Effects of Acid Hydrolysis on Microstructure of Cured Urea-Formaldehyde Resins Using Atomic Force Microscopy

Byung-Dae Park, Ho-Won Jeong

Department of Wood Science and Technology, Kyungpook National University, Daegu 702-701, Republic of Korea

ABSTRACT: This study investigated the effect of acid hydrolysis on the microstructure of cured urea-formaldehyde (UF) resins using atomic force microscopy (AFM) to better understand its hydrolytic degradation process which has been known to be responsible for the formaldehyde emission of wood-based composite panels. The AFM was scanned on both outer surface and facture surfaces of the thin films of cured UF resins that had been exposed to the etching of dilute hydrochloric acid to simulate their hydrolysis process. The AFM images showed two distinctive parts, which were classified as the hard and soft phases in cured UF resins. For the first time, this study reports the presence of thin filament-like crystalline structures on the fracture surface of cured UF resin. The soft phase of cured UF resins by ammonium chloride was much more easily hydrolyzed than those cured by ammonium sulfate, indicating that hardener types had a great impact on the hydrolytic degradation behavior of cured UF resins. The surface roughness measurement results also supported this result. The results of this study suggested that the soft phase was much more susceptible to the hydrolysis of cured UF resin than the hard phase. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 3255–3262, 2011

Key words: adhesives; atomic force microscopy; microstructure; thermosets; resins
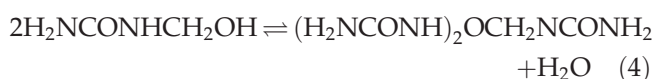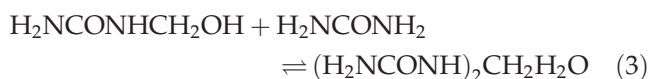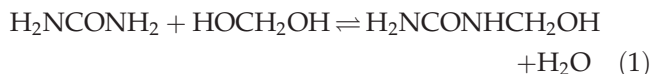
INTRODUCTION

One of the most important formaldehyde-based wood adhesives is urea-formaldehyde (UF) resins. Examples of formaldehyde-based resins such as melamine-urea-formaldehyde (MUF) resin, melamine-formaldehyde (MF) resin, or phenol-formaldehyde (PF) resin. As a polymeric condensation product formed by chemical reactions between formaldehyde and urea, UF resin adhesive is most widely used for the manufacturing of wood-based composite panel such as plywood, particleboard, or medium density fiberboard. Therefore, the wood panel industry is a major consumer of UF resin adhesive.

UF resin possesses some advantages such as a fast curing time, good performance in the panel, water solubility, and a lower price. However, a critical disadvantage of the UF resin is the formaldehyde emission from wood-based composite panels bonded with UF resin. As well, the lower resistance to water of UF resin limits to interior applications. Furthermore, formaldehyde emissions from the panels used for interior applications are known as one of the main causes, resulting in sick building syndrome in an indoor environment. Therefore, many authors have concentrated on the formaldehyde emission issue of UF resin.[1–8]

One of the causes of the formaldehyde emission from wood-based panels is free formaldehyde present in UF resin after its synthesis. For example, Park et al.[9] reported that the amount of free formaldehyde present in UF resin proportionately contributed to the emitted formaldehyde from particleboard even after hot-pressing at high temperature. The other important cause for the emission is the hydrolysis of UF resin under acidic and moisture conditions.[1] The hydrolysis of UF resins is reversible reactions of the synthesis reactions for UF resins. Typical synthesis reactions of UF resins are given as:

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

$$H_2NCONHCH_2OH + HOCH_2OH$$
$$\rightleftharpoons HOCH_2NCONHCH_2OH + H_2O \quad (2)$$

$$H_2NCONHCH_2OH + H_2NCONH_2$$
$$\rightleftharpoons (H_2NCONH)_2CH_2H_2O \quad (3)$$

$$2H_2NCONHCH_2OH \rightleftharpoons (H_2NCONH)_2OCH_2NCONH_2$$
$$+ H_2O \quad (4)$$

In UF resin synthesis, formaldehyde is added to urea to create monomethylol urea (Scheme 1). The monomethylol urea is further reacted to produce dimethylol urea (Scheme 2). The methylolated ureas then reacted with formaldehyde to form methylene-diurea (Scheme 3). In excess of formaldehyde, the monomethylol urea further reacted to form dimethylene ether link (Scheme 4). All these reactions produce water as a by-product of the condensation. In hydrolysis reaction, the chemical species go through reversible reactions when they are exposed to water.[10] Thus, these reversible reactions degrade the chemical species into a simpler species as shown in Schemes 1–4. In particular, the hydrolysis of cured UF resins in the composite seems inevitable because wood substance is hygroscopic material when UF resins are being used as a binder for wood-based composites.

