Colloidal Aggregation of Aminoplastic Polycondensation Resins: Urea–Formaldehyde Versus Melamine–Formaldehyde and Melamine–Urea–Formaldehyde Resins

A. Despres,[1,2] A. Pizzi[1,2]

[1]*ENSTIB, University of Nancy 1, Epinal, France*
[2]*LERMAB, UMR 1093, Epinal, France*

ABSTRACT: Colloidal particles formation followed by their clustering have been shown to be the normal way of ageing of aminoplastic resins, namely urea–formaldehyde (UF) resins, melamine–formaldehyde (MF) resins, and melamine–urea–formaldehyde (MUF) resins. Ageing or further advancement of the resin by other means such as longer condensation times causes whitening of the resin. This is a macroscopic indication of both the formation of colloidal particles and of their clustering. It eventually progresses to resins, which are mostly in colloidal, clustered state, followed much later on by a supercluster formation starting to involve the whole resin. The initial, filament-like colloidal aggregates formed by UF resins have different appearance than the globular ones formed by MF resins. MUF resins present a short rod-like appearance hybrid between the two. GPC has been shown to detect the existence of colloidal superaggregates in a UF resin, while smaller aggregates might not be detected at all. The star-like structures visible in the colloidal globules of MF resins are likely to be light interference patterns of the early colloidal structures in the resins. These star-like interference patterns become more complex with resin ageing or advancement due to the advancement of the resin to more complex aggregates, to eventually reach the stage in which filament-like and rod-like structures start to appear. The next step is formation of globular masses that are representative of the true start of physical gelation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1406–1412, 2006

Key words: colloids; resins; ageing; physical gelation; size distribution

INTRODUCTION

The wood panels and resin impregnated paper industries rely heavily on the use of synthetic polycondensation resins, a major class of these for such an application being the aminoplastic resins, namely urea–formaldehyde (UF), melamine–formaldehyde (MF), and melamine–urea–formaldehyde (MUF) resins. All formaldehyde-based resins, including aminoplastic resins, have been perceived for a long time to be in colloidal state.[1–11] Performance improvements and shelf life of these resins appear to be closely linked to their colloidal state or to their disruption.[3–11] Their colloidal state, however, up to now has been studied in detail only for MF and MUF resins.[6–11] For example, ageing of MUF resins was shown to proceed from clear resin (molecular colloidal aggregation) to superclusters of a whitened thixotropic resin, which is the beginning of physical gelation to, finally, liquid/clusters separation, which is the terminal stage of physical gelation.[10,11]

Colloidal particles formation followed by their clustering have been shown to be the normal way of ageing of MUF resins,[10] and optical microscopy and other evidence for it has also been obtained.[10,11] Ageing, or further advancement of the resin by any other means, such as longer condensation times, causes whitening of the resin. This is a macroscopic indication of both the formation of colloidal particles and of their clustering. Some clustering appears rather early in this process, even when the great majority of the resin does visually appear to be in colloidal state, being transparent. However, it eventually progresses to resins, which are mostly in colloidal, clustered state, followed much later on by a supercluster formation starting to involve the whole resin.

While the behavior observed for MUF resins appeared to be indicative of what could be obtained for MF resins, some discrepancies are evident when comparing the results obtained with the two resins, namely the shape of the aggregates obtained by different researchers.[9,10] As regards the most common UF resins, no in depth research record on their colloi-

dal state can be found in the literature. It is necessary to compare then what occurs with UF resins, to try to understand the differences in behavior noted between MUF and MF resins. This study then deal with an optical microscopy investigation of the shape of the colloidal superaggregates obtained for the three resins and reports on the detection of the presence of these superaggregates by GPC.

EXPERIMENTAL

Preparation of UF, MF and MUF resins

The MF resin of F/M molar ratio of 1.85 was prepared by mixing 80 g melamine with 92.8 g 37% formalin (methanol-stabilized) solution and 115.2 g water in a glass reactor equipped with reflux condenser and mechanical stirrer. The pH was initially adjusted between 9.0 and 9.5, and the temperature was raised to 92–93°C under continuous mechanical stirring. The mixture was allowed to react for 1 h, then the pH was adjusted to 7.2 by the addition of acetic acid and left to react until a water-tolerance value of 200% was reached. The pH was then adjusted to 10–10.5 by using 33% NaOH water solution; the resin cooled rapidly down to ambient temperature, the pH was checked and adjusted to 10.5, if needed.

