

^{13}C -NMR Spectroscopy of Urea-Formaldehyde Resin Adhesives with Different Formaldehyde/Urea Mole Ratios^{*1}

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ABSTRACT

As a part of abating formaldehyde emission of urea-formaldehyde (UF) resin adhesive, this study was conducted to investigate chemical structures of UF resin adhesives with different formaldehyde/urea (F/U) mole ratios, using carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectroscopy. UF resin adhesives were synthesized at four different F/U mole ratios such as 1.6, 1.4, 1.2, and 1.0 for the analysis. The analysis of ^{13}C -NMR spectroscopy showed that UF resin adhesives with higher F/U mole ratios (i.e., 1.6 and 1.4) had two distinctive peaks, indicating the presence of dimethylene ether linkages and methylene glycols, a dissolved form of free formaldehyde. But, these peaks were not detected at the UF resins with lower F/U mole ratios (i.e., 1.2 and 1.0). These chemical structures present at the UF resins with higher F/U mole ratios indicated that UF resin adhesive with higher F/U mole ratio had a greater contribution to the formaldehyde emission than that of lower F/U mole ratio. Uronic species were detected for all UF resins regardless of F/U mole ratios.

Keywords : ^{13}C -NMR spectroscopy, urea-formaldehyde resin adhesive, mole ratio

1. INTRODUCTION

Urea-formaldehyde (UF) resin is a polymeric condensation product of the chemical reaction of formaldehyde with urea, and it is regarded as one of the most important types of adhesives in the wood-based panel industry. Among the formaldehyde-based resin adhesives, UF resin adhesives have been extensively used in the

manufacture of particleboard (PB) or medium density fiberboard (MDF). So, UF resin adhesives are mainly consumed by the wood panel industry. In fact, the production of formaldehyde-based resin in 2005 was about 207,000 tons, which is 39% of the total production of adhesives in Republic of Korea. The production of UF resin adhesives was about 75% (i.e. about 155,000 tons) of the total pro-

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duction of formaldehyde-based resin adhesives. Compared to other wood adhesives, such as phenol-formaldehyde (PF) resins and diphenylmethane diisocyanate (MDI), UF resin adhesive possesses some advantages such as fast curing, good performance in wood panels, water solubility and lower price. The disadvantages of using the UF resin include formaldehyde emission (FE) from wood panels and a lower resistance to water. Lower resistance to water limits the use of wood-based panels bonded with UF resin to interior applications.

Free formaldehyde that is present in UF resin and hydrolytic degradation of UF resin under moisture and acidic conditions has been known to be responsible for the FE from wood-based panels (Dunky, 1983). In other words, the un-reacted formaldehyde in UF resin after its synthesis could be emitted from wood panels even after hot-pressing at high temperature. In addition, the reversibility of the aminomethylene link and its susceptibility to hydrolysis also explains the lower resistance against the influence of water and moisture, and subsequently the FE from wood-based panels (Seller Jr., 1999). Therefore, the FE issue has been one of the most important aspects of UF resin in the last few decades (Myer, 1983; Myer, 1984; Myers, 1986; Myers and Koutsky, 1987; Myers and Koutsky, 1990; Pizzi *et al.*, 1994).

Much attention has been paid to reduce or control FE from UF resin-bonded panels through resin technologies. In general, UF resins are synthesized by two-step reaction procedures (i.e., methylation under alkaline condition and condensation under acidic condition using a large amount of formaldehyde) (Dunky, 1983). This synthesis method has been widely employed for the preparation of UF resins for many years. In the early 1970's, however, this method faced with the serious problem of FE. So, lowering the formaldehyde to urea (F/U)

mole ratio for the synthesis of UF resin was adopted as one of the approaches to reduce the FE of UF resin-bonded panels (Myers and Koutsky, 1990). Thus, lower F/U molar ratios from 1.1 to 1.2 were employed for the resin synthesis. An excellent literature review on the influence of the F/U mole ratio on the FE, as well as panel properties, was published (Pizzi, 1983). According to the review, the gel time used increased with a decrease in the F/U mole ratio. In general, lower F/U mole ratios cause less FE resulted in a loss of panel properties, particularly internal bond (IB) strength as well as thickness swelling after the water immersion for 24 hours. Lower F/U mole ratios also reduced the modulus of rupture (MOR) (Myers, 1984). In recent years, it has been reported that a lower F/U mole ratio (i.e. 1.0) could reduce the FE of particleboards (Que *et al.*, 2007).

