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Characterization of Urea-Formaldehyde Resins by GPC/SEC and HPLC Techniques: Effect of Ageing

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Abstract

During the last 40 years, several analytical techniques have been developed/adapted to characterize urea-formaldehyde (UF) resins. However, a great part of the research about this kind of wood adhesives has been performed by industrial producers and, thus, the main part of the existing knowledge is retained within those companies.

This work describes a methodology for determining the molecular weight distribution (MWD) of UF resins using Gel Permeation Chromatography (GPC)/Size Exclusion Chromatography (SEC) with 2 detectors (differential refractive index (RI) and differential viscosity). This method permitted to characterize/distinguish commercial UF resins produced with different F/U molar ratios and to monitor the molecular weight and MWD with ageing.

An HPLC method was additionally used to evaluate the fraction of unreacted urea, monomethylolurea and dimethylolurea present in commercial UF resins and measure the evolution of these three compounds with ageing.

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Keywords

UF resins, characterization, polymerization reaction, ageing, GPC/SEC, HPLC

1. Introduction

The complex physics and chemistry of urea-formaldehyde (UF) resins has been the subject of several studies. These works have yielded further knowledge regarding these systems, but still many issues remain concerning their structure as well as the kinetics and mechanisms of their formation. The variety of randomly linked structural elements such as methylene bridges, ether bridges, methylol and amide groups,

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and possible cyclic derivatives makes their analysis a tough challenge. Moreover, these highly reactive chemical systems have tendency to change during preparation for the analysis, or during the analysis itself. The difficulty to find suitable solvents for these resins is an additional problem [1]. Fortunately, the availability of modern spectroscopic and chromatographic methods has led to considerable improvements in the characterization of these resins: more specifically, ^{13}C NMR [2] and FT-IR [3] for the structure and GPC/SEC [4–13] and even more recently MALDI-TOF-MS [14] for the determination of the detailed chemical constitution, although the true molecular weight distribution (MWD) remains elusive. More recently, Minopoulou *et al.* [15] explored the capabilities of FT-NIR spectroscopy [15, 16] for on-line monitoring of the amino resin synthesis. The cured system has been investigated by solid state ^{13}C CP MAS NMR [17], FT-IR [18] and Raman spectroscopy [19]. The reaction kinetics has been studied experimentally [20] and theoretically [19, 21, 22].

In this work, the characterization of UF resins is focused on the determination of the MWD. The mechanical and bonding properties of an adhesive are strongly dependent on its MWD [23, 24]. This can be done by GPC/SEC, but the low solubility of the colloidal fraction of these resins introduces unique features in the chromatograms that must be taken into account [25].

GPC/SEC is a controlled separation technique in which molecules are separated on the basis of their hydrodynamic molecular volume or size [26]. With proper column calibration or using molecular weight-sensitive detectors, such as light scattering, viscosimetry, or mass spectrometry, the MWD and the statistical molecular weight averages can be readily obtained. In their review, Barth *et al.* [26] mentioned that the GPC/SEC is the premier technique to evaluate these properties for both synthetic polymers and biopolymers.

The main problem using GPC/SEC is the choice of the proper solvent and mobile phase to ensure complete resin solubility. It is necessary to use dimethylformamide (DMF) or even dimethylsulfoxide (DMSO) to dissolve the higher molecular mass fractions. Salts such as lithium chloride (LiCl) or lithium bromide (LiBr) are often used to increase the solvent polarity and consequent polymer solubility, thus, minimizing the formation of aggregates. Another problem is related to the complex nature of the polymer present in UF resins, where linear and branched fractions coexist. The calibration standards cannot represent this accurately, leading to inaccuracies in the measured distribution of molecular masses. In contrast to methods such as the nowadays seldom used analytical ultracentrifugation, no exact molecular mass distribution can be extracted from chromatographic traces without several assumptions. But even for linear fractions of UF polymers, as there are no commercial standards for molecular mass calibration (UF compounds with a single molar mass and molecular structure), oligomers would have to be synthesized in the laboratory. GPC/SEC together with light scattering detection, which should avoid the need for external calibration, is not a viable solution, as only the high molar masses

are detected by the light scattering sensor [1] and for this reason, the calculation of averages such as weight and number molar masses is still much affected by the absence of a reliable calibration.

Some partial success has been claimed for the use of GPC/SEC in the analysis of UF polymers in previous research works. For instance, Dankelman *et al.* [5] have reported that GPC/SEC can estimate the ratio of low to high molecular mass components as well as the amounts of some oligomers. Billiani *et al.* [4] used this technique to characterize UF resins synthesized with different degrees of condensation. They found that measured average molecular mass increased with the duration of the condensation steps, from a few thousand up to more than 100 kDa.

In the present work, preliminary studies have pointed out that the Right Angle Laser Light Scattering (RALLS) signal is too weak in the low to moderate molecular weight fractions of the chromatograms obtained with UF resins. Additionally, preliminary tests with polystyrene standards indicated that this RALLS system was not able to detect molecular weights below about 7000 g/mol. This implies the need for using a traditional, universal calibration technique, with two detectors: differential refractive index and differential viscosity. The information provided by the RALLS detector was used only in a qualitative way.

