

KINETICS AND MECHANISM OF CURING EPOXY/ANHYDRIDE SYSTEMS

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ABSTRACT

The paper reports the results of studying the kinetics of DGEBA reactions with maleic anhydride catalyzed by N, N-dimethyl aniline (DMA). These stuffs are used as photoelastic model materials. The origination of monoester was studied separately on a model reaction of maleic anhydride with isopropyl alcohol. The subsequent reaction of epoxy groups with monoester was examined on a system of epoxy resin and isopropyl maleic monoester. The curing process depends significantly on the content of hydroxyl groups in the system.

KEYWORDS: epoxy resins, anhydrides, kinetics, catalyzed, model reactions

1. INTRODUCTION

Epoxy resins cured by anhydrides usually have better properties than resins cured by amines. They are less poisonous, display a higher glass transition temperature, and absorb less water, lower reaction exothermic, as well as their reaction shrinkage (Ellis, 1993; May, 1988; Lee and Seville, 1967). On the other hand, non-catalyzed epoxy-anhydride systems are very low reactive and, therefore, the curing has to be carried out at higher temperatures. Strong Lewis bases as tertiary amines catalyze the curing (Hagnauer and Pearce, 1992; Barton, 1986; Morgan, 1985; Steinmann, 1989).

A number of authors have studied the mechanism and kinetics of curing of epoxy resins. According to Fisch and Hofmann (1961, 1954) anhydride does not react with epoxy groups directly, but the anhydride ring is opened first by reaction with hydroxyl groups. The carboxyl group of monoester then reacts with epoxy one. Diester and a new OH group originate. Since the first reaction is faster, monoester accumulates in the reaction mixture. The authors also assume, to a minor extent, reaction of epoxy groups with hydroxyls. This reaction takes place at a measurable rate only at temperatures over 200 °C. On the contrary, basic catalysts such as tertiary amines, accelerate the reaction leading to esters, and the generation of ether formations is suppressed (Fisch and Hofmann, 1954; Fischer, 1960). Fischer (1960) studied the reactions of monoepoxies with anhydrides. He found that, within a certain time interval, the reaction was of the zero order with respect to both initial substances, i.e. that the reaction rate depended neither on the anhydride concentration, nor on the concentration of the epoxy

groups. On the other hand, an increase in the concentration of hydroxyl groups did not increase the reaction rate. Hence, Fischer (1960) did not assume alcoholysis which, according to Fisch and Hofmann (1954, 1961), preceded the reaction of the epoxy groups itself. Slightly different conclusions were drawn by Tanaka and Kakiuchi (1963, 1964) who studied the kinetics of curing of resin Epikote 828 analogous to Fischer (1960) they found that the epoxy groups and anhydride depleted at the same rate. In contrast to him, however, by analyzing the obtained kinetic dependences, they found the reaction was of the 1st order with respect to anhydride with tertiary amine without the presence of added alcohol. This is so because the existence of such complex was not proved, as claimed by the authors. In this case they refer to paper of Gold and Jefferson (1953) who found that the absorption of UV radiation in the principal absorption range of pyridine (230 – 280 nm) was additive for both substances. The same applies to the electric conductivity of their solutions in acetone. Similarly Jureček (1955) reported that anhydrides do not react with dry pyridine. However, Bender (1960) gives a reaction scheme of alcoholysis, in which the first step is the reaction of anhydride with pyridine. Sorokin (1968) studied the curing of epoxy resins on a model reaction of phenyl glycidyl ether with phthalic anhydride under catalysis with N,N-dimethylbenzylamine. He used n-butyl alcohol as an admixture containing hydroxyl groups. By studying of isolated reactions, he found that two reactions mainly run - alcoholysis of anhydride and the reaction of the nascent monoester with the epoxy compound. Both reactions take place with and without a catalyst. Reaction between epoxy groups and hydroxyls was

Table 1 Alcoholysis of maleic anhydride by isopropyl alcohol

T (°C)	K_3 (kg mol ⁻¹)	k_4' (kg ^{3/2} mol ^{-3/2} s ⁻¹)	k_7 (kg mol ⁻¹ s ⁻¹)
52	0.088	$1.07 \cdot 10^{-4}$	$4.69 \cdot 10^{-4}$
65	0.220	$1.60 \cdot 10^{-4}$	$1.06 \cdot 10^{-3}$
70	0.273	$5.21 \cdot 10^{-4}$	$1.38 \cdot 10^{-3}$
78	0.420	$2.45 \cdot 10^{-4}$	$2.18 \cdot 10^{-3}$
Preexponential factor	$1.40 \cdot 10^8$	20	$2.15 \cdot 10^5$
Activation energy (kJ)	57	30	54

