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Władysław Charmas^a

^a Department of Organic Chemistry and Technology, MCS University, Lublin, Poland

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THIOETHERGLYCIDYL RESINS. CURING OF ALIPHATIC, ALIPHATIC–AROMATIC, AROMATIC THIOETHERGLYCIDYL RESINS WITH ALIPHATIC AMINE AND ACID ANHYDRIDES

Władysław Charmas

Department of Organic Chemistry and Technology,
MCS University, Lublin, Poland

A main aim of the investigations was to determine the relations between structure and composition of cured substances, their stability and thermo-mechanical properties. Two kinds of thioetherglycidyl resins are used. In the first case thioether sulfur is directly bonded with the aromatic ring of naphthalene, isomeric xylene, diphenyl, combinations of diphenylmethane, diphenyloxide, diphenylsulfone, diphenylsulfide types and in the second case sulfur is bonded with the above mentioned compounds through the methylene group. Groups of thioetherglycidyl resins combined directly with the aromatic ring show greater reactivity with the amine curing agent compared with the aliphatic–aromatic systems. In the systems with the curing agents of acid anhydride type this dependence is reversed. Some properties were determined of the resin cured chemically as well as the compositions of thioetherglycidyl and commercial resins of diglycidylether of bisphenol-A.

Keywords: thioetherglycidyl resins, curing, properties

INTRODUCTION

Chemical crosslinking of epoxide resins takes place due to the reaction of functional groups in the resin with the suitably selected curing agent that is a crosslinking one. Choice of the curing agent depends on desirable curing conditions and required properties of the cured resin.

For curing at room temperature (“in cold”) aliphatic polyamines and at 80–100° tertiary amines as well as primary aromatic amines

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Address correspondence to Władysław Charmas, Department of Organic Chemistry and Technology, MCS University, ul. Gliniana 33, 20-614 Lublin, Poland.

("in hot") are used. The use of acid anhydrides requires curing of resins at higher temperatures *i.e.*, at 120–180°C ("in hot").

Kinds of resin and curing agent, curing process temperature and ratio of the resin and the curing agent are important for obtaining a polymer of favourable properties.

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 modulus and simultaneously very little unit elongation at rupture and slight impact strength. Unfavourable properties are exhibited at low temperatures and variable dynamic load.

In the materials of little elasticity and great rigidity, internal stresses are formed often causing cracking of the epoxy resin products.

The decrease of internal stresses so called elasticization can be achieved by means of external plasticization through chemical modification by addition into the resin–curing agent system long aliphatic chains, on ether or thioether compounds, decreasing in this way the vitrification temperature (T_g) of the cured composition.

Internal plasticization proved to be more effective. In this case elasticizing compounds are used, epoxide resin type containing long aliphatic fragments in the molecule, or curatives with similar units chemically built into the spatial lattice of the cured composition. Among the curatives worth mentioning are diamines of long aliphatic chains, polyetheramines, polyaminoamides as well as liquid polysulfides [1–3] (thiorubbers including mercaptan groups –SH) and polysulfides with anhydrides terminal units prepared by the addition of maleic anhydride to polysulfide with mercaptan terminal units [4].

Other elasticizing groups include long aliphatic chains with epoxide terminal units. The effective representatives of this group are diglycidyl ethers of polyglycols, diglycidyl esters of dicarboxylic acids as well as liquid polysulfides (thiorubbers) terminated with glycidyl groups on both sides.

Based on this method, we prepared in our laboratory thioether glycidyl resins by reacting epichlorohydrin in an alkaline medium in the presence of isopropane with the aromatic compound including –SH or –CH₂SH groups in a molecule [6–12].

At present some studies on curing this type of resins have been undertaken.

Unexpectedly, the large reactivity of monomeric thioetherglycidyl resins with curing agents of acid anhydrides type, encouraged the investigations of oxirane ring opening reaction under the effect of temperature.

STRUCTURE AND PROPERTIES OF CROSSLINKED THIOETHERGLYCIDYL RESINS

A main aim of investigations was to determine the relations between structure and composition of cured substances, their stability and thermo-mechanical properties. Knowledge of structure of the obtained thioetherglycidyl combinations together with a quantitative analysis of functional groups and determination of cured compounds properties make it possible to work out a convenient method for their curing.

