

A Study on the Colloidal Nature of Urea-Formaldehyde Resins and Its Relation with Adhesive Performance

João M. M. Ferra,¹ Adélio M. Mendes,¹ Mário Rui N. Costa,² Luisa H. Carvalho,³
Fernão D. Magalhães¹

¹LEPAE -Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

²LSRE -Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

³DEMAd -Departamento de Engenharia de Madeiras, Instituto Politécnico de Viseu, Campus Politécnico de Repeses, Viseu 3504-510, Portugal

Received 6 October 2008; accepted 3 July 2009

DOI 10.1002/app.31112

Published online 10 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Urea-formaldehyde (UF) resins present a swollen colloidal phase dispersed within a continuous water phase containing soluble oligomers. The main goal of the present investigation is to clarify the physical and chemical nature of those two phases and elucidate their impact on the bonding process. Optical and electronic microscopy has provided information on the morphology of the colloidal phase, showing primary particles and particle agglomerates. Mechanisms are suggested for the colloidal stabilization and dilution-induced flocculation. Three commercial UF resins with different *F/U* molar ratios were studied using particle size distribution (PSD) analysis. The results showed the influence of the resin's degree of condensation and the aging status on the size of the colloidal structures. Gel permeation chromatography

analysis was performed on samples of different resins and of the respective continuous and dispersed phases, separated by centrifugation. The quantified fraction of insoluble molecular aggregates present in the chromatograms was related to the resins synthesis conditions and age. Differential scanning calorimetry and tensile shear strength tests were performed to evaluate the reactivity and adhesive performance of each phase. It is suggested that the colloidal phase acts as a reactive filler at the wood joint interfaces, contributing for the resins bonding performance. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1956–1968, 2010

Key words: urea-formaldehyde resins; colloidal dispersion; biphasic structure; wood-bonding

INTRODUCTION

Urea-formaldehyde (UF) resins are still the most widely used adhesives in the manufacture of wood-based panels, mostly due to their high reactivity, low cost, and excellent adhesion to wood. Moreover, the impact of the resin limitations (potential formaldehyde emissions and low resistance to moisture due to the reversibility of aminomethylene link) has been considerably alleviated by improvements in the resin production technology.¹

The multiplicity of chemical and physical structures present in UF resins has made their study a complex task. In addition, these highly reactive chemical systems are prone to change during sample preparation for analysis or during the analysis itself. The difficulty to find suitable solvents is another serious problem.²

This article is mainly concerned with the physical structure of these resins and its influence on the resins

performance. Amino resins have been perceived for a long time to possess a colloidal structure.³ Pratt et al.⁴ were the first to admit the formation of an intermediate lyophobic colloidal sol, which subsequently coalesces to cause gelation during resin cure, concurrently with the conventional chemical gelation mechanism caused by step-growth polymerization. Dunker et al.⁵ suggested that the formation of insoluble aggregates is originated by the loss of hydrogen bonding potential between oligomers and water. This is caused by the decrease in the number of possible hydrogen bonding locations as the condensation reaction proceeds, together with the formation of intra- and intermolecular bonds.

Motter⁶ studied the mechanism of nucleation and growth of the colloidal phase in UF resins. The continuous and disperse phases were separated by centrifugation, and the relative molecular weight distribution (MWD) was determined by GPC/SEC. The results obtained indicate that the primary mechanism of disperse phase formation in this type of resins has to do with precipitation of linear, urea-terminated oligomers.

Grunwald⁷ observed a clear supernatant after centrifugation of UF samples at high velocities for long times (16 h at 40,000 rpm). The characterization of

Correspondence to: F. D. Magalhães (fdmagalh@fe.up.pt).

Contract grant sponsor: FCT (PhD grant); contract grant number: SFRH/BD/23978/2005.

TABLE I
Technical Data for UF Resins Analyzed in This Work

Resin	Molar ratio F/U	Resin solids content ^a (%)	Reactivity ^b (s)	pH range (25°C)	Viscosity ^c (25°C) (mPa s)
A	1.30	63 ± 1	45 ± 10	7.5–8.5	150–350
B	1.20	64 ± 1	80 ± 30	8.0–9.5	150–350
C	1.08	64 ± 1	80 ± 30	7.0–9.0	150–300
D	1.00	64 ± 1	70 ± 30	8.0–9.5	150–300

^a 105°C, 3 h.

^b Gel time at 100°C with 3% NH₄Cl.

^c Brookfield viscometer.

the continuous and disperse phases by GPC and¹ H-NMR indicated that the main difference between the phases is the fraction of urea and methylolureas.

Colloidal particle formation, followed by clustering, has been shown to be the normal way of aging of aminoplastic resins. Melamine-urea-formaldehyde (MUF) resins, in particular, have been the object of an extensive study done by Pizzi and co-workers.^{3,8-10} The work of Despres and Pizzi⁹ used optical microscopy to identify the colloidal structures, reporting considerable differences in shape for UF, MF, and MUF resins. Agglomerates were detected in SEC chromatograms of the UF resins. They have also observed that, at early stages, colloidal aggregate formation showed a star-like light interference pattern as in MF resins.¹¹

The main objective of this work is to obtain some additional insights on the nature of the colloidal particles present in UF resins and the role that these may play on the wood-bonding process. The structural analysis of the colloids was performed by optical microscopy, transmission electronic microscopy (TEM), and scanning electron microscopy (SEM). Particle size distribution (PSD) analysis gives information on the effects of condensation degree and aging on the formation of colloidal structures. Molecular weight distribution analysis based on GPC/SEC measurements are influenced by the heterogeneous structure of the resins, because the disperse phase cannot be completely solubilized. Still, the chromatograms provide information on the fraction of insoluble material present, and this can be related to the resins synthesis conditions. Reactivity and cure enthalpies are evaluated by DSC for a resin and the individual phases separated by centrifugation. Finally, the shear strength of glued joints is evaluated, allowing for some insights on the role of each phase on the wood-bonding process.

MATERIALS AND METHODS

Materials

Several commercial UF resins were characterized. They were produced by EuroResinas (Sonae Indús-

tria, Portugal), with different synthesis formulations under different operating conditions.

Table I shows the technical data of four UF resins, which were analyzed in this work. All of them are UF resins in water solution. The main differences in the synthesis of these resins are the duration of the condensation step and the final amount of urea added. For example, Resin D has the longer duration of the condensation step and a larger amount of final urea, whereas Resin A has the shortest duration of the condensation step and the lowest amount of final urea. These resins were available for analysis at different times along the work, within the context of an ongoing project. For this reason, the analysis techniques discussed below comprise different sets of samples. Nevertheless, when relevant, the results obtained are related to the nature of the resins under study.

To limit the aging of the resins for posterior analysis, they were stored at 5°C unless otherwise specified.

Methods

Morphology analysis

Direct visualization of UF resins was performed with a Leica DM LB2 microscope (Leica Microsystems) with 1000× magnification and equipped with a filter cube with the following characteristics: excitation filter 340–380 nm, dichromatic mirror 400 nm, and suppression filter LP 425, without oil immersion. The sample was prepared diluting approximately 1–2% of UF resin in water.

For visualization by TEM (50 kV; Zeiss), samples were adsorbed to glow-discharged carbon-coated collodion film on 400-mesh copper grids during 1 min. The sample was prepared diluting approximately 1–2% of UF resin in water.

SEM/EDS images were taken with a SEM-JEOL-JSM6301-F equipped with an Oxford INCA/ENERGY-350 microanalysis system. The deposition of resin droplets on the surface of a metallic sheet and on wood was also investigated. A water solution with 20 wt % of ammonium chloride was used

as hardener and mixed with the resin before spraying on a metallic sheet. The hardener concentration was 3 wt % (based on resin solids content) in the final mixture. The boards were then cured in an oven at 110°C for 8 min.¹² The samples were coated with gold by vaporization before the analysis.

