Comparison of UF Synthesis by Alkaline-Acid and Strongly Acid Processes

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ABSTRACT: This work discusses two processes for producing urea-formaldehyde (UF) resins. One is the alkaline-acid process, which has three steps: usually an alkaline methylolation followed by an acid condensation and finally the addition of a final amount of urea. The other process, the strongly acid process, consists of four steps, in which the first step involves a strongly acid condensation followed by an alkaline methylolation, a second condensation under a moderately acid pH and finally, methylolation and neutralization under a slight alkaline pH. Two resins were produced using the two above described processes. The molecular weight distribution (MWD) of the resins was monitored off-line by GPC/SEC and the final resins were characterized by GPC/SEC and HPLC. These studies showed that the two resins differ greatly in chemical structure, composition, viscosity, and reactivity. The monitoring of MWD indicated that the first condensation under a strongly acid environment leads to the production of a polymer with a distinctly different chemical structure, therefore increasing the flexibility of polymer synthesis and opening the way to the improvement of end-use properties. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1764–1772, 2012

Key words: urea-formaldehyde resins; alkaline-acid process; strongly acid process; GPC/SEC

INTRODUCTION

Owing to environmental concerns stemming from the formaldehyde emission in wood-based panels, the formulation of urea-formaldehyde (UF) resins has evolved towards a significant decrease in the mole ratio of formaldehyde to urea. Unfortunately, when the aim is to achieve particularly low formaldehyde contents, experience shows that compliance to this goal also brings about a drop in reactivity and in resin stability as well as the degradation in the mechanical properties of the finished boards. It is necessary to further optimize the synthesis of UF resins, studying how the production process can be adjusted to obtain the desired performances.

Several possibilities for the production of UF resins can be found in the literature.[1–8] The most common is the alkaline-acid process,[3,5,7,9] which has three steps—usually an alkaline methylolation followed by an acid condensation and finally the neutralization and addition of the last urea.

Maslosh et al.[10] reported that the alkaline-acid process produces resins with lower content of free formaldehyde as compared with the acid-alkaline process.

According to Christjanson et al.[3] the main advantage of this process consists in the first methylolation step, which allows a higher methylolurea content. The acid condensation step before the methylolation stage promotes the trisubstitution in urea through the formation of branched chains. These species decrease the compatibility with water and the adhesion performance, namely the reactivity.

Graves et al.[5] have found that the addition of triethanolamine in the first methylolation reaction improves not only the resistance to hydrolysis, but also the rate of cure and decrease the formaldehyde rate of release.

The strongly acid process was described for the first time by Williams,[2,8] who has developed a method for producing low emission UF resins, consisting of:

1. Carrying out the condensation of urea and formaldehyde under a highly acid environment and large excess of formaldehyde;

Figure 1 Reaction temperature (—) and pH (---) histories for resin UF-Exp7. These simplified history curves are based on the experimentally measured values. The urea addition (U_i) and sample collection (S_i) times are also indicated in the graph.
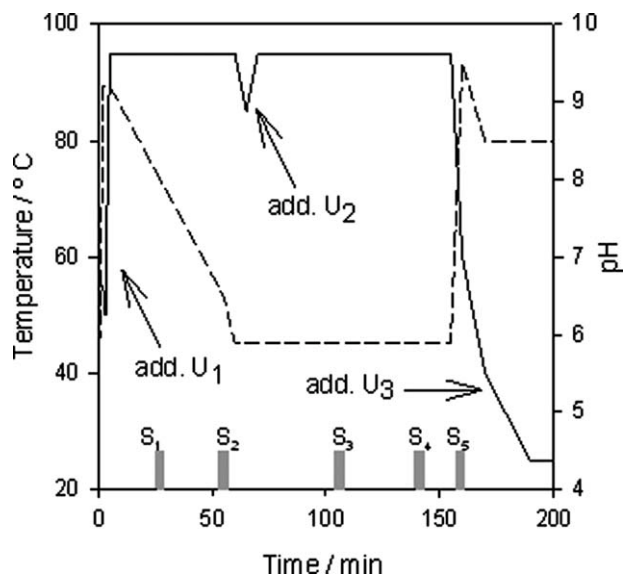

Figure 2 Reaction temperature (—) and pH (---) histories for resin UF-W6. These simplified history curves are based on the experimentally measured values. The urea addition (U_i) and sample collection (S_i) times are also indicated in the graph.

2. Pursuing the reaction in alkaline medium after urea addition, to achieve a predetermined F/U molar ratio;
3. Further carrying out the reaction under a pH of about 5 to allow a supplementary condensation until the desired viscosity is reached;
4. Neutralization and addition of a final amount of urea to obtain the intended low F/U molar ratio.

