

Colloidal Aggregation of MUF Polycondensation Resins: Formulation Influence and Storage Stability

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ABSTRACT: Colloidal particle formation followed by their clustering has been shown to be the normal way of ageing of aminoplastic resins, in particular 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 both of 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 by a supercluster formation starting to involve the whole resin. There appears to be clear correspondence between molecular mass increases as obtained by gel permeation chromatography (GPC), low-angle laser light scattering (LALLS) analysis, and observation by polarizing optical microscopy. LALLS, however, appears to indicate the dimensions of the colloidal particles themselves when the level of colloidal aggregation is rather low, but it indicates the dimensions of the clusters once these are mostly aggregated. The smaller visible colloidal particles, already aggregated, were found by polarizing optical microscopy to be of a mostly elongated,

rodlike shape, the length of which was shown to grow much further than their width with resin advancement and ageing. As their dimensions indicate, these are already clusters; this implies that the mainly linear increase of the polycondensate chains influences also the simpler colloidal clusters' growth direction, possibly explaining the resins' lack of tridimensional hardening while still in storage. It also explains why molecules such as free urea and acetals, by disrupting these colloidal aggregation mechanisms, allow both a much longer shelf life of the resin and its better performance in hardening. These findings explained the considerable difference in the behavior and performance of different MUF resin formulations. The ageing of the MUF resins of different preparation procedures appeared then to proceed from (1) clear resin (molecular colloidal aggregation) to (2) superclusters of a whitened, heavily thixotropic resin, which is the beginning of physical gelation to (3) liquid/cluster separation, which is the terminal stage of physical gelation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2690–2699, 2004

Key words: colloids; resins; ageing; gelation; particle size distribution; melamine; polycondensates; viscosity

INTRODUCTION

The wood-panel and resin-impregnated-paper industries rely heavily on the use of synthetic polycondensation resins, a major type among them for these application being melamine resins, in particular melamine–urea–formaldehyde (MUF) resins. Recently, several low-cost additives were shown to be capable of improving the performance of MUF resins, or of decreasing the consumption of MUF resins in the wood-panel-products industry.^{1,2} Such an improvement in performance appeared to be due to several changes induced in the MUF resins by these additives. Among these are their excellent solvent/cosolvent action and particularly their apparent disruption of the colloidal state of these resins observed by low-angle laser light scattering (LALLS). All formaldehyde-

based resin has been perceived for a long time to be in colloidal state,^{3–6} but only relatively recently has the concept of the colloidal state having a marked influence on the resin and its performance and stability started to emerge.² This latter has been particularly observed in the case of MUF resins,² although it is applicable to a different extent also to urea–formaldehyde (UF) and phenol–formaldehyde (PF) resins.¹

During the polycondensation of melamine, urea, and formaldehyde to form precondensates in water, the window of stability of the resins is rather narrow and strongly related to the advancement of the reaction. Unstable resins then could show mainly a loss of transparency with polycondensation advancement or with ageing in storage of the resin, as well as a marked increase or decrease of viscosity. All these effects appear to depend on the nature of the molecular interactions between the resin oligomers, although the physical reason for the effects are not well understood. Recently, evidence has been published that such interactions may involve crystallization, physical gelation, or liquid/liquid phase separation.^{7,8} Such resin behav-

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ior, however, was found to be due neither to crystallization nor to phase separation processes.⁸ Aggregation of some form was observed,⁸ and additives particularly apt to induce their disruption were found.^{2,8} The aggregation was shown to depend on the progressive increase of the resin colloidal state with its ageing on storage and/or with advancement on storage or during preparation.² Disruption by additives of the colloidal state of these resins was observed and studied by LALLS.²

This paper then deals with the influence of the resin formulation used on the development of the resin colloidal state, on the level of colloidal aggregation in itself and as a function of ageing time, and on its correlation with the gradual loss of transparency and storage stability of the resin.

