Hydrolytic Stability of Cured Urea-Formaldehyde Resins Modified by Additives

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ABSTRACT: Urea-formaldehyde (UF) resins are prone to hydrolysis that results in low-moisture resistance and subsequent formaldehyde emission from UF resin-bonded wood panels. This study was conducted to investigate hydrolytic stability of modified UF resins as a way of lowering the formaldehyde emission of cured UF resin. Neat UF resins with three different formaldehyde/urea (F/U) mole ratios (1.4, 1.2, and 1.0) were modified, after resin synthesis, by adding four additives such as sodium hydrosulfite, sodium bisulfite, acrylamide, and polymeric 4,4'-diphenylmethane diisocyanate (pMDI). All additives were added to UF resins with three different F/U mole ratios before curing the resin. The hydrolytic stability of UF resins was determined by measuring the mass loss and liberated formaldehyde concentration of cured and modified UF resins after acid hydrolysis. Modified UF resins of lower F/U mole ratios of 1.0 and 1.2 showed better hydrolytic stability than the one of higher F/U mole ratio of 1.4, except the modified UF resins with pMDI. The hydrolytic stability of modified UF resins by sulfur compounds (sodium bisulfate and sodium hydrosulfite) decreased with an increase in their level. However, both acrylamide and pMDI were much more effective than two sulfur compounds in terms of hydrolytic stability of modified UF resins. These results indicated that modified UF resin of the F/U mole ratio of 1.2 by adding acrylamide was the most effective in improving the hydrolytic stability of UF resin. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1011–1017, 2009

Key words: additives; adhesives; crosslinking; resins; thermosets

INTRODUCTION

Urea-formaldehyde (UF) resin forms strong bonds under a wider variety of conditions and cost less than phenol-formaldehyde (PF) resins.[1] UF resins are based on the manifold reactions of two components, that is, urea and formaldehyde.[2] By using different reaction conditions and preparation methods, a more or less innumerable variety of condensed structures is possible. UF resin is a thermosetting polymer and consists of linear or branched oligomeric and polymeric molecules, which always contain some amount of monomer[2] and it is one of the most important type of the so-called aminoplastic resins, because it has been widely used in manufacturing wood composites products such as plywood and particleboard as a binder[3] and also preferably a low pH for the condensation reactions that take place during the hardening process to yield a cross-linked state to develop the cohesion strength within the resin adhesive layer.[4] However, UF-bonded wood products are normally confined to interior nonstructural applications because UF resins undergo stress rupture and hydrolytic degradation under cyclic moisture or warm, humid environments.[1] Hydrolysis is often accompanied by formaldehyde emission, which constitutes a potential health hazard.[5] Hydrolysis of cured resin will cause splitting of ether bridges and terminal methylol groups, which seems to contribute the most in subsequent formaldehyde release from urea resin-bonded board.[6,7] Hydrolysis of UF resins is catalyzed by acids and increases in durability have been reported as a result of using materials that are capable of neutralizing the acid catalysts required for good UF resin cure. Examples include addition of glass powder to the adhesive, post-treatment of boards with sodium bicarbonate and addition of melamine that may act as a buffer.[8]

UF resin possesses some advantages, such as fast curing, good performance in wood panel, high reactivity, water solubility, and low cost. Disadvantages of using the UF resin are formaldehyde emission (FE) from the panels and lower resistance to water. Lower resistance to water limits the use of wood-based panels bonded with the UF resin to interior application.[9,10] Also, lower dimensional stability of wood-based panels bonded with UF resin is attributable to hydrolytic degradation.[3,11] Whereas poor durability and the emission of formaldehyde have been

recognized as an important drawback in the use of cured UF resin products.[7,12] It was shown that the reversibility of the aminomethylene links and susceptibility to hydrolysis were involved in the process of formaldehyde emission.[2] The structural factors responsible for these processes suggest that the stability of UF resin can be enhanced by modifying its structure and more random distribution of crosslinks.[1]