Four different UF resins were used. Two pure UF resins of F/U molar ratios 1.8 and 1.5, respectively, and a UF resin fortified with 4% melamine of final molar ratio 1.2. All these three resins were prepared in the laboratory, according to procedures outlined below. The fourth resin used was a commercial pure UF resin (from Atochem, France) of molar ratio F/U = 1.2.

The manufacturing procedure for the two UF resins of 1.8 and 1.5M ratios is given here. For the 1.8M ratio resin: to 215.6 g of Formurea (precondensate of formaldehyde 54%, urea 23%, water 23%) were added 56.2 g urea and 84 g of water. The pH was set at 8.5, and the temperature brought to 92 to 93°C under mechanical stirring, while maintaining the pH at 7.3–7.6. After 0.5 to 1 h, the pH was dropped to 5.3 by the addition of formic acid and the reaction continued until a water-tolerance value of the resin of 200% was reached. The pH was then immediately increased to 8.5 by adding 33% NaOH water solution and 23.5 g urea added to the reaction mixture, and the resin cooled. After the resin cooled down to ambient temperature, the pH was adjusted to 8.5, if needed.

The manufacturing procedure for the UF resin with 4% melamine added was as follows: to 176.8 g of formurea (precondensate of formaldehyde 57.1%, urea 23%, water 23%) were added 40.6 g urea and 68.3 g of water. The pH was adjusted to 10–10.4, and the temperature brought to 92°C under mechanical stirring. After 30 min of reaction, the pH dropped to 5–5.3 by

adding formic acid, and the reaction continued until a water-tolerance value of the resin of 200% was reached. The pH was then adjusted to 9.5 with a 33% NaOH water solution. 19.6 g of melamine premixed with 52.5 g water and 7 g dimethylformamide were then added, and the reaction continued until a water-tolerance value of the resin of 150% was reached. This phase of the reaction was rather fast, and the reaction time was generally quite short, just a few minutes. The pH was then increased to between 9.9 and 10.2, 77 g of second urea added and the pH adjusted to 10.5. The resin was then cooled to ambient temperature, and the pH was adjusted again to 10.5, if needed.

In the MUF resin formulation used, the addition of melamine and urea was done according to their respective reactivities with formaldehyde with a known, sequential, manufacturing procedure.[12,13] This was done to ensure the maximum extent of copolymerization of melamine and urea. This type of formulation generally gives very strong bonds.

The MUF formulation, of molar ratio (M + U): F of 1:1.2 and of M:U weight ratios of 47:53 was prepared according to known sequential manufacturing procedures.[10] Herewith is given the manufacturing procedure for a resin of 1:1.2M ratio, M:U of 47:53: to 142.2 g of formurea (precondensate of formaldehyde 54%, urea 23%, water 23%) were added 16.4 g urea and 30.0–35.0 g of water. The pH was set at 10–10.4, and the temperature brought to 92–93°C under mechanical stirring. The pH was then lowered to 7.8, and the reaction continued at the same temperature, allowing the pH to fall by itself over a period of 1 h 30 min to a pH of 6.5–7 (the pH must never fall below 5). To bring the pH to 9.5 or higher, 30% NaOH solution was added, then 80 g of melamine premixed with 42.8 g of water was added. 1–2 g of dimethylformamide was then added to the reaction mixture, maintaining a temperature of 93°C. The percentage water tolerance of the resin was checked every 10 min while the pH was allowed to fall by itself. When the water-tolerance (the percentage of water that is possible to add to the liquid resin) value reached 180–200% (the pH reached was ~7.2), 42.8 g of urea was added, and the pH was again brought up to 9.5. The reaction was continued until the water-tolerance value reached was <150% (the pH reached 7.7 at this stage).

The pH was then corrected to 10.0–10.2 by the addition of NaOH solution, and the resin cooled and stored.