The GPC/SEC technique is useful for the characterization of MWD, but does not give complete information about the composition of the low molecular weight species present. For this purpose, HPLC can be effectively used for identifying low molecular weight components in UF resins [27, 28], and may contribute to a deeper understanding of UF chemistry.

Grunwald [29] mentioned the combination of HPLC with GPC techniques as a relevant area for future R&D on UF resins. In our present work HPLC was used successfully for determining urea, monomethylolurea and dimethylolurea in different resins.

2. Materials and Methods

2.1. Resins Preparation

All resins characterized in this work were produced according to the alkaline–acid process, which consists basically of three steps: methylation under alkaline conditions, condensation under acidic conditions, and neutralization and addition of the so-called final urea or last urea.

Samples of UF-R5 and UF-R2 were supplied by EuroResinas (Sonae Indústria, Portugal), while sample of UF-Exp17 was prepared in our laboratory according to procedure described elsewhere [30]. Table 1 shows the technical data collected for these three resins. All of them are UF resins in water solution with low amounts of melamine and hexamine. The main differences in the synthesis are the duration of the condensation step — leading to different kinds of polymers formed — and the final amount of urea added — leading to different final F/U ratios. Resin UF-R2 has the longest condensation step and the largest amount of final urea, while resin

Table 1.

Technical data on UF resins used

Resin	Molar ratio F/U	Solids content ¹ (%)	Gel time ² (s)	pH range (25°C)	Viscosity ³ (25°C) (mPa s)
UF-R5	1.30	63 ± 1	35–55	7.5–8.5	150–350
UF-R2	1.00	64 ± 1	40–100	8.0–9.5	150–300
UF-Exp17	1.12	64 ± 1	40–100	8.0–9.5	150–300

¹ 105°C, 3 h.² Gel time at 100°C with 3 wt% of NH₄Cl (20 wt% solution).³ Brookfield viscometer.**Table 2.**

Technical data on UF-resins used from different producers

Resin	Molar ratio F/U	Solids content ¹ (%)	Gel time ² (s)	pH value (25°C)	Viscosity ³ (25°C) (mPa s)
UF-A	1.03	67.4	56	8.25	220
UF-B	1.12	63.6	64	8.78	210
UF-C	1.11	69.0	54	8.33	310
UF-D	1.15	68.1	43	8.40	400
UF-E	n.a.	64.0	57	8.30	258

¹ 105°C, 3 h.² Gel time at 100°C with 3 wt% of NH₄Cl (20 wt% solution).³ Brookfield viscometer.

UF-R5 has the shortest condensation step and the lowest amount of final urea. Resin UF-Exp17 has a sequential addition of urea during the condensation step and the preparation procedure is completely described by Ferra *et al.* [30].

Some commercial resins from several major European producers were also studied. The principal characteristics are presented in Table 2.

2.2. GPC/SEC Analysis

The main instrument used was a Gilson HPLC system equipped with a Gilson Differential RI detector and a Viscotek Dual Detector (differential viscosity and a light scattering detector RALLS). A Rheodyne 7125 injector with a 20 µl loop was used for injection. The column used was a Waters Styragel HR1 5 µm column. 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 poly (ethylene glycol) standards from Polymer Laboratories Ltd., UK, with molecular weight between 106–12 140. The RALLS detector was not used for the determination of molecular weight, because of no response of the detector to lower molecular weights. However, the RALLS signals were analysed qualitatively.

The samples for GPC/SEC analysis were prepared by dissolving the resin in DMSO, then vigorously stirring and filtering through a 0.45 μm Nylon syringe filter. The addition of LiCl and the use of an ultrasonic bath in the preparation of the samples were also tested, but the differences found in chromatograms were slight or nonexistent.

2.3. 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 column used was a Waters Spherisorb silica column. A mixture of acetonitrile and 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 for HPLC analysis were prepared by dissolving the resin in 1 ml of DMF. After vigorous agitation for 1 min, it was diluted in 2 ml of mobile phase. When the mobile phase was added, flocculation occurred and the sample was allowed to rest for 10 min. The supernatant was finally withdrawn with a micropipette.

3. Results and Discussion

3.1. Characterization of UF Resins

3.1.1. Determination of Molecular Weight Distribution

In Fig. 1 one can see the GPC/SEC chromatograms of resins UF-R5 and UF-R2. In both cases, at least two samples were prepared and analysed in order to verify the reproducibility of the results.