For structural analysis by Cryo-SEM, the sample was placed on a copper Cryo-SEM sample holder in a circular hole. The set was dipped into liquid nitrogen (slush nitrogen) at -170°C; the freezing occurred under vacuum. After freezing, the sample was transferred to a Gatan Alto 2500 cryochamber of the microscope (JEOL, JSM-6700F). The sample was fractured in the cryostage with a knife at -130°C, after the aqueous phase sublimation was performed at -98°C under vacuum during 1 min. Finally, the sample was coated with gold by vaporization before the analysis. The sample was observed at a temperature of -130°C and a voltage of 10 kV.

Particle size analysis

A Beckman Coulter LS230 (LS230) with a wet module was used in this study. The dynamic range of the LS230 goes from 0.04 to 2000 μm . The LS230 instrument uses polarization intensity differential scattering (PIDS) method. The PIDS system uses three light wavelengths (450, 600, and 900 nm, obtained by filtering light from an incandescent bulb) at two polarizations. Measurements were performed at several scattering angles of the polarized vertical light to the scattering plane and the polarized horizontal light to the scattering plane. The samples were prepared diluting 5 drops of UF resin in 10 mL of distilled water, these were ultrasonicated for 1 min and analyzed in the Coulter-Counter.

Centrifugation

Phase separation of UF resin was performed by centrifugation. The samples were fractionated at 18,000 rpm during 3 h using a JA25.50 rotor in Beckmann Coulter Avanti J25 centrifuge at 12°C in 50 mL polyallomer bottles. The supernatant was withdrawn with a micropipette, whereas the sediment was withdrawn after removing the intermediate phase. The supernatant, sediment, and sample of resin were stored in closed vials at 5°C for future analysis.

Molecular weight distribution

A Gilson HPLC system equipped with a Gilson Differential RI detector and Viscotek's Dual Detector (differential viscometer and a light scattering detector RALLS). A Rheodyne 7125 injector with a 20 μL loop was used for sample introduction. The column

used was a Waters Styragel HR1 5 μm . Dimethylformamide (DMF) was used as the mobile phase. The column was conditioned at 60°C using an external oven, and the flow rate was 1 mL/min. The Universal Calibration was done using polyethylene glycol standards from PL with molecular weight between 12,140 and 106. The RALLS detector was not used for the tri-SEC molecular weight calculations because of the low response for lower molecular weights. However, the RALLS signals were qualitatively taken into account.

The samples for SEC analysis were prepared dissolving 100 mg sample of resin in 3 mL of dimethylsulfoxide (DMSO), then stirring vigorously and filtering through a 0.45 μm Nylon syringe filter.

Curing and bonding strength characterization

About 15 mg of each sample was mixed with 3 wt % (based on resin solids content) of hardener (20 wt % solution of ammonium chloride). A Setaram DSC 131 was used with a temperature ramp of 5°C/min, from 25 to 300°C. The samples were held in stainless steel crucibles with a crimpable seal and able to withstand 80 bars up to 550°C. The use of this crucible enables prevention of water evaporation in the scanning temperature range. The analysis was performed under nitrogen atmosphere.

The same mixtures used in the DSC were subjected to a tensile shear test in a Servosis universal testing machine. Approximately 150 g/m² adhesive were applied to the bonding surfaces of lap joints test pieces.

The test was performed according to the procedure described by EN 205. The loading speed was 10 mm/min. The loading was continued until a break or separation occurred on the surface of the test samples. The tensile shear strength was then calculated in N/mm².

RESULTS AND DISCUSSION

Disperse phase morphology

The resins are white opaque liquids, indicating the presence of an insoluble disperse phase in the aqueous medium. The colloidal nature of UF resins has been reported previously^{4,9,13,14} and is associated to the presence of insoluble molecular aggregates.* Furthermore, above about 100% dilution with water, flocculation takes place, originating a white precipitate and a translucent supernatant liquid. The

*In this article, we adopt the terminology suggested by Nichols et al.¹⁵ using the term aggregate to describe "an association of molecules into supramolecular structures, which in turn may develop into agglomerates." Along this article, the terms aggregate and primary particle are used indistinctly.

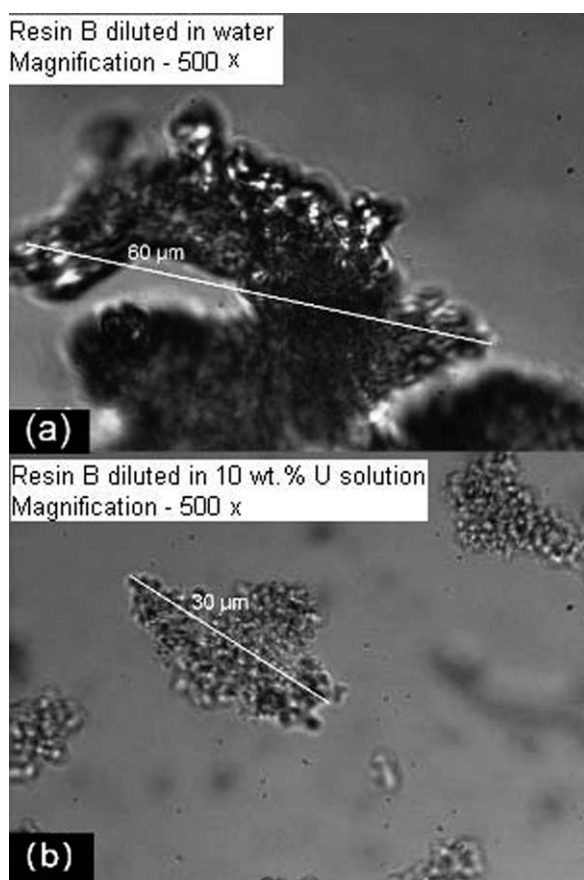


Figure 1 Optical microscopy image of Resin B: (a) diluted in water (1.6 wt % resin in water) and (b) diluted in 10 wt % urea solution (1.3 wt % resin in urea solution).

mechanism that originates this flocculation is not clearly identified and is certainly dependent on the particular nature of the resins considered.

Results from different microscopy techniques are presented below, providing a consolidated view of

the structure of the disperse phase and serving as a basis for the formulation of some hypothesis.

Optical microscopy is the easiest method to observe the morphology of the resins. Because of the high solids concentration, significant dilution is necessary for the microscopic visualization to be possible. Therefore, flocculation is inevitable, and particle agglomerates are formed, which were not present in the original resin. As an example, Figure 1(a) displays a sample of Resin B diluted in water (1.6% resin in water, resin had been stored at 5°C for about 90 days). A large agglomerate of smaller particles (primary particles) is visible.

Interestingly, when dilution is performed with a urea solution, instead of pure water, distinctly smaller floccules are formed. This difference is visible to the naked eye and is confirmed in Figure 1(b) (1.3% resin in urea solution at 10% concentration). The presence of excess urea may cause the solvation of the primary particles and minimizes interparticle interaction, namely hydrogen bonding, therefore decreasing the tendency toward agglomeration. This behavior is similar to the one observed in the well known chemical denaturation of proteins by urea solutions (e.g., Caballero-Herrera et al.¹⁶). The effect of urea on minimizing colloidal aggregation on MUF resins has previously been discussed by Zanetti and Pizzi.³

At this point, it is useful to formulate a descriptive model of the heterogeneous nature of these resins, which will be helpful in the interpretation of the results discussed throughout the rest of the article. Figure 2 presents a schematic view of the resin's heterophasic structure.

