J. Korean Wood Sci. Technol. 2017, 45(4): 471~481 pISSN: 1017-0715 eISSN: 2233-7180
https://doi.org/10.5658/WOOD.2017.45.4.471

Original Article

Effect of Analytical Parameters of Gel Permeation Chromatography on Molecular Weight Measurements of Urea-Formaldehyde Resins[1]

Bora Jeong[2] · Byung-Dae Park[2,3,†]

ABSTRACT

As the molecular weight (MW) of urea-formaldehyde (UF) resins had a great impact on their properties, this work was conducted to study effect of analytical parameters of gel permeation chromatography (GPC) on the MW measurement of UF resins. GPC parameters such as flow rate, column, detector temperature, and sample injection temperature were selected to compare number-average molecular weight (*Mn*), weight-average molecular weight (*Mw*), molecular weight distribution (MWD) and polydispersity index (PDI) of two UF resins with different viscosities. As expected, UF resin with higher viscosity resulted in greater *Mn* and *Mw* than those of low viscosity UF resin. When the flow rate increased, both *Mn* and *Mw* of UF resins decreased and MWD became narrower. By contrast, both *Mn* and *Mw* increased and MWD became wide when the column, detector, and sample injection temperature increased. The column, detector, and sample injection temperature of 50℃ at a flow rate of 0.5 mℓ/min resulted in the highest MW and broadest MWD for the GPC analysis. These results suggest that the apparent molecular size or a hydrodynamic radius of UF resin molecules dissolved in the mobile phase affect to *Mn*, *Mw* and MWD.

Keywords : urea-formaldehyde resin, molecular weight, molecular weight distribution, gel permeation chromatography

1. INTRODUCTION

Urea-formaldehyde (UF) resin is one of the most widely used adhesive in the manufacture of wood-based composite panels because it has several desirable characteristics such as low cost, fast curing, colorlessness, water solubility and high performance (Myers *et al*., 1990; Dunky, 1998; Park *et al*., 2006; Abdullah and Park., 2010). In general, the performance of UF resin heavily depends on molecular weight (MW) or molecular weight distribution (MWD) (Jeong and Park, 2016). Also, MW of the UF resin affects the adhesion (Jeremejeff, 2012). In order to have a good adhesion, low MW fraction of the resin should penetrate into wood cell walls, while high MW fraction should be remained in the bond-line between wood and adhesive (Arif

[1] Date Received July 4, 2017, Date Accepted July 17, 2017
[2] Department of Wood and Paper Sciences, Kyungpook National University, Daegu 41566, Republic of Korea
[3] Institute of Agricultural Science and Technology, Kyungpook National University, Daegu 41566, Republic of Korea
[†] Corresponding author: Byung-Dae Park (e-mail: byungdae@knu.ac.kr)

Table 1. Literature summary on parameters of GPC for the MW measurement of formaldehyde-based resins

Resin type	Flow rate (mℓ/min)	Column temp. (℃)	Detector temp. (℃)	Injection temp. (℃)	Reference
UF resin	1	25	25	-	Ludlam and King (1984)
	1	-	-	-	Despres and Pizzi (2006)
	1	60	60	-	Ferra *et al*. (2010)
	1	60	60	-	Ferra *et al*. (2012)
	-	50	50	-	Jeremejeff (2012)
MF resin	1	-	-	-	Despres and Pizzi (2006)
	1	-	-	-	Pendlebury *et al*. (2010)
MUF resin	1	-	-	-	Zanetti and Pizzi (2003)
	1	-	-	-	Despres and Pizzi (2006)
	1	-	-	-	Lei *et al*. (2006)
	1	60	-	-	Paiva *et al*. (2013)
PF resin	1				Holopainen, *et al*. (1997)
	0.8				Park *et al*. (1998)
PUF resin	3	60	-	-	Tomita and Hse (1993)
	1	25			Tyrynen *et al*. (2003)

et al., 2014).

