THERMOANALYTICAL STUDIES ON THE CURING OF EPOXY RESIN UNDER THE ACTION OF AQUEOUS SOLUTIONS OF HETEROPOLYACIDS OF TUNGSTEN AND MOLYBDENUM

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By means of DSC, DTA, TG and NMR it was established that the process of cure of epoxy resins induced by aqueous solutions of heteropolyacids consists of two stages, the first one being connected with a catalytic interaction between oligomer and water, and the second one with epoxy-hydroxyl etherification. Analysis of kinetic data shows that the first reaction is diffusion controlled, the second process can be described by pseudo-first order kinetics with activation energy about 40 kJ/M.

Keywords: epoxy resins, heteropolyacids of tungsten and molybdenium

Introduction

As it is known, the application of thermoanalytical methods (especially DTA and DSC) in studying the processes of cure of epoxy resins offers certain advantages both in the theoretical respect, for the detailed investigation of the mechanism of reactions, and in the determination of the practical schedules of thermal setting and the design of new compositions [1, 2]. From our point of view it is worth elaborating hardeners that combine high efficiency typical of catalytic curing agents and the possibilities of changing the physical-mechanical properties of polymeric products, which are characteristic of the crosslinking agents. The catalytic action of heteropolyacids (HPA) of the 12-row with common formula $H_{8-n}X_nM_{12}O_{40}$, where X signifies heteroatom (P, Si, B etc.) with valency n and M– Mo or W, was investigated in detail, particular attention has been given to the fact of their applicability in different polymerization and polycondensation processes [3, 4]. However, it was only in the early 80's that the use of HPA as the curing agents for epoxy resins was found to be perspective, and some technologically fitted compositions including organic solvents for HPA were

worked our [5]. The presence of active diluents in the above mentioned composi-
tions was obligatory for prolonging their pot life. In [6] the applicability of aque-
ous HPA solutions for the same purpose was shown. In that very case the
necessary decrease of the efficiency of the catalyst was achieved by the formation
of the diffusion barriers for the HPA in the initial heterophase system. The func-
tion of the solvent of HPA in this case can consist also in chemical interactions
with the oligomer. The influence of the initially added water in making the physi-
cal-mechanical properties of the systems in question flexible was studied in [7].
In the present study an attempt is made to investigate the role played by added
solvent in the catalytic reactions during the crosslinking of the resin via the-
rmoanalytical methods.

Experimental

In the present work aqueous solutions of 12–tungsten–phosphoric (PWA) and
12–molybdo–phosphoric (PMA) acids with formulae $H_3PW_{12}O_{40}$ and
$H_3PMo_{12}O_{40}$ were used. Industrially produced HPA of grade 'chemical pure'
(0.13% impurities) were recrystallized from water, PMA was also treated with
ether according to [8]. Epoxy resin ED–20 based on the diglycidyl ether of
Bisphenol–A (molecular weight 390–410, epoxy equivalent 205, T_g =258 K) [9]
was used without additional purification. The oligomer was heated for 2 h at
323 K before cure to remove crystallites. The preliminary check of the epoxy
equivalent was carried out by measuring the ratio between the integral intensities
of the phenyl and oxirane lines in the ^{1}H–NMR-spectra of high resolution. The
latter were recorded using a TESLA BS467 instrument. The compositions were
prepared by mechanical emulgation of the acid solution in the resin (30–40s) and
subsequent decontamination by a rapid centrifugation. The interval of the HPA
weight fractions (*m*) made up 0.5–4%. The usual setting procedure required iso-
thermal curing for 24 h at room temperature with a subsequent stepwise tempera-
ture rise up to 415 K.

Thermal analysis (TG, DTA, DSC) was carried out by a derivatograph
Q1500D (Hungary) and by a calorimeter DSM–2 (USSR). The instruments were
calibrated on the basis of the melting heat of diphenylketone and In, the experi-
ments were carried out in air atmosphere. To study the kinetics of reactions both
isothermal (303–343 K) and dynamic regimes with heating rates β =
2.5–50 deg/min were used.

Gel-times (τ_{gel}) were determined based on dynamic mechanical characteristic
measured on a direct pendulum. The extent of the curing process was examined
both by DSC and also by means of IR absorbance spectra obtained on a FTIR–IR
spectrometer Perkin–Elmer 1720X. Electron micrographs were made of the C/Pt
replicas of the freezed-fractured surface on a transmission microscope Philips
410. NMR spectra of broad lines were measured on a VARIAN WL–112 spec-

trometer. For the quantitative processing of the NMR spectra special calibrated capillaries-standards with determined amount of the solution of $MnSO_4$ in H_2O were prepared, the concentration of the salt was selected from the known breadth of the NMR-line.

