Thioether Glycidyl Resins. VII.* Products of Condensation of Bis(4-Mercaptophenyl)Sulfide and Bis(4-Mercaptophenyl)Sulfone with Epichlorohydrin

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Synopsis

New thioether glycidyl resins by condensation of bis(4-mercaptophenyl)sulfide or bis(4-mercaptophenyl)sulfone with epichlorohydrin were obtained by heterophase alkaline condensation in aqueous and isopropanol medium using sodium hydroxide. The detailed studies on their structures from elemental analysis and IR and[1]H-NMR spectra, physical and chemical properties, and curing conditions are presented. Thioether glycidyl resins compositions were also prepared using curatives typical for epoxy resins and after curing they were characterized from derivatographic, thermomechanical, and mechanical studies.

INTRODUCTION

Thioether glycidyl resins are obtained by heterophase alkaline condensation of dithiol derivatives of aromatic hydrocarbons with epichlorohydrin in the aqueous-isopropanol medium of alkaline hydroxide. To synthesize the resins of this type, mercaptocompounds including the thiol groups directly connected with the aromatic ring or separated by the methylene group can be used. In the investigations up till now, dithiol derivatives of naphthalene, diphenyl, xylenes, and combinations possessing benzene bridges in the form of a methylene group or oxygen between rings, i.e., diphenylmethane or diphenyloxide, were used.[1,2]

Within this field, studies on synthesis of new thioether glycidyl resin derivatives of dithiols including an additional sulfur atom or SO_2 group were undertaken using diphenylsulfide as an initial compound.

The main aim of this paper is synthesis, determination of structure, and basic physicochemical properties as well as applicability of thioether glycidyl resins prepared by condensation of dithiols–diphenylsulfide or diphenylsulfone derivatives with epichlorohydrin. Bis(4-mercaptophenyl)sulfide or bis(4-mercaptophenyl)sulfone were used as substrates.

Based on the results obtained from the model systems; the following resins were prepared: bis[4(2,3-epoxypropylthio)phenyl]-sulfide [bis(4-glycidylthiophenyl)-sulfide (BGTPhS)] and bis[4-(2,3-epoxypropylthio)phenyl]-

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sulfone[bis(4-glycidylthiophenyl)-sulfone (BGTPhSO$_2$)]. The investigations also covered determination of some properties of resins cured thermally or chemically by means of curatives typical for epoxy resins as well as determination of thermal and mechanical properties of the cured compounds.

It should be noted that thioether glycidyl resin of bis(4-mercaptophenyl)sulfide has already been obtained by condensation with epichlorohydrin in an aqueous solution of sodium hydroxide.[3] The resin prepared by this method was a brittle solid of a very reduced epoxide content.

EXPERIMENTAL

Reagents

During the synthesis of bis(4-mercaptophenyl)sulfide or bis(4-mercaptophenyl)sulfone, the products obtained by the methods given in the literature[4-9] proved difficult to be purified or exhibited too low a melting point.

The attempt to find suitable methods for the synthesis of the above-mentioned dithiols was successful employing reduction of bis(4-chlorosulfonylphenyl)sulfide or sulfone by stannous chloride in acetic acid saturated with gaseous hydrogen chloride by the Marvell–Caesar[10] method used to prepare bis(4-mercaptophenyl)oxide.

The initial product in the synthesis of both mercaptocompounds was diphenylsulfide, which was treated with sulphuric acid at 100–110°C for 12 h. Then the reaction mixture was neutralized by sodium carbonate solution and grained out by sodium chloride, giving sodium salt of diphenylsulfidedisulfone-4,4′ acid.[11] The salt was subjected to the action of phosphorus pentachloride in the presence of phosphorus oxychloride, giving bis(4-chlorosulfonylphenyl)sulfide, which after crystallization from acetic acid had the form of colorless plates of mp 157–158°C.[6]

Another initial compound to prepare bis(mercaptophenyl)sulfone, i.e., bis(4-chlorosulfonylphenyl)sulfone, was obtained by the method worked out in our laboratory by means of oxidation of bis(4-chlorosulfonylphenyl)sulfide with 30% hydrogen peroxide in acetic acid at 85°C. The crude reaction product after crystallization from acetic acid (1 g with 55 mL of the solvent) had a form of a colorless fine crystalline plate of mp 266–268°C[12] (lit.[13] mp 218–220°C).