In general, the hydrolysis of cured UF resin is believed to mainly contribute to the long-term formaldehyde emission of UF resin-bonded wood panels.[11–15] In efforts to gain better understanding, much attention has been paid to investigate the hydrolysis of UF resins to comprehend the mechanisms of the formaldehyde release from cured UF resin and UF resin-bonded wood panels.[16–20] The susceptibility of the hydrolytic degradation of cured UF resin depended on its chemical structure and the degree of crosslinking and could be accelerated by high temperature and strong acidic conditions.[18] For example, the infrared spectra study showed a major reduction of the content of methylol groups (CH_2OH) and an increase of the tertiary amide as the rate of hydrolysis increased upon the extent of cure, pH, and temperature.[14] A solid-state ^{13}C-NMR spectroscopic study on the hydrolytic stability of UF resins also reported that the dimethylene ether linkages, methylol groups attached to tertiary amides and poly(oxymethylene glycol) were the main formaldehyde emitters.[11]

Even though many studies concentrated on the hydrolysis of UF resins, there is limited research on the effects of hydrolysis on the microstructure of cured UF resins. To the authors' knowledge, no attempt has been made to investigate the influence of hydrolytic degradation process on the microstructure of cured UF resins using atomic force microscopy (AFM). Therefore, this study attempted to observe hydrolytic degradation effects on the microstructure of cured UF resin's using the AFM technique in efforts to understand the hydrolysis process of cured UF resins in terms of the formaldehyde emission.

EXPERIMENTAL

Materials

Both the urea and formalin (37%) used for the synthesis of UF resins were technical grade. Aqueous solutions of both formic acid (20 wt %) and sodium hydroxide (20 wt %) were used to adjust the pH level during the UF resin synthesis process. As hardener, aqueous solutions (20 wt %) of ammonium chloride (NH_4Cl) and ammonium sulfate (($NH_4)_2SO_4$) were used.

Methods

Preparation of UF resin and its properties

All UF resins used for this study were prepared in a laboratory, following the previous alkaline-acid two-step reaction.[9] The formalin was placed in the reactor and then adjusted to pH 7.8 with aqueous NaOH and then heated to 45°C. Subsequently, the first urea was added into the reactor in 1-min intervals to get the initial F/U mole ratio of 2.0. Then the mixture was heated to 90°C under reflux for 1 h to allow for methylolation reactions. The second stage of UF resin synthesis consisted of the condensation of the methylolureas under acidic condition. The acidic condition was obtained by adding formic acid (20%wt) to reach a pH of about 4.6, and the condensation reactions were carried out until a target viscosity of JK was reached. This was measured using a bubble viscometer (VG-9100, Gardner-Holdt Bubble Viscometer, USA). The final F/U mole ratio of 1.2 for the UF resin was adjusted by adding a certain amount of the second urea. Then, the UF resin was cooled to room temperature, later followed by adjusting the pH to 8.0.

The nonvolatile solids content was determined by measuring 1 g of UF resin in a disposable aluminum dish before and after drying in a convective oven at 105°C for 3 h. The nonvolatile solids content of the prepared UF resin was 54.9%. The viscosity of the UF resin was 250.7 mPa s when measured at 25°C by a cone-plate viscometer (DV-II +, Brookfield) with a No. 2 spindle at 60 rpm. The gel time of the UF resin prepared was 168 s when it was measured at 100°C by a gel time meter (Davis Inotek Instrument, Charlotte, NC) by adding 3% ammonium chloride.

Sample preparation and AFM observation

To observe the surfaces of the cured UF resins, first 0.1% hardener was thoroughly mixed with the liquid synthesized UF resin. And then films of the UF resin were prepared by casting the mixed liquid UF resin between two glass slides with a gap of 2 mm. Figure 1 shows a set-up rig used for the preparation of the cured UF resin films. After then, the liquid UF resin was cured at 60°C for 24 h in a drying oven, and then the rig was disassembled to remove the film specimens. To simulate the hydrolysis process, the
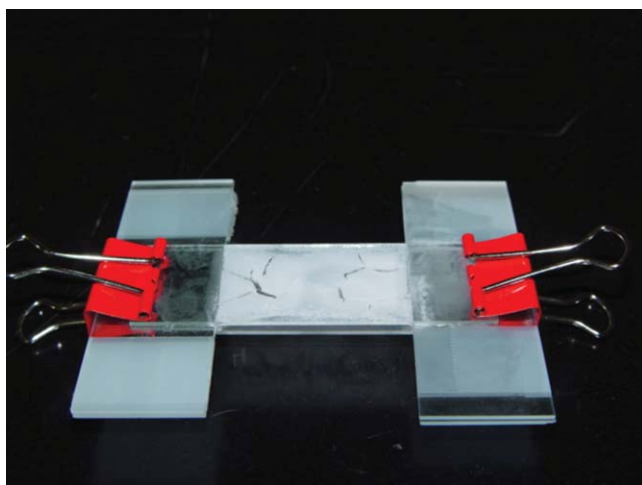
Figure 1 A set-up rig for the film preparation of cured UF resin using glass slides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

prepared film was etched by dipping the sample into $0.1N$ HCl solution for different durations of time. Next, the outer surface of the etched samples was scanned in the contact mode of an AFM (NanoScope IIIa, DI Instruments, Santa Barbara, CA). The tapping mode with a scan area of 125 μm × 125 μm was only used for the hardened UF resin without adding NH_4Cl. Fracture surfaces of the films were also prepared by immersing the films under liquid nitrogen. As well, the outer and fracture surfaces of the etched samples were also observed with the AFM.