In order to study the FE issue, many authors investigated the chemical structures of UF resins using ^{13}C -NMR spectroscopy to understand their reaction mechanisms, and chemical constitutions. To the authors' knowledge, Ebdon and Heaton (1977) have done the first work on the chemical structure of UF resin, showing that the ^{13}C -NMR spectroscopy was useful in providing information about the chemical constitution of UF resin. In the following year, Tomita and Hatono (1978) did an intensive ^{13}C -NMR work on UF resin by assigning the chemical shifts and quantifying the quantity of specific chemical species with a particular structure. Meyer (1979) also employed the same tool to relate chemical structures of UF resin to the FE issue, and mentioned that the formaldehyde release was due to the weakest chemical links in the resin like ether, or pendant methylol groups.

Kim and Amos (1990) also used the same tool to investigate the influence of initial F/U mole ratios with a fixed final F/U mole ratio of

1.0 to the chemical structures of UF resin prepared. They reported that the emitted formaldehyde level of particleboard decreased with a decrease in the initial F/U mole ratio. Gu *et al.* (1995) studied the chemical structures of UF resins prepared under different pH conditions, and reported that the content of branched structures increased as the pH decreased. Christjanson *et al.* (2002) applied the same tool for the investigation of structural changes of UF resins during storage, and showed that the main reaction during storage was the formation of methylene linkages.

A series of very extensive work on the chemical structures of UF resins using the ¹³C-NMR spectroscopy was done by Kim (1999, 2000, 2001) and Kim *et al.* (2001, 2003). Kim (1999) reported that monomeric hydromethylureas and methyl-ether derivatives were formed in the initial alkaline reaction while methylene bonds were formed in the subsequent acidic reaction, splitting formaldehyde from methylene-ether linkages. Kim (2000) also showed that the addition of the second urea during UF resin synthesis led various polymeric hydroxymethylureas migrates to monomeric hydroxymethylureas. Kim (2001) also found a decreasing number of side chain branches and increasing number of free amid group as the initial F/U mole ratio decreased from 2.4 to 1.8 with the final F/U mole ratio of 1.15. Kim *et al.* (2001, 2003) reported the relationship between the chemical structures of UF resins the formaldehyde emission of particleboard, depending on post-treatments and initial F/U mole ratios. Ferg *et al.* (1993) showed that a quantitative measurement of peak ratios could be used to predict UF resin strength and subsequent formaldehyde emission of the resultant particleboard. Tohmura *et al.* (2000) have studied the change of chemical structure of UF resins prepared under different reaction pH conditions using ¹³C-NMR technique.

One of the findings of these studies was the detection of uronic structures in the UF resin prepared under a strong acid condition.

As the number of publications on the analysis of formaldehyde-based resin using the established procedures of the ¹³C-NMR spectroscopy increased, the published papers showed different results with some inconsistencies in interpreting the data obtained. In order to explain the inconsistencies in many published results, Valdez (1995) reported important parameters in the quantitative measurement of ¹³C-NMR spectroscopy for formaldehyde-based resins such as adequate relaxation time, temperature, solvents, and the size of data files. Even though many authors investigated the chemical structure of UF resins prepared under different conditions, the work done to study the influence F/U mole ratio on the chemical structure of the resins has been limited. In particular, many researchers studied the influence of F/U mole ratio of UF resin that was adjusted by manipulating an initial F/U mole ratio. But, the F/U mol ratio influence of the second urea addition was limited. Therefore, this study was conducted to investigate the influence of F/U mole ratio on the chemical structures of the UF resin adhesives using ¹³C-NMR spectroscopy.

