

Thioetherglycidyl Resins. IV. Products of Condensation of Isomeric Di(mercaptomethyl)xylene with Epichlorohydrin*

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Synopsis

Thioetherglycidyl resins produced by condensation of isomeric di(mercaptomethyl)xylene with epichlorohydrin were obtained by heterophase alkaline condensation in water and isopropyl alcohol solution using sodium hydroxide. The structure of thioetherglycidyl resins was determined by elemental analysis, infrared, and NMR spectra, and their physical and chemical properties were defined. Some properties of the resins, cured chemically or thermally with typical for epoxy resins, and thermal and mechanical properties of the cured compounds were determined.

INTRODUCTION

The previous paper presented the studies on the synthesis, structure, and properties of thioetherglycidyl resins: derivatives of aliphatic-aromatic as well as aromatic thiols and dithiols, derivatives of hydrocarbons, i.e., naphthalene,¹ diphenylmethane,^{2,3} and diphenylether.^{2,3} The model studies on the resin synthesis showed that the method of heterophase, alkaline condensation of thiols with epichlorohydrin in water and isopropyl alcohol solution by sodium hydroxide was the most effective.

The investigations also covered the determination of some properties of resins, uncured and cured, possessing in their structure joined aromatic rings or various groups joining benzene rings, i.e., ethyl or methyl bridges.

This article gives the results of the studies on synthesis, structure, and physical and chemical properties of isomeric thioetherglycidyl resins, derivatives of di(mercaptomethyl)xylene with epichlorohydrin. The effect of structural isomerism of epoxy compounds, derivatives of *o*-, *m*-, and *p*-(mercaptomethyl)xylene on some properties of the resins cured chemically or thermally with typical curatives was defined. Thermal and mechanical properties of the cured compounds were determined.

It should be emphasized that thioetherglycidyl resin 2,5-di(mercaptomethyl)-*p*-xylene was prepared by condensation with epichlorohydrin through the metallic sodium in anhydrous ethanol.⁴ The resin obtained by this method possessed much lower epoxide content.

* Part III is Ref. 3.

EXPERIMENTAL

Reagents

4,5-Di(mercaptomethyl)-*o*-xylene (*o*-DMMX), which melts at 66–67°C, 4,6-di(mercaptomethyl)-*m*-xylene (*m*-DMMX), which melts at 33–36°C, and 2,5-di(mercaptomethyl)-*p*-xylene (*p*-DMMX), which melts at 74–77°C, were obtained from the corresponding chloromethyl derivatives through the thio-uronic salts using various methods, increasing the scale of the process several times and modifying the way of final product isolation.⁵⁻⁹

Epichlorohydrin (1-chloro-2,3-epoxypropane) boiling at 114–117°C, manufactured by Fluka AG, Buchs SG, 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 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 spectra (IR) were obtained with a Beckman 42-40 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 (val/100 g) of resin and determined according to the Polish Norm PN-69/C-8905 by HCl solution in dioxane.

Initial Products and Resin Synthesis

In this article the defined studies of resin synthesis, physicochemical properties of thioetherglycidyl resins, curing conditions, and thermal and mechanical properties of the cured composition were carried out on isomeric di(mercaptomethyl)xylene.

Based on the results of model compound studies¹⁻³ new resins were obtained: 4,5-di(2,3-epoxypropylthiomethyl)-*o*-xylene [4,5-di(glycidylthiomethyl)-*o*-xylene (*o*-DGTMX)], 4,6-di[(2,3-epoxypropyl)thiomethyl]-*m*-xylene [4,6-di(glycidylthiomethyl)-*m*-xylene (*m*-DGTMX)], and 2,5-di[(2,3-epoxypropyl)thiomethyl]-*p*-xylene [2,6-di(glycidylthiomethyl)-*p*-xylene (*p*-DGTMX)].

Isomeric Di(chloromethyl)xylene Synthesis

In a glass reactor "Simax" of 25 L volume equipped with a mechanical stirrer, reflux condenser, thermometer, and heating spiral, 1060 g (10 mol)

of ortho-, meta-, or paraxylene, 1800 g (60 mol) of paraform (aldehyd), and 10,800 mL of hydrochloric acid were placed.