Figure 2(a) shows particles formed by insoluble molecular aggregates, swollen by water, and soluble oligomers. These particles are not necessarily individualized, some agglomeration being possible. In

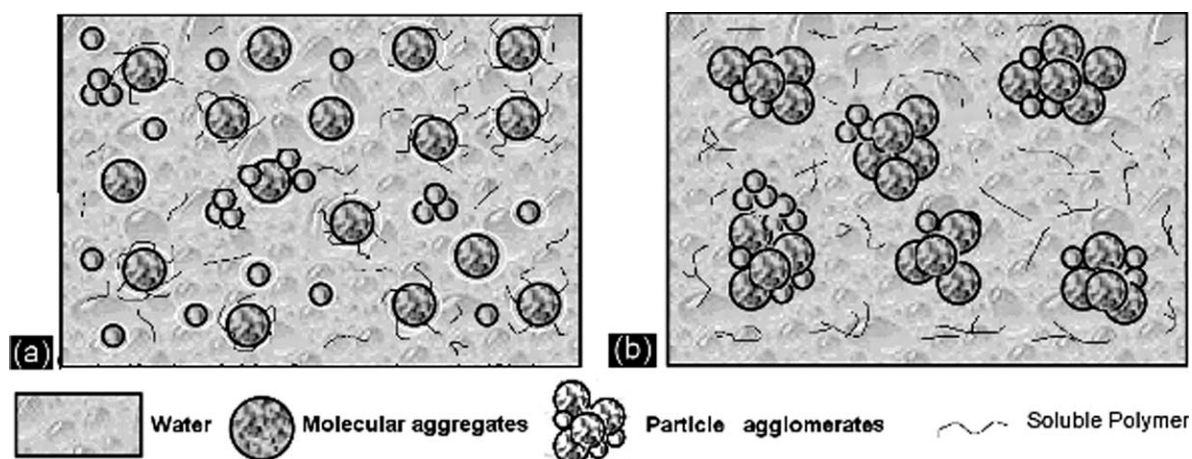


Figure 2 Simplified representation of a UF resin heterogeneous nature: (a) original resin and (b) resin after flocculation by water dilution.

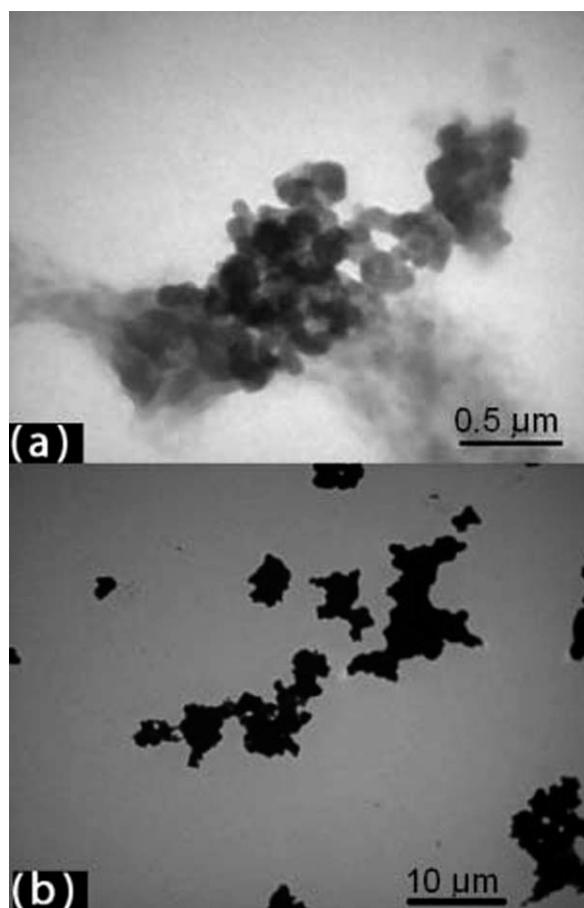


Figure 3 TEM images of Resin B diluted in water. (a) Fresh resin and (b) aged resin.

addition to this dispersed phase, the continuous phase contains unreacted urea and soluble polymer, ranging from small oligomers to medium molecular weight polymer.

Unreacted urea may form a solvation layer surrounding the particles, contributing to its stabilization toward agglomeration. On dilution-induced flocculation, particle agglomeration occurs, originating optically visible large floccules. This instability toward dilution can be associated to the depletion of the solvation layer due to diminishing urea concentration in the continuous phase. This explains why flocculation with urea solution is more difficult and originates much smaller floccules.

An additional colloidal stabilization mechanism may be taken into account, based on electrostatic repulsion associated to ionic species retained at the particle surface. A fraction of the polymeric species may have an intermediate hydrophilic character which causes it to be distributed between the dispersed and continuous phases. These species should have higher contents of very hydrophilic terminal hydroxymethylene and primary urea groups than the insoluble fraction. This makes possible the

capture of ionic species, i.e., sodium cations, at the particle surface, thus originating electrostatic stabilization. On dilution, the polymer at the surface is partially displaced toward the aqueous medium, depleting the surface from ionic species. This leads to agglomeration and flocculation.

TEM images for Resin B fresh and aged (stored for approximately 2 months at 5°C) are shown in Figure 3. Because TEM analysis implies significant dilution, we are again looking at the flocculated samples. These agglomerated structures are evident in both samples. The primary particles have dimensions in the tenths of micron. Interestingly, the aged sample showed larger agglomerates, whereas in the fresh sample these were smaller and less numerous. This relation between floccules dimensions and aging will be further discussed later.

In the case of Cryo-SEM analysis, resin dilution is not necessary. Additionally, no particle coalescence occurs because the sample is kept frozen. Figure 4 shows an agglomerate with approximately 3 μm. The relatively large size is probably associated with the aging process. The primary particles have dimensions in the tenths of micron, in agreement with the TEM observations. Interestingly, the particle geometry does not seem to be only spherical but also lamellar. These two types of geometries seem to be also present in the results reported by Despres and Pizzi.⁹

An example of the SEM images collected for the resin sprayed and cured on a metal plate is shown in Figure 5. Two different phases are visible, as expected: a continuous phase, corresponding to cured soluble polymer, and a dispersed phase made of individualized primary particles and small agglomerates. The particles have sizes in the range of few tenths of microns. In the agglomerates, some particle coalescence due to heating is visible. This

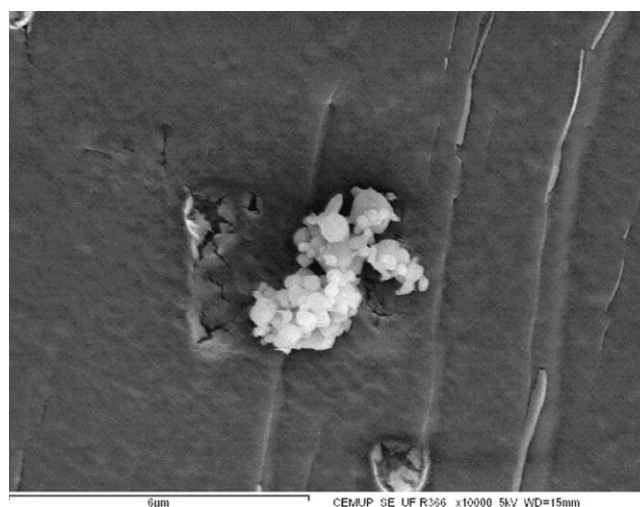


Figure 4 Cryo-SEM image aged Resin B.

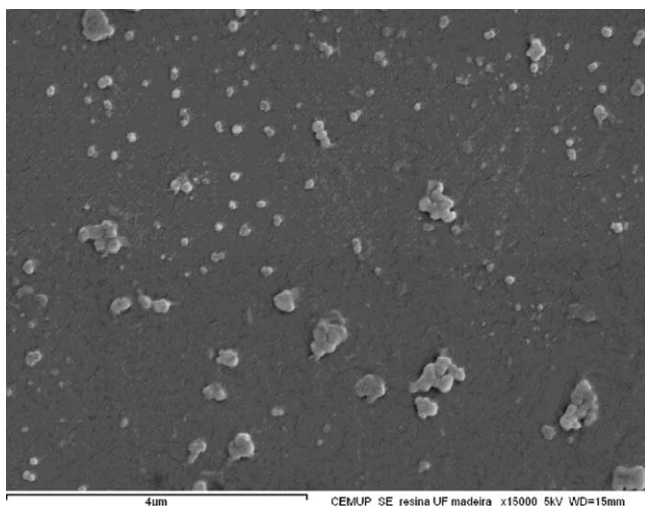


Figure 5 SEM image of UF Resin B sprayed and cured on a metal plate.

image somehow illustrates how the resin is deposited at the wood particle surface during the glue blending process. The continuous phase should penetrate to some degree within the wood structure, but the particles are likely to remain at the surface.