The Williams process[2,8] entails minimal energy consumption and involves relatively short (3–4 h) reaction times. The reduced formaldehyde emission and increased hydrolytic stability have been attributed to the predominance of the more stable methylene linkages in the cured resin, unlike the alkaline-acid process which leads to a larger amount of methylene ether linkages in the cured resin.

The main problem of this process lies in the control of the strongly acid condensation step, due to its exothermic character. According to Hatjiissaak and Papadopoulou,[4] this implies careful control, which may be difficult to achieve on an industrial scale, to prevent resin gelling in the reactor.

In this work, two resins were produced using the alkaline-acid and strongly acid processes.

The synthesis of the resins was monitored off-line by GPC/SEC and the different results obtained are discussed. It is shown that this relatively simple technique provides relevant information that can be related to the progress of the different reactions taking place in each synthesis process. The resins produce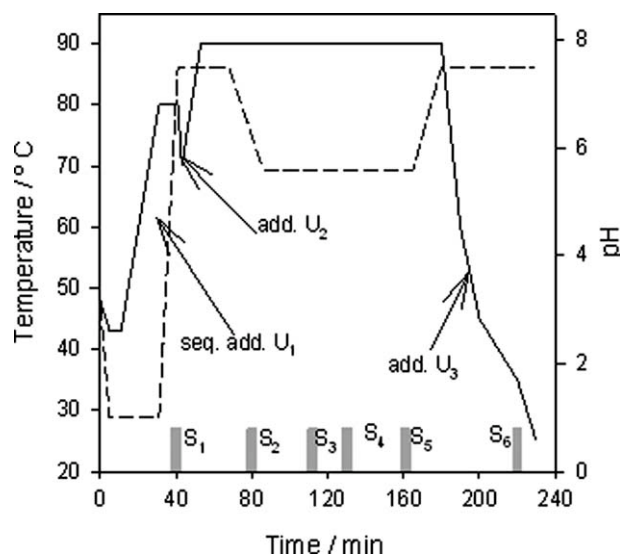d were also characterized by HPLC, to identify the different final compositions in unreacted urea, monomethylolurea, and dimethylolurea.

MATERIALS AND METHODS

Resin preparation

In the preparation of UF resins, industrial-grade raw materials were used, supplied by Euroresinas S.A. (Sines, Portugal), namely: urea, 50% formalin, melamine, hexamine, sodium hydroxide solution (50 wt % solution), acetic acid (25 wt % solution) and sulfuric acid (98 wt % solution). The synthesis of resins was carried out with a bench scale 5-L glass reactor. They were produced according to two synthesis methods.

Resin UF-Exp7 was produced according to the alkaline-acid process and resin UF-W6 according to the strongly acid process. The two procedures are described below.

The two resins are water dispersions with a low amount of melamine (0.3% based on total weight of liquid resin) and hexamine (0.1% based on total

TABLE I
Technical Data of UF-Resins

Resin	Molar ratio F/U	Solids content[a] (%)	Reactivity[b] (s)	pH value (25°C)	Viscosity[c] (mPa s)
UF-Exp7	1.12	64.1	71	8.64	150
UF-W6	1.10	63.3	112	8.16	270

[a] 120 °C, 3 h.
[b] Gel time at 100°C with 3 wt % NH₄Cl (20 wt % solution).
[c] Brookfield viscometer at 25°C.

TABLE II
Identification of Different Stages During the Synthesis (UF-Exp 7)

Stage	Reaction time (min)	Reaction step	T (°C)	pH
Sample 1	27	At the middle of methylolation step	90–100	9.0–9.4
Sample 2	55	At the end of methylolation step	90–100	9.0–9.4
Sample 3	106	During condensation step, when visc. $\sim$ 80 mPa·s at 25 °C	90–100	5.6–6.2
Sample 4	141	During condensation step, when visc. $\sim$ 400 mPa·s	90–100	5.6–6.2
Sample 5	159	Before addition of last urea	<60	>8.5

weight of liquid resin) which are typically added for improving hydrolysis resistance and increase the buffering capacity, respectively.

Alkaline-acid process (synthesis of UF-Exp7)

The reaction of urea and formaldehyde consists basically in a three step process:

i. methylolation step at alkaline conditions;
ii. condensation step at acidic conditions (pH about 5.6) until a viscosity of 350-450 mPa s is attained;
iii. neutralization (pH > 7.5) of the product and addition of a final amount of urea to obtain a desired low formaldehyde/urea ratio.