Many research results have reported on the measurement of the MW of formaldehyde-based resins, using gel permeation chromatography (GPC) (Ludlam and King., 1984; Tomita and Hse., 1993; Park *et al*., 1998; Zanetti and Pizzi., 2003; Despres and Pizzi., 2006; Laborie *et al.,* 2006; Lei *et al*., 2006; Ferra *et al*., 2010; Pendlebury *et al*., 2010; Jeremejeff, 2012; Ferra *et al*., 2012; Paiva *et al*., 2013) and were summarized in Table 1. For example, Ludlam and King (1984) measured MWs of UF resins to understand its aging characteristics over time, using size exclusion chromatography (SEC) at a flow rate of 1 mℓ/min. and columns and detector temperature of 25℃. Despres and Pizzi (2006) also determined MWs of UF resin, melamine-urea-formaldehyde (MUF) resin, and melamine-formaldehyde (MF) resin to study the presence of super-aggregates by GPC, and confirmed the formation of colloidal super-aggregates. Using GPC/SEC analysis, Ferra *et al*. (2010) also studied the colloidal phase in UF resins at a flow rate of 1 mℓ/min. and a column temperature of 60℃. And they found that it acted as reactive filler of improving bonding performance at the wood joint interfaces, indicating that the sediment and supernatant obtained by the centrifugation was related to strengthening of the adhesive bond. Ferra *et al*. (2012) also employed GPC/SEC method to compare two synthesis methods of UF resins: alkaline-acid and strong acid processes. Jeremejeff (2012) studied changes in the MW of UF resins to understand the effect of formaldehyde/urea molar ratio during the synthesis. Pendlebury *et al*. (2010) also analyzed MF resins by GPC to understand their

performance, and found that the GPC result was compatible with the density profile of panels bonded with the resin.

Zanetti and Pizzi (2003) measured MWs of MUF resins, and found that the whitening of these resins was related to the apparent average degree of polymerization of the resin with ageing. Two rather different MUF resin formulations yielded different variations in molecular mass fractions during the progress of the reaction and during the so-called ambient temperature "maturing" of the resin was investigated by Lei *et al*. (2006). Paiva *et al*. (2013) also performed GPC/SEC analysis for MUF resins, and reported that high molecular weight of MUF resins was due to a higher degree of the condensation.

In addition to amino resins, various GPC work has been done for PF resins. For example, Holopainen *et al*. (1997) studied that the effects of the condensation F/P molar ratio on the structure and properties of the resins. Park *et al*. (1998) reported that a mixture ratio of 40% low molecular weight (LMW) and 60% high molecular weight (HMW) resulted in the highest adhesion for medium density fiberboard (MDF). Lavorie *et al*. (2006) showed that a LMW PF resin interacted with wood cell wall polymers on the nanometer scale, as demonstrated by enhanced intermolecular coupling near the main glass transition of wood lignin. Tomita and Hse (1993) also investigated the effects of acidity on the reaction of urea and a methylolphenol using GPC analysis. Turunen *et al*. (2003) studied that modifications with corn starch, a lignin reagent, or urea were proven to increase MW values with respect to the values of the reference resol.

Although many literatures reported on the MW measurements of UF resins using GPC or SEC, the level of GPC parameters were different and inconsistent, depending on the authors and equipment. Thus, this study investigated the effect of GPC parameters on the MW measurements of UF resins by adjusting flow rate, detector, column, and sample injection temperature.

2. MATERIALS and METHODS

2.1. Materials

Materials used for the synthesis of UF resin adhesives in this work were technical grade of urea granules (99%) and formalin (37%). Aqueous solutions of formic acid (20 wt%) and sodium hydroxide (20 wt%) were used to adjust the pH during the resin synthesis process. Aqueous solution (20 wt%) of NH_4Cl were used as a hardener. High purity ($\geq$ 99.9%) high performance liquid chromatography (HPLC) grade of both *N,N*-dimethyl formamide (DMF) and dimethylsulfoxide (DMSO) were purchased from Sigma-Aldrich without further treatment.