Figure 6 presents the elementary analysis performed at different points in the cured resin surface. The particle surface shows a significantly higher content in sodium, chlorine, and potassium because of the adsorption of ions present in water. The ability for the surface to capture sodium cations may play an important role on the colloidal stabilization process, as discussed previously. The surface also shows higher nitrogen content relatively to carbon and oxygen. This could be related with the presence of urea in the disperse phase, as also suggested before.

Summarizing some of the conclusions derived from the previous observations:

The colloidal structures are agglomerates of elementary particles. These are a few tenths of micron in diameter and exhibit spherical and lamellar geometries.

Urea can play an important role on the stabilization of the colloidal particles, through the formation of a solvation layer. Adsorption of ionic species at the particles surface may also contribute to electrostatic stabilization.

Water dilution causes the weakening of both types of stabilization mechanisms, due to surface depletion, and originates agglomeration/flocculation.

When a resin is sprayed over a porous substrate, such as wood, the particles will remain at the surface while the soluble fractions should be absorbed together with water. This will have an

effect on the bonding mechanism, as discussed later.

Particle size distribution

The purpose of these PSD measurements was to analyze the effect of the degree of condensation and aging. It must be noted that the Coulter-Counter system implies dilution of the samples above the flocculation limit. Therefore, one is looking at flocculated samples and not at the original PSD. Figure 7(a,c) shows the volume PSD obtained for Resins A, B, and C, relatively fresh (stored for 30 days at 5°C) and aged (stored for 170 days at 5°C). For the fresh samples, it is clear that Resin A originates a different type of flocculate than Resins B and C. The volume distribution for Resin A lies mostly between 0.2 and 12 μm, whereas the others are displaced toward the right, in the region of hundreds of micron but still showing a small peak below 10 μm. On the other hand, after aging all resins show similar PSDs.

The much larger dimensions of the flocculates in the less aged Resins B and C, in relation to Resin A, evidenced in the volume distributions, may be related to the lower degree of condensation of Resin A. The colloidal phase present in fresh Resin A will be composed of less numerous and not very agglomerated particles that do not yield such large floccules. With aging, more molecular aggregates are formed and more agglomeration takes place,

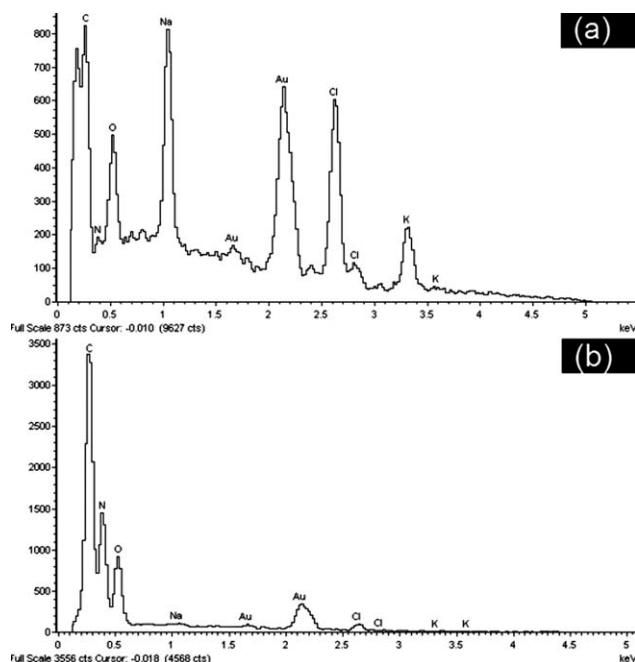


Figure 6 Elementary analysis for UF Resin B cured on a metal plate. (a) particle surface and (b) in continuous phase.

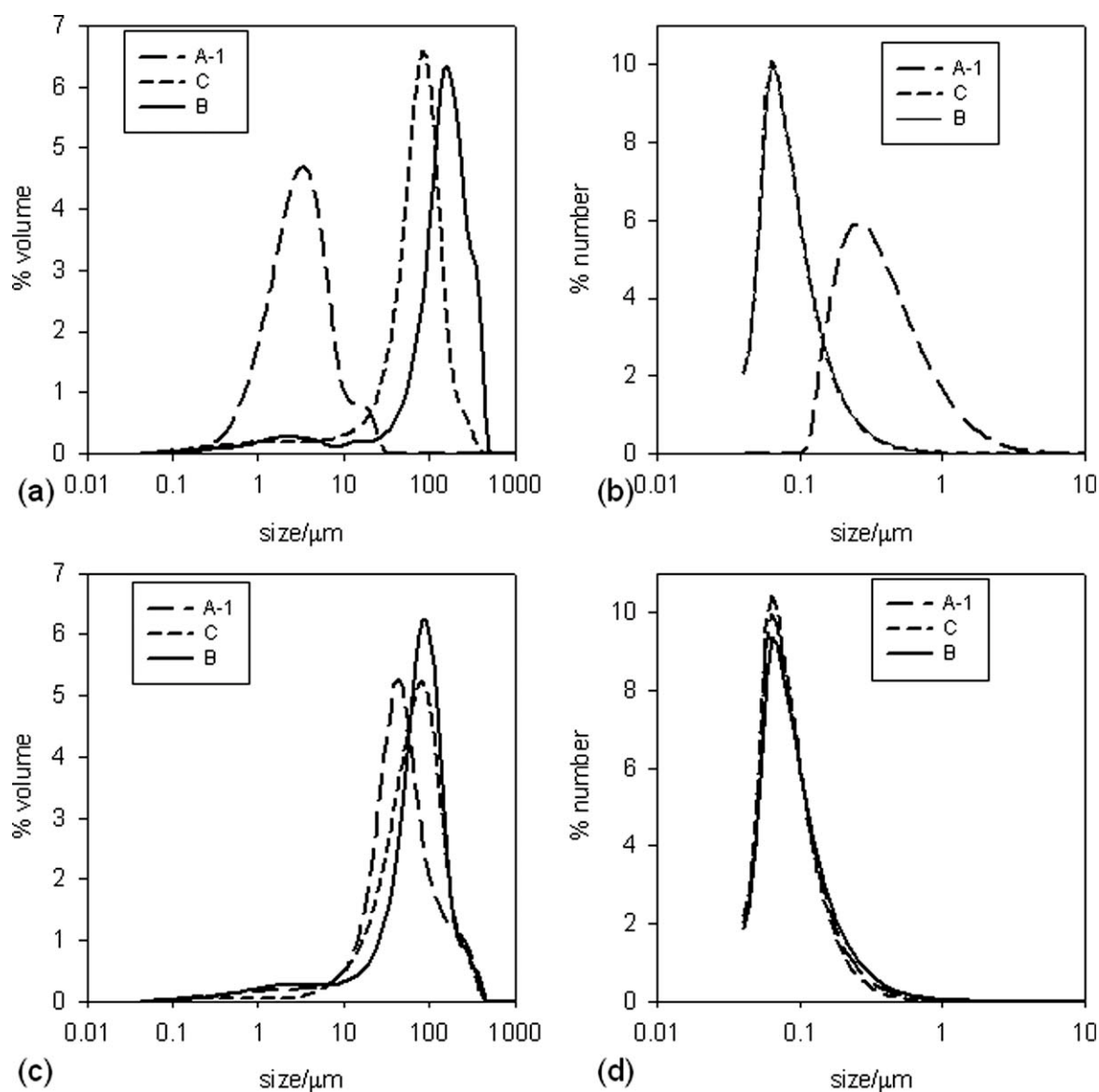


Figure 7 Particle size distribution for three UF resins stored at 5°C. (a) PSD in volume for 30 days, (b) PSD in number for 30 days—note that the curves for Samples B and C are nearly superimposed, (c) PSD in volume for 170 days, and (d) PSD in number for 170 days.

therefore approaching the morphology of Resins B and C and originating flocules with a similar PSD.

