

Hydrolytic Degradation of Cured Urea-Formaldehyde Resin

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Synopsis

The degradation of cured urea-formaldehyde (UF) resin in aqueous suspension was investigated by gravimetric analysis of the changes in the content of nonextractable low-molecular components. In acid conditions (pH 4.0) at 47°C the consecutive processes of post-curing and of polymer breakdown (activation energy 90 kJ/mol) are detectable whereas at 80°C and 97°C only the formation of the extractable hydrolysates is observed. The degraded polymer contains less carbonyl groups than does the original resin substrate as shown by means of infrared (IR) analysis. In contrast to the results of the tests carried out in acid conditions, in neutral and basic aqueous media the hydrolytic decomposition of UF macromolecular network is less significant. During the hydrolysis of UF polymer at 30°C–45°C the concentration of formaldehyde released from the resin to the aqueous phase increases initially (2 days) at a relatively high rate both at acid and alkaline pH. Then its growth slows down but is still detectable in acid conditions, whereas in basic medium no further liberation of HCHO is observed.

INTRODUCTION

The process of aging of cured UF resins involves the liberation of formaldehyde and gradual deterioration of their use properties. The latter may be a decrease of the mechanical strength, disintegration of the material,¹ loss of its adhesion characteristics,² or, e.g., of wrinkle-resistance effect in UF-resin-impregnated textile fabrics.³ In general, UF resins are less stable in humid conditions and at higher temperatures. It was shown in the previous work⁴ that the acidity of UF foam insulation is a very important factor in the hydrolytic breakdown of the polymer network and in the emission of formaldehyde from the material. Those studies were performed in humid-air conditions. The present paper deals with the investigation of the degradation of gelled UF resins in an aqueous medium.

EXPERIMENTAL

Preparation of UF Resin. The pH of 130 g formaline (38%) was adjusted to 7.5 with an aqueous solution of sodium hydroxide (10%), and 60 g urea was added. The mixture was stirred and heated under reflux for 2 h. Then about 40 mL water was distilled off to obtain a resin of 70% solids, 2.7% free formaldehyde, and 9.4% *N*-methylol formaldehyde (as analyzed by Kelly's method⁵). Thus obtained liquid resin was treated with 0.3*N* acetic acid to a pH of 4.0 and

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cured under reflux for additional 3 h. The moisture content of the gelled product was found by drying it at 45°C–50°C and 0.1–0.2 kPa for 2–3 h.

Hydrolysis of Cured UF Resin. Grains (ϕ 5 mm) of freshly cured resin (2 g) were suspended in 100 mL water and maintained in various conditions of temperature, pH, and time. Then the suspension was neutralized if necessary with diluted aqueous solution of sodium carbonate or acetic acid and filtered off. The solid residue was washed with water to neutral reaction and dried at 45°C–50°C under reduced pressure (0.1–0.2 kPa) for 2–3 h. The ratio of the weight of the dry solid residue of the hydrolyzed resin sample to its original dry weight before extraction was assumed to correspond to the nonextractable fraction of the resin.

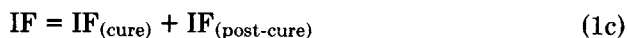
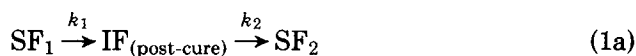
Analysis of Formaldehyde Released from UF Resin. Cured UF resin was washed with acetone, dried at ambient temperature, and ground up (less than 25 mesh). Then it was suspended in 60 mL water in various conditions of pH, temperature, and time. This test was followed by filtration of the suspension, and the filtrate was analyzed for formaldehyde by the chromotropic acid method.⁶

IR Analysis. Aliquots (1.5–2 mg) of UF resin, its water-extractable and nonextractable fractions were used to prepare pellets with KBr (200 mg). The IR analysis was performed with aid of a Model IR-10 Beckmann instrument.