Gel permeation chromatography

Samples of each of the UF, MF, and MUF resins described earlier were analyzed by gel permeation chromatography (GPC) (Waters 515 HPLC pump) through a Styragel HR1 column (for determination of M_w between 100 and 5000) at an elution rate of 1 mL/min,
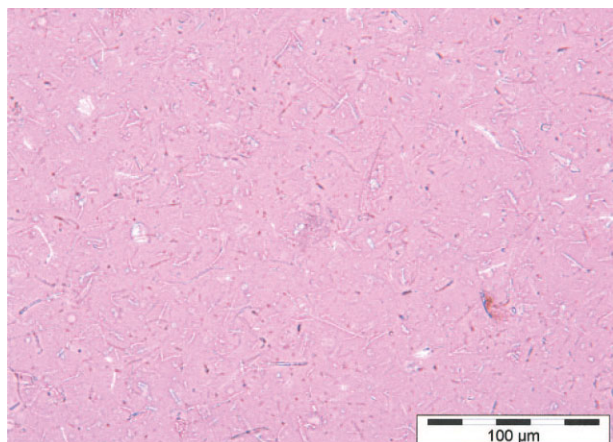
Figure 1 Optical microscopy micrograph of a whitened UF resin of molar ratio F/U = 1.8. Note the presence of long filament-like aggregates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

after polyethylene glycol (PEG) calibration of the column. The PEG samples used for calibration had M_w of 200, 300, 400, 600, 1000, 2000, 3400, 8000, and 10,000. Each resin sample, after having been dissolved in dimethylformamide, was tested without having been filtered, to ensure that the colloidal aggregates were not lost, but resulted in the chromatogram. A Waters 410 refractometer was used as the detector.

Polarized light optical microscopy

The samples of MUF resins were spread in thin film on glass and examined by optical microscopy through a polarizing Olympus BH2 microscope equipped with a Color View Soft Imaging System, of a high resolution
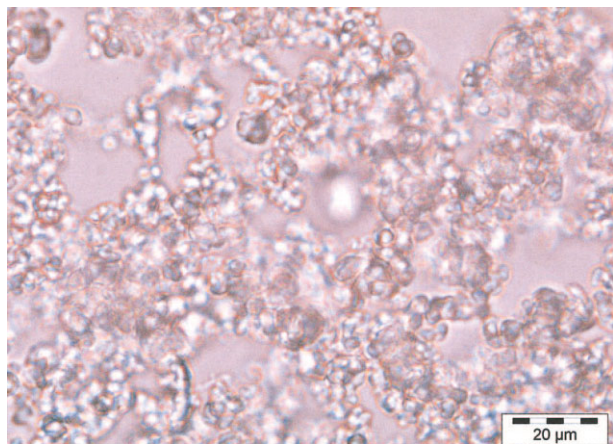

Figure 3 Polarizing light optical microscope micrograph of the very diffuse superclusters of colloidal particles in a whitened, nonsequential MUF resin. Resin is 2 months old. Note the size of particles at ~3.0–5.0 μm. Note that great majority of the resin is in colloidal cluster form. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(3.3 megapixels) digital camera and equipped of cooling by Petier effect. The program used for the elaboration of data was analySIS.

DISCUSSION

The polarized optical microscopy micrographs in Figures 1–3 show considerable differences in the shape of the colloidal superaggregates formed by UF, MF, and MUF resins. In Figure 1, elongated rod-like and filament-like structures are clearly visible, in the case of the UF resin. This resin is cloudy/opaque, but still

Figure 2 Optical microscopy micrograph of a whitened pure MF resin of molar ratio F/M = 1.8. Note the presence of globular aggregate superclusters. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
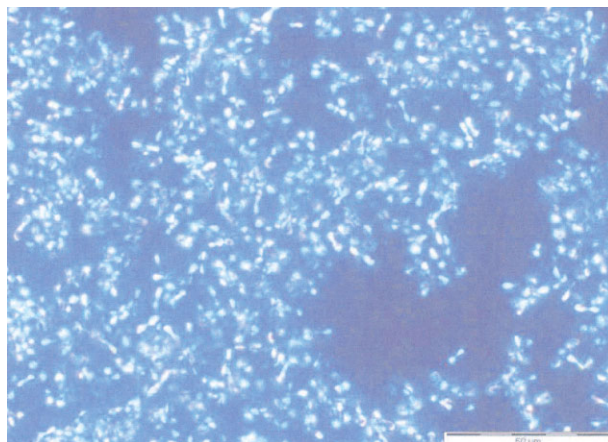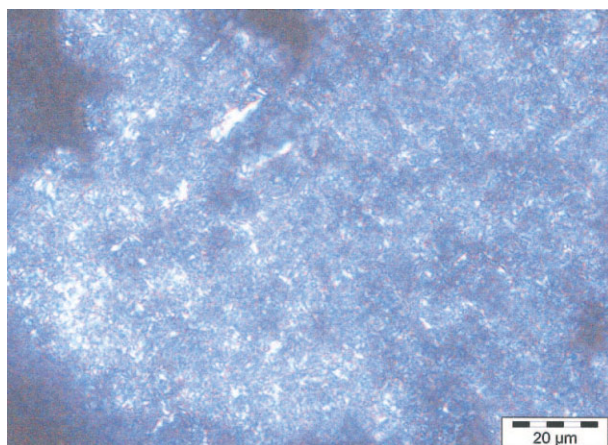