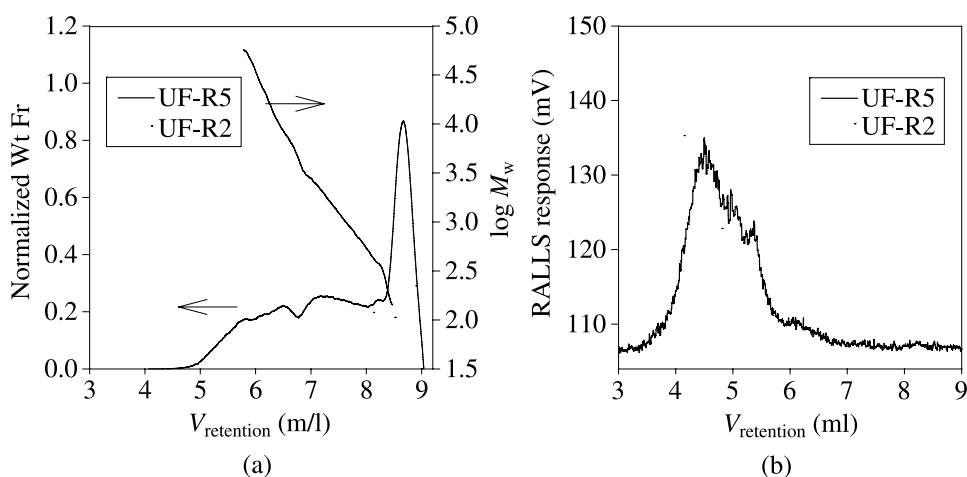


Figure 1. Chromatograms for UF-R5 and UF-R2 diluted 3% in DMSO and stored for 5 days at 25°C. (a) Normalized weight fraction (Wt Fr); (b) RALLS response.

Figure 1(a) shows the normalized weight fraction (Wt Fr) for resins UF-R5 and UF-R2 after 5 days. The general features of the chromatograms are similar to those found in the literature on UF resins. Three zones can be identified in the chromatograms, as discussed in a previous work [25]. Zone I (elution volume between 8 and 9 ml) corresponds to the low molecular weight species. Zone II (elution volume between 5.8 and 8 ml) corresponds to intermediate molecular weight species, with molecular weights ranging from about tens of thousands Da to about 600 Da. Zone III (elution volume below 5.8 ml) would correspond to species with quite high molecular weights, eluting before the exclusion limit of the GPC/SEC column. It has been suggested that these are molecular aggregates and not individual polymer molecules [9, 31]. These aggregates would be insoluble in the original aqueous medium, probably forming larger colloidal structures which become partially disaggregated in the DMSO solvent.

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

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

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

f_1 reflects the amount of low molecular weight species in the sample, while f_2 indicates the fraction of high molecular weight species, probably in the form of molecular aggregates in the polymerized material.

The main difference between the chromatograms for resins UF-R5 and UF-R2 (Fig. 1(a)) is observed in the zone of low molecular weights, which probably originated from the larger amount of the urea added in the last step of the reaction for resin UF-R2. In addition, resin UF-R2 shows a more pronounced tail for low elution volumes, corresponding to Zone III. This probably reflects the higher condensation state of this resin, which induces higher molecular aggregation [32]. Other than this, the two chromatograms are generically very similar. However, as will be discussed below, ageing will introduce more pronounced differences.

The RALLS response (Fig. 1(b)) gives qualitative information on the insoluble particles present in solution [32]. One can see that the RALLS chromatograms are similar for the two resins, but the trace for resin UF-R2 is more intense at lower elution volumes, once again indicating a more significant aggregation.

The quantitative data shown in Table 3 confirm the previous analysis: resin UF-R2 presents a higher fraction of lower molecular weight species (f_1) as well as a higher fraction of insoluble aggregates (f_2). Resin UF-R2 is the most condensed of the resins studied in this work, but this feature is not evidenced from the molecular weight results, because of the larger addition of urea in the last step of the reaction. Nevertheless, this resin shows the highest value of parameter f_2 , which is indeed relatable to the highest degree of condensation.

3.1.2. Determination of the Fractions of Urea and Methylolureas

Figure 2 presents a typical chromatogram obtained for a UF resin in HPLC. The three first peaks correspond to urea, monomethylolurea and dimethylolurea, respectively. This was confirmed by injection of the isolated compounds. The other peaks in the chromatogram correspond to oligomeric species.

Table 3.

Values of M_n , M_w , polydispersity (M_w/M_n), and parameters f_1 and f_2 , obtained by SEC for UF-R5 and UF-R2 stored for 5 days at 25°C

Resin	M_n	M_w	M_w/M_n	f_1	f_2
UF-R5	3.77×10^2	3.59×10^3	9.5	0.356	0.171
UF-R2	2.90×10^2	3.44×10^3	11.9	0.410	0.193

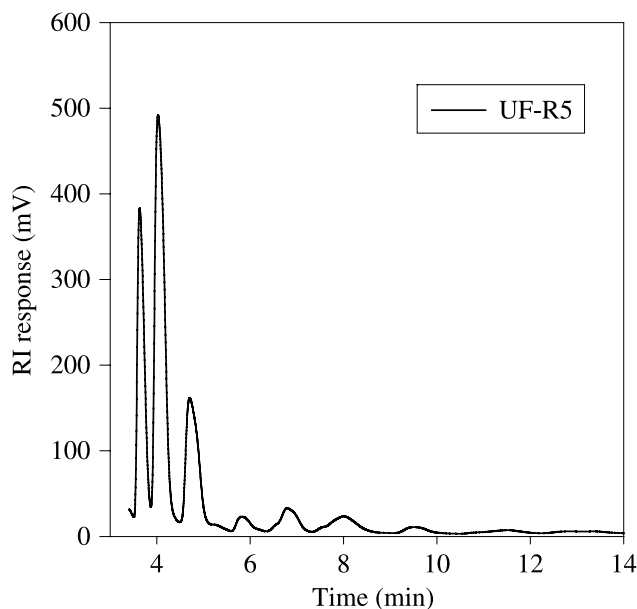


Figure 2. Chromatogram obtained for resin UF-R5.

