

Thioetherglycidyl Resins. III. Products of Condensation of Bis(4-Mercaptophenyl)ether and Bis(4-Mercaptophenyl)methane with Epichlorohydrin*

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Synopsis

Thioetherglycidyl resins produced by condensation of bis(4-mercaptophenyl)ether and bis(4-mercaptophenyl)methane with epichlorohydrin were obtained by heterophase alkaline condensation. To define the optimal conditions of condensation, the following factors that influence the process were studied: the kind of organic phase and the mole ratios of epichlorohydrin:mercaptan, alcohol:mercaptan, and alkaline hydroxide:mercaptan. For all syntheses yield and the epoxide content were found. The structure of thioetherglycidyl resins with the highest epoxide content was determined by elementary analysis, infrared IR, and NMR spectra. The physical and chemical properties were also defined. The investigations covered the determination of some properties of resins, cured chemically or thermally with different curatives and thermal and mechanical properties of the cured compounds.

INTRODUCTION

Studies of Bring,¹ Lidarik,² Fisch,³ Wiesner,^{4,5} and lately Rozentuler⁶⁻⁸ on the kinetics and mechanism of bisphenol A condensation at large excess of epichlorohydrin showed that the resin synthesis proceeded in the stages of addition and dehydrogenation. It has been stated that the greatest effect on the average value of polycondensation was exerted by the mole ratio of epichlorohydrin and bisphenol used in the reaction. The rate of addition and dehydrogenation as well as of oligomerization depends on the way of introduction of alkaline hydroxide to the mixture and of additional solvents, particularly alcohols of high dielectric constants.

Among the resins obtained from epichlorohydrin in which the oxirane ring is a part of glycidyl group besides the typical resins of glycidyl ether type, their homologs, thioetherglycidyl resins, can be found. To obtain this kind of resins, aliphatic, aliphatic-aromatic, cycloaliphatic-aromatic, and aromatic dithiols are used.

Thioetherglycidyl resins were prepared from aromatic dithiols of benzene, diphenylether, and diphenylmethane by condensation with epichlorohydrin in the aqueous solution of sodium hydroxide^{9,10} and through the sodium salts of durene and diphenyl mercapto- compounds formed earlier in the reaction of dithiol and metallic sodium in anhydrous ethanol.¹⁰

The resins obtained by this method were mostly solid and sparingly soluble and possessed lower epoxide content in comparison with the theoretical calculations.

* For Paper II see Ref. 12.

It should be emphasized that patents give only methods of thioetherglycidyl preparation from aromatic mercaptans with the reaction yield and epoxide and chlorine contents, but they do not give a detailed description of synthesis conditions, resin structure, physicochemical properties, and curing conditions.

For this reason it seemed useful to study the synthesis of thioetherglycidyl resins, derivatives of bis(4-mercaptophenyl)ether and bis(4-mercaptophenyl)-methane by heterophase, alkaline condensation with epichlorohydrin which was used effectively to obtain resins from aliphatic-aromatic dithiols, derivatives of naphthalene,¹¹ diphenylether,¹² and diphenylmethane.¹²

The investigations also covered the determination of some properties of resins cured thermally or chemically with curatives typical for epoxy resins and thermal and mechanical properties of the cured compounds.

EXPERIMENTAL

Reagents

Bis(4-mercaptophenyl)ether (BMPE) and bis(4-mercaptophenyl)methane (BMPM) were obtained from the corresponding disulfonyl chlorides through the reduction by stannous chloride in glacial acetic acid saturated with the gaseous hydrogen chloride.¹³⁻¹⁷

Mercapto- compounds with crystallized from the mixture of 10 parts of glacial acetic acid and one part of the concentrated hydrochloric acid [1 g of BMPE and 12 mL of solvent, amorphous plates at mp 100–101°C (Ref. 18: mp 98–100°C), 1 g of BMPM and 16 mL of solvent, thick crystalline plates at mp 79–80°C).