RESULTS AND DISCUSSION

Kinetic Changes of Water-Extractable Fraction in UF Resin

In the previous paper⁴ it was suggested that during the hydrolytic decomposition of cured UF foams containing phosphoric acid as a hardening agent, in humid-air conditions, the diffusion-controlled post-cure is accompanied by random degradation reactions. A similar situation is observed in the case of maintaining the hardened UF resin in water at 47° and pH of 4.0 (Fig. 1). An initial drop of the water-extractable low-molecular fraction due to the post-curing of ungelled components is followed by its subsequent increase resulting from the disruption of the polymer network. For practical purposes, it was found convenient to treat these kinetic changes as a combination of simultaneously occurring hydrolytic degradation of the originally cured UF resin and consecutive reactions of the uncured fraction involving its post-cure and breakdown:



where SF_1 is the initial water-soluble fraction representing the content of uncured material in the UF resin, IF is the nonextractable species, which is assumed to be the crosslinked polymer formed both in the original polycondensation $IF_{(\text{original cure})}$ and during the diffusion-controlled post-cure $IF_{(\text{post-cure})}$ and SF_2 symbolizes the soluble products resulting from the hydrolytic degradation of

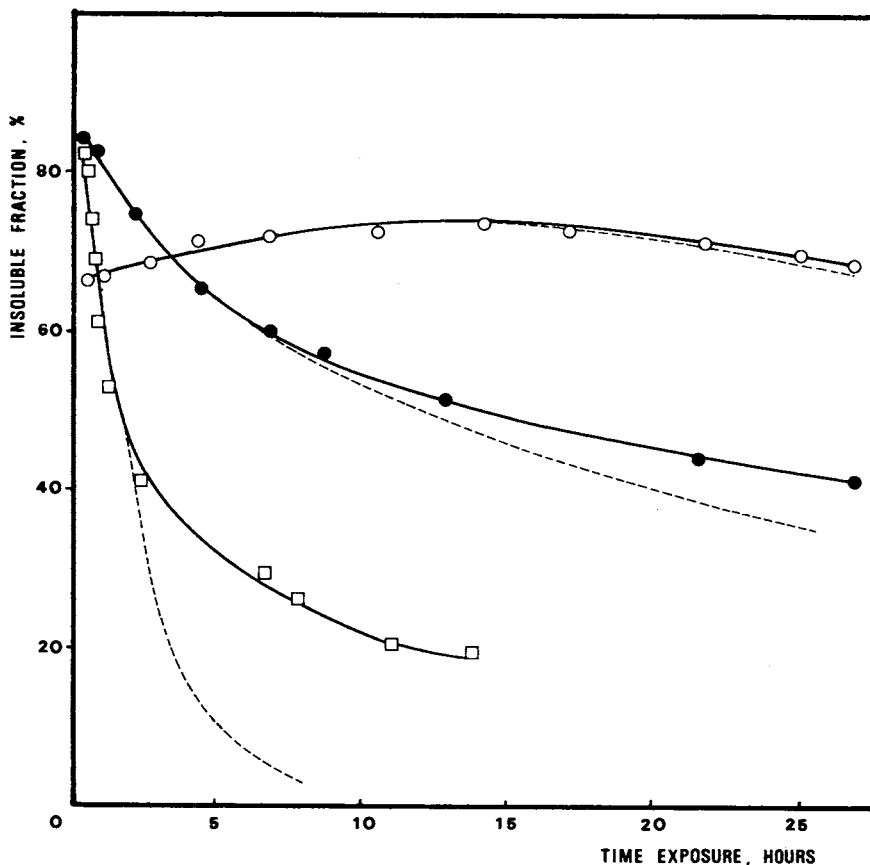


Fig. 1. A comparison of the experimental results and the theoretical values (dotted lines) predicted from eqs. (2) and (5) for the amount of the insoluble fraction in cured UF resin suspended in water in acid conditions (pH 4.0) and heated at temperatures of 47°C (O), 80°C (●) and 97°C (□) for various periods of time.

IF. The constants k_1 and k_2 are those of the insoluble-fraction formation and of the formation of water-extractable products, respectively.

The cured resin particles used in the experiments were highly porous and due to this property their interior parts should have been readily accessible to the water during the test performances. Therefore, the hydrolyzed, soluble resin fragments were believed to be quickly leached out and not alter the time dependence of degradation in the weight-loss tests. The same related to the acid cure catalyst, the pH of the mixtures being constant all the time.