A subtle additional difference exists between the fresh resins and is more visible when looking at the number PSDs, shown in Figure 7(b,d). The PSD for fresh Resin A does not show particles below 0.1 μm, contrary to resins B and C. After aging, however, the three resins again show similar number PSDs, all starting below that size. The number distributions put into evidence the lower particle sizes present, certainly displaying primary particles that have remained unagglomerated. Resins B and C display a large number of particles with sizes around 0.1 μm, which is consistent with the dimensions of the individual particles identified in the previous microscopy sections. Resin A, on the other hand, being a

less condensed resin, contains a lower concentration of agglomerates, which is confirmed by the lower amount of sediment observed after flocculation. Therefore, a lower amount of the original primary particles remain after flocculation.

The reproducibility of these results, both for fresh and aged conditions, has been confirmed with other batches of the same resins, not shown here.

In summary, even though these PSD analysis combines information on the original primary molecular aggregates and on the agglomerates formed on dilution, some qualitative conclusions can be withdrawn. More condensed resins display larger, more agglomerated, colloidal structures. On dilution, also larger flocules are formed. A less condensed resin will approach this morphology along time, as more

TABLE II
Solids Content of Original Resins, Sediment and Supernatant Phases for UF Resins A-2 and D

Resin	Resin Age (days at 25°C)	Resin solids (wt %)	Sediment solids (wt %)	Supernatant solids (wt %)
A-2	20	62.2	66.2	61.0
	50	63.0	67.8	60.2
D	20	65.0	72.2	63.7

particles (molecular aggregates) and particle agglomerates are formed.

To clarify the nature of the two phases present in these UF resins, some samples were centrifuged and the sediment and supernatant phases separated. Coulter-Counter analysis was performed on the supernatant and compared with the results from the original resins. The sediment consisted of a gel-like mass, which could not be redispersed for this analysis. These samples were also analyzed in the chromatographic and calorimetric studies described later in the article.

A completely clear supernatant has never been obtained, indicating that a residual colloidal phase was still dispersed in the continuous medium. On the other hand, the sediment is expected to still contain, in addition to water, soluble polymer, and oligomers, entrapped in inter and intraparticle voids, or retained due to surface adsorption on the dispersed phase.⁶

Resin A was studied for two different ages: 20 and 50 days at 25°C, whereas Resin D was analyzed only for 20 days, because it was gellified after 50 days at 25°C. Table II displays the results obtained for the solids content (after evaporation at

105°C for 3 h) in the original resins and in the separated phases.

The PSD results obtained are shown in Figures 8 and 9. The results for the resins before centrifugation are qualitatively similar to the ones described before, even though the aging times are not comparable due to the different storage temperatures. Resin A with 20 days shows a narrower PSD than the more condensed Resin D. As before, Resin A with this lower age [Fig. 8(a)] does not exhibit particles in the neighborhood of 0.1 μm, contrary to Resin D (Fig. 9). As Resin A ages [Fig. 8(b)], however, the PSD of the flocculated material widens, and the mean value is significantly displaced toward the right. Particles in the neighborhood of 0.1 μm are now displayed in the analysis.

The PSD of the flocculated supernatant, on the other hand, is similar for all resins. Interestingly, as can be seen in Figure 8(a), this distribution is almost the same as for the fresh uncentrifuged Resin A. This was somehow expected, considering that the supernatant should contain only small unagglomerated molecular aggregates, similar to the ones present in the fresh low-condensed resin. Agglomeration caused by aging leads to a broader PSD of the flocculate, as seen in Figures 8(b) and 9.

Molecular weight distribution

The work below attempts to relate the information obtained from conventional GPC/SEC analysis with the known heterogeneous character of these resins. This may provide additional information for the characterization of the resins molecular and colloidal structures. Chromatograms for Resins A-1 and D

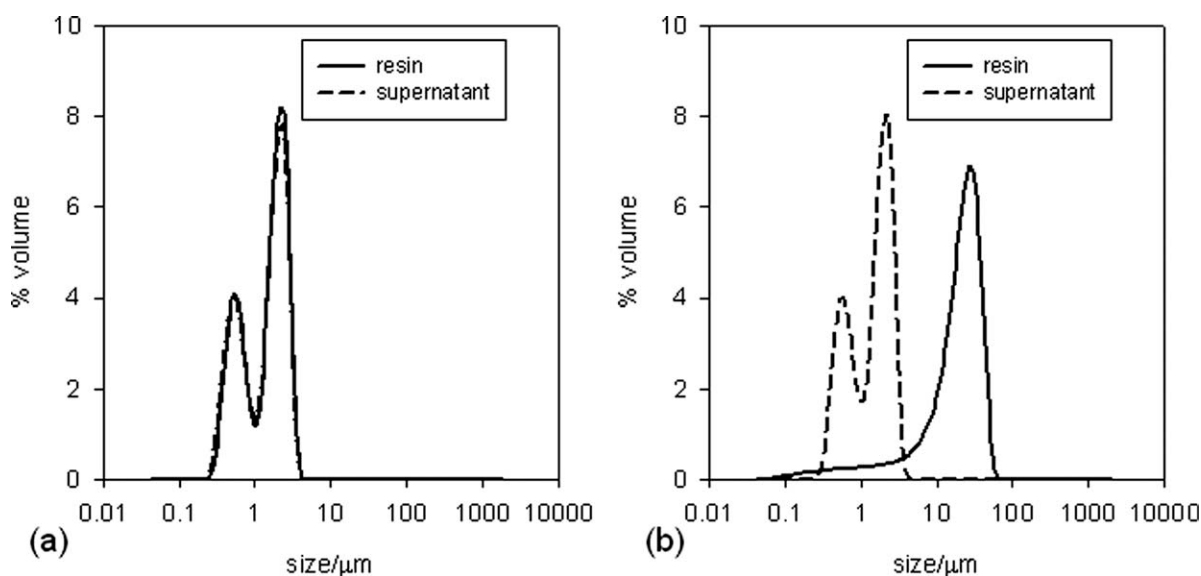


Figure 8 Particle size distribution in volume for UF Resin A-2 and supernatant. (a) resin stored for 20 days at 25°C and (b) resin stored for 50 days at 25°C.

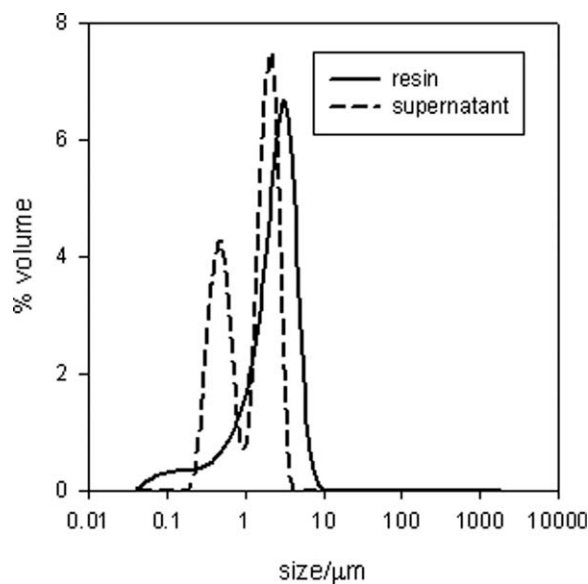


Figure 9 Particle size distribution in volume for UF Resin D and supernatant stored for 20 days.

and the corresponding supernatant and sediment phases, obtained after centrifugation, are shown in Figures 10 and 11. In all cases, at least two samples were prepared and analyzed to verify the reproducibility of the results.