2.2. Methods

2.2.1. Synthesis UF Resins of Different Viscosities

Formalin (37%) was placed in the reactor equipped by a mantle heater. The first addition

Table 2. Properties of UF resins with different viscosities

Sample	pH	Viscosity (mPa · s)	Non-volatile solids content (wt%)	Gel time (s)
UF resin #1	8.3	260	62 ± 0.2	240 ± 2
UF resin #2	8.1	760	62 ± 0.1	208 ± 1

Table 3. Different sets of column and detector temperature for the GPC analysis

Condition	Column temperature (℃)	Detector temperature (℃)
# 1	35	35
# 2	35	50
# 3	50	50

of urea was added into the reactor under stirring, and heated to 40℃. We adjusted the pH of 7.8-8.0 for addition reaction using sodium hydroxide. The reaction was heated at 90℃ for 60 min. The temperature was then brought down to 80℃. When the temperature reached 83℃, the pH had to be adjusted to 4.6 for the condensation reaction. The temperature was kept at 80℃ to determine the viscosity. The target viscosity was between 'J' and 'K' scale as measured by a bubble viscometer (VG-9100, Gardner-Holdt Viscometer, FL, USA). When the desired condition was reached, the second addition of urea was added to the reactor to adjust a F/U mole ratio of 1.0. After all the urea was dissolved, the UF resin was cooled to room temperature, and then the pH was adjusted to 8.0 to terminate the condensation reaction. And another UF resin was synthesized under the same procedure but with the target viscosity between 'S' and 'T' scale using the same bubble viscometer.

2.2.2. Properties of UF Resins Prepared

The viscosity of all resins was measured with a cone-plate viscometer (DV－II+, Brookfield, Middleboro, MA, USA), using a spindle #2 at 25℃ and 60 rpm. The non-volatile solids content of all UF resins were calculated by weighing resin samples before and after drying in the oven for 3 hours at 105℃. The gelation time of all resins were measured at 100℃ with 3 wt% of NH_4Cl (20 wt%) as hardener, using a gel time meter (DAVIS, Sunshine Instruments, US/22A-240). Properties of UF resins are summarized in Table 2.

2.2.3. MW Measurements of UF Resins Using GPC

A GPC (YL9100, Younglin, Korea) system equipped with a refractive index (RI) detector was used in this study. The columns used were the KD801, 802, and 806 M products from SHODEX. As shown Table 3, different sets of the column and detector temperature from 35℃ to 50℃ were used. And three flow rates of the mobile phase such as 0.5, 0.8 and 1 mℓ/min. were employed for the GPC analysis. A HPLC grade DMF was used as the mobile phase. Liquid UF resin samples were dissolved in the

Table 4. MWD of UF resin #1 as a function of the flow rate

Flow rate (mℓ/min)	*Mn* (g/mol)	*Mw* (g/mol)
0.5	851	905
	548	551
	403	405
	291	293
	227	228
	158	159
0.8	552	555
	401	403
	287	288
	228	229
1.0	504	553
	378	380
	221	225

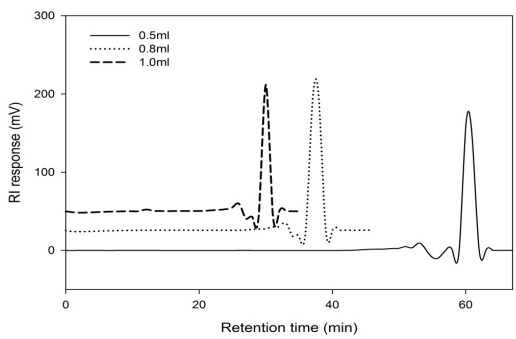

Fig. 1. GPC chromatograms of UF resin #1 as a function of the flow rate.

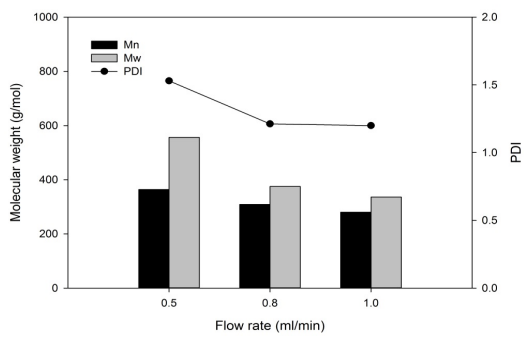

Fig. 2. *Mn*, *Mw* and PDI of UF resin #1 as a function of the flow rate of GPC.

mixture of 10% DMSO and 90% DMF and kept them in the oven at 50℃ for 3 hours before the injection. The sample solution was introduced to the injection loop of the GPC after the filtration through a 0.45 mℓ filter.

