

Epoxy Resins Based on Aromatic Glycidylamines.

V. Shelf Life of TGDDM-Based Epoxy Resins

Š. PODZIMEK,¹ I. DOBÁŠ,¹ and M. KUBÍN²

¹Research Institute for Synthetic Resins and Lacquers, CS-532 07 Pardubice, Czechoslovakia, and ²Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, CS-162 06 Prague, Czechoslovakia

SYNOPSIS

The effect of aging on resin composition was investigated as a part of a study concerned with the evaluation of epoxies containing *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM). Long-term stability of three different epoxy resins based on TGDDM and their mixtures with 4,4'-diaminodiphenylsulfone (DDS) was followed at $23 \pm 2^\circ\text{C}$ at a relative humidity ranging from 45% to 55%, by means of GPC and HPLC; short-term stability of the resins was evaluated at 125°C .

INTRODUCTION

Storage stability is an important property of TGDDM-based epoxy resins. The stability of *N*-glycidyl derivatives of aromatic amines is in general lower than that of glycidylethers.¹ Some results concerning the stability of TGDDM-based epoxy resins have already been published.^{2,3} It is the aim of this work to follow the changes which take place during storage of TGDDM-based epoxy resins and of their mixtures with DDS, the most common curing agent, as well as to determine the influence of by-products on their stability.

EXPERIMENTAL

To determine the influence of resin composition on its stability, three different resins were tested: resin A—prepared by a special procedure from 4,4'-diaminodiphenylmethane (DDM),⁴ resin B—a technical product from DDM,⁴ and resin C—a product prepared from aniline.⁵ Some characteristics of the resins are listed in Table I. The stability of mixtures containing 25 wt % of DDS was followed, together with the stability of resins without hardener.

GPC and HPLC

The instrumental equipment for GPC and HPLC as well as the conditions for separation by HPLC of TGDDM-based resins were described in a previous paper of this series.⁴ An aqueous gradient with increasing amounts of methanol and tetrahydrofuran (THF) (30% methanol from 0 to 6 min; 12% THF, 40% methanol at 9 min; 18% THF, 43% methanol at 28 min; 100% THF from 31 to 35 min) was employed for HPLC analysis of the mixtures of resins with DDS. Photometric detection at 275 nm was used for quantitative determination of TGDDM and DDS, because the detector response factors of the two components are approximately the same at this wavelength.

Number-Average Molecular Weight and Viscosity Determination

Viscosity of resins was measured at 25°C with a rotary viscometer Viscotester VT-24 (Haake) in the cone-plate arrangement. A Hewlett-Packard osmometer Model 302-B VPO was used to determine the number-average molecular weights (M_n).

Evaluation of Changes during Storage

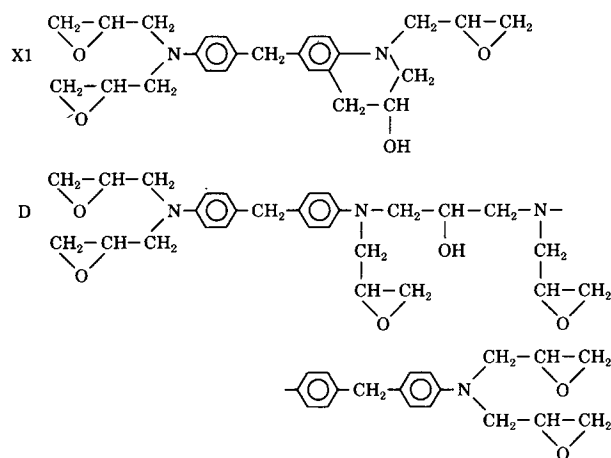
Changes in the composition of resins were followed by determining the contents of TGDDM, 1,2,3,4-