not proved. As the author reports, his results did not prove the conclusions of Tanaka and Kakiuchi (1963, 1964), or Fischer (1960). Indeed, he found that the anhydride depleted during the reaction substantially faster than the epoxy compound. This agrees with the experiments of Fisch and Hofmann (1954, 1961). Sorokin considers the reaction of the epoxy compounds with monoester to be the crucial step. This reaction is of the 1st order with respect to the epoxy compound and catalyst, and of the zero order with respect to monoester. The author does not mention how the tertiary amine works under alcoholysis, referring the reader to the paper of Gold and Jefferson (1953). At present is cure kinetics of epoxy resin studied in general by the help of physical methods as thermogravimetric analysis (Wang and Shi, 2005), DSC (Chen et al., 2004; Kim and Lee, 2002), dielectric analysis (Chen et al., 2004) or Raman spectroscopy (Rocks et al., 2004).

In this paper we study the mechanism and kinetics of epoxy resins cured via anhydrides on model reactions. The changes in the concentration of reaction components were monitored by chemical methods.

2. EXPERIMENTAL

DGEBA (CHS Epoxy 15 (present name is CHS Epoxy 520), epoxy group content 5.193, OH groups 0.610 mol kg⁻¹, SpolChemie, a.s. Czech Republic) was used as the initial resin. Maleic anhydride purris, isopropyl alcohol anhydrous (Sigma-Aldrich), N,N-dimethyl aniline purris. (Sigma-Aldrich). Mono(isopropyl) maleic ester was prepared by non-catalyzed reaction of maleic anhydride and isopropyl alcohol in equimolar amount as described in Ernest et al. (1959). All reactions took place in closed flasks at temperatures of 65 to 100 °C under mixing with a magnetic mixer. Samples collected in the course of the reaction were dissolved in benzene, and the content of epoxy groups was determined by HBr titration in acetic acid Durbetaki (1956). The contents of anhydride and monoester were determined simultaneously by sodium hydroxide and sodium methanolate titration described in Jureček (1955). The concentration of hydroxyl groups in the initial resin was determined by acetylation after Chachapuridze (1969).

3. RESULTS AND DISCUSSION

ALCOHOLYSIS

The generation of monoester was modeled by the reaction of maleic anhydride with isopropyl alcohol. The reactions provided at temperatures of 52, 65 and 78 °C. The course of the reactions was monitored by determining the concentrations of anhydride and monoester by double titration after Smith and Bryant (details in Jureček (1955)). The sigmoid shape of time dependence of the maleic anhydride conversion for systems without DMA indicates that the reaction was catalyzed by a reaction product (see Fig. 1). The generation of diester was not observed under the given conditions.

The active substance is evidently the proton produced by the dissociation of the generated monoester. The proton is first bound to the anhydride molecule under generation of an oxonium cation, which then reacts with alcohol and monoester originates (Ernest et al., 1959).

The dissociation of monoester is very fast in both ways so that, soon after the beginning of the reaction, equilibrium sets up. The control step, therefore, is the reaction of the oxonium cation with alcohol. The

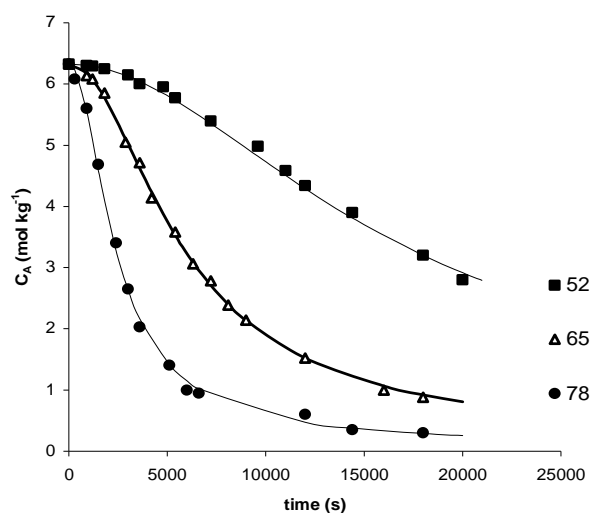


Fig. 1 Alcoholysis of maleic anhydride by isopropyl alcohol without DMA, numbers at curves are reaction temperature in °C.

following equation can then be derived for the alcoholysis kinetics:

$$-\frac{dC_A}{dt} = C_A C_{OH} (k_1 + k'_4 K_3) \sqrt{\frac{C_M}{1 + K_3 C_A}} \quad (1)$$

where

$$k'_4 = k_4 \sqrt{K_2}$$

At the beginning of the reaction the rate of the alcoholysis is very low, hence the inequality $k_1 \ll k'_4 K_3$. Equation (1) was solved by numerical integration using the Runge-Kutta method. Constants k'_4 and K_3 were optimized using Marquardt's method. The values of the constants found are given in Table 1. Figure 1 shows the time dependence of anhydride concentration fitted with integrated function (1). The temperature dependence of the constants was determined using Arrhenius' and van Hoff's relations.