3. RESULTS and DISCUSSIONS

Fig. 1 shows the GPC chromatograms of UF resin #1 at different flow rates. The results display that high flow rate reduced retention time. However, when the flow rate was fast, the detection of the MW was insufficient. There are the *Mn*, *Mw* and MWD according to different flow rates of the same UF resin #1 in Fig. 2. As a result, *Mn*, *Mw* and PDI decreased as the flow rate increased, because there was insufficient time for the MW analysis. The slower the flow rate was, the longer the retention time in the column was. Thus, the higher MW could

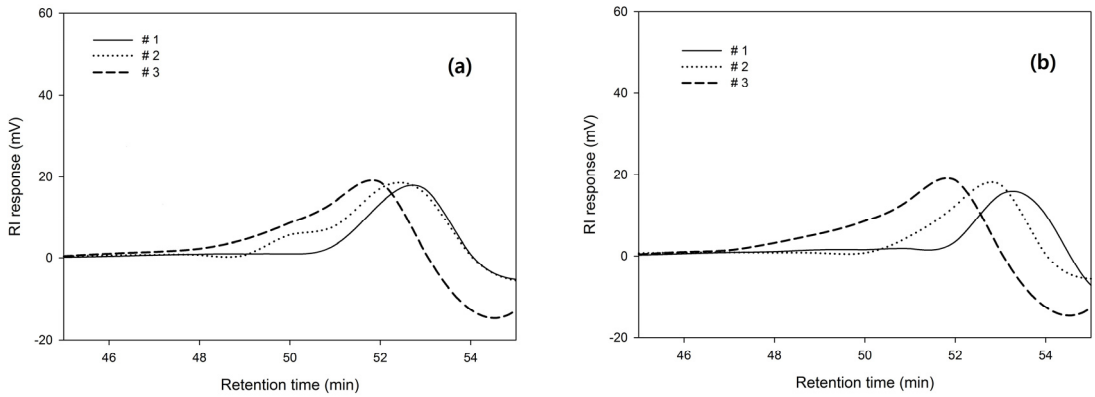

Fig. 3. GPC chromatograms of UF resin # 1 (a) and # 2 (b) at different sets of column and detector temperature.

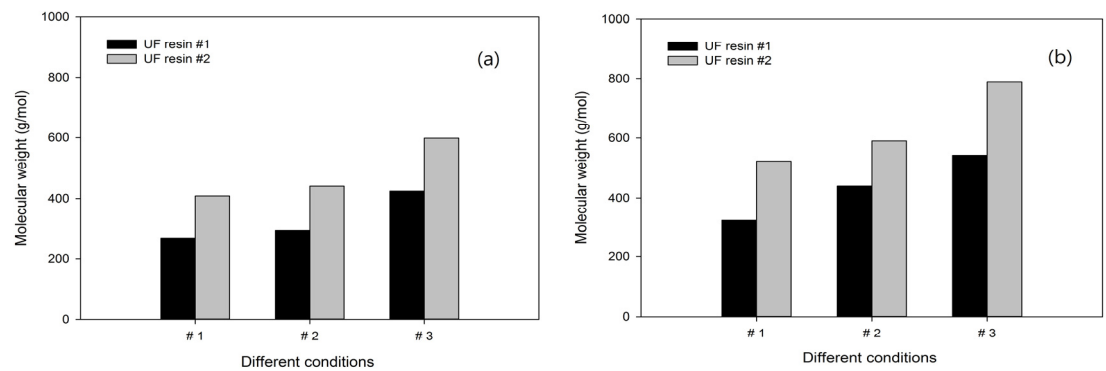

Fig. 4. *Mn* (a) and *Mw* (b) of UF resins at different temperatures of column and detector.

be analyzed. Another fact the MWD had showed narrower MWD as the flow rate became faster as presented in Table 4.

If the equilibrium assumption of GPC was valid, then the elution volume should be independent of flow rate (Iler and Mcqueston, 1974). But, many studies had shown that the elution volume increased or decreased with the flow rate, depending on the experimental conditions (Unger and Janzen, 1986; Majors, 1980). Despite the inconsistency between flow rate and elution volume in the literatures, it was generally accepted that as the flow rate reduced, the retention time and elution volume increased, resulting in high MW and wider MWD. By contrast, the elution volume is distorted and decreased, as the flow rate increased. At higher flow rate, the diffusion rate into micro pores is insufficient, and then the elution curve becomes skewed (Uglea, 1996). Therefore, the elution curve became more skewed and the peak area of the molecular weight curve of the sample decreased as the flow rate increased.