At continuous stirring and addition of gaseous hydrogen chloride from the generator, the temperature of 85°C inside the reactor was kept for 10 h, and then it was increased to 90°C. Stirring was continued for a further 3 h. Then the reaction mixture was cooled to 20°C while stirring aqueous solution was decanted and the chloromethyl compound evolved as precipitate (rice consistency) was dissolved at the temperature of 80°C in cyclohexane (for the isomers: ortho 3500 mL of solvent, meta 4000 mL of solvent, and para 4500 mL of solvent).

Cyclohexane solution after washing with hot water ($2 \times 1,5$ L, 70°C) was left to crystallize. The solvent was decanted from above the sediment, which was then filtered and dried in air. The following compounds were obtained: 4,5-di(chloromethyl)-*m*-xylene, mp 96–98°C, yield 1150 g (lit.¹⁰ 97–98°C); 2,5-di(chloromethyl)-*p*-xylene, mp 130–132°C, yield 900 g (lit.¹⁰ 133°C); 4,5-di(chloromethyl)-*o*-xylene, mp 103–105°C, yield 750 g, (lit.¹⁰ 105–106°C).

Isomeric Di(mercaptomethyl)xylene Synthesis

Into a flask of 2 L volume, 168 g (2.2 mol) of powdered thiocarbamide and 800 mL of dioxane were placed. The hot solution in the amount of 203 g (1 mol) of ortho, meta, or para of di(chloromethyl)xylene in 400 mL of dioxane was added at 80°C with continuous stirring. Shortly afterwards, the evolved sediment of thiouronic salt was further heated for 1 h, and then filtered and dried in air. Then 356 g of isomeric ortho, meta, or para of thiouronic salt was dissolved in 1600 mL of water and 240 g (6 mol) of NaOH dissolved in 300 mL of water was added at 40°C.

After heating for 1 h till mild boiling took place, the solution was cooled to room temperature, filtered, and then 600 mL of hydrochloric acid was added. Evolved as oil, mercapto compound which after cooling and stirring solidified was washed with water, filtered, and dried in air. The yields of the isomers, ortho, meta, and para, were 180 g, 175 g, and 185 g, respectively.

After twice done crystallization from isopropyl alcohol there were obtained: 4,5-di(mercaptomethyl)-*o*-ksylene, mp 66–68°C (lit.^{6,9} 68–69°C); 4,6-di(mercaptomethyl)-*m*-xylene, mp 46–48°C (lit.^{7,9} 48–50°C); and from ethanol there was obtained 2,5-di(mercaptomethyl)-*p*-xylene, mp 75–77°C (lit.⁸ 74.5–77.5°C).

TABLE I
Results of Elemental Analysis

| Thioetherglycidyl resins | Analysis | | | | | |
|-----------------------------|----------|-------|-------|-------|-------|-------|
| | % C | | % H | | % S | |
| | Calcd | Found | Calcd | Found | Calcd | Found |
| <i>o</i> -DGTMX | | 61.88 | | 6.68 | | 20.79 |
| <i>m</i> -DGTMX | 61.89 | 61.73 | 7.14 | 7.62 | 20.65 | 20.28 |
| <i>p</i> -DGTMX | | 61.70 | | 7.57 | | 20.53 |

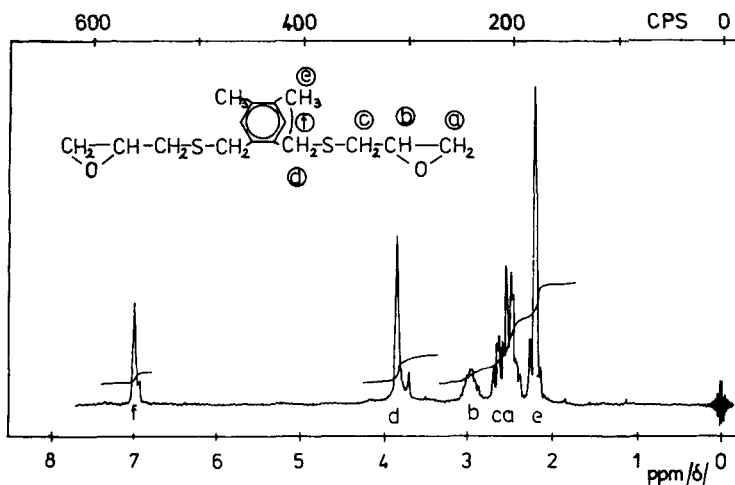


Fig. 1. NMR spectra of *o*-DGTMX resin. Assignments (ppm): $\delta_e = 2.17$; $\delta_{ac} = 2.30$ – 2.82 ; $\delta_b = 2.95$; $\delta_d = 3.82$; $\delta_f = 6.95$.

