

Thioether Glycidyl Resins. II. Products of Condensation of Bis(4-Mercaptomethylphenyl) Ether and Bis(4-Mercaptomethylphenyl)methane with Epichlorohydrin

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Synopsis

New thioether glycidyl resins produced by condensation of bis(4-mercaptomethylphenyl) ether and bis(4-mercaptomethylphenyl)methane with epichlorohydrin were obtained by heterophase alkaline condensation in water and isopropyl alcohol solution. To define the optimal conditions of condensation, the following factors that influence the process were studied: the mole ratios of epichlorohydrin-mercaptan, alcohol-mercaptan, alkaline hydroxide-mercaptan. For all reaction products, yield, epoxide content, and chlorine content were determined. The structure of thioether glycidyl resins with the highest epoxide content was determined by elemental analysis and infrared and NMR spectra. The physical and chemical properties were defined. Some properties of the resins, cured chemically or thermally with different curatives, and thermal and mechanical properties of the cured compounds were determined.

INTRODUCTION

An earlier article¹ contains a survey of our studies on the preparation of thioether glycidyl resins, derivatives of bis(mercaptomethyl) compounds, and epichlorohydrin and the achievements of other investigators in this subject.

The purpose of this article is to give the results of the studies on synthesis, structure, and physical and chemical properties of pure thioetherglycidyl resins and derivatives of bis(mercaptomethylphenyl)methane with epichlorohydrin obtained by heterophase, alkaline condensation in water, and isopropyl alcohol solution using sodium hydroxide.

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

The thioether glycidyl resin of bis(4-mercaptomethylphenyl) ether had already been obtained by condensation with epichlorohydrin in aqueous solution of sodium hydroxide.² The resin obtained by this method had a lower epoxy content and much greater viscosity probably because of side reactions and thermal curing characteristic for this type of epoxy resins, as was shown in the previous article.¹

EXPERIMENTAL

Reagents

Bis(4-mercaptomethylphenyl) ether (BMMPE), which melts at 34–35°C, and bis(4-mercaptomethylphenyl)methane (BMMPM), which melts at 81–82°C were obtained from the corresponding chloromethyl derivatives^{3,4} through the thiouronic salts. Epichlorohydrin (1-chloro-2,3-epoxypropane), boiling at 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 triethylenetetramine (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.

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).

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

RESULTS

Determination of Optimal Conditions of Resin Synthesis

In this article, studies of physical and chemical properties of thioether glycidyl resins, their curing conditions, and thermal and mechanical properties of the cured compounds were carried out on aliphatic-aromatic bis(mercaptomethyl) compounds and derivatives of diphenyl ether and diphenylmethane. Under optimal conditions, new resins were obtained: bis[*p*-(2,3-epoxypropylthiomethyl)phenyl]ether –bis(4-glycidylthiomethylphenyl ether (BGTMPPE) and bis[*p*-(2,3-epoxypropylthiomethyl)phenyl]methane –bis(4-glycidylthiomethylphenyl)methane (BGTMPM).

TABLE I
 Conditions of BGTMPPE and BGTMPM Resin Preparation

Synthesis no.	Mercaptan		Epichlorohydrin		Isopropyl alcohol		Addition 15% NaOH		Dehydrohalogenation, 15% NaOH		Yield, g	Epoxy content	Chlorine, %	
	Kind	g	mol	g	mol	g	mol	mL	mol	mL				mol
1	PMMPE	39.4	0.15	139	1.50	90	1.5	5.5	0.02	120	0.45	51	0.52	
2	BMMPE	39.4	0.15	35	0.37	90	1.5	5.5	0.02	120	0.45	50	0.51	
3	BMMPE	39.4	0.15	139	0.50	90	1.5	5.5	0.02	90	0.34	51	0.51	
4	BMMPE	39.4	0.15	35	0.37	90	1.5	5.5	0.02	90	0.34	50	0.50	
5	BMMPE	39.4	0.15	139	1.50	90 ^a	1.5	5.5	0.02	120	0.45	50	0.51	
6	BMMPE	39.4	0.15	139	1.50	—	—	5.5	0.02	120	0.45	50	0.22	9.18
7	BMMPM	39.0	0.15	139	1.50	60	1.0	5.5	0.02	120	0.45	55	0.51	
8	BMMPM	39.0	0.15	92	1.00	60	1.0	5.5	0.02	120	0.45	55	0.50	
9	BMMPM	39.0	0.15	161	1.75	60	1.0	5.5	0.02	94	0.35	55	0.50	
10	BMMPM	39.0	0.15	92	1.00	60	1.0	5.5	0.02	94	0.35	55	0.50	
11	BMMPM	39.0	0.15	139	1.50	60	1.0	5.5	0.02	94	0.35	54	0.49	
12	BMMPM	39.0	0.15	139	1.50	60 ^a	1.0	5.5	0.02	120	0.35	54	0.50	
13	BMMPM	19.5	0.07	70	0.75	—	—	3.0	0.01	60	0.23	29	0.21	9.49

