

Preparation of Cured Urea-Formaldehyde Resins of Low Formaldehyde Emission

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Synopsis

Several polymers containing amino or amido groups and biuret were tested as additives to urea-formaldehyde (UF) resin in order to neutralize its inherent acidity and combine free formaldehyde released upon hydrolysis of cured UF polycondensate. Each modifier was incorporated to liquid methylolureas at weight ratios of 1:100, 2:100, and 3:100 prior to curing with the aid of acetic acid. Over 10 days of maintaining aqueous suspensions of the ground-up resultant solid resins at ambient temperature, a neutralizing effect was exhibited most visibly by polyacrylamide, polymethacrylamide, and biuret, the test with chitosan and casein giving results slightly different from those obtained for the control nonmodified cured UF polymer. Polyacrylamide, biuret, and casein proved to be excellent inhibitors of formaldehyde release from the hardened resins which were suspended in water at ambient temperature. On the other hand, chitosan did not reduce the evolution of HCHO but, instead, augmented it when its content was 1 g/100 g of the original liquid resin before cure.

INTRODUCTION

A number of approaches have already been made to improve the hydrolytic stability of UF polymeric materials more or less with success.¹⁻³ However, in practice, there still occur problems particularly associated with the emission of formaldehyde resulting from the deterioration of the resins in hot and humid conditions.⁴ The gravity of this issue is sometimes important with respect to air pollution in dwellings containing UF-based products such as particle board, foam insulation, resin-impregnated fabrics, etc.

In order to eliminate the formaldehyde odor many trials involved the use of additional amounts of urea just before curing the resin.⁵⁻¹⁵ The urea thus introduced reversibly binds free formaldehyde producing rather unstable *N*-hydroxymethyl derivatives. Other amine or amide components proposed as additives to UF resins included melamine,^{6,7,16} thiourea,^{7,17-20} dicyanodiamide,^{7,17-19} ϵ -caprolactam,⁷ *m*-phenylenediamine,⁷ albumine,⁷ and other proteins.²¹ The reported results of such modifications are often contradictory. For instance, dicyanodiamide is cited by some authors⁷ as a formaldehyde-release inhibitor better than urea and by others the very agent is rejected.⁶

A treatment of UF resins with ammonia^{17,18,22-28} involved its reactions with free formaldehyde, which result in hydrolyzable urotropine and other methylene- and methylamines giving off formaldehyde again.²⁹

The experimental results of the studies on the longterm degradation of UF

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resins have been discussed in previous reports^{30,31} led to the conclusion that a reduction of the inherent acidity of cured UF materials has a beneficial effect on their hydrolytic stability and lowers the emission of formaldehyde. Having this in mind, it seemed plausible to look for methods of neutralizing acid-curing catalyst remaining in the product after it has done its work. In this way its adverse hydrolytic effect should be nullified. The approach described here toward reaching this goal consisted in including into the UF formulation a latent base, capable of *slowly* neutralizing acid-hardening agents. In order to minimize the formaldehyde emission from UF resin even more efficiently, several materials of high reactivity toward this gas were also tested as possible additives to the resin composition. Such ingredients were used to constitute an internal chemical trap for the evolved formaldehyde. Several substances having the properties mentioned above have already been tested in the previous work³² dealing with the modification of UF foam insulation. For instance, good results were obtained with some base polymers containing amino and hydroxyl groups.

EXPERIMENTAL

Materials and Their Preparation

Polyacrylamide used for UF-resin modifications was prepared by the method described previously.³³ Its intrinsic viscosity was 1.88 dL/g (aqueous solution, 25°C).

Polymethacrylamide, whose preparation technique was similar to that for polyacrylamide, had an intrinsic viscosity of 1.75 dL/g (aqueous solution, 25°C).

Biuret (mp 189–190°C) was obtained by heating urea at 160°C for 3 h. It was isolated from the reaction mixture by thoroughly washing off the byproducts and the remaining urea with cold water (2–3°C).

