

DETERMINATION OF PARAFORMALDEHYDE REACTIVITY AND ITS RELATIONSHIP TO PRF RESIN GELATION

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ABSTRACT

A titration procedure is described for determining paraformaldehyde reactivity in aqueous solution using common chemical reagents of Na_2SO_3 and NaH_2PO_4 . This reactivity is a measure of the monomeric formaldehyde released by the depolymerization of paraformaldehyde. Under certain experimental conditions, a curvilinear relationship was established between paraformaldehyde titration values and gelation times in a PRF resin. By utilizing a stepwise version of this titration method, the total reactivity distribution within paraformaldehyde samples could be determined and compared.

Keywords: Paraformaldehyde, PRF, titration, gelation reactivity.

INTRODUCTION

Paraformaldehyde is a mixture of polymethylene glycols containing 8 to 100 formaldehyde units per molecule (Walker 1964a). Commercial grade powders are commonly used in the hardener component of phenol-resorcinol-formaldehyde (PRF) adhesives. The reactivity of paraformaldehyde can vary considerably depending on how it was manufactured and the age of the material. When hardener and resin components are mixed, the paraformaldehyde breaks down to release monomeric formaldehyde, which rapidly reacts with the PRF polymer to first cause gelation and ultimately resin cure. The amount of paraformaldehyde present and its rate of decomposition have a major effect on PRF cure speed. In addition, recent concerns about formaldehyde emissions make control of paraformaldehyde decomposition an important parameter during manufacture and use of glued-wood-products.

The room temperature curing capabilities of PRF adhesives make them the adhesive of choice for bonding timber laminates of large dimension (Chow 1977). With these adhesives, gelation time at moderate temperatures provides a reliable indicator of system reac-

tivity because this test condition closely parallels conditions used during bond formation. However, gelation evaluations can be time-consuming and require the use of a test resin system that exhibits a characteristic, time-dependent curing property. This property is determined primarily by the manner in which the resin was synthesized. A more universal indication of hardener reactivity should result from a direct measure of paraformaldehyde decomposition to formaldehyde in aqueous solution.

Since cleavage of the formaldehyde polymer is believed to occur primarily at the end of the paraformaldehyde polymer chain, depolymerization will depend upon the number and accessibility of end groups. Consequently, paraformaldehyde materials of similar molecular weight may release formaldehyde at significantly different rates, depending upon whether the polymer chain end groups are exposed outside or inside the polymer chain bundles. The rate of formaldehyde release should also be dependent upon molecular weight, particle size, temperature, and pH.

This paper reports on a procedure for rapidly determining formaldehyde release into

aqueous solution and relates this data to gelation time measurements in a PRF resin system.

EXPERIMENTAL

The pH change in all experiments was monitored on an Accumet model 750 pH meter with attached chart recorder. Measurements were performed at ambient temperature (22 ± 2 C) in an unthermostated beaker. Reaction mixtures were magnetically stirred. Reagent grade sodium sulfite (Na_2SO_3) (Fisher Scientific) and reagent grade sodium dihydrogenphosphate (NaH_2PO_4) (Fisher Scientific) and distilled water were used throughout. The PRF resin used was LT-75, a 50% solids solution supplied by Borden Chemicals.

Titration of a formaldehyde solution against aqueous sodium sulfite

A 0.10 M HCHO solution was prepared by diluting 8.1 ml of a 37% formalin solution (containing 0.2% methanol) to one liter. This was titrated against 25 ml of 1.0 M Na_2SO_3 or a 25 ml solution containing 1.0 M Na_2SO_3 and 0.001 M of NaH_2PO_4 .

Standard titration procedures

A standard $\text{Na}_2\text{SO}_3/\text{NaH}_2\text{PO}_4$ solution was prepared by dissolving 63.02 g of anhydrous Na_2SO_3 and 13.8 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in distilled water to make a final volume of 1,000 ml. A 50-ml portion of the sulfite/phosphate solution was pipetted into a 400-ml beaker. The stirred solution was diluted with 175 ml of distilled water and 25 ml of methanol. The solution was vigorously stirred and 0.500 g of paraformaldehyde quickly added while a timer and recorder were simultaneously started. It is important that the paraformaldehyde be quickly dispersed into the reaction medium. The presence of methanol was found to eliminate the formation of lumps during the dispersion process. The reaction pH was monitored, and the timer was stopped after a rapid pH change to 11 (endpoint) was obtained. Two replicates were titrated for each sample.