Figure 4 Polarizing light optical microscope micrograph of a whitened UF resin of molar ratio F/U = 1.8. Note the presence of both filament-like and globular aggregates present in the mass of resin. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]
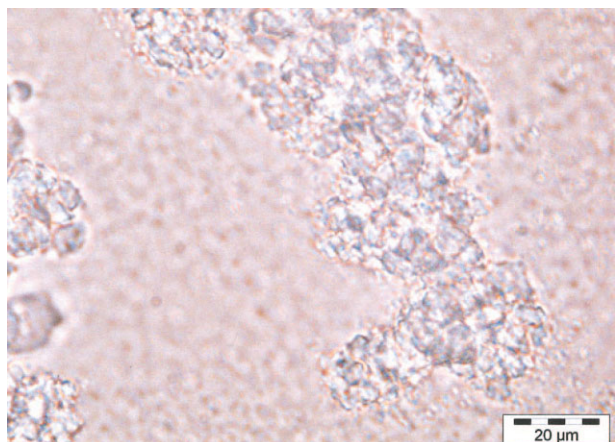
Figure 5 Optical microscopy micrograph of a whitened UF resin of molar ratio F/U = 1.8 already at or very near the stage of physical gel. Note the globular aggregates present in comparison with the same resin in Figure 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
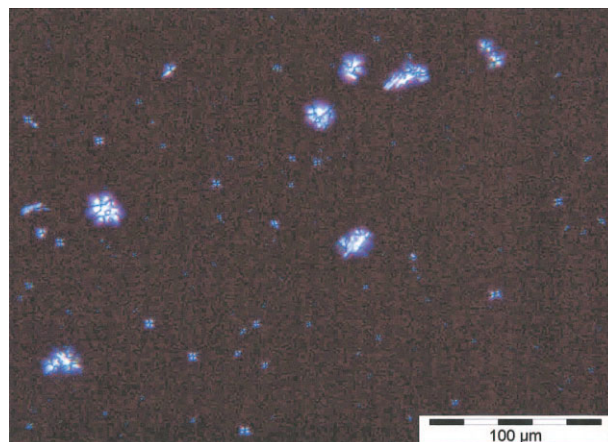

Figure 7 Same as Figure 6 but for a commercial UF resin of F/U molar ratio of 1.2. showing more complex polarized light patterns due to the resin being slightly more advanced than that in Figure 6. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley. com.]

perfectly fluid and a usable commercial UF resin of molar ratio 1.2. Such extreme rod-like and filament-like structures have never been observed in either MF or MUF resins. The appearance of this UF resin is rather different from the globular appearance, in Figure 2, of a MF resin of a similar state of advancement, indicating a different type of interaction between colloidal particles. The colloidal globular aggregates of the MF resin, in Figure 2, confirm what has been already reported by other authors on the appearance of pure MF resins.[9] The appearance of the MUF resin, in Figure 3, a resin where melamine and urea have

