

Department of Chemical Engineering
Indian Institute of Science
Bangalore-560012, India

Monitoring the Curing of Furan Resins through the Exothermic Heat of Reaction

Manas Chanda and S. R. Dinesh

(Received 27 July 1977)

SUMMARY:

The curing reaction of furan resins was monitored through the exothermic heat of reaction by means of a simple technique. *p*-Toluene sulphonic acid dissolved in acetone was used to catalyse the curing reaction. A 'cure rate index', defined as the maximum temperature rise per unit time per unit mass of the resin, was used as a measure of the rate of cure. The index value increases exponentially with the catalyst concentration. Interestingly, for the same catalyst concentration the index value also increases significantly with the period of ageing of the catalyst solution. A method is developed for deriving the activation energy for the curing reaction from the exothermic heat data for non-isothermal cure. The activation energy is found to increase with resin viscosity and to decrease exponentially with increasing catalyst concentration. Quantitative expressions are derived relating activation energy with catalyst concentration.

ZUSAMMENFASSUNG:

Die Härtingsreaktion von Furanharzen wurde durch die exotherme Reaktionswärme mit Hilfe einer einfachen Technik überwacht. In Aceton gelöste *p*-Toluolsulfonsäure wurde als Katalysator zur Härtung eingesetzt. Ein „Härtungsgeschwindigkeitsindex“, der als maximale Temperaturerhöhung pro Zeit- und Masseneinheit des Harzes definiert wurde, wurde zur Messung der Härtungsgeschwindigkeit herangezogen. Dieser Index steigt exponentiell mit der Katalysatorkonzentration. Interessanterweise steigt der Indexwert bei gleicher Katalysatorkonzentration merklich mit der Alterungszeit der Katalysatorlösung. Es wurde eine Methode zur Bestimmung der Aktivierungsenergie der Härtingsreaktion aus den Daten für die exotherme Reaktionswärme bei nichtisothermer Härtung entwickelt. Die Aktivierungsenergie steigt mit der Harzviskosität und fällt exponentiell mit zunehmender Katalysatorkonzentration. Quantitative Zusammenhänge wurden hergestellt, die die Aktivierungsenergie als Funktion der Katalysatorkonzentration beschreiben.

Introduction

Furfuryl alcohol in presence of acid catalysts yields resinous products, known as furan resins. In the cured state furan resins possess exceptional resistance to acids, alkalies, chemicals, and solvents and also exhibit excellent heat resistance. There are numerous patents covering the methods of preparation and a wide variety of applications of furfuryl alcohol resins. Rathi and Chanda¹ presented an exhaustive review of the literature in this field. Dunlop and Peters² reviewed the published literature up to 1951 on the chemistry of the polymerisation of furfuryl alcohol. Barr and Wallon³ reported the chemical composition of furfuryl alcohol resins. More recently, Chanda et al.⁴⁻⁶ reported on the kinetic aspects of furfuryl alcohol polymerisation.

For commercial use, a partially condensed furan resin (prepolymer) is normally prepared in the form of a dark, free flowing viscous liquid by the polymerisation of furfuryl alcohol. Final cure of the prepolymer is carried out in situ, usually by the addition of acid catalysts, which include para-toluene sulphonic acid (PTSA), HCl, H₂SO₄, maleic anhydride, phosphoric acid, etc. There is hardly any literature on curing studies of the resin in spite of curing being one of the major steps in its application. Some results of curing studies are presented in this paper.

As the curing reaction is an exothermic one, measurement of heat liberated in course of the reaction provided the modus operandi. A simple apparatus was set up and a method was developed for the measurement of heat of reaction. The reliability of the method was confirmed by conducting experiments with systems whose enthalpy data are known. A suitable index was defined for the rate of cure of furan resins and its value was measured as a function of the catalyst (PTSA) concentration. The effect of ageing of PTSA solution in acetone on the rate of cure of furan resins was studied. A method was developed for deriving the activation energy of the curing reaction from the data of heat of cure as a function of time. The effect of catalyst concentration on the activation energy was determined.

Experimental Details

Materials

Technical grade furfuryl alcohol BDH (England) was used for preparing furan resins. The furfural content of the furfuryl alcohol, as determined by the bisulphite method⁷,

Curing of furan resins

was 0.14% and its cloud point⁷, which is a measure of the amount of polymer present, was found to be 8.5°C. (For commercial furfuryl alcohol the cloud point should not exceed 10°C.)