2. MATERIALS and METHODS

2.1. Resin Preparation

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 heated to 60°C and then adjusted the reaction pH to 7.5 with sodium hydroxide (20 wt%). Subsequently, urea was added in equal parts at 1-min intervals, and the mixture was heated to 90°C for 1 hour. Then, the reaction pH was adjusted to 4.5

Table 1. Properties of the UF resin adhesives prepared at different F/U mole ratios

F/U mole ratio	Specific gravity	Non-volatile resin solids content (%)	Viscosity (mPa · s)	Free formaldehyde content (%)
1.6	1.26	50.1	240	0.70
1.4	1.25	51.7	248	0.38
1.2	1.25	53.3	254	0.30
1.0	1.21	54.5	160	0.27

with formic acid (20 wt%) for the condensation. The second urea was again placed in the reactor at 40°C before rapid cooling to 25°C terminated the reaction. Different amounts of the second urea were added for the synthesis in order to obtain F/U mole ratios of 1.6, 1.4, 1.2, and 1.0. For all resins prepared, final pH was adjusted to 8.0 after the cooling. Properties of the prepared UF resins with different F/U mole ratios were summarized in Table 1.

2.2. ^{13}C -NMR Spectroscopy

The prepared UF resins were freeze-dried without further pH adjustment, ground to a fine powder, and thoroughly oven-dried at 60°C overnight. The powder UF resins were also dissolved in deuterated dimethyl sulfoxide (DMSO-*d*6) as an internal standard (~1% concentration) for ^{13}C -NMR spectroscopy. The ^{13}C -NMR spectra were obtained with 9.5 seconds pulse width (30) and a pulse delay of 4 seconds, using 300 MHz model (Bruker AMX-R300) at the Korea Basic Science Institute in Seoul, Korea. By using the gated decoupling method to minimize the nuclear Overhauser effect, about 20,000 scans were accumulated to obtain reliable spectra.

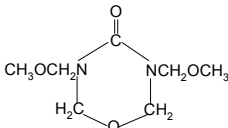
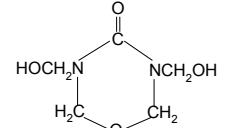
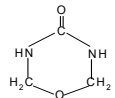
3. RESULTS and DISCUSSION

The ^{13}C -NMR spectra of the UF resins with different F/U mole ratios were shown in Figs. 1

to 4. Also, the assignments of chemical structures from the ^{13}C -NMR spectra were summarized in Table 2. The ^{13}C -NMR spectra of UF resins with different F/U mole ratios showed a peak at around 45 ppm. This chemical shift (around 45 ppm) was assigned to the carbon of methylene linkages, according to published information (Hse *et al.*, 1994; Kim, 1999; Kim 2001; Tohmura *et al.*, 2000; Tomita and Hatono, 1978; Soulard *et al.*, 1999). The chemical shift of around 54 ppm could be attributed to the carbons of methylene linkage such as dimethylene urea, trimethylene tetraurea, or tetramethylene pentaurea (Tomita and Hatono, 1978). But, these methylene linkages were not detected for the UF resin with the F/U mole ratio of 1.0. This result indicates that the chemical structure of UF resin with the F/U mole ratio of 1.0 was much less branched polymer without trimethylene tetraureas, or tetramethylene pentaureas. These species were known to contribute the formation of branched network polymer structures (Pascault *et al.*, 2002).

The chemical shift at around 63 ppm was assigned to various methylol carbons of the resins with different F/U mole ratios. The chemical shifts could be due to the carbons of monomethylol ureas, or dimethylol ureas. This result was well in the agreement with the published report (Gu *et al.*, 1995). The dimethylene ether carbon occurred at around 68 ppm for the UF resins with the F/U mole ratios of both 1.6 and 1.4. In other words, this peak was fairly weak

Table 2. Chemical shift assignment of ¹³C-NMR spectra of UF resins synthesized under different reaction pH conditions