Chitosan provided by Instytut Morski (Gdynia, Poland) had a weight-average molecular weight of 850,000 (found by Lee's method³⁴), degree of deacetylation 67%, and ash content of 0.9%.

Casein was obtained from an aqueous solution (10%, 200 mL) of Nido Nestle powder milk (Nestle Netherlands, Amsterdam, Holland) by its precipitation with aqueous acetic acid (10%, 10 mL) at 30°C for 2 h. The crude precipitate was treated with an aqueous solution of sodium hydroxide (1%, 5 mL) and the resultant paste again with 75 mL of the same solution at 30°C for 1 h. After maintaining the mixture overnight, two layers were separated and the aqueous one was treated with 2 mL glacial acetic acid to precipitate casein. The solid was subsequently filtered off and washed several times with water. It was dried in a desiccator for 24 h and then at 50°C for 4 h.

Preparation and Modification of UF Resins

An aqueous solution of formaldehyde (38%, 130 g) was brought to a pH of 7.5 with use of aqueous sodium hydroxide (10%), and then 60 g urea was added. The mixture was stirred and heated under reflux for 2 h. After that time about 40 mL water was distilled off to obtain a liquid UF resin containing 70% solids.

The following additives, polyacrylamide, polymethacrylamide, chitosan, and biuret, were dissolved in an aqueous solution of acetic acid (2%), each except for chitosan, in proportions of 0.7, 1.4, and 2.1 g/100 mL of the acid solution, and chitosan at ratios of 0.5, 1.0, and 1.5 g/100 mL acid solution. Aliquots of such mixtures were combined with the liquid UF resin to get contents of the said additives of 1, 2, and 3 g/100 g of the original resin. If necessary, additional amounts of acetic acid were used to achieve in each case a final pH of 4.0. The resins containing the above ingredients were cured under reflux for 3 h.

In the case of modifying the resin with casein the protein was first dissolved in various proportions in a diluted sodium hydroxide solution (0.5%). Aliquots (25 mL) of the prepared mixtures were combined with the liquid UF resin (10 mL) to get casein contents of 1%, 2%, and 3% by weight of the original resin. The obtained compositions were acidified in each case with aqueous acetic acid (2%) to get a pH of 4.0 and cured under reflux for 3 h.

The control nonmodified liquid resin was treated with an aqueous acetic acid solution (2%) and cured in the same way as the modified samples.

Analysis of Formaldehyde Liberated from the Resins

The gels of the UF resins prepared in the above manner were washed with acetone, dried at 23°C for 24 h and ground up (less than 25 mesh). Then their aliquots (0.5 g) were suspended in 60 mL water at 23°C and thus maintained with agitation for various periods of time. The tests were followed by the filtration of the suspensions, and the filtrates obtained were analyzed quantitatively for formaldehyde by the chromotropic acid method.³⁵ The validity of the analytical results thus obtained was verified in the previous work.³¹

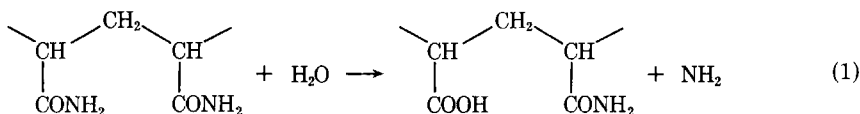
RESULTS AND DISCUSSION

The substances tested in this study as additives to UF resins contain amino and amido functions which can create crosslinks with methylolureas during the cure process. Thus they can be built into the macromolecular network of the resultant UF polymer. Polyfunctional ingredients such as polyacrylamide, polymethacrylamide, chitosan, and casein seemed to be especially interesting because they can form additional bonds with UF resin and still be abundant in base groups reactive toward formaldehyde. The agents used for modification experiments were tested in two respects, i.e., for their ability to neutralize the inherent acidity of UF polymer and to lower the formaldehyde emission resulting from its hydrolysis.

