^{13}C NMR Study of Presence of Uron Structures in Amino Adhesives and Relation with Wood-Based Panels Performance

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ABSTRACT: The chemical structure of amino adhesives produced by the strongly acid process was investigated by ^{13}C Nuclear Magnetic Resonance spectroscopy. This technique allowed the identification of functional groups and its quantitative determination. Concentration of cyclic polymeric structures (urons) was shown to be related with adhesive performance and with particleboard physico-mechanical properties and formaldehyde content. Higher urons concentration presented lower viscosity and reactivity. Particleboards produced with resins with lower urons concentration presented lower formaldehyde content, but also lower internal bond strength. Wood-based panels produced fulfilled E1 class requirements for formaldehyde emissions, indicating that strongly acid process is an alternative to the conventional alkaline–acid process. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 4500–4507, 2013

INTRODUCTION

Urea-formaldehyde (UF) resins are the most important type of adhesives for wood-based panels, such as particleboard, medium density fiberboard, or plywood, because of their excellent adhesion to wood, fast curing, good performance, and low cost. However, poor durability under high-humidity or high-temperature environments and formaldehyde emission levels from panels are important disadvantages for these resins. Formaldehyde emissions result not only from residual unreacted formaldehyde, but also from formaldehyde production by condensation reactions between methylol groups during cure, and from hydrolytic degradation of weak chemical bonds (reversibility of aminomethylene links) in cured resins.[1,2] Rammon[3] reported that the ether linkages on UF resins are related to formaldehyde emission, and their formation are related to synthesis variables such as pH or condensation step. Costa et al.[4] reported that the hexamine formed during cure decomposes during the life-time of the panel contributing for formaldehyde emission specially in low formaldehyde emitting boards. Formaldehyde emission has been recognized as a potential source of indoor air pollution that may lead to possible health problems.

This has led to stricter standard regulations and has been forcing the wood-based panels industry to reduce the level of emitted formaldehyde from UF resin-bonded panels.

The conventional UF resins synthesis procedure, so called alkaline–acid process, consists of two main steps: an alkaline methylolation followed by an acid condensation.[1] After these, urea is usually added under alkaline environment, reacting with free formaldehyde and forming new methylolureas. Williams studied the alternative strongly acid process,[5,6] which consists of simultaneous methylolation and condensation under highly acidic environment and large excess of formaldehyde, followed by a neutralization and addition of more urea (known as second urea). Then, a second condensation under moderate acidic environment takes place until the desired viscosity is attained. Finally, the resin is neutralized with sodium hydroxide and more urea (known as final urea) is added to attain the desired final F/U molar ratio. According to Williams,[5] the strongly acid process entails minimal energy consumption and involves a shorter batch time reaction, when compared with the conventional process. Hatjiissaak and Papadopoulou[7] reported the extremely exothermic reaction of the strongly acid step and the

difficulty to transpose this process from the laboratory to the industrial scale. Ferra et al.[8] also observed the high exothermicity of the reaction and compared the reactivity of resins obtained by both processes, reporting lower reactivity of resins produced by the strongly acid process when compared with the alkaline–acid procedure.

The complex structure and chemistry of UF resins has been subject of numerous research studies, but their physical, morphological, and chemical properties are not yet fully understood. The large variety of structural elements such as methylene bridges, ether bridges, methylol and amide groups or possible cyclic compounds makes their analysis very difficult.[9] In the same way, the effect of changing synthesis parameters (for example, pH, temperature, F/U molar ratios) on the chemical structure of the resin has not been well established.