To prepare a furan resin, 200 ml of furfuryl alcohol was taken in a 1 l beaker and to this an equal volume of distilled water containing 0.25 ml of conc. H₂SO₄ was added, mixed thoroughly and heated over a water bath until two layers formed. Prolonging the heating at this stage resulted in a furan resin of higher viscosity. The bottom resin layer was separated from the aqueous layer with a separating funnel and washed thoroughly with an equal volume of 1% sodium bicarbonate solution. The alkaline resin layer was then subjected to vacuum distillation to remove the accompanying water completely. The residue in the flask was the furan resin. Furan resins of three different viscosities were prepared, viz., 150, 540 and 1380 centipoise at 30°C. The variations of viscosity with temperature for the three resins, as measured with a Höppler falling ball viscometer, are shown in Fig. 1. PTSA from Riedel de Haën, Hannover, Germany, was used as the curing catalyst.

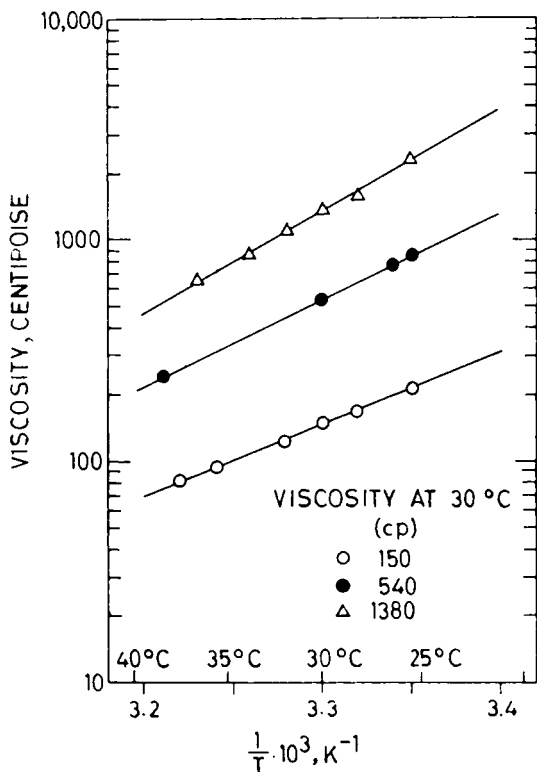


Fig. 1. Temperature dependence of viscosity of furan resins of different average molecular weights.

Apparatus

A diagrammatic sketch of the apparatus is shown in Fig. 2. The apparatus consisted of a 5 l capacity corning glass beaker covered at the top with a perspex sheet having four peripheral holes and a central hole of 1.5 cm diameter. A glass cell of 1.5 cm diameter and 5.5 cm height was projected vertically into the beaker through the central hole. A calibrated thermocouple was placed in a 6 mm diameter thin-walled glass tube (thermowell) containing a small amount of graphite powder. The thermocouple and thermowell were supported in a two-piece wooden block resting on the perspex sheet in such a way that the tip of the thermowell was at the centre of the cell. A heating coil was wound round the beaker to maintain the ambient temperature around the cell at 30°C. The thermocouple was connected to a potentiometric strip chart recorder through an amplifier for continuous recording of millivolt output.