Results and discussion

Aqueous HPA solutions are capable of providing rather high rates of setting of ED–20 at room temperature, the temperature of the bulk samples containing 1.6 g of composition may be raised even up to 440 K within a few minutes. Analysis of some species that underwent usual curing demonstrate an excellent degree of conversion of epoxies ($\alpha > 0.93$) and no sign of their isomerisation.
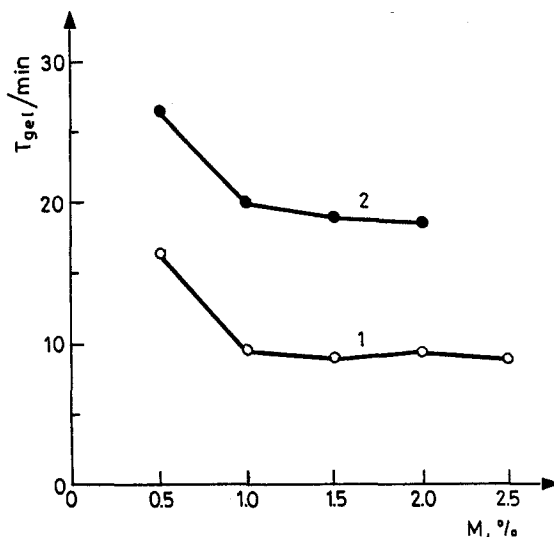

Fig. 1 Dependences of τ_{gel} on m' for the isothermal cure of ED–20 ($T = 295$ K) by 0.45 M(1) and 0.3 M(2) PWA solutions

The consideration of the isothermal kinetics of gel formation ($T = 295$ K) for the systems with PWA (Fig. 1) shows that the character of the dependence $\tau_{gel}(m)$ is different for different catalyst weight fractions. For low m the values of τ_{gel} are changing fast, reaching 10–15 days at $m = 0.3\%$. For m greater than some optimum value of 0.8–1% the dependence shows practically no change. Evidently in the latter case the rate of reaction is limited by the initial induction period connected with the processes of diffusion of HPA into the resin phase, this retardation being determined only by the concentration of acid (C) in the aqueous solution. The electron-microscopic study confirms the diffusional nature of the first stage

of the reaction. The micrographs of the samples show that the size of formations, which made up 130±30 nm at the beginning and was weakly dependent upon C, approaches 215±30 nm at the gel-point and acquires a vague boundary. The above mentioned stage of the reaction is also responsible for a certain increase in the hydrogen bond intensity*, which suggests that water can participate in the curing processes.
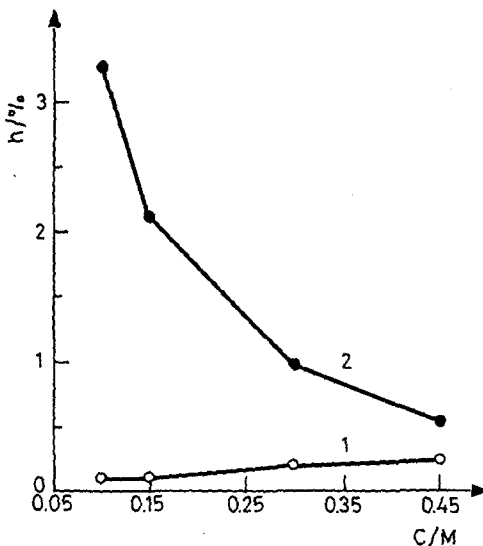

Fig. 2 Results of measurements of humidity obtained from NMR–spectra of broad lines for the compositions with PWA (m =1%) (1) and initial humidity (2)

The state of water in the fully cured polymers prepared in sealed glass tubes was studied by considering the temperature dependence of the ^{1}H–NMR–spectra of broad lines; some of the species on heating to 320–330 K revealed a narrow component with a breadth of about $8 \cdot 10^{-2}$ Gauss. The results of measurements of humidity (h) performed for this component are given in Fig. 2. It is obvious that the available water fraction is considerably smaller than the initial one and changes in a way reverse to the expected. On the basis of the known behaviour of sorbed water in epoxy polymers [10, 11] it can be stated that the possibility of the presence of bound fraction of water [12] with an amount as high as 3–3.5% is completely excluded. Thus it is demonstrated that initially emulgated water can participate in the catalytic processes of crosslinking.