Both the film outer and fracture surfaces were observed with an AFM in the contact mode with a scan rate of 0.220 Hz and a tip velocity of 35.2 μm/s

using a silicon nitride tip (OTR8-35, Veeco, USA). The scan area was 100 μm ×100 μm. Image analysis software (iSolution Ver. 8.3, Image and Microscope Technology Inc., NY) was used to measure the area percentage of the hard and soft phases. Duplicate measurements were made to obtain an average surface roughness using the AFM. Scanning of the surfaces provided two parameters of the surface roughness, i.e., arithmetic average surface roughness (R_a) and root mean squared surface roughness (R_q) expressed below:

$$R_a = \frac{1}{n}\sum\nolimits_{i=1}^{n}|y_i| \tag{5}$$

$$R_q = \sqrt{\frac{1}{n}\sum\nolimits_{i=1}^{n}(y_i^2)} \tag{6}$$

where n is the number of measurement and y is surface roughness value.

RESULTS AND DISCUSSION

Outer surface of cured UF resin

Prior to looking the outer surface of the cured UF resin films, comparison was made between the AFM image of the hardened UF resin film without adding NH_4Cl and that of the cured UF resin films by adding NH_4Cl as shown in Figure 2. The AFM image of the hardened UF resin films without adding NH_4Cl shows very rough surfaces with two distinctive regions, i.e., bright and dark areas [Fig. 2(a)]. This rough surface could be the result of the spherical structures of the UF resins that have been reported for the low formaldehyde/urea mole ratio of 1.2.[21]
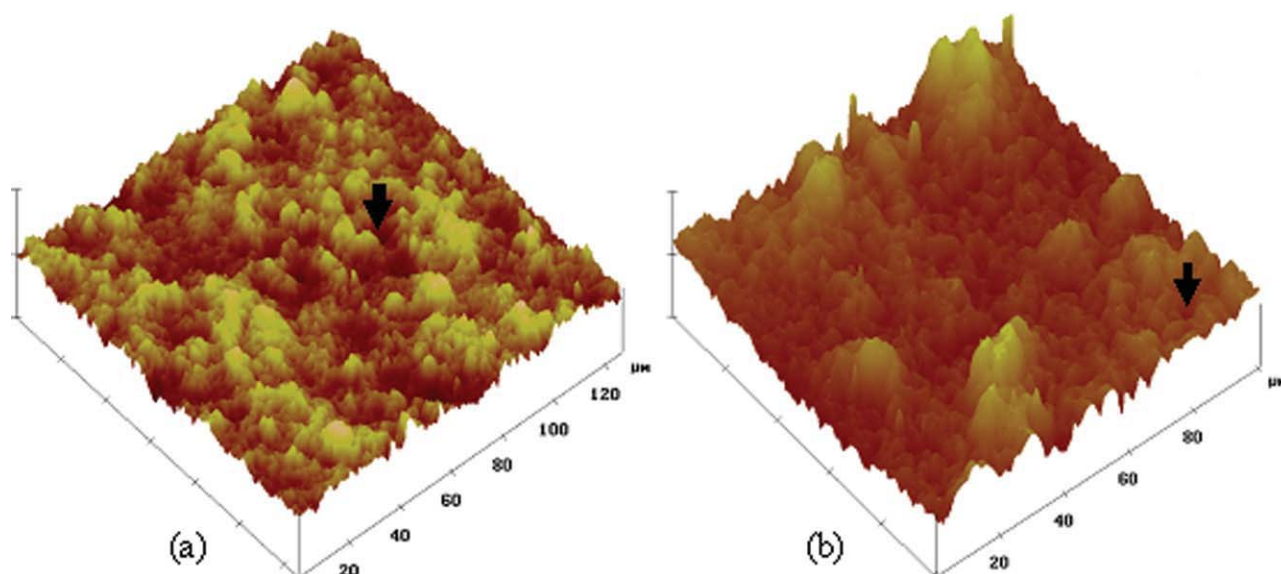

