

The effect of tertiary amines on the network formation of bisphenol-A diglycidyl ether in reaction with 4,4'-diaminodiphenyl methane

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SUMMARY

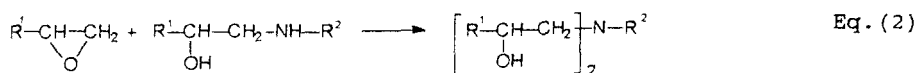
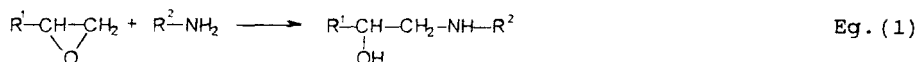
The structure-property relationships of crosslinking systems consisting of bisphenol-A diglycidyl ether and 4,4'-diaminodiphenyl methane were investigated by following the network formation and characterization of cured samples in dependence on the molar ratio and on the curing temperature. Gelation times, soluble parts and glass transition temperatures of the cured systems were determined. The influence of *N,N*-dimethylbenzylamine as an accelerator was discussed.

INTRODUCTION

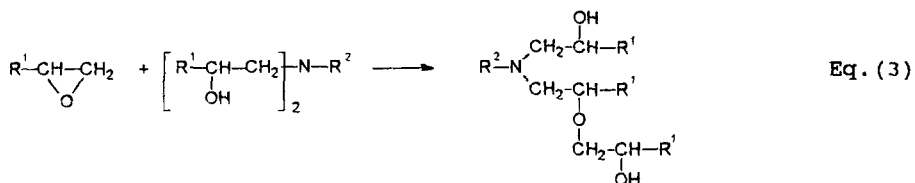
Epoxy resins are a class of polymer materials used in various fields. The large variety of applications depend on the fact that physical and mechanical properties are variable by the nature of the epoxy prepolymer, the nature of the curing agent and the accelerator, the molar ratio and the curing conditions. In order to optimize the properties of the final products it is necessary to understand the curing process and structure-property relationships of the cured resin.

We are interested in investigation of the system consisting of bisphenol-A diglycidyl ether (BADGE) and 4,4'-diaminodiphenyl methane (DDM).

The addition reactions which occur during the curing of glycidyl ethers with primary amines (Eqs.1 and 2) were already described by several authors [1-3]. But there are questions to be answered concerning the etherification reaction between the secondary hydroxylic groups of the products according to Eqs.1 and 2 and the oxirane group (Eq.3).



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Generally, the hydroxylic group should react slower than the amines in the absence of an accelerator [4-6]. Thus the reactivity of the OH-groups can have a significant effect only when there is an initial excess of the epoxy over the amine. We were interested in the effect of such etherification reactions on the network formation dependent on the molar ratio of components and the curing conditions.

Furthermore, we will discuss the effect of a tertiary amine used as an accelerator for the epoxy ring opening on the reaction of the complex system consisting of BADGE, DDM and N,N-dimethylbenzylamine (DMBA).

Some laboratories have paid attention to the oligomerization reactions of the epoxide in the presence of tertiary amines [1,7,8]. Another aspect in this connection is the acceleration of these oligomerizations and the reactions of the hydroxylic groups with epoxide during the curing of epoxides with primary and tertiary amines [1,9,10].

We contributed to this phenomenon by investigation of the model system of phenyl glycidyl ether, aniline and DMBA and could establish that oligomerization and etherification are significantly dependent on the reaction temperature [11]. The reaction of the secondary hydroxylic group is preferred to the reaction of the secondary amine hydrogen at relatively low temperatures. Also, by oligomerization many products were formed. The competition of such reactions to the addition of epoxy and amine will be smaller if the reaction temperature increases.

The reactions caused by the accelerator lead to new structures which in a network are marked by longer and more flexible chain segments. Their influence on the network formation process and the properties of cured samples was tested at the crosslinking system.

EXPERIMENTAL

BADGE (Leuna AG) was purified by recrystallization from acetone/methanol (m.p. 42 °C), and DDM (Merck-Schuchardt) by recrystallization from methanol/water (m.p. 89 °C). DMBA was dried with KOH pellets, purified by the addition of small amounts of phenyl isocyanate and distilled under reduced pressure (b.p. 55-56 °C/ 1.2 kPa).

Gelation times were determined according to ref. [12].

For preparation of cured samples BADGE and DDM were mixed in several ratios of epoxy groups per amine hydrogen (e/a) at 80 °C. The accelerator concentration was applied to the epoxy group. The samples were cured for 48 hours at 70 °C and for 5 hours at 120, 150 or 180 °C, respectively.

HPLC was run on a KNAUER apparatus using RP technique and an acetonitrile/water mixture as eluent.