A limited ability of UF resin to resist moisture is mainly caused by: (1) the brittleness of resin, which allows the cured resin to crack and allow moisture to penetrate into the bonded-wood product and (2) the chemical breakdown of the amino bonds within the cured resin.[10] These limitations were evidenced, for example, in the strength loss of UF resin-bonded joints, owing to irreversible swelling of UF resin-bonded composite panels and formaldehyde release.[8] A significant improvement in the durability of UF resin would broaden the application and markets for UF resin-bonded wood products.[1] Greater moisture resistance has also been reported when additives, such as amines or thermoplastics, were incorporated into the UF resin.[10] The samples with high-crosslink density would be expected to have lower moisture sorption rates and equilibrium moisture uptake than those with low-crosslink density, mainly due to the extra bonds within a given area, which would need to be hydrolyzed to allow moisture to penetrate the sample.[10]

Several methods have been used to study hydrolytic stability of cured UF resins.[6,12,13] A common and effective method to reduce formaldehyde release is to build vapor barriers by coating or painting. Chemical treatments such as soaking or fumigation with ammonia have been proposed and used. This reaction consumes formaldehyde yielding hexamethylene-tetra amine. Many resin manufacturers have modified their formulations, often by the addition of excess urea during the second or condensation stage of resin manufacture or later. This procedure decreases formaldehyde release in the press, but makes the cured resin more vulnerable to formaldehyde release by hydrolysis, because it increases the concentration of methylol-terminal groups in the resin. Another method invlolves addition of lignosulfonates or similar materials to the resin formulation. Such lignosulfonate-containing resins have excellent weather resistant properties, but tend to be more brittle, their main drawback is that they must be cured longer and at a higher temperature than unmodified UF resins.[13] Other methods recorded formaldehyde concentration in filtered fractions of aqueous slurries of cured ground resin.[6] It was reported that UF resin with lower F/U mole ratio decreased methylol content and branching, leading to lower water sorption, greater interchain

bonding,[8] and also, affects internal bond (IB) and thickness swelling of particleboard.[12] The hydrolytic resistance appears decreasing with increasing F/U mole ratio. The UF resins with F/U mole ratio higher than 4.0 probably favors the formation of trimethylolurea. This may result in increased methylene-ether linkage concentration in the hardened resin and consequently to lower the hydrolytic stability.[6] In general, UF resins prepared from starting mixtures with a formal F/U mole ratio of 1.0 show a high degree of stability toward hydrolysis. Crosslinking methylene linkages in the UF resins show a higher susceptibility to hydrolytic treatments at pH 4 and 86°C than do linear methylene linkages. Whereas UF resins prepared with F/U mole ratio of 2.0 are susceptible to hydrolysis at the same condition. Dimethylene ether linkages, methylols attached to tertiary amides, and poly(oxymethylene glycol) moieties are probably the main formaldehyde emitters in UF resin products.[7] A variety of modifiers have been examined and some have been found to be beneficial for durability; few modifiers such as melamine, furfuryl alcohol, and certain fillers, were used in commercial applications. The mechanisms of these materials contribution were not clear; and it was postulated to increase in hydrolytic stability as an alteration of the polymer network increased in flexibility.[8] UF resins were modified either by (i) incorporating urea-terminated di- and tri-functional flexible amines into the resin structure or (ii) curing the resins with hydrochloride derivates of some of the amines. The results showed that the UF resin modified with urea-terminated hexamethylenediamine, bishexamethylenetriamine, and poly(propylene oxide) at 13, 16, and 28 wt %, respectively, resulted in excellent stability of the UF resin.[1,14] It has been reported that greater the melamine content and higher the F/U mole ratio will result in lower hydrolytic stability. It might be attributed to the chemical structure of UMF resins, which provided more branched and pendant hydroxymethyl groups and more ether linkages in UF resins because of higher F/U mole ratio.[15] Besides the modification of UF resin structures in reducing liberated formaldehyde concentration, the catalysts, hardener, and acid scavengers also have an important effect on liberated formaldehyde concentration.[6]

