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Thermochemistry

Thermochemistry of Model Curing Reactions of Epoxy Resins

Vladimír Špaček[1]*, Jan Biroš[1], Julius Pouchlý[1], and Ivan Dobáš[2]**

[1] Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, CS-162 06 Prague 6, Czechoslovakia

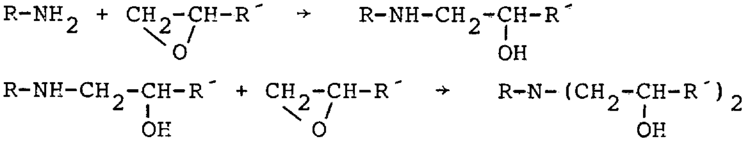
[2] Research Institute of Synthetic Resins and Lacquers, CS-53207 Pardubice, Czechoslovakia

Summary

The heats of reaction of phenylglycidyl ether and N,N-methylglycidylaniline as model systems for two different types of epoxy resins with primary and secondary amine were determined. In all cases the heat of reaction was found to be dependent on the ratio of the reactant components. This dependence is probably due to the formation of various complexes via a hydrogen bond. It was also found that, while the heats of reaction of phenylglycidyl ether with primary and secondary amine are the same, the heats of reaction of N,N-methylglycidylaniline with primary and secondary amine differ significantly from each other.

Introduction

Epoxides react with amine according to the scheme



$$R\text{-}NH_2 + \underset{\diagdown O \diagup}{CH_2\text{-}CH}\text{-}R' \rightarrow R\text{-}NH\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}R' \qquad (I)$$

$$R\text{-}NH\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}R' + \underset{\diagdown O \diagup}{CH_2\text{-}CH}\text{-}R' \rightarrow R\text{-}N\text{-}(CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}R')_2$$

The heats of these reactions were investigated in various papers already in the past, e.g. (1-6), using polyfunctional epoxy resins and amines, and also model monofunctional compounds. By using the latter, it is possible to avoid complications due to the polyfunctionality of commercially employed epoxides and amines, i.e. to the increase in viscosity and to the formation of a crosslinked structure in the reaction of such compounds.

In the papers published so far there are striking differences between the values of measured heats of reaction of similar systems (4,5). Also, some problems regarding the heats of reaction of the amine/epoxide systems still remain unsolved:

a) While in some papers (1,2) the dependence of the experimentally determined heat of reaction (H_e) on the ratio of both reactants was not ascertained, in others (4) it was. The dependence was also found to exist in an excess of amine functionalities, where no side reaction capable of explaining it could be assumed.

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* On leave of absence from the Research Institute of Synthetic Resins and Lacquers, Pardubice

** To whom offprint requests should be sent

b) Little attention has so far been devoted to the possible difference in the H_e value of the reaction of primary and secondary amine with epoxide. The difference, if any, is of basic importance, e.g., for the subsequent kinetic treatment of the calorimetric experiment.

Recently, there has been an increased interest in resins based on epoxides derived from N,N-diglycidylaniline. The heats of reaction of monofunctional models of such compounds have not yet been measured.

We therefore attempted the determination of the heats of reaction of phenylglycidyl ether and N,N-methylglycidylaniline with decyl- and dibutylamine as a function of temperature and of the ratio of reactants. We also measured the heat of mixing of one reaction product with the reactants. The dependence of the heats of reaction on the molar ratio of reactants may be explained by the not negligible magnitude of the heat of mixing.

Experimental

Dibutyl amine (DBA) and *decyl amine* (DA), analytical purity grade, produced by Fluka,AG,Buchs, were used without purification; according to the gas-chromatographic analysis, they were respectively 99.82 and 99.07%.

Phenylglycidyl ether (PGE) was of GC purity 99.53%.