Isomeric Thioetherglycidyl Resin Synthesis

Into a round-bottom flask of 1 L volume, equipped with a mechanical stirrer, reflux condenser, thermometer, and dropper, 69.3 g (0.35 mol) of *o*-DMMX, *m*-DMMX, or *p*-DMMX, 185 g (2.0 mol) of epichlorohydrin, 120 g (2.0 mol) of isopropanol were added and heated in the water bath to 60°C. Then the first portion, 12 mL of 15% solution of sodium hydroxide as an addition catalyst, was dropped in carefully. After 10 min the second portion, 280 mL 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 epichlorohydrin were distilled under the reduced pressure (12 Torr). The remaining epichlorohydrin was distilled in an azeotropic way

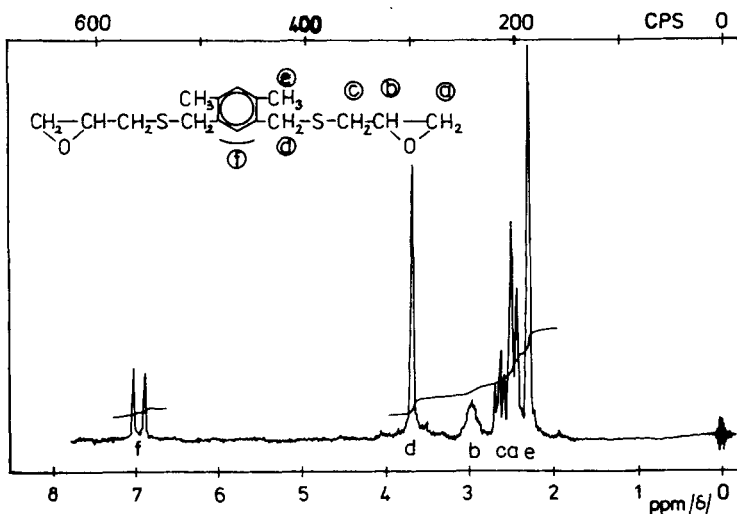


Fig. 2. NMR spectra of *m*-DGTMX resin. Assignments (ppm): $\delta_e = 2.30$; $\delta_{ac} = 2.35$ – 2.70 ; $\delta_b = 2.97$; $\delta_f = 6.95$.

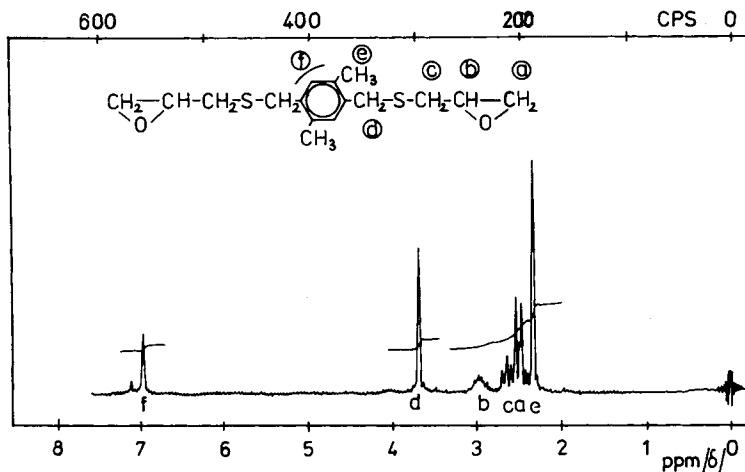


Fig. 3. NMR spectra of *p*-DGTMX resin. Assignments (ppm): $\delta_e = 62.32$; $\delta_{ac} = 2.37-2.72$; $\delta_b = 2.97$; $\delta_f = 6.95$.

under the reduced pressure adding 2×20 mL of toluene into resin and filtered when heated. There were obtained 115 g of *o*-DGTMX as oil of the epoxide content, 0.60 val/100 g or 113 g of *m*-DGTMX as oil of the epoxide content, 0.59 val/100 g or 108 g of *p*-DGTMX as solidifying oil of the epoxide content 0.60 val/100 g.

