

# Hydrolytic Stability of Cured Urea-Melamine-Formaldehyde Resins Depending on Hydrolysis Conditions and Hardener Types<sup>1</sup>

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## ABSTRACT

As a part of abating the formaldehyde emission of amino resin-bonded wood-based composite panels, this study was conducted to investigate hydrolytic stability of urea-melamine-formaldehyde (UMF) resin depending on various hydrolysis conditions and hardener types. Commercial UMF resin was cured and ground into a powdered form, and then hydrolyzed with hydrochloric acid. After the acid hydrolysis, the concentration of liberated formaldehyde in the hydrolyzed solution and mass loss of the cured UMF resins were determined to compare their hydrolytic stability. The hydrolysis of cured UMF resin increased with an increase in the acid concentration, time, and temperature and with a decrease in the smaller particle size. An optimum hydrolysis condition for the cured UMF resins was determined as 50°C, 90 minutes, 1.0 M hydrochloric acid and 250 μm particle size. Hydrolysis of the UMF resin cured with different hardener types showed different degrees of the hydrolytic stability of cured UMF resins with a descending order of aluminum sulfate, ammonium chloride, and ammonium sulfate. The hydrolytic stability also decreased as the addition level of ammonium chloride increased. These results indicated that hardener types and level also had an impact on the hydrolytic stability of cured UMF resins.

**Keywords :** amino resin, hydrolysis condition, hydrolytic stability, hardener types

## 1. INTRODUCTION

Amino resins such as urea-formaldehyde (UF) resin, urea-melamine-formaldehyde (UMF) resin, melamine-urea-formaldehyde (MUF) resin and melamine-formaldehyde (MF) resins are polymeric condensation products of the chemical reaction of formaldehyde with urea, copoly-

mers of urea and melamine, or melamine. The UMF and MUF resins are different in terms of the relative mass proportions of melamine to urea. In general, the relative mass proportions of melamine to urea in MUF resins are ranged from 50 : 50 to 40 : 60 (Clad and Schmidt-Hellerau, 1977). Thus, commercial MUF resins are synthesized with much higher

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levels of melamine than those of UMF resins, and are being used for different wood-bonding applications that require a higher resistance to water.

These amino resins are most widely used for the manufacture of wood-based composite panel, particularly plywood, particleboard or medium density fiberboard. Therefore, amino resin adhesives are considered one of the most important wood adhesives. So, the wood panel industry is a major user of amino resin adhesives. For example, the production of formaldehyde-based resin in 2010 was about 225,620 tons, which was 37.7% of the total production of adhesives in the Republic of Korea. In particular, the production of UF resin adhesives was about 77% (i.e. 174,061 tons) of the total production of formaldehyde-based resin adhesives.

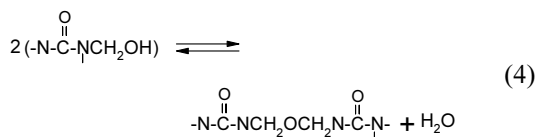
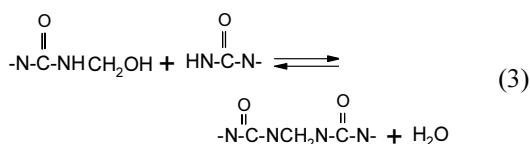
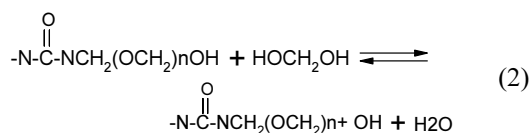
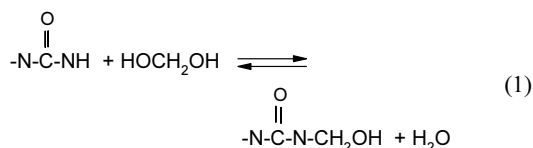
UF resin adhesive possesses some advantages, such as fast curing, good performance in the panel, water solubility and lower price. Disadvantages of using the UF resin are formaldehyde emission from the panels and lower resistance to water. Lower resistance to water limits the use of wood-based panels bonded with UF resin to interior applications. Furthermore, the formaldehyde emission from the panels used for interior applications was one of the factors, affecting sick building syndrome in an indoor environment. Therefore, the formaldehyde emission issue has been one of the most important aspects of UF resin in the last few decades (Myers and Koutsky, 1987; Myers, 1986a; Myers, 1986b; Pizzi *et al.*, 1994;

Hse *et al.*, 1994; Gu *et al.*, 1995).

