Crosslinking behaviour of diolmodified epoxies
2. DSC measurements

W. Tänzer[1], M. Szesztay[2], Zs. László-Hedvig[2], and M. Fedtke[1]*

[1]Technische Hochschule "Carl Schorlemmer" Leuna-Merseburg, Otto-Nuschke-Strasse,
DDR-4200 Merseburg, German Democratic Republic
[2]Central Research Institute for Chemistry of the Hungarian Academy of Sciences,
Pusztaszeri út 59–67, H-1525 Budapest, Hungary

Summary
        Diglycidyl ether of bisphenol A (BADGE) reacts with alipha-
tic alcohols to form different products, depending on the type
of accelerator. Using isothermal and dynamic DSC, magnesium
perchlorate proved to be a more selective accelerator in
comparison with N,N-Dimethylbenzylamine (DMBA). In the presence
of DMBA, Arrhenius plots of log t_c (t_c-cure times) versus
inverse cure temperature show a changing reaction order over a
wide range of temperatures.

Introduction
        Diglycidyl ether of bisphenol A (BADGE) only reacts with
aliphatic alcohols if suitable accelerators are used. In the
reaction of BADGE with butane-1-ol, $Mg(ClO_4)_2 \cdot 2H_2O$ proved to be
a   more   selective   accelerator   in   comparison   with   N,N-
dimethylbenzylamine (DMBA). In the first case, mainly one single
type of starting reaction proceeds independently of the reaction
temperature. Using DMBA as accelerator, the number of starting
steps increases as the reaction temperature rises.   Furthermore,
the ratio of the reactivity of primary and secondary hydroxyl
groups in the amine-accelerated system changes and leads to
superimposed reaction orders (1).
        The temperature dependence of the reaction mechanism of
diolmodified epoxies can be proved by DSC as well. For this
purpose it is necessary to synthesize prepolymers with a homo-
geneous state, because epoxide and diol are not soluble into one
another and cannot be stirred during the DSC-measurements. These
prepolymers contain about 80% of the epoxide group content of
the unreacted compounds. Then, the crosslinking reaction was
investigated using DSC.   The times until the crosslinking
reactions have finished can be measured under isothermal
conditions, making it possible to calculate the activation
energies of the reactions concerned (2-5). Arrhenius plots of
log t_c versus inverse cure temperature provide some information
about the validity of the reaction mechanism dependent on the
reaction temperature (6).

Experimental
        Chemicals: Diglycidyl ether of bisphenol A (BADGE), butane-
1,4-diol, magnesium perchlorate and N,N-dimethylbenzylamine
(DMBA) are commercially available products. BADGE was
recrystallized from acetone-methanol (m.p.=42°C). Preparation of
prepolymers: BADGE, butane-1,4-diol and the accelerator were

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* To whom offprint requests should be sent

mixed in a given molar ratio in a thermoregulated glass reactor. The reaction proceeded at 100°C if magnesium perchlorate was used as accelerator and at 60°C if DMBA was used. The reaction was interrupted at an epoxide consumption of approximately 20% and the reaction products were stored at -20°C.

Analysis: DSC: Du Pont Instruments Type 910. Heating rate: 10 K*min^{-1}, open capsules.

Results and Discussion

To get some general information about the crosslinking behaviour, acidic and basic accelerated systems were measured at 10 K*min^{-1} (Fig. 1)
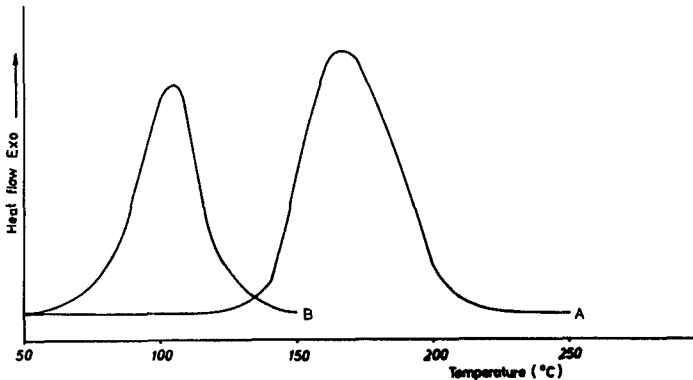

Fig.1.Dynamic DSC for acidic and basic accelerated systems (10 K*min^{-1})
A-BADGE:butane-1,4-diol:Mg(ClO$_4$)$_2$*2H$_2$O=1:1:0.03
B-BADGE:butane-1,4-diol:DMBA   =1:1:0.05

The overall reaction heat is 300 J*g^{-1} (A) and 226 J*g^{-1} (B) respectively.