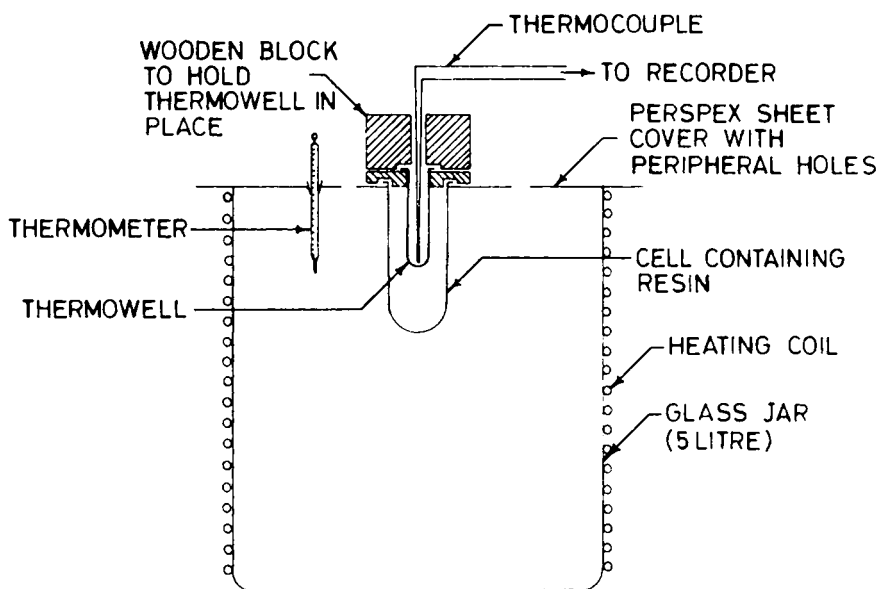


Fig. 2. Apparatus for curing studies.

Cooling Characteristics

The method of calculation of the heat of cure required a knowledge of the cooling characteristics of the system. In order to determine the cooling characteristics a series of experiments were conducted by pouring a hot medium into the cell and recording the corresponding cooling curves. Furan resins at a pH of 9.0 were used as the hot

Curing of furan resins

medium and cooling curves with different initial temperatures of the medium were recorded. Each cooling curve was fitted to an equation of the type

$$(T - T_2)/(T_0 - T_2) = Ae^{-Bt}$$

where T is the instantaneous temperature at time t , T_2 is the ambient temperature and T_0 is the initial temperature. For each curve the constants A and B were obtained and $-dT/dt$ and T were calculated for different values of time t . Fig. 3 shows a plot of $-dT/dt$ versus T . Since all points corresponding to different initial temperatures cluster around a straight line representing the instantaneous rate of temperature fall as a function of instantaneous temperature, this functional relationship may be assumed, to a fair degree of accuracy, to be independent of the preceding thermal history of the cooling system.

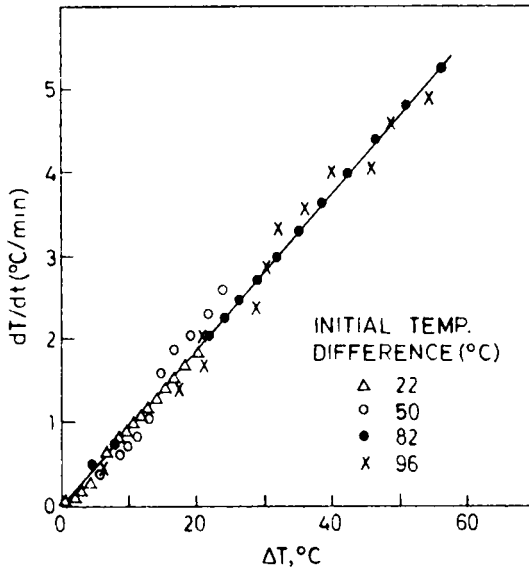


Fig. 3. Plot of -rate of fall of temperature versus instantaneous temperature.

Heat of Reaction

The recorder output corresponding to a reaction taking place in the cell is transformed into a temperature-versus-time curve. The curve is divided into a number of small time intervals. Assuming that the rate of heat loss over a small time interval is uniform, the cumulative heat of reaction (ΔH_t) over a period of time t is given by

$$\Delta H_t = \sum_{i=0}^{i=t} mc_p(-dT/dt)_i \Delta t_i k + mc_p(T_{t=t} - T_{t=0})k \quad (1)$$

Tab. 1. Heat of hydration of sulphuric acid: Comparison of results.

Wt. of water (g)	Wt. of acid (g)	Strength of acid (wt.-%)	Final H ₂ O:H ₂ SO ₄ molar ratio	Heat liberated (cal/g)	
				calculated	literature*
0.970	6.387	98.73	0.908	65.08	60.62
0.931	6.387	98.73	0.874	60.74	59.72
1.187	6.113	98.73	1.141	69.20	68.28

* O. T. Fasullo, Sulfuric Acid, McGraw-Hill, New York 1965, p. 294.

where $(dT/dt)_i$ is the rate of temperature drop, obtained from Fig. 3, corresponding to the mean temperature T_i of the i^{th} time interval; m and c_p are the mass and heat capacity of the reaction system; k is a factor to account for the heat taken up by the cell and the thermowell.