The Effect of the Additives on the Acidity of UF Resin

Polyacrylamide can be easily introduced to the UF resin formulation by dissolving it in the acid hardening agent prior to curing. However, the concentration of the polymer in such a mixture is restricted by its viscosity. On the other hand, this property may be controlled to some extent by using a material of a lower molecular weight. Of course, these restrictions concern as well other possible water-soluble polymeric additives.

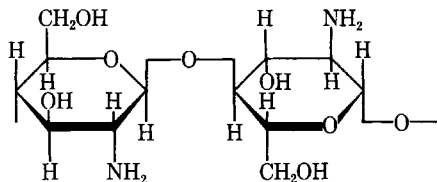
The amide groups of polyacrylamide can slowly hydrolyze liberating ammonia³⁶:



It was anticipated that NH_3 thus formed would gradually neutralize the acid curing agent contained in the resin gel. The real effect found by experiment is illustrated in Table I as an increase of pH of an aqueous suspension of the cured resin after 10 days of maintaining it at ambient temperature.

Polymethacrylamide and biuret can also neutralize partially the UF resin as seen from Table I. They are soluble in aqueous acid solutions of curing agents, and in this form may also be easily incorporated into the aminoplast before its hardening.

Chitosan is a linear polyaminosaccharide constituted of the units belonging to 2-amino-2-deoxy- β (D)-glucose bound one with another with one to four glucoside links:



This material is obtained by deacetylation of chitin,³⁷ a natural polymer common both in animal and vegetal organisms.³⁸ Recently, chitosan gained much practical interest due to its diverse use properties.^{37,39,40} However, its solutions in aqueous acetic acid are exceptionally viscous so that their direct application to UF resins is rather difficult. Besides, the neutralizing effect of chitosan which contains base amino groups (Table I) is less evident than those observed for polyacrylamide, polymethacrylamide, and biuret.

No significant change of pH was observed (Table I) for the resin modified with casein over 10 days of maintaining it at ambient temperature in water suspension.

TABLE I
Effect of Various Additives on pH^a of Cured UF Resin

Additive	Amount of additive (%) ^b	Initial pH	pH after 10 days ^c
—	0	4.3	4.5
Polyacrylamide	3	4.2	4.8
Polymethacrylamide	3	4.2	4.9
Biuret	3	4.3	5.1
Chitosan	3	4.4	4.7
Casein	3	4.4	4.5

^a pH of ground-up (25 mesh) cured UF resin (2 g) in water (150 mL) suspension.

^b By weight of liquid resin before cure.

^c Samples maintained in water at 23°C.