To study the effect of temperature and chemical composition of individual compounds on reactivity, the gelation time was determined. The obtained results are presented in Figures 1 and 2.

Groups of thioetherglycidyl resins combined directly with the aromatic ring show greater reactivity with the amine curing agent compared with the aliphatic-aromatic systems. In the systems with acid anhydride curing agents this dependence is reversed. Aliphatic-aromatic resins exhibit shorter gelation times than the aromatic analogues due to smaller stability of the epoxide group ring at the increased temperature.

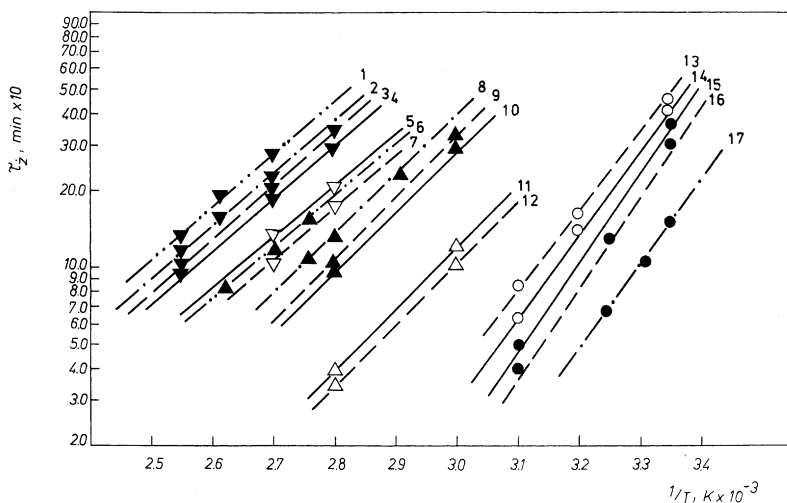


FIGURE 1 Dependence of gelation time of resins with curing agents on temperature: 1-BGTPhSO₂ + NMA, 2-BGTPhS + NMA, 3-DGTPhM + NMA, 4-DGTPhE + NMA, 5-DGTMPPhE + NMA, 6-BGTPhSO₂ + HY-905, 7-DGTMPPhM + NMA, 8-BGTPhS + HY-905, 9-DGTPhM + HY-905, 10-DGTPhE + HY-905, 11-DGTMPPhE + HY-905, 12-DGTMPPhM + HY-905, 13-DGTM-PhM + HY-905, 13-DGTMPPhM + TECZA, 14-DGTMPPhE + TECZA, 15-DGTPhE + TECZA, 16-DGTPhM + TECZA, 17-DGTPhS + TECZA.