N.N-Methylglycidylaniline was synthesized by the following procedure: 53.6 g (0.5 mol) N-methylaniline, 92.5 g (1 mol) epichlorohydrin, 50 g methyl-isobutyl ketone and 4 g water were mixed and left to react at room temperature for two weeks. After that, the reaction mixture was stirred at 50°C for 30 h. After this, 60 g of a 50% NaOH solution in water was added, again at 50°C during 30 min. with intensive stirring. The mixture was left to react under stirring for another nine hours. After that, 150 ml water was added, and the separated organic phase was washed three times with 50 g of a 5% NaCl solution. The reaction mixture was freed from methyl-isobutyl ketone by distillation at reduced pressure (1330 Pa) and a temperature up to 100°C. By this procedure, 73 g of the product, i.e. 89.4% of the theoretical yield was obtained. The raw product was purified by triple distillation at reduced pressure (1330 Pa) at the b.p. 90-92°C. Purity according to GC was 99.34%.

The "reaction product", *1-(dibutylamino)-3-phenoxy-2-propanol* ($PhOCH_2CH(OH)CH_2NBu_2$), was prepared by heating 30 g PGE with 28 g DBA under a reflux to 80°C. Complete conversion was reached by additional heating to 120°C for one hour. The amine in excess was distilled off at reduced pressure; the resulting product was repurified by a twofold addition of active charcoal and filtration (GPC purity 99.67%).

The heats of reaction were measured by using a Perkin-Elmer DSC 2 calorimeter under isothermal conditions at 80°C - 160°C (according to the type of the reaction system). Samples of the reaction mixture, about 10 mg each, were prepared by direct weighing of the reaction components dosed with syringes into hermetically sealed aluminium vessels. The output signal from the calorimeter was digitized and computerized by Wang 2200 C.

The completion of the reaction, the number and type of the reaction products formed were proved by infrared spectroscopy and by the GPC method.

The heats of mixing were determined by using a standard model of the Calvet calorimeter (Setaram) at 25°C in stainless steel mixing vessels with an Al membrane and provided with a mechanical stirrer with a perforator. In view of the very low vapour tensions of the compounds, corrections for the non-zero vapour space were neglected.