It is reported in the literature that the polyacrylamide and polymethacrylamide can create crosslinks with methylolureas during the curing process.[16] The additional bond that is formed with the resin and is still abundant in the base groups will react with formaldehyde. Ammonia that are liberated slowly from the amide groups of polyacrylamide and polymethacrylmaide can neutralize the acid curing agent contained in the resin. These agents were used to lower the formaldehyde emission resulting from its

hydrolysis by firmly binding on the free formaldehyde evolved. The reaction between the additives and formaldehyde lead to stable cyclic structures.[16]

General bond-degradation processes that appear to be responsible for the poor durability of UF resin-bonded products are hydrolytic degradation and brittleness of cured UF resin. Over the past decade, much progress had been made in improving the formaldehyde emission from wood products such as particleboard, hardwood plywood, and medium-density fiberboard.[17] Nevertheless, there are limited studies on the improvement of the hydrolytic stability of UF resin in terms of formaldehyde emission. The hydrolytic stability of UF resin could be enhanced if the structure of UF resins was modified by incorporating comonomers into the polymer chains and also incorporating some suitable modifiers and buffers into the resin that are capable of neutralizing the acid catalysts are used as curing agents.[8] So this study has attempted to investigate the hydrolytic stability of UF resins that are modified with additives. In this work, four additives such as sodium bisulfite, sodium hydrosulfite, pMDI, and acrylamide have been added to UF resins with different F/U mole ratios to modify the chemical structure of UF resins as a method of improving hydrolytic stability of UF resin.

EXPERIMENTAL

Materials

Four additives used in this study were all technical grade regents. Sodium bisulfite ($NaHSO_3$) (DC Chemical Co., Korea), sodium hydrosulfite ($Na_2S_2O_4$) (75.0%, Samchun Pure Chemical Co., Korea), acrylamide ($H_2C{=}CH{-}CO{-}NH_2$) (pH 6.6, 71.08 M_w, Yongsan Mitsui Chemicals, purity 50.2 wt %, Korea), and polymeric 4,4'-diphenylmethane diisocyanate (pMDI) (80 $\sim$ 140 mPa s, density 1.23, 350 M_w) were used as received. Formaline (37%) was used for UF-resin synthesis as received.

Preparation of UF resins

All UF resins used for this study were prepared in the laboratory, following traditional alkaline-acid two-step reaction. Formaldehyde (37%) was placed in the reactor and then adjusted to pH 7.8 with sodium hydroxide (20 wt %) then heated up to 45°C, subsequently, a certain amount of urea was added equally at 1 min intervals, and the mixture was heated to 90°C under reflux for 1 h to allow the methylolation reactions to proceed. The second stage of UF-resin synthesis consisted of the condensation of the methylolureas. The reaction mixture is brought to the acid side, with a pH of about 4.6, and
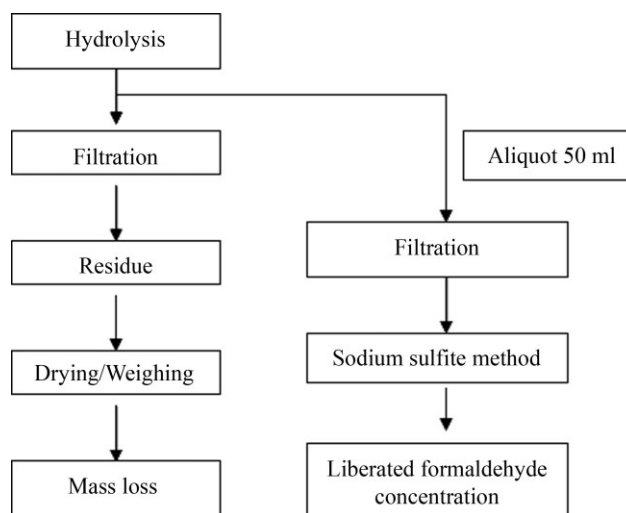

Figure 1 Schematic diagram of hydrolysis procedures to determine the mass loss and liberated formaldehyde concentration of cured UF resins.

the condensation reactions were carried out until a target viscosity of JK using a bubble viscometer (VG-9100, Gardner–Holdt Bubble Viscometer, USA). Different amounts of the second urea were added during the condensation step to obtain different UF resin with F/U mole ratios of 1.4, 1.2, and 1.0. Then, the UF resin was cooled to room temperature by adjusting the final pH to 8.0.