Among the NMR spectroscopy methods, liquid-state ^{13}C NMR has provided the most complete information on the chemical structures present in UF resins (that can be dissolved in appropriate solvents) and the reactions occurring in their formation. In a ^{13}C NMR experiment, the chemical shift (δ) is a sensitive probe of the chemical structure and the large chemical shift range makes ^{13}C NMR an attractive technique for the analysis of these resins. In addition, this analytical method allows the identification of several functional groups present in the resins and its quantitative determination.[10] Over the years, many works have been performed by different researchers using ^{13}C NMR to identify the chemical structure of UF resins synthesized under different pH conditions.[2,9,11–14] Some authors have shown that uronic structures are present in the resins when strongly acidic conditions are employed. Gu et al.[12] showed that substituted uronic structures are formed only for resins synthesized at pH equal to 1 and a smaller amount of methylol group than the other resins produced at higher pH. Soulard et al.[13] determined that the pH ranges that favor formation of urons and its derivatives are above six and below four and that the reactivity of methylol groups in uronic structures is much lower that for methylol groups on the noncyclic structures of urea. Tohmura et al.[14] concluded that resins prepared under strongly acidic conditions have better heat stability than those produced under weakly acidic and alkaline conditions, possibly because of some aromatic character present in the urons formed.

However, the influence on physico-mechanical properties and formaldehyde emission of wood-based panels are not well understood. Hse et al.[11] reported that resins produced in strongly acid environment produce boards with lower internal bond (IB) strength, lower bending strength, and lower formaldehyde emission. Gu et al.[12] found that resins produced under strongly acid environment were less reactive and wood-based panels produced with these resins had lower bond strength and lower formaldehyde emission. Park et al.[2] also reported the lower viscosity and lower free formaldehyde concentration in UF resins produced at low pH. Obviously, the results of formaldehyde emissions reported by these authors are significantly higher than those nowadays considerer as "low", as the emissions levels on wood-based panels have been continuously reduced along the last decades.[15]

This work uses liquid state ^{13}C NMR to study the chemical structure of liquid UF resins synthesized under different pH and temperature conditions. This information was related to the performance of the resins, in terms of viscosity and reactivity. Particleboards produced with these resins were characterized in terms of physico-mechanical properties and formaldehyde content (FC) by perforator method.

MATERIAL AND METHODS

Materials

Seven UF resins were provided by EuroResinas S. A. (Sines, Portugal). All resins were produced according to the strongly acid process, as described by Ferra et al.[8] The reaction steps involved are described in detail in Costa et al.[16] (no additives were added); for the resins used in the current work, the synthesis conditions differed only in the first step (condensation step). Two production series were considered. In the first series (resins A, B, C, and D) different condensation pH values were used, between 2.0 and 0.5. In the second series (resins E, F, and G) different condensation temperatures were used, between 80°C and 90°C,

Wood particles, paraffin, and ammonium sulfate were supplied by Sonae Indústria PCDM (Oliveira do Hospital—Portugal) for the production of particleboards.

Methods

Liquid ^{13}C NMR Experiments. The ^{13}C NMR spectra of the liquid resins were obtained with a Bruker Avance III 400 NMR spectrometer, at a frequency of 100.6 MHz. Chemical shifts (δ) were calculated relative to TSP (3-(trimethylsilyl) propionic acid sodium salt), as the external reference, dissolved in D_2O for NMR control. At about 1 mL of liquid 63% solids resin was added to 0.4 mL of deuterium oxide and then the mixture was placed in an NMR tube. The high concentration of the samples allowed very good signal/noise ratios.

To acquire quantitative peak intensities (integrated areas) from ^{13}C NMR spectra, sufficient delay time between pulses must be used to allow total relaxation of all carbon resonances. This requires the knowledge of the range of spin-lattice relaxation times, T_1. Tomita and Hatono[17] used an inversion recovery experiment to determine the T_1 and suggested that a pulse interval of 5 s was needed to obtain a reliable spectrum. So, all spectra were run with a relaxation delay of 5 s. The quantitative analysis was performed through a decoupling process of proton–carbon interactions without introducing NOE effect (nuclear Overhauser effect) on the peak intensities. The quantitative spectra were obtained with about 8200 scans and took approximately 16 h to accumulate.

Resin Characterization. Viscosity was measured with a Brookfield DV-III Ultra viscometer with a 62 spindle at 60 rpm. Samples were previously cooled until 25°C.

The gel time of the final resins was measured in a laboratory test tube immersed in boiling water, corresponding to the time necessary to attain the onset of gelification. A 20% wt ammonium sulfate solution was used as catalyst.