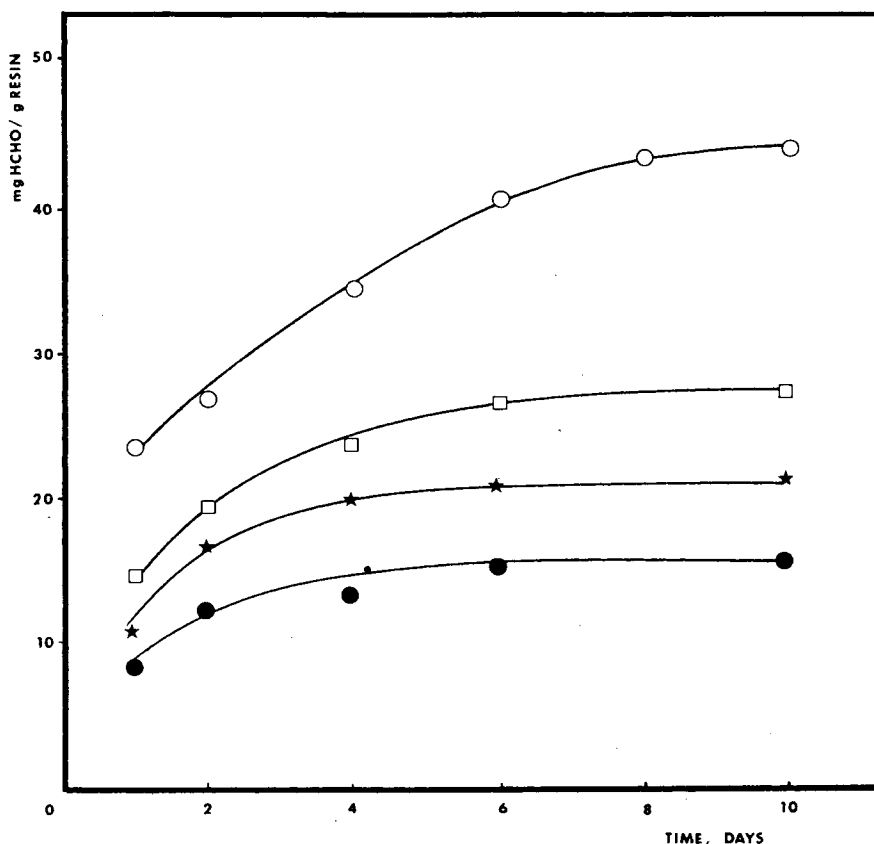


Fig. 1. A comparison of the kinetic changes of formaldehyde concentration in aqueous suspensions of cured UF-resin control and polyacrylamide-modified samples at a temperature of 23°C. Contents of polyacrylamide in the resin (by weight of the liquid UF resin before cure): (○) 0%; (□) 1%; (★) 2%; (●) 3%.

Formaldehyde Release from the Modified UF Resins

The effect of polyacrylamide on the liberation of formaldehyde from cured UF resins suspended in water, at ambient temperature, is illustrated in Figure 1. Each time before the test, free formaldehyde had been removed from the material according to the procedure described in the Experimental section. All the experiments were carried out in such a way that each data point (Figs. 1-5) was the result of a measurement upon a separate 0.5-g sample in its own solution. Once the control UF polymer is submerged into water, it releases formaldehyde again up to a certain equilibrium level. It is seen from Figure 1 that the higher the amount of polyacrylamide contained in UF resin, the sooner the equilibrium is reached and the lower the final HCHO concentration in the aqueous suspension. The maximum content of polyacrylamide used in the aminoplast corresponded to a ratio of about 1 mol of the amido function of the polymer additive to 2 mol of formaldehyde released from the control resin over a period of 10 days.