Alcoholysis of anhydrides is catalyzed by tertiary amines. Whereas the product of the reaction of acetic anhydride with pyridine was not proved [10] the reaction of maleic anhydride with N,N-dimethyl aniline undoubtedly takes place. Evidence of this is the intensively orange coloration appearing after the two substances have been mixed. Neither maleic anhydride, nor N,N-dimethyl aniline absorb in the visible part of the spectrum. Let us assume the reaction:



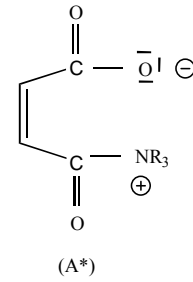
The equilibrium concentration $MA(DMA)_n$ depends on the molar fraction DMA as:

$$\begin{aligned} [MA(DMA)_n] &= K_6 \{C^0 (1 - X_{DMA}) - [MA(DMA)_n]\} \\ \{C^0 X_{DMA} - n[MA(DMA)_n]\}^n & \quad (3) \end{aligned}$$

where X_{DMA} is the molar fraction of DMA and $C^0 = C_A^0 + C_{DMA}^0$, superscript 0 indicates the initial concentrations.

Maximum of function (3) is at $X_{DMA} = n/(n+1)$. Using the Lambert-Beer's law we altered Equation (3) for absorbances. The solutions of MA and DMA in benzene were mixed in ratios to produce mixtures of different DMA molar fractions at constant total concentration of both components C^0 . These solutions were measured in the visible part of the spectra at several wavelengths. The maxima of the curves corresponded to $X_{DMA} = 0.5$, and thus $n=1$. It may be assumed that the substances to be generated will have the following structure see scheme 1.

Alcoholysis is a nucleophilic reaction and it is evident to take place advantageously, via semiproduct A^* , in the presence of tertiary amine due to increase of



Scheme 1: Structure of the MA (DMA)

the positive partial charge on the carbon neighboring to nitrogen. Let us assume a reversible reaction, in which the initial substances and the product are in scheme 2.

The system of equations, describing the kinetics of these reactions, can be simplified if one assumes stationary concentrations C_{A^*} , C_{M^*} and constant concentration of active DMA particles:

$$\frac{dC_A}{dt} = -\frac{k_7 K_6 C_{DMA}^0 C_A C_{OH}}{1 + K_6 C_A + K_8 C_M} + r_0 \quad (4)$$

where r_0 is the rate of non-catalyzed reaction (Equation (1)).

Equation (4) can be conveniently approximated by a 1st-order equation, to which it will transfer, if $K_6 C_A \gg 1 + K_8 C_M$:

$$\frac{dC_A}{dt} = -k_7 C_{DMA}^0 C_{OH} + r_0 \quad (5)$$

The time dependences of maleic anhydride for various amounts of catalyst at a temperature of 65 °C are shown in Fig. 2. Rate constants k_7 determined by Marquardt's method are given in Table 1.