Epichlorohydrin (1-chloro-2,3-epoxypropane), boiling temperature 114–117°C, manufactured by Fluka AG, Buchs SG, was used. We also used methylbicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic anhydride-NMA (Allied Chemical Dye Corp.), anhydride HY-905 (Ciba-Geigy), and triethylenetetraamine (TETA) (curative Z-1 produced by Chemical Plant Sarzyna).

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.

Measurement of Properties

Spectral Analysis

The infrared (IR) spectra were obtained with a Unicam SP-200 spectrophotometer. NMR spectra were carried out with a Tesla BS-487-C apparatus, frequency 80 MHz, reference TMS, solvent CCl₄, temperature 25 °C.

Thermogravimetric Analysis

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

TABLE I
Conditions of BGTPPE and BGTPM Resin Preparation

Synthesis no.	Mercaptan		Epichlorohydrin		Solvent		Addition (mL)	Dehydrogenation,		Yield (g)	Epoxy content	Chlorine (%)		
	Kind	(g)	(mol)	(g)	(mol)	Kind		(g)	(mL)				(mol)	
1	BGTPPE	22.4	0.1	92	1.0	Isopropyl alcohol	60	1.0	4	80	0.3	31	0.54	0.74
2	BGTPPE	22.4	0.1	92	1.0	Isopropyl alcohol	60 ^a	1.0	4	80	0.3	30	0.53	0.83
3	BGTPPE	22.4	0.1	92	1.0	<i>n</i> -butanol	74 ^a	1.0	4	80	0.3	30	0.52	1.64
4	BGTPPE	22.4	0.1	92	1.0	Acetone	60 ^a	1.0	4	80	0.3	31	0.40	4.40
5	BGTPPE	22.4	0.1	92	1.0	Toluene	90 ^a	1.0	4	80	0.3	34	0.04	13.95
6	BGTPPE	22.4	0.1	92	1.0	—	—	—	4	80	0.3	33	0.19	10.12
7	BGTPPE	44.8	0.2	48 ^b	0.5	Isopropyl alcohol	120	2.0	6	160	0.6	61	0.52	—
8	BGTPPE	44.8	0.2	185	2.0	Isopropyl alcohol	90	1.5	6	120	0.45	62	0.51	—
9	BGTPPE	44.8	0.2	185	2.0	Isopropyl alcohol	60	1.0	6	160	0.6	61	0.52	—
10	BGTPM	23.2	0.1	92	1.0	Isopropyl alcohol	60	1.0	5	80	0.3	34	0.55	—
11	BGTPM	23.2	0.1	56	0.6	Isopropyl alcohol	60	1.0	5	80	0.3	33	0.54	—
12	BGTPM	23.2	0.1	28 ^b	0.3	Isopropyl alcohol	60	1.0	5	80	0.3	34	0.52	—
13	BGTPM	23.2	0.1	110	1.2	Isopropyl alcohol	60 ^a	1.0	5	60	0.3	33	0.53	—

^a Isopropyl alcohol dropped in after addition, i.e., before the second portion of NaOH.

^b 30 g of epichlorohydrin was additionally introduced after dehydrohalogenation, i.e., before mixture delamination.

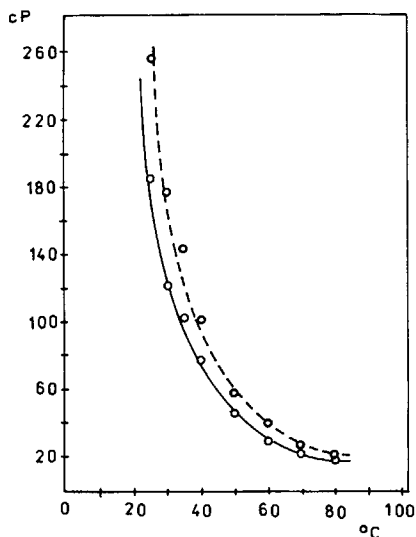


Fig. 1. Viscosity of BGTPE (—) and BGTMPM (---) resins in relation to temperature.

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 of resin and determined according to the Polish Norm PN-69/C-8905 by HCl solution in dioxane.