The system under examination, i.e., an aqueous suspension of solid UF resin, is rather complex from the kinetic point of view. As the first approximation, (1a) and (1b) are both considered first-order transformations.⁴ Besides, the presented scheme does not take into account any reversible reactions that might alter the amount of SF_1 , SF_2 , or IF. In the previous work it was found that their role is initially not significant but may increase with time and temperature. So, the application of the first-order consecutive model equations will have to be understood as rather a simplified mathematical description of the post-cure and degradation processes. Thus, the amount of IF after time t will be given by

$$IF = IF_0 e^{-k_2 t} + SF_0 k_1 (e^{-k_1 t} - e^{-k_2 t}) / (k_2 - k_1) \quad (2)$$

IF_0 and SF_0 are, respectively, the initial quantities of IF and of the water-extractable material SF_1 in the resin, found by extrapolating the experimental lines to "zero" time. Here and later in the further considerations slight changes of the overall UF-resin weight are neglected. In Figure 1 the extremum point (IF_{\max} , t_{\max}) of the kinetic curve, illustrating the 47°C test, can be described by the following equations:

$$t_{\max} = 1/(k_2 - k_1) \ln(k_2/k_1) - IF_0 k_2 (k_2 - k_1) / SF_0 k_1^2 \quad (3)$$

$$IF_{\max} = IF_0 e^{-k_2 t_{\max}} + SF_0 k_1 (e^{-k_1 t_{\max}} - e^{-k_2 t_{\max}}) / (k_2 - k_1) \quad (4)$$

The values of k_1 and k_2 are given in Table I. At temperatures of 80°C and 97°C, the initial growth of the UF insoluble fraction can no more be observed in Figure 1. Presumably in such conditions the said process is too rapid to be monitored with aid of the experimental technique employed. Nevertheless, the amounts of nonextractable UF components found at the beginning of these tests are higher than those analyzed for the material treated at 47°C. This could account for the fact that some fast post-curing of the freshly hardened resin should have taken place at higher temperatures. From the data obtained for 80°C and 97°C only the approximative values of k_2 for the initial times were calculated from eq. (5) and given in Table I:

$$\ln(IF_0/IF) = k_2 t \quad (5)$$

The overall activation energy for the formation of water-extractable UF hydrolysates, calculated from the Arrhenius plot was 90 kJ/mol. This value is higher than that (50 kJ/mol) found for the degradation of UF foam which was more acidic (pH 2.7).⁴ This is consistent with the statement previously made⁴ that the decomposition of UF polymer in the studied range of humid conditions has a character of an acid-catalyzed hydrolysis.

Mechanism of Hydrolytic Degradation of UF Polymer

In Figure 1 the experimental kinetic curves are compared with the theoretical ones found from eqs. (2) and (5). There are some deviations between them which increase with time and temperature. They result primarily from the approximations made above and may be also a consequence of the reactions which do not fit to the proposed scheme (1a)–(1c). These are reversible dissociations of ether linkages and of methylene bonds in the UF polymer structure. So, the amount of the low-molecular products formed over the degradative hydrolysis is actually smaller than that predicted on the basis of eqs. (2) and (5). The ni-

TABLE I
Rate Constants k_1 and k_2 Calculated from eqs. (2) and (5) for the Tests Performed at pH 4.0

Temperature (°C)	$10^5 k_1$, (s ⁻¹)	$10^5 k_2$ (s ⁻¹)
47	1.9	0.33
80	—	1.2
97	—	18.0