Glass transition temperatures were determined with DSC and TMA

measurements with a Perkin Elmer DSC/TMA 7 apparatus. FTIR spectra were recorded with a NICOLET FTIR spectrometer 205. Samples were prepared in chloroform (0.1mm). The conversion was followed by an evaluation of the ratios of infrared absorption of epoxy groups at 917 cm^{-1} and of the aromatic structure at 1601 cm^{-1} .

The soluble parts were established at 1g sample (reduced to small pieces) by extraction with chloroform for 16 hours using a soxhlet apparatus.

DISCUSSION

The gelation time is a decisive point in the process of network formation because it determines the maximal possible treatment time. The values for this time depend on the ratio of epoxy groups per amine hydrogen, on the curing temperature and on the concentration of an accelerator. In the unaccelerated system consisting of BADGE and DDM an excess of the epoxy compound leads clearly to a slower gelation (Fig.1). The effect is significant if the curing temperature is relatively low (100°C).

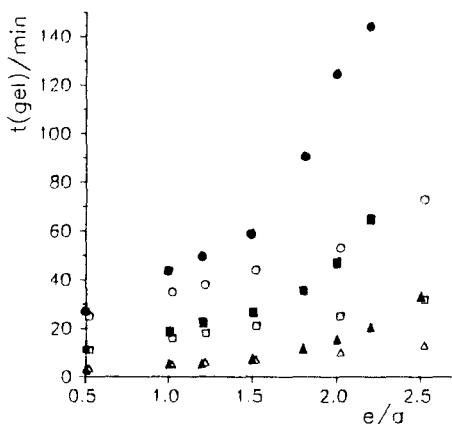


Figure 1: Gelation time $t(\text{gel})$ of BADGE/DDM systems in dependence on the ratio of epoxy groups per amine hydrogen e/a and on the curing temperature

- without DMBA, $T=100^\circ\text{C}$
- without DMBA, $T=120^\circ\text{C}$
- ▲▲▲▲ without DMBA, $T=150^\circ\text{C}$
- ×××× +1mole% DMBA, $T=100^\circ\text{C}$
- ×××× +1mole% DMBA, $T=120^\circ\text{C}$
- △×××× +1mole% DMBA, $T=150^\circ\text{C}$

It seems the surplus of epoxy will not entirely be included in the network formation. This also shows the investigation of soluble parts of cured systems. Soluble parts were always found in systems which were cured with an excess of epoxy. For instance, the sample consisting of 2 epoxy groups per amine hydrogen contains 40% soluble products and 30% unreacted epoxy groups in her sol fraction [12]. BADGE was detected by HPLC as part of the sol fraction.

Glass transition temperatures are closely connected with network properties. In Figure 2 it is visible that T_g has the highest value for the sample consisting of epoxy and amine in a molar ratio [12]. The temperature decreases extremely if there is an excess of epoxy functions.

We suppose that the soluble parts are the reason for this behaviour. But the measurement of the glass transition temperature for the gel part by DSC results, surprisingly, in nearly the same value for the whole network. In this case the low T_g value is attributed to a low network density.

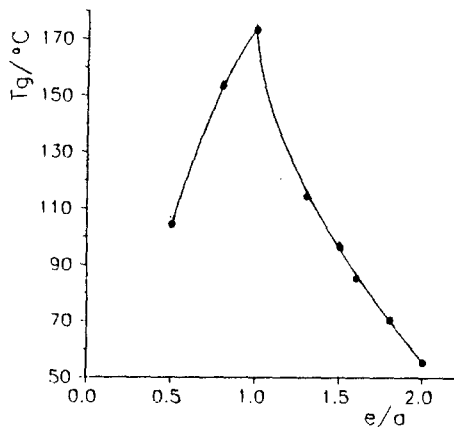


Figure 2: Glass transition temperature T_g of BADGE/DDM systems (cured at 120 °C) which depend on the ratio of epoxy groups per amine hydrogen e/a

At high temperatures (150 °C) the gelation time was not so strongly dependent on the epoxy amine ratio (Fig.1). We assumed that the excess of epoxy groups was consumed by etherification. Investigations by HPLC showed no difference in the product formation during the reaction at 120 and 150 °C. However, the chemical analysis of the network structures is limited by the insolubility of the products which arise.

Kinetic curves show also an independence of the conversion of epoxy groups at the gelation time on the reaction temperature for the unaccelerated system (see Fig.3). Approximately 40% conversion of epoxy groups in the system with a ratio of 2 epoxy groups per amine hydrogen were achieved.