RESULTS AND DISCUSSION

Determination of Optimal Conditions of Resin Synthesis

In this article studies of resin synthesis, physicochemical properties of thioetherglycidyl resins, curing conditions, and thermal and mechanical properties of the cured compositions were carried out on aromatic di(mercapto-) compounds, derivatives of diphenylether and diphenylmethane. In the optimal conditions new resins were obtained: bis[*p*(2,3-epoxypropylthio)phenyl]ether [bis(4-glycidylthiophenyl)ether (BGTPE)] and bis[*p*(2,3-epoxypropylthio)phenyl]methane [bis(4-glycidylthiophenyl)methane (BGTMPM)].

Thioetherglycidyl Resin Synthesis

To determine the optimal conditions of resin synthesis by heterophase, alkaline condensation of aromatic dimercaptans with epichlorohydrin, yield, epoxide, and chlorine content were studied. The influence of the following factors on the process—type of phase and the mole ratios of epichlorohydrin:mercaptan, alcohol:mercaptan, alkaline hydroxide:mercaptan—was investigated. To prepare BGTMPPE and BGTMPM resins, the following method was used.

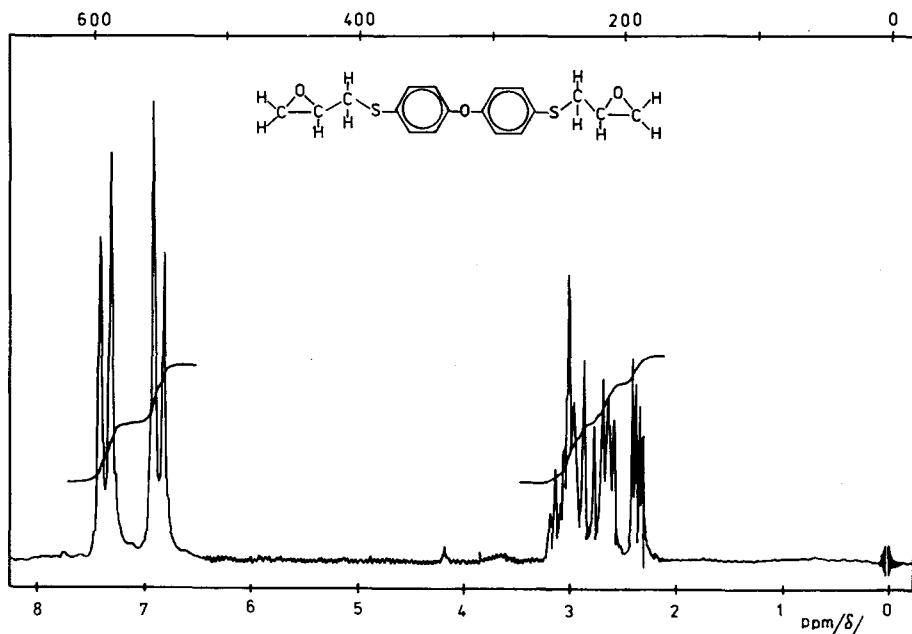


Fig. 2. NMR spectra of BGTPE resin.

Into a four-necked round-bottom flask of 500 cm³ volume, equipped with a mechanical stirrer, reflux condenser, thermometer, and dropper di(mercapto-) compound, epichlorohydrin and solvent in the amounts given in Table I were poured. After heating in the water bath to 60°C, the first portion of 15% solution of sodium hydroxide as an addition catalyst was dropped in very carefully. When the solution changed from brown-green into light beige, the second portion of 15% solution of sodium hydroxide was added for 5 min and stirred for another 10 min. The organic layer was separated, and the solvent and excess of epi-