Chemical structure	Chemical shift (ppm)				References
	F/U = 1.6	F/U = 1.4	F/U = 1.2	F/U = 1.0	
NH-CH ₂ -NH	45.26	45.23	45.27	45.40	6, 7
N(CH ₂ -)CH ₂ N-(CH ₂ -)-	54.19	54.14	54.18		2, 12, 31
NH-CH ₂ OH	63.39	63.39	63.39	63.41	6, 7
N(CH ₂ -)CH ₂ OH	63.97	63.54	63.54	63.56	
-NH-CH ₂ -O-CH ₂ -NH-	68.91	68.91			2, 12, 31
HO-CH ₂ -OH	81.89	81.88			2, 31
	156.75				
	156.90	156.89	156.89	156.94	6, 7, 10, 22
	157.15		157.36		6, 7, 28
HOCH ₂ NHCON(CH ₂ OH) ₂	158.07	158.06	158.06	158.12	2, 6, 7
-HN-CO-NH-, NH-CO-NH ₂		159.44	159.44	159.51	6, 7, 30

for the resins prepared at the F/U mole ratios of 1.2 and 1.0. This result indicates that UF resins with higher F/U mole ratios tend to form dimethylene ether linkages. These linkages were also reported by other published papers (Chung and Maciel, 1994; Gu *et al.* 1996; Tomita and Hatono, 1978; Kim, 2001). These structures were known to be susceptible to hydrolytic degradation under acidic environment (Chung and Maciel, 1994).

The chemical shift of around 81.8 ppm was observed for UF resins with the F/U mole ratios of 1.6 and 1.4 (arrows in Figs. 1 and 2). However, this was not detected for the UF resins with the F/U mole ratios of 1.2 and 1.0. This chemical shift was assigned to methylene glycols that were a dissolved form of free form-

aldehyde in the resin. Chung and Maciel (1994) reported the chemical shift of 87-92 for the methylene glycols while Gu *et al.* (1996) reported the range of from 83 ppm to 95 ppm as the methylene glycol species. This result shows that higher F/U mole ratio produces more free formaldehyde than lower F/U mole ratio for the synthesis of UF resins.

The chemical shifts around 156 ppm could be assigned to the carbonyl carbons of uronic structures (Ebdon and Heaton, 1977; Gu *et al.*, 1995, 1996; Park *et al.*, 2002). The peak at 156.7 ppm could be assigned to the carbonyl carbons of urons with the di-substitutions of dimethylene methyl ether groups (CH₃OCH₂N-C-O-NCH₂(₂)OCH₂(₃)), while the one at 156.9 could be assigned to the carbonyl carbons of ur-

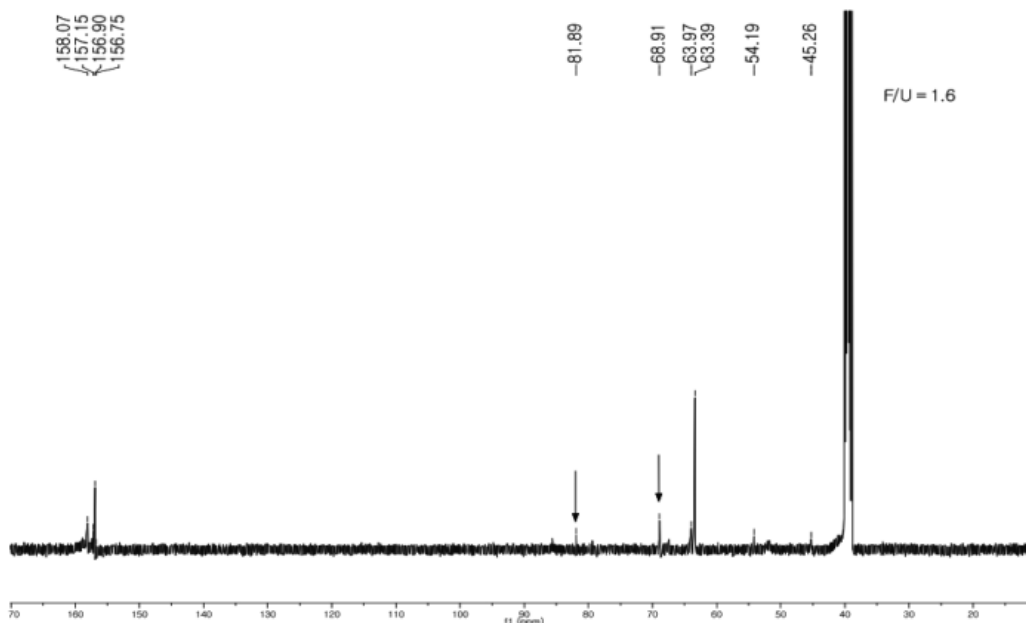


Fig. 1. ^{13}C -NMR spectrum of UF resin adhesive with the F/U mole ratio of 1.6.