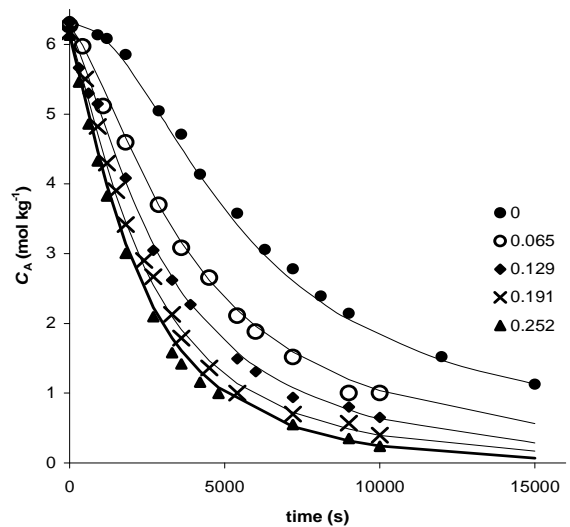
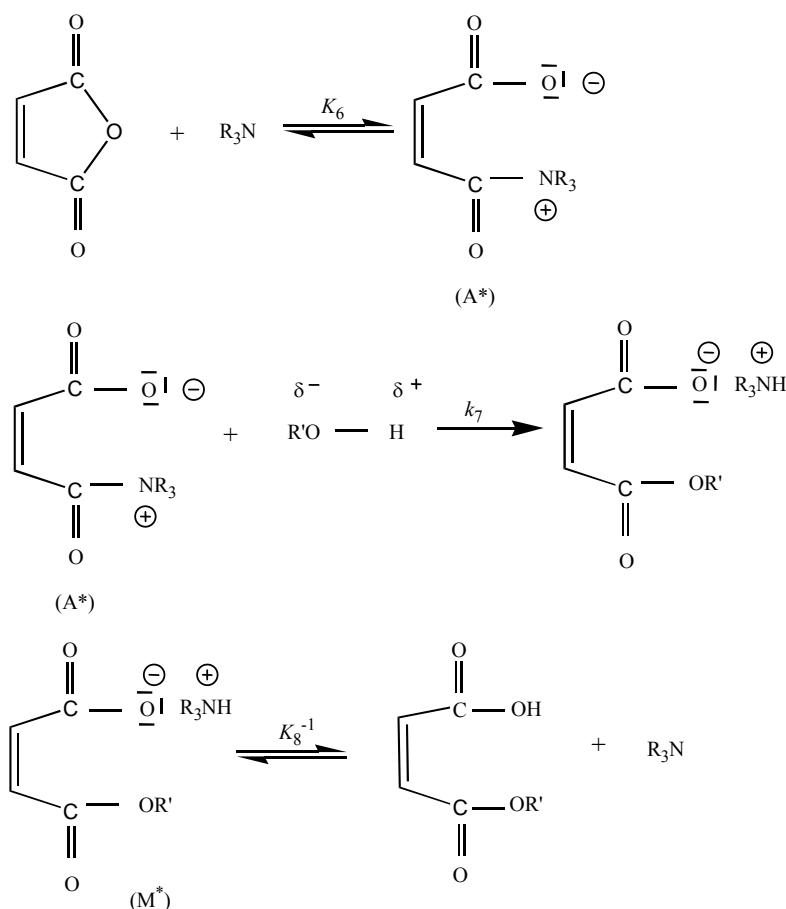


Fig. 2 Alcoholysis of maleic anhydride by isopropyl alcohol catalyzed DMA, numbers at curves are catalyst contents in mol kg^{-1} .



Scheme 2: Catalytic reaction of alcoholysis.

REACTION OF CHS EPOXY 15 RESIN WITH MONO(ISOPROPYL) MALEIC ESTER

The reaction of monoester (generated by alcoholysis) with epoxy groups was studied on the model reaction of CHS Epoxy 15 resin with Mono(isopropyl) maleic ester (M). The reactions took place in present DMA catalyst as well as without a catalyst, at temperatures of 65, 78, 89 and 100 °C. The reactions were monitored by measuring the concentration of epoxy groups and of monoester. The epoxy groups were determined by HBr titration in acetic acid (Durbetaki, 1956). The content of monoester was determined by double titration after Smith and Bryant (Jureček, 1955). The rate of depletion of both reaction components is identical. On the whole, the reaction is of the second order:

$$-\frac{dC_E}{dt} = -\frac{dC_M}{dt} = k_9 C_E C_M \quad (6)$$

where C_E and C_M are the concentrations of epoxy groups and monoester, respectively.

The kinetic constants for the monitored temperatures are given in Table 2. The time dependences of the conversion of epoxy groups for various reaction temperatures are shown in Fig. 3. The

kinetics observed correspond to the data reported in the literature. According to (Ernest et al., 1959) the epoxy groups react with weak acids mostly with the S_N2 mechanism. Kinetics of the second order in general was also observed by Sorokin, when he studied the non-catalyzed reaction of phenyl glycidyl ether with caproic acid (Sorokin, 1968).