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

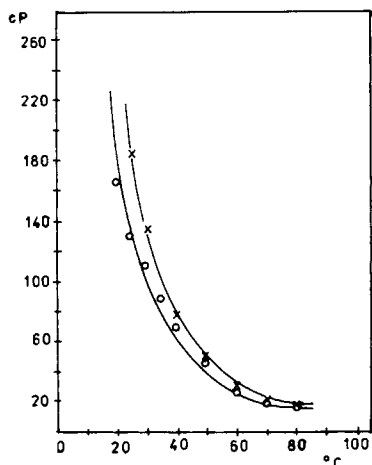


Fig. 1. Viscosity of (O) BGTMPPE and (X) BGTMPM resins in relation to temperature.

Thioether Glycidyl Resin Synthesis

In the determination of optimal conditions for resin synthesis by heterophase alkaline condensation of aromatic-aliphatic dimercaptans with epichlorohydrin in water and isopropyl alcohol solution, the yield, the epoxide content, and the chlorine content were investigated. The influence of the following factors on the process was studied; the mole ratios of epichlorohydrin:mercaptan, alcohol:mercaptan, and alkaline hydroxide:mercaptan. The influence on resins and derivatives of naphthalene¹ of other factors was also investigated: the amount of the addition catalyst, time of the addition and dehydrohalogenation, concentration of the alkaline hydroxide solution, temperature of the reaction, and kind of alcohol.

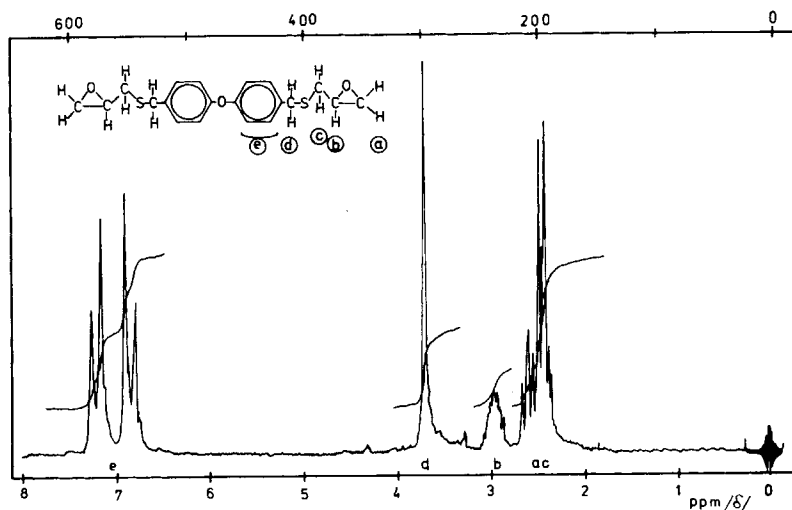


Fig. 2. NMR spectra of BGTMPPE resin. Assignments: $\delta_{a,c} = 2.35 \dots 2.70$, $\delta_b = 2.97$, $\delta_d = 3.72$, $\delta_e = 6.75 \dots 7.35$.