Figure 2 Outer surface AFM images of the cured UF resin film. (a) 0% NH_4Cl and (b) 0.1% NH_4Cl. [Color figure can be
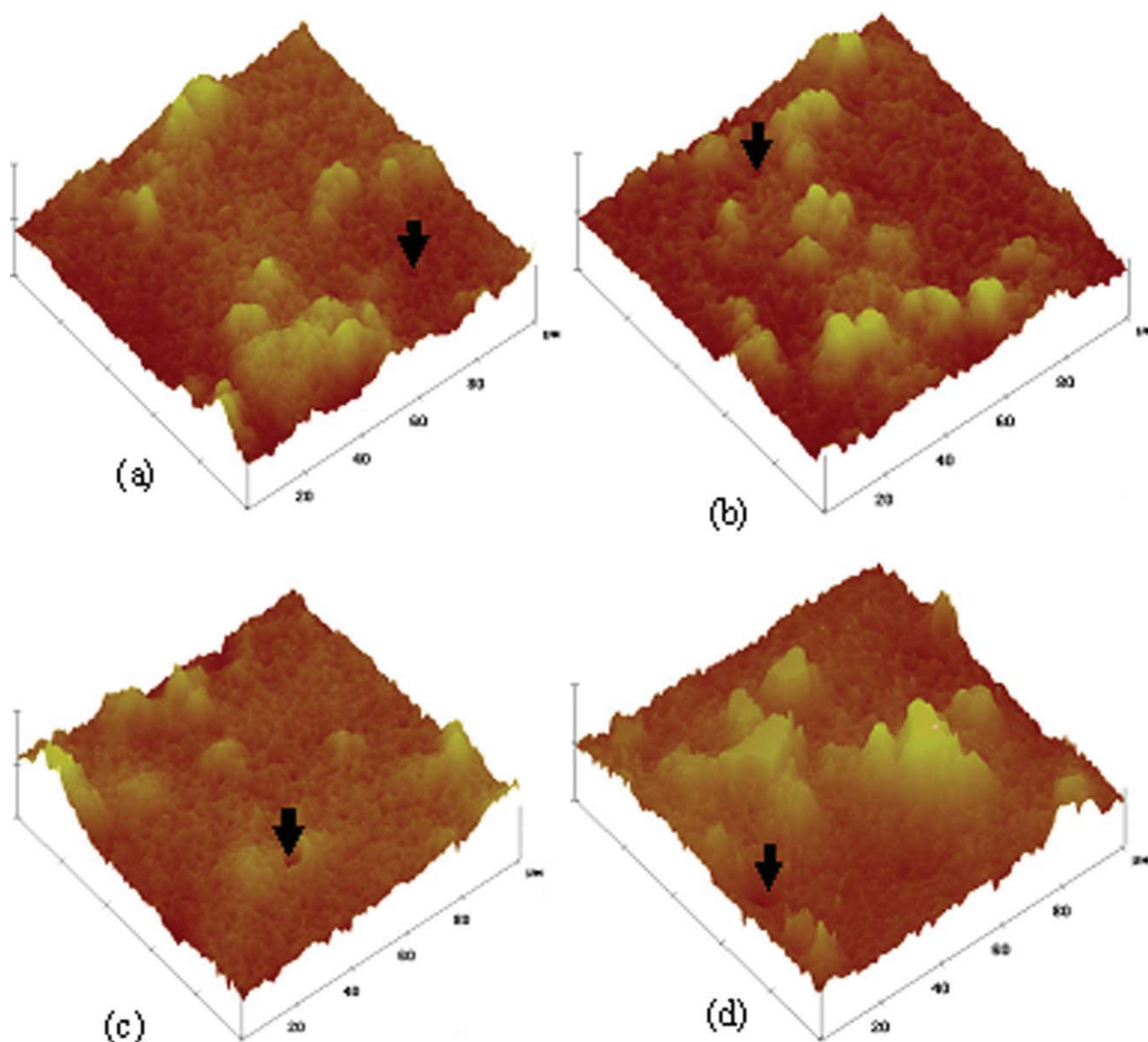
Figure 3 Outer surface AFM images of the cured UF resin film as a function of etching time. (a) 10 s, (b) 20 s, and (c) 40 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

In other words, lower F/U mole ratio UF resin has colloid particles, which are coalesced into clusters in the aging process. These clusters were known to form spherical structures in UF resin.[22] In the imaging by the AFM, higher forces tend to enhance the phase contrast, which is a function of the elastic and viscoelastic properties of the sample.[23] In other words, harder, less viscoelastic phases will be brighter than softer, more viscoelastic phases. Thus, the bright and dark areas were classified as the hard phase and soft phase, respectively. In addition, there were pores (black arrows) at the outer surface of the UF resin (Fig. 2). These pores could be the result of the evaporation of water of formaldehyde during its curing process.

When the UF resin was cured by adding 0.1% NH_4Cl based on the resin solids, the outer surface became much rougher than that of its counterpart. In fact, the R_a increased from 303.6 to 433.9 nm and the R_q increased from 389.5 to 574.2 nm when the NH_4Cl was added. The greater surface roughness of the cured UF resin films could be due to the formation of crosslinks during it curing process.

To simulate the hydrolysis process in cured UF resin responsible for formaldehyde emission, the prepared UF resin films were etched by dilute hydrochloric acid in different times, ranging from 0 to 40 s. Typical AFM images obtained by the scans on the outer surface were shown in Figure 3. As expected, the hard and soft phases appeared for all AFM images, which were analyzed by software to obtain the hard phase area percentage.

Figure 4 shows the measurement results of the hard phase areas on the outer surfaces of the cured
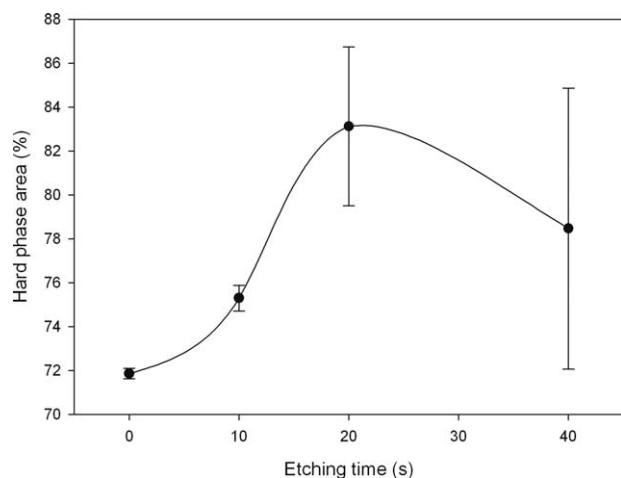
Figure 4 Hard phase area of the cured UF resin film as a function of etching time. (a) 0 s, (b) 10 s, (c) 20 s, and (d) 40 s.