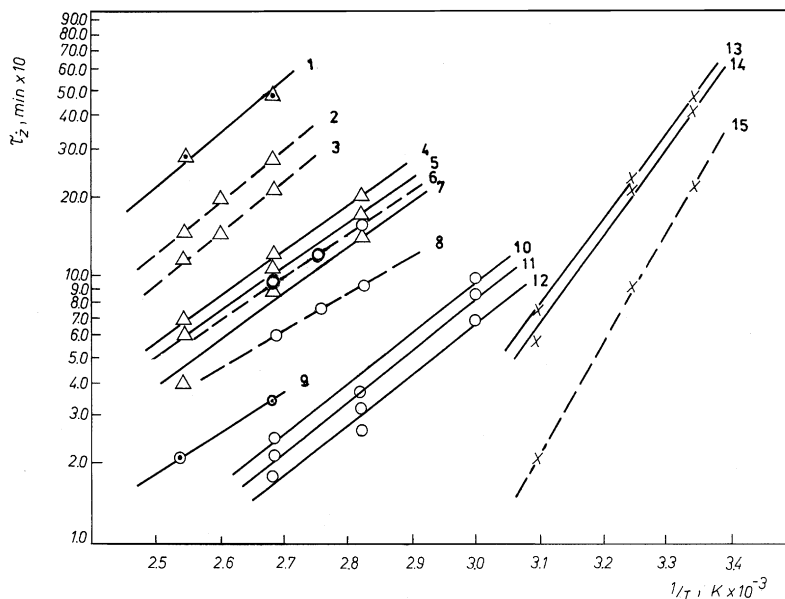


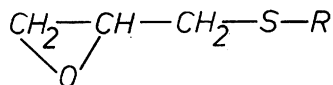
FIGURE 2 Dependence of gelation time of resins with curing agents on temperature: 1-DGTDPh + NMA, 2-1, 4-DGTN + NMA, 3-1, 5-DGTN + NMA, 4-n-DGTMX + NMA, 5-o-DGTMX + NMA, 6-1, 4-DGTN + HY-905, 7-p-DGTMX + NMA, 8-1, 5-DGTN + HY-905, 9-DGTDPh + HY-905, 10-p-DGTMX + HY-905, 11-m-DGTMX + HY-905, 12-o-DGTMX + HY-905, 13-o-DGTMX + TECZA, 14-m-DGTMX + TECZA, 15-1, 4-DGTN + TECZA.

As will be shown below, saturated and unsaturated alcohols are formed more readily from aliphatic–aromatic resins which, in turn, enter the estrification reaction of anhydride groups giving shorter gelation times.

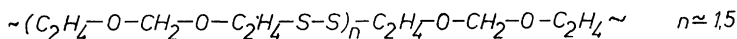
Two kinds of thioetherglycidyl resins are used. In the first case the thioether sulfur is directly bonded with the aromatic ring of naphthalene, isomeric xylene, diphenyl, combinations of diphenylmethane, diphenyloxide, diphenylsulfone, diphenylsulfide types and in the second case the sulfur is bonded with the above mentioned compounds through a methylene group.

The addition reaction of epoxide compounds with curing agents proceeds at high yield, giving crosslinked products whose structural features are important:

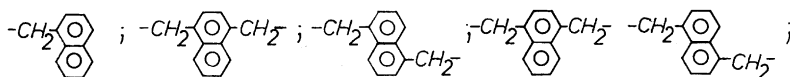
- structure of lattice points and their closest surrounding
- isomerism of rigid fragments location
- crosslinking density



-aliphatic



-aliphatic-aromatic

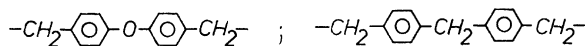


1-GTMN

1,4-DGTMN

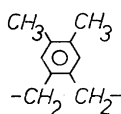
1,5-DGTMN

1,4-,1,5-DGTMN

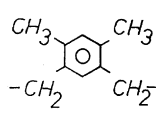


BGTMPHE

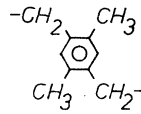
BGTMPHM



o-DGTMX



m-DGTMX



p-DGTMX

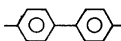
-aromatic



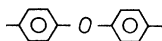
1,4-DGTN



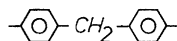
1,5-DGTN



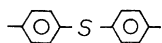
DGTDPH



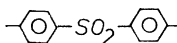
BGTPhE



BGTPhM



BGTPhS



BGTPhSO₂

SCHEME 1

Based on several dozen examples, the possibility of affecting physical and thermomechanical properties of crosslinked compositions using structurally related thioetherglycidyl resins and selected curing agents was pointed out [5–12].

To compare the properties of cured compounds there were applied the amine curing agent triethylenetetraamine (TETA) and the acid