RESULTS AND DISCUSSION

Studies of Thioetherglycidyl Resin Structure

Chemical structure of the resins: *o*-DGTMX of the epoxide content 0.59 val/100 g (the theoretical epoxide content 0.64 val/100 g) and viscosity 225 cP at 25°C, *m*-DGTMX of the epoxide content 0.60 val/100 g and viscosity 260 cP at 25°C, and *p*-DGTMX of the epoxide content 0.60 val/100 g and mp 93°C (derivatographic analysis) was defined from the analytical and

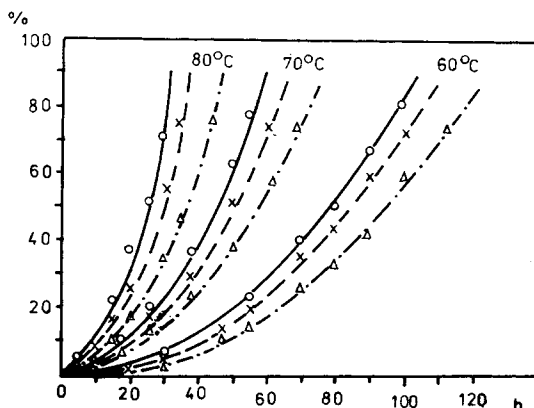


Fig. 4. Loss (%) of epoxy groups of *o*-DGTMX (---), *m*-DGTMX (—), and *p*-DGTMX (- · -) resins in relation to heating time (h) at 60, 70, and 80°C.

TABLE II
Thermal Resistance of the Resins and Compositions

| Resin | Kind | Epoxy content | Thermal analysis (°C) | | | | | T_5^f |
|---------|----------------|---------------|-----------------------|---------|---------|---------|-------|---------|
| | | | T_1^a | T_2^b | T_3^c | T_4^d | U^e | |
| o-DGTMX | Uncured | 0.59 | — | 190-260 | 240 | 260 | 14 | 310 |
| | Thermal curing | 0.14 | — | — | — | 250 | 4.0 | 320 |
| m-DGTMX | Uncured | 0.60 | — | 190-270 | 240 | 280 | 12 | 310 |
| | Thermal curing | 0.12 | — | — | — | 280 | 5.0 | 310 |
| p-DGTMX | Uncured | 0.60 | 93 | 210-290 | 250 | 280 | 6.0 | 320 |
| | Thermal curing | 0.35 | — | 180-240 | 210 | 270 | 6.0 | 310 |
| o-DGTMX | Thermal curing | 0.20 | — | — | — | 270 | 5.0 | 310 |
| | TETA | — | — | — | — | 230 | 4.0 | 315 |
| m-DGTMX | HY-905 | — | — | — | — | 250 | 1.0 | 310 |
| | NMA | — | — | — | — | 260 | 1.0 | 340 |
| p-DGTMX | TETA | — | — | — | — | 270 | 1.5 | 330 |
| | HY-905 | — | — | — | — | 280 | 1.0 | 330 |
| p-DGTMX | NMA | — | — | — | — | 260 | 1.5 | 340 |
| | HY-905 | — | — | — | — | 280 | 1.0 | 340 |
| | NMA | — | — | — | — | 290 | 1.5 | 340 |

^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 in the temperature T_4 from the curve TA.

^e Mass loss in the temperature T_4 from the curve TG.

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

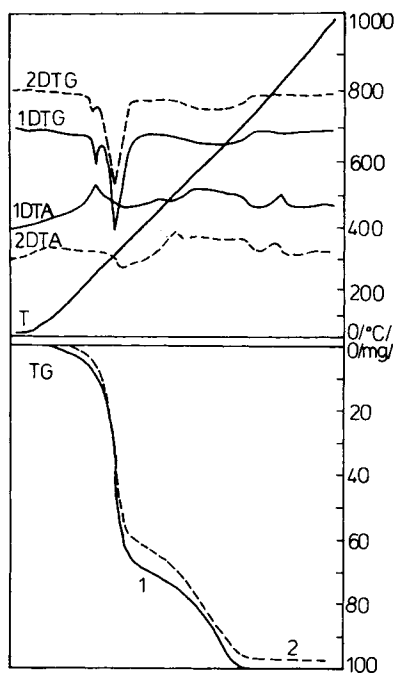


Fig. 5. TGA and DTA of uncured and thermally cured resin *o*-DGTMX of epoxy contents 0.59 (—) and 0.14 (---). Heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 mg; measurements related to Al_2O_3 .