UF resin films. Average values with standard deviation for each etching time were presented. As the etching time increased, the hard phase area increased up to 20 s, and then decreased with an etching time of 40 s. These results indicate that the hard phase area increases with an increase in the etching time because the soft phase area decreases due to hydrolytic degradation of the cured UF resin by the acid etching. However, the decreased hard phase area with an etching time of 40 s could also be due to the hydrolysis of both the hard and soft phases at the same time. In other words, the hydrolysis of cured UF resin starts at the soft phase first and then moves on to the hard phase. However, it is believed that longer etching times result in the simultaneous removal of both the soft and hard phases. It is interesting to note that the standard deviation of the measurements increase with an increase in the etching time. This suggests that the outer surface of the cured UF resin films become rougher as each etching time is extended because the hydrolysis exposes a new hard phase area during the etching process.

So, the surface roughness values of the samples are presented in Figure 5. As the etching time increased, the surface roughness expressed by R_a and R_q slightly decreased at an etching time of 10 s, and then increased at 20 s of etching followed by a level-off. After 10 s of etching, the surface roughness had not much changed even though the hard phase area increased. However, the surface roughness increased with 20 s, which was consistent with the measurements of the hard phase area as shown in Figure 4. These results also suggest that the hydrolysis simulated by acid etching removes the soft phase first and then hard phase.

Facture surface of cured UF resins with different hardener types

To compare the outer surface's microstructure, the AFM was also applied to the fracture surface of cured UF resin by adding 0.1% NH_4Cl. The AFM image is shown in Figure 6, (a). As expected, the AFM image also showed the hard and soft phases. The AFM scans also found a pore [black arrow in Fig. 6(a)], which was believed to be formed by the evaporation of water during its curing process. An interesting point is that the hard phase, i.e., brighter region, shows filament-like sharp structures (white arrows) with various dimensions [Fig. 6(a)]. These brighter structures in the AFM images mean a lot of hard and less viscoelastic regions. Thus, these are believed to be crystalline structures in the cured UF resins.

For the first time, this article reports the three dimensional shapes of the filament-like thin structures on the fracture surface of the cured UF resins. Although the reason is not clear, the formation of these structures could be due to the presence of colloids of the UF resins with low F/U mole ratios. In other words, it was reported that filament-like colloidal aggregates were initially formed in UF resin, and then eventually changed to superclusters by the coalescence in later during the ageing process.[21,22] And the presence of crystalline structures in UF resin has been reported by several authors.[24–27]

In particular, UF resins with lower F/U mole ratio of 1.2 are supposed to have colloidal structures, which constitute crystalline structure.[22,27] Dunker et al.[28] also reported that UF resin contained colloidal regions of semicrystalline nature, and ascribed the origin of the crystal structure to a high degree of order due to hydrogen bonding. They also mentioned the possibility that the crystalline regions
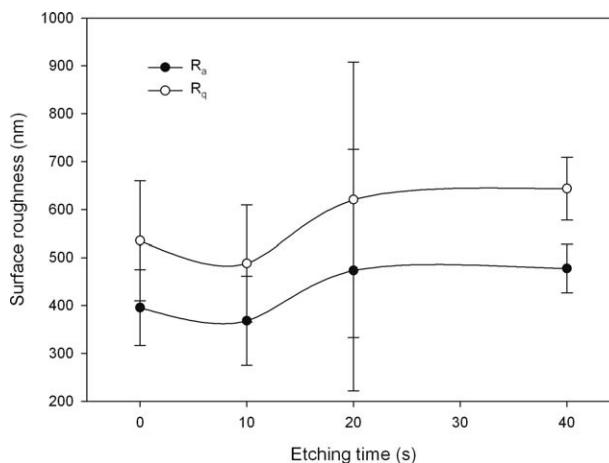
Figure 5 Outer surface roughness of the cured UF resin film as a function of etching time. (a) 0 s, (b) 10 s, (c) 20 s, and (d) 40 s.
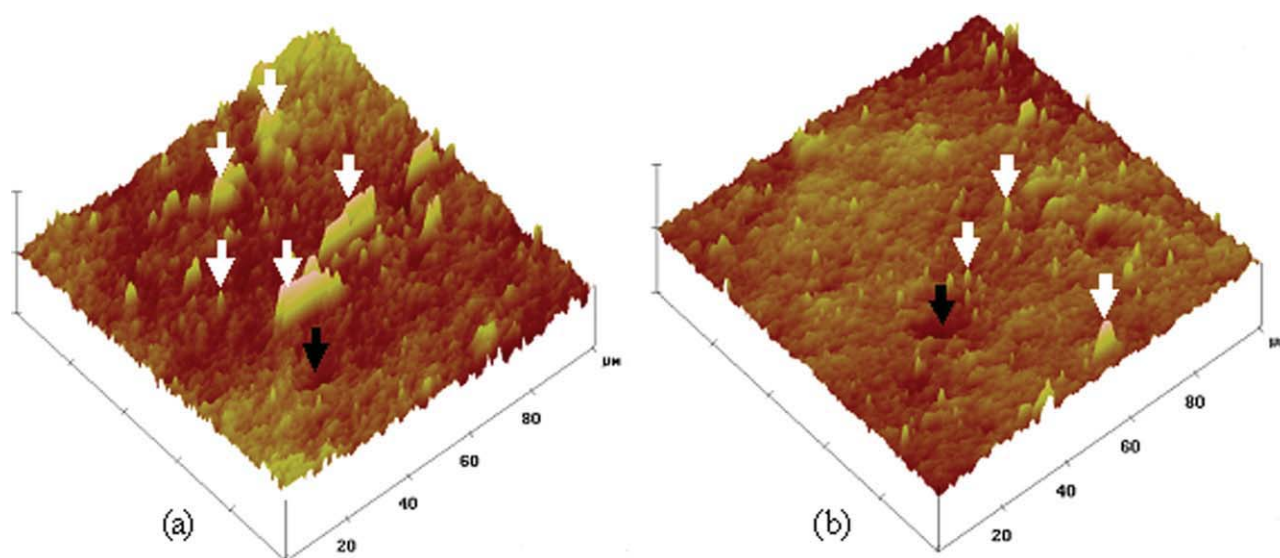
Figure 6 Fracture surface AFM images of the cured UF resin film by adding ammonium chloride as a function of etching time. (a) 0 s, and (b) 10 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