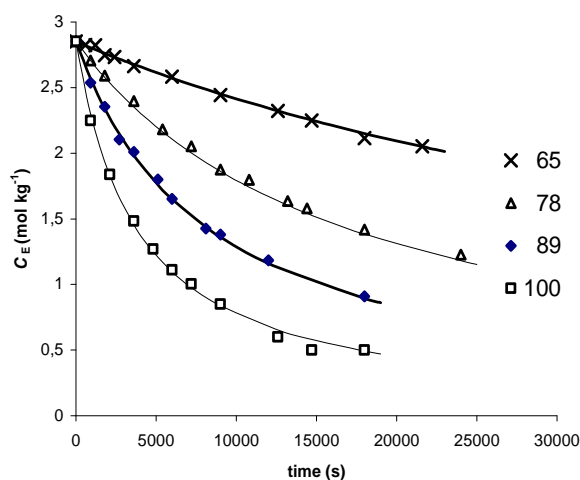
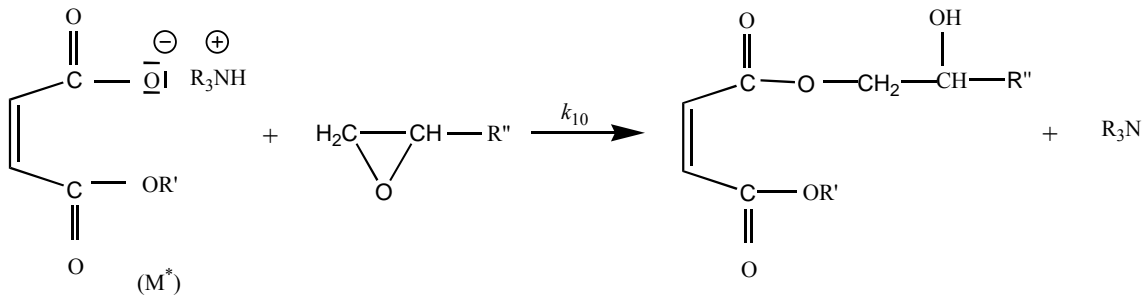


Fig. 3 Reaction of CHS Epoxy 15 resin and mono(isopropyl) maleic ester without a catalyst.

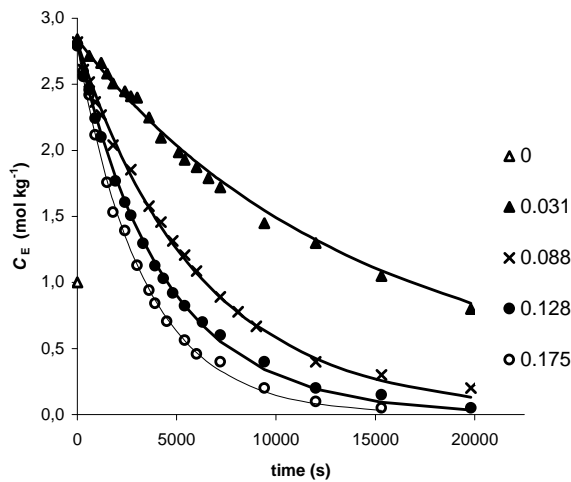
Table 2 Reaction of CHS Epoxy 15 resin and mono(isopropyl) maleic ester

T (°C)	k_9 (kg mol s ⁻¹)	k_{10} (kg mol s ⁻¹)
65	$6.35 \cdot 10^{-6}$	$1.67 \cdot 10^{-3}$
70	$9.97 \cdot 10^{-6}$	$2.43 \cdot 10^{-3}$
78	$2.07 \cdot 10^{-5}$	$3.35 \cdot 10^{-3}$
89	$4.27 \cdot 10^{-5}$	$5.57 \cdot 10^{-3}$
100	$9.33 \cdot 10^{-5}$	$8.98 \cdot 10^{-3}$
Preexponential factor	$1.37 \cdot 10^7$	$6.56 \cdot 10^4$
Activation energy (kJ)	80	49

**Scheme 3:** Reaction schema of epoxy and M^* .

The presence of N,N dimethyl aniline leads to the acceleration of the reaction. Fig. 4 shows the concentrations of the epoxy groups at a temperature of 65 °C and various catalyst concentrations as functions of time.

Let us consider the reaction scheme 3. The corresponding mathematical model can be simplified by assuming C_{M^*} to be stationary and the concentration of active particles DMA to be constant:

**Fig. 4** Reaction of CHS Epoxy 15 resin and mono(isopropyl) maleic ester with DMA catalyst

$$\frac{dC_E}{dt} = -\frac{k_{10}K_8C_{DMA}^0C_EC_M}{1+K_8C_M} \quad (7)$$

Since the DMA concentration as compared to the monoester concentration is very low, all of the catalyst is certain to be practically present in bound form. The rate equation can then be simplified as:

$$\frac{dC_E}{dt} = -k_{10}C_{DMA}^0C_E \quad (8)$$

This agrees with Sorokin's results (Sorokin, 1968) who found that the reaction of n-butyl phthalate with phenyl glycidyl ether under catalysis by tertiary amines displayed kinetics of the first order with respect to the epoxy compound and of zero order with respect to monoester. Kinetics of the 1st order was also observed for the basic catalyzed reaction of epoxy compounds with caproic acid (Sorokin, 1968). The equation for the overall rate of epoxy groups depletion was solved by numerical integration using the Runge-Kutta method, and constants k_9 and k_{10} were optimized by Marquardt's method. The values of the constants are given in Table 2.