The formulation of resin UF-Exp7 was based on a previously reported[11] optimization study of the traditional alkaline-acid process. From the design of experiments procedure employed, UF-Exp7 yielded the highest value of internal bonding while maintaining an acceptably low formaldehyde emission value.[11]

After the required amount of 55.5% formaldehyde solution and urea were loaded into a reactor (F/U molar ratio of 2.00–2.15), the reaction mixture was held at the final temperature ($T = 95°C$) for about 30 min under alkaline conditions (pH = 8.5–9.5).

The pH was then adjusted to about 5.6–6.1 with acetic acid solution and the second urea was added sequentially to the previous reaction mixture (four additions of urea and 13 min between additions). The F/U molar ratio after this step is $\sim$ 1.8.

After the desired viscosity being reached, the reaction was stopped by alkalinization with sodium hydroxide solution and cooled down. The third (final) urea was then added at 60°C, yielding a final F/U ratio of 1.12. Figure 1 shows a diagram describing the temperature and pH histories during resin preparation.

Strongly acid process (synthesis of UF-W6)

The reaction consists basically in a four step process:

i. condensation of urea and formaldehyde under a strongly acid environment and a large excess of formaldehyde;
ii. methylolation step at alkaline medium;
iii. condensation at a low pH (about 5) as soon as the desired viscosity was reached;
iv. neutralization (pH > 7.5) and fast cooling; final addition of urea to obtain the specified low F/U molar ratio.
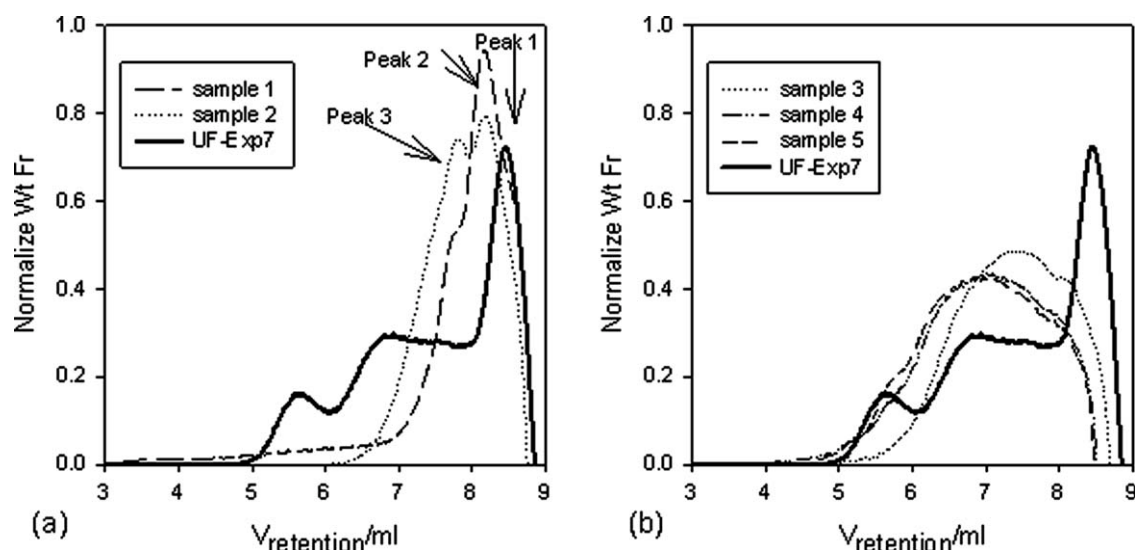

Figure 3 Monitoring of UF-Exp 7 synthesis by GPC/SEC: (a) samples collected during methylolation step, including the chromatogram of the final resin; (b) samples during condensation step, including the chromatogram of the final resin.
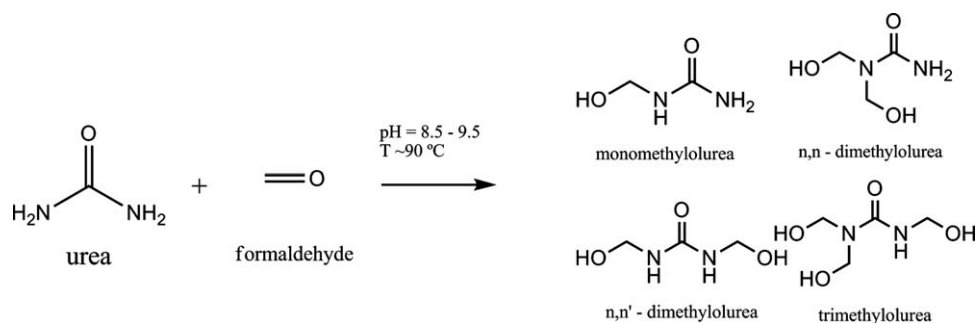
Figure 4 Formation of methylolureas (mono-, di-, and trimethylolurea) by the addition of formaldehyde to urea.