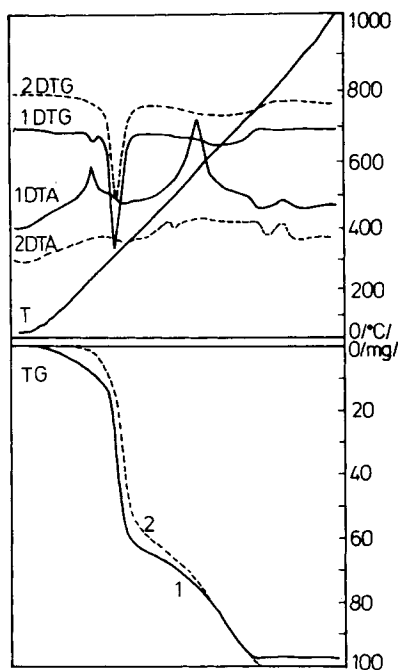


Fig. 6. TGA and DTA of uncured and thermally cured resin *m*-DGTMX of epoxy contents 0.60 (—) and 0.12 (---). Heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 mg; measurements related to Al_2O_3 .

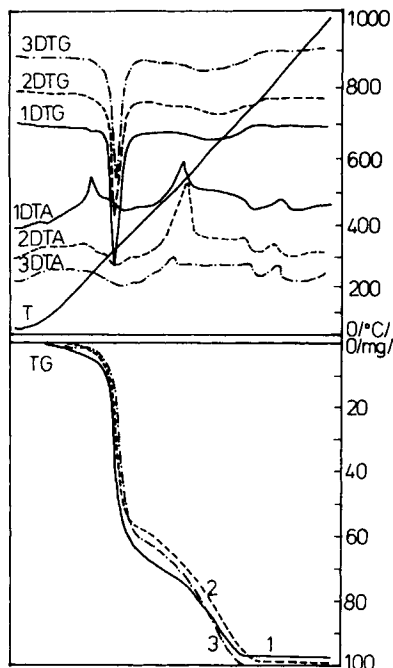


Fig. 7. TGA and DTA of uncured and thermally cured resin *p*-DGTMX of epoxy contents 0.60 (—), 0.35 (---), and 0.20 (- · -). Heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 mg; measurements related to Al₂O₃.

spectral data. Elemental analysis (Table I) for C, H, and S showed the agreement with the theoretical values.

IR spectra of the resins showed strong adsorption at 1240–1260, 925–950, and 850–840 cm⁻¹, which are characteristic of the epoxy valency band and at 1420–1410 and 1240–1220 cm⁻¹, which is characteristic of —S—CH₂ groups.

The ¹H-NMR spectroscopic studies of the resins (Figs. 1–3) show three

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

| Resin | Composition no. | | | | | | | |
|-----------------|-----------------|-----|-----|-----|-----|-----|-----|------|
| | I | II | III | IV | V | VI | VII | VIII |
| <i>o</i> -DGTMX | 100 | 100 | 100 | — | — | — | — | — |
| <i>m</i> -DGTMX | — | — | — | 100 | 100 | 100 | — | — |
| <i>p</i> -DGTMX | — | — | — | — | — | — | 100 | 100 |
| TETA | 14 | — | — | 14 | — | — | — | — |
| HY-905 | — | 100 | — | — | 100 | — | 100 | — |
| NMA | — | — | 95 | — | — | 95 | — | 95 |

^a Cure schedules: (I and IV) 48 h at room temperature, 24 h at 60°C; (II, V, and VII) 6 h at 90°C, 16 h at 120°C, 4 h at 140°C, and 3 h at 150°C; (III, VI and VIII) 6 h at 90°C, 16 h at 120°C, 4 h at 140°C, and 3 h at 160°C.