clearly been shown to be cocondensed,[10,12,13] is again different. In this resin (Fig. 3), rather short rod-like structures are clearly visible, as well as some globular ones. The short rod-like structure are then likely to be hybrid colloidal aggregates of cocondensed urea and melamine, conserving some of the long rod-like appearance of UF polycondensate, but with their length limited by coreaction with melamine, thus true MUFs. The globular structures, which in Figure 3 appear to be in the minority, are instead likely to be pure MF resin aggregates. MUF resins, which have been shown to be composed almost exclusively of a pure MF resin drowned in unreacted urea,[10] have already been
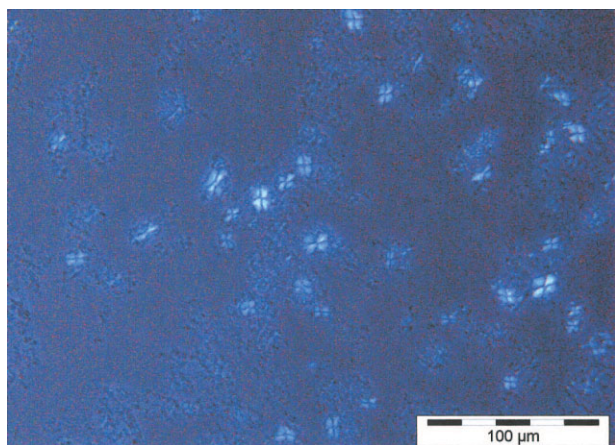

Figure 6 Polarizing light optical microscope micrograph of a whitened UF + 4% melamine resin of molar ratio F/U = 1.2 at the beginning of whitening. Note the star-like polarized light interference patterns noticed in the early stages clusters due of the whitening to physical gelation process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
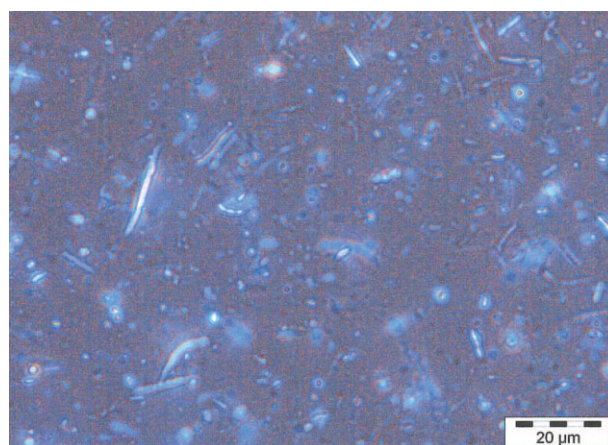

Figure 8 Polarizing light optical microscope micrograph of a whitened UF resin of molar ratio F/U = 1.8 (same resin as in Fig. 1, but less advanced/aged). Note the start of the formation of filament-like aggregates. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
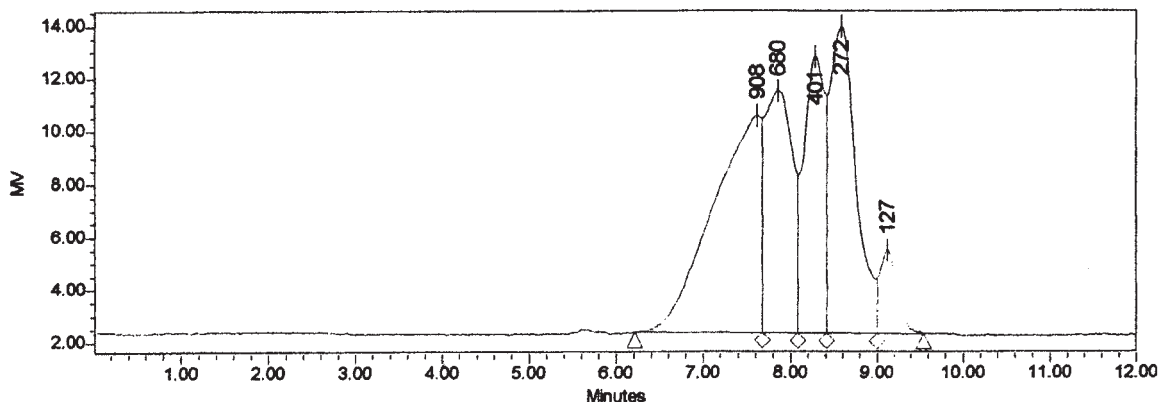
Figure 9 A standard appearance GPC of the sequential MUF resin used. The figure shows elution time and the number average molecular mass (M_n) of the different resin fractions eluted. No absurd values of the molar mass are present.

shown to be present exclusively as globular structures too.[9]

However, the filament-like appearance of UF resins is rapidly lost at greater levels of advancement of the resin. Thus, in Figure 4, the next stage of advancement of the UF resin can be observed where the great majority of the resin starts to acquire globular structure, but where some short rod-like structures still persist, but very much in the minority. The rod-like structures are very much shorter than what is observed in Figure 1. The UF resin structures in Figure 4 change further to acquire the condensed globular structure visible in Figure 5 once the UF resin has advanced enough to have reached, or to be near to the stage of, complete physical gelation.