Furthermore, crosslinking reactions were carried out under isothermal conditions, permitting the determination of cure times t_c (Fig. 2). The measuring technique involves pre-heating the DSC to the desired temperature, starting the time base scan, and loading the sample into the cell as rapidly as possible. At A, the DSC-cell has been opened and the sample inserted. At B, the sample has reached the isothermal value and commences curing. Curing is complete at C, and the cure time t_c is taken as C-B (6).

The overall reaction heats were determined after previous calibration (Fig. 3).

There is a linear dependence in the temperature range from 140 to 180 °C. At 120 °C no reaction heat could be determined, showing the latent properties of the acidic-accelerated system.

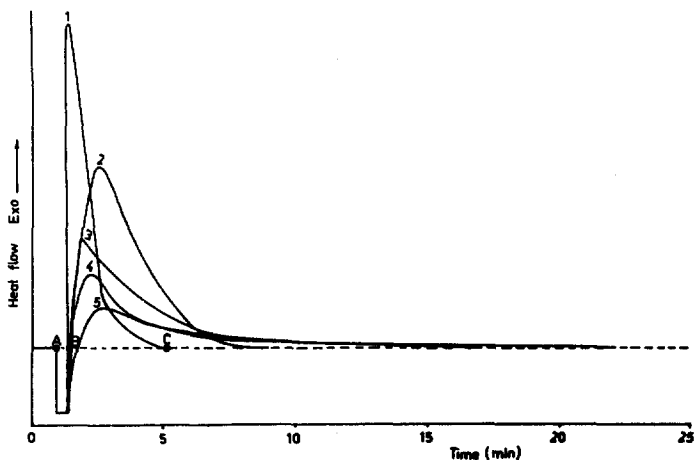The values for t_c at different temperatures are summarized in Table 1.

Fig.2.Thermogram, system BADGE:butane-1,4-diol:Mg(ClO$_4$)$_2$*2H$_2$O= 1:1:0.03.1-200 °C, 2-180 °C, 3-170 °C, 4-160 °C, 5-150 °C
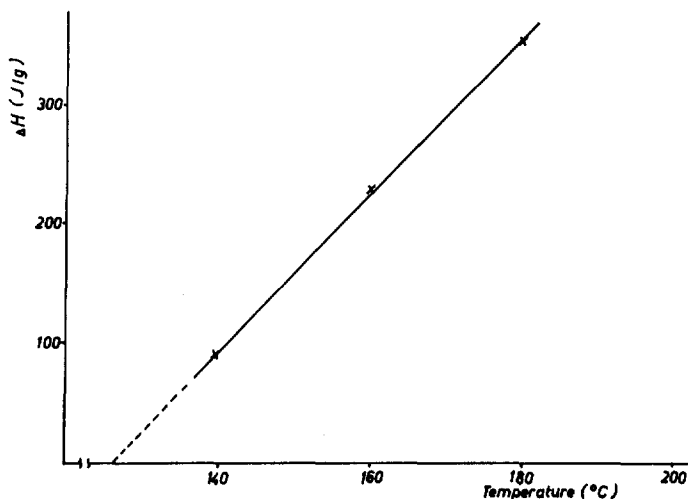
Fig.3.Overall reaction heats (J*g^{-1}), system BADGE:butane-1,4-diol:Mg(ClO$_4$)$_2$*2H$_2$O=1:0.5:0.03 dependent on the temperature

temperature °C	cure times t_c min	
	A1	A2
200	3.6	6.5
180	7.3	12.0
170	11.4	16.0
160	14.7	22.3
150	20.2	32.0

Table 1.Cure times t_c for systems
A1-BADGE:butane-1,4-diol:Mg(ClO$_4$)$_2$*2H$_2$O=1:   1:0.03
A2-BADGE:butane-1,4-diol:Mg(ClO$_4$)$_2$*2H$_2$O=1:0.25:0.03

The cure times are dependent on the decreasing amount of butane-1,4-diol and they increase significantly.

Arrhenius plots of log t_c versus inverse cure temperature will be linear if the overall reaction order is constant. Lines with the same slope were found for systems A1 and A2 (Fig.4).
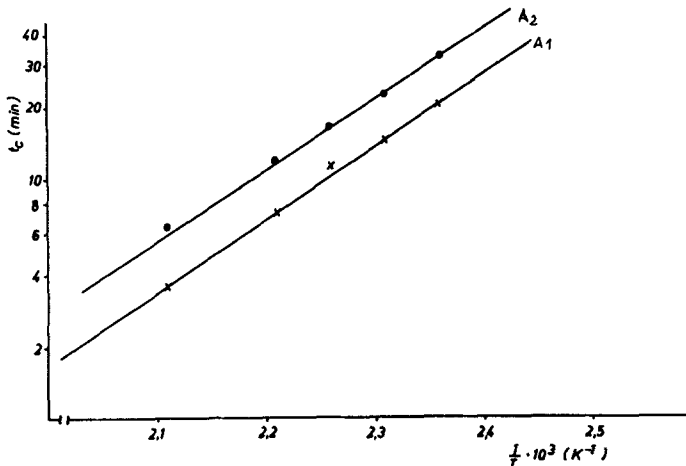