REACTION OF CHS EPOXY 15 RESIN WITH MALEIC ANHYDRIDE

The course of the curing of CHS Epoxy 15 resin was studied. The content of the epoxy groups during curing was monitored by HBr titration in acetic acid (Durbetaki, 1956). The contents of anhydride and monoester were determined by double titration (Jureček, 1955). The reaction of the epoxy groups

Table 3 Reaction of maleic anhydride with CHS Epoxy 15 resin

T (°C)	k_7 (kg mol s ⁻¹)	k'_{10} (kg mol s ⁻¹)
65	$1.53 \cdot 10^{-02}$	$5.71 \cdot 10^{-03}$
70	$2.23 \cdot 10^{-02}$	$8.45 \cdot 10^{-03}$
78	$3.24 \cdot 10^{-02}$	$1.61 \cdot 10^{-02}$
Preexponential factor	$7.8 \cdot 10^6$	$9.0 \cdot 10^9$
Activation energy (kJ)	56	79

runs via monoester, generated by the reaction of anhydride with OH groups (always present in epoxy resins). The fact that these reactions, i.e. alcoholysis and reaction of epoxy groups with monoester, do indeed take place was verified, on the one hand, by analysis of curing mixtures, and on the other by studying both reactions separately. The following balances exist among the concentrations of the epoxy groups, maleic anhydride, OH groups, DMA, monoester and diester:

$$\begin{aligned}
 C_E^o &= C_E + C_D \\
 C_A^o &= C_A + C_M + C_D \\
 C_{OH}^o &= C_{OH} + C_M \\
 C_{DMA}^o &= C_{DMA} + C_{A^*} + C_{M^*}
 \end{aligned} \quad (9)$$

Based on the reaction schemes proposed above, one is able to derive the rate equations of depletion of epoxy groups and anhydride in the following form:

$$-\frac{dC_A}{dt} = \frac{k_7 K_6 C_{DMA}^o C_A C_{OH}}{1 + K_6 C_A + K_8 C_M} \quad (10)$$

$$-\frac{dC_E}{dt} = \frac{k_{10} K_8 C_{DMA}^o C_E C_M}{1 + K_6 C_A + K_8 C_M}$$

The used CHS Epoxy 15 resin is characterized by a very low content of OH groups, and the curing rate is limited by their low concentration. Also the concentration of monoester will be low throughout the whole period of the reaction. Assuming that no other reactions are taking place, in which these substances occur, the inequality $C_M \leq C_{OH}^o$ holds between the concentrations. Based on the approximation of the steady state (Kraus et al., 1978) we assume that, after a brief induction period, the concentrations of monoester and of the OH groups will stabilize at a constant value, and that the following equations will hold for the rate of depletion of the epoxy groups and anhydride:

$$\frac{dC_A}{dt} = -k_7 C_{DMA}^o C_{OH}$$

$$\frac{dC_E}{dt} = -k'_{10} C_{DMA}^o C_M$$

$$\text{where } k'_{10} = \frac{k_{10} K_8}{K_6} \quad (11)$$

Hence, if the content of the OH groups in the epoxy resin is very low, the reaction may be referred to as of zero order with respect to both initial substances. Fischer (1960) describes the kinetics of the reaction of monoepoxy substances with anhydrides by a zero-order equation. Tanaka and Kakiuchi (1963, 1964) found that the Epikote 828 resin (0.8 mol OH/kg) displayed the same depletion of anhydride and epoxy groups.

Kinetics of reaction of maleic anhydride with CHS Epoxy 15 resin are in Fig. 5. Rate constants k_6 and k'_{10} of reactions CHS Epoxy 15 resin and MA were determined from integrated equations (11). The results are given in Table 3.

To determine the effect of the OH concentration on the curing process, we added an amount of isopropyl alcohol to the reaction mixture to bring its concentration corresponding to the concentrations of anhydride and of the epoxy groups. The time functions of the concentration of monoester display a shape typical for the subsequent reactions with one

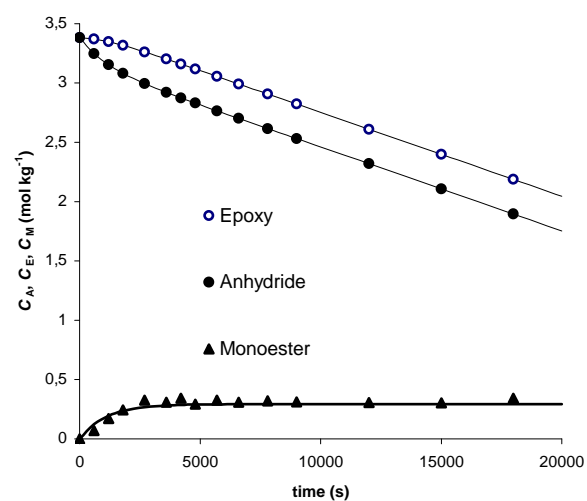


Fig. 5 Curing of Epoxy 15 resin by maleic anhydride ($C_E^o = C_A^o = 3.38$, $C_{OH}^o = 0.397$, $C_{DMA}^o = 0.029$ mol kg⁻¹), time dependence of epoxy groups, maleic anhydride and monoester.