As regards, the star-like structures visible in the colloidal globules of the MF resins are reported by other authors (but not commented on);[9] these are likely to be light interference patterns caused by the early colloidal structures in the resins. Thus, in Figures 6–8, the variation as a function of resin ageing time of

UF resin is shown as an example. In Figure 6, at the early stages of colloidal aggregate formation, polarized light microscopy shows clearly the same type of star-like light interference pattern, as already shown in the micrographs by other authors for MF resins.[9] In Figure 7, the star-like interference patterns become slightly more complex, indicating the advancement of the aggregation process of the resin to more complex aggregates. Finally, in Figure 8, the advancement of the aggregation process of the resin is reaching the stage in which the filament-like and rod-like structures start to appear.

Surprisingly, the presence of a considerable proportions of colloidal aggregates in these resins can also been noticed by GPC. In Figure 9 is shown, for example, the GPC chromatograph of a standard-type sequential MUF resin, as given in the Experimental part. The GPC mass distribution observed is quite the usual one for this resin, and only the usually expected peaks are noticeable. However, this is not the case for the GPC chromatographs of the UF resins used. Thus, in
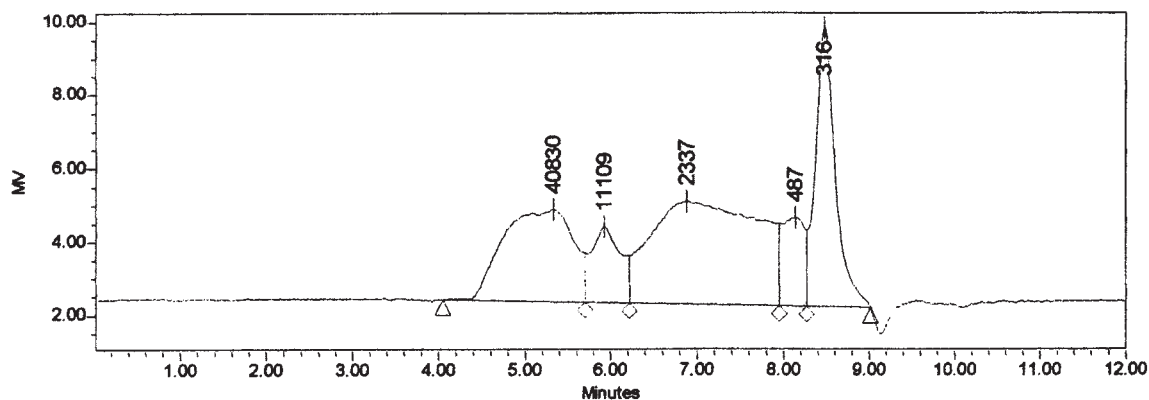