GPC chromatograms of UF resins at different sets of column and detector temperatures with

Table 5. MWD of UF resins at different sets of column and detector temperature

Condition	UF resin #1		UF resin #2	
	Mn (g/mol)	*Mw* (g/mol)	*Mn* (g/mol)	*Mw* (g/mol)
# 1			687	741
	471	481	306	309
	277	278	291	293
	216	217	226	227
# 2			742	901
	498	503	313	316
	274	276	257	258
	214	215	160	161
# 3	845	914	876	1012
	502	505	485	499
	368	369	221	235
	288	290	135	139

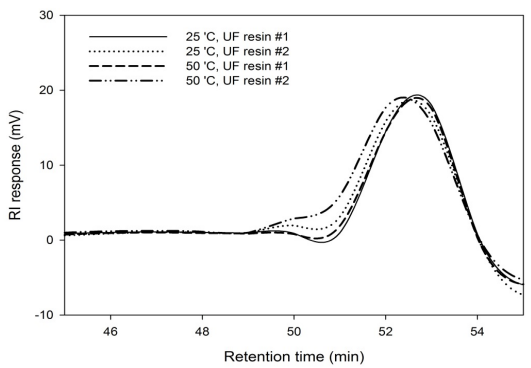

Fig. 5. GPC chromatograms of UF resins with different sample injection temperatures.

low and high viscosities are shown in Fig. 3. Regardless of the resin viscosity, higher temperature of the column and detector resulted in higher MW for UF resins, indicating that column and detector temperature directly influenced the resolution of GPC. It depends on the expansion of the polymer and it's diffusion in the column. When the temperature increased, the viscosity of the solvent decreased and the mobility of the sample in solution increased. As the mobility of the molecule increases, the mass transfer in the column becomes easier. As expected, both *Mn* and *Mw* increased with an increase in the column and detector temperature as shown in Fig. 4. Both *Mn* and *Mw* of the condition #2 were higher than those of the condition #1, and the condition #3 had the highest *Mn* and *Mw* values.

As shown in Table 5, the MWD of UF resins became wider as the temperature of column and detector increased. The range of MWD of the condition #2 was wider than that of the condition #1, and the condition #3 was broader than the condition #2. This was because the diffusion coefficient of the mobile solution increased as the temperature of column and detector increased. And seeing as the diffusion coefficient increased, mobility solution improved. Because the mobility solution increased, the mass transfer became easier.

The result shows that temperature changes in

Table 6. PDI values of the UF resins with different sets of column - detector temperature and sample injection temperature

Parameter	Temperature (℃)	PDI	
		UF resin #1	UF resin #2
Column - Detector set	35 - 35	1.204	1.281
	35 - 50	1.488	1.341
	50 - 50	1.279	1.320
Sample injection	25	1.032	1.030
	50	1.542	1.558

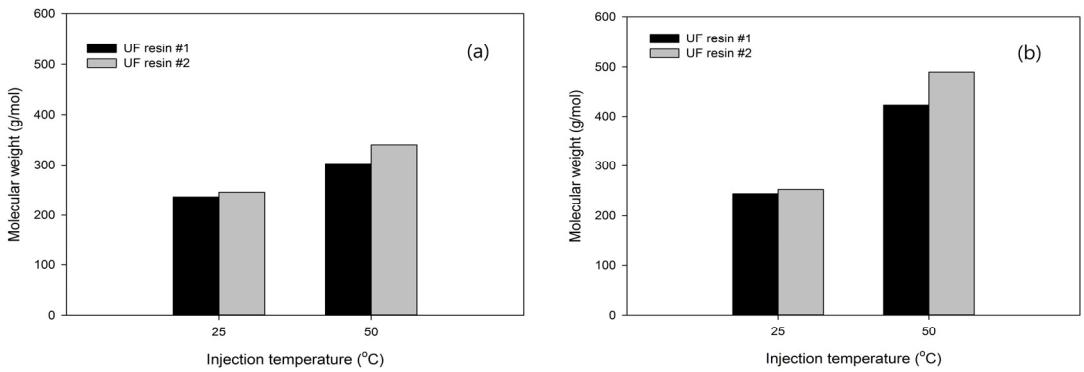

Fig. 6. *Mn* (a) and *Mw* (b) of UF resin #1 and #2 with different sample injection temperatures.