The reliability of the above method was checked using the H₂SO₄—H₂O system. Sulphuric acid of known strength was added to the cell containing a known quantity of water and the heat of dilution was calculated by the above method. Tab. 1 shows a comparison of values derived in this way with those obtained from the literature. The good agreement observed testifies to the reliability of the method.

Catalyst Ageing and Concentration

A 50% (wt./vol.) solution of PTSA in acetone was used as catalyst in all cure experiments. PTSA solution with different periods of ageing (at 27°C) was used to determine the effect of ageing on the rate of cure of furan resins of different viscosities.

To determine the effects of PTSA concentration (wt.%) in furan resin on its rate of cure, different amounts of 50% (wt./vol.) solution of PTSA in acetone, each of one hour age, were added to the furan resin and the corresponding T vs t curves were obtained.

Results and Discussion

Effect of concentration of PTSA

Non-isothermal cure curves for furan resins of viscosities 150, 540 and 1380 cp (at 30°C) catalysed by different amounts of PTSA are shown in Fig. 4 to 6. An index, γ , has been defined as

$$\gamma = \Delta T_{\max} / m \cdot t \quad (2)$$

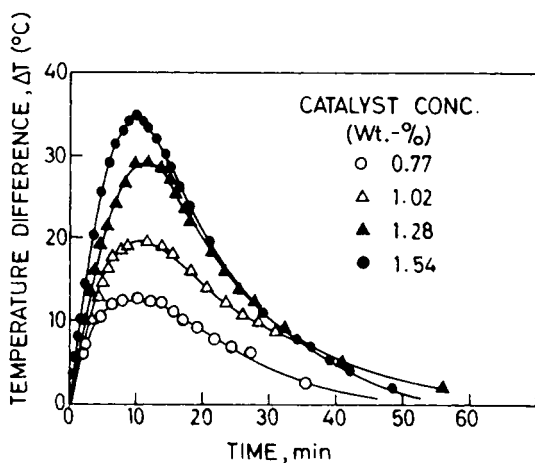


Fig. 4. Temperature rise versus time curves for non-isothermal cure of furan resin of viscosity 150 cp (at 30°C) with different amounts of catalyst (PTSA).

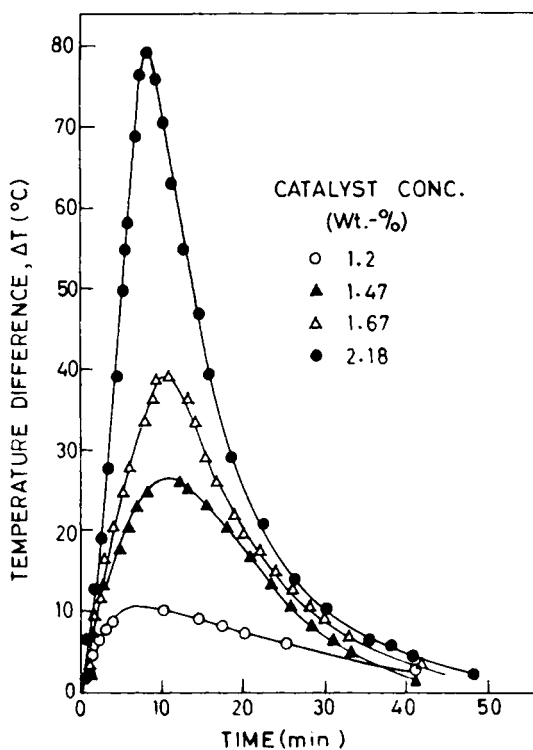


Fig. 5. Temperature rise versus time curves for non-isothermal cure of furan resin of viscosity 540 cp (at 30°C) with different amounts of catalyst (PTSA).