Free formaldehyde present in UF resin and hydrolytic degradation of UF resin under moisture condition is known to be responsible for the formaldehyde emission from wood-based panels (Myers, 1983). For example, the amount of free formaldehyde present in UF resin proportionately contributed to the formaldehyde emission from particleboard even after hot-pressing at high temperature (Park *et al.*, 2006). However, Myers (1983) reported that hydrolysis of cured UF resin was a major factor affecting formaldehyde emission of UF resin-bonded wood panels. Specifically, the reversibility of the curing reactions under acidic hydrolysis also explained lower resistance against the influences of water and moisture, and subsequent formaldehyde emission (Myers, 1983).

Much attention has been paid to investigate the hydrolysis of UF resins to understand the mechanisms of formaldehyde released from cured UF resins (Myers, 1983; Myers, 1986b). Hydrolysis of cured UF resin under acidic conditions splits ether bridges or terminal hydroxymethyl groups, which has been known to mainly contribute to the subsequent formaldehyde emission from UF resin-bonded wood panels (Neusser and Schall, 1970; Myers and Koutsky, 1990; Elbert, 1995). The susceptibility of hydrolytic degradation of cured UF resin depended on its chemical structure and the degree of cross-linking, and could be accelerated by high temperature and strong acidic conditions (Robitschek and Christensen, 1976). For exam-

ple the following reactions are reversible to play a role in the emission of formaldehyde from cured UF resin:



In scheme (1), urea is reacted with formaldehyde under alkaline conditions to produce mono-hydroxymethylurea, which is an addition reaction and reversible to produce formaldehyde. In addition, different types of hydroxymethylureas such as di- or tri-hydroxymethylureas are also reversible reactions. The scheme (2) shows that either hemiformal ( $-\text{NH}-\text{CH}_2-\text{OCH}_2\text{OH}$ ), or formal ( $-\text{NH}-(\text{CH}_2\text{O})_n-\text{CH}_2\text{OH}$ ) are also reversible to split into formaldehyde moieties in the end. In scheme (3), the hydroxymethylureas are converted to methylene linkages in the condensation reaction, which is also reversible to provide hydroxymethylureas that are susceptible

to hydrolysis. The scheme (4) also shows a reversible reaction of dimethylene ether linkage to hydroxymethylurea.

A conventional method of measuring hydrolytic stability of amino resin, particularly UF resin is to use an acid solution and compare the mass loss or liberated formaldehyde concentration (Myers, 1982; Rigena *et al.*, 2006). A different method of evaluating hydrolytic stability of cured UF resins was also introduced by exposing the resins to the air with controlled temperature and relative humidity (Kavvouras *et al.*, 1998). Tohmura *et al.* (2000) reported that an increase in the formaldehyde emission was related to a decreased amount of hydroxymethylurea.

Even though numerous research have been done on UMF resins, few reports in recent years have been published about the synthesis, thermomechanical curing, and performance of UMF resin (No and Kim, 2004; No and Kim, 2005; No and Kim, 2007). In spite of research work on the UMF resin, there is limited data available for hydrolytic stability of UMF resin in terms of formaldehyde emission. Therefore, this study was conducted to investigate hydrolytic stability of UMF resins with different hydrolysis conditions, hardener types, and hardener levels as a part of abating the formaldehyde emission of amino resin-bonded wood products.

## 2. MATERIALS and METHODS

A commercial UMF resin donated from a local particleboard mill was used in this study,

**Table 1.** Properties of a commercial UMF resin adhesives used in this study

F/(U+M) mole ratio	Melamine content (%wt)	Gel time (s)	Non-volatile resin solids content (%)	Viscosity (mPa · s)	Free formaldehyde content (%)
1.3	20	132	65.0	135.0	0.15

and its properties were shown in Table 1.

### 2.1. Determination of free formaldehyde

Free formaldehyde in the prepared UMF resins was determined by a slightly modified sodium sulfite method (McCaffery, 1970). The solution of 25 ml 1 M sodium sulfite mixed with 10 ml HCl was added to 2-3 grams of UMF resin sample dissolved in 100 ml of distilled water. The mixed solution containing about 10 drops of 0.1% thymolphthalein was neutralized with 1 N sodium hydroxide. The percent of free formaldehyde was determined by the equivalent of the amount of the consumed sodium hydroxide in titration.