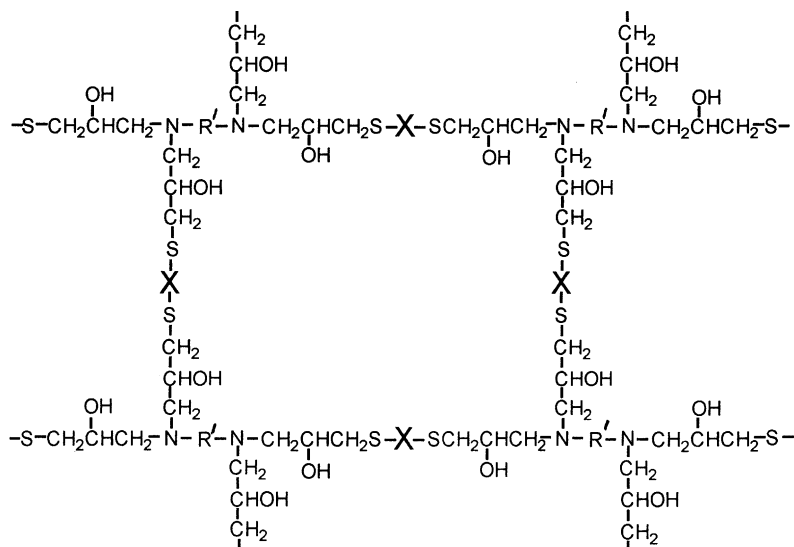
anhydride curing agents: methylbicyclo (2,2,1)hept-5-ene-2,3-dicarboxylic anhydride (NMA) and HY-905 anhydride produced by CIBA.

After mixing and heating (in the case of anhydride curing agents) of specified amounts of resin and curing agent there is formed a cross-linked material of chemical structure determined by the reaction in which rigid fragments (aromatic rings) and aliphatic chain characterized by the areas of higher and lower crosslinking degrees, as in the case of etherglycidyl resins, are found.

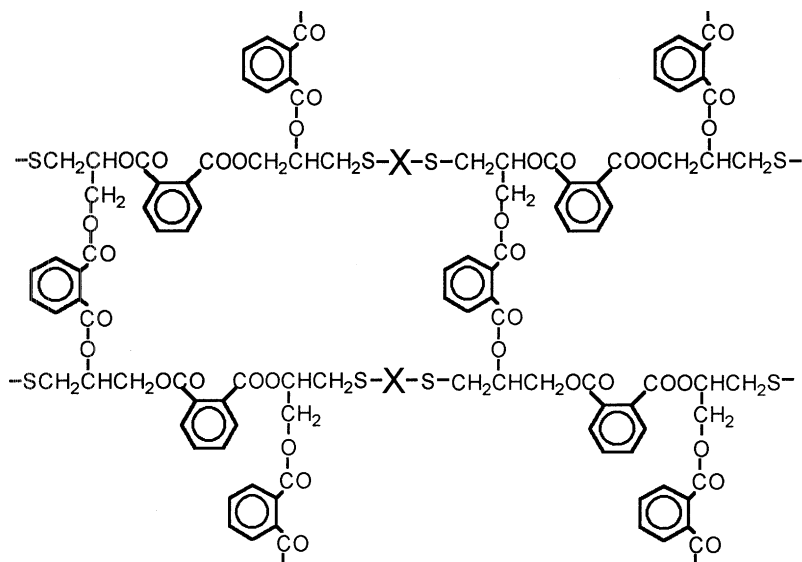
The structure of cured epoxide resin is usually considered in the schematic two-dimensional system while actually 3-dimensional crosslinking occurs. Using such a simplified scheme it is possible to present the chemical structure and length of segments between the lattice points and share of various elements in the structure.

In the case of amine curing in the crosslinked composition at the nitrogen atom constituting a junction point there are four or five mobile groups $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{S}-$ or $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{S}-\text{CH}_2-$

However, in the case of anhydride curing at the junction points there are found $-\text{CH}_2-\text{CH}_2-\text{S}-$ or $-\text{CH}_2-\text{S}-\text{CH}_2-$ groups of reduced motional freedom compared with the previous structure causing significant intensification of thermomechanical properties.