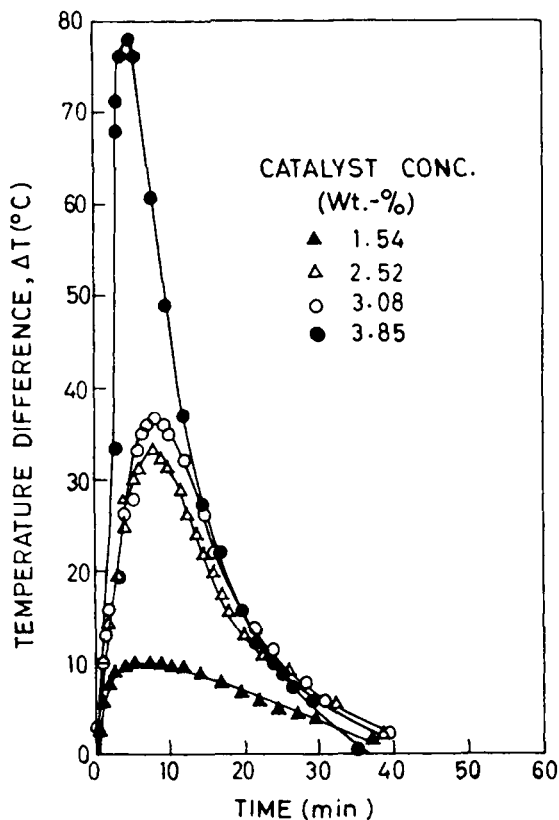


Fig. 6. Temperature rise versus time curves for non-isothermal cure of furan resin of viscosity 1380 cp (at 30°C) with different amounts of catalyst (PTSA).

where ΔT_{\max} , which corresponds to the peak of a cure curve, is the maximum temperature difference attained between the cell contents and the ambient air in a cure experiment and t is the time at which this maximum occurs; m is the mass of the resin. The index, γ , thus gives a measure of the maximum rate of cure. The values of the index, γ , calculated from Fig. 4 to 6 are plotted against wt.-% concentration of PTSA in resin. The rate of cure increases exponentially with catalyst concentration. It is significant that for an equal catalyst concentration, furan resins of lower viscosity, and hence lower average molecular weight, exhibit a higher index value (Fig. 7). This may be attributed to a larger content of reactive groups per unit mass in a lower molecular weight resin.

Curing of furan resins

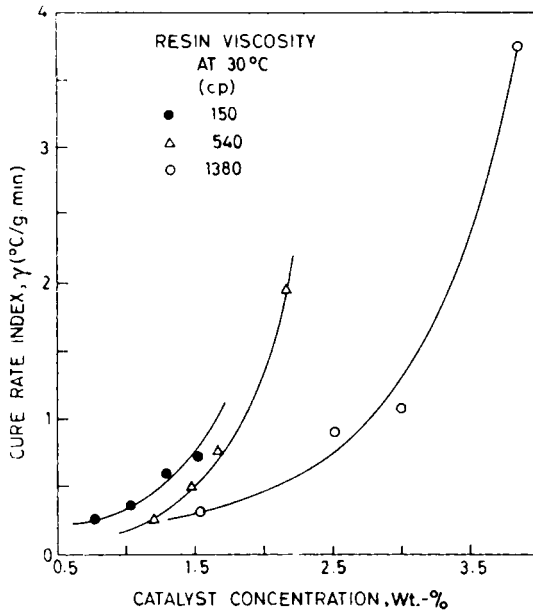


Fig. 7. Cure rate index versus catalyst (PTSA) concentration.

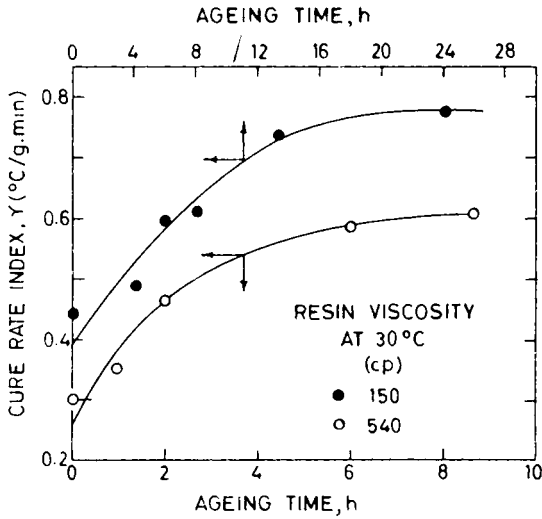


Fig. 8. Cure rate index versus ageing time of catalyst (PTSA) solution.