UF resin modification

Neat UF resin was physically mixed with different levels of additives at 1, 3, and 5 wt % of the UF resin immediately before mixing with 3 wt % of NH_4Cl as catalyst. In this study, additives were sodium bisulfite, sodium hydrosulfite, pMDI, and acrylamide. The mixture was then quickly and vigorously stirred. At all levels, the additives were easily dissolved except the pMDI. All the modified resins were cured in the oven at 105°C for 3 h. Two replications of modified UF resins for every each F/U mole ratio with four additives were prepared.

Resin hydrolysis

After curing, the resins were ground into particles using a grinding mill (MF 10 basic, IKA WERKE, Germany) and then sieved using a sieve shaker (CG-211-8, Korea) to obtain 250 m size particles. UF-resin samples for hydrolytic stability measurement were prepared by adding 2 g of the cured resin into 250 mL beaker and 50 mL of 0.1N HCl. Then, the mixture was hydrolyzed by continuously and vigorously stirring with a magnetic bar, at 50°C for 90 min (two replications for each sample). Figure 1 shows the flow diagram of the hydrolysis and further analysis.

TABLE I
Properties of UF Resins with Different F/U Mole Ratios

F/U mole ratio	Nonvolatile solid content (wt %)	Viscosity (mPa s, 25°C)	Gel time (s)
1.4	52.8	350	114
1.2	55.7	286	257
1.0	59.0	205	315

Determination of liberated formaldehyde concentration

Liberated formaldehyde concentration after the hydrolysis was determined by the sulfite method. A total of 50 mL of filtered solution was placed in 250 mL beaker and carefully neutralized by titrating with 0.1N sodium hydroxide. Then, 50 mL of sodium sulfate were added to the solution. The solution was stirred for 5 min; then, the mixture was slowly titrated with 1N hydrochloric acid.

Determination of mass loss

To determine the total mass loss of cured UF-resin sample after hydrolysis, the suspension was filtrated using filter paper (Whatman #1). The solid residue was washed with distilled water to remove residual hydrochloric acid. After drying (105°C, 3 h), the sample residue was weighed. The mass loss was determined by weighing the difference of the weights before and after the hydrolysis.

Properties of modified UF resins

About 1 g of UF resin was poured into a disposable aluminum dish, and then dried in a convective oven at 105°C for 3 h. Nonvolatile solids content was determined by measuring the weight of UF resin before and after drying. An average of three replications was presented.

To compare reactivity of UF resins synthesized, the gel time of resins were measured, with 3% NH_4Cl (20 wt %) as a hardener, at 100°C using a gel time meter (Davis Inotek Instrument, Charlotte, NC). The measurements were done with three replications for each UF resin with different F/U mole ratios.

The viscosity of UF resins at 25°C was measured using a cone-plate viscometer (DV-II +, BROOK-FIELD, US) with No. 2 spindle at 60 rpm.

RESULTS AND DISCUSSION

The properties of UF resins prepared at different F/U mole ratios were summarized in Table I. The nonvolatile solid contents of UF resins prepared at different F/U mole ratios were ranging from about 50–60 wt %. The resin viscosity showed a large differ-

ence between the F/U mole ratios of 1.4 and 1.0. This might be due to greater amount of the second urea for lower F/U mole ratio during the resin synthesis. The addition of the second urea dissolved at later stage of UF-resin synthesis could reduce the viscosity of UF resin.[18] An increase of the F/U mole ratio resulted in an increase in the resin molecular weight, whereas an increase of the sulfur material in the UF resin led to decrease in its molecular weights.[19]

The gel time of the UF resins prepared increased with a decrease in the F/U mole ratio. As shown in Table I, the gel time increased when the F/U mole ratio decreased from 1.4 to 1.0. These results indicate that the reactivity of UF resin decreased with a decrease in the F/U mole ratio. This might be explained by a decrease in the availability of free formaldehyde at lower F/U mole ratio.[19]

Figure 2 shows liberated formaldehyde concentration of modified UF resins at different F/U mole ratios and different levels of sodium bisulfite. It shows that liberated formaldehyde concentration of UF resin with the F/U mole ratio of 1.4 and 1.2 increased with an increase in the sodium bisulfite level, whereas UF resin with the F/U mole ratio of 1.0 initially decreased and then stabilized. Figure 3 also shows that UF resin at all F/U mole ratios showed an increase in mass loss with increasing sodium bisulfite levels. Among these, three F/U mole ratios, the UF resin of F/U mole ratio of 1.0 was found to be most resistant to hydrolysis. These results showed that the hydrolytic stability of cured modified UF resin decreased as the sodium bisulfite level increased.

