Morphology and Chemical Elements Detection of Cured Urea–Formaldehyde Resins

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ABSTRACT: As a part of understanding the hydrolysis of cured urea–formaldehyde (UF) resins that has been known as responsible for the formaldehyde emission, leading to sick building syndrome, this study attempted to investigate the morphology and to detect chemical elements of the cured UF resins of different formaldehyde/urea (F/U) mole ratios and hardener (NH$_4$Cl) levels, using field emission-scanning electron microscopy and energy-dispersive spectroscopy. Cured UF resins of low F/U mole ratio showed spherical structure whose diameter increased with an increase in the hardener level, whereas this was not observed for high F/U mole ratio UF resins regardless of the hardener levels. The energy-dispersive spectroscopy results showed five different chemical elements such as carbon, nitrogen, oxygen, chloride, and sodium in cured UF resins. The chloride distribution assumed as the presence of residual acid in the cured UF resins suggested that the hydrolysis of cured UF resins could initiate at the sites of chlorides on the surface of the spherical structures. As the hardener level increased, the quantities of both carbon and oxygen decreased, whereas those of nitrogen and chloride increased as expected. But the quantity of sodium was within measurement error. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1475–1482, 2011

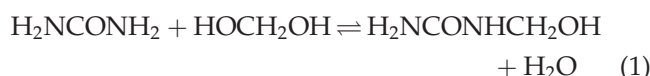**Key words:** adhesives; microstructure; resins; catalyst; electron microscopy

INTRODUCTION

Urea–formaldehyde (UF) resin is a polymeric condensation product of the chemical reaction of formaldehyde with urea, and a kind of amino resin. UF resins are most widely used for the manufacture of wood-based composite panel such as plywood, particleboard, or medium-density fiberboard.[1] Therefore, wood panel industry is a major consumer of UF resin adhesive, which is considered as one of the most important wood adhesives.

UF resin posses some advantages such as fast curing, good performance in the panel, water solubility, and lower price. Faster curing provides a short production time because of reduced hot-pressing time in the manufacture of wood-based panels. Water solubility also provides a flexibility of adjusting the resin solids content, which has a great impact on the moisture content of furnish materials to be hot-pressed. However, UF resin adhesives possess critical disadvantages such as formaldehyde emission from the panels and lower resistance to water.[2,3]
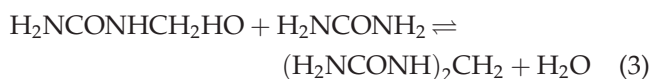
Lower resistance to water reduces the durability of wood-based panels, which excludes their uses in exterior applications. Thus, lower water resistance of UF resins limits the use of wood-based panels bonded with UF resin adhesives for interior applications.[1] Furthermore, the formaldehyde emission 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.[4–11]

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.[4] For example, the amount of free formaldehyde present in UF resin proportionately contributed to the emitted formaldehyde from particleboard even after hot-pressing at high temperature.[12] But, it was reported that hydrolysis of cured UF resin was a major factor affecting long-term formaldehyde emission of UF resin-bonded wood panels.[3] The hydrolysis of UF resins is reversible reactions of UF resin synthesis reactions.[13,14] Typical synthesis reactions of UF resins are given as:

$$H_2NCONH_2 + HOCH_2OH \rightleftharpoons H_2NCONHCH_2OH + H_2O \quad (1)$$

$$H_2NCONHCH_2HO + HOCH_2OH \rightleftharpoons$$
$$HOCH_2NCONHCH_2OH + H_2O \quad (2)$$

$$H_2NCONHCH_2HO + H_2NCONH_2 \rightleftharpoons$$
$$(H_2NCONH)_2CH_2 + H_2O \quad (3)$$

$$2H_2NCONHCH_2HO \rightleftharpoons H_2NCONCH_2OCH_2NCONH_2$$
$$+ H_2O \quad (4)$$

In UF resin synthesis, formaldehyde is added to urea to give monomethylol urea [eq. (1)]. The monomethylol urea is further reacted to produce dimethylol urea [eq. (2)]. Methylolated ureas react with formaldehyde to form methylenediurea [eq. (3)]. In excess of formaldehyde, monomethylol urea further reacts to form dimethylene ether link [eq. (4)]. All these reactions produce water as a by-product of the condensation.