Effect of Ageing of PTSA Solution

Ageing of PTSA solution in acetone, unlike other solutions of PTSA such as in alcohol or dioxane, has been observed to have a significant promotional effect on the rate of cure of furan resins. The effect is however more pronounced in the case of lower viscosity resins (Fig. 8). The ageing effect may be attributed to reactions between PTSA and acetone resulting in the formation of more reactive species. The colour of the solution becomes darker on ageing.

Kinetic Treatment

It is assumed that the overall rate of cure is given by

$$d\alpha/dt = kf(\alpha) \quad (3)$$

where α is the fractional conversion and k is the rate constant. The quantity $f(\alpha)$ depends on the reaction mechanism. Assuming a first order reaction, Eq. (3) becomes

$$d\alpha/dt = k(1 - \alpha) \quad (4)$$

For the present work, α can be expressed as

$$\alpha = \Delta H_t / \Delta H_0 \quad (5)$$

where ΔH_t is the heat of cure up to time t and ΔH_0 is the overall heat of cure.

Substituting for α from Eq. (5) into Eq. (4) and assuming the rate constant to have the usual Arrhenius form: $k = A \exp(-E/RT)$, Eq. (4) can be written in the form

$$dH/dt = \Delta H_0(1 - \Delta H_t/\Delta H_0)A \exp(-E/RT) \quad (6)$$

In the initial period of curing, $(1 - \Delta H_t/\Delta H_0) \simeq 1$, and Eq. (6) then simplifies to

$$dH/dt = (A\Delta H_0) \exp(-E/RT) \quad (7)$$

For testing the validity of Eq. (7), the integral heat of reaction versus time data, calculated from Eq. (1) for the initial period, were fitted to an

Curing of furan resins

equation of the form $\Delta H_t = bt + ct^2$ and the constants b and c , evaluated by least squares technique, were then utilised to obtain $dH/dt = b + 2ct$. Thus for each cumulative time, t , in the initial period the corresponding dH/dt was calculated and a semilog plot of dH/dt versus $1/T$ was made. Fig. 9 to 11 show these plots for furan resins of different viscosities and different catalyst concentrations. A straight line fit in each case confirms that the

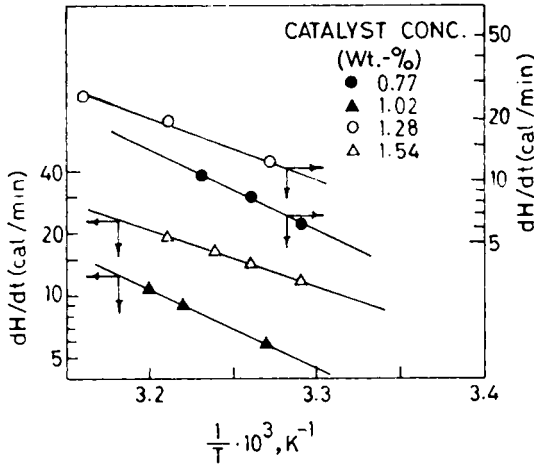


Fig. 9. Test of Eq. (7) for non-isothermal cure of furan resin of viscosity 150 cp (at 30°C).

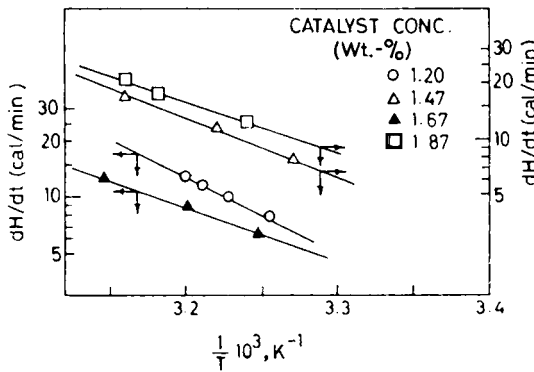


Fig. 10. Test of Eq. (7) for non-isothermal cure of furan resin of viscosity 540 cp (at 30°C).