SCHEME 2

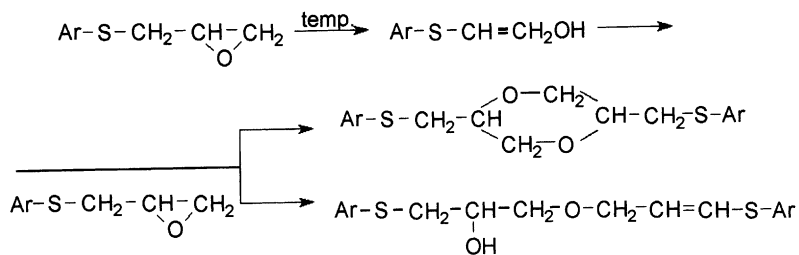


SCHEME 3

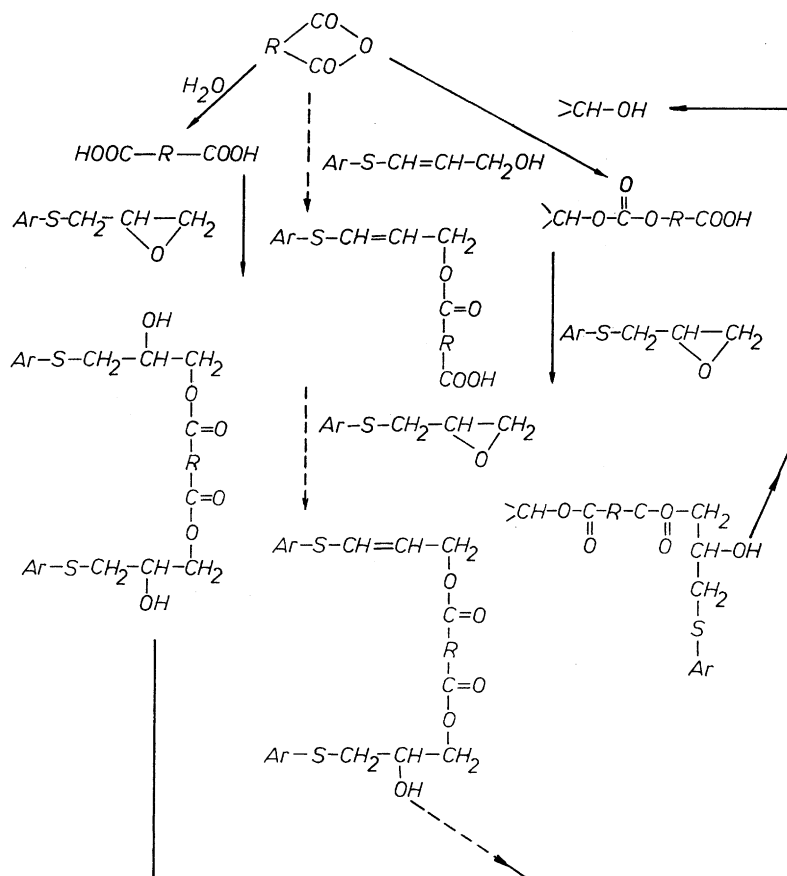
Further stiffening of the network is achieved by introducing endomethylene (NMA anhydride) bridges which make changes of cyclohexane ring shape impossible.

The influence of rigid fragments and net mesh sizes on thermomechanical properties of the cured composition was traced using epoxide compounds of various molecular structure for a given curing agent. The compounds cured using thioetherglycidyl resins-aliphatic-aromatic dimercaptans derivatives are characterized by lower values of thermomechanical resistance than their aromatic analogues. The results of measurements indicate that the increase of crosslinking density (net mesh reduction) using aromatic thiophenols causes a significant increase of Marten's deflection temperature, and Vicat's softening temperature with a simultaneous slight increase of resistance to bending and stretching while impact resistance increases.

The influence of position isomerism was studied using *o*-, *m*- and *p*-xylene derivative resins built into the structural lattice of the material. As follows from the numerical data obtained from derivatographic, thermomechanical and mechanical studies, the compositions are characterized by similar values independent of the kind of isomer. This indicates lack of significant differences in the order level of crosslinked compounds.



SCHEME 4



SCHEME 5

Based on thioetherglycidyl resins it was shown that besides the structures characteristic for etherglycidyl resins there can appear fragments formed due to thermal opening of the oxirane ring *i.e.*, the structure of dioxane type as well as fragments formed from the epoxide group and unsaturated alcohols.

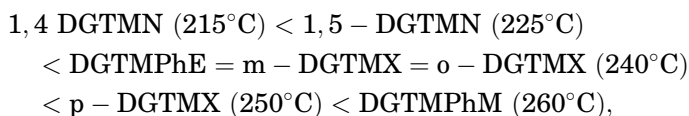
Based on the investigations a cyclic process was proposed of anhydride curing of thioetherglycidyl resins in which the broken line was used to mark the start of curing with moisture and hydroxyl groups derived from high molecular resins. In this circular process all hydroxyl groups formed take part in curing which enables complete reaction of the anhydride curing agent.