UF resins were analyzed by gel permeation chromatography (GPC)/SEC using a Gilson Differential RI detector and a
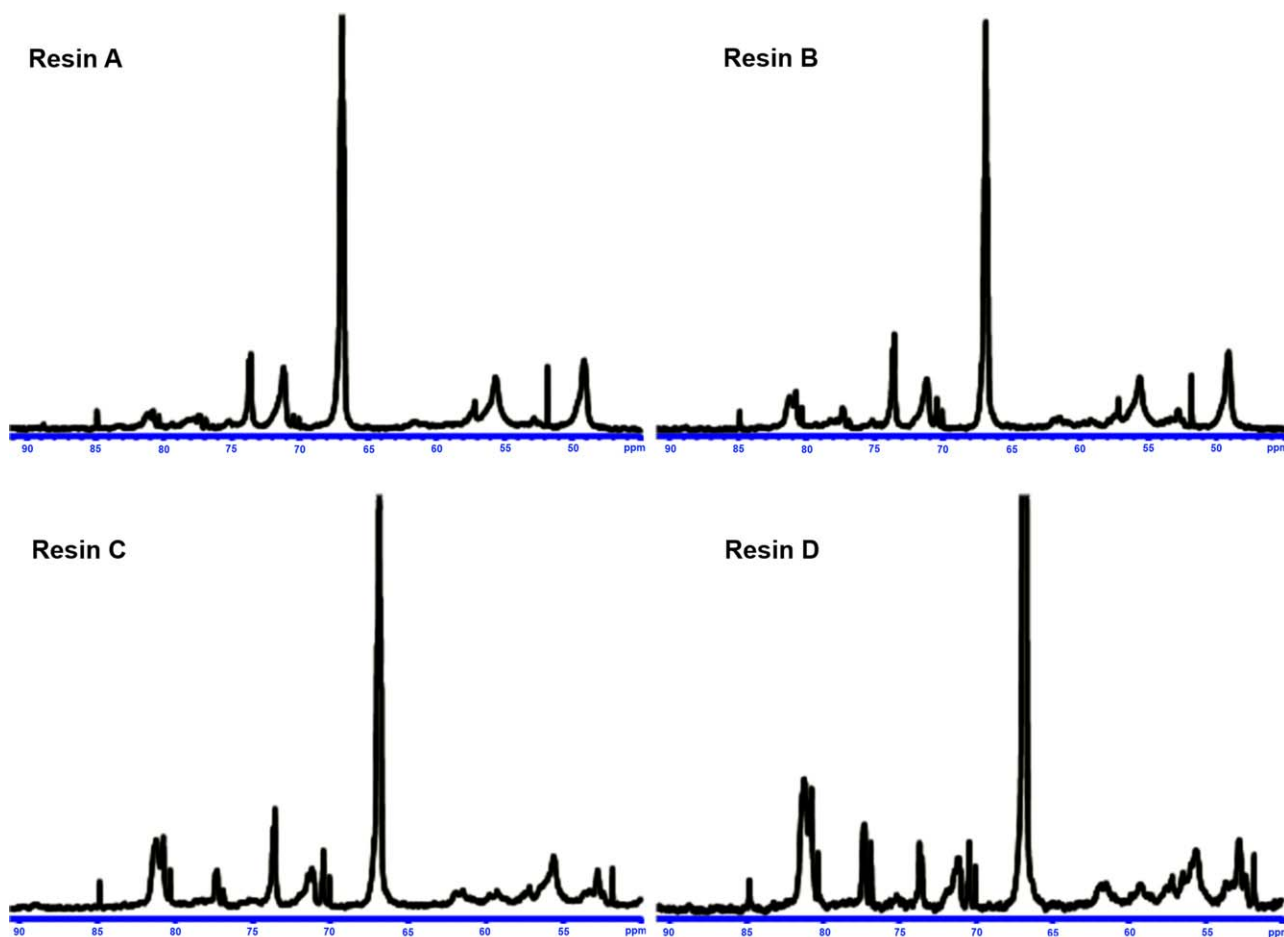
Figure 1. ^{13}C NMR spectra of resins A, B, C, and D. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Rheodyne 7125 injector with a 20 μL. The columns were PSS Protema 100 and 300 μm placed in an external oven at 60°C. A flow rate of 1 mL/min of dimethylformamide was used as mobile phase. Samples for analyses were prepared dissolving a small amount of resin in dimethylsulfoxide (DMSO), followed by vigorous stirring. Subsequently, the sample was left to rest and filtered with a 0.45-μm nylon syringe filter, following the protocol described by Ferra et al.[18]