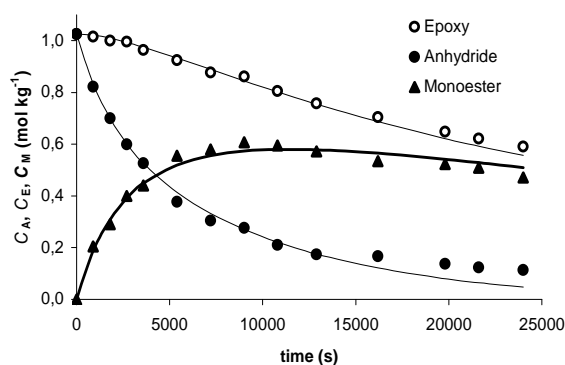


Fig. 6 Curing of Epoxy 15 resin by maleic anhydride in presence of isopropyl alcohol ($C_E^0 = C_A^0 = C_{OH}^0 = 2.842$, $C_{DMA}^0 = 0.026 \text{ mol kg}^{-1}$), time dependence of epoxy groups, maleic anhydride and monoester.

Table 4 Reaction of maleic anhydride with CHS Epoxy 15 resin enriched in hydroxyls.

	1)	2)
k_7 ($\text{kg mol}^{-1} \text{ s}^{-1}$)	$3.13 \cdot 10^{-4}$	$1.04 \cdot 10^{-3}$
K_6 (kg mol^{-1})	13.20	8.30
k_{10} ($\text{kg mol}^{-1} \text{ s}^{-1}$)	$1.10 \cdot 10^{-2}$	$2.31 \cdot 10^{-2}$
K_8 (kg mol^{-1})	0.14	0.08

¹⁾ CHS Epoxy 15 resin with isopropyl alcohol

²⁾ CHS Epoxy 15 resin reacted formerly with mono(isopropyl) maleic ester

semiproduct (see Fig. 6). The rate of alcoholysis is not limited, in this case, by the low concentration of hydroxyls, the depletion of anhydride is faster than the depletion of the epoxy groups, and monoester, therefore, accumulates in the reaction mixture. The experimental points were fitted with integrated functions (10). The values of the constants are shown in Table 4.

The concentration of the hydroxyl groups was effected also by partial reaction of the epoxy resin with mono(isopropyl) maleic ester in an amount, in which the resultant hydroxyl concentration would correspond to the concentration of the remaining epoxy groups. The resin treated in this manner, was subjected to reaction with maleic anhydride. The reaction took place in xylene with 0.156 mol DMA/kg as catalyst, at a temperature of 75 °C. The appropriate time dependences of concentrations of E, A and M are shown in Fig. 7.

Fisch and Hofmann (1954, 1961) detected dependences of this type. These authors studied the reaction kinetic of curing Araldite 6060 resin, which has a comparable content of hydroxyl and epoxy groups (2.8 and 2.5 mol/kg). Also Sorokin (1968) who studied the reaction of equimolar amounts of phenyl

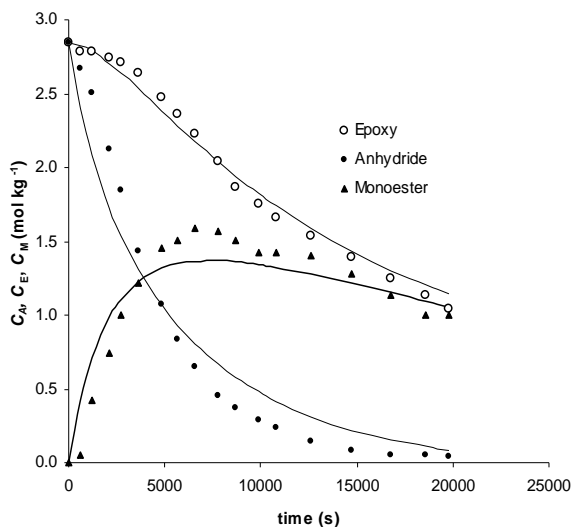


Fig. 7 Curing of Epoxy 15 resin reacted formerly with mono(isopropyl) maleic ester, ($C_E^0 = C_A^0 = C_{OH}^0 = 1.026$, $C_{DMA}^0 = 0.029 \text{ mol kg}^{-1}$).

glycidyl ether, phthalic anhydride and n-butyl alcohol arrived at the same results.