Gelatin time determination

Three paraformaldehyde samples, A, B (both powders), and C (flakes) were obtained as reagent grade material from BDH Chemicals, Fisher Scientific and BDH Chemicals, respectively. Specifications for this grade of material indicated a minimum of 97% paraformaldehyde content. A fourth sample, D, was a hardener mixture (FM 282) supplied by Borden Chemicals and used to cure PRF resins. Analysis of total formaldehyde, by the standard Na_2SO_3 method (Walker 1964b) showed this hardener, D, to contain 35% formaldehyde, with the rest being walnut shell filler. Paraformaldehyde with higher levels of polymerization were prepared by heating powder A in a closed container at 92 C. Samples 2A and 3A were produced by heating for 9 and 16 days, respectively. During this heating period, the samples were monitored daily, and the reactivity was found to cycle between low and high titration values in an unpredictable manner. Addition of a small quantity of CaCl_2 into the powder during heating helped to stabilize this fluctuation. The CaCl_2 likely acts as a desiccant and catalyst for this reaction. Samples 4A, 5A, 6A, and 7A were produced by heating a mixture of sample A with 0.1% CaCl_2 at 67 C for 0.5, 1, 3 and 6 h, respectively.

Gelation times were determined by quickly mixing 1.58 g of paraformaldehyde with 25 g of LT 75 and placing the mixture in a 50-ml test tube that was held in a water bath at either 30 or 45 C. The measurement was accomplished by manually moving a stirring rod through the mixture using an up and down motion (about 5 cycles per minute). The period between when the test was initiated and when the rod could no longer be moved in the mixture was the gelation time. Duplicate samples were run for each mixture. When the FM 282 hardener was evaluated, 4.5 g of this material (equivalent to 1.58 g of paraformaldehyde) was used for testing gelation.

Stepwise titration of paraformaldehyde

A 7-ml rapid filling pipette with a reservoir containing a 0.48 M solution of NaH_2PO_4 was

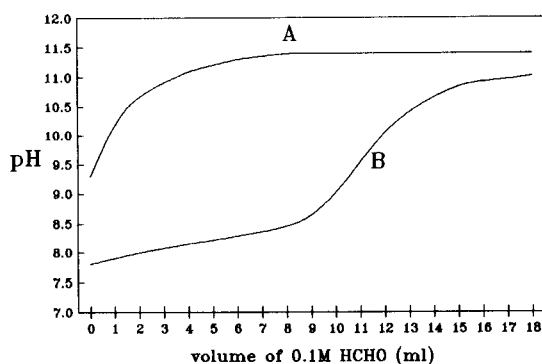


FIG. 1. Titration of 0.10 M HCHO solution against A, 25 ml of 1.0 M Na_2SO_3 and B, 25 ml of both 1.0 M Na_2SO_3 and 0.001 M NaH_2PO_4 .

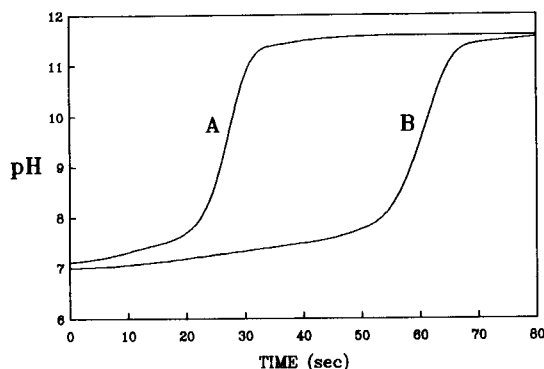


FIG. 2. Change in pH with time resulting from addition of A, 0.500 g paraformaldehyde (BDH type) or B, 0.500 g paraformaldehyde (heated 9 days at 92 C) to a 50-ml aqueous solution of 0.025 M Na_2SO_3 and 0.005 M NaH_2PO_4 .

positioned above a 400-ml beaker containing 25 ml methanol and 225 ml of 0.10 M Na_2SO_3 . A 7-ml volume was added from the pipette. The pH electrodes were immersed, and the mixture was vigorously stirred. A 0.5-g sample of paraformaldehyde was added at once, and at the same time, the chart recorder was started. Reaction was continued until the pH reached a value of 10.5, whereupon another 7-ml volume of NaH_2PO_4 solution was rapidly added from the pipette. This caused the pH to return to about 8, after which the reaction continued until the pH again reached 10.5 and another 7-ml portion of NaH_2PO_4 solution was added. A total of four 7-ml portions were added for each paraformaldehyde tested. Since each 7-ml addition represents 20% of the total paraformaldehyde present, up to 80% of the polymer reactivity was measured.