Epichlorohydrin (1-chloro-2,3-epoxypropane) boiling at 114–117°C, manufactured by Fluka AG, Buchs SG, 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.

Measurement of Properties

Spectral Analysis. The infrared (IR) spectra were obtained with a Beckman 42-40 spectrophotometer.^{1}H-NMR spectra were carried out with a Tesla BS-487-C apparatus, frequency 80 MHz: reference, TMS; solvent, CDCl^3; temperature, 25°C.

Thermogravimetric Analysis. Measurement of weight loss was conducted in a MOM derivatograph (Paulik, Paulik, and Erdey, Budapest). Heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 mg; measurements related to Al_2O_3.

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

Bis(4-Mercaptophenyl)Sulfide Synthesis. Into a flask of 2 L volume, equipped with a stirrer and thermometer, 400 g (1.8 mol) of dihydrate stannous chloride and 1600 mL of glacial acetic acid were placed which were saturated with gaseous hydrogen chloride. Then the flask content was heated to 75°C, and 55 g (0.114 mol) of bis(4-disulfonylphenyl)sulfide were added in portions. Heating was continued at 80–90°C for 30 min. After cooling to 50°C, the flask content was poured into 1200 mL of 36% hydrochloric acid. The separated sediment was filtered and crystallized with cyclohexane (300 mL). Slightly yellow plates of mp 116–118°C (lit.[6] mp 118°C) and a yield of 30 g (83%) were obtained.

The same reaction was also carried out in the reactor of 15 L volume produced by Simax using seven times as many reagents. The yield of the obtained bis(4-mercaptophenyl)sulfide was 88%.

Bis(4-Mercaptophenyl)Sulfone Synthesis. Bis(4-mercaptophenyl)sulfone was also prepared by reduction of bis(4-chlorosulfonylphenyl)sulfone in the same way as bis(4-mercaptophenyl)sulfide. In this case, 32 g (0.077 mol) of sulfonylchloride were reduced. The crude product (20 g) after crystallization from benzene (1 g of the product from 7 mL of the solvent) had mp 142–144°C (lit.[9] mp 138–140°C) and yield 16 g (73%).

Bis[4-(2,3-Epoxypropylthio)Phenyl]-Sulfide Resin Synthesis. Into a four-necked flask of 500 mL volume, equipped with a mechanical stirrer, reflux condenser, thermometer, and dropper, 50 g (0.2 mol) of bis(mercaptophenyl)sulfide, 180 g (1.9 mol) of epichlorohydrin, 120 (2.0 mol) of isopropanol were placed and heated in the water bath to 60°C. Then the first portion of 50 mL of 20% sodium hydroxide solution was dropped in very carefully as an addition catalyst. After 10 min, another portion of 120 mL of 20% sodium hydroxide solution was added for 5 min and stirred for another 10 min. The organic layer was separated in a distributor and the solvent and epichlorohydrin excess were distilled off under the reduced pressure (12 Torr). The remaining epichlorohydrin was distilled off in an azeotropic way under the reduced pressure, adding 2 × 20 mL of toluene into the resin before filtration while heating. Seventy-eight grams of light brown thioether glycidyl resin of the epoxide content 0.53 val/100 g (the theoretical epoxide content 0.55 val/100 g) and viscosity 180 cP at 25°C were obtained.