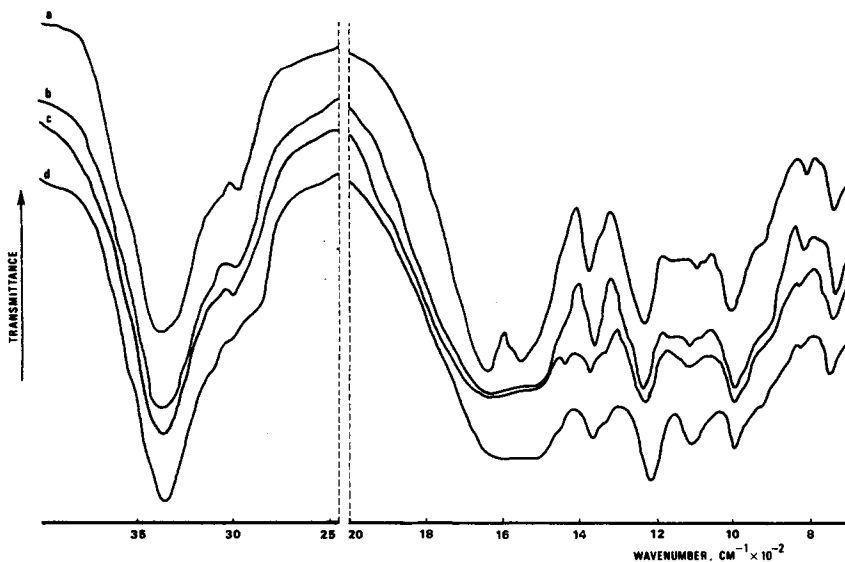
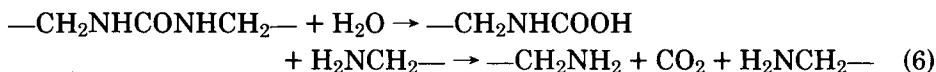


Fig. 2. IR spectra of cured UF resin (a) and of the products of its degradation in water at 97°C and pH 4.0 after 6 h, [insoluble fraction (b), water-extractable fraction (c)] and after 30 h [insoluble fraction (d)].

trogen-methylene link is relatively stable so the deviation of the theoretical graphs is more significant only at higher temperatures.

Reactions which do fit to scheme (1a)–(1c) involve probably the hydrolysis of less stable amide bonds between nitrogens and carbonyl carbon atoms. This can be described as follows:



The occurrence of such a reaction was suggested in the previous paper⁴ and supported by the IR analysis and GLC data. Figure 2 shows the IR spectra of the undegraded resin and of the water-soluble decomposition products. It may be seen that the hydrolytic destruction of UF polymer is associated with the loss of its carbonyl groups. This observation is in agreement with reaction (6).

Effect of the Acidity of UF Resin on Its Hydrolytic Stability

The results of the tests involving a storage of suspensions of cured UF resins in water at pH 4.0 (Fig. 1) as well as at pH 9.0 (Fig. 3) support the presumption that the acidity is an important factor determining the decomposition of UF polymer in aqueous media. In neutral and basic conditions at 80°C there are no significant quantitative changes of the water-extractable fraction of the resin, and at 95°C the increase of the low-molecular water-soluble components is rather small. On the contrary, at pH 4.0 the destruction of the polymer is quite visible as the hydrolysis continues.

Decomposition of UF resin is accompanied by evolution of formaldehyde.^{7–10} In order to follow its formation, the free unreacted HCHO had to be first removed from the freshly cured material. It was accomplished by washing the samples