In the hydrolysis reaction, the chemical species go through reversible reactions when these species are exposed to water.[14] Thus, these reversible reactions degrade the chemical species into a simpler species as shown in eqs. (1–4). In particular, the hydrolysis of cured UF resins in the composite seems inevitable because wood substance is a hygroscopic material when UF resins are being used for wood-based composites as a binder.

Much attention has been paid to investigate the hydrolysis of UF resins to understand the mechanisms of formaldehyde released from cured UF resins. The 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.[15–18] 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.[18] Even though many researches focused on the chemical structure of UF resins,[19–22] there is a limited research in relation to its hydrolysis process. For example, Chuang and Maciel[23] reported that dimethylene ether linkages, methylols attached to tertiary amides, and poly(oxymethylene glycol) moieties were the main emitters in cured UF resins. Using the same technique, Tohmura et al.[24] reported that formaldehyde emission from cured UF resin was mainly ascribed to decreased hydroxymethyl groups and dimethylene ether linkages.

UF resin adhesives are cured by the addition of a hardener, which makes acidic condition by producing an acid through the reaction between free formaldehyde and a component of a hardener. For example, the chloride of ammonium chloride reacts with free formaldehyde and produces hydrochloric acid, which stays in cured resin as a residual acid. It is known that the residual acid in cured resin could play a role in accelerating hydrolytic degradation, or hydrolysis.[16]

In a study to understand the microstructure or morphology of UF resins, Pratt et al.[25] reported that UF resin of low formaldehyde/urea (F/U) mole ratio formed colloid particles and postulated that the colloidal particles were covered by double layers of formaldehyde. But, the particles were not observed for high F/U mole ratio UF resins. After that, Stuligross and Koutsky[26] also found colloidal particles that consisted of four to eight units of urea, depending on F/U mole ratios.

Despite extensive research work on the hydrolytic degradation of UF resin adhesive, the morphology and detection of chemical elements in cured UF resin adhesive was not investigated to explain the hydrolysis of the resin that subsequently would influence formaldehyde emission of UF resin adhesive-bonded wood panels. In particular, the distribution of residual acid in the cured resin has not yet been studied. Therefore, this study attempted to observe the morphology and to detect the chemical elements of the cured UF resin adhesives at different F/U mole ratios and hardener levels as a part of abating the formaldehyde emission of UF resin adhesive for bonding wood-based composite panels.

MATERIALS AND METHODS

Materials

Both commercial urea (99 wt %) and formalin (37 wt %) were used for the synthesis of UF resins. Aqueous solutions of both formic acid (20 wt %) and sodium hydroxide (20 wt %) were used to adjust the pH during the UF resin synthesis. Aqueous solution of ammonium chloride (NH_4Cl) as hardener was used. Four different levels of the hardener (i.e., 0, 1, 3, and 10%) were added into the synthesized UF resin based on the nonvolatile resin solids.

Methods

UF resin synthesis

All UF resins used for this study were prepared in the laboratory, following traditional alkaline-acid two-step reaction. Formalin was placed in the reactor, adjusted to pH 7.8 with sodium hydroxide, and 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 hr 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 by

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

F/U mole ratio	Nonvolatile solids content (%)	Viscosity (mPa sec, 25°C)	Free formaldehyde (%)	pH (25°C)	Gel time (sec)
1.4	54.1	276	0.699	8.0	72
1.0	57.6	248	0.271	8.0	201

adding formic acid to a pH of about 4.6, and the condensation reactions were carried out until it reached a target viscosity of JK, which was measured using a bubble viscometer (VG-9100, Gardner-Holdt Bubble Viscometer, USA). Then, different amounts of second urea were added during the condensation step to obtain different UF resin of F/U mole ratios of 1.4 and 1.0. Then, the UF resin was cooled to room temperature and adjusted to the final pH of 8.0.

Measurement of UF resin properties

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 hr. Nonvolatile resin 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 was measured with three replications for each UF resin of different F/U mole ratios by adding 3 wt % NH_4Cl as a hardener at 100°C using a gel time meter (Davis Inotek Instrument, Charlotte, NC). The viscosity of UF resin adhesives at 25°C was measured using a cone-plate viscometer (DV-II+, Brookfield, USA) with no. 2 spindle at 60 rpm.

