

Completion of Alkaline Cure Acceleration of Phenol-Formaldehyde Resins: Acceleration by Organic Anhydrides

Recently, the mechanism of acceleration of the curing of phenol-formaldehyde (PF) resins by esters under very alkaline conditions has been clarified.¹ This is the mechanism responsible for the so-called α -set acceleration of alkaline PF resins in foundry core binders^{1,2} and in other applications.³ The mechanism was shown to depend on the decomposition of the ester and on the non-site-selective ionic attack of one of its fragments on the aromatic nuclei of the phenol. This led to a cross-linking mechanism superimposed onto the methylene bridges formation that is characteristic of the PF reaction. This mechanism, in effect, increases the functionality of the phenol, leading to early tridimensional networking and more rapid curing of the PF resin. Many esters such as propylene carbonate, glycerol triacetate, and phenyl acetate were shown to induce the same acceleration mechanism, although to a different extent.¹

The characteristic ester fragment shown to attack the phenolic nuclei indicated that chemical compounds unrelated to esters, but which also on decomposing produced the same type of fragment, should also be capable of accelerating the curing of PF resins under alkaline conditions by means of the same mechanism. The compounds used to show such a correlation were organic acid anhydrides, in particular, acetic and maleic anhydride.

EXPERIMENTAL

Phenol-Formaldehyde (PF) Resin Preparation and Gel Times Determination

Ninety-four parts by mass of phenol were mixed with 40 parts (20/80) methanol/water solution and 55 parts by mass of 96% paraformaldehyde powder. After stirring for 30 min at 40°C, the temperature was slowly, over a period of 30 min, increased to reflux (93°C). A total of 20 parts by mass of 33% sodium hydroxide solution was added in four equal parts at 15 min intervals over the previous total of 60 min. The reaction mix was kept at reflux for 60 min and then cooled. The resin solids content was 60% and viscosity 3100 centipoises at 25°C and the final pH was 10.8.

The gel-time dependence at pH 10.8 at 94°C was determined at a constant resin solids content of 50% using the following method: Gelation is defined by the point at

which the resin ceases to be a viscous liquid and becomes a soft, elastic, rubbery solid. Ten grams of liquid resin is weighed in a glass test tube. A wire spring is placed in the resin within the test tube and the resin (and anhydride accelerator when used) gently mixed for a few seconds at ambient temperature. The test tube is then placed in a boiling water bath, the wire spring is manually moved rapidly by upward/downward hand movements, and the time taken to gel is measured using a stopwatch. The test is repeated a few times and has good reproducibility as shown from the standard deviation values in Table I. The gel-time measurement has been shown to be inversely proportional to the rate of polycondensation and cross-linking of the resin,⁵ under the same reaction conditions, and has been adopted by some product associations as a standard due to its simplicity and reproducibility in relation to methods such as steady-shear viscosity.⁵ The gel times of the PF resin alone and of the PF resin to which 5 and 10% acetic anhydride, 5% maleic anhydride, 10% glacial acetic acid, and 10% acetic anhydride plus 10% of a 50% water solution of a surfactant were measured (see Table I), the percentages being expressed as percentages by mass on mass of PF resin solids content. The pH of the different mixtures was maintained constant at 10.8 by addition of small amounts of 40% sodium hydroxide solution, when needed.