Interesting results were obtained from the studies of thermal stability of thioetherglycidyl resins and their compositions cured by isothermal and dynamic methods.

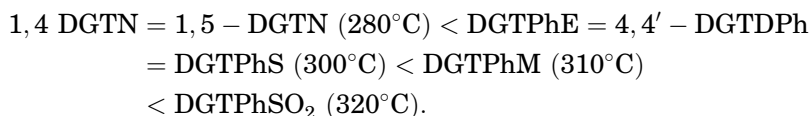
Isothermal investigations were made tracing the epoxide group loss during heating. As follows from the comparison of the curves obtained at different temperatures the temperature affects the oxirane rings reactivity. Comparing the time of 50% epoxide group loss in resin, significant influence of molecular structure on thermal stability can be observed. Resins of aliphatic–aromatic structure are characterized by higher reactivity of the oxirane ring than the aromatic series resins.

The decomposition temperature of the studied resins for the aliphatic and aliphatic–aromatic series is in the range 290–325°C, regardless of the fact that it is estimated from the differential thermal analysis (DTA) curve or from the derivatographic (DTG) curve. It was stated that on the DTA curve there occurs a very distinct exothermic effect characteristic for this type of resins connected with the oxirane ring opening. Projections of this effect on the temperature curve (*i.e.*, exothermic maxima) can be made depending on the resin type as follows:

- resins of the aliphatic–aromatic series:



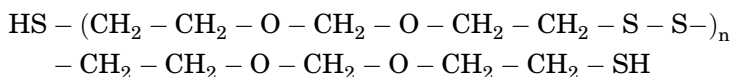
- resins of the aromatic series:



In most cases this order corresponds to the rate of 50% epoxide group loss in the statistical studies and to the time of gelation with anhydride curing agents.

THIOETHERGLYCIDYL RESINS AS MODIFIERS OF ETHERGLYCIDYL RESINS

Based on the method for thioetherglycidyl resins preparation worked out in our laboratory, a new synthesis method was elaborated and the main physico-chemical properties of diglycidyl resin of aliphatic polysulfide of 17% mercaptan group content of the structure:



where $n = 0 - 1$ were determined [12].

There were also determined some properties of thermally or chemically cured resin and the composition of thioetherglycidyl resin with the commercial etherglycidyl resin of bisphenol-A (Epidian-5) (commercial resins of diglycidyl ether of bisphenol-A, produced by Chemical Plant Sarzyna, Poland) was proved and after curing it was characterized by means of derivatographic, thermal-mechanical and mechanical studies.

Moreover, to establish applicability there were determined gelation times of the resin and curing agents (TETA, HY-905 and NMA) compositions depending on temperature. As follows from the obtained results, the aliphatic resin only and its composition with etherglycidyl resin (Epidian-5) are cured by means of common curing agents used for etherglycidyl resins. The determined gelation times exhibit useful technological processing properties in the temperature range 25–40°C curing with amine and at 80–140°C curing with anhydrides.

The compositions cured with NMA are characterized by long gelation times. The increase of aliphatic thioetherglycidyl resin content in the composition with etherglycidyl resin and curing with amine (TETA) causes longer gelation times but curing with anhydride (HY-905, NMA) makes them shorter compared with the pure resin Epidian-5. As shown in the aliphatic–aromatic and aromatic systems of thioetherglycidyl resins this is caused by formation, under the influence of temperature, of unsaturated and saturated alcohols which along with the temperature increase initiate the anhydride curing reaction [6].

Based on the studied compositions a significant influence of such groups as thioether sulfur and aliphatic chains of thioetherglycidyl

resin built into the cured structure was shown. The obtained results of thermal (T_g) and thermal-mechanical (Martens, Vicat) investigations confirm the evident plasticizing effect. The good dilution effect with only a slight decrease of epoxide group content and a significant reduction of pungent smell of the initial thiorubber material was obtained. This indicates good applicability for production of laminar plastics, glues, varnishes and particularly its application as self-spreading floors.

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