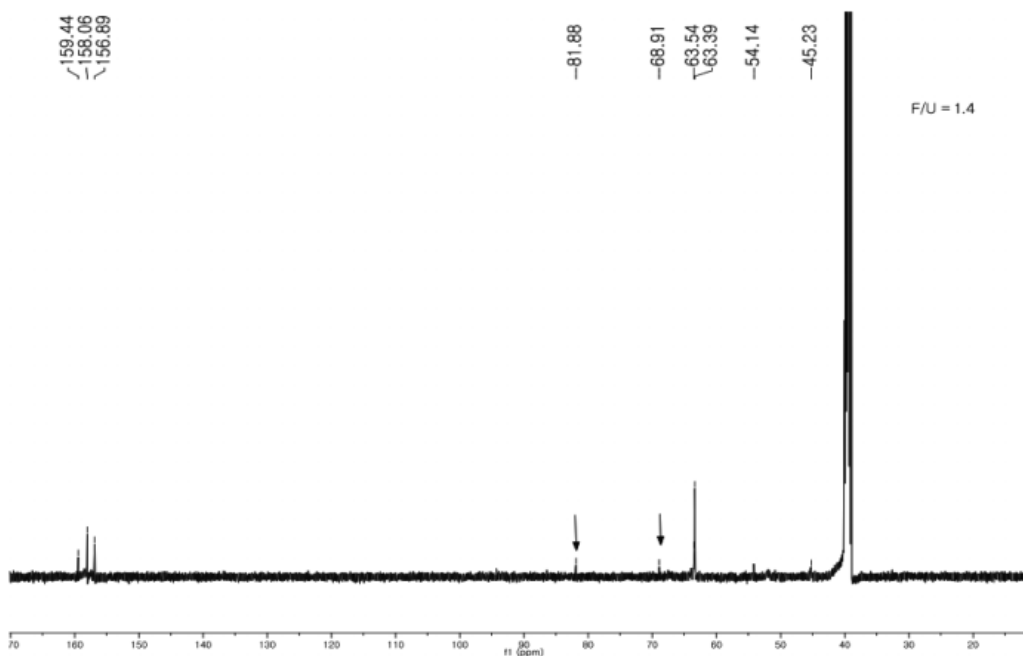


Fig. 2. ^{13}C -NMR spectrum of UF resin adhesive with the F/U mole ratio of 1.4.

¹³C-NMR Spectroscopy of Urea-Formaldehyde Resin Adhesives with Different Formaldehyde/Urea Mole Ratios