Sample preparation

Cured UF resin samples were prepared by placing liquid UF resin on a disposable aluminum dish and cured at 120°C for 1 hr in a convection drying oven. Different amounts (i.e., 0, 1, 3, and 10%) of NH_4Cl as hardener were added before curing the resin based on the nonvolatile resin solids. After curing, the cured UF resins were partially film shaped. These films were fractured to make new surfaces, which were exposed to energy-dispersive spectroscopy (EDS) and FE-SEM. But, the control UF resin without adding NH_4Cl was hardened at 120°C for 24 hr.

FE-SEM and EDS examination

FE-SEM (S-4300, Hitachi, Japan) coupled with an EDS (EMAX 6853-H, Horiba, UK) with a X-ray source (Kα1) was used to examine both morphology and chemical elements detection of the cured UF resins with different addition levels of ammonium chloride. The fractured surfaces of the cured UF resins obtained after the curing were coated with platinum, and then observed at different magnification levels using the FE-SEM, with an acceleration voltage of 15 kV. Diameter of spherical structures of the cured UF resins of the F/U mole ratio of 1.0 was determined by image analysis software using FE-SEM images. An average diameter of the sphere was presented by measuring at least 25 spheres per image. Quantities of chemical elements were determined using the EDS at 20 kV by measuring at least three surface areas (i.e., three replications), and an average value was presented. Total acquisition time was 60 sec per replication.

RESULTS AND DISCUSSION

Properties of UF resins prepared are summarized in Table I. As the F/U mole ratio decreased from 1.4 to 1.0, the nonvolatile solids content increased about 3%. The resin viscosity decreased as the F/U mole ratio decreased. This result could be due to the amount of the second urea added. In other words, a higher F/U mole ratio UF resin has much greater degree of the condensation, which gives a greater viscosity and low nonvolatile solids content. But, a low F/U mole ratio UF resin requires more amount of the second urea that could react with formaldehyde or methylolated ureas into smaller species in the resin. This produces a low viscosity. However, the amount of free formaldehyde was much greater for the high F/U mole ratio UF resin than that of the low F/U mole ratio. As expected, the gel time was much shorter for the high F/U mole ratio UF resin that that of the low F/U mole ratio. This result means that the reactivity of the higher F/U mole ratio UF resin is much greater than that of the counterpart. This result was in the agreement with the published work.[12]

Figure 1 shows FE-SEM micrographs of cured UF resins of both F/U mole ratios of 1.4 and 1.0 when no NH_4Cl was added. These resins were hardened under a similar condition to the curing condition of UF resins by adding NH_4Cl. As shown, the fracture surface of high F/U mole ratio UF resin was quite flat and smooth. In other words, the cured UF resins of the F/U mole ratio of 1.4 without the hardener
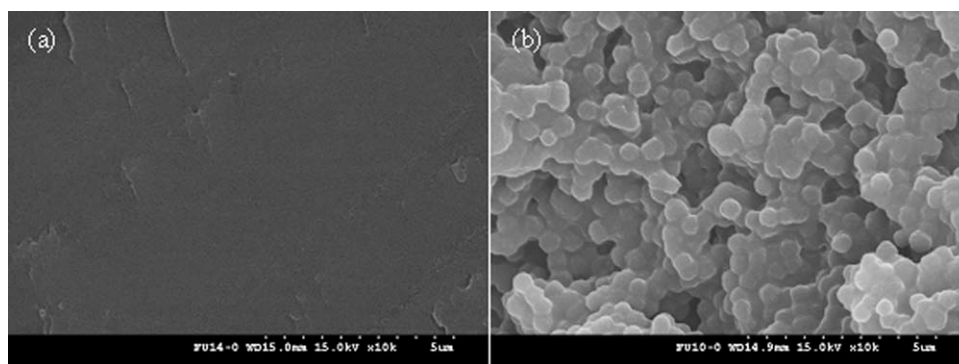
Figure 1 FE-SEM micrographs (×10,000) of cured UF resins of different F/U mole ratios at 0% NH_4Cl level. (a) 1.4 F/U mole ratio and (b) 1.0 F/U mole ratio.

did not show any particular morphology. This could be because UF resin was solidified by evaporation of water at elevated temperature without curing reaction. There were small holes that resulted from the evaporation of water during its hardening. But, the morphology of hardened UF resin of the F/U mole ratio of 1.0 was quite contrasting. In other words, low F/U mole ratio UF resin showed spherical structures on the fracture surface.