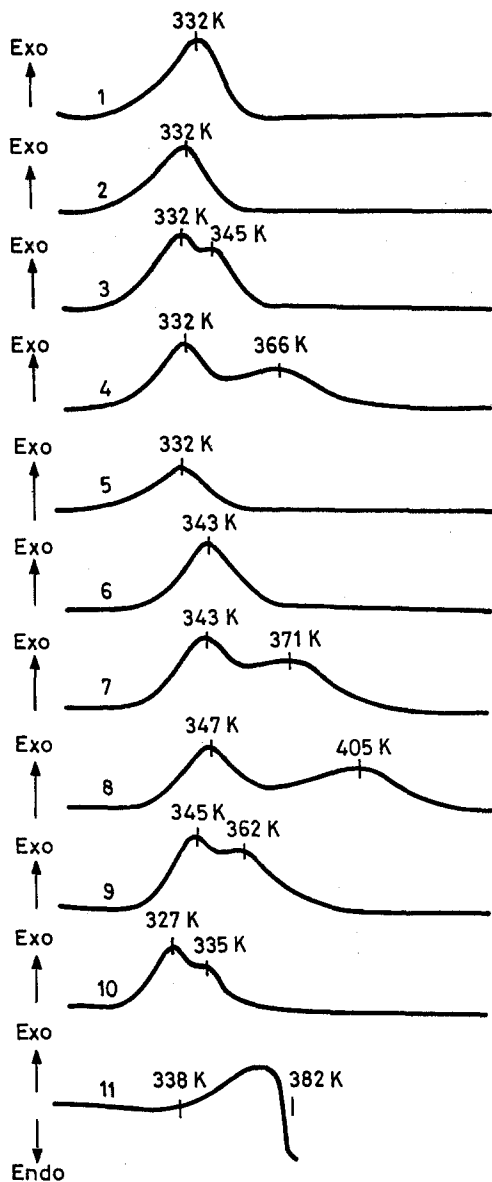*   correlations between initial humidity and the shift of the OH valence band are given in [7].

Fig. 3 DTA curves (β =5 deg/min) corresponding for the interaction between ED–20 and PWA 0.15 M, m being equal to 1.5%(1), 0.8%(2), 0.6%(3), 0.4%(4), 0.2%(5); PMA 0.085 M, m being equal to 0.4%(6), 0.3%(7); PWA 0.05 M, m =0.2%; DSC curves for the system with 1% 0.3 M PWA β =50 deg/min (9), β =12 deg/min (10); and for the system with PWA 0.05 M, m =0.1%, β =50 deg/min

DTA and DSC curves corresponding to the interaction of ED–20 with two HPA solutions (0.15 M PWA and 0.085 M PMA) added in different amounts to the system are given in Fig. 3 (1–5,6–7). The curves shown ($\beta = 5$ deg/min) confirm our supposition about the stage character of the curing process: a decrease in m leads to the division of the single exothermal effect into two effects, called first and second. The exothermal effects can also be divided by variation of β (Fig. 3, curves 9–10). However, at fixed β the position of the first signal on the tempera-ture scale ($T_{1, max}$) is dependent only on C and that of the second ($T_{2, max}$) is shifted to the high-temperature region as m decreases. The parameters of both processes were calculated for the scans exhibiting sufficiently separated exothermal peaks.

The first process

The results of TG demonstrated that the first reaction resulted in complete water conversion, moreover it was established that the thermal yield of this pro-cess (ΔH_1) was determined by h and was independent of m. The function $\Delta H_1(h)$ for compositions differing in m and C is shown in Fig. 4. The stoichiometry of the process in question may be received from the slope of the experimental line (27±3 kJ/mole %H$_2$O) taking into account literature data for the heat of the epoxy polymerization reactions (94–103 kJ/mole [13]): H$_2$O +2·epoxy g. So the first re-action appeared not to be the simple hydrolysis of epoxies [14] and probably it in-cludes as well the stages of the condensation and/or etherification of the generated end OH groups. The given interpretation is in accord with the fact that
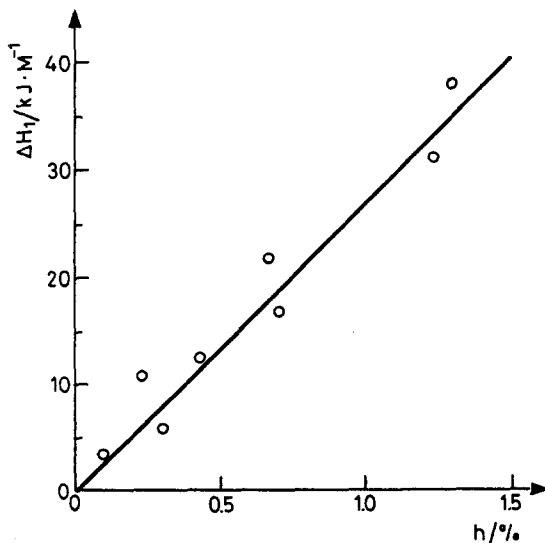