the column and detector are one of the important parameters in GPC analysis. As the diffusion coefficient of the polymer in solution increased, the mobility increased, and then the resulting sample peaks appear sharper and narrower. However, the PDI values shown in Table 6 were inconsistent. For the condition #2 which the column-detector temperature was 35-50℃, the PDI value increased as the difference in both *Mn* and *Mw* values became widened. The both *Mn* and *Mw* values widened that because the diffusion coefficient of the molecules increases as the detector temperature increases. On the other hand, conditions #1 and #3 with the same column and detector temperatures did not show a significant difference in PDI values. In Consequence, as column and detector temperatures increases, the diffusion of the molecules becomes easier and wider range of the MW can be measured.

Both UF resins #1 and #2 with different viscosities were used for the sample injection temperatures of 25℃ and 50℃. Fig. 5 displays GPC chromatograms of two UF resins at different sample injection temperatures. As expected, high MW was detected at greater viscosity resin like UF resin #2 with greater viscosity resulted in high MW. And higher sample injection temperature also resulted in high MW. By contrast, low MW was detected for UF res-

Table 7. MWD of UF resins at different sample injection temperatures

Sample injection temperature (℃)	UF resin #1		UF resin #2	
	Mn (g/mol)	*Mw* (g/mol)	*Mn* (g/mol)	*Mw* (g/mol)
25			846	952
	404	406	423	426
	275	277	285	287
	215	216	222	223
50	817	898	926	1118
	419	422	418	422
	283	284	282	284
	220	222	216	218

in #1 with low viscosity resin at low sample injection temperature. Similarly, Fig. 6 shows that the high viscosity resin had high *Mn* and *Mw*, and the high sample injection temperature resulted in the high *Mn* and *Mw*.

In other words the higher viscosity of a resin is, the larger MW is. Park *et al*. (1998) reported blending LMW and HMW resins in different proportions to investigate the influence of *Mw* of PF resin. They concluded that as the proportion of HMW increased, *Mw* and hence the viscosity of adhesives increased. As showed in Table 6, the PDI increased because the difference between *Mn* and *Mw* was high at high sample injection temperature. The sample injection temperature also affected the MWD of UF resins as presented in Table 7. An increase in the sample injection temperature increased the solubility of UF resins and confirmed a wider MWD using GPC analysis.

When the sample injection temperature increased, the sample has an increased dispersion in the elution solvent and diffusion coefficient is increased. If the diffusion coefficient of a polymer increases in solution, the resulting sample peaks appear sharper and less broad.

4. CONCLUSION

In the words, UF resins of different viscosities were prepared to optimize the parameters of GPC analysis. GPC analysis parameters were very important in obtaining a proper MW and MWD for UF resins. The GPC analysis of UF resin showed that a faster flow rate resulted in smaller MW and narrower MWD. And the diffusion of resins and mobility increased, affecting the MW and MWD measurement, as the column and detector temperature increased. We also found that the sample injection temperature affected the MW and MWD of the sample because it influenced the dissolution of sample. As a result of this study, the greatest MW and wider MWD were observed at a flow rate of 0.5 mℓ/min with the column, detector and sample injection temperature of 50℃. The flow rate affects the diffusion rate of analyte molecule, and column, detector, and sample injection tem-

peratures affect molecular mobility and their diffusion.

ACKNOWLEDGEMENTS

This work was supported by the Basic Science Research Program through the National Research Foundation (NRF) of Korea funded by the Ministry of Education, Science and Technology (Grant #: 2016R1D1A1A09917782).

REFERENCES

Abdullah, Z.A., Park, B.D. 2010. Influence of acrylamide copolymerization of urea-formaldehyde resin adhesives to their chemical structure and performance. Journal of Applied Polymer Science 117(6): 3181～3186.

Arif, N., Park, B.D., Adya, P.S. 2014. Penetration of urea-formaldehyde resins with different formaldehyde/urea mole ratios into softwood tissues, Wood Science and Technology 48: 889～902.