Using FE-SEM images of the cured UF resins of F/U mole ratio of 1.0, an image analysis was done to measure the diameter of the spherical structure as a function of the NH_4Cl level. The results are shown in Figure 2. As the NH_4Cl level increased, the diameter increased up to 3% NH_4Cl and then leveled off. This might be due to an increase in the cross-linking density in the cured resin as the NH_4Cl level increased. In other words, the more NH_4Cl was added, the more acidic condition in curing UF resin, which provided a greater cross-linking density. As reported by Johns and Dunker,[8] colloidal structure of UF resin with low F/U mole ratio was formed by the presence of double layer of formaldehyde. Thus,
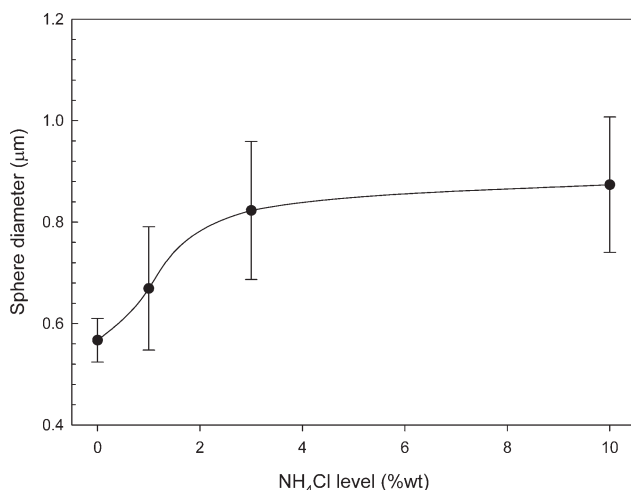
an increased amount of NH_4Cl in UF resin could disrupt the double layer of formaldehyde, which subsequently increased the diameter of the spherical structure of the UF resin. But, the level-off of the diameter from 3% to 10% NH_4Cl levels could be related to the amount of free formaldehyde in the UF resin. In other words, 10% NH_4Cl addition level did not influence the spherical structure because 1.0 F/U mole ratio UF resin contained much smaller amount of the free formaldehyde than that of the counterpart. Thus, low free formaldehyde did not disrupt the double layer although high NH_4Cl was added in the resin.

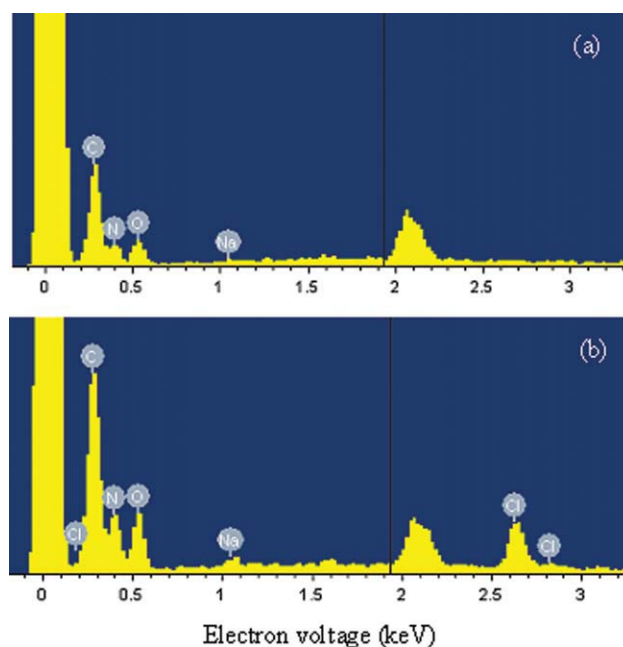Figure 3 shows a typical EDS result of cured UF resins of F/U mole ratio of 1.0 at different NH_4Cl