EXPERIMENTAL

Preparation of MUF resins

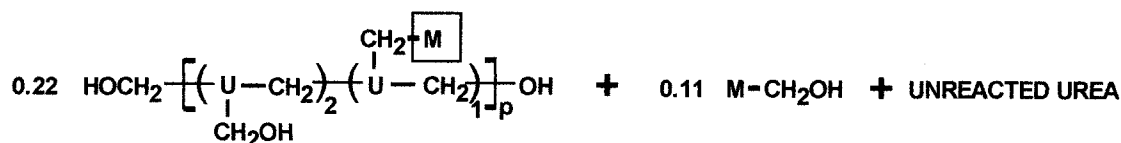
Two basically different MUF resin formulations were used for the experiments. One is a resin formulation in which the additions of melamine and urea are done according to their respective reactivities with formaldehyde by means of known sequential manufacturing procedures.² This is done to ensure the maximum extent of copolymerization of melamine and urea. This type of formulation generally gives very strong bonds. The second one is an almost pure melamine–formaldehyde (MF) formulation where a relatively low proportion of urea, in defect, too little to be reactive enough in relation to melamine to participate in the reaction, is added at the beginning of the reaction. This MF resin with unreacted urea in relatively high proportion is then “drowned” at the end of the reaction period in a considerable excess of urea. This approach is the same one that has been used in some present-day commercial PUF resins. In the case of MUF resins prepared in this way, the high amount of unreacted urea gives a resin of weaker strength but of lower formaldehyde emission. For ease of understanding, we will call this second resin a nonsequential MUF resin.

For the first formulation, a MUF resin with a molar ratio (M+U):F of 1:1.2 and a M:U weight ratio of 47:53 was prepared according to known sequential manufacturing procedures.⁹ Herewith is given the example for a resin of a 1:1.2 molar ratio and a M:U of 47:53: To 142.2 g of formurea (precondensate of formaldehyde 54%, urea 23%, and water 23%) are added 16.4 g of urea and 30.0–35.0 g of water. The pH is set at 10–10.4, and the temperature is brought to 92–93°C under mechanical stirring. The pH is then lowered to 7.8, and the reaction continued at the same temperature, allowing the pH to fall by itself over a period of 90 min to 6.5–7 (the pH must never fall below 5). To bring the

pH to 9.5 or higher, 30% NaOH solution is added, and then 80 g of melamine premixed with 42.8 g of water is added. Dimethylformamide (1–2 g) is then added to the reaction mixture, maintaining a temperature of 93°C. The percentage water tolerance of the resin is checked every 10 min while the pH is allowed to fall by itself. When the water tolerance (the percentage of water that it is possible to add to the liquid resin) reaches a value of 180–200 % (the pH reached is around 7.2), 42.8 g of urea is added, and the pH is again brought up to 9.5. The reaction is continued until the water tolerance reached is lower than 150% (the pH has reached 7.7 at this stage). The pH is then corrected to 10.0–10.2 by the addition of NaOH solution, and the resin is cooled and stored.

The second MUF adhesive formulation, a so-called non-sequential (NS) formulation having the same (M+U):F molar ratio and the same M:U weight ratio as the resin above, was prepared as follows. To 390 g of formurea (precondensate of formaldehyde 54%, urea 23%, and water 23%) are added 190 g water, and the pH of the mixture is adjusted to 9 by adding a few drops of 33% NaOH solution. The temperature is brought to 30°C, and then 175 g of melamine powder is added. The reaction is conducted throughout in a glass reactor equipped with a reflux condenser and under mechanical stirring. The temperature of the reaction mixture is brought to 94°C over a period of 1 h, and the pH generally goes down to 8.5. The reaction is kept at 94°C for 30 min, and the pH decreases to 7.5. The turbidity point, measured at 30°C, is generally reached at this stage. The pH is adjusted to 8.95 by addition of 33% NaOH solution, and then a second portion of 46 g of melamine is added to the reaction mixture. Small amounts of 33% NaOH solution are added continuously to prevent the pH from decreasing too much. The reaction is continued for 15 min, and then 155 g of urea is added. The reaction mixture is kept at 74°C for 3–5 minutes, and the pH is maintained at 9. The reaction mixture is then cooled slowly to reach a temperature of 45°C after approximately 1 h. The pH is then 9.3. monoethanolamine (7.7 g) is added as a buffer to maintain the long shelf life of the resin, and the pH obtained is 9.65. About 15–20 min later, once the resin has cooled down to 30°C, the resin is stored. The MUF obtained has a final (M+U):F molar ratio of 1:1.2 and a M:U weight ratio of 47:53. In reality, if one calculates according to the relative reactivities of melamine and urea with formaldehyde, this is in reality a (M+U):F molar ratio of 1:2.15 and a M:U weight ratio of 70:30, drowned in urea. This is done to reduce the high formaldehyde emission that would be expected from such a high-molar-ratio resin when applied to wood panels.