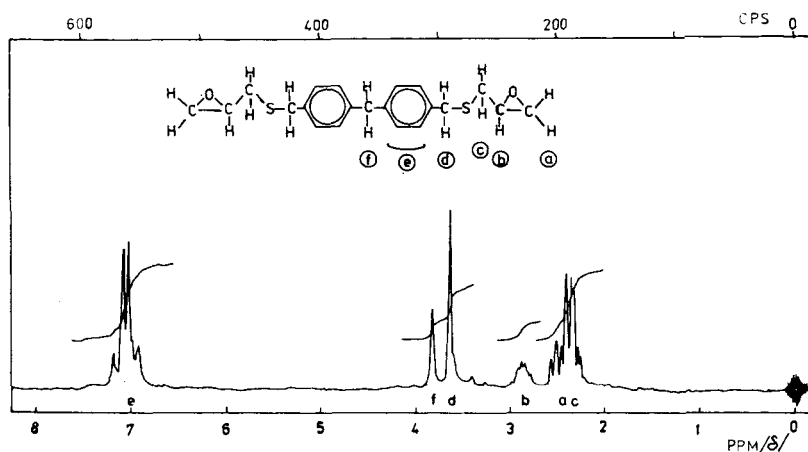


Fig. 3. NMR spectra of BGTMPM resin. Assignments: $\delta_{a,c} = 2.27 \dots 2.57$, $\delta_b = 2.87$, $\delta_d = 3.62$, $\delta_f = 3.82$, $\delta_e = 6.89 \dots 7.22$.

To prepare BGTMPE and BGTMPM resins, the following method was used. In a four-necked 500-ml flask equipped with a mechanical stirrer, reflux condenser, thermometer, and dropper, di(mercaptomethyl) compound, epichlorohydrin, and isopropanol were placed in the amounts given in Table I. After

TABLE II
Results of Elementary Analysis

Thioether glycidyl resins	%C		%H		%S	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
BGTMPE	64.14	63.92	5.87	5.70	17.12	17.34
BGTMPM	67.70	67.99	6.49	7.02	17.21	17.06

TABLE III
Thermal Resistance of the Resins and Compositions

Resin	Kind	Epoxy content	Thermal analysis				
			$T_1,^a \text{ } ^\circ\text{C}$	$T_2,^b \text{ } ^\circ\text{C}$	$T_3,^c \text{ } ^\circ\text{C}$	$U,^d \%$	$T_4,^e \text{ } ^\circ\text{C}$
BGTMPE	uncured	0.52	180-280	240	210	1.0	320
	thermal curing	0.17	140-230	—	220	1.5	320
BGTMPM	uncured	0.50	180-320	280	250	0.5	325
	thermal curing	0.17	—	—	240	0.5	325
BGTMPE	TETA	—	—	—	220	4.0	290
	HY-905	—	—	—	240	2.0	310
	NMA	—	—	—	245	2.0	320
BGTMPM	TETA	—	—	—	220	3.0	290
	HY-905	—	—	—	250	2.0	305
	NMA	—	—	—	240	2.0	310

^a Homopolymerization temperature from DTA curve.

^b Maximum homopolymerization temperature from DTA curve.

^c Initial mass loss temperature from DTG curve.

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

^e Temperature of intensive mass loss from DTG curve.

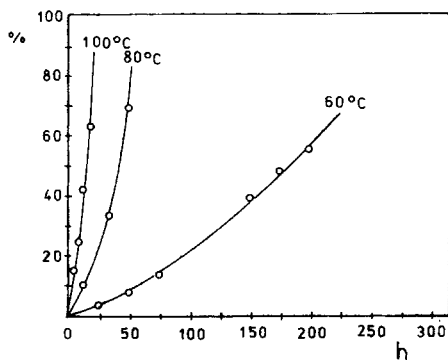


Fig. 4. Percent loss of epoxy groups of BGTMPPE resin in relation to heating time h at 60, 80, and 100°C.

heating in a water bath to 60°C, the first portion of a 15% solution of sodium hydroxide as addition catalyst was added very carefully for 10 min, so that the temperature of the mixture did not exceed 84°C. Then another portion of the 15% sodium hydroxide solution was added for 5 min and stirred for another 10 min.

The organic layer was separated and the alcohol and excess epichlorohydrin were distilled under reduced pressure (12 torr). Then it was filtered through filter paper. 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.