Table I Characteristics of Tested Resins^a

Parameter	Resin		
	A	B	C
Content of epoxy groups (mol/100 g)	0.894	0.858	0.768
Chlorine content (%)	0.26	0.33	0.46
M_n (VPO)	470	500	530
TGDDM content (%)	92.7	73.2	56.1
X1 [HPLC relative area (%)]	0	5.2	17.9
X2 [HPLC relative area (%)]	0.7	1.5	0.1
D [HPLC relative area (%)]	2.1	12.9	—
Oligomers [GPC relative area (%)]	0.4	6.5	7.2

^a For structure of compounds X1, X2, D, and oligomers see reference 4.

tetrahydro-3-hydroxy-quinoline derivative X1, the dimer D, and the oligomers (trimer and higher). The compounds X1 and D were identified in previous work.⁴



The TGDDM content was determined by means of HPLC; the detector response factor was measured with pure TGDDM obtained by semipreparative HPLC. In the determination of compounds X1 and D by HPLC, the response factors of TGDDM, X1 and D were supposed to be the same. The content of oligomers was estimated as the relative area of the oligomer peaks in GPC chromatograms. The stability of resin-DDS mixtures was evaluated from the measured contents of TGDDM and DDS. The detector response factors for the two components were determined by measurements on pure TGDDM and DDS.

RESULTS AND DISCUSSION

Figures 1 and 2 show the changes in the content of TGDDM and of oligomers in resins kept at $23 \pm 2^\circ\text{C}$.

It is apparent that resin A with a low content of byproducts is highly stable, its composition remaining constant over a one-year period. The storage stability decreases with increasing content of byproducts. The increase in the content of oligomers leads to a considerable increase of viscosity (Fig. 3). Figure 4 illustrates the variation in the content of compound X1 in resin C, and of dimer D in resin B. It is apparent that, together with the decrease of TGDDM content, the content of compounds X1 and D also decreases. *N,N,N'*-triglycidyl-4,4'-diaminodiphenylmethane (X2) in resin B fully disappeared after 10 months. It is evident from the results obtained that pure TGDDM is stable at ambient temperature and normal humidity and the instability of resins is caused by the presence of side-products containing functional groups (mostly hydroxyl) capable of reacting with epoxy groups. The formation of a hydrogen bond between the oxygen of the ep-

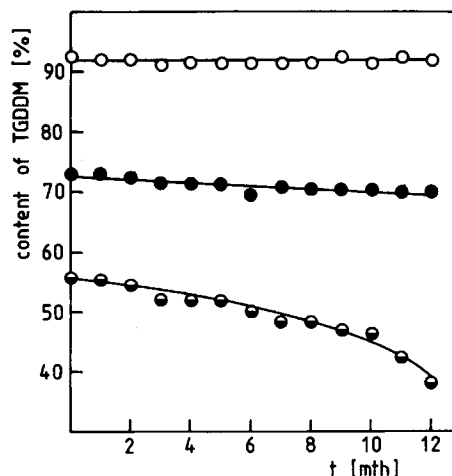


Figure 1 Content of TGDDM in resins as a function of time of exposure at $23 \pm 2^\circ\text{C}$: (○) A; (●) B; (◐) C.

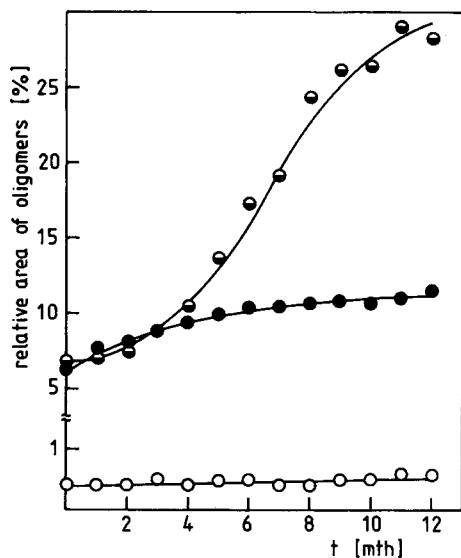


Figure 2 Relative area of oligomers (trimer + higher) in GPC chromatograms of resins plotted against time of exposure at $23 \pm 2^\circ\text{C}$: (O) A; (●) B; (◐) C.

oxide and the hydrogen of the hydroxyl group, is followed by opening the epoxy ring. Products of the reaction of TGDDM with byproducts contain the hydroxyl group and are able to react further with TGDDM and other components in the resins.