It is presumed that polyacrylamide acts in UF resin in two ways: on the one

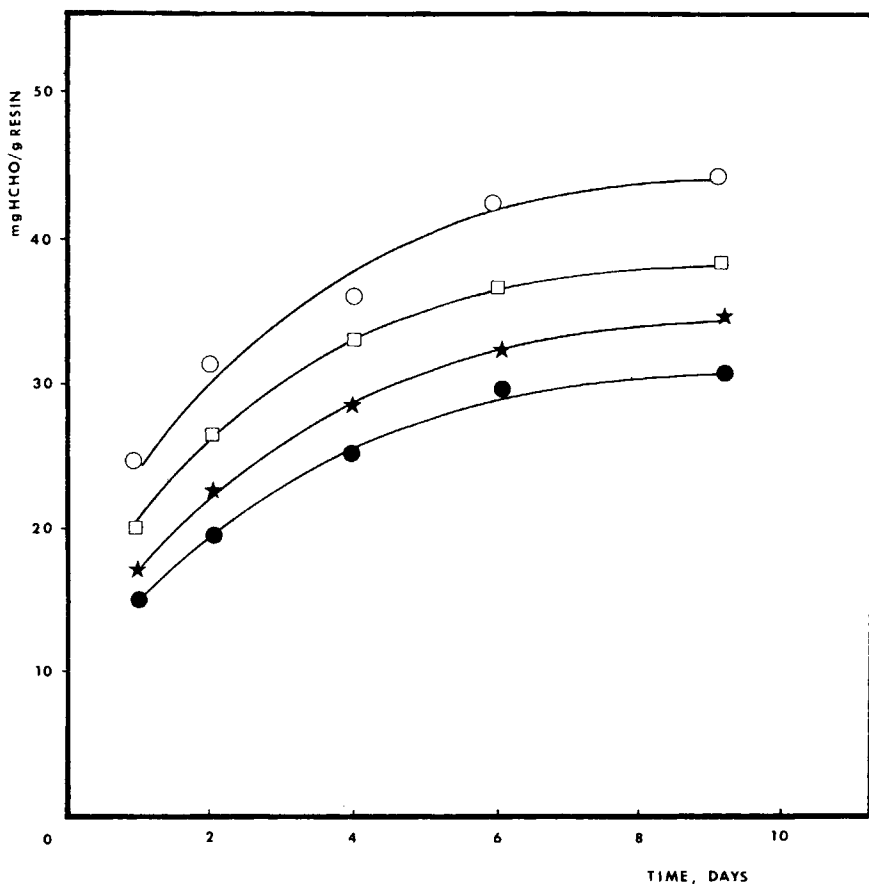
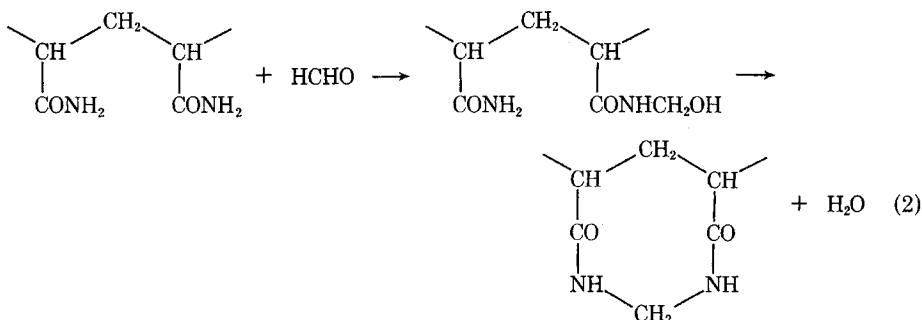


Fig. 2. A comparison of the kinetic changes of formaldehyde concentration in aqueous suspensions of cured UF-resin control and polymethacrylamide-modified samples at a temperature of 23°C. Contents of polymethacrylamide in the resin (by weight of the liquid UF resin before cure): (○) 0%; (□) 1%; (★) 2%; (●) 3%.

hand, it neutralizes slowly the acid curing catalyst as mentioned above, and, on the other hand, it binds firmly the free formaldehyde evolved. The reaction between this additive and HCHO may possibly lead to fairly stable cyclic structures according to the following scheme⁴¹:



Rather surprisingly, it was found (Fig. 2) that polymethacrylamide is much

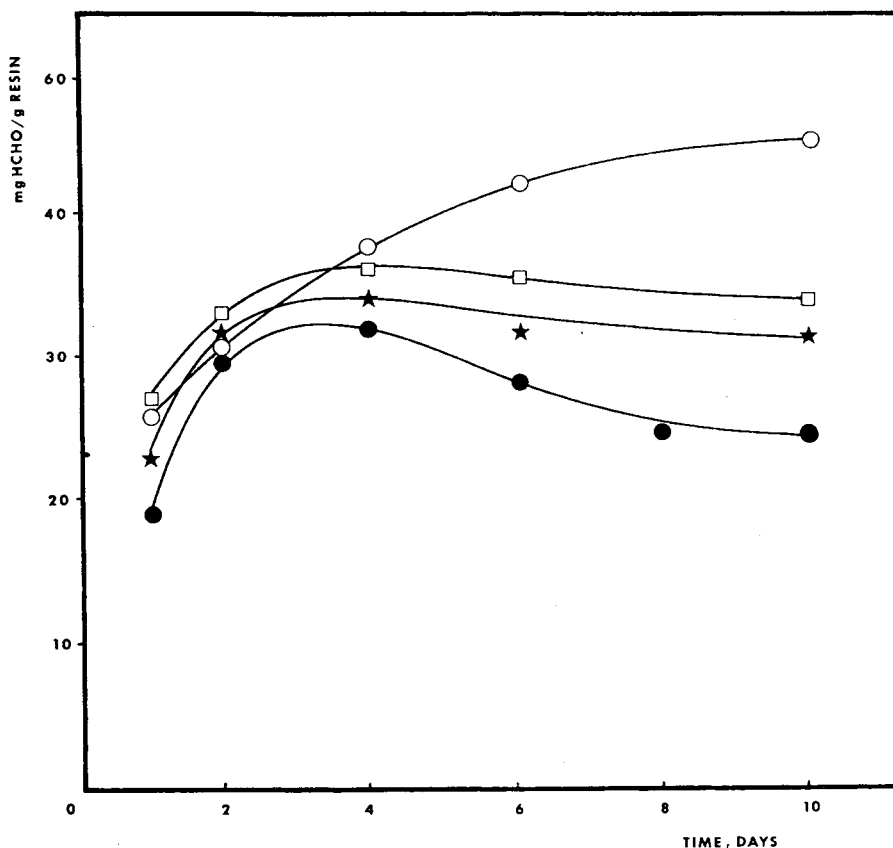
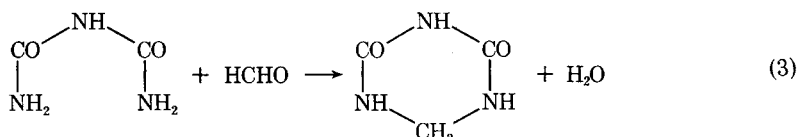


Fig. 3. A comparison of the kinetic changes of formaldehyde concentration in aqueous suspensions of cured UF-resin control and biuret-modified samples at a temperature of 23°C. Contents of biuret in the resin (by weight of the liquid UF resin before cure): (○) 0%; (□) 1%; (★) 2%; (●) 3%.

less efficient as a formaldehyde scavenger than polyacrylamide. Presumably the former polymer does not undergo the intramolecular cyclization reactions similar to those shown in eq. (2) to such an extent as does polyacrylamide.

The application of biuret as an additive to UF resin gave a different pattern of the formaldehyde-evolution kinetic curves (Fig. 3) than those observed in the previous cases. Here, the maximum level of biuret in the resin was adjusted at a ratio of 1 mol of the additive to about 1 mol of formaldehyde liberated from the control UF material to its aqueous suspension at 23°C over 10 days. It was anticipated that, in reaction with HCHO, biuret would form a stable cyclic derivative according to the following equation:



Supposedly, such a cyclic product can be partially built into the UF polymer network through its secondary amino groups. From Figure 3 it is seen that the