### 2.2 Resin curing and sample preparation

About 20 grams of the commercial UMF resin was thoroughly mixed with 3% hardener (20% ammonium chloride solution), and then cured at 120°C for 60 minutes in a convective drying oven. The cured resins subsequently went through a grinding mill to obtain fine particles in powder form.

### 2.3. Hydrolysis of the cured UMF resin

About 2 grams of the cured UMF resins pre-

pared in powdered form were added to a 250 ml Erlenmeyer flask that contained 200 ml of 0.1 M (0.01 M or 1.0 M) hydrochloric acid. The mixture was hydrolyzed on a hot-plate with continuous stirring using a magnetic bar at different temperatures (25°C, 50°C, or 60°C) for different times (30 min., 60 min., or 90 min.). The hydrolyzed mixture was separated by filtering into the solution and resin particle residues. Then, hydrolytic stability of cured UMF resins was evaluated by determining both the concentration of liberated formaldehyde in the solution, and the mass loss of the cured resin particle residue.

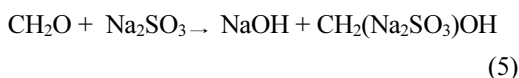
### 2.4. Determination of particle size of cured UF resins

About 2 grams of the cured UMF resins were ground using a mill (MF 10, IKA, Werke, Germany) to obtain powdered particles. And the particles were screened with a RoTap Shaker to classify different sizes of particles.

### 2.5. Determination of the concentration of liberated formaldehyde

After the hydrolysis, the filtered solution was used to determine the concentration of formaldehyde liberated during the hydrolysis ac-

according to the sulfite method (Walker, 1964). In brief, 50 ml of the solution was neutralized with 0.1 M NaOH, and then 50 ml of sodium sulfite was added to the solution. The mixed solution was titrated with 1.0 M HCl to calculate the concentration of formaldehyde liberated. As shown in the scheme (5) below, the sodium sulfite reacted with liberated formaldehyde to produce sodium hydroxide, which was titrated with hydrochloric acid.

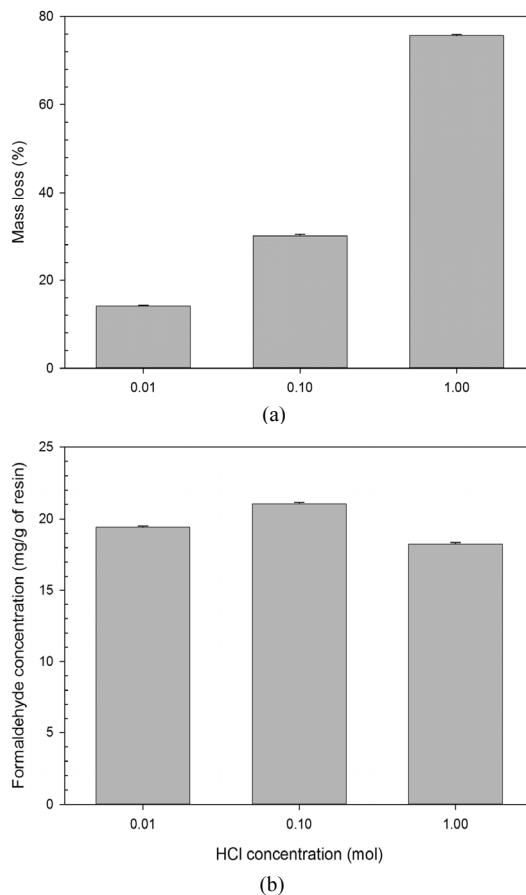


## 2.6. Determination of mass loss

In order to determine the mass loss of cured UMF resin, the particles of cured resins after the acid hydrolysis were filtered with a filter paper (Whatman #1), and then dried at 105 °C for 3 hours. After drying, the mass loss of cured resins was determined by weighing the masses of cured resins before and after the hydrolysis.