When sodium bisulfite was added to UF resin, it could react with free formaldehyde that had been existed in UF resin to form sulfonate groups.
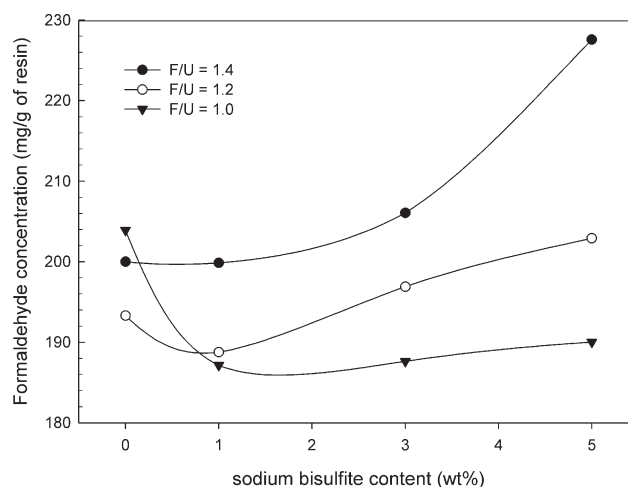

Figure 2 Liberated formaldehyde concentration of modified UF resin at different F/U mole ratios and sodium bisulfite levels after the hydrolysis.
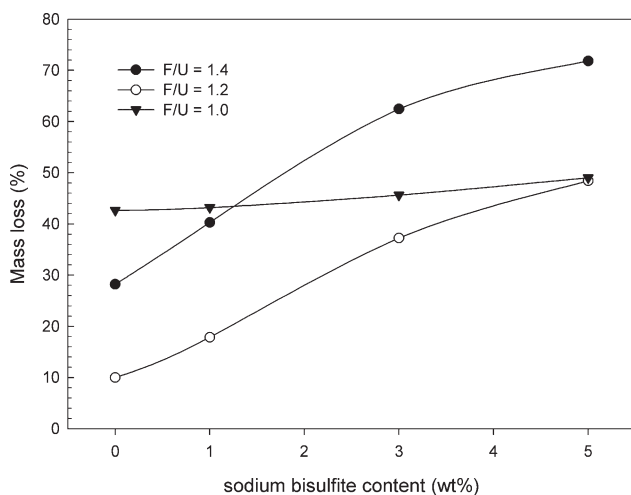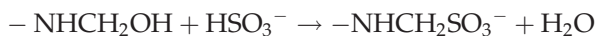
Figure 3 Mass loss of modified UF resin at different F/U mole ratios and sodium bisulfite levels after the hydrolysis.
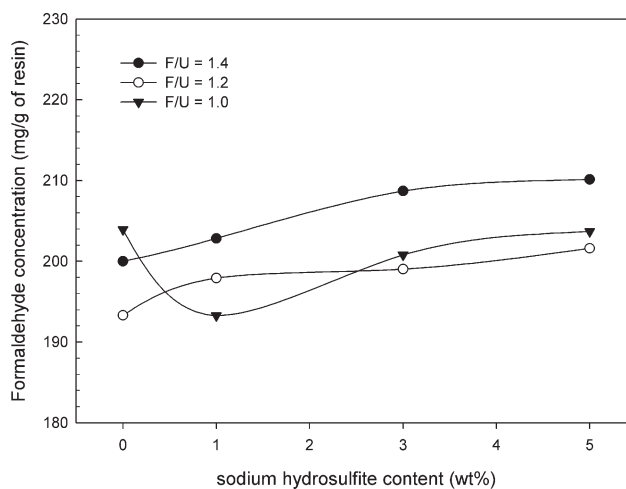

Figure 4 Liberated formaldehyde concentration of modified UF resin at different F/U mole ratios and sodium hydrosulfite levels after the hydrolysis.

