and simultaneously of very little unit elongation at rupture and slight impact strength. Unfavourable properties are revealed at low temperatures and variable dynamic load.

In so little elastic and very rigid materials, internal stresses are formed and they often cause cracking of epoxide resin products.

Decrease of internal stresses, called elasticizing, can be obtained by external or internal plasticization, chemical modification (adding to the system resin-curative long aliphatic chains ether or thioether compounds), decreasing in this way vitrification temperature (T_g) of the cured composition.

Internal plasticization proved to be more effective. In this case there are used elasticizing compounds, epoxide resin type including long aliphatic fragments in a molecule or curatives with similar units chemically built into the spatial lattice of the cured composition. Among the curatives worth mentioning are diamines of a long aliphatic chain, polyetheramines, polyaminoamides as well as liquid

* For Paper VII see Ref. 9. Patrz [9].

polysulfides [1-9] (thiorubbers including mercaptan groups ($-\text{SH}$) and polysulfides with anhydride terminal units prepared by the addition of maleic anhydride to polysulfide with mercaptan terminal units [4].

Other groups constituted by elasticizing means including long aliphatic chains with epoxide terminal units. The effective representatives of this group are diglycidyl ethers of polyglycols, diglycidyl esters of diacarboxylic acids as well as liquid polysulfides (thiorubbers) terminated with glycidyl groups on both sides. The first attempts at diglycidyl thioether preparation were published by B e n d e r and F a r n h a m [5] in 1956.

Basing on this method, we prepared in our laboratory thioether glycidyl resins by reacting epichlorohydrin in an alkaline medium in the presence of isopropane with aromatic compounds including $-\text{SH}$ or $-\text{CH}_2\text{SH}$ groups in a molecule [6-9], we then undertook investigations on synthesis and main physical-chemical properties of diglycidyl resin from the aliphatic polysulfide of the content of 17% of mercaptan group ($-\text{SH}$) on the ends of the chain prepared according to the patent by D o j k a *et al.* [10].

Some properties of the resin cured chemically or thermally were determined and the compositions of thioether glycidyl resins and commercial resins of diglycidyl ether of bisphenol —A (Epidian-5) were prepared. After curing them with common curatives they were characterized by thermogravimetric, thermomechanical and mechanical studies.

EXPERIMENTAL

REAGENTS

Aliphatic dithiol of the structure $\text{HS}-(\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{S})_n-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2\text{SH}$ where $n=0-1$ and the content of 17% of mercaptan groups was prepared from β , β -dichlorodioxymethane and sodium hydroxide according to the method by D o j k a and co-workers [10].

Small molecular weight epoxide resin diglycidyl ether of bisphenol—A (Epidian-5) was produced by Chemical Plant Sarzyna. Its basic properties are given in Table 1.

Epichlorohydrin (1-chloro-2,3-epoxypropane) boiling at $114-115^\circ\text{C}$, manufactured by Fluka AG, Buchs, methylbicyclo-(2,2,1)-hept-5-ene-dicarboxylic anhydride-NMA (Allied Chemical Dye Corp.), anhydride HY-905 (Ciba-Geigy), and triethylenetetraamine (TETA) were used.

Caution: The above-mentioned mercaptans have a slightly unpleasant smell. In their preparation and handling some care must be taken to prevent dermatitis. This does not refer to the newly obtained resins.

Table 1. Results of studies on properties of uncured DGTEF resin, DGBA resin and their mixtures

Property	Norm of studies	Kind of Composition			
		DGBA	DGTEF	DGBA : DGTEF	
				100 : 10	100 : 50
Viscosity 20°C [cP] 25°C	PN-66/C-89085	39923	139.0	13384	1931
		16112	101.6	6429	1263
Density 20°C [g/cm ³] 25°C	PN-66/C-04004	1.167	1.220	1.173	1.186
		1.165	1.218	1.170	1.188
Epoxy content [val/100g]	PN-74/C-89085	0.512	0.355	0.502	0.458

MEASUREMENT OF PROPERTIES

Spectral Analysis. The infrared (IR) spectra were obtained with a Beckman 42-40 spectrophotometer. ¹H—NMR spectra were carried out with a Tesla BS-487-C apparatus, frequency 80 MHz reference, TMS; solvent, CDCl₃; temperature, 25°C.