RESULTS AND DISCUSSION

Reaction of formaldehyde and paraformaldehyde

In reactions where the only source of formaldehyde is paraformaldehyde, the reaction rate will be limited by the rate at which formaldehyde is generated from its polymeric form. The sodium sulfite method has long been used as a quantitative analytical procedure for determining free formaldehyde in aqueous solution. This process is described by the equation:



with stoichiometric generation of NaOH resulting in a pH increase during the reaction. Titration of hydroxide by acid allows determination of the original formaldehyde content. To utilize this technique for estimating paraformaldehyde reactivity, the presence of high alkalinity in the solution must be controlled since the rate of paraformaldehyde decomposition increases rapidly in this environment. By incorporating an appropriate weak acid into the mixture, the titration can be performed *in situ* and the time taken to consume the acid is related to the breakdown of paraformaldehyde.

The typical behavior of pH during the titration of aqueous formaldehyde solution against excess sodium sulfite is shown in curve A of Fig. 1. A limiting pH of about 11.4 is reached well before the stoichiometric endpoint of 250 ml of 0.1 M HCHO for 25 ml of 10 M Na_2SO_3 . By incorporation of the acid salt NaH_2PO_4 to consume the generated base, curve B of Fig. 1 is obtained.

These reactions proceed rapidly when monomeric formaldehyde is present in aqueous solution. However, if the formaldehyde is some condensed polymeric form such as paraformaldehyde, its rate of reaction may be found by

TABLE 1. Effect of particle size on titration times of paraformaldehyde.

Mesh size range	Titration time (sec)	
	Sample	
	1	2
1 to 5	234	246
>5 to 20	173	167
>20 to 35	106	102
>35 to 80	41	43
>80 to 200	21	21
>200	12	13

determining the time needed for a stoichiometric excess of this polymer to consume a given amount of dihydrogen phosphate in the presence of sulfite. To ensure that a large pH change occurs at some stage, a deficiency of acid relative to both paraformaldehyde and sulfite is necessary. The experimental results for two paraformaldehyde samples indicating the change in pH with time are shown in Fig. 2. The combination of sulfite and dihydrogen phosphate acts as a buffer until the latter is consumed, whereupon the pH rises steeply. The generation of hydroxide will continue until one of the reactants, either sulfite or paraformaldehyde, is depleted. As long as the sulfite concentration is in excess, titration time will depend primarily on the quantity of paraformaldehyde present and the reactivity of the polymeric form.

TABLE 2. Titration times and gelation times for paraformaldehyde samples.

Paraformaldehyde sample	Titration time* (sec)	Gelation time* (min)	
		30 C	45 C
1A	26, 25	143, 145	32, 33
B	16, 15	— —	29, 33
C	12, 13	128, 120	27, 28
D	16, 16	136, 138	32, 30
2A	62, 68	200, 200	57, 52
3A	46, 46	225, 205	35, 39
4A	110, 106	>300	85, 85
5A	169, 170	>300	97, 112
6A	219, 232	>300	103, 101
7A	376, 402	>300	98, 96

* Duplicate tests carried out on each sample.

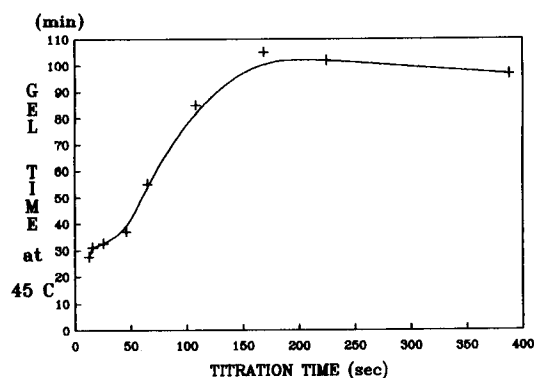


FIG. 3. Gelation time vs. titration time for paraformaldehyde samples.

Particle size effects

Since this reaction involves a solid-liquid phase interaction, the accessibility of reagents to reactive sites on the polymer is expected to be an important factor influencing titration times. Consequently, the mixture must be well stirred during reaction. In addition, the effect of particle surface area on accessibility must be considered. Table 1 shows the influence of paraformaldehyde particle mesh size on titration times. Reactivity increases by an order of magnitude as accessible surface is increased by converting paraflake from the largest to smallest particle size. A standardized particle size range of >80 to 200 mesh was chosen for this study.

Correlation of titration times with gelation times

After some initial experimentation with a range of reactant concentrations, a standard condition was established that provided some spread in titration results with various paraformaldehyde samples. Table 2 lists titration times and gelation times for three commercial paraformaldehyde samples (A, B, and C) and heated samples made from them (2A–7A). Figure 3 indicates the relationship found between room temperature titration times and gelation times at 45 C. The graph displays two distinct regions. Between gelation times of 35 and 85 minutes, an almost linear relationship exists between titration and gelation times ($r^2 = 0.96$).