Particleboards Production and Characterization. Wood particles were blended with resin, catalyst, and a hydrophobic agent (paraffin) in a laboratory glue blender. Surface and core layers were blended separately. The amount of solid resin was 7.0, in surface and core layers (based in oven dry wood). The catalyst level in the core layer was 3 wt % (g dry catalyst per g solid resin).

After blending, a three-layer particleboard mat was hand formed in a deformable aluminum container (220 × 220 × 80 mm^3). Wood amount was determined in order to obtain boards with target densities of 650 kg/m^3. Surface and core layer differ in particle size distribution and moisture content (MC). The mass distribution was 20% for the upper surface layer, 62% for the core layer, and 18% in the bottom surface layer.

The mats were pressed in a computer-controlled laboratory batch hot-press equipped with a linear variable displacement transducer (LVDT), a pressure transducer and thermocouples. Five boards were produced for each synthesized resin. The pressing time of particleboards was 120 s and the final board thickness was 16 mm.

After production, boards were hermetically conditioned until performance evaluation. All tests were carried out according to the European Standards for particleboard testing: IB (EN 319), MC (EN322). FC was evaluated according to EN 120. The values were corrected for 6.5% of MC, according to the EN 312 standard.

RESULTS AND DISCUSSION

Liquid ^{13}C NMR Interpretation

The ^{13}C NMR spectra of analyzed UF resins can be split into four main areas:

1. from 45 to 60 ppm are observable signals from carbons on methylene groups;
2. from 65 to 72 ppm are observable signals from carbons on methylol groups;
3. from 69 to 90 ppm are observable signals from carbons on methylene-ether groups;

4. from 160 to 170 ppm are observable signals from carbons on substituted and unsubstituted urea carbonyl groups.

An expansion of the quantitative ^{13}C NMR spectra of the resin produced under different acidic pH, where some of the regions mentioned above can be observed, is shown in Figure 1.

The structural assignments of chemical shifts of resins and the corresponding integrated areas are summarized in Tables I and II.

The interpretation of the spectra is complex, but can give a good indication on the structure and nature of the linkage groups present in the resins, and can also help in relating the

Table I. Structural Assignments of Chemical Shifts of Resins (A, B, C, and D) and the Corresponding Integrated Areas