Figure 3 Types of chemical elements detected in the cured UF resins at different NH_4Cl levels. (a) 0% NH_4Cl and (b) 10% NH_4Cl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2 Sphere diameter of the cured UF resins of F/U mole ratio 1.0 at different NH_4Cl addition levels.
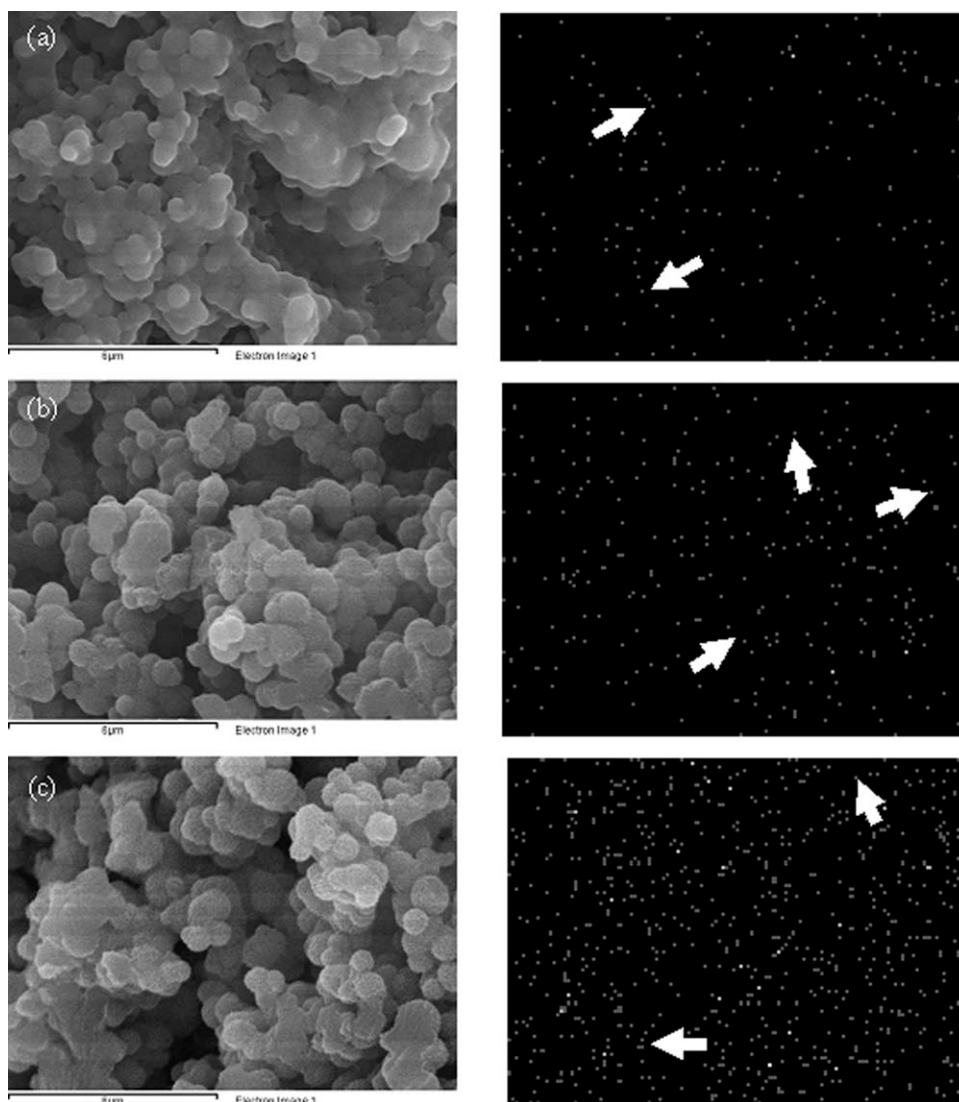
Figure 4 FE-SEM micrographs and corresponding Cl distributions of cured UF resins of the F/U mol ratio of 1.0 at different NH$_4$Cl levels. (a) 1% NH$_4$Cl, (b) 3% NH$_4$Cl, and (c) 10% NH$_4$Cl.

levels. As expected, four chemical elements such as carbon (C), nitrogen (N), oxygen (O), and sodium (Na) were detected for the resins hardened without adding NH$_4$Cl. The N element resulted from the urea, whereas both C and O elements were from either urea or formaldehyde, used as raw materials. The Na element resulted from sodium hydroxide (NaOH) that has been used for the pH control during UF resin synthesis. The C distribution was the most abundant among the four elements. This could be because both urea and formaldehyde used as two major raw materials had carbon in common, and cured UF resin also had hydroxymethyl groups (CH$_2$OH) and methylene linkages (-CH$_2$-). The N element was obviously from the amine groups of urea, whereas the O element was carbonyl groups of both urea and formaldehyde. Both N and O elements were less abundant than that of the C element. As expected, the Na element was the least abundant among the four elements.