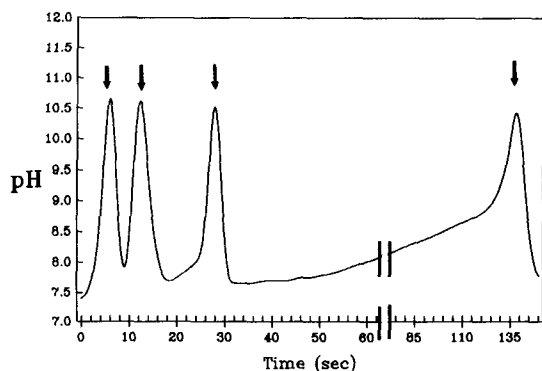


FIG. 4. Stepwise titration to constant pH for FM282 hardener. Arrows represent times where additional NaH_2PO_4 solution, molar equivalent to 20% HCHO , is added.

from linear regression analysis in this region). Above 120 sec titration time, where the paraformaldehyde samples have been more extensively heat treated, the gelation times remain almost invariant. It should be recognized that the shape of the curve in Fig. 3 is highly dependent on titration conditions chosen. In this case, about 30% of the paraformaldehyde sample needs to be reacted to generate a large change in pH.

Uniformity of paraformaldehyde samples

Since a given paraformaldehyde sample is a mixture of polymer chains, nonuniformity in reactivity is likely to occur. A stepwise titration method was utilized in an attempt to delineate this distribution in reactivity. The technique involves successive measurement of titration times for each fractional component of the sample. The reactivity is measured for the first 20% of the sample, then the second 20%, and so on until the entire sample is consumed. The result, as shown in Fig. 4, is a sawtooth shape titration curve with the distance between two successive peaks being the time needed to consume 20% of the paraformaldehyde. It is evident from this figure that the time interval is increasing, and hence the rate of polymer breakdown is decreasing for each successive increment of paraformaldehyde reacted.

While the very nature of this method of step-

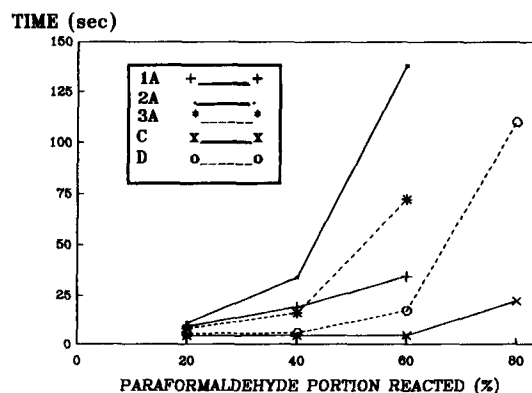


FIG. 5. Relationship between titration times for successive stages in the stepwise titration sequence and the proportion of paraformaldehyde reacted. Samples 1A, 2A, and 3A are, respectively, a paraformaldehyde powder heated for 0, 9, and 16 days at 92 C. Samples C and D are, respectively, a flake paraformaldehyde and FM 282 hardener (Borden Chemicals).

wise titration precludes conventional kinetic analysis, useful information for comparing different paraformaldehyde forms can be obtained. Figure 5 shows time intervals measured for sequence titrations involving 20, 40, 60, and 80% of the total of different paraformaldehyde samples. The shape of these responses can in part be explained in terms of the reactivity distribution in each sample.

The short time intervals needed to consume up to 80% of the flake sample (C) indicate the rapid breakdown of this polymer into highly reactive monomeric formaldehyde. In contrast, only the first 20% of the paraformaldehyde sample heated for 9 days (2A) depolymerized at a similar rate, while the fraction between 40 and 60% yielded monomeric formaldehyde about 30 times slower than the flake sample. This result indicates that heat treatment converts some of the lower molecular weight polymers into higher molecular weight ones.

A consequence of these differences in decomposition rate for portions of a sample is that it is possible to make one paraformaldehyde appear more reactive for gelation than another by using an excess in the reaction with PRF resin. Since gelation precedes cure, the

fraction of the total paraformaldehyde controlling gelation time will be a function of resin formulation. Information about these fractional reactivity differences between samples provides a useful guide for controlling both adhesive pot life and presence of excess paraformaldehyde, which may result in preventable formaldehyde emissions both during and after resin cure.

CONCLUSION

The reaction of paraformaldehyde with sulfite can be monitored by *in situ* titration with a weak acid. This technique allows a rapid and convenient method for determining total and fractional paraformaldehyde reactivity. Titration results can, in part, be correlated with gelation times. Temperature, pH, and paraformaldehyde particle size are parameters that

need careful consideration when utilizing this technique.

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