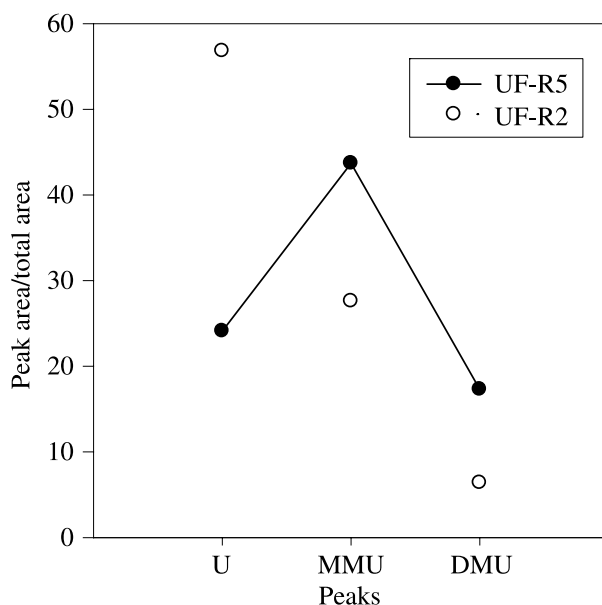


Figure 3. Peak areas normalized by total chromatogram area for UF-R5 and UF-R2 stored at 25°C.

Figure 3 shows the distribution of the urea, monomethylolurea and dimethylolurea present in solution for the two resins stored at 25°C for 5 days after synthesis. UF-R2 has a much larger fraction of unreacted urea than resin UF-R5. The last urea was added in order to react with the free formaldehyde present, but as the added amount was large, most of the urea remained unreacted in the final resin. However, this unreacted urea may play another role, since it may form a solvation layer surrounding the colloidal aggregates surface, contributing to its stabilization against agglomeration [25].

3.1.3. Analysis of Commercial UF Resins

Five commercial UF resins from different European producers were analysed. Figure 4(a) shows the normalized Wt Fr obtained by GPC/SEC. One can see that UF-D presents a distinctly larger fraction of insoluble aggregates (Zone III) and a higher fraction of oligomers in the elution volume range 7.8–8.2 ml. On the other hand, resin UF-B has the lowest fraction of insoluble aggregates and a larger fraction of polymer with moderate molecular weight. Resins UF-A, UF-C and UF-E present similar chromatograms, but some differences in the three zones of the chromatograms were found, namely the large amount of polymer with low molecular weight present in UF-A and a large amount of insoluble aggregates existing in UF-E.

The chromatographic trace from the RALLS detector shown in Fig. 4(b) agrees qualitatively with the previous analysis concerning the presence of insoluble aggregates in the different resins.

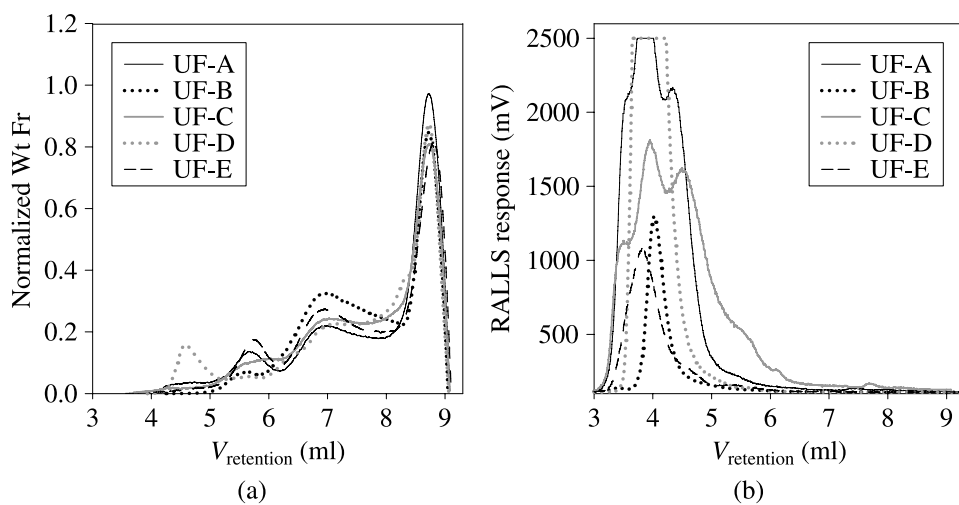


Figure 4. Chromatograms for five UF resins from different manufacturers in Europe. (a) Normalized weight fraction; (b) RALLS response.