Thermogravimetric Analysis. Measurement of weight loss was conducted in a MOM derivatograph (Paulik, Paulik and Erdey, Budapest).

Differential Thermal Analysis. Measurement of vitrification temperature was made by the differential registering calorimeter produced by Perkin-Elmer under the following conditions: weighed amount of the sample was 6 mg, heating rate 32 K/min, apparatus sensitivity 4 m·cal/s, nitrogen flow 30 ml/min.

Mechanical Analysis. The analysis was conducted in a resistance machine 1231-U-10 produced in the Soviet Union.

Epoxy Content. Epoxy content was expressed in epoxy gram-equivalent content in 100 g (val/100 g) of resin and determined according to the Polish Norm PN-69/C-8905 by HCl solution in dioxane.

RESIN SYNTHESIS

Into a four-necked flask of 1 l volume, equipped with a mechanical stirrer, reflux condenser, thermometer, and dropper, 200 g of dithiol [bis(β-mercaptoethyl)-formal], 160 g of epichlorohydrin 200 g of isopropanol were placed. The

mixture was heated in the water bath to 60°C. Then the first portion 20 ml of 20% solution of sodium hydroxide as an addition catalyst was dropped in very carefully not to exceed 75°C. After 10 min when the temperature of the mixture began to decrease, another portion of 335 ml 20% aqueous solution of NaOH was added for 5 min and stirred for another 20 min.

The organic layer was separated in a distributor, the solvent and excess of epichlorohydrin were distilled under reduced pressure (12 Torr). The remains of epichlorohydrin were distilled azeotropically under reduced pressure adding 2×20 ml of toluene into resin.

The reaction product after filtration was subjected to common physical-chemical analysis and the results are presented in Table 1. The yield of the reaction was 260 g.

RESULTS AND DISCUSSION

The chemical structure of DGTEF resin of the epoxide content 0.36 val/100 g and viscosity 102 cP at 25°C (Fig. 1) were determined from the analytical and spectral data. Elemental analysis showed the presence of 43.23% C, 6.98% H and 28.97% S.

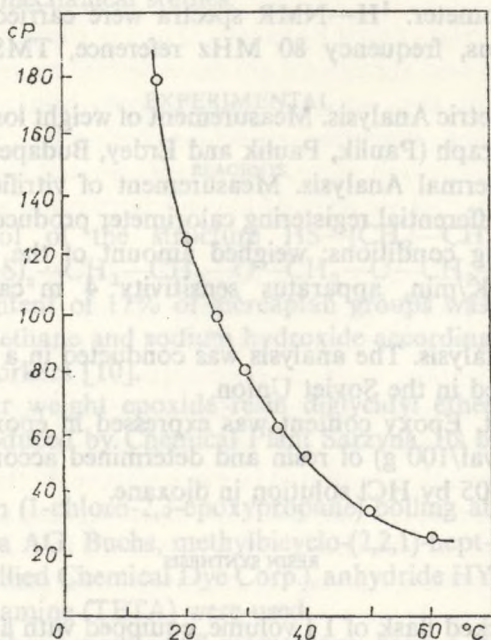


Fig. 1. Viscosity of DGTEF resin in relation to temperature

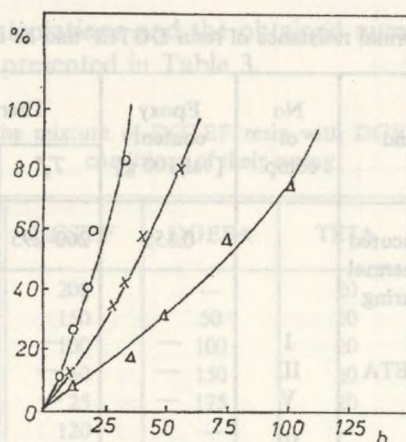


Fig. 2. Loss [%] of epoxy groups of DGTEF resin in relation to heating time [h] at 80°C (Δ), 90°C (×), and 100°C (○)

IR spectra of the resin showed strong absorptions at 1,290, 925 and 840 cm^{-1} which are characteristic of the epoxy group.