The chloride (Cl) element was detected when the NH$_4$Cl was added. As expected, the peak intensity of Cl at 10% NH$_4$Cl was greater than those of either 1% or 3% NH$_4$Cl. Three peaks of Cl element observed at 0.25, 2.65, and 2.8 keV by the EDS resulted from the electron valence of K_a, K_b, and L, respectively. This could be ascribed to different X-ray radiation energy from different electron valences of the Cl.[27] The EDS was also used to map the chemical elements at the facture surface, i.e., element distribution. The peak at 2.1 keV was attributed to the presence of platinum, which had been used for coating the facture surface.

In general, UF resin is polymerized under acidic condition through a curing process. Usually, a hardener or catalyst is added into the UF resin to obtain
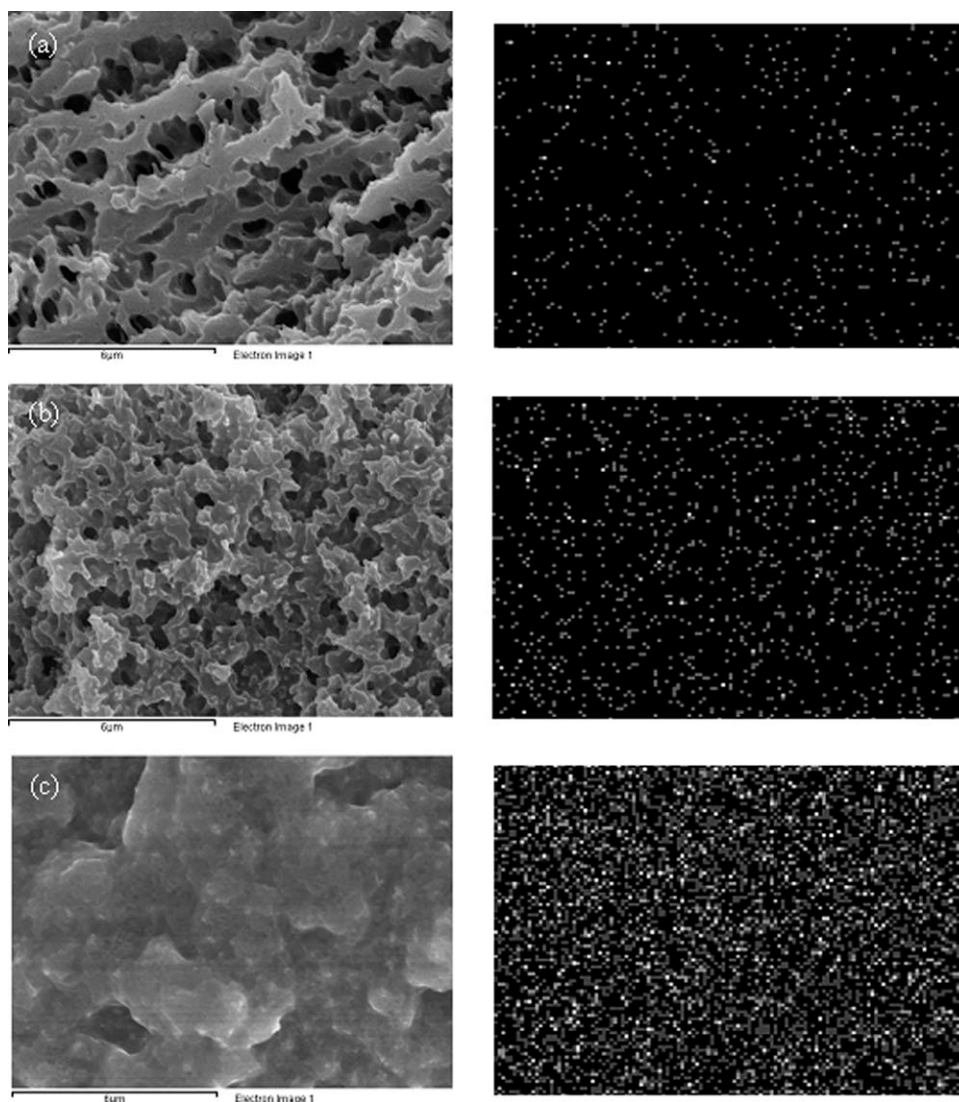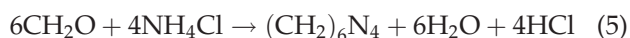
Figure 5 FE-SEM micrographs and corresponding Cl distributions of cured UF resin of the F/U mol ratio of 1.4. (a) 1% NH_4Cl, (b) 3% NH_4Cl, and (c) 10% NH_4Cl.