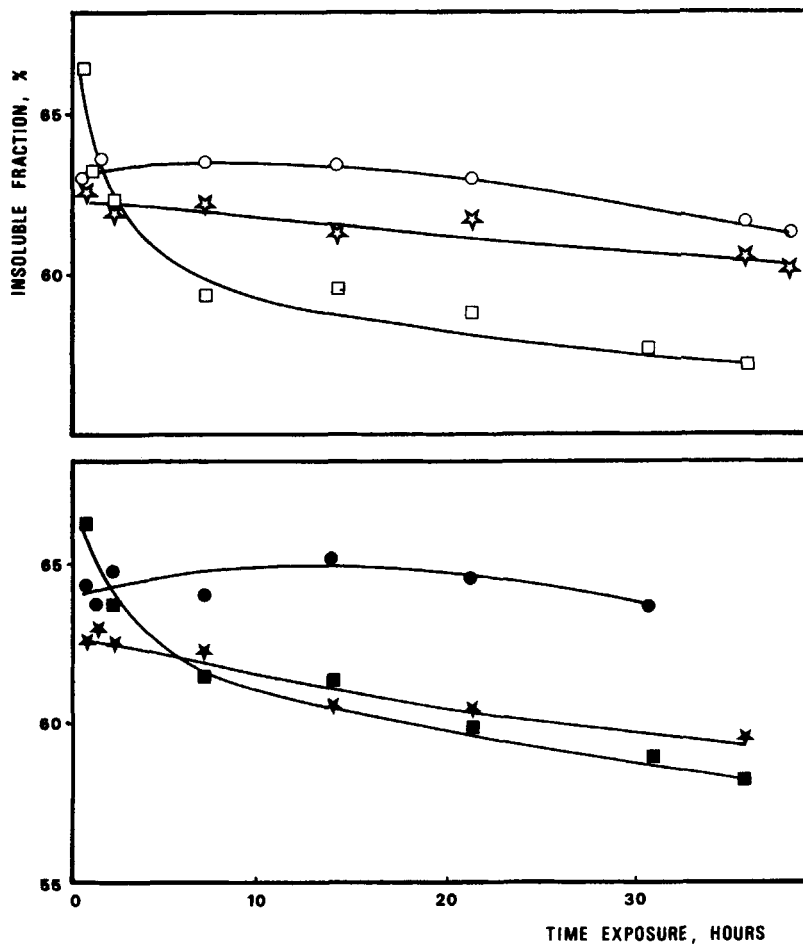


Fig. 3. A comparison of the amount of insoluble fraction in cured UF resin at pH 7.0 (O, ☆, □) and 9.0 (●, ★, ■) at temperatures of 47°C (O, ●), 80°C (☆, ★), and 97°C (□, ■) for various periods of time.

with acetone and drying them. At the same time the cured species IF_0 was separated from the uncured low-molecular material SF_0 . As seen from Figures 1 and 3, at a relatively low temperature (47°C) the overall amount of the soluble fraction, $SF_1 + SF_2$, changes rather slightly with time both at pH 4.0 and 9.0. The filtrates obtained after the tests, which contained the released formaldehyde, had therefore, negligible concentrations of UF hydrolysates and uncured material. Hence, practically, they did not have an important influence on the quantitative analysis of the HCHO by the chromotropic acid method. This was confirmed indirectly in the preliminary trials by comparing the results of the analyses of free formaldehyde in the filtrates, conducted by the bisulfite and chromotropic acid techniques. The two series of data thus obtained did not differ significantly one from another. As a conclusion, either method could have been adopted in the study.

The resin samples washed with acetone were ground up and suspended in water at pH 4.0 and 9.0, in either case at temperatures of 30°C and 45°C. Be-

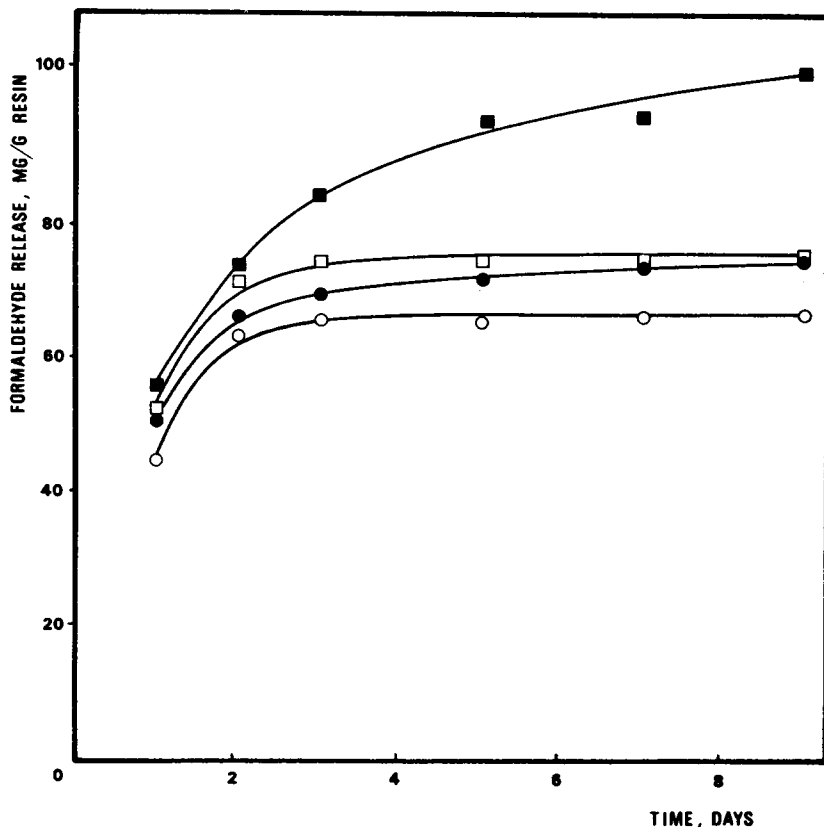


Fig. 4. A comparison of the kinetic changes of formaldehyde concentration in aqueous suspension of cured UF resin at pH 4.0 (●, ■) and 9.0 (○, □) and at temperatures of 30°C (○, ●) and 45°C (□, ■).