Very strong exothermic effects in the first stage of the resin preparation probably indicate the addition reaction of thiol and epichlorohydrin epoxide groups and that the alkaline hydroxide is not bound stoichiometrically but acts as a catalyst. As in the case of thioether glycidyl resins derived from naphthalene,¹ the beneficial effects of isopropanol on the dehydrohalogenation process, i.e.,

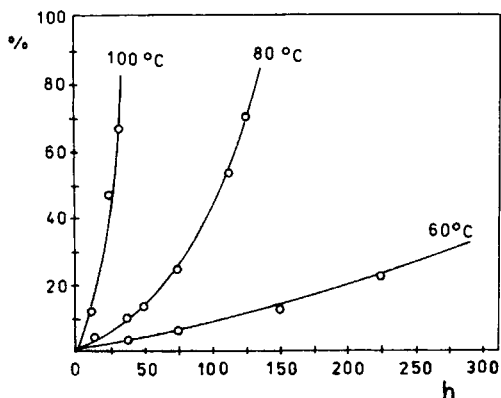


Fig. 5. Percent loss of epoxy groups of BGTMPM resin in relation to heating time h at 60, 80, and 100°C.

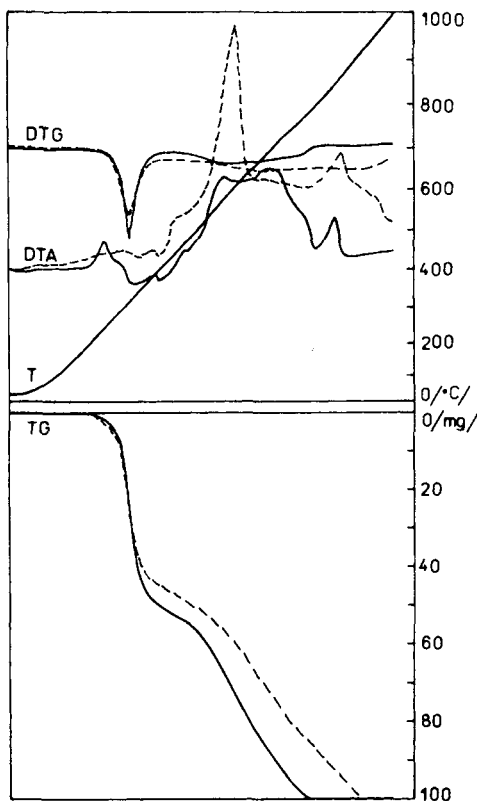


Fig. 6. TGA and DTA of uncured and thermally cured resin BGTMPPE of epoxy contents 0.52 (—) and 0.17 (- -). Heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 mg; measurements relate to Al_2O_3 .

in the second stage of the reaction, were observed (syntheses 5, 6, 12, and 13, Table I).

IR and NMR spectra were made for BGTMPPE of epoxide content 0.52 (theoretical epoxide content 0.53) and viscosity 110 cP at 25°C and for BGTMPM of epoxide content 0.51 (theoretical epoxide content 0.53) and viscosity 110 cP at 25°C. (The relation between viscosity and temperature is given in Fig. 1.)

IR spectra of the resins showed strong absorptions at 935–920 and 845–840 cm^{-1} , which are characteristic of the epoxy valency band; at 760–750 cm^{-1} , which is characteristic of —C—S— stretching; and at 1435–1420 cm^{-1} , which is characteristic of — CH_2 —S— groups.

The NMR spectra of the resins (Figs. 2 and 3) consist of five separate groups of signals for BGTMPPE and BGTMPM. The ratio of their intensity in the direction of the increasing field according to the drop of the integral curve is 4:4:4:2:8 for BGTMPPE, which equals 22 protons, and 8:2:4:2:8 for BGTMPM, which equals 24 protons. The values of the chemical shifts are given under the figures presenting the spectra.

On the basis of good agreement of the found and calculated analytical data (Table II), the observed thermal effects of the reaction, and the IR and NMR