could have arisen from the crystallization of some minority components of UF resin, like urons or other ring structures. A physical association in the UF resin solution was related to the crystalline region in solid form.[25]

However, it is not certain what process is playing a role in the formation of these filament-like thin structures. Further research is required to find more conclusive evidence on how the filament-like thin structures are formed by the colloidal particles in the UF resins.

The facture surface was etched by dilute hydrochloric acid for 10 s, and then the AFM image obtained was presented in Figure 6(b). As expected,

both the hard and soft phases were observed, and the filament-like thin structures of the hard phase was also detected. In general, the fracture surface became much smoother after the acid etching for 10 s than before the etching. Also, the size of the hard phase's thin structure decreased after the acid etching. Although the size of the filament-like thin structure decreased, the occurrence frequency of the structure increased greatly. This phenomenon could be ascribed to the hydrolysis process in that the acid removed either the hard phase, showing the remaining crystalline structures with a decreased size; or the soft phase, emerging new the crystalline structures at the fracture surface. Regardless of the
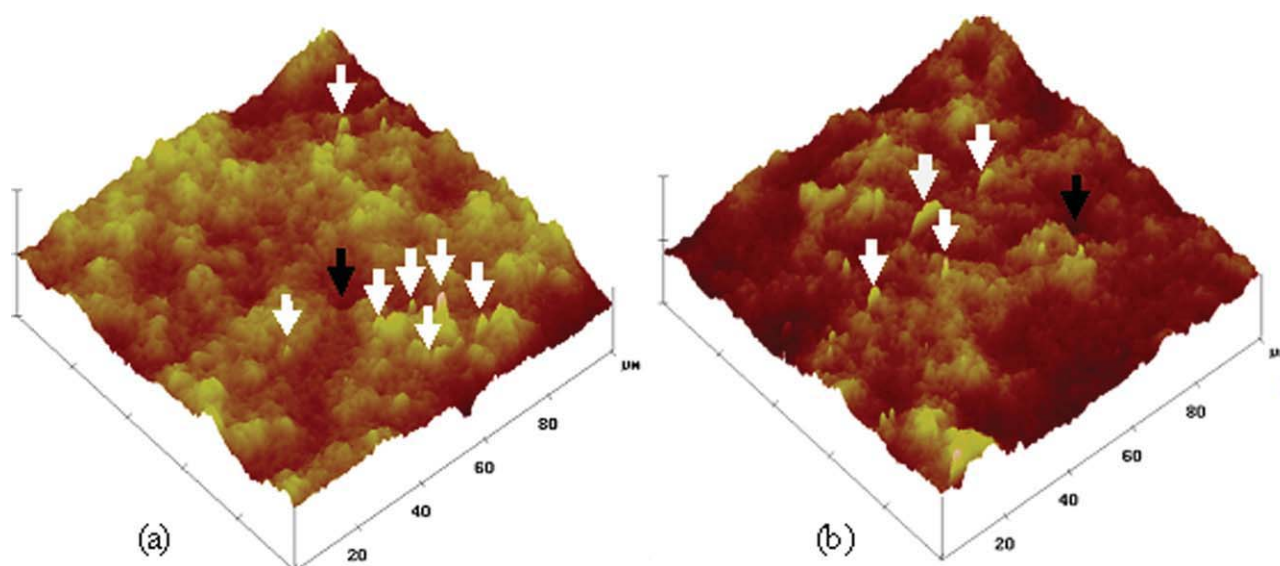

Figure 7 Fracture surface AFM images of the cured UF resins by adding ammonium sulfate as a function of etching time. (a) 0 s and (b) 10 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]
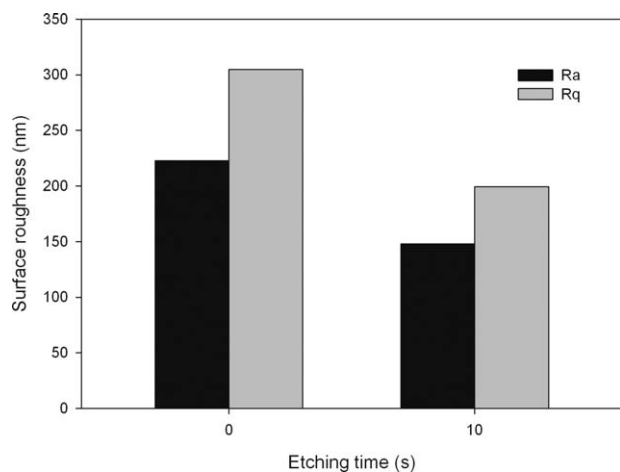
Figure 8 Fracture surface roughness of the cured UF resin film by adding ammonium chloride as a function of etching time.