cause of high porosity of the UF resin particles the liberated formaldehyde was believed to be leached out quickly by the water from the suspended material. The results of the quantitative analyses of HCHO released to the aqueous system in the test conditions are illustrated graphically in Figure 4. The initial burst of emission is caused probably by the dissociation of chain-end *N*-methylol groups. In the case of the experiments conducted at pH 9.0 the equilibrium of this reaction is reached fairly soon, and further heating of the suspension does not lead to any significant increase of the formaldehyde concentration. Similarly, relatively rapid initial evolution of HCHO during the first 2 days is observed as well at the acid pH. Over the period of the next 9 days the release is slowed down; however, it does not cease to continue. The dissociation constant for the *N*-hydroxymethyl functions essentially does not depend on the pH over a wide range.¹¹ Hence, it is justifiable that at the beginning formaldehyde reaches the same level of concentration regardless of the pH conditions. Further release of HCHO at pH 4.0 results presumably from the hydrolytic degradation of the interior fragments of the UF macromolecular structure. On the other hand, as already stated above (Fig. 3), in alkaline conditions (pH 9.0) such a destruction is much less significant.

SUMMARY AND CONCLUSIONS

The results of the present investigation give some more evidence that during the aging of cured UF resins in humid acid media the consecutive processes of post-cure and hydrolytic degradation take place. This decomposition is much less significant in neutral and alkaline conditions.

The mechanism of the hydrolytic destruction of UF polymer involves presumably, as one of the possible reactions, the scission of C—N amide bonds, which leads to a decrease in the carbonyl function content in the resin composition.

The evolution of formaldehyde that accompanies the hydrolysis of UF resins is associated with the dissociation of *N*-methylol groups and with the breakdown of the UF polymer network. The former reaction, as known from the literature,¹¹ takes place both in acid and alkaline conditions, whereas the latter occurs more probably at lower pH.

The findings of this investigation and of the preceding studies⁴ provide a basis for further research into the ways of imparting higher stability to UF resins. The results of this work will be the subject of the next paper.

References

1. W. J. Rossiter, R. G. Mathey, D. M. Burch, and E. T. Pierce, *Urea-Formaldehyde Based Foam Insulations: An Assessment of Their Properties and Performance*, NBS Technical Note 946, U.S. Department of Commerce and National Bureau of Standards, U.S. Government Printing Office, Washington, D.C. 1977.
2. G. E. Troughton, *Wood Sci.*, **1**, 172 (1969).
3. H. Petersen, "The Relationship between Crosslinkers, Catalysts, Liberation of Formaldehyde and Degree of Conversion during Finishing of Fabrics by *N*-Methylol Compounds," AATCC National Technical Conference, Philadelphia, September 28–30, 1972.
4. G. G. Allan, J. Dutkiewicz, and E. J. Gilmartin, *Environ. Sci. and Technol.*, **14**(10), 1235 (1980).
5. F. L. Kelly and R. L. Wells, U.S. Pat. 3,231,525 (1966).
6. J. F. Walker, *Formaldehyde*, Reinhold, New York, 1964, pp. 469–471.
7. Z. Wirpsza and M. Piwińska, *Przem. Chem.*, **52**, 187 (1973).
8. E. Roffael, *Holz Roh-Werkst.*, **34**, 385 (1976).
9. C. Y. Hse, *Mokuzai Gakkaishi*, **20**, 483 (1974).
10. H. Petersen, W. Reuther, W. Eisele, and O. Wittmann, *Holz Roh-Werkst.*, **30**, 429 (1972).
11. J. I. De Jong, and J. De Jonge, *Rec. Trav. Chim.*, **71**, 661 (1952).

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