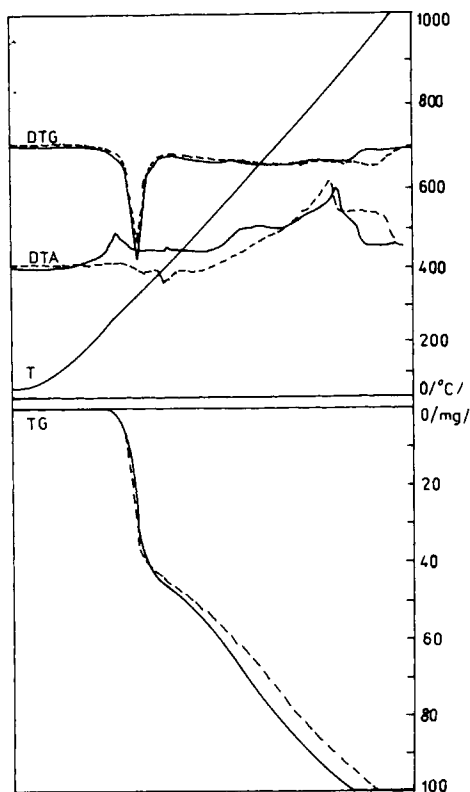


Fig. 7. TGA and DTA of uncured and thermally cured resin BGTMPM of epoxy contents 0.50 (—) and 0.17 (- - -). Heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 mg; measurements relate to Al_2O_3 .

spectra, a resin structure of the type of a pure monomeric compound is assumed.

Thermal Stability

The thermal stability of new resins was determined during controlled heating at different temperatures from the epoxy group loss (Figs. 4 and 5) and deriva-

TABLE IV
Composition and Cure Conditions for the Epoxy Resin^a

Resin	Composition					
	I	II	III	IV	V	VI
BGTMPPE, g	100	100	100	—	—	—
BGTMPM, g	—	—	—	100	100	100
TETA, g	13	—	—	12	—	—
HY-905, g	—	85	—	—	84	—
NMA, g	—	—	79	—	—	78

^a Cure schedules: Compositions I and IV, 24 h at room temperature, 10 h at 60°C; II and V, 2 h at 70°C, 8 h at 100°C, 13 h at 130°C, and 4 h at 150°C; III and VI, 6 h at 80°C, 15 h at 100°C, 6 h at 140°C, and 6 h at 160°C.

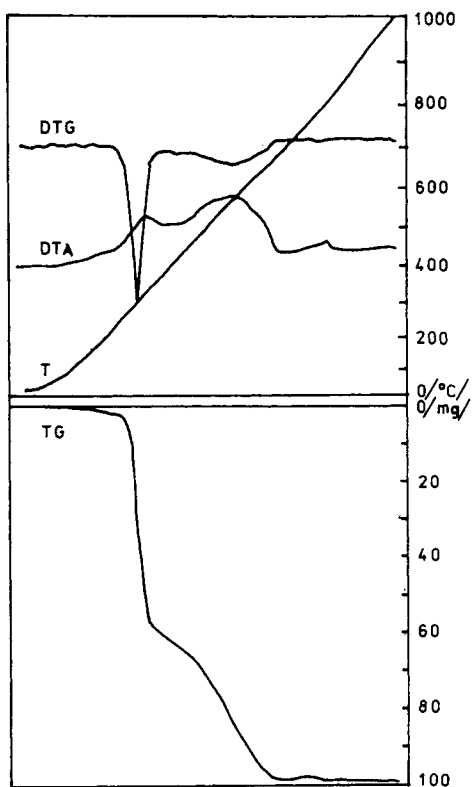


Fig. 8. TGA and DTA of the cured composition BGTMPPE with HY-905. Heating time in air, 100 min; heating rate, 10°C/min; amount of composition, 100 mg; measurements relate to Al_2O_3 .

tographic analysis (TGA) for uncured resins and those cured in a thermal or chemical way. From the curves presented in the figures, it can be seen that temperature affects the rate of thioether glycidyl resin thermal curing. BGTMPPE reactivity is twice as much as that of BGTMPM, and in both cases the reactivity is much smaller than the reactivity of the resins that are derivatives of naphthalene.¹

Some results of derivatographic analysis are presented in Figures 6–9. As

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

Composition	Gelation time, min					
	25°C	40°C	50°C	60°C	80°C	100°C
BGTMPPE						
TETA I	415	145	65	—	—	—
HY-905 II	—	—	—	128	40	—
NMA III	—	—	—	—	205	135
BGTMPM						
TETA IV	460	165	75	—	—	—
HY-905 V	—	—	—	108	35	—
NMA VI	—	—	—	—	175	105