Despres, A., Pizzi, A. 2006. Colloidal aggregation of aminoplastic polycondensation resins: urea-formaldehyde versus melamine-formaldehyde and melamine-urea-formaldehyde Resins, Journal of Applied Polymer Science 100: 1406～1412.

Dunky, M. 1998. Urea-formaldehyde (UF) adhesive resins for wood. International Journal of Adhesion and Adhesives 18(2): 95～107.

Ferra, J., Mendes, A., Costa, M.R., Carvalho, L., Magalhães, F.M. 2010. Characterization of urea-formaldehyde resins by GPC/SEC and HPLC techniques: effect of ageing. Journal of Adhesion Science and Technology 24: 1535～1551.

Ferra, J., Henriques, A., Mendes, A., Costa, M.R., Carvalho, L., Magalhães, F.D. 2012. Comparison of UF synthesis by alkaline-acid and strongly acid processes. Journal of Applied Polymer Science 123(3): 1764～1772.

Iler, R., Mcqueston, H.J. 1974. U.S. Patent No. 3,855,172. Washington, DC: U.S. Patent and Trademark Office.

Jeong, B., Park, B.D. 2016. Measurement of molecular weights of melamine-urea-formaldehyde resins and their influences to properties of medium density fiberboards. Journal of the Korean Wood Science and Technology 44(6): 913～922.

Jeremejeff, J. 2012. Investigation of UF-resins-the Effect of the Formaldehyde/Urea Molar Ratio during Synthesis. Stockholm. Sweden.

Laborie, M.P.G., Salmén, L., Frazier, C.E. 2006. A morphological study of the wood/phenol-formaldehyde adhesive interphase. Journal of adhesion science and technology 20(8): 729～741.

Lei, H., Pizzi, A., Du, G., Despres, A. 2006. Variation of MUF and PMUF resins mass fractions during preparation. Journal of Applied Polymer Science 100(6): 4842～4855.

Ludlam, P.R., King, J.G. 1984. Size exclusion chromatography of urea formaldehyde resins in dimethylformamide containing lithium chloride. Journal of Applied Polymer Science 29(12): 3863～3872.

Majors, R.E. 1980. Recent advances in HPLC packings and columns. Journal of Chromatographic Science 18(10): 488～511.

Paiva, N.T., Pereira, J., Ferra, J.M., Cruz, P., Carvalho, L., Magalha, F.D. 2013. Study of influence of synthesis conditions on properties of melamine-urea formaldehyde resins. International Wood Products Journal 3: 51～57.

Park, B.D., Riedl, B., Hsu, E.W., Shields, J. 1998. Effects of weight average molecular mass of phenol-formaldehyde adhesives on medium density fiberboard performance. Holz als Roh-und

Werkstoff 56(3): 155～161.

Park, B.D., Kang, E.C., Park, J.Y. 2006. Effects of formaldehyde to urea mole ratio on thermal curing behavior of urea-formaldehyde resin and properties of particleboard. Journal of Applied Polymer Science 101(3): 1787～1792.

Pendlebury, E., Lei, H., Antoine, M.L., Pizzi, A. 2010. Melamine-Formaldehyde Resins without Urea for Wood Panels. Journal of Adhesion Science and Technology 24(8-10): 1415～1422.

Tomita, B., Hse, C.Y. 1993. Syntheses and structural analyses of cocondensed resins from urea and methylolphenols, Mokuzai Gakkaishi 39(11): 1276～1284.

Turunen, M., Alvila, L., Pakkanen, T.T., Raninio, J. 2003. Modification of phenol-formaldehyde resol resins by lignin, starch, and urea. Journal of Applied Polymer Science 88(2): 582～588.

Uglea, C.V. 1996. Liquid chromatography of oligomers (Vol. 72). Chaptet 4, 288-289. CRC Press. New York. USA.

Unger, K.K., Janzen, R. 1986. Packings and stationary phases in preparative column liquid chromatography. Journal of Chromatography A 373: 227～264.

Zanetti, M., Pizzi, A. 2003. Colloidal aggregation of MUF polycondensation resins: formulation influence and storage stability. Journal of applied polymer science 91(4): 2690～2699.