In the case of the sequential resin, monoethanolamine was also added in one case to observe the effect. The resins, after GPC analysis, were then stored



Scheme 1

in the fridge at 0°C for 1 year of ageing before being tested by means of LALLS, polarizing optical microscopy, and viscometry. The resins were tested for viscosity at a stable 25°C with a Brookfield microviscometer at 20 rpm and spindle 21, the measurement being conducted continuously for 1 h. The resin solid contents at which the two resins were tested for the determination of the intrinsic viscosity were 58%, 57%, 53%, 51.8%, 46.4%, 45.6%, 41.4%, and 40.7%.

Low-angle laser light scattering (LALLS)

The measures of granulometry of MUF resins with a molar ratio (M+U):F of 1:12 and a weight ratio M:U of 47:53 of nonsequential, sequential, and sequential+monoethanolamine formulations were carried out with an 18-mm-diameter Malvern laser and a helium/neon source. The detector was positioned at 90° to the light beam, and the area scanned was 50 μm². The different resins were dispersed in water in 1:1 proportion by volume. The translational diffusion coefficient was obtained from the Stokes-Einstein equation, $d(H) = KT/(3\eta\pi D)$, where $d(H)$ is the hydrodynamic radius, D is the diffusion coefficient, K is the Boltzmann constant, T is the absolute temperature, and η is the viscosity.

Gel permeation chromatography (GPC)

Samples of each of the two MUF resins described above were analyzed by gel permeation chromatography (GPC) (Waters 515 HPLC pump) through a Styragel HR1 column (for determination of M_w values between 100 and 5000) at an elution rate of 1 mL/min, after polyethylene glycol (PEG) calibration of the column. The PEG samples used for calibration had M_w values of 200, 300, 400, 600, 1000, 2000, 3400, 8000, and 10,000. Each resin sample after having been dissolved in dimethylformamide was tested after having been filtered through a 0.45-μL filter. A Waters 410 refractometer was used as the detector.

Polarized light optical microscopy

The samples of MUF resins were spread in thin films on glass and examined by optical microscopy through a polarizing Olympus BH2 microscope equipped with Soft Imaging System's ColorView high-resolution (3.3

megapixels) digital camera and a Peltier cooling device. The program used for the elaboration of data was analySIS.

RESULTS AND DISCUSSION

The two MUF formulations present some considerable differences both in structure as well as in performance.¹⁰⁻¹²