Bis[4-(2,3-Epoxypropylthio)Phenyl]-Sulfone Resin Synthesis. Into a four-necked flask of 500 mL volume equipped with a mechanical stirrer, reflux condenser, and dropper, 56 g (0.2 mol) of bis(4-mercaptophenyl)sulfone, 180 g

(1.9 mol) of epichlorohydrin, and 120 g (2 mol) of isopropanol, were placed and heated in the water bath to 60°C. Then 5 mL of 20% solution of sodium hydroxide as an addition catalyst was dropped in. After 10 min another portion 120 mL of 20% solution of sodium hydroxide was added and stirred for another 10 min. The organic layer was separated in a distributor; the solvent and epichlorohydrin excess were distilled off under the reduced pressure (12 Torr).

The resin was dissolved in 50 mL of benzene and filtered, and, after stripping under the reduced pressure, thioether glycidyl resin, solidifying at room temperature, of the epoxide content 0.49 val/100 g was obtained. After crystallization from carbon tetrachloride (1 g of substance in 50 mL of solvent), 49 g of crystalline compound (plates) of mp 73–75°C and epoxide content 0.50 val/100 g were obtained. The resin dissolves well in toluene, epichlorohydrin, and dioxane, moderately in carbon tetrachloride, and poorly in methanol and ethanol.

RESULTS AND DISCUSSION

Studies on Thioether Glycidyl Resin Structures

The chemical structure of BGTPhS resins of the epoxide content 0.53 val/100 g and viscosity 180 cP at 25°C (Fig. 1) and BGTPhSO$_2$ of the epoxide
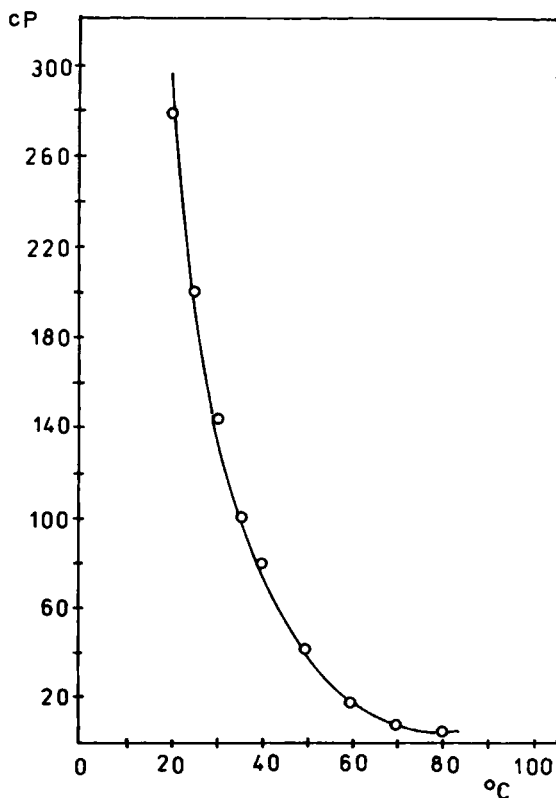

Fig. 1.   Viscosity of BGTPhS resin in relation to temperature.

TABLE I
Results of Elemental Analysis

Thioether glycidyl resins	Analysis					
	%C		%H		%S	
	Calcd	Found	Calcd	Found	Calcd	Found
BGTPhS	59.63	59.41	5.00	4.82	26.53	26.76
BGTPhSO$_2$	54.80	54.98	4.60	4.68	24.38	24.45

content 0.50 val/100 g and 73–75°C was determined from the analytical and spectral data. Elemental analysis (Table I) for C, H, and S showed the agreement with theoretical values.