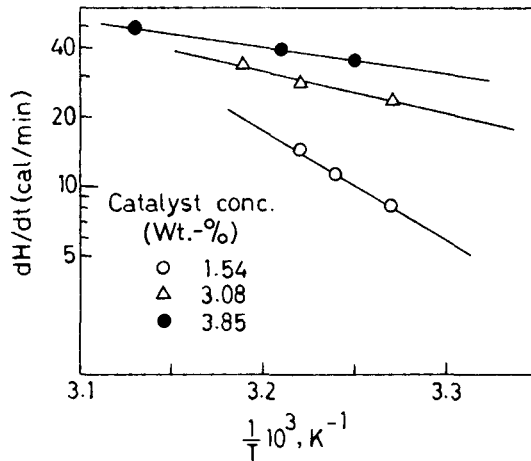


Fig. 11. Test of Eq. (7) for non-isothermal cure of furan resin of viscosity 1380 cp (at 30°C).

assumption of first order reaction is valid at least in the initial period. From the slope the corresponding activation energy can be calculated.

The activation energy values corresponding to different resin viscosities and catalyst concentrations are listed in Tab. 2. The activation energy is

Tab. 2. Activation energies for curing reaction corresponding to different resin viscosities and catalyst concentrations.

Resin viscosity at 30°C (cp)	Catalyst conc. (wt.-%)	Activation energy kcal/mol
150	0.77	18.31
	1.02	16.70
	1.28	13.61
	1.54	12.34
540	1.20	18.00
	1.47	14.80
	1.67	13.82
	1.87	12.60
1380	1.54	25.88
	3.08	8.38
	3.85	5.18

Curing of furan resins

seen to decrease considerably with increasing catalyst concentration. The logarithm of activation energy bears a linear relationship with catalyst concentration (wt.-%) for all the three resins, as shown by the plots of Fig. 12. The relationships are derived as

$$E_{150} = 27.15 \exp(0.511 w) \text{ (kcal/mol)} \quad (8)$$

$$E_{540} = 35.48 \exp(0.564 w) \text{ (kcal/mol)} \quad (9)$$

$$E_{1380} = 70.79 \exp(0.679 w) \text{ (kcal/mol)} \quad (10)$$

where w represents wt.-% concentration of PTSA in furan resin and the subscript for E indicates the resin viscosity.

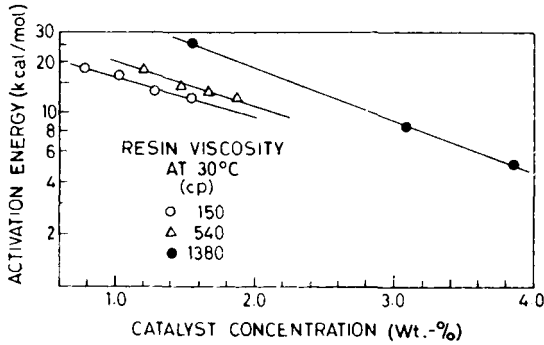


Fig. 12. Semilog plot of activation energy versus catalyst (PTSA) concentration.

Conclusions

The rate of cure of furan resins catalysed by PTSA in acetone has been monitored through the exothermic heat of cure. The rate of cure increases exponentially with catalyst concentration and for the same catalyst concentration, a resin of lower viscosity exhibits a higher rate of cure.

Ageing of PTSA solution in acetone has a strong promotional effect on the rate of cure of furan resins, especially those of lower viscosities. The promotional effect indicates the formation of more reactive species by reaction between PTSA and acetone to catalyse the cure of furan resins.

The activation energy for the curing reaction of furan resins decreases exponentially with increasing catalyst concentration. For the same catalyst concentration, however, the activation energy is higher for a resin of higher viscosity.

Acknowledgement

The authors thank Prof. R. Kumar for his interest in the work.

- ¹ A. K. A. Rathi, M. Chanda, *Pop. Plast.* **18/12** (1973) 28
- ² A. P. Dunlop, F. N. Peters, *The Furans*, ACS Monograph, Reinhold, New York 1953, p. 213
- ³ J. B. Barr, S. B. Wallon, *J. Appl. Polym. Sci.* **15** (1971) 1079
- ⁴ A. K. A. Rathi, M. Chanda, *J. Appl. Polym. Sci.* **18** (1974) 1541
- ⁵ M. Chanda, T. A. Krishnan, A. K. A. Rathi, *J. Indian Inst. Sci.* **56** (1974) 422
- ⁶ T. A. Krishnan, M. Chanda, *Angew. Makromol. Chem.* **43** (1975) 145
- ⁷ G. M. Kline, *Analytical Chemistry of Polymers*, Interscience Publishers, New York 1959, p. 203