Results and Discussion

Figs 1 to 4 show the measured heats of reaction (H_e) as a function

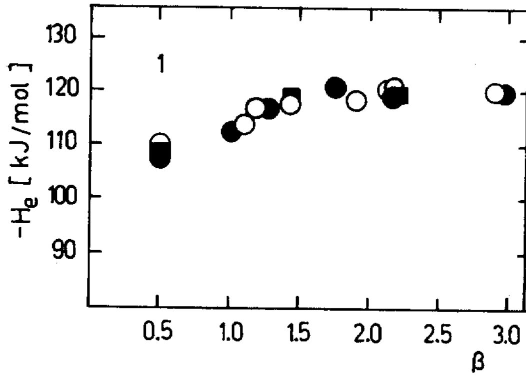


Fig.1 DBA/PGE
■100°C,○110°C,●120°C

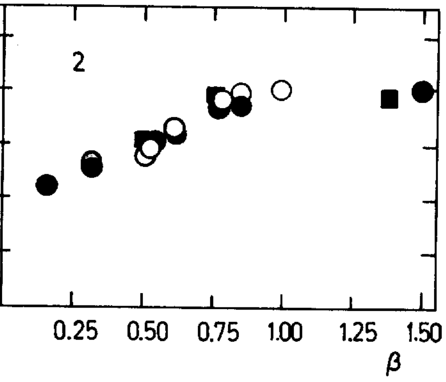


Fig.2 DA/PGE
■80°C,○90°C,●100°C

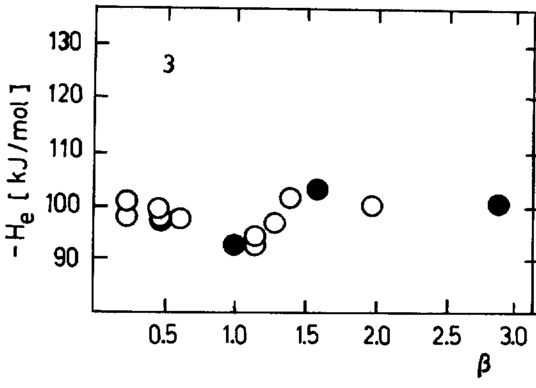


Fig.3 DBA/MGA
○150°C,●160°C

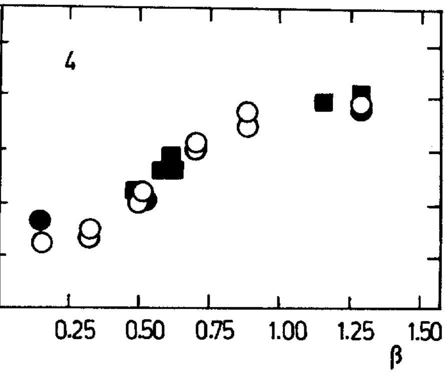
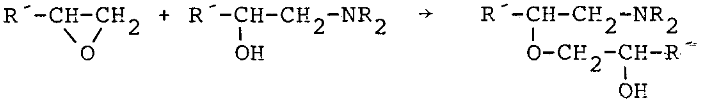


Fig.4 DA/MGA
■130°C,○140°C,●150°C

of the amine/epoxide mole ratio (β). (For the system butylamine - PGE which is the closest to our systems, the H_e values reported for 70°C are (4): 115.6 kJ/mol for $\beta = 0.5$ and 128.5 kJ/mol for $\beta = 1$). Figs 1 through 4 show the dependence of H_e on β in all the four cases. In our opinion, the increase in the heat measured in an excess of amine functionalities may be due to the formation of a complex between the reaction product, i.e., alcohol (I) and amine in excess. The formation of this complex via a hydrogen bond is very exothermal. This is also suggested by the heat of mixing (H_M) of DBA with the reaction product of DBA and PGE measured by us. The heat of mixing of these components at 25°C (for $x_1=0.4-0.6$) approximately obeys the relation $H_M=-10.7.x_1x_2$ kJ/mol, where x_1 and x_2 are mole fractions of both components. We assume that H_M depends little on temperature, as is also corroborated by some data obtained using similar systems (7) at elevated temperatures (90°C).

At the ratio of the amine and epoxide functionalities 1:1, only the product (alcohol) capable of self-association is eventually present in the reaction mixture. This is why also the heats of reaction determined at this ratio of the starting components are higher by the heat of self-association of the reaction product; the latter, however, obviously is not as high as that of formation of the amine-alcohol complex. The H_e values of the individual reaction systems at the initial ratio of the amine and epoxide functionalities $\beta=1$ are: for DBA/PGE=-111.1 kJ/mol, for DA/PGE=-109.6 kJ/mol, for DBA/MGA=-92.5 kJ/mol and for DA/MGA=-100.8 kJ/mol. It can be seen from these data that the heat of reaction of PGE with both amines is approximately the same within the limits of experimental error, while that of the reaction of MGA with DBA is lower than that of the reaction with DA.

In an excess of epoxide functionalities in the systems DA/PGE and DA/MGA (Figs 2 and 4) one can see a decrease in H_e with decreasing β. This is in agreement with the heat of mixing of 1-(dibutylamino)-3-phenoxy-2-propanol with PGE $H_M=5.25.x_1x_2$ kJ/mol). The DBA/PGE system was the only one for which a certain small participation of the consecutive etherification reaction (II) has been demonstrated in PGE in excess. Hence also H_e in the range $\beta < 1$ is somewhat higher than one may expect.



$$R'\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} + R'\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}NR_2 \rightarrow R'\text{-}\underset{O\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}R'}{CH}\text{-}CH_2\text{-}NR_2$$

(II)

On the other hand, the behaviour of MGA with DBA at $\beta < 1$ where H_e increases again with decreasing β is different. The causes of such behaviour have not been elucidated, however.

For all the four measured systems, H_e are virtually independent of temperature within the temperature range used.

Using the time dependence of the isothermally released heat, it is possible to calculate the time dependence of the reaction and to evaluate the kinetic parameters. At the same time, the released heat is assumed to be directly proportional to the degree of conversion. In our case, of course, the magnitude of the measured heat is considerably affected by the simultaneously released heat of interaction which is not a linear function of the degree of conversion. Hence, in principle, in an exact calculation of the degree of conversion from the measured heat these nonlinear terms should be considered, as will be shown in a forthcoming communication.

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