^1H -NMR spectroscopic studies of the resin show three basic groups of signals. The first signal at $\delta=4.70$ ppm comes from the fragment of $-\text{O}-\text{CH}_2-\text{O}-$ group. The second signal is a quartet at 3.65–3.82 ppm characteristic of $-\text{CH}_2-$ group in the terminal unit $-\text{O}-\text{CH}_2-\text{CH}_2-\text{S}$. The third signal at 2.53–3.25 ppm (multiplet) is common for the glycidyl group and the remaining part of the terminal unit $-\text{O}-\text{CH}_2-\text{CH}_2-\text{S}-$.

Intensity ratios for each band calculated from the integration curve for the first and second signals are in agreement with the number of magnetically nonequivalent protons in a molecule. However, the third signal coming from the glycidyl terminal unit is lowered which points to polysulfide character of the initial product chain.

THERMAL STABILITY

Thermal stability of DGTEF resin was studied by isothermal and dynamic methods and its compositions were cured chemically by the dynamic method. Isothermic studies were carried out controlling epoxy group loss during heating at 80, 90 and 100°C (Fig. 2). Compared with thioether glycidyl resins of aliphatic–aromatic dithiols, DGTEF resin is more reactive and the temperature of the processes affects the rate of thermal curing.

Results of studies of uncured and thermally or chemically cured resin using the dynamic method by means of a thermogravimetric (temperature increase of 10°C/min in air) are presented in Table 2.

Table 2. Thermal resistance of resin DGTEF and its compositions

Resin	Kind	No of comp.	Epoxy content [val/100 g]	Thermal analysis [°C]				
				T_1^a	T_2^b	T_3^c	U^d	T_4^e
DGTEF	Uncured		0.355	260–295	275	220	15.0	300
	Thermal Curing		—	—	—	225	1.0	290
DGTEF	TETA	I	—	—	—	200	1.0	270
DGTEF + DGEBA		III	—	—	—	205	2.0	290
DGTEF + DGEBA		V	—	—	—	240	3.0	315
DGTEF	HY-905	VI	—	—	—	210	1.0	300
DGTEF + DGEBA		VIII	—	—	—	225	2.0	330
DGTEF + DGEBA		X	—	—	—	240	1.0	375
DGTEF	NMA	XI	—	—	—	205	1.0	310
DGTEF + DGEBA		XIII	—	—	—	200	1.0	325
DGTEF + DGEBA		XV	—	—	—	210	1.0	360

^a Homopolymerization temperature from the DTA curve;

^b Maximum homopolymerization temperature from the DTA curve;

^c Initial mass loss temperature from the DTG curve;

^d Mass loss in the temperature T_3 from the TG curve;

^e Temperature of intensive mass loss from the DTG curve.

From the curves of thermal gravimetric analysis (TGA), homopolimerization temperature, maximum homopolimerization temperature, initial decomposition temperature, mass loss in percentage, and the temperature at which the highest rate of resin or its composition decomposition takes place have been determined. From differential thermal analysis (DTA) of uncured resin exothermic reaction of epoxy group opening under the effect of temperature takes place in the range of 260–295°C. A fairly sharp onset of G curves at 290–310°C, indicates the intense mass loss. The upper limit of stability of both uncured and thermally or chemically cured resin depends mainly on stability of thioether linkage.

CHEMICAL CURING OF RESIN AND ITS COMPOSITION

Chemical curing of DGTEF resin and its blend with epoxide resin DGEBA was carried out in cold using aliphatic amine (TETA) and in hot by means of acid anhydrides (HY-905 and NMA). The chemical composition was established

from stoichiometric calculations and the obtained numerical values as well as curing conditions are presented in Table 3.