Fig.4.log t_c versus inverse cure temperature for systems A1 and A2 (according to Table 1)

Activation energies, calculated from the slopes of the Arrhenius plots, were 57.3 kJ*mol^{-1}. These activation energies largely fall in the range of 50-59 kJ*mol^{-1} (glycidyl ethers + aliphatic amines) or 59-63 kJ*mol^{-1} (glycidyl ethers + alcohols) (6), regardless of the use of prepolymers (see experimental section). The reaction mechanism does not change in the temperature range under observation. If this behaviour is also valid for lower temperatures, then an extrapolation gives a cure time of 133 h at 40 °C for system A1. Consequently, the system can be taken into consideration as a latent system at room temperature.

The DMBA-accelerated system is more reactive. According to Fig. 1, lower reaction temperatures are required. The isothermal cure times are summarized in Table 2.

temperature °C	cure times t_c min	
	B1	B2
170	–	4.7
150	7.2	7.5
130	8.7	10.4
110	13.2	11.4
90	20.0	14.1
70	54.1	18.6

Table 2.Cure times t_c for systems
B1-BADGE:butane-1,4-diol:DMBA=1: 1:0.05
B2-BADGE:butane-1,4-diol:DMBA=1:0.25:0.05

The course of the cure times is rather different from that for the acidic-accelerated system. Arrhenius plots of log t_c versus inverse cure temperature are illustrated in Fig. 5.
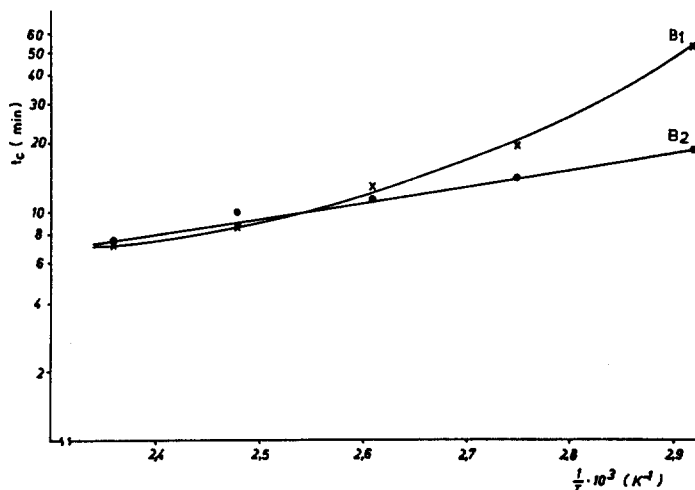

Fig.5. log t_c versus inverse cure temperature for systems B1 and B2 (according to Table 2)

Whereas the system with the lower amount of butane-1,4-diol shows a linear dependence, for the stochiometric mixture a non-linear dependence was observed. The activation energy for system B2 is 13.5 kJ*mol^{-1}, owing to the use of prepolymers, in which some reactions took place before DSC-measurements were performed. In the case of DMBA-accelerated systems, a considerable amount of the exotherm reaction was already released. Thus, a slight temperature rise was observed during the preparation of these prepolymers (see experimental section). The system considered is not latent and reacts even at room temperature. An extrapolation gives a cure time of 40 min at 40 °C.

In system B1 the reaction mechanism is dependent on the temperature. In a temperature range from 70 to 170 °C no uniform reaction order was found. This corresponds with the results of kinetic measurements of model systems (1). Here, two different reaction mechanisms were found between 60 and 100 °C. The main reason for this behaviour is the low selectivity of the accelerator DMBA, leading to more different starting steps with an increasing reaction temperature.

Reactions taking place at temperatures above 100 °C would be of interest for further investigations.

Conclusions

Differential scanning calorimetry (DSC) proved to be a suitable method for the investigation of the selectivity of accelerators. In the reaction of diglycidyl ether of bisphenol A (BADGE) with aliphatic alcohols, $Mg(ClO_4)_2*2H_2O$ causes one single reaction mechanism independent of the temperature. In the presence of N,N-Dimethylbenzylamine (DMBA), Arrhenius plots of log t_c (t_c-cure time) versus inverse cure temperature indicate superimposed reaction orders between 70 and 170°C. This behaviour confirmed the results of kinetic investigations (1).

References

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