Figure 10 GPC of the UF resin of F/U molar ratio = 1.8 used. The figure shows elution time and the number–average molecular mass (M_n) of the different resin fractions eluted. Note the low, real average molar masses values corresponding to oligomers of the resin and the other, absurdly high values that indicate the presence of big cluster aggregates without any correspondence to the molar mass of the oligomers present.
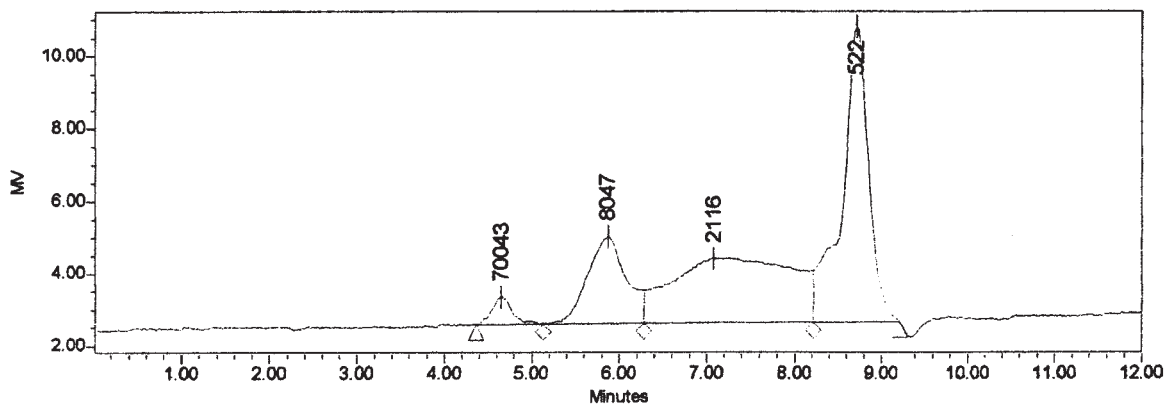
Figure 11 GPC of the UF resin of F/U molar ratio = 1.5 used. The figure shows elution time and the number–average molecular mass (M_n) of the different resin fractions eluted. Note the low, real average molar masses value of the first, real peak, corresponding to oligomers of the resin and the other, absurdly high values that indicate the presence of big cluster aggregates without any correspondence to the molar mass of the oligomers present.

Figures 10–13 are shown the GPC chromatographs of a UF resins of F/U molar ratios of 1.8 (Fig. 10), 1.5 (Fig. 11), of a commercial UF resin of molar ratio 1.2 (Fig. 12) and of a commercial UF resin fortified with 4% of melamine (Fig. 13), today a very common type of commercial UF resin. In all these figures, on top of the expected peaks and mass distribution up to M_n values of ~500, which are expected and quite normal for these resins, also peaks at absurdly high molar masses appear. These peaks do not correspond at all to either any molar mass or to the molar mass values indicated. They only indicate the elution of very big structures that the GPC system mistakenly interprets as absurdly high molar masses. In reality, the existence of these "absurdly high masses" indicates clearly the elution of the colloidal aggregates and superaggregates present in the resin. This is a clear indication that, in UF resins, the formation of colloidal superaggregates is much more common and more noticeable than that in MUF

resins. It is also clear that the long filament-like structures observed for UF resins, the length of which can be as much as ~50–60 μm, can be observed by GPC in this way, while the much shorter rod-like structures in MUF resins (Fig. 3)[10] at 3–5 μm are too short to be easily picked up by this technique.

CONCLUSIONS

In conclusion, the initial, filament-like colloidal aggregates formed by UF resins have different appearance than the globular ones formed by MF resins, with MUF resins presenting a short rod-like appearance hybrid between the two. GPC can detect the existence of colloidal superaggregates in a UF resin, while smaller aggregates might not be detected at all. The star-like structures, visible in the colloidal globules of MF resins, are likely to be light interference patterns of the early colloidal structures in the resins. These star-
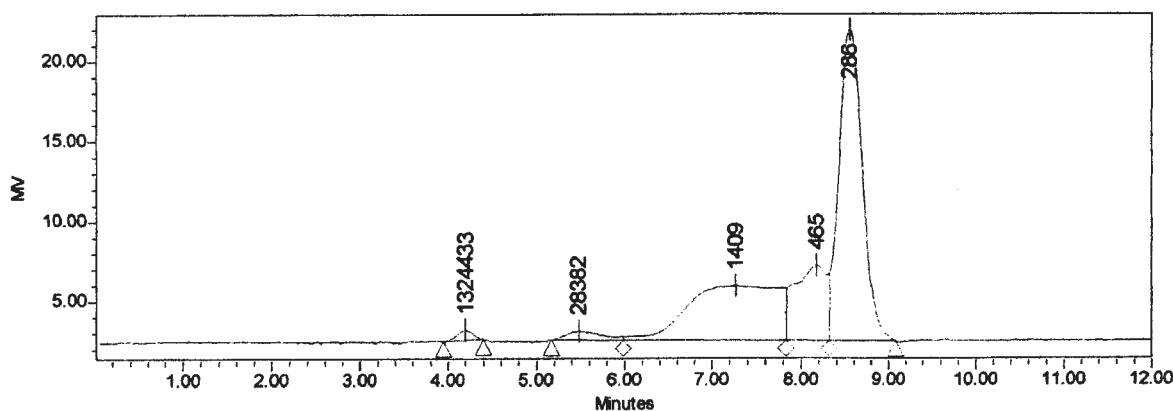