IR spectra of the resins showed characteristic valency vibrations of the molecule aromatic fragments ν 3070 cm^{-1} and deformation vibrations of the benzene ring which have sharp peak forms of various intensities below ν 1600 cm^{-1}. Combination vibrations at ν 817 cm^{-1} characteristic for the benzene ring, which univocally confirm para substitution, are of particular importance. ν (C—S—C) assignment in IR spectra proves to be difficult.[14]

However, IR spectra of BGTPhSO$_{22}$ show characteristic valency and —SO$_2$— deformation vibrations: ν_{as} at 1310 cm^{-1}, ν_s at 1160 cm^{-1}, and deformation vibrations at 580 cm^{-1} or at ν 550 cm^{-1}, which correspond to bending and oscillatory vibrations of the —SO$_2$— group.

The spectra of both resins showed strong adsorption bands at 1270–1250, 950–920, and 840–820 cm^{-1} characteristic of the epoxy valency vibrations.

^{1}H-NMR spectroscopic studies of the resins (Figs. 2 and 3) show two basic group signals. The first group δ7.12–7.32 for BGTPhS and δ7.36–7.64 ppm for BGTPhSO$_2$ comes from the aromatic ring protons. The second group δ2.67–3.15 and δ2.76–3.17 comes from glycidyl groups. Intensity ratios for each band calculated from the integration curve are in agreement with the number of magnetically nonequivalent protons in a resin molecule and are 4:4:6:2:2, which equals 18 protons. It should be noted that in the sulfone structure (Fig. 3), multiplet separation corresponding to aromatic protons is observed, which indicates the twist of aromatic ring planes towards each other caused probably by —SO$_2$— group which is in agreement with literature data for this group of compounds.[15,16] Values of proton chemical shifts are given under the spectrum illustrations. Good agreement of elemental analyses and IR and NMR spectra assumes a pure monomeric structure of resins.

Thermal Stability

Thermal stability of new resins was studied by isothermal and dynamic methods. Isothermic studies were carried out, controlling epoxy group loss during heating at 100°C, 110°C, and 120°C. From the curves presented in Figures 4 and 5 it can be seen that reactivity of BGTPhSO$_2$ resin is considerably higher than that of BGTPhS and the rate of thermal curing is affected by temperature.