Fig. 4 Correlation between the thermal yield of the first reaction and initial humidity ($\beta=5$deg·min^{-1})

for the systems whose first process was not over up to 373 K, DSC revealed the endothermal effect which accounts for the explosion-like evaporation of part of the water (Fig. 3, curve 11).

To calculate the kinetic parameters of the first process some methods based on the treatment of the dynamic as well as isothermal data were employed. It should be noted that no difficulty arose in the evaluation of the isotherms (303–343 K) which might be caused by vitrification, the corresponding T_g remained remarkably below 295 K. The results of calculation show that the representation of the $f(\alpha)$ function in the form of $(1 - \alpha)^n$ in the equation $\ln K = \ln r - n \cdot \ln (1 - \alpha) = \ln \frac{d\alpha}{dt} \cdot n \cdot \ln (1 - \alpha)$, where r, K, n are rate, rate constant and order of reaction does not describe the real process. Thus the attempts to fit a straight line for the dependence $\ln K / T^{-1}$ [15] by means of the least squares method varying n in wide range lead to lines characterized by relatively low correlation coefficients. Besides there was found considerable non-linearity of the dependence $\ln r / \ln (1 - \alpha)$ for the isothermal experiments. The reasons accounting for the difficulties in the interpretation of DSC data likely consist in

1) the diffusional character of the first reaction (since it is known that diffusional equations may even not have a reaction order [16]);

2) changes in the reaction mechanism going on together with α. The detailed analysis of kinetic data brings us to the conclusion that both phenomena take place.

Table 1 E_a–α dependence for the first process for the compositions ED–20/PWA

α	(1) E_a (kJ/mole)	(2) E_a (kJ/mole)	(3) E_a (kJ/mole)
0.1	76.5	—	95.0
0.2	73.0	—	86.4
0.3	71.4	85.0	82.4
0.4	70.1	84.2	79.8
0.5	69.1	83.0	77.5
0.6	67.8	81.9	75.8
0.7	66.2	77.4	74.2
0.8	59.6	71.3	72.3
0.9	56.2	60.3	70.9

Ways of determination of E_a:

(1), (2) Evaluation by the dynamic [16] ($\beta = 2.5, 6, 25, 50$ deg/min) and isothermal experiments ($T = 313, 323, 333, 343$ K) for the system: $m = 0.2\%$, $C = 0.15\ M$;

(3) Concentrational shift of the exothermal effect with changing concentration for compositions with $m = 0.1–0.2\%$, $C = 0.05–0.3\ M$
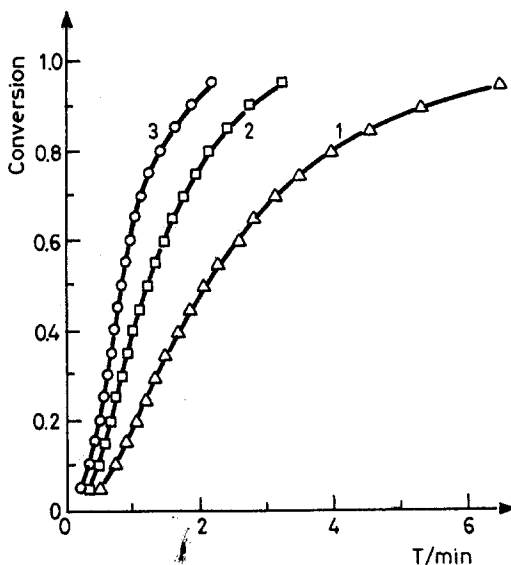
Fig. 5 Isotherms of the first process (T =333 K) corresponding to the interaction with PWA
0.05 M (1), 0.15 M (2) and 0.3 M (3)

The dependence of activation E_a (α) on the conversion for the first process received for the series of dynamic [17] and isothermal scans are given in Table 1; they demonstrate the decrease of E_a. At the same time the process can be described within the diffusional model: qualitatively the correlation between the rate of the process and C is obvious, the corresponding isotherms (333 K) are given in Fig. 5. Quantitatively we can suppose that the reaction is controlled by the diffusional flow of HPA particles, that is f (α)~C. Then the values of $E_a(\alpha)$ can be determined from the shift of the effect with changing concentration, i.e. by the slopes $\ln r_\alpha - \ln C/T_\alpha^{-1}$ (r_α, T_α– rate and temperature at conversion α) for dynamic scans at constant β. The E_a (α) values obtained (Table 1) correlate with data received by other methods.