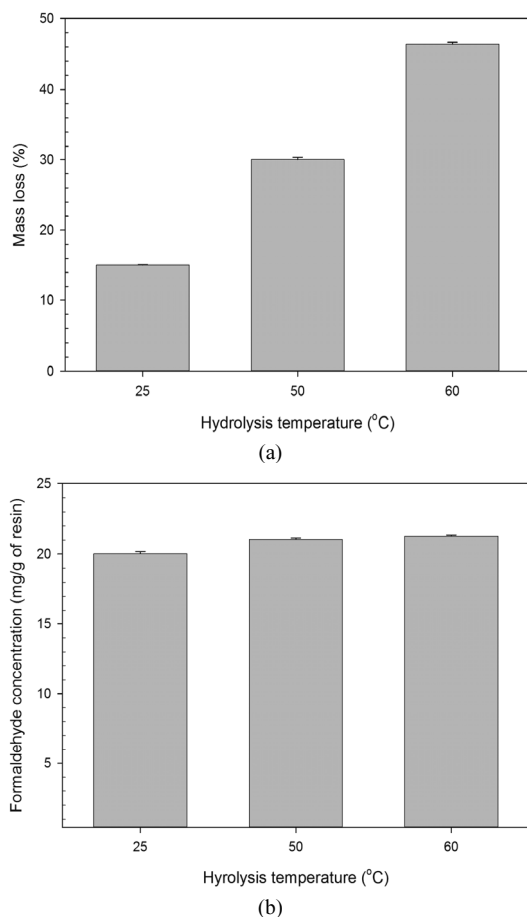
## 3. RESULTS and DISCUSSION

Prior to measuring hydrolytic stability of the cured UMF resins, the parameters such as acid concentration, time, temperature and particle size should be determined to obtain an optimum condition. Fig. 1 shows the mass loss and liberated formaldehyde concentration of cured UMF resins at different hydrochloric acid concentration levels. For this experiment, other



**Fig. 1.** Mass losses and liberated formaldehyde concentration at different acid concentrations. (a) Mass loss, and (b) liberated formaldehyde concentration.

hydrolysis conditions such as time, temperature and particle size were 50 °C, 90 minutes, and 250 μm, respectively. As expected, an increase in the hydrochloric acid concentration resulted in an increase of the mass loss after the hydrolysis. As the hydrochloric acid level increased from 0.01 M to 0.1 M, the mass loss of cured UMF resin increased two times from about 15% to 30%. And the mass loss increased to five times (about 75%), as the acid



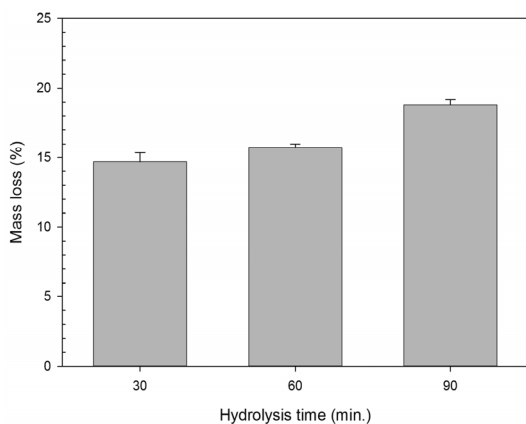
**Fig. 2.** Mass losses and liberated formaldehyde concentration at different hydrolysis temperatures. (a) Mass loss, and (b) liberated formaldehyde concentration.

level increased from 0.1 *M* to 1.0 *M*. These results suggested that hydrolysis stability of cured UMF resin was more dominant at higher levels of hydrochloric acid than lower ones. But, the concentration of liberated formaldehyde increased to a maximum at 0.1 *M* level, and then decreased afterwards. This result was inconsistent with the mass loss changes after the acid hydrolysis. This inconsistency in the measured

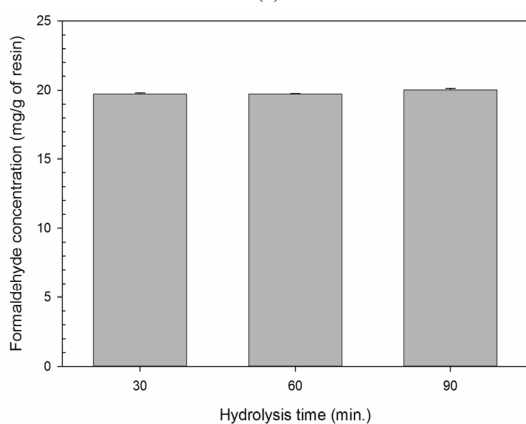
formaldehyde concentration could be ascribed to a larger variation of liberated formaldehyde concentration of the cured UMF resins as observed in the resin particle size (Fig. 4). Another reason could be that high acid concentration could have hydrolyzed cured UF resins into oligomers that had not been detected by the titration.