Figure 10(a) shows the normalized refraction index (RI) chromatogram for Resin A-1. The general features of the chromatogram are similar to those found in the literature for UF resins.^{1,7,9,17-19} Three zones, based on the apparent limits of detectable peaks, can be defined in the chromatograms:

Zone I—Elution volume between 8 and 9 mL. Corresponds to the lower molecular weight species, i.e., unreacted urea, methylolureas, and oligomeric species, such as methylenediurea, monomethylolmethylenediurea, dimethylolmethylenediurea, and others. The methylenediurea was synthesized with Kadowaki's method²⁰ in laboratory and analyzed in SEC. Molecular weight should be below about 600.

Zone II—Elution volume between 5.8 and 8 mL. Corresponds to intermediate molecular weight species, with molecular weights ranging from a few tens of thousand to about 600.

Zone III—Elution volume below 5.8 mL. This would correspond to polymer with quite high molecular weights, eluting before the exclusion limit of the SEC column. It has been suggested by some authors that this portion of the chromatograms actually refers to molecular aggregates and not individualized polymer molecules.^{9,18} These aggregates would be insoluble in the original aqueous medium, probably forming larger colloidal structures that partially disaggregated

in the DMSO solvent. In this article, we present some evidence in favor of this hypothesis.

Because the chromatograms may reflect the presence of insoluble molecular aggregates, a straightforward computation of average molecular weights would be misleading. Two different approaches were therefore taken to quantitatively represent the chromatographic data. On one hand, assuming that Zone III corresponds essentially to insoluble material, molecular weights were computed neglecting this portion of the chromatograms. On the other hand, the two following parameters were introduced to complement the description of the particular features of these chromatograms:

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

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

f_1 should reflect the amount of low molecular weight species in the sample, whereas f_2 is expected to be related to the relative importance of what would be high molecular weight species in the polymerized material. Table III shows the numerical values obtained for these parameters in all the chromatograms.

Qualitatively, the RI chromatograms (Figures 10 and 11) display similar features for the original resins and the supernatant and sediment phases. Two discrete peaks in the lower molecular weight region are common to all samples, with retention volumes of 8.5 and 8.2 mL. The first peak represents urea and methylolureas, as was confirmed by direct injection of urea and dimethylolurea. The fraction which eluted at 8.2 mL is probably a polymer formed by reaction of urea and methylolureas. The chromatogram of the sediment phase displays a peak for a retention volume of 7.5–8.0 mL ($M_w \sim 600$ –1000), which does not seem to be present in the supernatant. A similar behavior was observed by Motter⁶ for the SEC analysis of the sediment and supernatant phases. This author associates this peak to insoluble linear urea-terminated oligomers, 4–8 urea units in length. These oligomers would correspond to a critical molecular size for solubility in water, above which the formation of primary colloidal particles takes place.

Considering the data in Table III, for Resin A-2 with 20 days at 25°C, the sediment shows the highest molecular weights and the supernatant the lowest. The original resin shows intermediate values. On the other hand, the fraction of low molecular weight species, f_1 , is highest for the supernatant and lowest for the sediment. Once again, the original resin shows an intermediate value. Similar results are seen in Table III for the other samples. It was

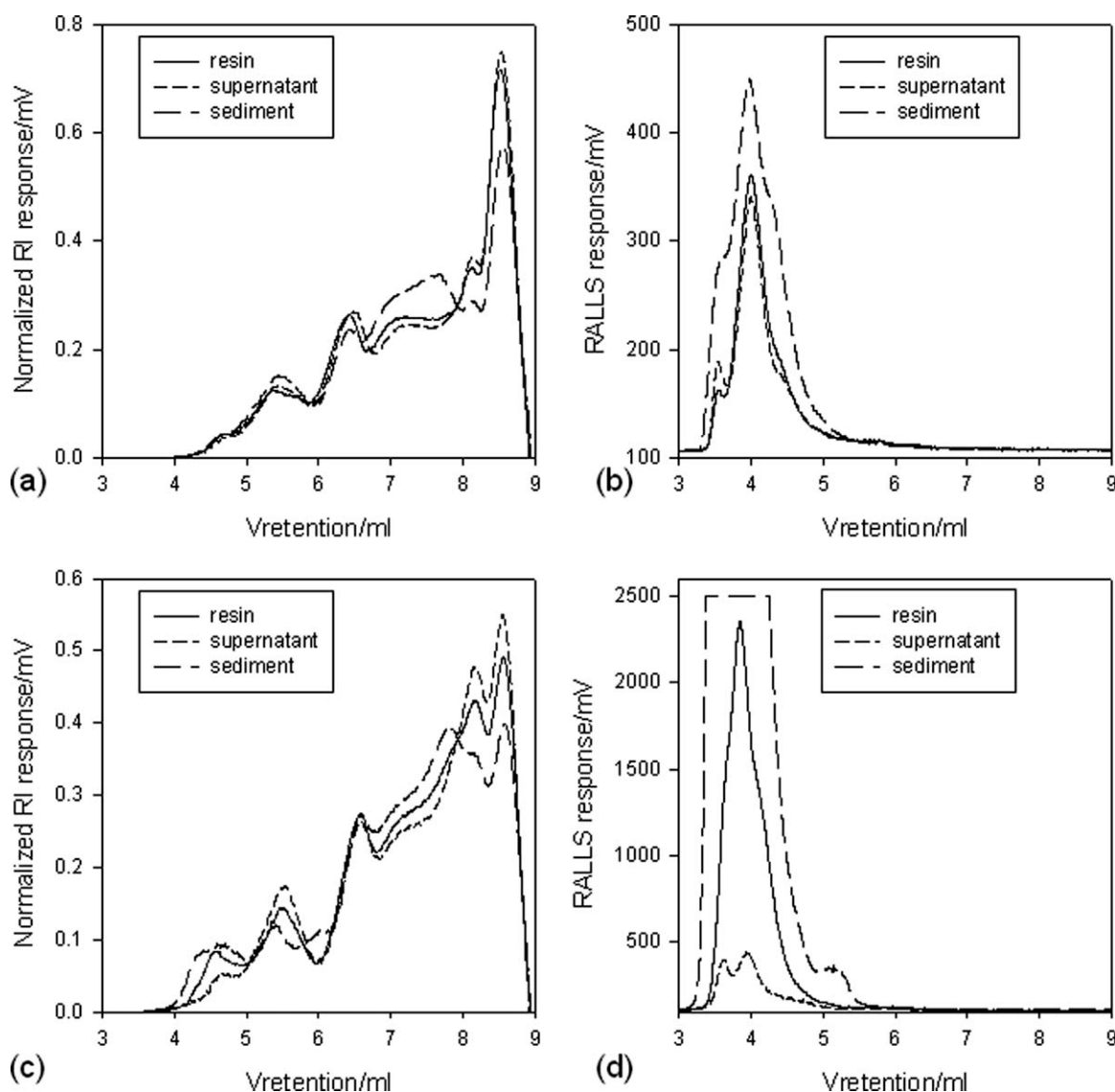


Figure 10 Chromatogram for UF Resin A-2 with 20 and 50 days, sediment, and supernatant diluted 3% in DMSO. (a) normalized response of RI sensor for 20 days, (b) response of RALLS sensor for 20 days, (c) normalized response of RI sensor for 50 days, and (d) response of RALLS sensor for 50 days.

expected that the supernatant would exhibit the highest fraction of low molecular weight material, which was dissolved in the aqueous medium of the original resin. The sediment also contains some of this material, in lower proportion, because it was sorbed within the solid phase or was retained in the interparticular space. Therefore, one concludes that centrifugation does not lead to complete separation of the disperse and continuous phases.