Some results of studies of uncured and thermally or chemically cured resins using the dynamic method (temperature increase of 10°C/min in air) are presented in Table II.
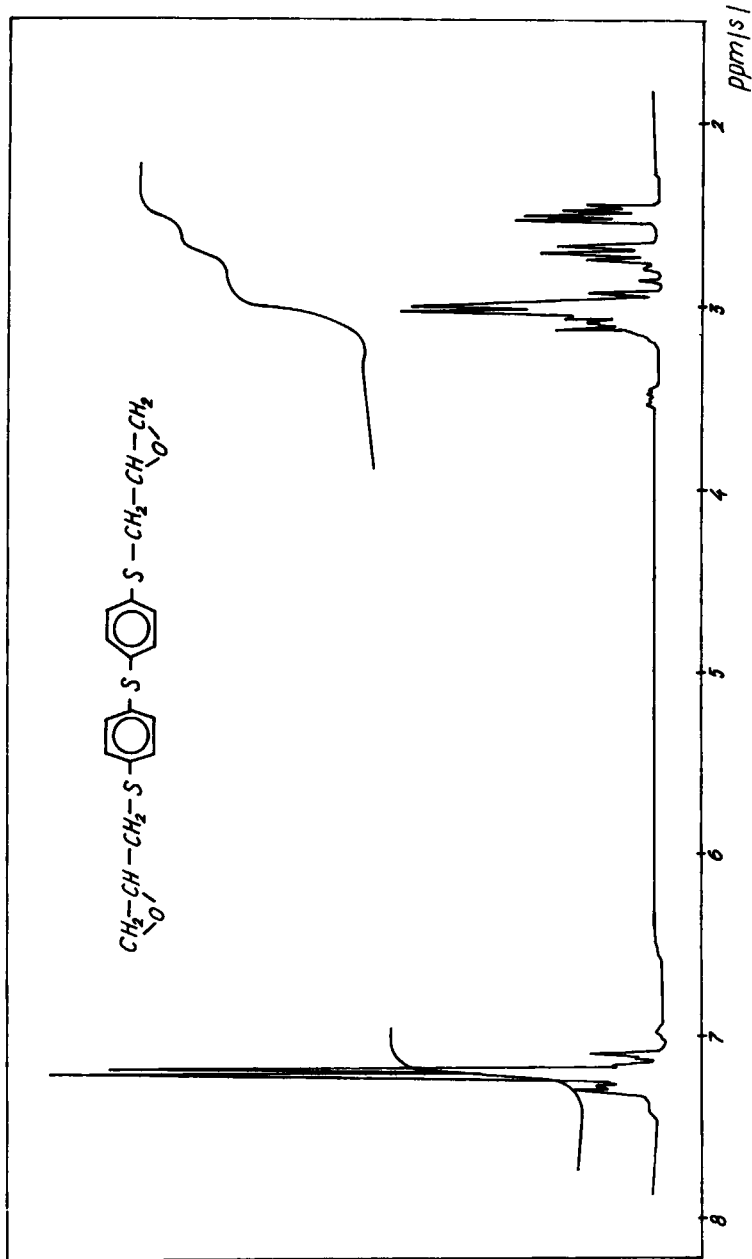
Fig. 2. ^{1}H-NMR spectra of BGTPhS resin. Assignments: δ(aromatic) = 7.32...7.12, δ(CH$_2$—O) = 2.51...2.49, δ(CH$_2$—S) = 3.15...2.92, and δ(CH) = 2.87...2.67 ppm (solvent CDCl$_3$).
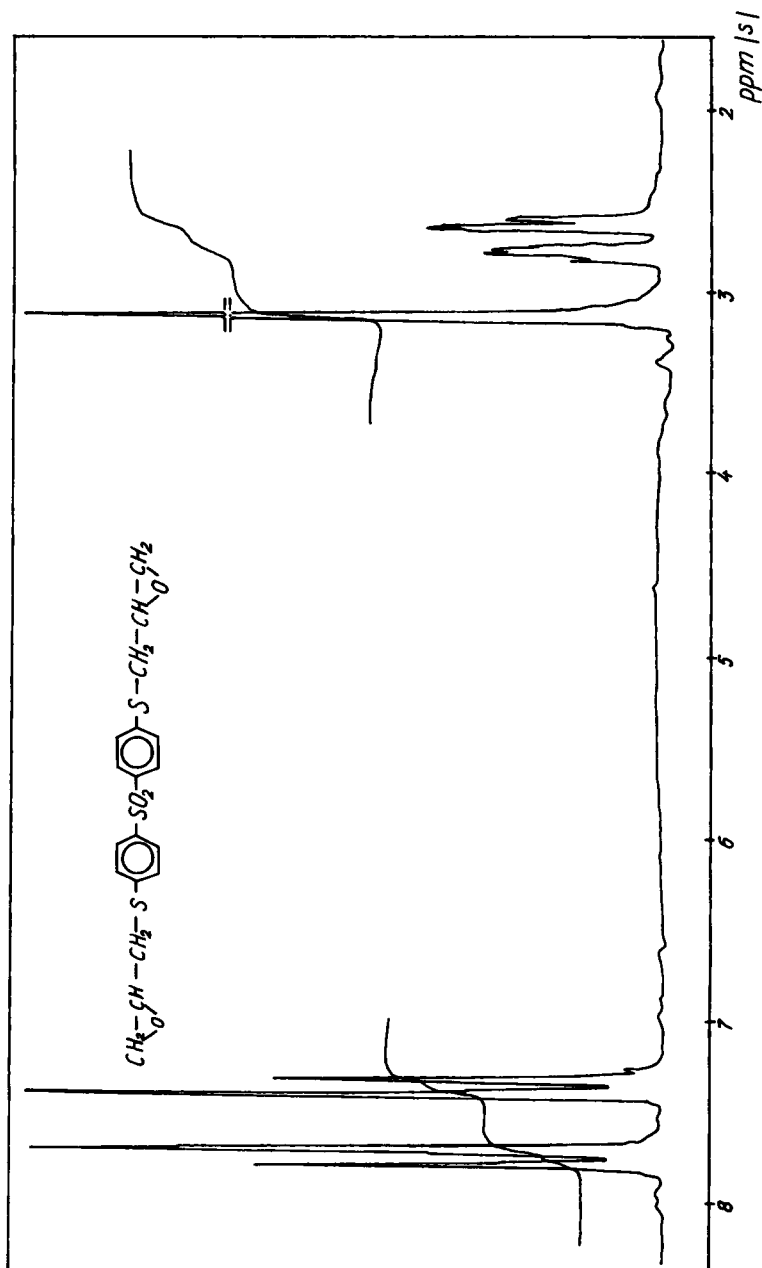
Fig. 3. ^{1}H-NMR spectra of BGTPhSO$_2$ resin. Assignments: δ(aromatic) = 7.84...7.36, δ(CH$_2$—O) = 2.67...2.62, δ(CH$_2$—S) = 3.17...2.96, and δ(CH) = 2.80...2.76 ppm (solvent CDCl$_3$).
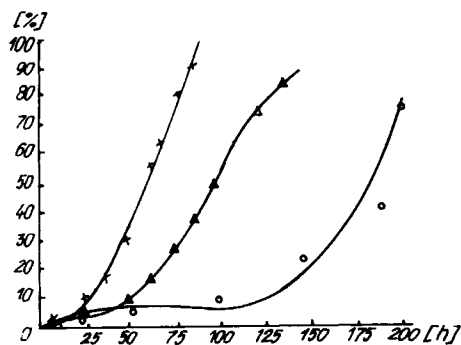
Fig. 4. Loss (%) of epoxy groups of BGTPhS resin in relation to heating time (h) at: (○) 100°C; (△) 110°C; (×) 120°C.
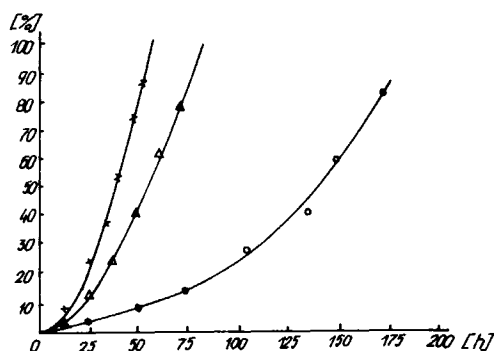