Formaldehyde 55.5% solution was charged into the reactor and the pH value was adjusted to 1-2 using sulfuric acid. Urea ($F/U \sim$ 3.00–3.25) was added in 15 equal parts over a time span of 15 min. The reaction is very exothermic and the temperature increased to 80°C without external heat supply. The temperature was kept at 80°C for 10 min. After 10 min of reaction the pH was adjusted to 7.3–7.5 with a 50% sodium hydroxide solution. A second amount of urea and melamine were charged into the reactor and the temperature was increased to 95°C and the reaction followed during 15 min. The pH was again adjusted to 5.2–6.0 with 25% acetic acid solution and the polymer was condensed until the desired viscosity (450–550 mPa s) was reached. The pH was then adjusted to 7.5 with 50% sodium hydroxide solution and the reacting media was cooled down. At 60°C, the last amount of urea and hexamine were added to the reactor to obtain the specified F/U molar ratio (1.10), and again the pH was adjusted to obtain a pH 7.5–8.5. After the whole amount of urea was dissolved the solution was cooled to room temperature. The temperature and pH histories along resin preparation are shown in Figure 2.

GPC/SEC analysis

A Gilson HPLC system equipped with a Gilson Differential RI detector, a Viscotek Dual Detector (differential viscometer and a light scattering detector RALLS) and a Rheodyne 7125 injector with a 20-μL loop have been used. The selected column was a Waters Styragel HR1 with 5μm particle size, using DMF as eluent. The RALLS detector was not used for the triSEC molecular weight calculations because of the weak response for lower molecular weights. The analysis conditions and sample preparation procedure have been described in detail elsewhere.[12]

HPLC analysis

A JASCO HPLC system equipped with a JASCO Differential RI detector, and a Rheodyne 7725i injector with a 100-μL loop was used. The separation column selected was a Waters Spherisorb NH_2 with 5 μm nominal particle size. Acetonitrile/water (90/10) was used as the mobile phase. The column was conditioned at 30°C using an external oven and the flow rate was 1.5 mL/min.

The samples were prepared according to the procedure described in Ferra et al.[12].

RESULTS AND DISCUSSION

Characteristics of the produced resins

Table I shows the technical data of the two UF resins characterized in this work. The UF resins were stored at 25°C for the chemical analysis in GPC/SEC
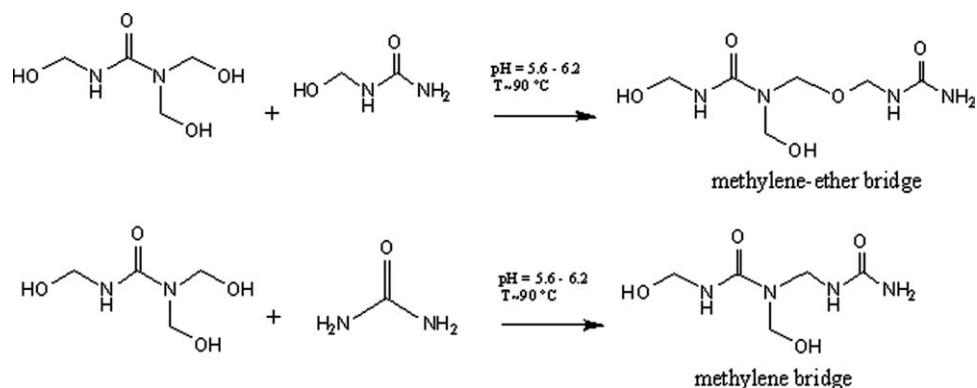

Figure 5 Condensation of the methylolureas and urea to form methylene-ether bridges and methylene bridges.

TABLE III
Values of M_n, M_w, Polydispersity (M_w/M_n) Obtained by GPC/SEC for Samples Collected During the Synthesis of UF-Exp7

Sample	M_n	M_w	M_w/M_n
Sample 1	5.70×10^3	6.18×10^3	1.1
Sample 2	2.98×10^3	4.66×10^3	1.6
Sample 3	3.51×10^3	1.20×10^4	3.4
Sample 4	8.70×10^3	3.18×10^4	3.7
Sample 5	7.39×10^3	3.04×10^4	4.1
UF-Exp7	5.50×10^2	2.78×10^3	5.1

and HPLC. It should be noticed that resin UF-W6 had a high gel time (low reactivity), while viscosity was comparable to the UF-Exp7.