Figure 10 Hard phase area of the cured UF resins by adding ammonium chloride and ammonium sulfate as a function of etching time.

degradation behavior, these results clearly indicate that the hydrolysis of UF resin caused by etching degrades the hard and soft phases.

To compare the microstructure of cured UF resins depending on the type of hardener, AFM images of cured UF resins by adding ammonium sulfate were presented in Figure 7. As expected, the pore for water evaporation (black arrow) was also observed for both the control and etched samples. When the UF resin was cured by adding ammonium sulfate, the topography of the facture surface was quite different from that of the cured UF resin by adding ammonium chloride [Fig. 7(a)]. In other words, a limited number of the crystalline structures (white arrows) occurred even though the coverage of the brighter hard phase was apparently much larger. The acid etching of the cured UF resin by ammonium sulfate exposed a greater number of the crystalline structures on the facture surface. This result indicates that
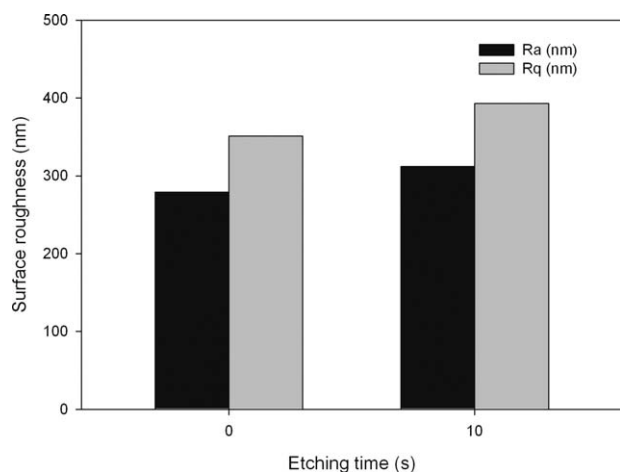

Figure 9 Fracture surface roughness of the cured UF resin film by adding ammonium sulfate as a function of etching time.
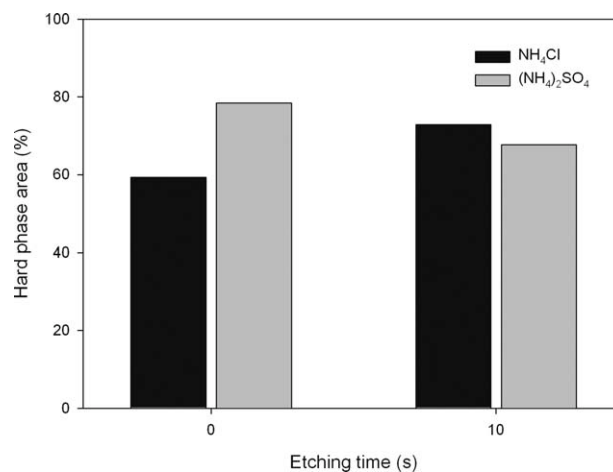
the molecular structure of UF resins cured by ammonium sulfate is much more resistant to hydrolysis than those cured by ammonium chloride. This result is quite compatible with the measurement of the hydrolytic stability of cured UF resins.[21] The authors reported that cured UF resins by ammonium sulfate chloride had greater hydrolytic stability than cured UF resins by ammonium chloride.

Fracture surface roughness and hard phase area of cured UF resin with different hardener types

The AFM scans of the fracture surface of the cured UF resins also provided two different surface roughness results (i.e., R_a and R_q) as shown in Figures 8 and 9. The surface roughness values of the cured UF resins by ammonium chloride after the etching decreased as presented in Figure 8. As discussed in the previous section, this result could be due to the hydrolysis of the cured UF resin by ammonium chloride. In other words, the surface roughness decreases because the hydrolysis due to etching simultaneously degrades the hard phase area with crystalline structure and the soft phase area as shown in Figure 6. However, the surface roughness increased after the etching for the cured UF resin by ammonium sulfate as presented in Figure 9. In fact, the R_a value increased from 279.2 to 312.3 nm and the R_q value increased from 350.8 to 393.2 nm. These results suggest that the hydrolysis of UF resins cured by ammonium sulfate dominantly degrades the soft phase area and exposes a greater number of crystalline structures on the fracture surface as discussed in Figure 7. A greater susceptibility to the hydrolytic degradation of UF resins cured by ammonium chloride than those by ammonium sulfate also supports the observed hydrolysis behavior by the AFM, depending on the hardener types.[27]

In addition, the hard phase area percentage obtained by image analysis of the AFM images before and after the etching is presented in Figure 10. The percentage of the hard phase area increased from 59.3 to 72.8% after the etching of the fracture surface of UF resins cured by adding ammonium chloride. As mentioned in the previous paragraphs, an increase in the hard phase area after the etching could be the result of a greater susceptibility to the hydrolysis of ammonium chloride cured UF resins. In other words, the soft phase of cured UF resins by ammonium chloride was easily hydrolyzed, which resulted in a greater area of the hard phase being exposed after the etching. However, the hard phase area slightly decreased after the etching when the UF resin was cured by adding ammonium sulfate. This could be due to a greater resistance to hydrolysis of the cured UF resins by ammonium sulfate. The soft phase was slightly degraded by the hydrolysis caused by the etching, which reduced the hard phase area after the etching.