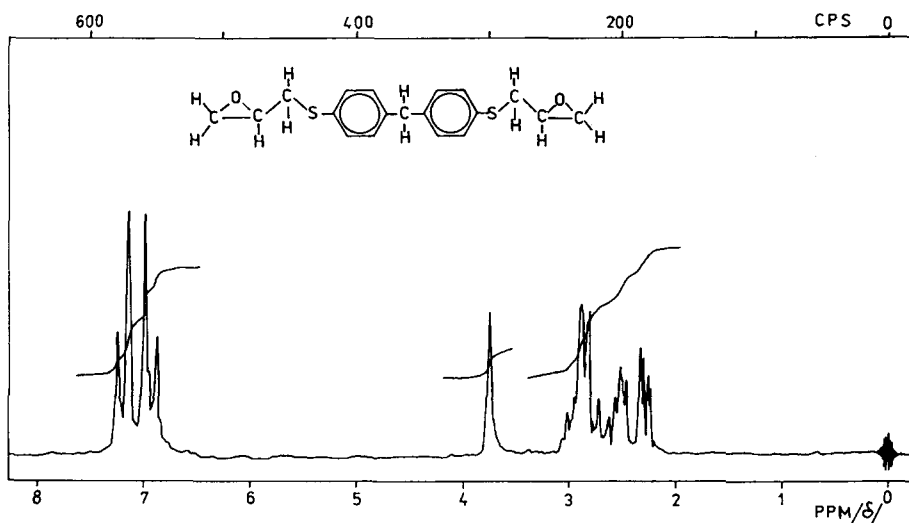


Fig. 3. NMR spectra of BGTTPM resin.

TABLE II
Results of Elementary Analysis

Thioetherglycidyl resins	Analysis					
	% C		% H		% S	
	Calcd	Found	Calcd	Found	Calcd	Found
BGTPE	62.40	62.21	5.23	4.89	18.51	18.92
BGTPM	66.24	65.77	5.85	6.21	18.61	18.23

chlorohydrin were distilled under reduced pressure (12 Torr). Then it was filtered. In every synthesis the resin yield and its epoxy and chlorine contents were determined when the Bekstein test was positive. Numerical values are given in Table I.

Because of very strong exothermic effects of the addition reaction, the resin synthesis was carried out only when alkaline hydrogen oxide was introduced by stages. In the case of thioetherglycidyl resins derived from aliphatic-aromatic mercaptans, the synthesis takes place through the stages of addition and dehydrohalogenation.^{11,12} It can be more clearly observed in the case of aromatic mercapto- compounds because, besides a very strong exothermic effect, change of the mixture color takes place.

It seems that epichlorohydrin excess which influences the direction and kinetics in etherglycidyl resin synthesis is not so effective in thioetherglycidyl resin preparation. The mole ratio increase of epichlorohydrin and mercaptan points rather to physical activity resulting in reaction mass viscosity decrease and in facilitating of resin isolation.

It follows from Table I that the reaction medium influences the direction of thioetherglycidyl resin synthesis. The resins of the highest epoxide content are obtained with solvents of higher dielectric constants, particularly with alcohols which cause increase of alkaline hydroxide solubility in an organic phase and have beneficial effect on chlorohydrin thioether dehydrohalogenation.

IR and NMR spectra were made for BGTPE of the epoxide content 0.54 (the theoretical epoxide content 0.58) and melting temperature 37°C and for BGTPM of the epoxide content 0.55 (the theoretical epoxide content 0.58) and viscosity 255 cP at 25°C (the relation between viscosity and temperature is given in Fig. 1).

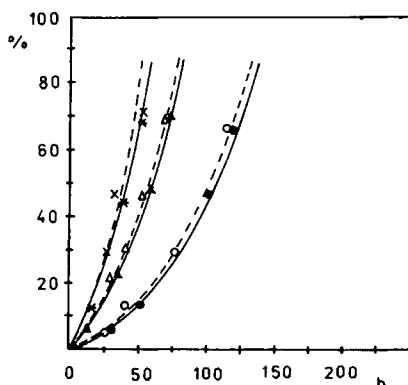


Fig. 4. Loss (%) of epoxy groups of BGTPE (—) and BGTPM (---) resins in relation to heating time (h) at 100°C (O, ●), 110°C (Δ, ▲), and 120°C (×, *).