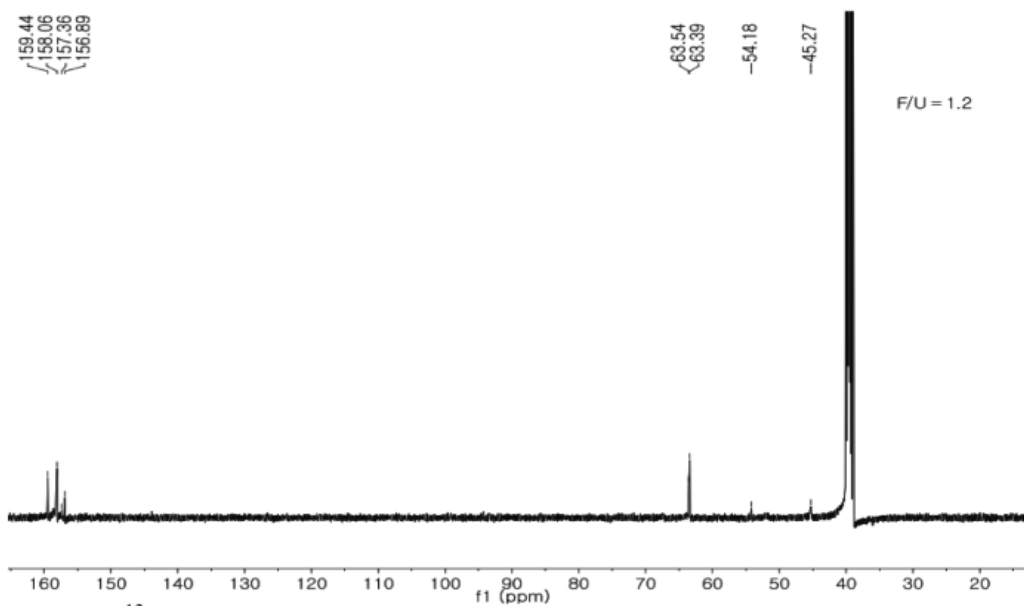


Fig. 3. ¹³C-NMR spectrum of UF resin adhesive with the F/U mole ratio of 1.2.

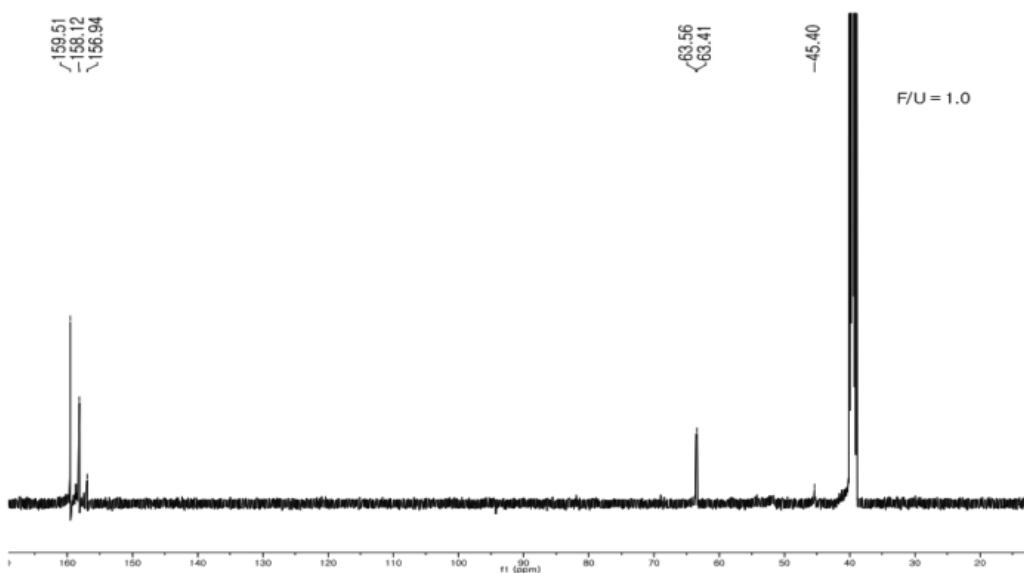


Fig. 4. ¹³C-NMR spectrum of UF resin adhesive with a F/U mole ratio of 1.0.

ons with the di-substitutions of dimethylol groups (HOCH₂N-C-O-NCH₂OH). And the che-

mical shift at around 157 ppm was assigned to the carbonyl carbons of uronic structures with-

out any substitutions (Ebdon and Heaton, 1977; Gu *et al.*, 1995, 1996). This assignment is in a good agreement with the published results.

Three peaks at 158 ppm and 159 ppm were appeared prominently for all four UF resins. The peak at around 158 ppm was assigned to the carbons of carbonyl group of tri-methylated ureas (Chung and Maciel, 1994; Gu *et al.*, 1995, 1996). The one at around 159 ppm was assigned to the carbons of substituted carbonyl groups of ureas (Tohmura *et al.*, 2000; Tomita and Hatono, 1978; Soulard *et al.*, 1999). The peak at 159 ppm was assigned to the carbons of carbonyl group of various urea residues (Gu *et al.*, 1995, 1996).