| | Resins | | | | | | | |
| | Resin A | | Resin B | | Resin C | | Resin D | |
Functional groups	δ (ppm)	Area	δ (ppm)	Area	δ (ppm)	Area	δ (ppm)	Area
Urea {U}								
NH$_2$CONH$_2$	165.4	1.00	165.4	1.00	165.4	1.00	165.4	1.00
Carbonyl Group {C}								
NH$_2$CONH-{C1}	163.7	1.21	163.7	1.06	163.7	0.61	163.7	0.74
NH$_2$CONH = {C2}	163.2	0.09	163.2	0.06	163.2	0.04	163.2	0.02
-NHCONH-{C3}	162.1	1.01	162.2	0.81	162.2	0.54	162.1	0.61
=NCONH-{C4}	161.7	0.35	161.7	0.36	161.7	0.20	161.7	0.19
=NCON = {C5}	–	–	–	–	–	–	–	–
Methylene Group {Me}								
-NHCH$_2$NH-{Me1}	49.1	0.41	49.1	0.37	49.1	0.17	49.0	0.16
N(CH$_2$)-CH$_2$NH-{Me2}	55.6	0.43	55.6	0.32	55.6	0.24	55.6	0.22
NH(CH$_2$-)CH$_2$N(CH$_2$-)-{Me3}	61.6	0.06	61.5	0.10	61.5	0.05	61.5	0.09
Methylol Group {Mo}								
-NHCH$_2$OH-{Mo1}	66.8	1.28	66.8	0.95	66.8	0.72	66.8	0.95
-N(CH$_2$-)CH$_2$OH {Mo2}	71.2	0.32	71.2	0.23	71.2	0.11	71.1	0.13
Ether Group {E}								
-NHCH$_2$OCH$_3$ {E1}	73.6	0.19	73.6	0.21	73.6	0.13	73.6	0.06
-N(CH$_2$-)CH$_2$OCH$_3$ {E2}	77.4	0.13	77.4	0.06	77.3	0.06	77.3	0.12
-NHCH$_2$OCH$_2$OH {E3}	–	–	–	–	–	–	–	–
-NHCH$_2$OCH$_2$NH-{E4}	70.5	0.03	70.5	0.05	70.4	0.04	70.4	0.05
-N(CH$_2$-)CH$_2$OCH$_2$NH-{E5}	–	–	–	–	–	–	–	–
Methoxy Group								
-NHCH$_2$OCH$_3$	57.2	0.11	57.2	0.09	57.2	0.07	57.2	0.09
Methanol								
CH$_3$OH	51.8	0.04	51.8	0.03	51.8	0.01	51.8	0.02
Free Formaldehyde {F}								
HOCH$_2$OH	84.8	0.01	84.8	0.01	84.8	0.01	84.8	0.01
Uron {UR}								
HN - CO - NH $\mid$ $\mid$ {UR1} CH$_2$ - O - CH$_2$	157.9	0.13	157.9	0.21	157.7	0.22	157.9	0.36
HN - CO - NH $\mid$ $\mid$ {UR2} CH$_2$ - O - CH$_2$	80.8	0.11	80.8	0.22	80.7	0.27	80.8	0.40
- N - CO - N - $\mid$ $\mid$ {UR3} CH$_2$ - O - CH$_2$	–	–	–	–	–	–	–	–
Acids {A}								
H-COO$^-$ {A1}	–	–	–	–	–	–	173.7	0.01
Acid {A2}	–	–	–	–	–	–	188.1	0.01

Table II. Structural Assignments of Chemical Shifts of Resins (E, F, and G) and the Corresponding Integrated Areas

	Resins					
	Resin E		Resin F		Resin G	
Functional groups	δ (ppm)	Area	δ (ppm)	Area	δ (ppm)	Area
Urea {U}						
NH$_2$CONH$_2$	165.3	1.00	165.2	1.00	165.2	1.00
Carbonyl Group {C}						
NH$_2$CONH-{C1}	163.5	1.29	163.5	1.27	163.5	1.08
NH$_2$CONH = {C2}	163.0	0.09	163.0	0.08	163.0	0.07
-NHCONH-{C3}	161.9	1.22	161.9	1.20	161.9	1.01
= NCONH-{C4}	161.5	0.43	161.5	0.44	161.5	0.46
= NCON = {C5}	–	–	–	–	–	–
Methylene Group {Me}						
-NHCH$_2$NH-{Me1}	49.0	0.39	49.0	0.43	49.0	0.28
N(CH$_2$)-CH$_2$NH-{Me2}	55.5	0.51	55.5	0.55	55.5	0.29
NH(CH$_2$-)CH$_2$N(CH$_2$-)-{Me3}	61.4	0.05	61.3	0.09	–	–
Methylol Group {Mo}						
-NHCH$_2$OH-{Mo1}	66.7	1.90	66.7	1.84	66.7	1.34
-N(CH$_2$-)CH$_2$OH {Mo2}	71.0	0.31	71.0	0.32	71.0	0.22
Ether Group {E}						
-NHCH$_2$OCH$_3$ {E1}	73.6	0.29	73.6	0.28	73.6	0.24
-N(CH$_2$-)CH$_2$OCH$_3$ {E2}	77.6	0.10	77.7	0.14	77.6	0.09
-NHCH$_2$OCH$_2$OH {E3}	–	–	88.7	0.01	–	–
-NHCH$_2$OCH$_2$NH-{E4}	70.3	0.01	70.3	0.03	70.3	0.02
-N(CH$_2$-)CH$_2$OCH$_2$NH-{E5}	–	–	–	–	–	–
Methoxy Group						
-NHCH$_2$OCH$_3$	57.1	0.09	57.1	0.12	57.0	0.05
Methanol						
CH$_3$OH	51.7	0.03	51.7	0.04	51.7	0.01
Free Formaldehyde {F}						
HOCH$_2$OH	84.7	0.01	84.7	0.02	84.7	0.01
Uron {UR}						
HN - CO - NH | | {UR1} CH$_2$ - O - CH$_2$	157.8	0.01	157.8	0.04	157.8	0.08
HN - CO - NH | | {UR2} CH$_2$ - O - CH$_2$	80.7	0.05	80.6	0.09	80.7	0.09
- N - CO - N - | | {UR3} CH$_2$ - O - CH$_2$	159.8	0.01	159.8	0.02	159.8	0.02
Acids {A}						
H-COO$^-$ {A1}	–	–	–	–	–	–
Acid {A2}	–	–	–	–	–	–