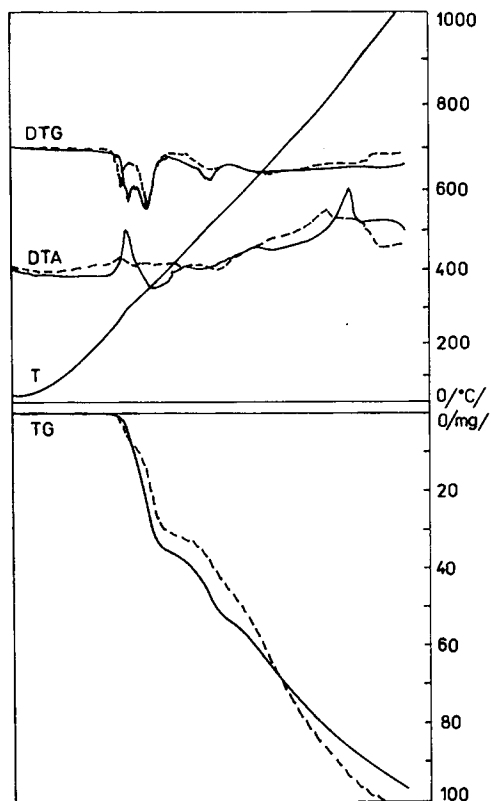


Fig. 5. TGA and DTA of uncured and thermally cured resin BGTPE of epoxy contents 0.54 (—) and 0.26 (---). Heating time in air, 100 min; heating rate, 100°C/min; amount of resins, 100 mg; measurements related to Al_2O_3 .

IR spectra of the resins showed strong adsorption at 930–220 cm^{-1} and 840–835 cm^{-1} , which are characteristic of the epoxy valency band; at 1100–1090 cm^{-1} which are characteristic of Ar—S— stretching and at 1420–1410 cm^{-1} and 1240–1220 cm^{-1} , which is characteristic of —S—CH₂— groups.

The proton NMR spectroscopic studies of the resins show that the resin BGTPE (Fig. 2) has two group signals: One signal, between δ 6.85 and 7.38 ppm, had a characteristic A_2B_2 pattern and was assigned to the *p*-substituted phenylene ring; the other, assigned to the glycidyl group, and δ 2.30 ··· 3.20 ppm. But the resin BGTPE (Fig. 3) has three distinct group signals: One signal, between δ 6.92 and 7.17 ppm, was assigned to the *p*-substituted phenylene ring; the other of the —CH₂— group between the phenylene groups and δ 3.72 ppm and the third of the glycidyl group had between δ 2.20 and 3.05 ppm.

The integration of the aromatic and aliphatic groups shows a proton number ratio of 2:2:5 for BGTPE and of 2:2:1:5 for BGTPE. On the basis of these results it is apparent that both resins have the same basic structure of bis(4-glycidylthiophenyl) compound.

On the basis of good agreement of the found and calculated analytical data (Table II), the observed thermal effects of the reaction, and IR and NMR spectra, the resin structure of the type of a pure monomeric compound is assumed.

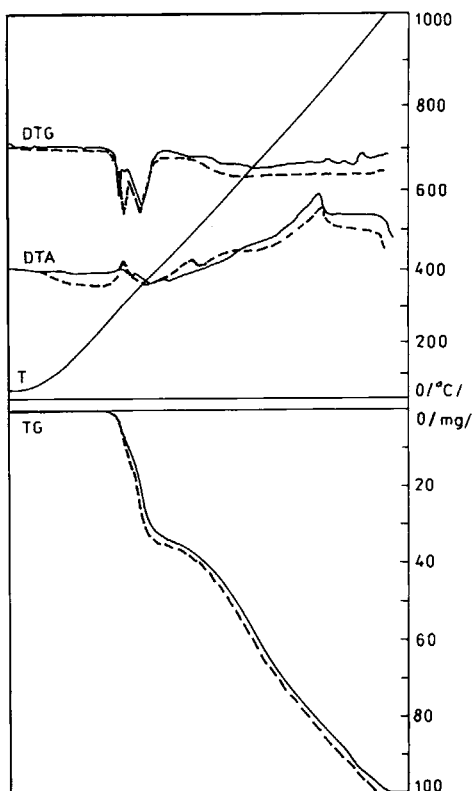


Fig. 6. TGA and DTA of uncured and thermally cured resin BGTPM of epoxy contents 0.55 (---) and 0.21 (—). Heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 mg; measurements related to Al_2O_3 .