Table 3. Composition of the mixture of DGTEF resin with DGEBA resin and curatives and conditions of their curing

No	Composition	DGTEF	DGEBA	TETA	HY-905	NMA
I		200	—	20	—	—
II		150	50	20	—	—
III		100	100	20	—	—
IV		50	150	20	—	—
V		25	175	20	—	—
VI		120	—	—	90	—
VII		80	40	—	90	—
VIII		60	60	—	90	—
IX		40	80	—	90	—
X		20	100	—	90	—
XI		130	—	—	—	80
XII		86	43	—	—	80
XIII		65	65	—	—	80
XIV		43	86	—	—	80
XV		21	108	—	—	80

* Cure schedules: (I–V) 72 h at room temperature and 24 h at 80°C; (VI–XV) 5 h at 80°C, 17 h at 110°C, 5 h at 140°C and 2 h at 150°C.

Moreover, to study the application, gelation time of resin compositions with curatives in relation to temperature was determined (Table 4).

Cast profiles obtained according to Polish standards were studied thermally, thermo-mechanically and mechanically. The obtained values are collected in Tables 5 and 6. From the results of the investigations it can be seen that aliphatic resin and its blend with DGEBA (Epidian-5) can be cured by means of common curatives used for ether glycidyl resins. On the basis of the determined gelation time it can be said that the compounds reveal good technological processing properties at 25–40°C cured by amine and at 80–140°C cured hot by anhydrides. The compositions cured by NMA are characterized by longer gelation time.

There is a distinct effect of aliphatic thioether glycidyl resin on gelation rate in the blend with DGEBA (Epidian-5). The increase of aliphatic resin content in the composition cured by amine (TETA) causes gelation time lengthening and by anhydrides (HY-905, NMA) — shortening. As indicated by the aliphatic—aromatic and aromatic systems (part VI) this is caused by formation of aliphatic resin under the effect of temperature of saturated and nonsaturated

alcohol type compounds which with the temperature increase initiate the anhydride curing reaction.

Table 4. Gelation time compositions [min] in relation to temperature

DGEBA : DGTEF (weight ratio)			Gelation time [min]						
			45°C	50°C	60°C	70°C	80°C		
	I	0 : 1	—	77	39	17	—		
	II	1 : 3	—	60	20	11	—		
TETA	III	1 : 1	—	29	15	7	—		
	IV	3 : 1	43	28	14	—	—		
	V	7 : 1	39	23	11	—	—		
			80°C	90°C	100°C	110°C	120°C	140°C	160°C
	VI	0 : 1	30	19	12	—	—	—	—
	VII	1 : 2	28	16	10	—	—	—	—
HY-905	VIII	1 : 1	33	20	13	—	—	—	—
	IX	2 : 1	47	25	17	—	—	—	—
	X	5 : 1	—	—	—	85	52	43	23
			80°C	90°C	100°C	110°C	130°C	140°C	160°C
	XI	0 : 1	105	64	40	30	—	—	—
	XII	1 : 2	90	51	35	25	—	—	—
NMA	XIII	1 : 1	99	58	40	—	—	—	—
	XIV	2 : 1	—	66	48	35	—	—	—
	XV	5 : 1	—	—	—	—	120	—	80

On the basis of the studied compositions, the effect of such terminal units as sulphur and aliphatic chains built in to the cured structure was shown. The results obtained from thermal (T_g) and thermomechanical (Martens, Vicat) studies (V–VI) confirm the distinct plasticizing effect.

The good dilution effect (Table 1) obtained by aliphatic thioether glycidyl resin with simultaneous slight decrease of epoxide group content and significant decrease of unpleasant smell compared with the raw material of which resin is prepared i.e. thiorubber point to its application in production of layer polymer compositions, glues, surfacers, varnishes, but particularly in building industry.