Fig. 5. Loss (%) of epoxy groups of BGTPhSO$_2$ resin in relation to heating time (h) at: (○) 100°C; (△) 110°C; (×) 120°C.

TABLE II
Thermal Resistance of Resis and Composition

Resin	Kind	Epoxy content (val/100 g)	T^a	T^b	T^c	T^d	U^e	T^f
				Thermal analysis (°C)				
BGTPhS	Uncured	0.53	—	260–350	310	265	1.5	345
	Thermal curing	0.10	—	—	—	260	1.0	350
BGTPhSO$_2$	Uncured	0.50	75	280–360	320	285	1.5	360
	Thermal curing	0.15	—	—	—	275	1.0	360
BGTPhS	TETA	—	—	—	—	235	1.5	320
	HY-905	—	—	—	—	230	2.0	335
	NMA	—	—	—	—	200	2.0	340
BGTPhSO$_2$	HY-905	—	—	—	—	270	3.0	345
	NMA	—	—	—	—	230	2.0	360

[a] Melting temperature from the curve DTA.
[b] Homopolymerization temperature from the curve DTA.
[c] Maximum homopolymerization temperature from the curve DTA.
[d] Initial mass loss temperature from the curve DTG.
[e] Mass loss in the temperature T_4 from the curve TG.
[f] Temperature of intensive mass from the curve DTG.