Thermal Stability

Thermal stability of new resins was determined during controlled heating at different temperatures, from the epoxy group loss and derivatographic analysis (TGA) for uncured resins and those cured in a thermal or chemical way. From the curves presented in Figure 4 it can be seen that temperature affects rate of thioether glycidyl resin thermal curing. Reactivity of both resins is similar and considerably lower than that of their aliphatic-aromatic analogs, i.e., resins derived from bis(4-mercaptomethylphenyl)ether and bis(4-mercaptomethylphenyl)methane.

Some results of derivatographic analysis are presented in Figures 5–7. As follows from the values given in Table III, thermal resistance of other resins and compositions are similar. Melting temperature, homopolymerization temperature, maximum homopolymerization temperature, initial decomposition temperature, mass loss in percentage, and the temperature at which the highest rate of resin decomposition takes place have been determined from the curves of thermal derivatographic analysis (TGA).

From differential thermal analysis (DTA) of uncured resins exothermic reaction is detected in the range 230–240°C and indicates a homopolymerization reaction of epoxy groups. A fairly sharp onset of weight loss is noted at 220–285°C. The upper limits of stability of both uncured resins and resins cured

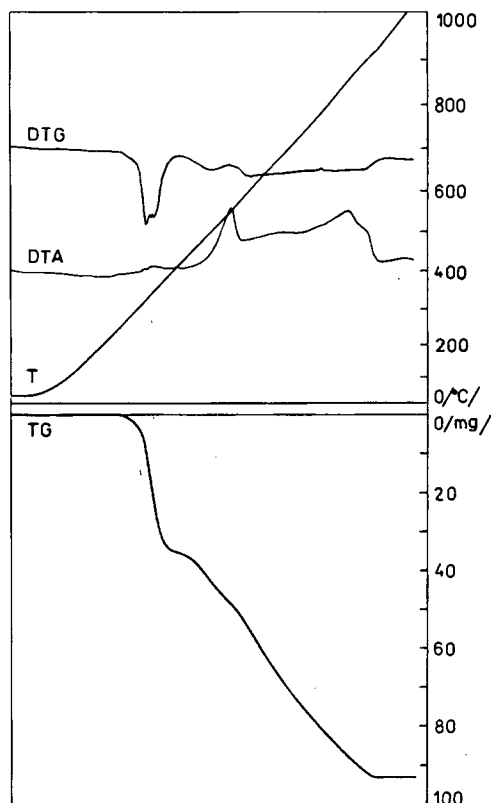


Fig. 7. TGA and DTA of the cured composition BGTPE with TETA. Heating time in air, 100 min; heating rate, 10°C/min; amount of a composition, 100 mg; measurements related to Al_2O_3 .

thermally or chemically appear to be governed mainly by the stability of thioether linkage.

Chemical Curing of Resins

Chemical curing of thioetherglycidyl resins was carried out in hot setting using acid anhydride and in cold setting using aliphatic amine. Chemical structure of the compound was determined from stoichiometric calculations (0.85 mol of anhydride per epoxide equivalent). Numerical values and curing conditions are given in Table IV.

The time of resin gelation with curatives in relation to the temperature has been determined (Table V). To examine the application of cured resins, some cast profiles have been prepared. After mixing the component, at the increased temperature, the compound was vented in the vacuum desiccator, poured into a metal mold covered with antiadhesive coating of silicone varnish and cured in the conditions given in Table IV. Cast profiles obtained according to Polish standards were studied to determine their thermal mechanical properties, which are presented in Table VI.

From the results of these investigations, it can be seen that BGTPE and BGTPM resins can be cured by means of common curatives used for etherglycidyl resins.