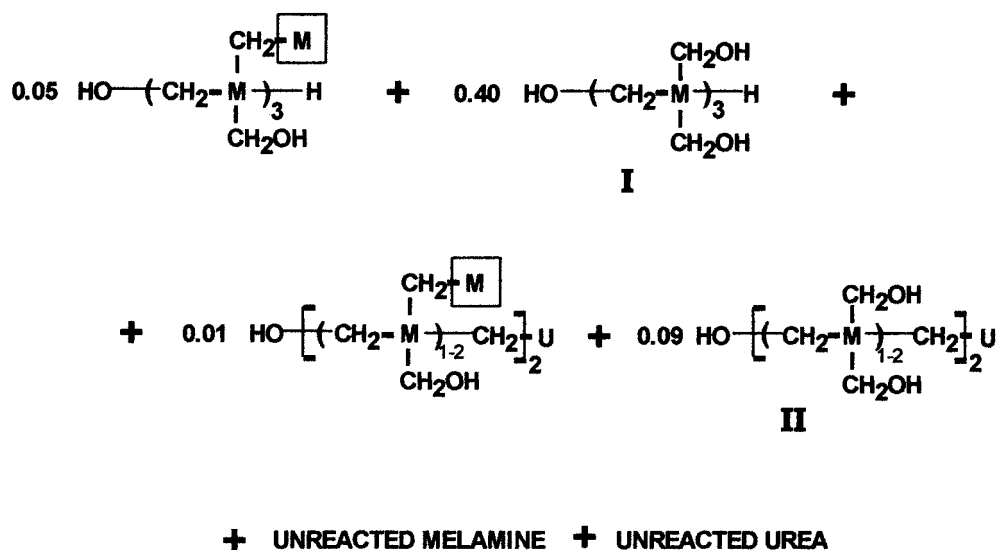
The differences in the behavior of the two MUF resins examined, and hence the level of their performance as binders of wood panels, are due both to their differences at the level of the resin structure and type and distribution of the molecular species formed before hardening, as well as to the differences in the structure of the final hardened networks. The two MUF resins examined were

- (1) A sequential MUF in which the UF was prepared first and then melamine coreacted afterwards once the UF polymer had been formed, a last small urea addition also being carried out for a final (M+U):F molar ratio of 1:1.2 and a M:U weight ratio of 47:53; and
- (2) A MUF resin in which the great majority of the urea and the melamine were premixed and then reacted simultaneously to form the resin, followed by the addition of small amounts of both melamine and urea for a (M+U):F molar ratio of 1:1.2 and a M:U weight ratio of 47:53.

The proportion and type of chemical species formed which can be calculated by the molar proportions of the reagents, the manner in which these are combined during the reaction under different conditions, and the rate reaction constants of urea and melamine with formaldehyde lead to the conclusion, confirmed by ¹³C-NMR, that the distribution of species for the sequential and nonsequential resins and their relative proportions are as indicated in Schemes 1 and 2.

Case (1) above presents the predominant chemical species indicated in Scheme 1, where framed M attached to the UF polymer is in the form of both a single melamine as well as in the form of a melamine-formaldehyde short oligomer.

Case (2) above, presents the predominant chemical species indicated in Scheme II, where M attached to the UF polymer is in the form of both a single mel-



Scheme 2

amine (M and M framed) as well as in the form of a melamine formaldehyde short oligomer (M framed). It means that while the sequential resin is a proper copolymerized MUF resin, the nonsequential resin is mainly a MF or a MUF resin with a M:U equal to or higher than 70:30 and a (M+U):F molar ratio higher than 1:2 drowned in unreacted or underreacted urea. It is the same principle used in some PUF resins today.^{13,14}

When any of the two different MUF resins are freshly prepared, their appearance is clear/transparent, and no colloidal aggregates can really be detected. The results in Table 1, however, show that the nonsequential formulation remains almost clear, presenting only some slight haziness, even after 2 months of ageing, whereas the sequential formulation becomes first hazy and then assumes the characteristic whitish appearance of MUF resins after only about 1 week of ageing. This is supported by GPC results which show the sequential MUF resin as presenting M_n , M_w , and M_w/M_n values of 578, 1021, and 1.77, respectively, compared to values of 437, 666, and 1.52 for the non-

TABLE I
Ageing Behavior and Intrinsic Viscosity $[\eta]$ for
Three MUF Resins

Resin	Days before whitening	$[\eta]$
MUF sequential	5-7	— ^a
MUF sequential + monoethanolamine	>20	
Initial viscosity		-57.6
Viscosity after 30 min shear		-29.3
MUF nonsequential	>60	-1.76

^a Not measured; water tolerance was too low after 1 year of ageing in the refrigerator.

sequential MUF resin (Fig. 1). Resin whitening is related to the progressive increase in the apparent average degree of polymerization of the resin with ageing. Equally so is the resins' increase in viscosity. These differences between the two MUF resins indicate that the phenomenon of formation and aggregation of colloidal particles in MUF resins is related to the progressive increase of their average degree of polymerization with ageing and/or with their further advancement during their preparation.