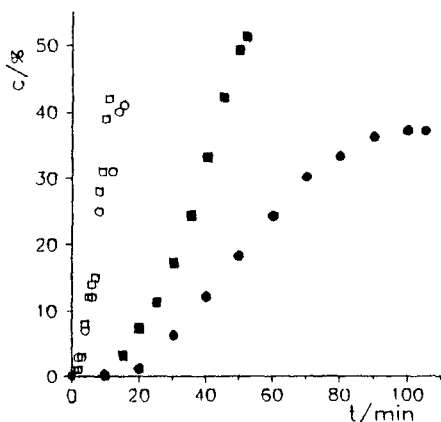


Figure 3: Kinetic curves of the conversion c of epoxy groups in the reaction with amine ($e/a=2$)

- without DMBA, $T=100$ °C
- without DMBA, $T=150$ °C
- ■ ■ ■ +1mole% DMBA, $T=100$ °C
- □ □ □ +1mole% DMBA, $T=150$ °C

Table 1a shows that are the glass transition temperatures of cured samples with a stoichiometric ratio of functional groups and with epoxy excess are independent of the curing temperature. It seems equal that if the curing temperature was 70 or 180 °C

the T_g values averaged 174 and 54 °C, respectively. The crosslinked samples have also had the same insoluble parts. The systems cured with a stoichiometric ratio of epoxy per amine hydrogen contained no soluble parts and the systems with epoxy excess ($e/a=2$) contained independently of the reaction temperature 40 % sol and 30 % unreacted epoxy groups in the sol fraction.

Table 1: Glass transition temperatures T_g of BADGE/DDM systems a) without DMBA, b) in the presence of 1 mole% DMBA, in dependence on the curing temperature T

a)			b)		
$T_g/^\circ\text{C}$			$T_g/^\circ\text{C}$		
$T/^\circ\text{C}$	$e/a=1$	$e/a=2$	$T/^\circ\text{C}$	$e/a=1$	$e/a=2$
70	176	56	70	126	150
120	173	55	120	137	128
150	174	51	150	167	129
180	176	54	180	173	128

These investigations indicate that in the systems without an accelerator etherification doesn't occur if there is also an excess of epoxy groups.

In the presence of 1 mole% DMBA the gelation point will be achieved faster in comparison with the unaccelerated system (see Fig.1). In this case the epoxy excess hasn't so great an effect. It seems the excess of epoxy became a part of the network. It wasn't possible to find soluble parts of the cured reaction system when the system also consisted of two epoxy groups per amine hydrogen.

At a greater concentration of accelerator the effects will be clearer (Fig.4).

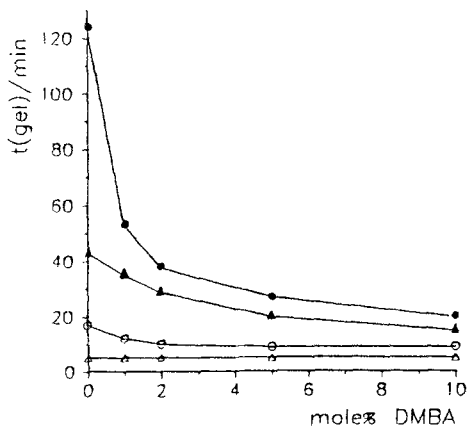


Figure 4: Dependence of the gelation time $t(\text{gel})$ of BADGE/DDM systems on the concentration of DMBA per epoxy group

- ▲▲▲▲▲ $e/a=1, T=100\text{ }^\circ\text{C}$
- △△△△△ $e/a=1, T=150\text{ }^\circ\text{C}$
- $e/a=2, T=100\text{ }^\circ\text{C}$
- ○ ○ ○ ○ $e/a=2, T=150\text{ }^\circ\text{C}$

If there is an excess of NH functions the presence of accelerator shows no effect on the gelation time. The value was always 25 min at 100 °C and 5 min at 150 °C curing temperature. At stoichiometric ratio of epoxy and amine an acceleration of

gelation is only visible at relatively low temperatures (100 °C).

The presence of DMBA in the system with an epoxy excess ($e/a=2$) effects always a faster gelation. But also in this case is the acceleration at 100°C clearer than at 150°C.

That fact that part of etherification and oligomerization reactions is higher than all at relatively low temperatures shows the measurement of conversion of epoxy groups at gelation time (see Fig.3). At 150°C at the gelation time will have achieved the same conversion in the presence and in the absence of DMBA. However, in the system reacted at 100°C the conversion at the gelation time is already 10 % higher in the presence of an accelerator. We suppose that in the presence of an accelerator at lower temperatures reactions take part on the network formation which do not contribute so effectively to the formation of networks.

This is typical for etherification and oligomerization. During these reactions epoxy compounds were consumed forming longer chain segments.

A band for the aliphatic ether structure will be visible in the FTIR spectra of the reaction systems at gelation time (Fig.5).