The second process

It is supposed that HPAs dissociate in the phase of epoxy resin and the second process consists in the specific acid catalysis of the epoxy–hydroxyl etherification. It is known that the latter is facilitated in the presence of H^+–donors [18] (entering the reaction in our case after the first homogenization stage). This fact can be fixed by the shift of $T_{2, max}$ (m)(Fig. 3, curves 1–5, 6–7). The process can also be accelerated by increasing concentration of OH–groups which is connected with the initial h (Fig. 3, curves 5, 8). The determination of kinetic param-

eters according to [15] gives the values E_a=40±5 kJ/M and n =1.0±0.1. Evidently n may have a physical meaning if we suppose that hydroxyls are not consumed in side reactions. Thus we can check the shift of $T_{2,\,max}$ (m) (β, C are constant) using equations

$$r = K\,(1-\alpha)=A\cdot[H^+]\cdot[OH]\cdot exp(-E_a/RT)\cdot(1-\alpha); \quad [OH]\sim m; \quad [H^+]\sim m.$$

Then from Kissinger's formula [19]

$$E_a\,\beta\,/\,RT^2_{max} = A\cdot n\cdot(1-\alpha\,(T_{max}))^{n-1}\cdot exp(-E_a/RT_{max})$$

(where A signifies the frequency factor) it simply follows:

$$\Delta(\,\ln m^2 + \ln T^2_{max}) = \Delta(\,E_a/RT_{max}). \tag{1}$$

Dependences for the calculation of E_a of the second process by the method in [19] and by Eq. (1) are given in Fig. 6. The E_a values obtained are close: 43.6 and 39.4 kJ/M, which is in favour of the given interpretation of the second process.
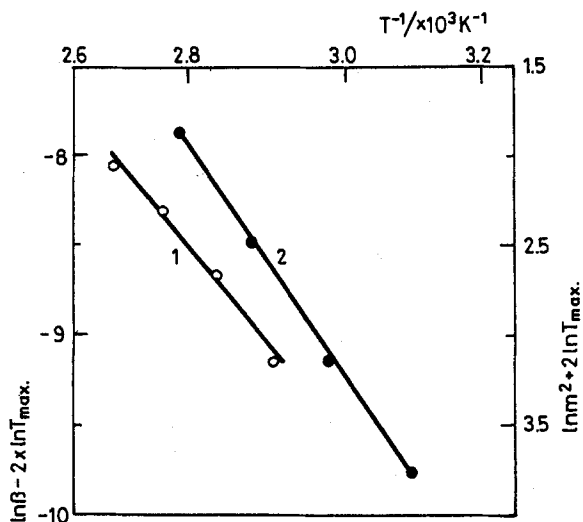

Fig. 6 Dependences $\ln m^2 + 2\cdot\ln T_{max}/T^{-1}_{max}$ (1) and $\ln\beta - 2\cdot\ln T_{max}/T^{-1}_{max}$ (2) for the second process in the systems with PWA 0.3 M (1) and 0.15 M (2)

Conclusions

It is established using DTA, DSC, TG and NMR techniques that the process of cure of epoxy resin ED–20 induced by aqueous solutions of heteropolyacids con-

sists of two stages, which can be separated on the DSC or DTA curves by variation of the composition of the systems or of the heating rate. The kinetics of the first stage is connected with a catalytic interaction between epoxy groups and water and is diffusion controlled. The second stage can be described by a pseudofirst order reaction with activation energy about 40 kJ/mol.

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Zusammenfassung — Mittels DSC, DTA, TG und NMR wurde festgestellt, daß der durch wäßrige Lösungen von Heteropolysäuren induzierte Aushärtungsprozeß von Epoxyharzen aus zwei Schritten besteht, der erste steht im Zusammenhang mit einer katalytischen Wechselwirkung zwischen Oligomer und Wasser, der zweite mit einer Epoxy-Hydroxyl-Etherbildung. Eine Analyse der Kinetik ergab, daß der erste Teilschritt diffusionskontrolliert ist, der zweite kann mit einer Reaktionskinetik pseudo-erster Ordnung mit einer Aktivierungsenergie von etwa 40 kJ/M beschrieben werden.