Fig. 2 shows the mass loss and liberated formaldehyde concentration of cured UMF resin, depending on hydrolysis temperatures. As expected, the mass loss after the hydrolysis increased with an increase in the hydrolysis temperature (Fig. 2, a). The liberated formaldehyde concentration also increased with an increase in the temperature, although the increase was not much different between temperatures. Since the mass loss and liberated formaldehyde concentration of cured UMF resin after the hydrolysis were consistent with increasing hydrolysis temperature, we selected 50°C as an optimum hydrolysis temperature.

The mass losses and liberated formaldehyde concentrations of cured UMF resin depending on hydrolysis time were shown in Fig. 3. The mass loss of the cured resin slightly increased when the hydrolyzing time increased from 30 minutes to 60 minutes (Fig. 3, a). However, the mass loss was much more increased when the hydrolyzing time increased from 60 minutes to 90 minutes. By contrast, the liberated formaldehyde concentration of the cured resin after the hydrolysis did not change much among the temperatures although the highest concentration was found at 90 minutes (Fig. 3, b). In general,



(a)

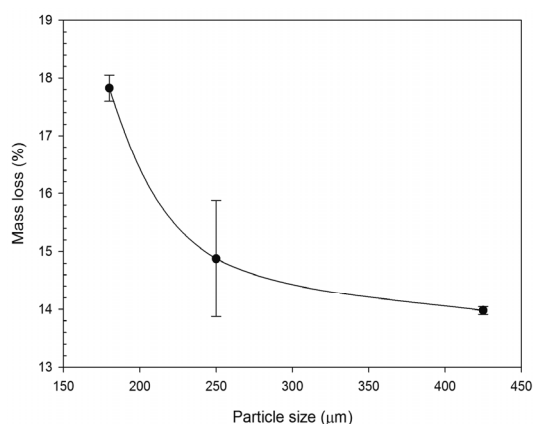


(b)

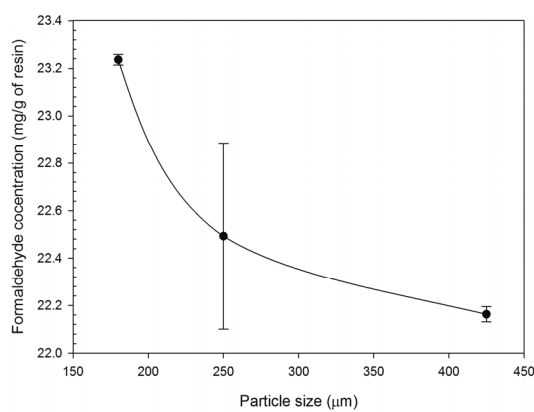
**Fig. 3.** Mass losses and liberated formaldehyde concentration at different hydrolysis times. (a) Mass loss, and (b) liberated formaldehyde concentration.

the hydrolytic stability of cured UMF resin decreased with an increase in the hydrolyzing time. This result was quite compatible with the published result (Ringena *et al.*, 2006). These results suggested an optimum hydrolysis time as 90 minutes for the cured UMF resin.

The effect of particle sizes of cured UMF resin was presented in Fig. 4. Both mass loss (Fig. 4, a) and liberated formaldehyde concen-



(a)



(b)

**Fig. 4.** Mass losses and liberated formaldehyde concentration at different particle sizes of cured UMF resin. (a) Mass loss, and (b) liberated formaldehyde concentration.

tration (Fig. 4, b) of the cured UMF resins decreased, as the particle size increased. These results could be due to the fact that smaller sizes particles possess larger surface areas than those of larger sized particles, resulting in a greater susceptibility of the smaller particle sizes to the acid hydrolysis. And these results also showed that the particle size of the cured UMF resin affected the degree of its hydrolytic