an acidic condition. For example, the NH_4Cl as a hardener reacts with free formaldehyde in UF resin to form hydrochloric acid in the cured state.[28] The reaction is given as eq. (5):

$$6CH_2O + 4NH_4Cl \rightarrow (CH_2)_6N_4 + 6H_2O + 4HCl \quad (5)$$

The produced acid remains as residual acid in the cured UF resin. The residual acid facilitates the hydrolytic degradation of UF resins, which is eventually responsible for the formaldehyde emission. In this study, the distribution of Cl element was assumed as residual acid in the cured UF resin although there were Cl elements from the unreacted NH_4Cl. We expected that the Cl distribution could provide useful information on the process of its hydrolytic degradation.

Figure 4 shows FE-SEM images and Cl distributions of cured UF resins of F/U mole ratios of 1.0.

All FE-SEM images of the UF resins showed spherical structures regardless of the NH_4Cl addition levels. These structures were quite similar to those hardened without adding NH_4Cl (Fig. 2). This result indicated that the spherical structure had been formed in the UF resin of F/U mole ratio of 1.0 after its synthesis. In fact, Johns and Dunker[8] reported a similar result and mentioned that these structures were due to colloidal particles in the UF resin of low F/U mole ratio. But, the influence of hardener on the spherical structure has not been reported yet.

The distribution of the Cl element was becoming denser as the NH_4Cl addition level increased (Fig. 4). An interesting point was the fact that the Cl element distribution clearly showed an arc shape. The frequency of arc shape increased at both 1% and 3% NH_4Cl levels, but it was infrequent at 10% NH_4Cl level (white arrows). These results indicated that the residual acid existed on the surface of the spherical

structure of cured UF resin of F/U mole ratio of 1.0. These results also suggest that the hydrolysis of cured UF resin could start at the surface of the spherical structures. In addition, these results also support the hypothesis of forming colloidal particles in UF resin proposed by Pratt et al.[25]

FE-SEM images and Cl distributions of the cured UF resins of F/U mole ratios of 1.4 at different NH$_4$Cl addition levels are shown in Figure 5. When the UF resin of F/U mole ratio of 1.4 was cured by adding 1% NH$_4$Cl, the cured UF resin showed irregular shape at the fracture surface [Fig. 5(a)]. As the NH$_4$Cl content increased, the irregular shape of UF resin showed a more compacted morphology with much smaller empty spaces between them [Fig. 5(b,c)].