The increase in the apparent average degree of polymerization of the resins leads then to further colloidal particle formation and aggregation. In this regard, Figure 2 compares the LALLS results obtained for 2-month-old resins: a nonsequential formulation MUF resin (NS) (which always contains monoethanolamine) and a sequential formulation MUF resin without and with monoethanolamine (to compare with the NS case which always contains it). The peaks in the average particle or aggregate size distribution of the two sequential MUF resins are at 40,087 nm (interval 32,812 to 59,822 nm) and 49,602 nm (interval 41,844 to 58,800 nm), respectively, with the presence of monoethanolamine having no significant effect on the sequential formulation (Fig. 2). The nonsequential MUF resin instead presents its particle aggregate size distribution peak at the much lower value of 502 nm (interval 199 to 1002 nm) (Fig. 2).

In Figure 3 are shown the LALLS results when an acetal is used to disrupt colloidal aggregation in a sequential MUF resin. Laser light scattering of MUF + 10% methylal resins and of MUF and MUF + H₂O control resins has confirmed these findings and added a different dimension to the solubility effect of acetals on MUF resins. A fairly aged (2 months old), already

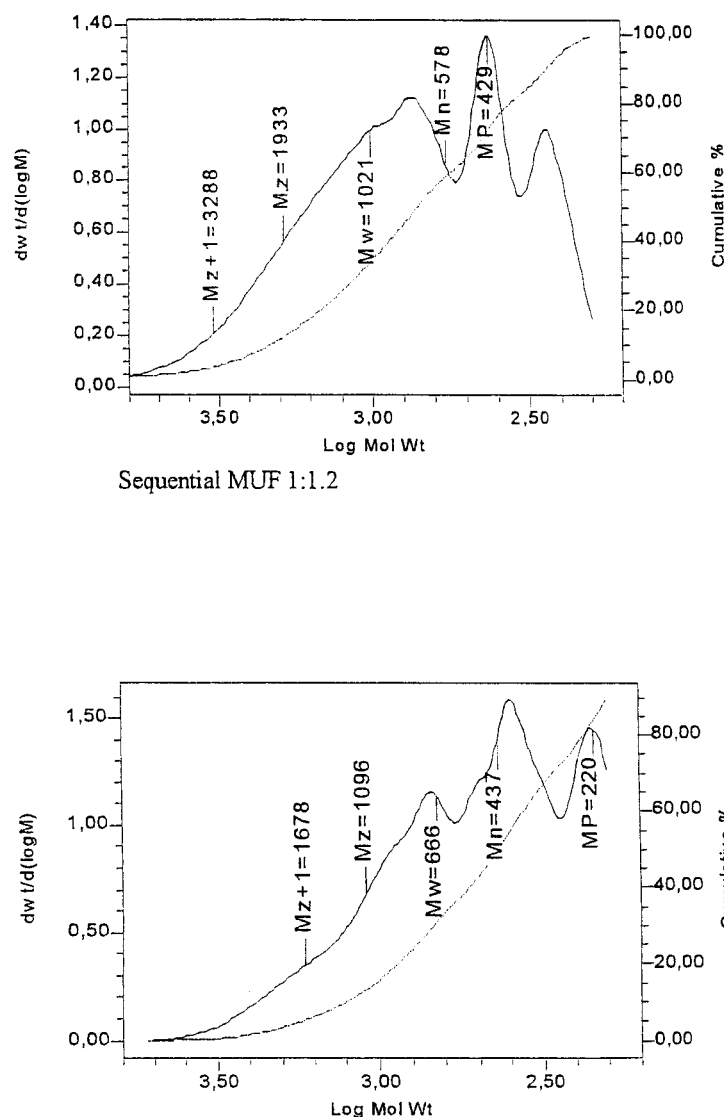


Figure 1 GPC of (a) the sequential MUF resin and (b) the nonsequential MUF resin used. The figure shows $dwt/d(\log M)$ and as a function of the log molecular weight of the resin fractions eluted. The number average molecular mass (M_n), weight average molecular mass (M_w), and z-average molecular mass (M_z) are indicated for the two MUF resins.