synthesis conditions with the resulting structures. Thus, each signal observed in the spectra of all resins was identified according to chemical shifts reported earlier by other authors.[13,17,19]

The peaks in the low-field resonance, 160–170 ppm, were assigned to the carbonyl carbons of substituted and unsubsti-tuted urea. In the case of substituted urea, two peaks of high intensity are visible, but each one has another smaller peak overlapped. In the same way as Kim and Amos[20] had already reported, we assigned each signal in this range to the different species of urea: unsubstituted urea, monosubstituted urea, simultaneously di and tri-substituted urea, and finally a very
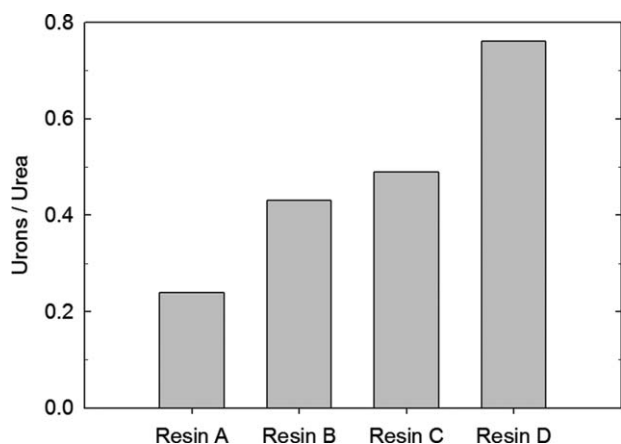
Figure 2. Relative proportion between urons and urea for resins produced under different acidic environments.
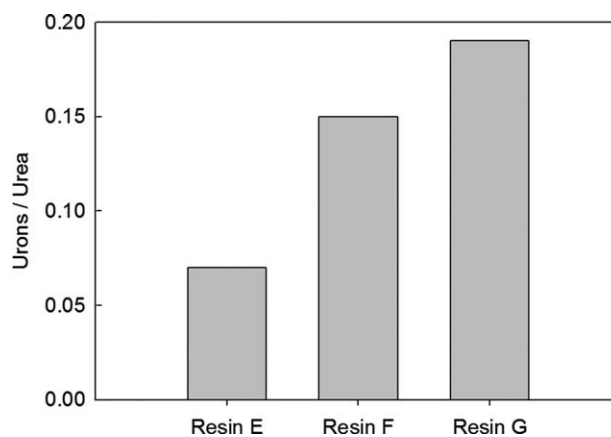

Figure 3. Relative proportion between urons and urea for resins produced under different condensations temperatures.

low intensity peak corresponding to tetrasubstituted urea, which is not identified in all spectra.