Monitoring of UF resins synthesis

To improve the knowledge on the polymerization reactions occurring in alkaline-acid and strongly acid processes, each synthesis was monitored off-line by GPC/SEC.

Alkaline process

Samples were collected at the moments of the synthesis: start and end of methylolation stage, start, and end of condensation stage and before the addition of the last urea. The complete description of the sampling procedure is presented in Table II. The instants when the samples were collected are also shown on Figure 1.

Figure 3 shows the GPC/SEC chromatograms obtained for the different samples. It is interesting to follow the evolution of the low molecular weight species during the reaction, taking into account the assignment of the peaks, discussed in a previous work[12,13]: Peak 1, urea and methylolureas; Peak 2, methylolureas and some oligomeric species; Peak 3, other oligomeric species. In Figure 3(a) it is possible to observe the formation of methylolureas and oligomeric species in the methylolation stage (see Fig. 4).

The chromatograms obtained for the samples collected during the condensation reaction are presented in Figure 3(b). During this process, the methylolureas are condensated to form linear and/or branched polymers linked by methylene-ether and methylene bridges (see Fig. 5). The almost complete disappearance of the peaks of urea and methylolureas indicates the progress of the condensation reaction. At the same time, moderate molecular weight polymer is formed. The chromatogram of Sample 4 shows the presence of a small amount of insoluble molecular aggregates in solution (elution volume below 5.8 mL).[12,13] Samples 4 and 5 do not differ significantly indicating that the reaction was blocked by the neutralization and cooling of the solution. Comparing the chromatograms for Sample 5 and the final resin, we can see that methylolureas were formed by reaction of the last urea added with free formaldehyde in solution. Note that Peak 1 has been identified as a combination of urea and methylolureas and not urea alone.[12] In addition, some condensation of higher polymer has occurred.

The values of the molecular weight averages (based on polystyrene standards) have been computed for all samples collected during the synthesis and are presented in Table III. According to Ferra et al.[12] the chromatogram fraction corresponding to elution volumes below 5.8 mL corresponds essentially to insoluble material, so the molecular weights were computed neglecting this portion of the chromatograms. The obtained results show the increase of polydispersity of the polymer with the progress of reaction. It is evident the growth of the polydispersity from Sample 2 (methylolation reaction) to Sample 3 (condensation reaction) and the stabilization of polydispersity along the condensation step. The final increase, from Sample 5 to the end product, is related to the last urea addition.

Strongly acid process

Table IV summarizes the information about the samples collected during the monitoring of the synthesis of UF-W6, at key points of the synthesis path: first strongly acid condensation reaction, methylolation reaction, second condensation reaction, and after the addition of the last urea (final methylolation).

As it can be seen from the GPC/SEC analysis in Figures 3–6, the polymerization reactions that take by this process are very different from the ones that take place by the alkaline-acid process.