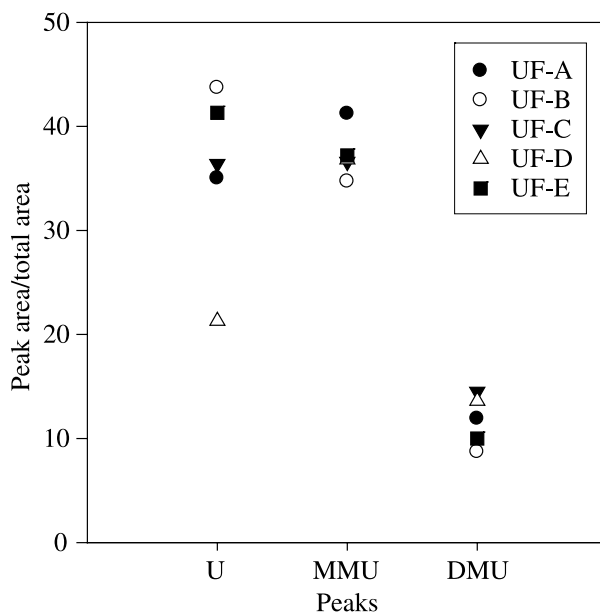


Figure 5. Ratios of peak areas/total area of urea (U), monomethylolurea (MMU) and dimethylolurea (DMU) for five UF resins from different producers.

The distributions of urea and methylolureas present in the five commercial resins are shown in Fig. 5. The main difference among the resins is the fraction of unreacted urea. In particular, the fraction of urea in resin UF-D is approximately half of

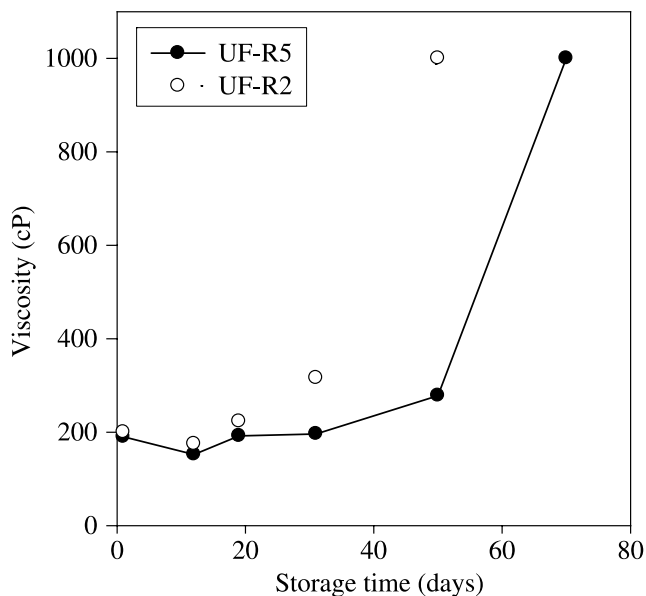


Figure 6. Viscosity of UF-R5 and UF-R2 with storage time at 25°C.

the value for the other resins. The final percentages of urea and methylolureas as shown above are related to the amount of last urea added and the free formaldehyde present in the final condensation step.

The results obtained by GPC/SEC and HPLC indicate that each producer had likely used different processes for the production of UF resins.

3.2. Monitoring the Ageing of UF Resins

Two UF resins were analysed after ageing, using GPC/SEC and HPLC techniques. The pH and viscosity of resins were also monitored.

Figure 6 depicts the evolution of viscosity for resins UF-R2 and UF-R5 during storage at 25°C. The initial slight decrease in viscosity is related to the migration of hydroxymethyl groups (methylolureas) from the polymeric UF resin components to the last urea as reported by Kim [33]. Resin UF-R2 gels faster than UF-R5, but both are stable up to 30 days, which is the normal specification for UF resins. The storage time limit for UF-R2 is about 40 days, while for UF-R5 it is about 60 days. The higher degree of condensation of the resin UF-R2 can explain this behaviour.

UF-R5 and UF-R2 resins were monitored at six different ageing periods (5, 12, 19, 32, 50 and 53 days). Figures 7 and 8 show the chromatograms for some selected storage times. Note that no significant changes in the molecular weight distributions were observed for the first two storage times (5 and 12 days). This is consistent with the stable viscosity measurements for the first 20 days. Kim *et al.* [34] reported similar results by monitoring the storage of UF resins using ^{13}C NMR. They showed