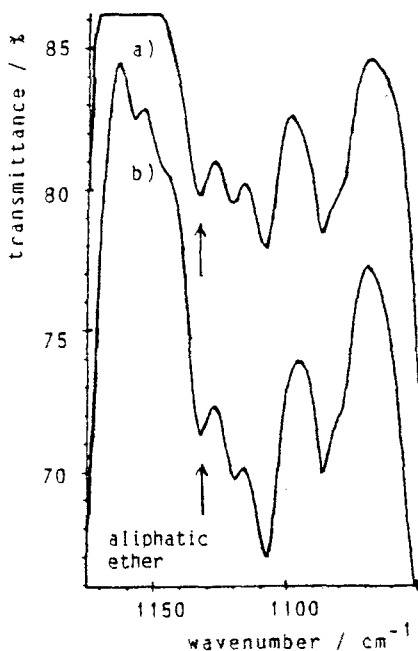


Figure 5: Section from the FTIR spectra of the system BADGE/DDM ($e/a=2$) at $t(\text{gel})$
 a: reacted at 100 °C
 b: reacted at 150 °C

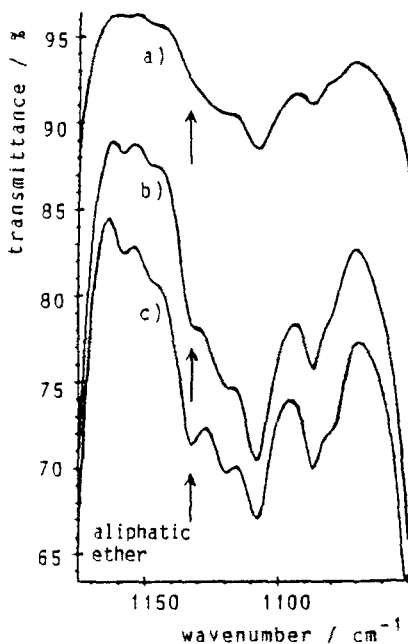


Figure 6: Section from the FTIR spectra of the systems consisting of BADGE and DDM
 a: $e/a=0.5$, b: $e/a=1.0$,
 c: $e/a=2.0$ at $t(\text{gel})$ at 150 °C

For the reaction at 150°C the band is smaller than for the reaction at 100°C. This correspond with the result of following

the epoxy conversion.

The differences are extreme when comparing systems with a different e/a ratio (Fig.6). With an increase of the content of the epoxy the band for an aliphatic ether became greater.

The competition between reactions leading to ether structures and the addition of epoxide and amine has an important effect on the glass transition temperatures.

In the system consisting of epoxy and amine in stoichiometric ratio T_g is lower in the presence of DMBA (Tab.1). The part of etherification and oligomerization decrease if the curing temperature is increased. Therefore the system cured at 180°C has the same T_g as the unaccelerated system. The reason for the lower values for networks with ether structures are the longer chain segments which should be more flexible. For samples with an excess of epoxide the glass transition temperature isn't so strongly dependent on the curing temperature because the excess of epoxide is available for the competition reactions at any temperature.

Furthermore, we investigated the dependence of glass transition temperature on the DMBA concentration at a curing temperature where the accelerator also has an effect on the system with stoichiometric ratio of epoxy and amine (Fig.7).

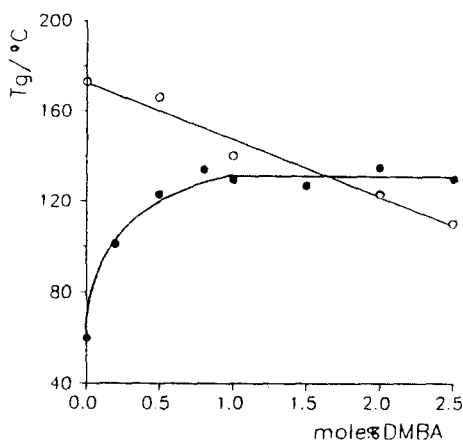


Figure 7: Glass transition temperature T_g of BADGE/DDM systems (cured at 120°C) on the DMBA concentration per epoxy group

○ ○ ○ ○ e/a=1
● ● ● ● e/a=2

As the samples with stoichiometric ratio increase the part of etherification and oligomerization with increasing DMBA concentration and glass transition temperature decrease. For the samples with epoxy excess there is a great difference between the presence and the absence of DMBA, but the concentration of the accelerator has only an effect on the gelation time, not on the glass transition temperature, because still with a small amount of accelerator the excess of epoxy became a part of the network.

CONCLUSIONS

We can establish that in the presence of an accelerator etherification and oligomerization take place in the network formation corresponding to the model investigations [11].

The part of these reactions will be greater at relatively low temperatures and if there is an excess of epoxy groups. The competition between these reaction types and the addition of epoxide and amine has an important effect on the properties of the network.

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