It is somewhat surprising that, in all samples, a not very substantial difference is obtained for the computed molecular weights of sediment and supernatant. Significantly higher molecular weights would, in principle, be expected for the sedimented phase. Because this is not the case, we are led to believe that the colloidal phase is actually composed

of aggregated polymer with molecular weights not too different from the polymer in solution. The more relevant difference between the soluble and insoluble fractions may lie on chemical composition, namely hydroxyl group content.

Even though the purpose of this article is not to study the effect of aging, when looking at Resin A-2 with 20 and 50 days (Table III), it is noticeable that the molecular weights increase and f_1 decreases with aging. This indicates that condensation progresses with time, consuming urea, and oligomers. Furthermore, f_2 has increased, indicating the presence of more insoluble aggregates.

Resin D (Table III) is the most condensed of the resins studied. This fact is not evident from the computed molecular weights, because it is masked by the

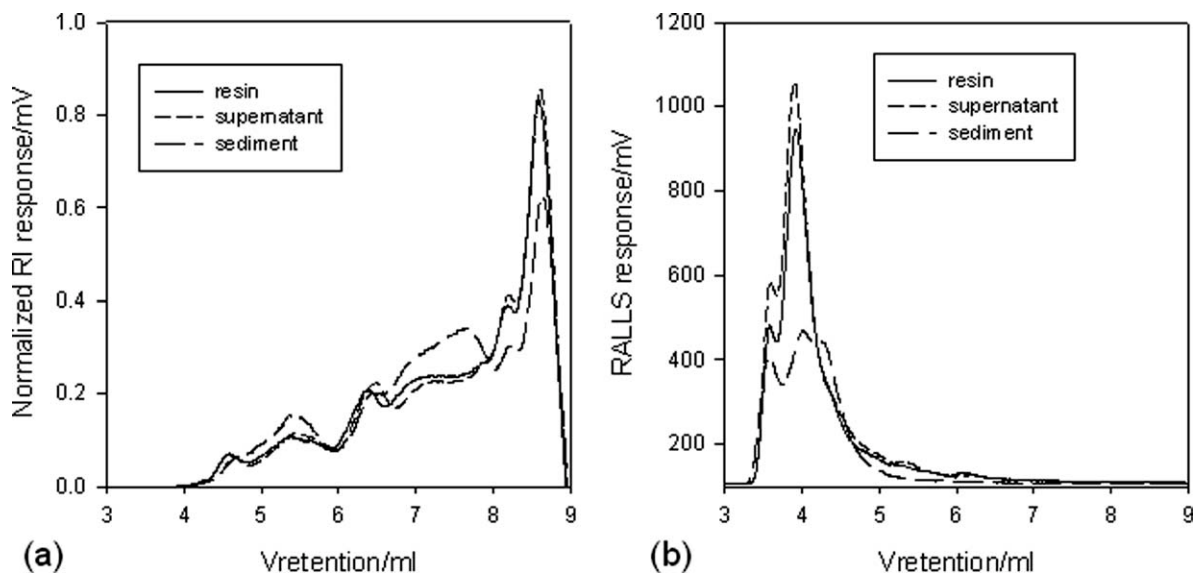


Figure 11 Chromatogram for UF Resin D with 20 days, sediment, and supernatant diluted 3% in DMSO. (a) Normalized response of RI sensor and (b) response of RALLS sensor.

larger amount of final urea added, as confirmed by the higher value of f_1 . However, this resin shows the highest values for parameter f_2 , which may indeed be related to the higher degree of condensation.

It is also interesting to look at the RALLS responses obtained in the different cases. For Resin A-2 after 20 days, Figure 10(b) shows several peaks roughly in the region corresponding to Zone III, attributable to the molecular aggregates present in the samples. The peak magnitude is higher for the sediment, as this sample is expected to be more concentrated in insoluble material. This difference becomes much more significant when the resin is aged 50 days, as seen in Figure 10(d), where the RALLS signal is actually saturated for the sediment, while it maintains approximately the same magnitude for the supernatant. As expected, the original resin

displays an intermediate chromatogram. This indicates that the aging process has originated a significantly higher concentration of insoluble molecular aggregates, in agreement with the PSD results discussed previously. These aggregates would actually be agglomerated into larger structures in the original resin, sedimenting during centrifugation. Contact with DMSO solvent caused desagglomeration into particles visible to the RALLS detector.

On the other hand, for Resin D, Figure 11(b), the RALLS chromatogram for the sediment is less intense than for the supernatant. This more condensed resin may form insoluble particles that cannot be easily disaggregated in DMSO and are therefore retained in the precolumn 0.45 μm filter.

Some key conclusions can be extracted from these SEC results:

TABLE III
Values of M_n , M_w , Polydispersity, and Parameters f_1 and f_2 , Obtained by SEC for Resin, Sediment, and Supernatant of the UF Resin A-2 with 20 and 50 Days and UF Resin D with 20 Days Storage at 25°C

Sample	M_n	M_w	M_w/M_n	f_1	f_2
Resin A-2 with 20 days storage					
Resin A-2	4.69×10^2	3.40×10^3	7.2	0.296	0.168
Supernatant	4.17×10^2	2.84×10^3	6.8	0.313	0.167
Sediment	5.63×10^2	3.50×10^3	6.2	0.248	0.180
Resin A-2 with 50 days storage					
Resin A-2	5.10×10^2	2.74×10^3	5.4	0.225	0.185
Supernatant	4.91×10^2	2.53×10^3	5.2	0.246	0.185
Sediment	6.39×10^2	3.64×10^3	5.7	0.190	0.192
Resin D with 20 days storage					
Resin D	3.91×10^2	2.87×10^3	7.3	0.342	0.182
Supernatant	3.62×10^2	2.53×10^3	7.0	0.355	0.184
Sediment	5.19×10^2	3.06×10^3	5.9	0.269	0.200

TABLE IV
Cure Temperatures and Enthalpies for UF Resin A-2, Supernatant, and Sediment

Sample	Peak temperature (°C)	Enthalpy (J/g)
Resin A-2	83.25	77.57
Supernatant	81.58	85.38
Sediment	83.04	72.18

The lower retention volume portion of the RI chromatograms reflects the presence of insoluble molecular aggregates. This fraction of the chromatogram can be quantified and related to the resins degree of condensation and aging condition.

Based on the analysis of centrifuged samples, the polymer aggregates present in the colloidal phase do not seem to have higher molecular weight than the water-soluble polymer. The cause for insolubility may have to do with differences in chemical composition.

A larger degree of condensation may not translate into a significantly higher molecular weight but into a higher fraction of insoluble aggregates formed.

Resin aging leads to the formation of a higher fraction of insoluble molecular aggregates.

The RALLS chromatograms confirm the presence of insoluble particles in the samples and its relation with aging.

Curing behavior and bonding strength

DSC is an often used tool to evaluate the reactivity of UF resins. However, the analysis conditions are different from those observed in the bonding process, so it cannot be directly related to the process of mechanical strength development.

The same separate analysis for resin, supernatant, and sediment was performed for Resin A. Figure 12 shows the DSC curves obtained, and Table IV summarizes the results. The supernatant is more reactive, having a slightly lower cure temperature than the resin and sediment, which show similar results.

TABLE V
Values of Tensile Shear Strength and Percentage of Cohesive Failure Within Wood for UF Resin A-2, Supernatant, and sediment

Sample	Tensile shear strength (N/mm ²)	% cohesive failure in wood
Resin A-2	13.4	90
Supernatant	11.3	60
Sediment	14.6	90

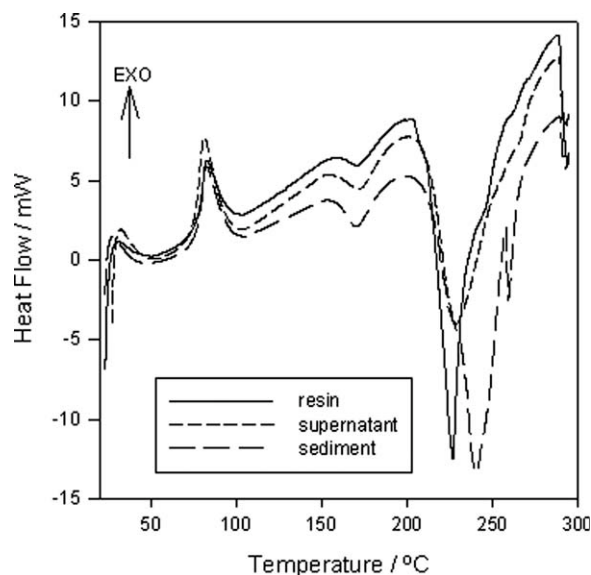


Figure 12 DSC curves for UF Resin A-2, supernatant, and sediment. Resin had been stored for 50 days.