CONCLUSIONS

This article reports the effect of acid hydrolysis on microstructures of cured UF resins with the aid of AFM to better understand the hydrolysis process that has been known to be responsible for the formaldehyde emission in wood-based composite panels. The AFM scanned either on the outer surface or facture surfaces of the thin films of cured UF resins that had been exposed to the etching of dilute hydrochloric acid to simulate their hydrolysis process. The following conclusions were obtained from this study:

1. The AFM images showed two distinctive areas, which were classified as the hard and soft phases in cured UF resin. For the first time, this study reports the presence of filament-like sharp crystalline structures on the fracture surface of cured UF resin, which was more resistant to the hydrolytic degradation than the soft phase after the acid etching.
2. The hydrolytic degradation behavior of the two phases was highly dependent on the types of hardeners used. The soft phase of the UF resins cured by ammonium chloride was much more easily hydrolyzed than those cured by ammonium sulfate. The hard phase area percentage also depended on the types of hardeners. Surface roughness measurements also supported these results.

3. The results of this study suggested that the soft phase of cured UF resins was much susceptible to the hydrolysis and depended on hardener type, which was compatible with the measurements of the surface roughness and hard phase area.

References

1. Myers, G. E. For Prod J 1983, 33, 27.
2. Myers GE. In Formaldehyde Release from Wood Products;-Meyer, B.; Andrews, B. A. K.; Reinhardt, R. M., Eds.; American Chemical Society, 1986; p 87.
3. Marutzky, R. In Wood Adhesives: Chemistry and Technology; Pizzi, A., Ed.; Marcel Dekker Inc., 1986; Vol.2., p 307.
4. Park, B. D.; Lee, S. M.; Roh, J. K. Eur J Wood Prod 2009, 67, 121.
5. Pizzi, A.; Lipschitz, L.; Valenzuela, J. Holzforschung 1994, 48, 254.
6. Hse, C. Y.; Xia, Z. Y.; Tomita, B. Holzforschung 1994, 48, 527.
7. Gu, J. Y.; Higuchi, M.; Morita, M.; Hse, C. Y. Mokkuzai Gakkaishi 1996, 42, 149.
8. Myers, G. E. For Prod J 1984, 34, 35.
9. Park, B. D.; Kang, E. C.; Park, J. Y. J Appl Polym Sci 2006, 101, 1787.
10. Myers, G. E. In Proceedings of Wood Adhesives in 1985: Status and Needs; Christiansens, A. W.; Gillespie, R.; Myers, G. E.; River, B. H., Eds.; Forest Products Research Society, 1986; p 119.
11. Chuang, I. S.; Maciel, G. E. J Appl Polym Sci 1993, 52, 1637.
12. Tohmura, S.; Hse, C. Y.; Higuchi, M. J Wood Sci 2000, 46, 303.
13. Ringena, O.; Janzon, R.; Pfizenmayer, G.; Schulte, M.; Lehnen, R. Holz als Roh-und Werkstoff 2006, 64, 321.
14. Myers, G. E. Wood Sci 1982, 15, 127.
15. Kavvouras, P. K.; Knoditsiotis, D.; Petinarakis, J. Holzforchung 1998, 52, 105.
16. Nessuer, H.; Schall, W. Holzforschung Holzverwert 1970, 22, 116.
17. Myers, G. E.; Koutsky, K. A. Holzforschung 1990, 44, 117.
18. Elbert, A. A. Holzforschung 1995, 49, 358.
19. Robitschek, R.; Christensen, R. L. For Prod J 1976, 26, 43.
20. Park, B. D.; Jeong, H. W. International Conference on Wood Adhesives, Harveys Resort Hotel & Casino, Lake Tahoe, Nevada, USA, September 28-30, 2009.
21. Stuligross, J.; Kousky, J. A. J Adhes 1985, 18, 281.
22. Johns, W. E.; Dunker, A. K. In Formaldehyde Release from Wood Products;Meyer, B.; Andrews, B. A. K.;Reinhardt, R. M., Eds.; The American Chem Society, 1986; p 76.
23. Vanlandingham, M. R.; Eduljee, R. F.; Gillespie, J. W., Jr. J Appl Polym Sci 1999, 71, 699.
24. Despres, A.; Pizzi, A. J Appl Polym Sci 2006, 100, 1406.
25. Pratt, T. J.; Johns, W. E.; Rammon, R. M.; Plagemann, W. L. J Adhes 1985, 17, 275.
26. Motter, W. K. Ph.D. Thesis, Department of Mechanical and Materials Engineering, Washington State University, Pullman, WA, USA, 1990.
27. Levendis, D.; Pizzi, A.; Ferg, E. Holzforschung 1992, 46, 263.
28. Dunker, A. K.; Johns, W. E.; Rammon, R.; Framer, B.; Johns, S. J Adhes 1986, 19, 153.