rather advanced MUF resins with a molar ratio (M+U):F of 1:1.9 and M:U weight ratios of 47:53 and 40:60 to which has been added 10% methylal have yielded average colloidal particle diameters of 588 nm (M:U = 47:53) and 387 nm (M:U = 40:60), respectively, while the same resins present average particle diameters of 3109 nm (a wide peak, 3001–3218 nm) in the absence of methylal (Fig. 3) for both types of resin. Furthermore, the size distribution is wider in the absence of methylal (2798 to 3451 nm) than when methylal is present (564 to 636 nm for the M:U 47:53 resin; 350 to 428 nm for the M:U 40:60 resin), indicating a much narrower polydispersity range. This means that the acetals are capable of either (1) disrupting the molecular clustering of the resin colloidal particles or (2) rearranging the size of the colloidal particles due to the decrease in surface tension of the system, or both.

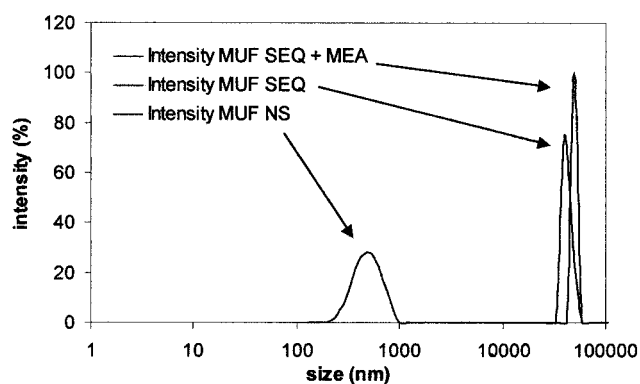


Figure 2 Colloidal particle/cluster diameter distributions measured by low-angle laser light scattering obtained for the sequential MUF adhesive resins, the sequential MUF resin+monoethanolamine, and the nonsequential MUF resin.

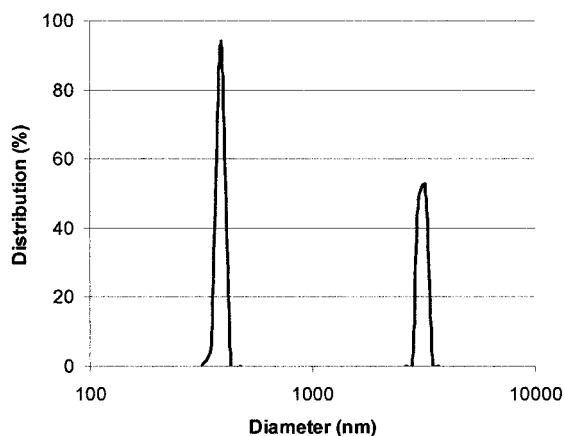


Figure 3 Colloidal particle diameter distributions measured by low-angle laser light scattering obtained for sequential MUF adhesive resins with a molar ratio (M+U):F of 1.1:9 and a weight ratio M:U of 40:60. At 3109 nm MUF resin alone. At 387 nm MUF resin + 10% methylal.

As the methylal is added to the MUF resin long after its preparation, the former appears to be the most likely explanation, especially in light of the recent observation that the progressive whitening of MUF resins on ageing is due to the appearance of colloidal

clusters and higher-molecular-weight fractions, which appear in the resin as the reaction slowly proceeds on ageing.⁸ However, the data do not allow us to eliminate the second explanation, which might be valid too.