Figure 12 GPC of the commercial UF resin of F/U molar ratio = 1.2 used. The figure shows elution time and the number–average molecular mass (M_n) of the different resin fractions eluted. Note the low, real average molar masses values of the first two real peaks, corresponding to oligomers of the resin and the other, absurdly high values that indicate the presence of big cluster aggregates without any correspondence to the molar mass of the oligomers present.
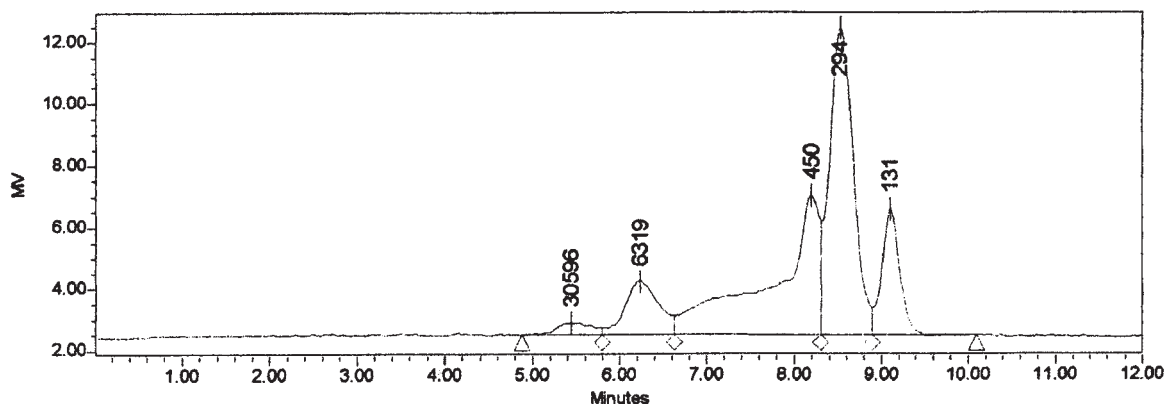
Figure 13 GPC of the UF + 4% Melamine resin of F/U molar ratio = 1.2 used. The figure shows elution time and the number–average molecular mass (M_n) of the different resin fractions eluted. Note the low, real average molar masses values of the first three real peaks, corresponding to melamine alone and to oligomers of the resin and the other, absurdly high values that indicate the presence of big cluster aggregates without any correspondence to the molar mass of the oligomers present.

like interference patterns become more complex with resin ageing or advancement due to the advancement of the resin to more complex aggregates, to eventually reach the stage in which filament-like and rod-like structures start to appear. The next step is formation of globular masses that are representative of the true start of physical gelation.

References

1. Pizzi, A.; Stephanou, A. J Appl Polym Sci 1994, 51, 2125.
2. Gay, K.; Pizzi, A. Holz Roh Werkstoff 1996, 54, 278.
3. Johns, W.E. Proc Forest Prod Int Symp; CSIR Council: Pretoria, South Africa, 1985; p 1. Paper 17-A.
4. Dunker, A. K.; Johns, W. E.; Rammon, R. M.; Farmer, B.; Johns, S. J Adhes 1986, 19, 153.
5. Dunker, A. K.; Johns, W. E.; Rammon, R. M.; Farmer, B.; Johns, S. J Adhes 1985, 17, 275.
6. Jahromi, S.; Litvinov, V.; Geladé, E. J Polym Sci Phys Ed 1999, 37, 3307.
7. Jahromi, S. Macromol Chem Phys 1999, 200, 223.
8. Jahromi, S. Polymer 1999, 40, 5103.
9. Mijatovic, J.; Binder, W.H.; Kubel, F.; Kantner, W. Macromol Symp 2002, 181, 373.
10. Zanetti, M.; Pizzi, A. J Appl Polym Sci 2004, 91, 2690.
11. Pizzi, A.; George, B.; Zanetti, M. J Appl Polymer Sci 2005, 96, 655.
12. Mercer, A.T.; Pizzi, A. J Appl Polym Sci 1996, 61, 1687.
13. Kamoun, C.; Pizzi, A.; Zanetti, M. J Appl Polym Sci 2003, 90, 203.