TABLE IV
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 |
| <i>o</i> -DGTMX | | | | | | | | |
| TETA | I | 470 | 235 | 75 | — | — | — | — |
| HY-905 | II | — | — | — | 68 | 26 | 18 | — |
| NMA | III | — | — | — | — | 180 | 110 | 65 |
| <i>m</i> -DGTMX | | | | | | | | |
| TETA | IV | 420 | 215 | 55 | — | — | — | — |
| HY-905 | V | — | — | — | 85 | 32 | 22 | — |
| NMA | VI | — | — | — | — | 200 | 120 | 70 |
| <i>p</i> -DGTMX | | | | | | | | |
| HY-905 | VII | — | — | — | 95 | 35 | 25 | — |
| NMA | VIII | — | — | — | — | 150 | 90 | 38 |

group signals: the first signal $\delta_{6.95 \text{ ppm}}$ comes from the aromatic ring, the second group of signals $\delta_{3.82-230 \text{ ppm}}$ comes from the glycidyl group and the third one $\delta_{2.32-2.17 \text{ ppm}}$ from CH_3 group. 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 2:4:2:8:6, which equals 22 protons. The values of proton chemical shifts are given under the figures presenting the spectra.

On the basis of good agreement of the found and calculated elemental analysis results and the IR and NMR spectra, a resin structure of the type of a pure monomeric compound is assumed.

TABLE V
Thermal and Mechanical Properties of Cured Composition

| Test | <i>o</i> -DGTMX | | | <i>m</i> -DGTMX | | | <i>p</i> -DGTMX | |
|---|-----------------|--------|------|-----------------|--------|-------|-----------------|-------|
| | TETA | HY-905 | NMA | TETA | HY-905 | NMA | HY-905 | NMA |
| Vicat thermal resistance after Martens (°C) | 61 | 65 | 95 | 62 | 68 | 100 | 72 | 102 |
| Softening temp. after Vicat (°C) | 74 | 75 | 109 | 73 | 78 | 114 | 79 | 128 |
| Bending strength (MPa) | 59.5 | 62.6 | 53.2 | 45.6 | 57.6 | 36.7 | 88.4 | 56.7 |
| Compressive strength (MPa) | 135.0 | 118.5 | 66.6 | 130.9 | 107.9 | 117.7 | 145.2 | 155.2 |
| Tensile strength (MPa) | 18.8 | 10.3 | 13.9 | 36.8 | 28.8 | 25.0 | 16.7 | 23.6 |
| Brinnell hardness (MPa) | 21.3 | 10.6 | 15.2 | 16.8 | 17.7 | 12.3 | 15.2 | 16.2 |
| Charpy impact (kJ/m^2) | 6.4 | 5.8 | 5.0 | 11.6 | 5.2 | 5.6 | 13.1 | 5.7 |

Thermal Stability

The thermal stability of new resins was determined during controlled heating at the temperatures 60°C, 70°C, and 80°C 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 reactivity of isomeric resins is similar and temperature affects the rate of thermal curing.

Some results of derivatographic analysis are presented in Figures 5–7. As follows from the values given in Table II, the thermal resistances of the compositions are similar. Melting temperature, 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 190–290°C and indicates a homopolymerization reaction of epoxy groups. A fairly sharp onset of weight loss is noted at 250–290°C. The upper limits of stability of both uncured and thermally or chemically cured resins appear to be mainly governed by the stability of the thioether linkage.

Chemical Curing of Resins

Chemical curing of thioetherglycidyl resins was cold-setting using aliphatic amine and hot-setting using acid anhydride. The chemical structures of the compounds determined from stoichiometric calculation and curing conditions are given in Table III. Time of resin gelation with curatives in relation to temperature was determined (Table IV).

To examine the application of cured resins, some compositions of resins and curatives were prepared and cured in the conditions given in Table III. The obtained cost profiles of the cured compositions were studied to determine their thermal mechanical properties according to Polish standards, and the results are presented in Table V. It can be seen that isomeric xylene 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 30–40°C and those cured in hot-setting with anhydride at 80–100°C. The compounds cured by NMA are characterized by a longer gelation time. The resin with the some curatives possess similar thermal mechanical and mechanical properties.

The technological processing and mechanical properties of resin compositions are dependent on the 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 modifiers of other epoxy resins.

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