The cure enthalpies based on the samples solids content (from Table II) are significantly different. The values increase in the following order: sediment < resin < supernatant. This may be attributed to the higher molecular mobility and lower condensation (more reactive groups) of the soluble material present in the supernatant.

The endothermic peaks that appear between 160 and 190°C can be attributed to the release of entrapped water from the cured polymer.²¹ It is also possible to observe, above 200°C, endothermic peaks associated to thermal degradation of the methylene ether.^{22,23}

For evaluating the bonding behavior of Resin A-2, supernatant, and sediment, a tensile shear test of lap joints was performed. The tensile shear strengths measured are shown in Table V, together with the percentages of cohesive failure in substrate, obtained by visual inspection of the joint after fracture. Qualitatively similar results were obtained for Resin D.

More relevant than looking at the actual tensile strengths measured may be comparing the percentages of cohesive failure within wood. These are much higher for the original resin and the sediment (about 90%). This indicates that in these samples the failure started within the wood material and not at the adhesive joint. The measured strength values may therefore be limited by the tensile strength of the wood substrate. On the other hand, the joint glued with supernatant appears more fragile, showing lower percentage of cohesive failure in wood and lower tensile shear strength, which indicated that the failure was initiated at the adhesive joint. The poorer performance of the supernatant may be associated to its ability to penetrate to some degree

into the substrate, depleting the interface from glue. Recalling Figure 5, the colloidal structures, which are significantly present in the sediment, are expected to remain in the wood surface. The presence of these structures in the joint interface may play an important role in the bonding process, acting as a reactive reinforcing filler.

There is a generalized concept that a well performing UF resin should incorporate low molecular weight species, which are important for substrate wetting and penetration, and higher molecular weight species, which have an important contribution to cohesive strength.^{1,17} Our results emphasize that the "high molecular weight" component of the resin may actually take the form of insoluble molecular aggregates.

CONCLUSIONS

Different microscopy techniques allowed for the visualization of colloidal structures in the UF resins analyzed. Primary particles have dimensions in the order of tenths of micron having spherical or lamellar shapes. These particles are found to be agglomerated to some degree in the original resin. On water dilution, flocculation occurs, originating much larger agglomerates. Two colloidal stabilization mechanisms were suggested, based on solvation by unreacted urea, hindering interparticle hydrogen bonding and electrostatic repulsion due to cations adsorbed at the particle surface. Both mechanisms explain the dilution-flocculation process in terms of depletion of the stabilizing entities from the particle surface.

PSD analyses of different resins showed distinct PSDs, which can be related to the way how the degree of condensation affects the formation of the dispersed solid phase. These differences tend to vanish as the resins age, indicating that molecular aggregation and particle agglomeration proceed along time on a less condensed resin.

The size exclusion chromatography analysis encompasses information on the molecular weight distribution of the soluble polymer and on molecular aggregates from the original dispersed phase that have not been completely solubilized in the solvent. The quantification of the fraction of the RI chromatogram corresponding to molecular aggregates is related to the resins degree of condensation and the aging status. The information from the RALLS sensor confirms qualitatively the presence of insoluble material. Analysis of partially separated phases, obtained by centrifugation, shows that the insoluble portion of the resins does not seem to have a significantly different molecular weight, in relation to the soluble material. The formation of colloidal structures may have to do with aggregation caused by

intermolecular interactions and not with precipitation due to critical molecular weight.

Tensile shear strength experiments performed with the original resin and the centrifugation products (sediment and supernatant) indicated that the presence of the dispersed phase may be relevant for the strengthening of the adhesive bond, acting as a reactive reinforcing filler.

Future work will be focused on the analysis of the resin aging processes on the resins characteristics, particularly on its heterogeneous morphology. In addition, it will be important to study in more detail the bonding mechanism of this biphasic structure in the wood composite production.

The authors thank EuroResinas (Portugal) for providing the resin samples.

References

1. Dunky, M. *Int J Adhes Adhesives* 1998, 18, 95.
2. Dunky, M. 1st European Panels Products Symposium; Llandudno: North Wales, UK, 1997; p 9-11.
3. Zanetti, M.; Pizzi, A.; Faucher, P. *J Appl Polym Sci* 2004, 92, 672.
4. Pratt, T. J.; Johns, W. E.; Rammon, R. M.; Plagemann, W. L. *J Adhes* 1985, 17, 275.
5. Dunker, A. K.; John, W. E.; Rammon, R.; Farmer, B.; Johns, S. J. *J Adhes* 1986, 19, 153.
6. Motter, W. K. Ph.D. Dissertation, Washington State University, 1990; p xi.
7. Grunwald, D. *Kombinierte Analytische Untersuchungen von Klebstoffen für Holzwerkstoffe*; Mensch & Buch Verlag: Berlin, 2002.
8. Zanetti, M.; Pizzi, A.; Beaujean, M.; Pasch, H.; Rode, K.; Dalet, P. *J Appl Polym Sci* 2002, 86, 1855.
9. Despres, A.; Pizzi, A. *J Appl Polym Sci* 2006, 100, 1406.
10. Pizzi, A.; George, B.; Zanetti, M.; Meausoone, P. *J Appl Polym Sci* 2005, 96, 655.
11. Mijatovic, J.; Binder, W. H.; Kubel, F.; Kantner, W. *Macromol Symp* 2002, 181, 373.
12. Carvalho, L. M. H. In Ph.D. Dissertation, University of Porto: Portugal, 1999.
13. Kim, M. G.; No, B. Y.; Lee, S. M.; Nieh, W. L. *J Appl Polym Sci* 2003, 89, 1896.
14. Stulgross, J.; Koutsky, J. A. *J Adhes* 1985, 18, 281.
15. Nichols, G.; Byard, S.; Bloxham, M. J.; Botterill, J.; Dawson, N. J.; Dennis, A.; Diart, V.; North, N. C.; Sherwood, J. D. *J Pharm Sci* 2002, 91, 2103.
16. Caballero-Herrera, A.; Nordstrand, K.; Berndt, K. D.; Nilsson, L. *Biophys J* 2005, 89, 842.
17. Kumar, R. N.; Han, T. L.; Rozman, H. D.; Daud, W. R. W.; Ibrahim, M. S. *J Appl Polym Sci* 2007, 103, 2709.
18. Hlaing, T.; Gilbert, A.; Booth, C. *Br Polym J* 1986, 18, 345.
19. Zeppenfeld, G.; Grunwald, D. *Klebstoffe in der Holz- und Möbelindustrie*; Drw Verlag Weinbrenner 2005.
20. Kadowaki, H. *Bull Chem Soc Jpn* 1936, 11, 248.
21. Xing, C.; Deng, J.; Zhang, S. Y.; Riedl, B.; Cloutier, A. *J Appl Polym Sci* 2005, 98, 2027.
22. Szesztay, M.; Laszlohedvig, Z.; Kovacsovics, E.; Tudos, F. *Holz als Roh- und Werkstoff* 1993, 51, 297.
23. Zorba, T.; Papadopoulou, E.; Hatjiissaak, A.; Paraskevopoulos, K. M.; Chrissafis, K. *J Therm Anal Calorimetry* 2008, 92, 29.