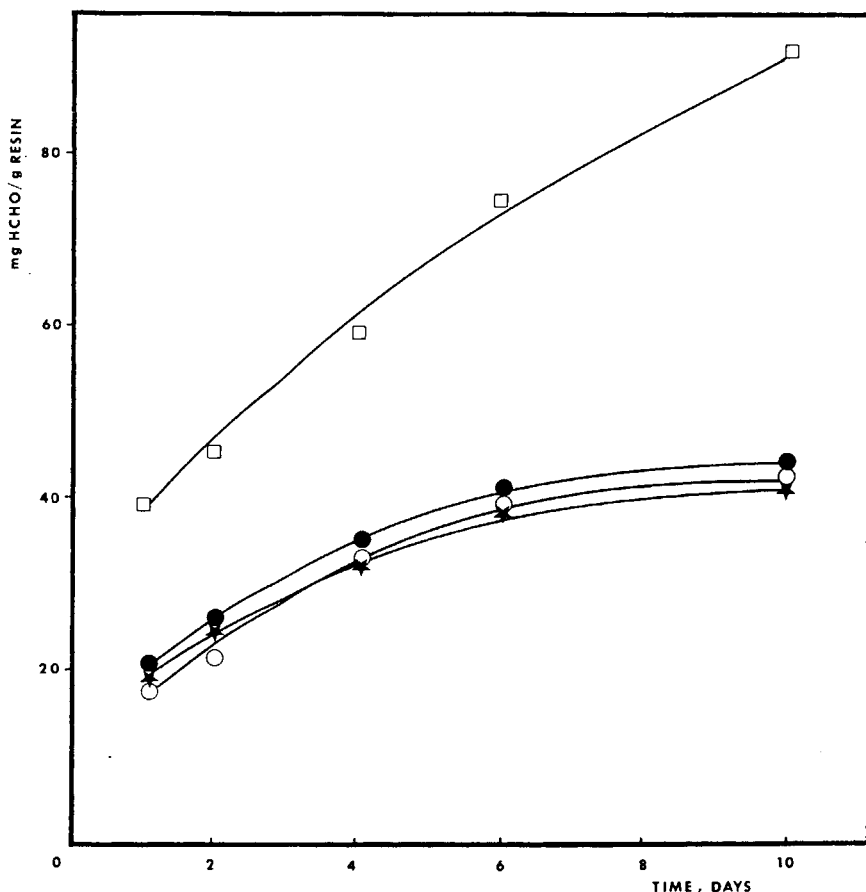


Fig. 4. A comparison of the kinetic changes of formaldehyde concentration in aqueous suspensions of cured UF-resin control and chitosan-modified samples at a temperature of 23°C. Contents of chitosan in the resin (by weight of the liquid UF resin before cure): (O) 0%; (□) 1%; (★) 2%; (●) 3%.

concentration of formaldehyde released from the biuret-modified resin to its aqueous dispersion is much lower after 10 days than that for the control sample. However, initially the HCHO concentration reaches some maximum and only then begins to fall down. The reason of this phenomenon is not clear, and perhaps some additional study should be made to find the explanation for the observed shape of the experimental curves.

Another candidate for an additive to UF resins, i.e., chitosan, gave somewhat unexpected results. Not only did it not inhibit the emission of formaldehyde from the cured UF polymer, but it had just the opposite effect when its content in the resin was 1% by weight of liquid methylolureas before hardening. This situation is depicted in Figure 4. A similar behavior of chitosan had been already observed as it was used for modification of UF foam insulation.³² This phenomenon is not clear yet.

A natural polymer of a high reactivity toward carbonyl compounds is casein. Due to this property it is utilized for the production of aminoplasts.⁴² In Figure