In the cured UF resins of F/U mole ratios of 1.4, the formations of irregular empty spaces at low NH$_4$Cl level and compacted structure at high NH$_4$Cl level could be related to two different phenomena. In other words, the water molecules formed by the condensation need to make empty spaces to be evaporated, whereas the curing of UF resin molecules need to crosslink them, leading to a compacted structure. Thus, it was believed that the morphology of cured UF resin of F/U mole ratios of 1.4 resulted from the combination of water evaporation and curing process. Thus, large empty spaces formed at 1% NH$_4$Cl level could be due to water evaporation at a slow curing process. In other words, a slow curing process allows the water molecules to evaporate, leading to the formation of irregular morphology. However, a compacted structure at 10% NH$_4$Cl level could be because a faster curing process did not allow much time for the water molecules to evaporate from the UF resin.
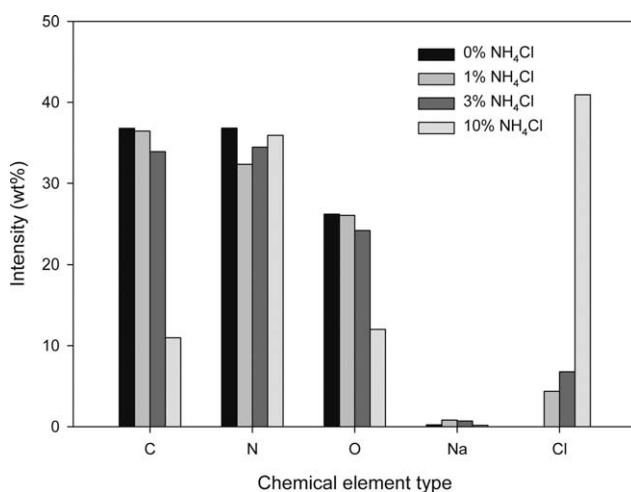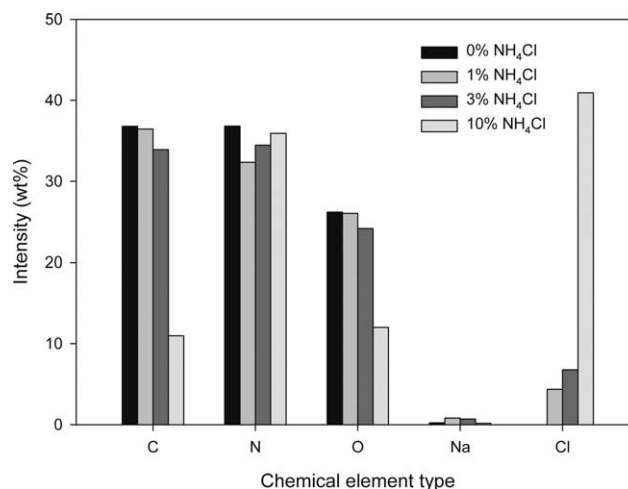

Figure 7 Quantitative results of chemical elements in cured UF resin of the F/U mole ratio of 1.0 on the basis of the number of their atoms.

The Cl element distribution in cured UF resin of F/U mole ratio of 1.4 is also shown in Figure 5. As expected, the abundance of Cl element was much greater than those UF resins of F/U mole of 1.0. These results could be due to greater amount of free formaldehyde in the resin, which produced much more hydrochloric acid. In general, higher F/U mole ratio resulted in a greater amount of free formaldehyde after UF resin synthesis.[8] Thus, the arc-shape distribution of Cl element was hardly observed for the cured UF resin of higher F/U mole ratio.

For comparison, we also quantified the amount of each chemical element for cured UF resins. The quantitative results of each element in the cured UF resins at different F/U mole ratios as well as NH$_4$Cl levels are presented in Figures 6 and 7. The quantity of each element based on their weights was given because the results based on the atom percent were quite similar. Regardless of the F/U mole ratio, the quantity of C decreased as the NH$_4$Cl level increased. This result could be due to the evaporation of formaldehyde in UF resins during the curing process. But, the N element showed an increased quantity with an increase in the NH$_4$Cl level as expected, although it slightly decreased at 1% NH$_4$Cl level. This could be due to the N element of the NH$_4$Cl added. The quantity of O element in the cured resin decreased with an increase in the NH$_4$Cl level. This result might be attributed to the condensation reaction of hydroxymehtyl groups into methylene linkages by splitting water as a by-product. In other words, the oxygen in the hydroxymehtyl groups disappeared during the curing of the resin, which reduced the quantity of oxygen in the cured UF resin. But, the quantity of chloride increased as the NH$_4$Cl level increased as expected. However, the amount of Na element was within 1%, which was

Figure 6 Quantitative results of chemical elements in cured UF resin of the F/U mole ratio of 1.4 on the basis of their weights.

the least amount among the elements detected in the cured UF resins.

CONCLUSIONS

This article reports the morphology and detection of chemical elements in cured UF resins of different F/U mole ratios and NH$_4$Cl addition levels as an effort of understanding the hydrolysis of UF resin adhesives for wood-based panel products. The cured UF resins of low F/U mole ratio showed spherical structure, whose diameter increased with an increase in the hardener level, whereas this was not the case for high F/U mole ratio UF resin regardless of the hardener levels. The EDS results showed the presence of four main chemical elements such as carbon, nitrogen, oxygen, and chloride, whereas sodium was sparsely detected within the range of quantification error. The distribution of Cl element as a proof of the residual acid suggested that the hydrolysis of cured UF resin of the low F/U mole ratio could initiate at the surface of the spherical structures. When the addition level of NH$_4$Cl increased, the quantities of both carbon and oxygen decreased, but those of nitrogen and chloride increased as expected.

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