4. CONCLUSION

This study was undertaken to investigate the influence of F/U mole ratio to the chemical structures of UF resin adhesives using carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectroscopy as a part of abating formaldehyde emission of UF resin adhesive. UF resin adhesives were synthesized at four different F/U mole ratios such as 1.6, 1.4, 1.2, and 1.0 for the analysis. The analysis of ^{13}C -NMR spectroscopy showed that UF resin adhesives with higher F/U mole ratios (i.e., 1.6 and 1.4) had two distinctive peaks, indicating the presence of dimethylene ether linkages and methylene glycols (a dissolved form of free formaldehyde). But, these peaks were not detected at the UF resins with lower F/U mole ratios (i.e., 1.2 and 1.0). These chemical structures present at the UF resins with higher F/U mole ratios indicated that UF resin adhesive with a higher F/U mole ratio had a greater contribution to the formaldehyde emission than that of a lower F/U mole ratio. Uronic species were detected for all UF resins regardless of F/U mole ratios.

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REFERENCES

1. Christjanson, P., K. Siimer, T. Pehk, and I. Lasn. 2002. Structural changes in urea-formaldehyde resins during storages, *Holz als Roh-und Werkstoff*, 60: 379~384.
2. Chung, I. and G. E. Maciel. 1994. NMR study of the stabilities of urea-formaldehyde resin components toward hydrolytic treatments, *J. Appl. Polym. Sci.*, 52: 1637~1651.
3. Dunky, M. 1983. Urea-formaldehyde (UF) adhesive resins for wood. *Int. J. Adhesion & Adhesives*, 18: 95~107.
4. Ebdon, J. R. and P. E. Heaton. 1977. Characterization of urea-formaldehyde adducts and resins by ^{13}C -n.m.r. spectroscopy, *Polymer*, 18: 971~974.
5. Ferg, E. F., A. Pizzi, and D. C. Levendis, 1993. ^{13}C NMR analysis method for urea-formaldehyde resin strength and formaldehyde emission, *J. Appl. Polym. Sci.*, 50: 907~915.
6. Gu, J. Y., M. Higuchi, M. Morita, and C. Y. Hse. 1995. Synthetic conditions and chemical structures of urea-formaldehyde resins I. Properties of the resins synthesized three different procedures. *Mokkuzai Gakkaishi*, 41(12): 1115~1121.
7. Gu, J. Y., M. Higuchi, M. Morita, and C. Y. Hse. 1996. Synthetic conditions and chemical structures of urea-formaldehyde resins II. Synthetic procedures involving a condensation step under strongly acidic conditions and the properties of the resins obtained. *Mokkuzai Gakkaishi*, 42(2): 149~156.
8. Hse, C. Y., Z. Y. Xia, and B. Tomita. 1994. Effects of reaction pH on properties and performance of urea-formaldehyde resins. *Holzforchung*, 48(6): 527~534.
9. Kim, M. G. and L. W. Amos. 1990. Quantitative