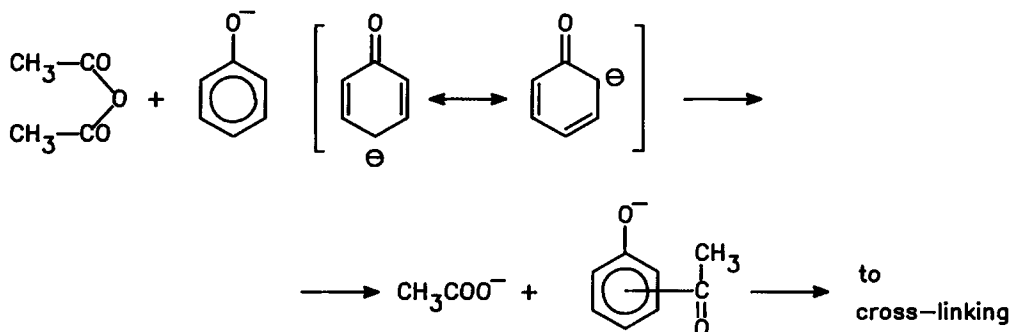
Calculation of Apparent Rate Constant

The calculation of the apparent rate constant of condensation due to the PF autocondensation and to the anhydride fragment attack was obtained by measuring the rate constants of the polycondensation of *o*-hydroxybenzyl alcohol (saligenin) under alkaline conditions,⁴ by measuring by IR spectroscopy the appearance of the 1420 cm⁻¹ band characteristic of a hydroxybenzyl alcohol and the decrease of the 840 and 715 cm⁻¹ band characteristic of the disubstituted aromatic nuclei.¹

DISCUSSION

The values of gel-time tests of a PF resin and of the apparent rate constants of polycondensation shown in Table I indicate that both acetic and maleic anhydride are capable of accelerating significantly the curing of PF resins. The pH of the mixes was maintained constant in all tests at a value of 10.8. From Table I it is also interesting to note that while the extent of acceleration appears to de-

pend on the proportion of anhydride used the correlation between acceleration and amount of anhydride is not linear. Thus, addition of 5% acetic anhydride shortens significantly the PF gel time from 40 to 32 min. However, by increasing the quantity of anhydride from 5 to 10% only shortens further the gel time to 29 min. Maleic anhydride also appears to accelerate PF resins curing better



Organic anhydrides hydrolyze in water solutions, and PF resins are in water solutions: A method to diminish the extents of hydrolysis, thus to diminish the proportion of the reactive fragment transforming into acid, should then also shorten further the PF resin gel time. To this purpose, 10% of a surfactant was added to the phenolic resin in order to form micelles in which some PF resin would be entrapped. On addition of anhydride, which is not miscible with water, for the part of the anhydride capable of migrating within the micelles, transformation to

than does acetic anhydride. That acceleration is not due to the acid formed from anhydride hydrolysis is shown by the gel time remaining unaltered when only acetic acid, rather than anhydride, is used (Table I). The proposed mechanism, which could then be presented from the cure acceleration behavior, appears then to be the same as that in the ester acceleration of PF resins curing.¹ The attacking fragment is also likely to be the same. Thus,

Table I Gel-time Values and Apparent Rate Constants of Polycondensation of a PF Resin with Anhydrides, pH 10.8

	Gel Time (Min)	Apparent Rate ^a Constant k ($L \times mol^{-1} \times s^{-1}$)
PF resin alone	40 ± 0.11	9.9 × 10 ⁻⁶
PF resin + 5% maleic anhydride	27 ± 0.07	7 × 10 ⁻⁵
PF resin + 5% acetic anhydride	32 ± 0.09	6 × 10 ⁻⁵
PF resin + 10% acetic anhydride	29 ± 0.08	1 × 10 ⁻⁵
PF resin + 6% glacial acetic acid	40 ± 0.12	1 × 10 ⁻⁵
PF resin + 10% acetic anhydride + 10% surfactant solution	26 ± 0.08	7 × 10 ⁻⁵

^a Calculated by model compounds (saligenin) autocondensation reaction at 85°C.

acid is decreased. This would lead to a more efficient use of the mechanism on which the acceleration effect is based. This appeared to be the case: Acetic anhydride in a micellar environment shortened the PF resin gel time even further from 29 to 26 min.

The use of anhydrides as cure accelerators of alkaline PF resins is not practical, the use of ester accelerators being far more significant.^{1,2} It was, however, of some interest to show that compounds other than esters, also able to produce some amount of the same reactive fragment, can also accelerate, by the same mechanism, the curing of alkaline PF resins.

References

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5. FESYP, Federation Europeenne des Syndicats de Fabricants de Panneau de Particules.

A. PIZZI

A. STEPHANO

Department of Chemistry
University of the Witwatersrand
Johannesburg, South Africa

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