TABLE IV
Identification of Different Stages During the Synthesis

Stage	Reaction time (min)	Reaction step	T (°C)	pH
Sample 1	40	At the end of the 1st condensation step	76	2.0
Sample 2	80	At the end of the 1st methylolation step	74	7.4
Sample 3	112	At the 2nd condensation step, viscosity $\sim$ 200 mPa s	89	5.5
Sample 4	130	At the 2nd condensation step, viscosity $\sim$ 300 mPa s	90	5.5
Sample 5	161	At the 2nd condensation step, viscosity $\sim$ 500 mPa s	88	5.5
Sample 6	220	After addition of the last urea	35	>7.5
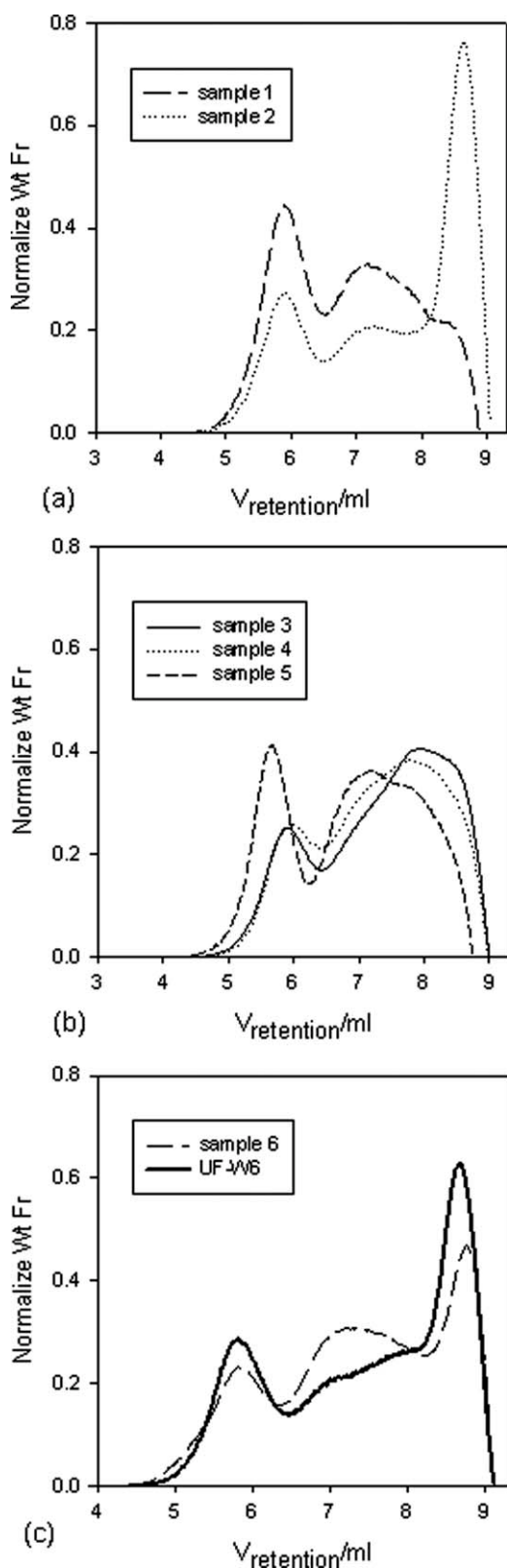
Figure 6 Monitoring of UF-W6 synthesis by GPC/SEC: (a) $\hat{1}$ condensation step and $\hat{1}$ methylolation step; (b) $\hat{2}$ condensation step; (c) $\hat{2}$ methylolation step and final resin.

Figure 6 shows the MWD of the products obtained. High molecular weight material can be seen, which should be constituted by extensive methylene or methylene-ether bridges chains and urons.

In the first condensation reaction under strongly acid conditions the methylolureas were formed, but condensate rapidly to form methyleneureas (e.g., methylene-diurea, dimethylenetriurea, trimethylenetetraurea, etc.)[14] Kadowaki[15] has reported the synthesis of methylene-diurea by the reaction of formaldehyde and urea at acid conditions. The progress of the reaction produces linear products with methylene bridges. Motter[16] has suggested that this polymer is insoluble above 4–8 urea units in the chain. Probably, uron groups are also formed in this step. The formation of uron groups in strongly acid condensation of urea and formaldehyde was reported by Beachem et al.[17] The main reactions taking place in this first stage are presented in Figure 7.

After the condensation reaction, the synthesis proceeds by the methylolation of unreacted formaldehyde and urea (second amount of urea was added in these stage) to form methylolureas (see Fig. 4). This is shown in Figure 6(a) by development of the right most peak in the chromatogram of Sample 2.

Then, the new condensation reaction takes place, forming chains of methylene and methylene-ether bridges, the product of the reaction containing preferentially methylene bridges according to Williams.[2,8] Chromatograms in Figure 6(b) show the condensation of methylolureas forming polymer with larger molecular weight. The polymerization reaction proceeds until the desired viscosity is reached forming a large amount of polymer with high molecular weight, which might be in the form of insoluble molecular aggregates [see chromatograms of Samples 3, 4, and 5 in Figure 6(b)].

Finally, Figure 6(c) shows the last reaction that takes place. The appearance of the peak corresponding to urea and methylolureas (Sample 6) indicates the presence of unreacted urea and its reaction with the remaining formaldehyde.

The values of the apparent molecular weight averages (see Table V) show the broad distributions of the polymer present in the resin UF-W6. This resin has a large fraction of higher polymer, which is particularly important for the cohesive strength of the resins.[9]