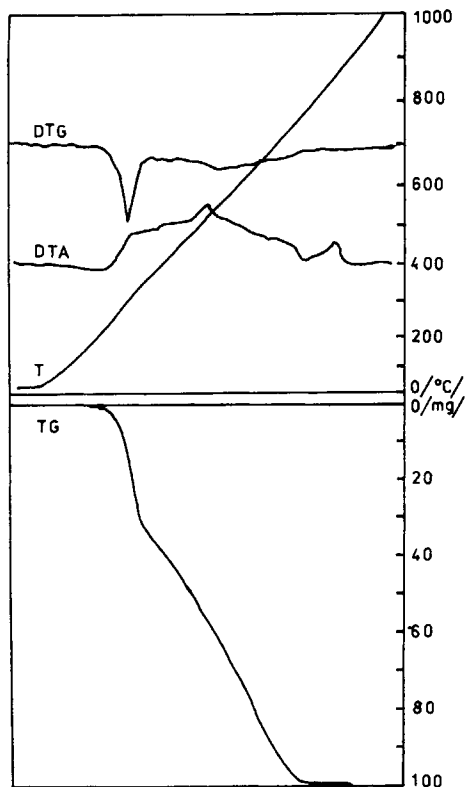


Fig. 9. TGA and DTA of the cured composition BGTMPM with NMA. Heating time in air, 100 min; heating rate 10°C/min; amount of composition, 100 mg; measurements relate to Al₂O₃.

follows from the values given in Table III, the thermal resistances of other resins and compositions are similar. Homopolymerization temperature, maximum homopolymerization temperature, initial decomposition temperature, mass loss in percentage, and temperature at which the highest rate of resin decomposition takes place were determined from the curves of thermal derivatographic analysis (TGA).

From differential thermal analysis (DTA) of uncured resins, an exothermic reaction is detected in the range 180–320°C and indicates a homopolymerization reaction of epoxy groups. A fairly sharp onset of weight loss is noted at 210–250°C. The upper limits of stability of both uncured and thermally or chemically cured resins appear to be governed by the stability of the thioether linkage. Decomposition of polymers gives hydrogen sulfide which identifies the thioether linkage as the weakest linkage in the chain.

Chemical Curing of Resins

Chemical curing of thioether glycidyl resins was hot-setting using acid anhydride and cold-setting using aliphatic amine. The chemical structures of the compounds determined from stoichiometric calculations (0.85 mol anhydride per epoxide equivalent) and curing conditions are given in Table IV. Time of

TABLE VI
Thermal and Mechanical Properties of the Cured Compositions

Test	BGTMEPE			BGTMPM		
	TETA	HY-905	NMA	TETA	HY-905	NMA
Vicathermal resistance after Martens, °C	52	64	94	58	59	91
Softening temp. Vicat, °C	62	72	107	69	68	105
Bending strength, MPa	120.8	95.2	149.6	123.5	88.8	108.8
Compressive strength, MPa	101.6	126.5	129.2	111.1	111.7	113.3
Tensile Strength, MPa	67.5	37.8	30.6	70.5	57.6	44.3
Brinnell hardness, MPa	125	198	96	152	201	145
Charpy impact, kJ/m ²	137	203	97	126	157	87

resin gelation with curatives in relation to the temperature is shown in Table V.

To examine the application of cured resins, some cast profiles were prepared. After mixing the components at the increased temperature, the compound was vented in the vacuum desiccator, poured into a metal mold covered with an antiadhesive coating of silicone varnish, and cured. Cast profiles obtained according to Polish standards were studied to determine their thermal mechanical properties which are presented in Table VI. It can be seen that DGTMEPE and DGTMPM resins can be cured by means of common curatives used for ether glycidyl resins.

On the basis of the determined gelation time, we can say that compounds cured in cold-setting TETA reveal good technological and processing properties at 25–35°C, but those cured with anhydride are good at 60–70°C. The compounds cured by NMA are characterized by a longer gelation time.

DGTMEPE and DGTMPM resins are characterized by a lower temperature of deflection according to Martens, greater bending strength, and better impact strength compared to resin derivatives of naphthalene.¹ It is due to greater mobility of chain segments caused by additional bridges (—CH₂— or —O—) between resin aromatic rings, which gives elasticity to a polymer chain.

The technological, processing, and mechanical properties of thioether glycidyl resins are dependent on the curative. This fact should be taken into account in cast resin, laminated plastics, glue, and varnish coat production.

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