

DSC INVESTIGATIONS ON THE KINETICS OF THE LINEAR STEP GROWTH
POLYMERIZATION OF DIAN-BISGLYCIDYLETHER WITH AMINES

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ABSTRACT

Isothermal measurements were carried out using a Perkin-Elmer-DSC 2C with data station. A reaction scheme, which describes all experimental findings, is proposed for the epoxy-amine-curing.

INTRODUCTION

The kinetic characterisation of reaction between amines and epoxies is of great practical importance. A large amount of work has been reported in the literature concerning the nature of the reaction. Nevertheless there exists no simple rate equation, which can describe the full conversion-time curve. The cure reaction has sometimes been described by means of a simple n-th order expression governed by a single rate constant /e.g. 1/. This equation ignores the autocatalytic character of reaction. Therefore, the most authors use the original ideas of Smith /2/. The curing process is governed by two rate constants for a catalytic and an autocatalytic reaction. The original form of the corresponding rate equation gives good fits to the experimental data up to about 40-60% conversion. Typical attempts to extend the validity range of the rate equation are those of Ryan /3/ (parameter fitting of fractional reaction orders) and Barton /4/ (linear decrease of rate constants with conversion). The physical meaning of these assumptions is not very clear.

EXPERIMENTAL

Dian-bisglycidylether (DGEBA) was prepared from Epilox M 515^R by twofold vacuum distillation. A series from primary amines and dissecondary diamines were purified by distillation and/ or crystallization. The purity was checked by paper chromatography and thin-layer chromatography. The thermal and kinetic data

were obtained using a Perkin-Elmer DSC 2C with data station. Cure isotherms were obtained at temperatures well above the final glass temperature and below 150°C to avoid side reactions. Under these conditions the products are soluble and linear having molecular weights \bar{M}_n of 15000 to 20000. Software for isothermal measurements and experimental details were already described /5/. The reproducibility of isothermal runs is excellent and gives a reliable basis for a critical examination of reaction kinetics.

RESULTS AND DISCUSSION

Any attempt to describe the cure kinetics has to be regard the following features:

- The reaction is always autocatalytic. This is obviously clear in the case of equimolar mixtures (Fig. 1). But the reaction ist still autocatalytic, if nonstoichiometric mixtures (Fig. 1), increasing amounts of catalysts or increasing amounts of inert dilution substances (Fig. 2) are used. In the latter case the reaction rate is diminished by an amount proportional to the dilution of reactants.
- Substances with acid hydroxyls are powerful accelerators for the curing reaction. The initial reaction rate is proportional to the concentration of this catalyst.
- Nonstoichiometric mixtures with an excess of amine react faster (Fig. 1), those with more epoxy react slower compared with equimolar samples of the same system.
- Primary amines and dissecondary diamines show the same principal reaction curves.
- The final conversion after isothermal runs is typically 0.95 - 0.98. This has to be taken into account in all subsequent calculations.
- The initial reaction rate of most systems is relatively high. This can hardly explained by catalytic impurities of the high purified substances. Therefore, a noncatalytic reaction path has to be taken into consideration.

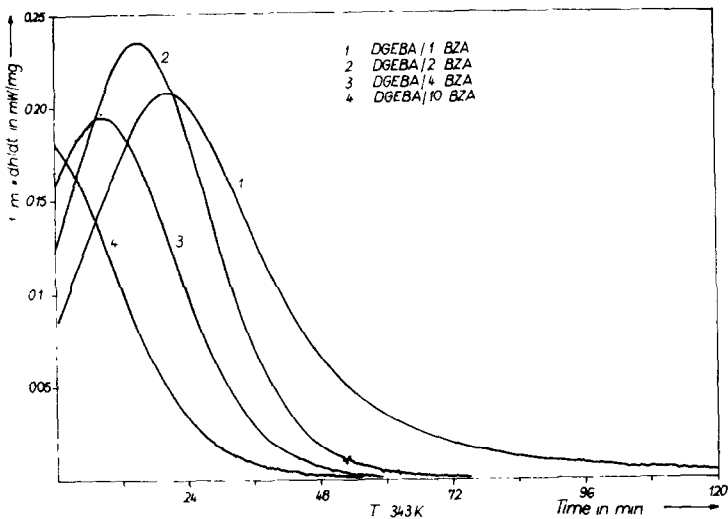


Fig. 1 Effect of initial epoxy-amine stoichiometries on the reaction rate of isothermal runs in the system DGEBA / Benzylamine

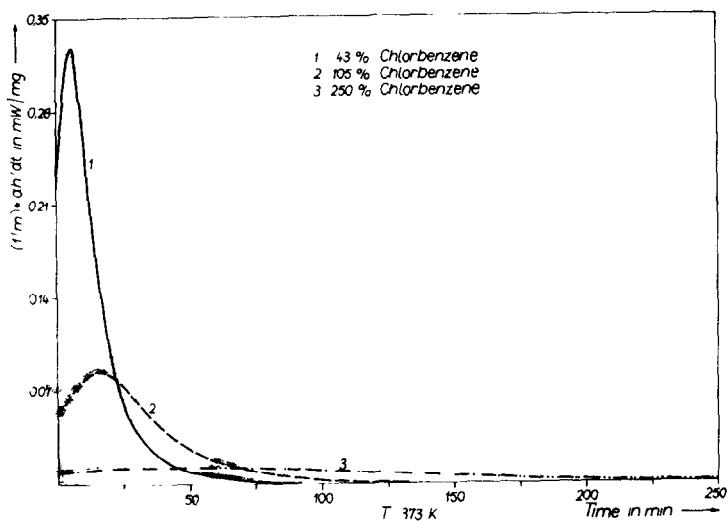
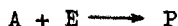


Fig. 2 Effect of increasing amounts of an inert dilution substance on the reaction rate in the system DGEBA Benzylamine

CONCLUSIONS

The following reaction scheme should be able to describe all experimental findings



where A is the amine, E is the epoxy, C is the catalyst, P and P' are the products with different chain length, K1 and K2 are hydrogen bond complexes between epoxy and hydroxyls, and TK1 and TK2 are the ternary transition state complexes. The scheme implies noncatalytic, catalytic and autocatalytic reactions.

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