Comparison of the two resins

Determination of molecular size distribution

In Figure 8 we can see the GPC/SEC chromatograms for two resins (UF-Exp7 and UF-W6), in terms of the normalized weight fraction (Wt Fr), measured five days after synthesis. In both cases, at least two samples were prepared and analyzed to verify the reproducibility of the results. Three zones, based on the apparent limits of detectable peaks in the chromatograms,
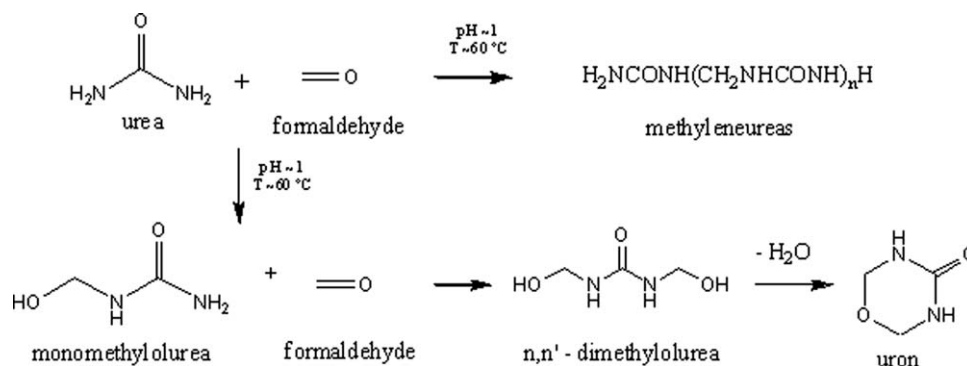
Figure 7 Condensation -reactions of urea and formaldehyde to form methylolureas that form methyleneureas and urons.

can be defined in the chromatograms.[12] The Zone I (elution volume between 8 and 9 mL) corresponds to the lower molecular weight species. Zone II (elution volume between 5.8 and 8 mL) corresponds to intermediate molecular weight species, with apparent molecular weights between about a few tens of thousand Da and about 600 Da. Zone III (elution volume below 5.8 mL) would correspond to polymer with quite high molecular weights, eluting before the exclusion limit of the GPC/SEC column. Ferra et al.[12] and, other authors[18,19] suggested that this portion of the chromatograms actually consists to molecular aggregates and not to solubilized polymer chains. These aggregates are insoluble in the original aqueous medium, forming larger colloidal structures that partially disaggregated in the DMSO solvent used in GPC/SEC sample preparation.[12]

Observing the two chromatograms it can be readily noticed that the UF-W6 resin presents a large fraction of insoluble aggregates as compared with UF-Exp7 and other resins produced according with this method and reported in Ferra et al.[12] It is clear that resin UF-W6 has a smaller fraction of polymer with moderate molecular weights, which reacted previously forming large linear chains of methylene bridges and urons. The fraction of low molecular weight species is superior for UF-Exp7 resin, therefore explaining the higher reactivity of this resin.

As it has been above stated, the molecular weights were computed neglecting the insoluble aggregates.

Ferra et al.[12] have defined two empirical parameters as an aid for quantifying the features of the MWD in UF resins;

- f_1 reflecting the amount of low molecular weight species in the sample;

$$f_1 = \frac{\text{Area of Zone I}}{\text{Total area of chromatogram}}. \qquad (1)$$

- f_2 related to the relative importance of what would be the high molecular weight species in the polymerized material.

$$f_2 = \frac{\text{Area of Zone III}}{\text{Area of Zone II} + \text{Zone III}}. \qquad (2)$$

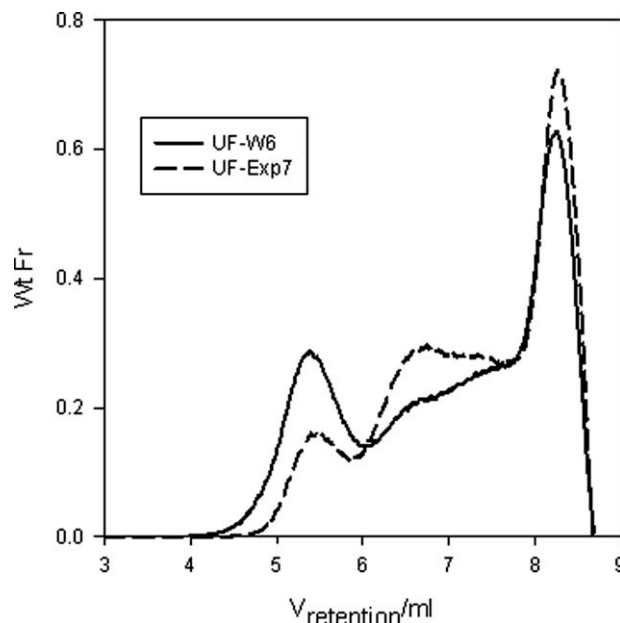Table VI shows the numerical values obtained of these parameters for the two resins studied in this

Figure 8 Chromatogram for four resins (UF-W6 and UF-Exp7) with five days (stored at 25°C).