The high-field region of each ^{13}C NMR spectrum, 45–90 ppm, indicates that besides the methylol groups resulting from urea and formaldehyde reaction, there are also methylene and dimethylene-ether structures and methylene glycol. The latter group corresponds to the free formaldehyde present in the resin. The highest peak in this region is assigned to the methylol group, which may indicate that methylolation was extensive in the synthesis. The identification of methylene linkages is relevant since these are more stable to hydrolytic degradation than methylene-ether bonds. The spectra also indicate the presence of methanol and methoxy groups resulting from the reaction of methanol with methylene glycol.

Uronic structures (cyclic compounds of urea and formaldehyde) were also identified in all spectra of resins. These assignments have been also previously reported by many authors.[11,13,17] Thus, urons displayed signals at about 158 ppm, attributed to carbonyl carbons, and at about 81 ppm, assigned to carbons in CH_2 groups.

The ^{13}C NMR signal areas of the various functional groups were determined by integration of the quantitative peak inten-

sities in the spectrum. To get the integrated areas of some severely overlapped peaks, a deconvolution process was used. However, it should be pointed out that the integrated areas or intensities of ^{13}C NMR peaks can never be taken as a measure of the abundance of a chemical group.

This work allowed studying the effect of reaction pH of the UF resins synthesized by the strongly acid process on the final resin structure and on the relative amount of produced urons. As shown in Figure 2, the quantitative amount of uronic structures increases as the acidity conditions increase. Although dimethylene ether group (E4) could be involved in the formation of uron rings, the difference between all resins is not relevant.

Uronic structures were also identified in all spectra of the UF resins prepared under different reaction temperatures. Figure 3 shows that the relative quantity of urons increases with the condensation temperature.

Soulard et al.[13] prepared UF resins using a procedure based on the conventional alkaline–acid process, in order to maximize the proportion of urons present at the end of the reaction. During the synthesis the pH was monitored. They found that the maximum quantity of urons at the end of reaction (pH 2.3) approached almost 50% of total urea present (uron + urea). These authors also stated that the uron amounts do not change

Table III. Relative Amount of Urons, Viscosity, and Gel Time of the Produced Resins and Corresponding Particleboard Properties

| Resin | Resins properties | | | Particleboards properties | |
	Urons/urea	Viscosity (cP)	Gel time (s)	Internal bond (N/mm^2)	Formaldehyde content (mg/100 g oven dry board)
A	0.24	150	56		
B	0.43	100	66		
C	0.49	80	97	a)	a)
D	0.76	70	104		
E	0.07	170	41	0.47	6.0
F	0.15	190	53	0.39	5.8
G	0.19	230	57	0.39	5.4

Particleboards were not produced because of the lower adhesive viscosity that will cause excessive penetration on wood particles.

much during the final neutralization procedure. In our work, and at pH values near 2, we achieved lower concentration values, which could indicate that, depending on reaction conditions, it is possible to decrease the formation of urons, even for the strongly acid process.

Resins Properties

Figure 2 shows that increasing acidic conditions during condensation leads to an increase in urons concentration. The resins with higher urons concentration present lower viscosity and higher gel time, as seen for resins A to D in Table III. An increase in gel time corresponds to a decrease in resin reactivity. Gu et al.[12] and Soulard et al.[13] have also shown that higher amount of urons implies lower reactivity. Resins A, B, and C presented a final viscosity below the standard requirements for adhesives for particleboards production. Usually, the target viscosity must lie between 150 and 500 cP, as lower viscosities cause excessive penetration of adhesive on wood, increasing the consumption of resin, and higher viscosities will bring flow problems in adhesive spray on the industrial plant.[21,22] On the other hand, lower reactivity will increase pressing time and therefore decrease productivity. As these resins presented reactivity and viscosity values below standard requirements for commercial manufacture, particleboards production was not performed.