Table 5. Curing conditions and results of studies on mechanical properties of some epoxide compositions

Property	Norm of studies	DGEBA + DGTEF + TETA 100 : 50 : 12 (A)		DGEBA + DGTEF + TETA 100 : 10 : 12 (B)	DGEBA + TETA 100 : 12 (C)
		(A ₁)*	(A ₂)*		
Deflection temp., by Martens method (°C)	PN-68/C-89025	59.5	97.0	105.5	115.0
Tensile strength (MPa)	PN-68/C-89034	61.4	95.8	38.4	24.9
Bending strength (MPa)	PN-69/C-89027	67.0	95.8	113.4	170.6
Compressive strength (MPa)	PN-68/C-89031	76.6	95.2	114.5	114.8
Brinnel hardness (MPa)	PN-68/C-89030	126.2	138.6	118.3	120.5
Charpy impact (kJ/m ²)	PN-69/C-89029	25.9	15.7	14.5	17.6
Hygroscopicity (%)	PN-66/C-89032	—	—	0.144	0.176

* (A₁) — 170 h at 25°C, (A₂) — 18 h at 25°C and 6 h at 100°C, (B) — 12 h at 25°C and 6h at 100°C, (C) — 18 h at 25°C and 6 h at 100°C

Table 6. Thermal and mechanical properties of cured composition

Property	TETA					HY-905					NMA				
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV
Vicat thermal resistance after Martens [°C]	—	—	27	68	95	—	—	40	52	74	—	—	38	56	69
Softening temperature after Vicat [°C]	—	32	52	70	90	—	40	54	65	83	—	32	52	70	84
Glass transition temp; range* [°C]	-28.5	-2.0	+65.5	+80.0	+101.0	+1.0	+28.0	+40.0	+55.0	+75.0	-4.0	+22.0	+41.5	+59.5	+79.0
Compressive strength [MPa]	—	11.2	70.6	124.4	124.2	—	25.2	92.4	105.7	113.4	—	—	82.1	110.9	116.3
Brinnel hardness [MPa]	—	—	63.3	132.1	140.4	—	—	118.1	138.1	136.2	—	—	117.3	137.5	160.5
Shore hardness [D]	15	30	76	84	84	21	62	81	83	84	17	67	75	76	84

* (I) -41 + -16; (II) -19 + +15; (III) +50 + +81; (IV) +63 + +94; (V) +93 + +109; (VI) -7 + +9; (VII) +20 + +36; (VIII) +32 + +48; (IX) +47 + +63; (X) +69 + +81; (XI) -11 + +3; (XII) +10 + +34; (XIII) +29 + +54; (XIV) +50 + +69; (XV) +71 + +87

REFERENCES

- [1] Lee H., Neville K., *Handbook of Epoxy Resins*, Mc Grow Hill Book Co., New York 1967.
- [2] Dachslt E., Thioplaste, *Deutscher Verlag für Grundstoffindustrie*, Lipsk 1971.
- [3] Szlezynghier W., *Polimery*, **11**, 546 (1974).
- [4] Penczek P., Staniak H., *Plaste u. Kautsch*, **17**, 259 (1970).
- [5] Bender H. L., Farnham A. G., *Pat. USA* 2 731 437 (1956).
- [6] Charmas W., Podkościelny W., *J. Appl. Polym. Sci.*, **25**, 2393 (1980); **27**, 1453 (1982); **29**, 4297 (1984).
- [7] Charmas W., *J. Appl. Polym. Sci.*, **27**, 2797 (1982); **30**, 411 (1985).
- [8] Charmas W., Podkościelny W., Brunn J., *J. Polym. Sci.: Polym. Chem. Ed.*, **27**, 2397 (1989).
- [9] Charmas W., Podkościelny W., Rudź W., *J Appl. Polym. Sci.*, **39**, 1623 (1990).
- [10] Dojka M. *et al.*, *Pat. PRL* 107 779 (1978).

STRESZCZENIE

Orzymano żywicę tioeteroglicydylową w wyniku kondensacji bis (β -merkptoetylo)formalu z epichlorohydriną metodą heterofazowej alkalicznej kondensacji w środowisku wodno-izopropanolowym za pomocą wodorotlenku sodowego. Przedstawiono badania dotyczące struktury na podstawie analiz: elementarnej i widm spektralnych IR i ^1H —NMR oraz określono podstawowe fizyko-chemiczne właściwości i warunki utwardzania. Sporządzono także kompozycje żywicy tioeteroglicydowej z żywicą diglicydylową bisfenolu A i po utwardzeniu przy użyciu typowych utwardzaczy dla żywic epoksydowych scharakteryzowano je na podstawie badań termicznych, termo-mechanicznych i mechanicznych.