TABLE V
Values of M_n, M_w, Polydispersity (M_w/M_n) Obtained by GPC/SEC for Samples Collected During the Synthesis of UF-W6

Sample	M_n	M_w	M_w/M_n
Sample 1	7.13×10^2	1.64×10^4	22.9
Sample 2	3.25×10^2	3.34×10^3	10.3
Sample 3	7.30×10^2	5.96×10^3	8.2
Sample 4	6.48×10^2	4.75×10^3	7.3
Sample 5	7.49×10^2	6.66×10^3	8.9
Sample 6	2.06×10^2	1.69×10^3	8.2
UF-W6	2.75×10^2	7.23×10^3	26.3

work. These results support the previous statements derived from the direct inspection of the chromatograms.

Determination of the fraction of urea and methylolureas

Following the procedure described by Ferra et al.[13] the fraction of free urea and methylolureas present in final resins was measured by HPLC, as seen in Figure 9.

The distribution of the unreacted urea, monomethylolurea, and dimethylolurea present in solution five days after the synthesis shows that the UF-W6 resin has a much larger fraction of unreacted urea than resin UF-Exp7. As the amount of last urea incorporated was similar for the two resins, other characteristics had an impact on the distribution of unreacted urea in the final resin. The main difference in the last step of the process is a rapid cooling that takes place after addition of the last urea for the strongly acid process. This action delays the consumption of urea, which remains unreacted in the final resin. However, this unreacted urea may play another role, since it may form a solvatation layer surrounding the colloidal aggregates surface, contributing to its stabilization towards agglomeration.[12] Recently, Park et al.[20] reported that the unreacted urea can also be a good scavenger of formaldehyde during the hot-pressing of the particleboards.

Resin UF-Exp7 has a large fraction of monomethylolurea as compared with the other resin, but the fraction of dimethylolurea is similar.

CONCLUSIONS

This work describes two pathways for producing UF resins, the alkaline-acid and the strongly acid processes; the synthesized resins were followed by GPC/SEC. It was found that the polymer formed by the two processes is quite different. At the first stage of the strongly acid process, polymer with high molar mass (containing essentially links of methylene groups) is formed, in contrast with the alkaline-acid process, where this has to be avoided because of possible resin gelling inside the reactor.

This study shows the capabilities of the GPC/SEC technique for monitoring and controlling the synthesis of UF resins. This is more evident when compar-
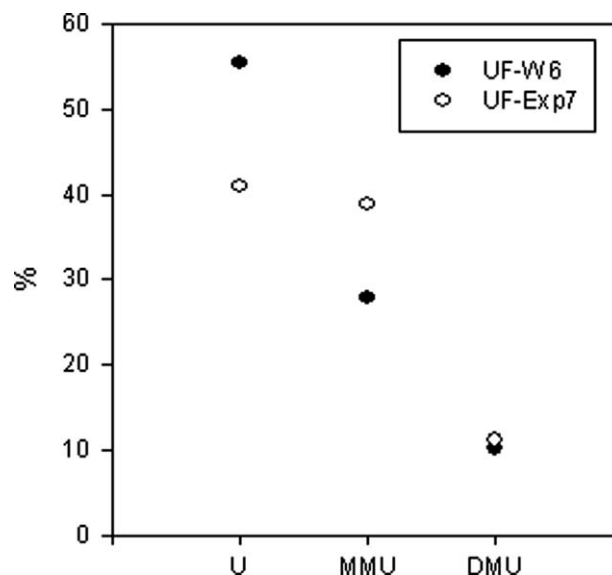

Figure 9 Ratios of peak areas/total area of the urea (U), monomethylolurea (MMU) and dimethylolurea (DMU) for UF-W6 and UF-Exp7 resins, with five days (stored at 25°C).

ing resins produced by different processes. The technique permits to quickly identify the evolution of polymer formation in different reaction steps, with a high reproducibility.

The measured molecular weight distribution of UF resins shows that the resin produced by the strongly acid process has a great fraction of insoluble molecular aggregates, which is believed to contribute to a higher resin cohesive strength. However, it has also a smaller fraction of low molecular weight species when compared with the alkaline-acid process, which might contribute to improve resin wettability on the wood substrate.

The results obtained by HPLC showed that the resins produced by the strongly acid process have a large fraction of unreacted urea and a small fraction of monomethylolurea in contrast with the alkaline-acid process.

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TABLE VI
Values of M_n, M_w, and Parameters f_1 and f_2, Obtained by GPC/SEC for Resins (UF-W6 and UF-Exp7)

Sample	M_n	M_w	f_1	f_2
UF-Exp7	5.50×10^2	2.78×10^3	0.40	0.045
UF-W6	2.75×10^2	7.23×10^3	0.35	0.13

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