Methylene bridges were obtained as main structural units. It was hydrolyzed in water to produce bisulfite ions, which reacted with methylol groups through their sulfonation as shown latter.[21]

$$-NHCH_2OH + HSO_3^- \rightarrow -NHCH_2SO_3^- + H_2O$$

As the level of sodium bisulfite in the UF resins increases, more sulfonate groups are formed. So, it was expected that less methylol groups were available in the condensation, which subsequently resulted in less number of methylene bridges in the modified UF resins.[8] Nevertheless, the sodium bisulfite was used as an additive in this study. So the sulfonation might be incomplete in the condensation that could have made more formaldehyde liberated from cured UF resins.

Figure 4 shows that liberated formaldehyde concentrations of UF resins with F/U mole ratios of 1.4 and 1.2 increased with an increase in the level of sodium hydrosulfite. However, for the UF resin with F/U mole ratio of 1.0 at all additives levels, the liberated formaldehyde concentration was below those of the control UF resins. From these three F/U mole ratios, UF resin with the F/U mole ratio of 1.2 seem to be more stable compared with F/U mole ratios 1.4 and 1.0 at lower sodium hydrosulfite levels. Figure 5 showed that, for all F/U mole ratios, the mass loss increased with an increase in the additives level. This result indicated that hydrolytic stability of the modified UF resin decreased with an increase in the sodium hydrosulfite. The sodium hydrosulfite reacts readily with formaldehyde solution and reduces formaldehyde release.[20] However, it was difficult to study this reaction because these compounds changed its structure in water on dissolution and were quickly decomposed.[21] So, it was

expected that a similar thing happened at lower levels of sodium hydrosulfite.

Figures 6 and 7 show hydrolytic stability of UF resins modified with acrylamide that contained amino- and amido-functions that could create crosslinks with methylolureas during the curing process. Thus, they could modify the macromolecular network of the resultant UF-resin polymer.[7] Figure 6 shows the changes of liberated formaldehyde concentration of the modified UF resin with the F/U mole ratios of 1.0 and 1.4 when acrylamide was added. The UF resin with the F/U mole ratio of 1.2 shows a slight decrease with an increase in the acrylamide and then slightly increased at its 5% level. In Figure 7, UF resin with the F/U mole ratio of 1.4 shows a very small increase with an increase in the acrylamide and slightly decreased at 5% level. In addition, UF resin
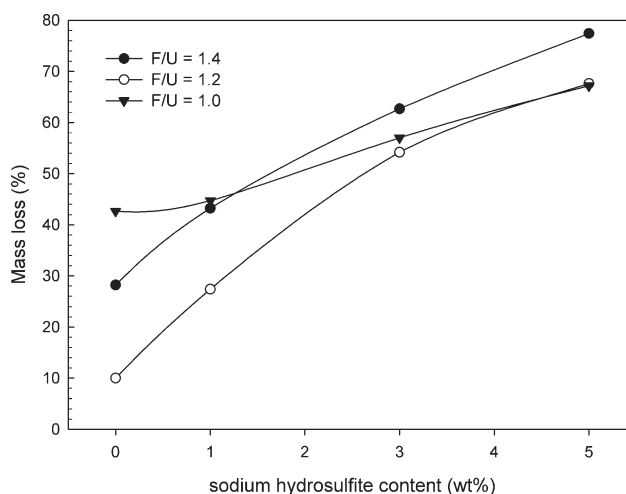