Figure 3 shows the effect of condensation temperature on urons formation during synthesis. Higher temperatures increase urons concentration in the final resin. In this study, a reduction of 10°C has reduced the urons concentration by one third. These resins were produced at a pH near to the resin A, to obtain a lower concentration of urons and maximize reactivity and viscosity properties. As seen in Figure 4, a linear relation was found between urons concentration and gel time. The gel time of these resins is below 60 s and viscosity above 150 cP.

GPC technique has been shown to allow differentiation of formaldehyde-based resin based on polymeric structure.[16,23] Chromatograms shown in Figure 5 evidence that the polymeric structure of resins E, F, and G is similar, supporting that the main differences are related to small oligomers, namely uron structures, as suggested.
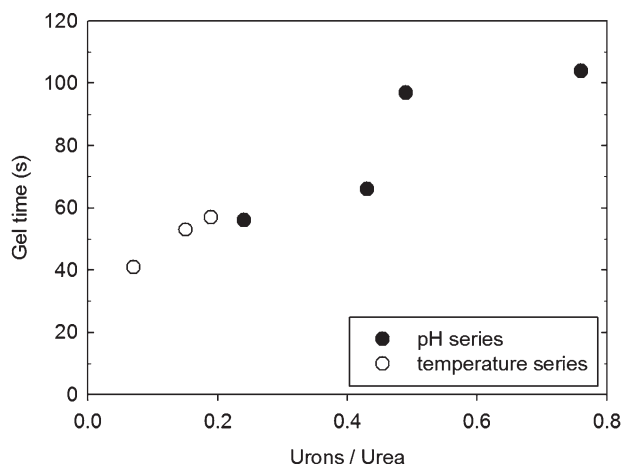
Figure 4. Relation between concentration of urons and gel time of resins produced.
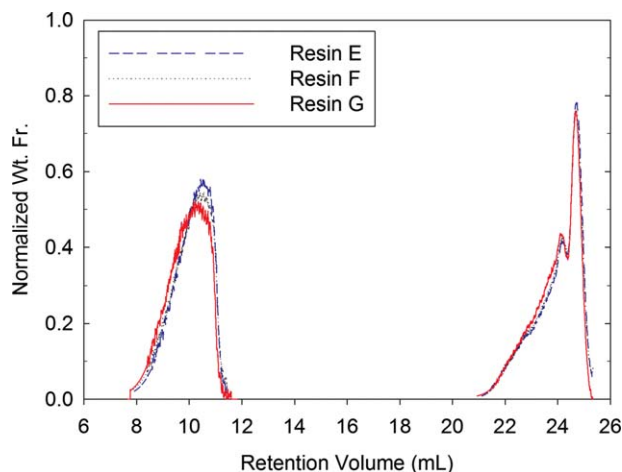
Figure 5. GPC chromatograms of resins E, F, and G. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The particleboard properties presented in Table III, for resins E, F, and G, shows that resins with higher urons concentration present lower FC, but also lower IB strength. Hse et al.[11] and Gu et al.[12] also obtained lower free formaldehyde on resins with higher amount of cyclic structures. These authors found that resins produced under strongly acid environments exhibited lower reactivity and the boards produced thereof presented lower formaldehyde emissions and IB strength. The apparent relation between decreasing FC and increasing urons concentration may be because of the higher stability of these species. On the other hand, lower IB strength may be related to lower reactivity.

CONCLUSIONS

^{13}C NMR spectroscopy was applied in the analysis of the amino adhesives synthesized by the strongly acid process at different reaction pH and temperature. This analytical technique allowed the identification of many functional groups present in the resins and its quantitative determination. A detailed description of the chemistry and polymer structure was obtained. Lower pH and higher temperatures originated higher concentrations of uronic structures.

A relation between resin properties and concentration of uronic structures was found: higher urons concentration lead to a decrease on resin viscosity and reactivity. Higher condensation temperatures also induced formation of urons. However, these resins presented lower reactivity and particleboards with lower IB strength, despite lower FC on particleboards.

All boards produced were according to the class E1 requirements, meaning that strongly acid process can be an alternative to the conventional alkaline–acid process and should not be disregarded in future studies.

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