REACTION OF EPOXY GROUPS WITH HYDROXYLS

The reaction of hydroxyls with epoxy groups was studied on the reaction of CHS Epoxy 15 resin with isopropyl alcohol under DMA catalysis, as well as without a catalyst at temperatures of 65 and 80 °C. During the monitored period (about 8 hours) not even in a single case did a provable depletion of epoxy groups occur. This agrees with the finding of Sorokin, who observed no reaction of epoxy groups with alcohols either (Sorokin, 1968).

4. CONCLUSION

The paper reports the results of research the kinetics of reactions of CHS Epoxy 15 resin with maleic anhydride and N,N-dimethyl aniline (DMA) catalyst. The origination of monoester was studied separately on a model reaction of maleic anhydride with isopropyl alcohol. This is acid catalyzed reaction, in which the proton concentration is determined by the dissociation of the originating monoester. The rate of the DMA catalyzed reaction can be described by a first-order equation. The subsequent reaction of the epoxy groups with monoester was modeled by an CHS Epoxy 15 resin and mono(isopropyl) maleic ester. The non-catalyzed reaction is of the first order with respect to both reactants. The rate of the DMA catalyzed reaction can be described by a first-order equation with respect to the epoxy groups and by a zero-order equation with respect to monoester.

The curing of epoxy resins by maleic anhydride catalyzed by DMA depends on the content of hydroxyls. If the concentration of anhydride, epoxy

groups and hydroxyls is comparable, the depletion of anhydride is faster than that of the epoxy groups. The time dependence of monoester has a form typical for the subsequent reactions. A relatively short time after the beginning of the reaction, the anhydride vanishes from the reaction mixture and only the reaction of epoxides with the monoester continues. In terms of kinetics this reaction is of the first order. The low concentration of OH groups restricts the rate of alcoholysis as well as the reaction of monoester with the epoxy groups. It appears that the discrepancies in curing kinetics and mechanism are related to the different content of OH groups in the resins studied.

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REFERENCES

- Barton, J.M. and Greenfield, D.C.L.: 1986, *British Polym. J.*, 18, 51.
- Bender, M.L.: 1960, *Chem. Rev.*, 60, 1.
- Chatchapuridze, N.A.: 1969, *Plast Massy*, 4, 57.
- Chen, W.Y. et al.: 2004, *Polymer*, 45, 6897–6908.
- Durbetaki, A.J.: 1956, *Anal. Chem.*, 28, 2000.
- Ellis, B.: 1993, *Chemistry and technology of epoxy resins*, Glasgow, Blakie Academic Professional.
- Ernest, I., Heřmánek, S. and Hudlický, M.: 1959, *Preparative reactions in organic chemistry*, Prague, Czechoslovak Academy of Sciences.
- Fisch, W. and Hofmann, W.: 1954, *J. Polym. Sci.*, 12, 497.
- Fisch, W. and Hofmann, W.: 1961, *Plastics Technology*, 28, 8, 29.
- Fischer, R.F.: 1960, *J. Polym. Sci.*, 44, 155.
- Gold, V.E. and Jefferson, C.J.: 1953, *J. Chem. Soc.*, 1049.
- Hagnauer, G.L. and Pearce, P.J.: 1992, *ACS Symp. Ser.*, 221, 193.
- Jureček, M.: 1955, *Organic Analysis*, Prague, Czechoslovak Academy of Sciences.
- Kim, W.G. and Lee, J.Y.: 2002, *Polymer*, 43, 5713–5722.
- Kraus, W., Schneider, P. and Beránek, L.: 1978, *Chemical kinetics for engineers*, Prague, SNTL.
- Lee, H. and Neville, K.: 1967, *Handbook of epoxy resins*, New York, McGraw-Hill.
- May, C.A.: 1988, *Epoxy resins*, New York, Marcel Dekker.
- Morgan, R.T.: 1985, *Adv. Polym. Sci.*, 72, 1.
- Rocks, J., Rintoul, L., Vohwinkel, F. and Georgie, G.: 2004, *Polymer*, 45, 6799–6811.
- Sorokin, M.F.: 1967, *Kinetika i kataliz*, 3, 512.
- Sorokin, M.F.: 1968, *Kinetika i kataliz*, 3, 548.
- Steinmann, B.J.: 1989, *Appl. Polym. Sci.*, 37, 1753.
- Tanaka, Y. and Kakiuchi, J.: 1964, *J. Polym. Sci.*, Part A, 3405.
- Tanaka, Y., Kakiuchi, J.: 1963, *J. Appl. Polym. Sci.*, 37, 1063.
- Wang, Q. and Shi, W.: 2005, *Polymer Degradation and Stability*.