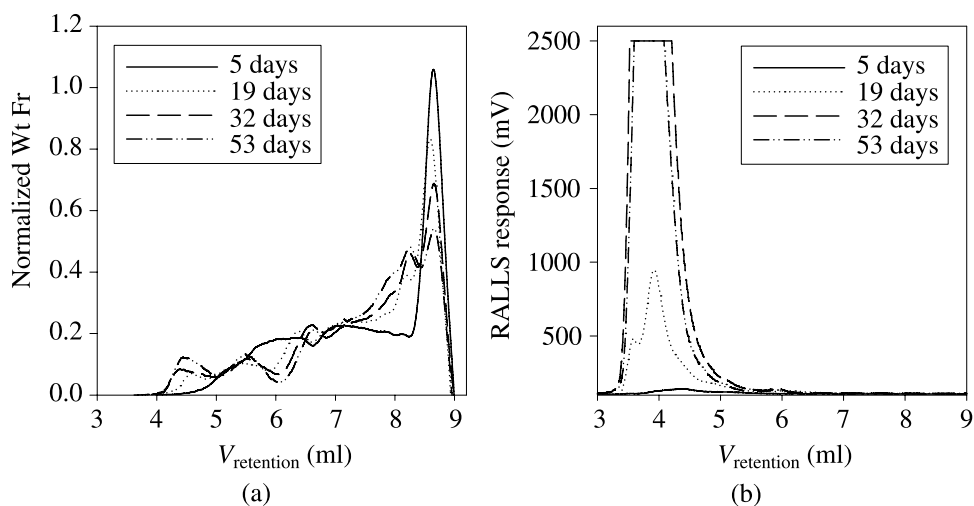


Figure 7. Chromatograms for UF-R2 diluted 3% in DMSO, for different storage periods at 25°C. (a) Normalized weight fraction; (b) RALLS response.

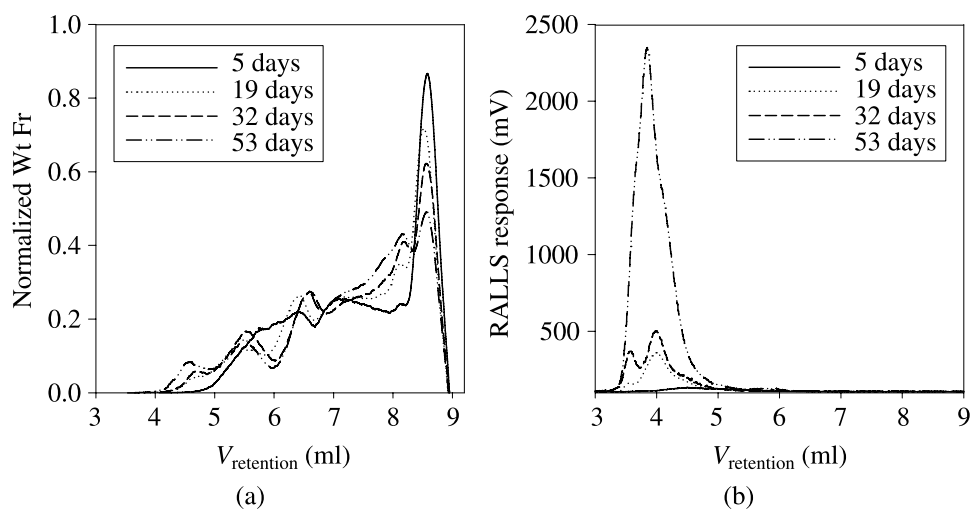


Figure 8. Chromatograms for UF-R5 diluted 3% in DMSO, for different storage periods at 25°C. (a) Normalized weight fraction; (b) RALLS response.

that the degree of polymerization remained stable for about 15 days but then increased rapidly until 30 days and remained constant afterwards until gelling.

On analysing the chromatograms for 4 selected storage times, we find that urea and methylolureas (peak at 8.5 ml) decrease with ageing while the peaks at 8.2 and 7.8 ml increase. This suggests that urea and methylolureas react during storage to produce a polymer with a narrow range of molecular mass/size (peak at 8.2 ml),

which, in turn, reacts to produce polymer eluting in the vicinity of 7.8 ml, visible as a broad peak. Globally, there is a decrease in Zone I of the chromatogram, yielding an increase in moderate to high molecular weight polymer (Zone II) and in molecular aggregates (Zone III). Interestingly, a well-defined separation between Zones II and III becomes apparent (at an elution volume of about 6 ml), which was also visible in the commercial resins (Fig. 4(a)). This might be associated with the process of agglomeration of smaller aggregates into larger particles, shifting towards the left portion of the chromatogram.

RALLS responses show a sharp increase in insoluble aggregates between 19 and 32 days for resin UF-R2 and between 32 and 53 days for resin UF-R5. This is related to the viscosity evolution previously measured for both resins (Fig. 6): the pre-gelling increase in viscosity for each resin is associated with a significant formation of insoluble molecular aggregates or, as mentioned above, to agglomeration of existent aggregates into larger particles. Zanetti and Pizzi [35] and Despres and Pizzi [31] reported that the continuing formation of colloidal structures followed by the formation of ‘superaggregates’ (globular masses) were the normal steps for physical gelation of MUF and UF resins.

From the data in Table 4 for resins UF-R2 and UF-R5 at different ages, one can see that the value of polydispersity decreases with time, due to the condensation of the low molecular weight species to form polymers with moderate and high molecular weights. This solubilized polymer might then form insoluble molecular aggregates, but the portion of the chromatogram corresponding to the insoluble molecular aggregates is not included in the molecular weight calculation, as mentioned above. The decrease of the low molecular weight fraction (f_1) and the increase of insoluble aggregates fraction (f_2) with ageing corroborates the idea that condensation progresses with storage time, consuming urea and oligomers. The decrease in f_2 observed for resin UF-R5 after 50 days is related to the large increase in fraction of the polymer with moderate molecular weight (Zone II).