The decreasing contents of TGDDM and DDS are shown in Figures 5 and 6. The stability of resin-DDS mixtures is much lower than that of pure resins. The reactivity of TGDDM with respect to DDS depends strongly on the content of by-products. The

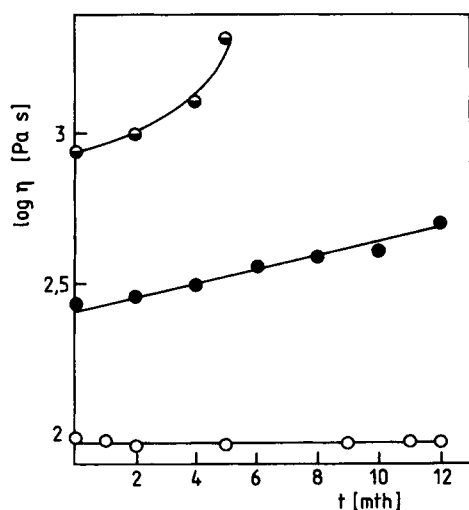


Figure 3 Viscosity of resins as a function of time of exposure at $23 \pm 2^\circ\text{C}$: (O) A; (●) B; (◐) C. (Newtonian behavior was observed up to a shear rate of 100 s^{-1})

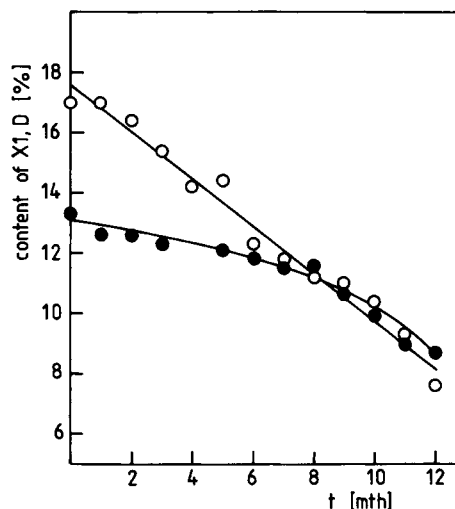


Figure 4 Content of 1,2,3,4-tetrahydro-3-hydroxyquinoline compound X1 (O) in resin C and of dimer D (●) in resin B as a function of time of exposure at $23 \pm 2^\circ\text{C}$.

presence of hydroxyl-containing byproducts accelerates ring-opening reactions by hydrogen bonding. As the mole shortage of DDS is significantly larger than that of TGDDM (see Figs. 5 and 6), some DDS is obviously reacting with byproducts and formed adducts TGDDM-DDS (or other adducts present in the mixture). The starting mole ratios of TGDDM : by-products for resin A and B can be estimated as 1 : 0.07 and 1 : 0.23, respectively. After 6 months the mole ratios of reacted TGDDM : DDS for A and B are 1 : 1.34 and 1 : 1.55. Consequently in both cases at least one-fifth of the lost DDS has reacted with TGDDM-DDS adducts. After one epoxy group

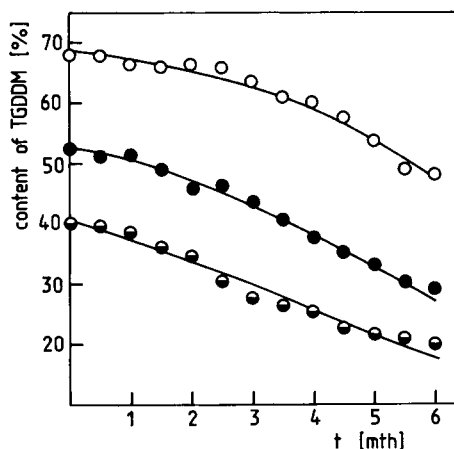


Figure 5 Content of TGDDM in mixtures of resins with DDS as a function of time of exposure at $23 \pm 2^\circ\text{C}$: (O) A; (●) B; (◐) C.