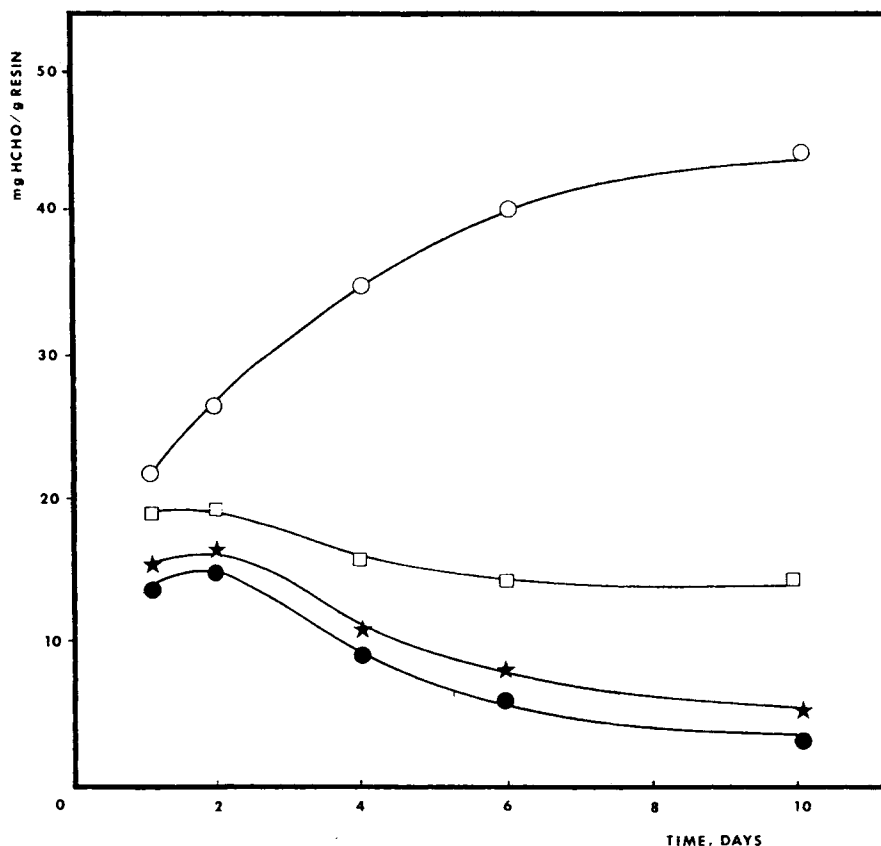


Fig. 5. A comparison of the kinetic changes of formaldehyde concentration in aqueous suspensions of cured UF-resin control and casein-modified samples at a temperature of 23°C. Contents of casein in the resin (by weight of the liquid UF resin before cure): (○) 0%; (□) 1%; (★) 2%; (●) 3%.

5 the experimental results indicate that casein can reduce substantially the amount of formaldehyde emitted from the cured UF polymer to its aqueous environment. The protein included in the resin may react with HCHO through its amino, amido, hydroxyl, aryl, and other functions already during the cure process. However, less stable structural units produced in such reactions are probably hydrolyzed in water in a similar manner as do the hydroxymethyl groups of the UF polycondensate. Perhaps, thus liberated formaldehyde is subsequently bound slowly by casein with the formation of more stable combinations. This could explain why the initial burst of HCHO from the modified materials, observed in Figure 5, is followed by a decrease of its concentration down to a relatively low level.

The results of the formaldehyde-release experiments presented above need some more comment. Sometimes partial loss of formaldehyde in pure water may be due to microbiological action. In our case the UF samples were prepared, and the tests performed in rather sterile conditions so that such a possibility was minor. Nevertheless, it cannot be totally excluded because no microbiological analyses were made. Perhaps they should be conducted in the future work. It seems, however, that even if the microorganisms had been responsible for some

small loss of formaldehyde, the qualitative observations concerning the effect of the used different additives on HCHO release from UF resins should have still remained valid since the experimental conditions were the same in each case.

SUMMARY AND CONCLUSIONS

The results obtained in this study showed that the emission of formaldehyde from UF resins, being mainly a consequence of their hydrolysis, can be reduced considerably when certain base additives are used which are capable of neutralizing the acid cure catalyst and of reacting irreversibly with HCHO. Polyacrylamide, biuret, and casein proved to be excellent formaldehyde chemical traps whereas quite an opposite effect was observed in the case of chitosan despite its well-known reactivity toward carbonyl compounds.³⁷ It follows from that fact that not only the reactivity of a modifier, but, obviously, also the stability of its possible combinations with formaldehyde has to be considered when selecting inhibitors of the HCHO emission from aminoformaldehyde resins. Quite surprisingly, from some references cited in this paper it may seem that this requirement was not always duly appreciated in the search for methods of modification of UF aminoplasts.

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