Figure 5 Mass loss of modified UF resin at different F/U mole ratios and sodium hydrosulfite levels after the hydrolysis.
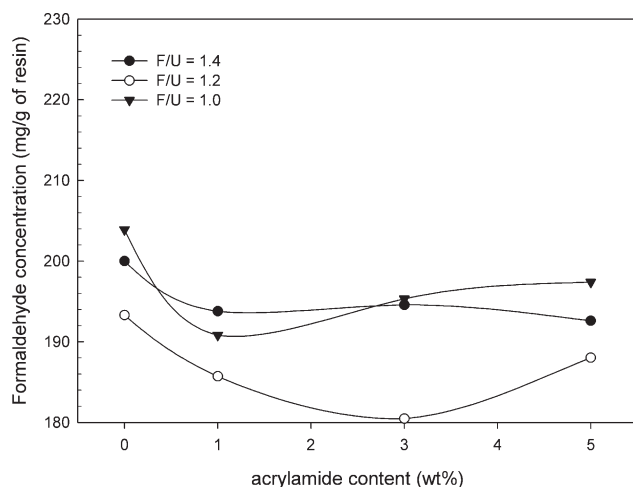
Figure 6 Liberated formaldehyde concentration of modified UF resin at different F/U mole ratios and acrylamide levels after the hydrolysis.

Figure 8 Liberated formaldehyde concentration of modified UF resin at different F/U mole ratios and pMDI levels after the hydrolysis.

with the F/U mole ratio of 1.2 also shows a very small increase at 1% level of acrylamide, then slightly decreased at 3% level, following an increase at 5% level of acrylamide. For the UF resin with F/U mole ratio of 1.0, the mass loss decreased at 1% level and then slightly increased with an increase of acrylamide level. These results indicated that the F/U mole ratio of 1.2 was more effective in improving the hydrolytic stability of UF resins compared with that of F/U mole ratios of 1.4 and 1.0.

Liberated formaldehyde concentration of modified UF resins with pMDI was shown in Figure 8. As expected, the addition of pMDI did not show much influence on the mass loss and liberated formaldehyde concentration. All UF resins of the three F/U mole ratios showed that the liberated formaldehyde decreased at 1% pMDI and increased again with an increase in the additive levels. Figure 9 showed that
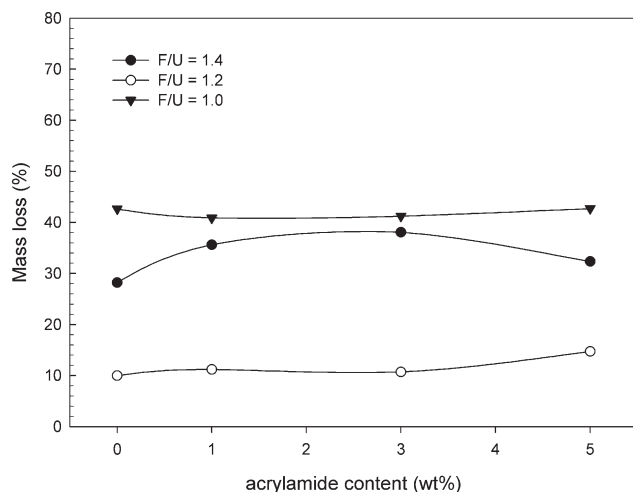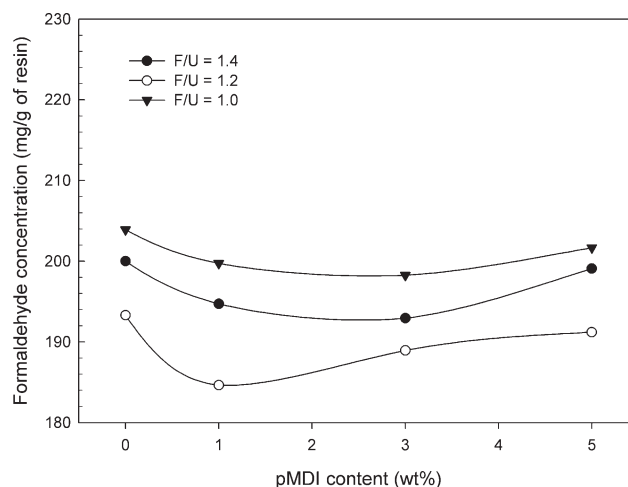
the UF resin with the F/U mole ratio of 1.0 had a decrease in the mass loss at 1 and 3% of pMDI, and then slightly increased at 5% level of pMDI. In contrast, UF resin with the F/U mole ratio of 1.2 showed an increase in the mass loss with an increase in the pMDI level. Mass losses of UF resin with the F/U mole ratio of 1.4 showed a fluctuation when the pMDI level increased. These results showed that UF resin with the F/U mole ratio of 1.2 was more stable than the resins with F/U mole ratios of 1.0 and 1.4.