TABLE III
Thermal Resistance of Resins and Compositions

Resin	Kind	Epoxy content	Thermal analysis					
			T_1^a	T_2^b	T_3^c	T_4^d	U^e	T_5^f
BGTMPPE	Uncured	0.54	37	230-330	300	280	1.0	350
	Thermal curing	0.26	—	230-300	265	260	1.0	340
BGTMPM	Uncured	0.55	—	240-340	310	285	0.5	350
	Thermal curing	0.21	—	250-280	270	280	1.0	350
BGTPE	TETA	—	—	—	—	240	0.5	330
	HY-905	—	—	—	—	240	1.0	350
	NMA	—	—	—	—	260	0.5	365
BGTMPM	TETA	—	—	—	—	230	1.0	300
	HY-905	—	—	—	—	220	1.0	310
	NMA	—	—	—	—	230	1.0	340

^a (°C): melting temperature from the curve DTA.

^b (°C): homopolymerization temperature from the curve DTA.

^c (°C): maximum homopolymerization temperature from the curve DTA.

^d (°C): initial mass loss temperature from the curve DTA.

^e (%): mass loss in the temperature T_4 from the curve TG.

^f (°C): temperature of intensive mass loss from the curve DTG.

On the basis of the determined gelation time we can say that the compounds reveal good technological processing properties at 30–40°C cured in cold setting (TETA) and at 80–120°C cured in hot setting with anhydrides. The compounds cured by NMA are characterized by longer gelation time.

TABLE IV
Composition and Cure Conditions for Epoxy Resin^a

Resin	Composition no.					
	I	II	III	IV	V	VI
BGTPE	100	100	100	—	—	—
BGTMPM	—	—	—	100	100	100
TETA	14	—	—	13	—	—
HY-905	—	90	—	—	90	—
NMA	—	—	85	—	—	85

^a Cure schedules: (I and IV) 24 h at room temperature, 10 h at 60°C; (II and V) 3 h at 80°C, 8 h at 90°C, 4 h at 110°C, 12 h at 140°C, and 4 h at 160°C; (III and VI) 6 h at 90°C, 6 h at 110°C, 12 h at 140°C, and 6 h at 160°C.

TABLE V
Gelation Time of Composition (min) in Relation to Temperature

Composition no.	Gelation time (min)						
	25 °C	35 °C	50 °C	60 °C	80 °C	100 °C	120 °C
BGTMPPE	TETA (I)	380	130	50	—	—	—
	HY-905 (II)	—	—	—	290	95	—
	NMA (III)	—	—	—	—	295	185
BGTMPM	TETA (IV)	310	90	40	—	—	—
	HY-905 (V)	—	—	—	345	105	—
	NMA (VI)	—	—	—	—	350	200

TABLE VI
Thermal and Mechanical Properties of Cured Composition

Test	BGTMPPE			BGTMPM		
	TETA	HY-905	NMA	TETA	HY-905	NMA
Vicat thermal resistance after Martens (°C)	65	75	95	53	74	93
Softening temp after Vicat (°C)	129	82	109	72	82	110
Bending strength (MPa)	131.2	139.2	83.2	132.0	100.0	84.8
Compressive strength (MPa)	161.1	133.3	141.6	121.5	127.8	123.9
Tensile strength (MPa)	69.2	25.4	24.0	35.0	20.4	24.0
Brinnell hardness (MPa)	12.3	14.5	11.0	11.8	16.0	12.8
Charpy impact (kJ/m ²)	25.9	10.0	5.8	12.0	13.0	7.6

BGTPE and BGTMPM resins except BGTPE—TETA reveal similar thermomechanical properties with the same curatives, greater resistance to temperature according to Martens and Vicat, greater bending and impact strength compared to aliphatic-aromatic compounds derived from bis(4-mercaptomethyl)ether and bis(4-mercaptomethyl)methane.¹² It is due to the increased density of a composition crosslink cured through the decrease of segment length between lattice nodes.

The technological, processing, and mechanical properties of the resins are dependent on a curative. This fact should be taken into account in constructional resin, insulating-hermetic resin, glue, laminated plastics, and varnish coat production. Thioetherglycidyl resins can also be applied as stabilizers in processing and other epoxy resin modifiers.

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