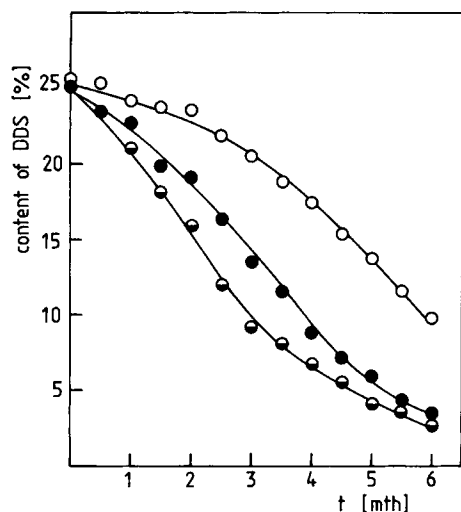
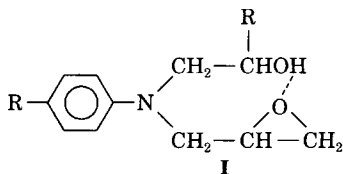


Figure 6 Content of DDS in mixtures of resins with DDS as a function of time of exposure at $23 \pm 2^\circ\text{C}$: (○) A; (●) B; (◐) C.

of TGDDM has reacted with DDS the other becomes activated and reacts more quickly. This positive substitution effect can be explained by the activation of the epoxy group of the adduct TGDDM-DDS by the adjacent hydroxyl group and has been observed in other studies (see structure I)⁶:



Figs. 7 and 8 show the changes in composition during storage at 125°C . An important practical finding is that resins can be heated at 125°C for a short period of time (to reduce their viscosity and to improve processability) without significant changes in their composition. After prolonged thermal treatment at this temperature the composition of all resins changes substantially. Resin C is again the least stable. The drop in TGDDM content in resin C was accompanied by a fall in the content of compound X1 (17% to 10%). The buildup in oligomers is about the same for resins A and B during thermal aging (14% for A and 16.5% for B). The relative loss in the TGDDM content is even greater for A than for B (A, 100% to 80%; B, 100% to 88%). These data indicate that, together with reaction between hydroxyl-containing impurities and TGDDM, other reactions take place at 125°C . The GPC trace for resin A before and after thermal treatment is shown in Figure 9. A dimer (peak 2) and higher oligomers

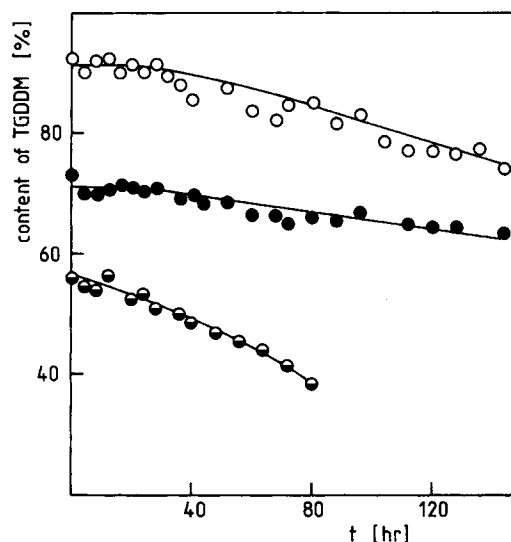


Figure 7 TGDDM content in resins thermostated at 125°C : (○) A; (●) B; (◐) C.