Table 4.

Values of M_n , M_w , polydispersity (M_w/M_n), and parameters f_1 and f_2 , obtained by GPC/SEC for UF-R2 and UF-R5 stored for different days at 25°C

Storage period	M_n	M_w	M_w/M_n	f_1	f_2
UF-R2					
5	2.90×10^2	3.44×10^3	11.9	0.410	0.193
32	3.79×10^2	2.50×10^3	6.6	0.315	0.201
50	4.14×10^2	2.03×10^3	4.9	0.303	0.217
UF-R5					
5	3.77×10^2	3.59×10^3	9.5	0.356	0.171
32	4.55×10^2	2.30×10^3	6.6	0.268	0.190
50	5.10×10^2	2.75×10^3	5.4	0.225	0.185

It is also interesting to look at the RALLS responses obtained for resins UF-R2 and UF-R5 with ageing. Figures 7(b) and 8(b) show a peak located roughly in the region corresponding to Zone III, assigned to molecular aggregates present in the samples. When resins were ‘fresh’ the peak magnitude was very low, but with ageing it increased sharply for both resins. This seems to indicate that the ageing process produces a significantly higher concentration of aggregated material. These aggregates might actually be agglomerated into larger particles in the resin.

Figures 9 and 10 show the evolution with ageing of the fractions of urea, monomethylolurea, dimethylolurea and three more oligomeric species present in the HPLC chromatograms, for resins UF-R2 and UF-R5, respectively. According to the results described by Ludlam *et al.* [28], who used the same analysis conditions (silica columns with NH_2 groups, mobile phase and sample preparation) for the identification of oligomeric species present in UF resins, the three unknown peaks can be identified as monomethylolmethylenediurea, monomethyloloxymethylenediurea and dimethylolmethylenediurea, respectively.

In both cases, the fraction of urea in the solution decreases significantly up to 30 days. It ends up becoming stable as the formaldehyde present in the solution is consumed. It is interesting to note that the evolution of dimethylolurea is different for the two resins. It remains almost constant for resin UF-R2 but it goes through a maximum at about 30 days for resin UF-R5. This behaviour is related

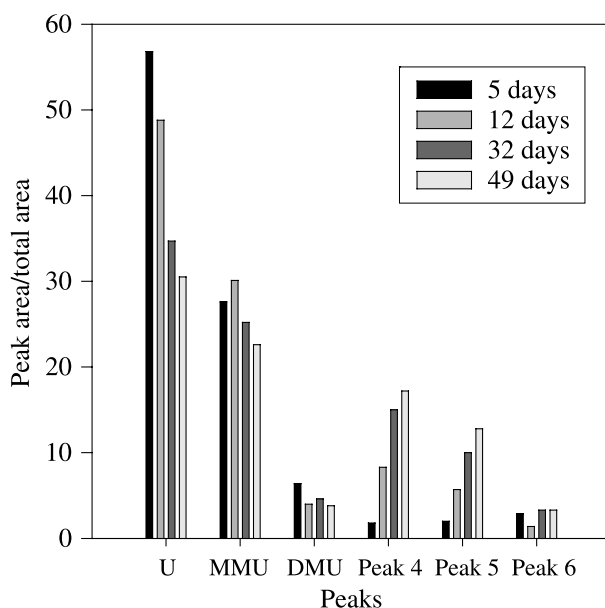


Figure 9. Evolution of the ratios of peak areas/total area of the urea (U), monomethylolurea (MMU), dimethylolurea (DMU) and three other oligomeric species for UF-R2 stored for various periods at 25°C.

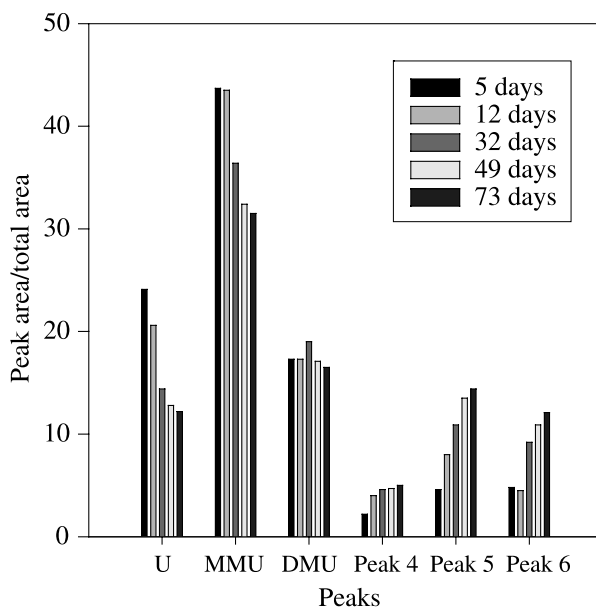


Figure 10. Evolution of the ratios of peak areas/total area of the urea (U), monomethylolurea (MMU), dimethylolurea (DMU) and three other oligomeric species for UF-R5 stored for various periods at 25°C.

to the existence of free formaldehyde in the solution for resin UF-R5, which reacts with urea and mostly with monomethylolurea (that is in excess in solution) forming dimethylolurea. These results indicate that the polymerization reactions between free formaldehyde, urea and methylolureas continue during the storage of the resin. Similar observations were reported by Kim *et al.* [34], which reported that the amount of monomethylolurea during storage could increase or decrease depending on the amount of free formaldehyde present in the solution.