For all F/U mole ratios, the mass loss and liberated formaldehyde concentration increased with an increase in the levels of sodium bisulfite, sodium hydrosulfite, and acrylamide. However, this was not the case when pMDI was added into the UF resins with F/U mole ratios of 1.4 and 1.0 and acrylamide was added in the UF resin with F/U mole ratio of 1.4. Generally, the modified UF resins with sodium
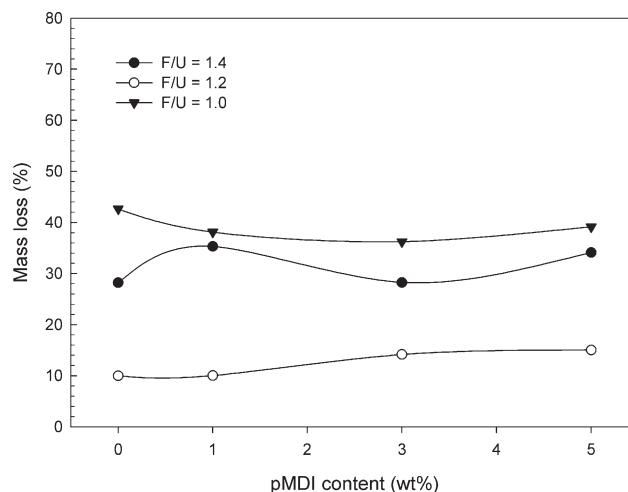

Figure 7 Mass loss of modified UF resin at different F/U mole ratios and acrylamide levels after the hydrolysis.

Figure 9 Mass loss of modified UF resin at different F/U mole ratios and pMDI levels after the hydrolysis.

bisulfite and sodium hydrosulfite at different levels increased liberated formaldehyde concentration with an increase in additives compared with the modified UF resins with either acrylamide or pMDI. Also, the relative increase of the mass loss was more pronounced compared with liberated formaldehyde concentration. For example, the mass loss of the modified UF resin by sodium bisulfite at the F/U mole ratio of 1.4 increased from 40.3 to 71.8%, whereas the amount of liberated formaldehyde concentration had very small increases. Sodium hydrosulfite showed a similar trend, whereas the other two additives (pMDI and acrylamide) did not increase the mass loss and liberated formaldehyde concentration to a greater extent. In some cases, the liberated formaldehyde concentration was not parallel to the extent of mass loss particularly for the pMDI and acrylamide. This might depend on the number of methylol groups exposed on the surfaces of cured UF resin during acid hydrolysis. However, the gravimetric method provides a clearer trend in measuring hydrolytic stability of the modified UF resins than liberated formaldehyde concentration.[21] Based on the results obtained, the hydrolytic stability of the modified UF resins was determined in the following order: pMDI < acrylamide < sodium bisulfite < sodium hydrosulfite as additives.

CONCLUSIONS

As a part of abating formaldehyde emission of UF resin, this study investigated hydrolytic stability of the modified UF resins by the addition of four different additives. The mass loss and formaldehyde concentration of sodium bisulfite and sodium hydrosulfite increased with an increase in the additives level. However, as the level of acrylamide and pMDI increased, the mass loss and liberated formaldehyde concentration decreased at 1 and 3% additives level, but it increased at 5% additive level. Modified UF resins of lower F/U mole ratios of 1.0 and 1.2 showed better hydrolytic stability than the UF resins of higher F/U mole ratio of 1.4, except the modified UF resins with pMDI.

In terms of hydrolytic stability, the UF resins modified by sulfur compounds (sodium bisulfite and sodium hydrosulfite) decreased with an increase in their level. However, both acrylamide and pMDI were much more effective than two sulfur compounds. However, pMDI was not homogeneously dispersed in neat UF resin. These results indicate that the modified UF resin of the F/U mole ratio of 1.2, by adding acrylamide, was the most effective in improving the hydrolytic stability of UF resin.

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