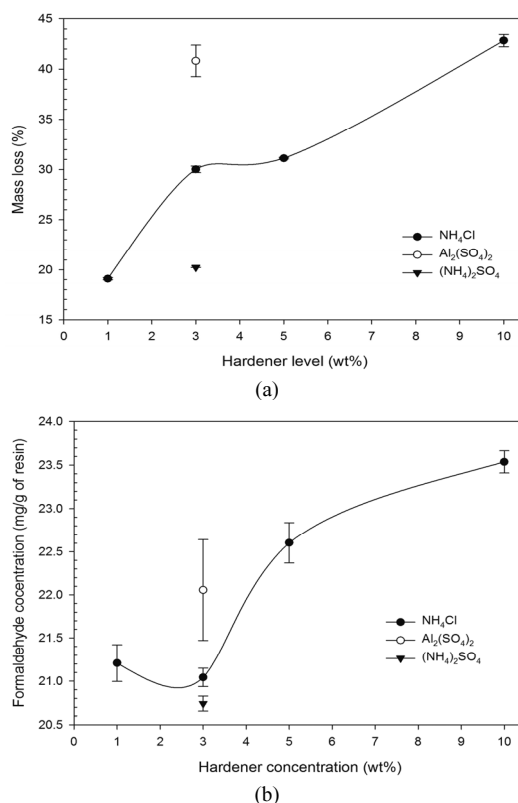
**Table 2.** Optimum conditions of hydrolysis parameters for cured amino resins

Hydrolysis parameters	Optimum level
HCl concentration ( <i>M</i> )	1.0
Temperature (°C)	50
Time (min.)	90
Particle size (μm)	250

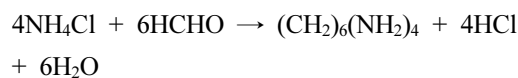
stability. From the above results, an optimum hydrolysis condition was determined to compare types of hardeners, and summarized in Table 2.

Fig. 5 (a) shows the mass loss and liberated formaldehyde concentration of cured UMF resin, depending on hardener types and hardener levels. The mass loss of the cured UMF resin was the greatest with the addition of aluminum sulfate, followed by ammonium chloride, and then ammonium sulfate. These results could be due to the reactivity of hardeners used. The greater the reactivity of a hardener is, the lower the hydrolytic stability of the cured resin is. The mass loss of cured UMF resin depending on the addition level of ammonium chloride was also shown in Fig. 5 (a). As shown, the mass loss increased with an increase in the hardener concentration. This result suggested that the hydrolytic stability of cured UMF resin decreased with an increase in the hardener concentration.

Fig. 5 (b) shows the liberated formaldehyde concentration of cured UMF resin after the acid hydrolysis. As expected, the liberated formaldehyde concentration of the cured resins also followed a similar trend as the mass loss. In other words, the hydrolytic stability of the cured resins was the highest for ammonium sul-

**Fig. 5.** Mass losses and liberated formaldehyde concentration at different hardener types. (a) Mass loss, and (b) liberated formaldehyde concentration.

fate, followed by ammonium chloride, and then aluminum sulfate. This result could be due to the reactivity of hardeners. Usually, hardener added into the UMF resin was supposed to react with free formaldehyde in the resin, producing an acid that stimulated the start of the cure of the resin. For example, ammonium chloride reacts with free formaldehyde in the resin to produce hydrochloric acid, as shown below:





So, the ability of providing protons that stimulate the formation of methylene linkages by reacting with the methylol groups in the resin would accelerate the cure of the resin. It is expected that a faster curing of the resin will produce a more branched structure in the cured resin than the slower ones. It was already reported that the branched structure of the cured UMF resin was more susceptible to acid hydrolysis than those of linear structure (Chung and Maciel, 1994). Therefore, a decrease in the hydrolytic stability of the cured UMF resin with an increase in the hardener level could be partially explained by the above curing reactions.

#### 4. CONCLUSION

This study was conducted to investigate hydrolytic stability of urea-melamine-formaldehyde (UMF) resin depending on various hydrolysis conditions and hardener types. Hydrolytic stability was determined by measuring the concentration of liberated formaldehyde in the hydrolyzed solution and mass loss of the cured UMF resins after the acid hydrolysis. The degree of acid hydrolysis of the cured UMF resin increased with an increase in the acid concentration, time, and temperature, and with a decrease in the particle size, resulting in an optimum hydrolysis condition of 50°C, 90 minutes, 1.0 M hydrochloric acid, and 250 μm particle size. Moreover, the hydrolytic stability of UMF resin was also affected by types of hardeners with a descending order of aluminum

sulfate, ammonium chloride, and ammonium sulfate. As the addition level of ammonium chloride increased, the hydrolytic stability of cured UMF resin decreased.

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