TABLE III
Composition and Cure Conditions for the Epoxy Resin[a]

Resin	Composition no.				
	I	II	III	IV	V
BGTPhS	100	100	100	—	—
BGTPhSO$_2$	—	—	—	100	100
TETA	14	—	—	—	—
HY-905	—	90	—	90	—
NMA	—	—	85	—	85

[a] Cure schedules: (I) 24 h at room temperature, 8 h at 60°C; (II and IV) 2 h at 80°C, 6 h at 120°C, 13 h at 140°C, and 1 h at 160°C; (III and V) 3 h at 80°C, 16 h at 110°C, 8 h at 140°C, and 3 h at 160°C.

Melting point, 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 were determined from the curves of thermal derivatographic analysis (TGA). From differential thermal analysis (DTA) of uncured resins, exothermic reaction is detected in the range 260–360°C and indicates an opening and polymerization reactions of epoxy groups. A fairly sharp onset of weight loss is noted at 230–285°C. The upper limit of stability of both uncured and thermally or chemically cured resins is mainly dependent on thioether linkage stability.

Chemical Curing of Resins

Chemical curing of resins was carried out in cold using aliphatic amine (TETA) and in hot using acid anhydrides (HY-905 and NMA). Chemical structure of the compounds was determined from stoichiometric calculations (0.85 mol of anhydride for an epoxide equivalent). Numerical values and curing conditions are given in Table III.

To examine the application of cured resins, the time of gelation with curatives in relation to the temperature has been determined (Table IV) and some compositions have been prepared whose curing conditions are given in Table III. Cast profiles obtained according to Polish standards were studied to determine their thermomechanical properties, which are presented in Table V.

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

Composition no.		Gelation time (min)								
		25	30	35	70	80 (°C)	90	100	110	120
BGTPhS	TETA (I)	155	110	68	—	—	—	—	—	—
	HY-905 (II)	—	—	—	235	140	110	—	—	—
	NMA (III)	—	—	—	—	—	—	230	155	115
BGTPhSO$_2$	HY-905 (IV)	—	—	—	—	—	—	155	115	85
	NMA (V)	—	—	—	—	—	—	280	180	130

TABLE V
Thermal and Mechanical Properties of Cured Composition

	BGTPhS			BGTPhSO$_2$	
Test	TETA	HY-905	NMA	HY-905	NMA
Vicat thermal resistance after Martens (°C)	46	68	78	76	130
Softening temp after Vicat (°C)	68	76	98	96	146
Bending strength (MPa)	136.2	142.6	90.2	128.8	92.6
Compressive strength (MPa)	128.5	130.7	142.6	143.5	154.6
Tensile strength (MPa)	42.2	23.8	22.4	24.6	20.8
Brinnell hardness (MPa)	13.8	15.4	16.2	13.5	16.6
Charpy impact (kJ/m^2)	15.8	11.6	6.6	10.2	6.2

From the results of these investigations it can be seen that the resins (BGTPhS and BGTPhSO$_2$) can be cured by means of common curatives used for ether glycidyl resins. The determined gelation time indicates good technological processing properties of BGTPhS–TETA at 25–30°C and while curing in hot with anhydrides at 80–120°C, whereas the compositions cured by NMA are characterized by longer gelation time.

From the studied resin and curative compositions, the significant effect of characteristic groups constituted by a sulfur atom or sulfone group placed between phenyl rings of a molecule or in a crosslinking structure can be observed.

Comparing the obtained results of thermomechanical studies (Table V) with those of the resins which are diphenyloxide and diphenylmethane derivatives[2] with the same curatives and under the same conditions, it can be seen that BGTPhS resin is characterized by the highest plasticizing effect while BGTPhSO$_2$ by the lowest.

Using NMA anhydride as a curative causes an increase in thermomechanical resistance and a slight increase in compression resistance while flexibility decreases, which is due to endomethylene bridges in the cured composition.

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