- carbon-13 NMR study of urea-formaldehyde resins in relation to the formaldehyde emission levels, *Ind. Eng. Chem.*, 29: 208~212.
- Kim, M. G. 1999. Examination of selected synthesis parameters for typical wood adhesive-type urea-formaldehyde resins by ¹³C NMR spectroscopy I, *J. Polym. Sci., Part A: Polym. Chem.*, 37: 995~1007.
 - Kim, M. G. 2000. Examination of selected synthesis parameters for typical wood adhesive-type urea-formaldehyde resins by ¹³C NMR spectroscopy. II, *J. Appl. Polym. Sci.*, 75: 1243~1254.
 - Kim, M. G. 2001. Examination of selected synthesis parameters for typical wood adhesive-type urea-formaldehyde resins by ¹³C NMR spectroscopy III, *J. Appl. Polym. Sci.*, 80: 2800~2814.
 - Kim, M. G., H. Wan, B. Y. No, and W. L. Nieh. 2001. Examination of selected synthesis parameters for typical wood adhesive-type urea-formaldehyde resins by ¹³C NMR spectroscopy IV, *J. Appl. Polym. Sci.*, 82: 1155~1169.
 - Kim, M. G., H. Wan, B. Y. No, S. M. Lee, and W. L. Nieh. 2003. Examination of selected synthesis parameters for typical wood adhesive-type urea-formaldehyde resins by ¹³C NMR spectroscopy IV, *J. Appl. Polym. Sci.*, 89: 1896~1917.
 - Marutzky, R. 1986. In: Wood Adhesives: Chemistry and Technology, Vol. 2. A. Pizzi, Ed., Marcel Dekker Inc., pp: 307~387.
 - Meyer, C. B. 1979. Formaldehyde release from urea-formaldehyde systems, In: Proc. of the 13th International Symposium on Particleboard, Washington State University, Pullman, WS, USA, Ed. by T. M. Maloney, pp: 43~354.
 - Myers, G. E. 1983. Formaldehyde emission from particleboard and plywood paneling: measurement, mechanism, and product standards. *For. Prod. J.*, 33(5): 27~37.
 - Myers, G. E. 1984. How mole ratio of UF resin affects formaldehyde emission and other properties: A literature critique. *For. Prod. J.*, 34(5): 35~41.
 - Myers, G. E. 1986. In: Formaldehyde Release from Wood Products, B. Meyer. B. A. K. Andrews, R. M. Reinhardt. Ed., American Chemical Society, pp: 8~14.
 - Myers, G. E. and K. A. Koutsky. 1987. Procedure for measuring formaldehyde liberation from formaldehyde-based resins. *For. Prod. J.*, 37(9): 56~60.
 - Myers, G. E. and K. A. Koutsky. 1990. Formaldehyde liberation and cure behavior of urea-formaldehyde resins. *Holzforschung*, 44(2): 117~126.
 - Park, B.-D., Y. S. Kim, W. T. So, and K. P. Lim. 2002. Effects of reaction pH and hardener types on reactivity, properties, and performance of urea-formaldehyde (UF) resin, *Mokchae Konghak*, 30(3): 1~11.
 - Pascault, J.-P., H. Sautereau, J. Verdu, and R. J. J. Williams. 2002. Thermosetting polymers, Marcel Dekker Inc., New York, USA.
 - Pizzi, A., L. Lipschitz, and J. Valenzuela. 1994. Theory and practice of the preparation of low formaldehyde emission UF adhesives. *Holzforschung*, 48(3): 254~261.
 - Pizzi, A. 1983. Wood Adhesives: Chemistry and Technology. Marcel Dekker Inc., New York, USA. pp. 59~104.
 - Pizzi, A. 1994. Advanced Wood Adhesives Technology. Marcel Dekker Inc., New York, pp. 19~66.
 - Que, Z., T. Furuno, S. Katoh, and Y. Nishino. 2007. Effects of urea-formaldehyde resin mole ratio on the properties of particleboard, *Building and Environment*, 42: 1257~1263.
 - Soulard, C., C. Kamoun, and A. Pizzi. 1998. Uron and uron-urea-formaldehyde interior wood adhesives, *Holzforschung Holzverwertung*, 50(5): 89~94.
 - Sellers Jr., T. 1999. In: International Contributions to Wood Adhesion Research, A. W. Christiansen, Ed., Pilato L. Forest Products Society, Madison, WI, USA. pp: 31~51.
 - Tohmura, S., C. Y. Hse, and M. Higuchi. 2000. Formaldehyde emission and high-temperature stability of cured urea-formaldehyde resins. *J. Wood Sci.*, 46: 303~309.
 - Tomita, B. and S. Hatono. 1978. Urea-formaldehyde resins. III. Constitutional characterization by ¹³C fourier transform NMR spectroscopy. *J. Appl. Polym. Sci.*, 16: 2509~2525.

32. Valdez, D. 1996. ^{13}C -NMR spectroscopy- A quantitative tool for wood adhesives, *In: Proc. of Wood Adhesives 1995*, Ed. by A.W. Christiansen and A. H. Conner, Forest Products Society, Madison, WI, USA, pp: 193~200.