are the major reaction products. The relative areas of peaks 1 and 2 increased gradually from 3 to 7.5% and from 5 to 12%, respectively. The addition of a small amount of water (0.1 to 0.5 wt %) into resins accelerated the formation of oligomers, dimer, and compound 1. Based on this result, we suppose that at 125°C the water present in resins opens epoxy groups forming 2,3-dihydroxypropyl groups and that the resulting hydroxyl groups react with epoxy groups. The same reaction was observed by Hag-

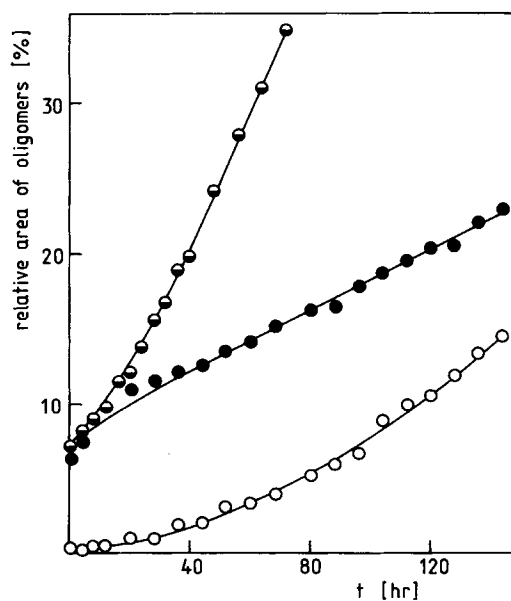


Figure 8 Content of oligomers (trimer + higher) in resins thermostated at 125°C : (○) A; (●) B; (◐) C.

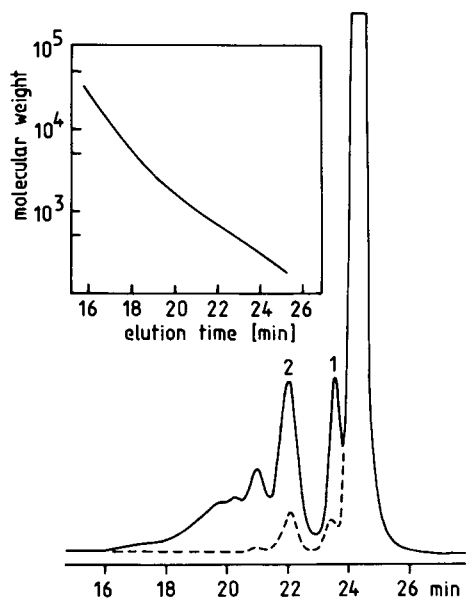


Figure 9 GPC chromatograms of resin A (---) before and (—) after 144 hours of heating at 125°C.

nauer.³ Moreover, a lot of other reactions can proceed in TGDDM resins at elevated temperatures;^{7,8} however, the detailed study of thermally induced reactions of TGDDM is not part of this stability investigation.

CONCLUSIONS

The following conclusions can be drawn from the investigations performed:

1. The resin with a high content of TGDDM (above 90%) is at room conditions highly stable. Its composition remains constant for at least a one-year period.
2. The resin stability is reduced by the presence of hydroxyl-containing by-products. The hydroxyl groups react with the epoxy groups and in addition catalyze this reaction by hydrogen bonding.

3. The stability of the mixtures of resins with DDS is significantly lower.
4. The reaction of epoxy and amino groups in the mixtures resin-DDS is accelerated by hydroxyl-containing impurities and autocatalyzed by intramolecular hydrogen bonds that are formed after one epoxy group has reacted with an amine.
5. A short thermal treatment (several hours) at 125°C does not cause pronounced changes in the resin composition.
6. Prolonged thermal treatment at 125°C results in a significant drop in TGDDM content and growth of oligomers.
7. The thermal stability of resins falls strongly with increasing content of water in resins.

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