3.3. Determination of Water Tolerance

UF resins are colloidal suspensions that tend to flocculate as they are diluted in water [25]. Figure 11 shows the GPC/SEC chromatograms obtained for the original resin UF-R5 after 5 days storage at 25°C and for the resin flocculated with a large excess of water. In this case the supernatant was collected after sedimentation of the precipitate and analysed. The corresponding chromatogram shows similar concentrations of moderate and low weight molecules (elution volumes between 7.0 to 9.0 ml), but a higher concentration of the zone that corresponds to high/moderate molecular weight (elution volumes between 5.8 to 7.0 ml) and a lower concentration of insoluble molecular aggregates (Zone III). Apparently, the transfer of molecules from the high to the intermediate molecular weight zone is related to disaggregation of the larger particles due to the dilution. It can also be seen from Fig. 11 that insoluble aggregates originally corresponding to Zone III form aggregates of

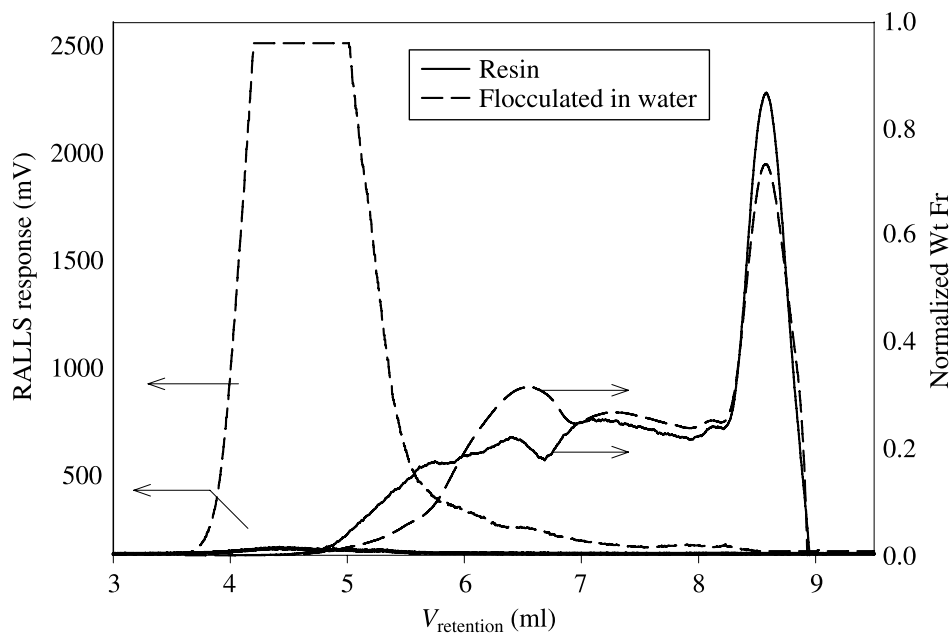


Figure 11. Chromatograms for UF-R5 aged for 5 days, diluted in DMSO and very diluted (floculated) in water.

larger dimensions after flocculation, thus, eluting earlier. These aggregates only are detected by the RALLS sensor due to their low concentration. However, it is necessary to use some caution in analysing the results from RALLS detector because it saturates in the zone between 3.5 to 4.5 ml of the chromatogram. A similar behaviour was observed for other UF resin, namely UF-R2.

These results demonstrate that the GPC/SEC is an interesting technique to evaluate the water tolerance. The evaluation of water tolerance using the common method, which consists in the addition of small amounts of water until the resin flocculation occurs, is very difficult and inaccurate. A high value of water tolerance confers good washdown properties to the product and allows easy cleaning of the apparatus used for production and storage of UF resins.

4. Conclusions

Different UF resins were characterized by GPC/SEC and HPLC techniques.

The GPC/SEC analysis encompasses information on the MWD of the soluble polymer as well as on insoluble molecular aggregates that constitute the original dispersed phase and have not been completely dissolved in the DMSO solvent. The information obtained by GPC/SEC is useful for characterization of the resins and allows to distinguish resins obtained from different production processes. The

information from the RALLS detector complements qualitatively the information on the insoluble material.

GPC/SEC and HPLC methods permitted to verify that UF resins produced by the European companies had distinct characteristics (MWD and relative amounts of U, MMU and DMU). These results suggest that each producer uses a particular process for the production of UF resin.

The GPC/SEC analyses of the resins at different ageing periods indicated that both polymer condensation and aggregation/agglomeration proceed during storage. This technique permits to monitor accurately the ageing of UF resins.

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