The picture that appears then is one of effectiveness of crosslinking between the lower-diameter-component colloidal particles leading to a better crosslinked network when methylal is added and to a crosslinked network between bigger colloidal aggregates where the weak point is indeed the possibility of network collapse due to disruption in the structure of the aggregate.

The changes intervening become much clearer when the resins are observed by polarizing optical microscopy. This method is able to detect particles down to 1 μm in size in transparent and semitransparent samples. When the resins were freshly prepared and transparent, no colloidal particles were observed. As the resins started to age, colloidal particles started to make an appearance and started to cluster immediately. For example, Figure 4 is the polarized light microscope image of the MUF nonsequential resin, which is still relatively clear after 2 months of ageing. The image shows isolated aggregates of colloidal particles, with the majority of the resin appear-

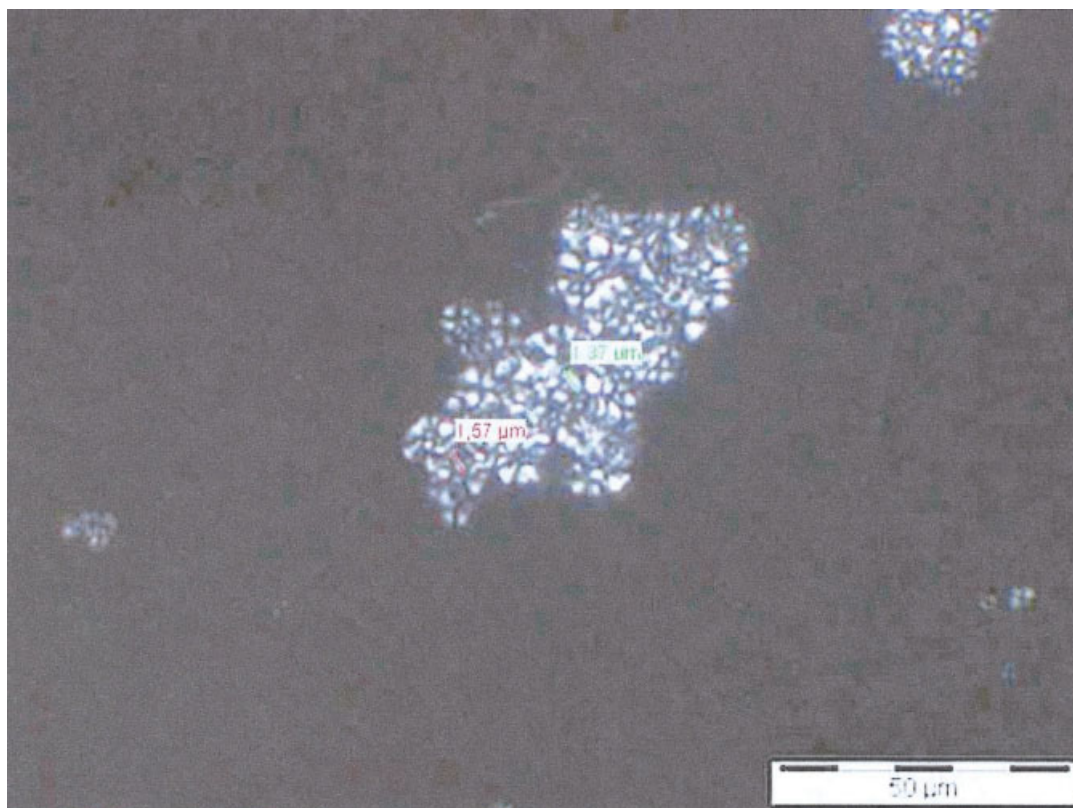


Figure 4 Polarizing light optical microscope micrograph of the rare clusters of colloidal particles in a still-clear, nonsequential MUF resin. Resin is 2 months old. Note that the size of particles is around 1.5 μm . The black part is the resin that is still in solution.

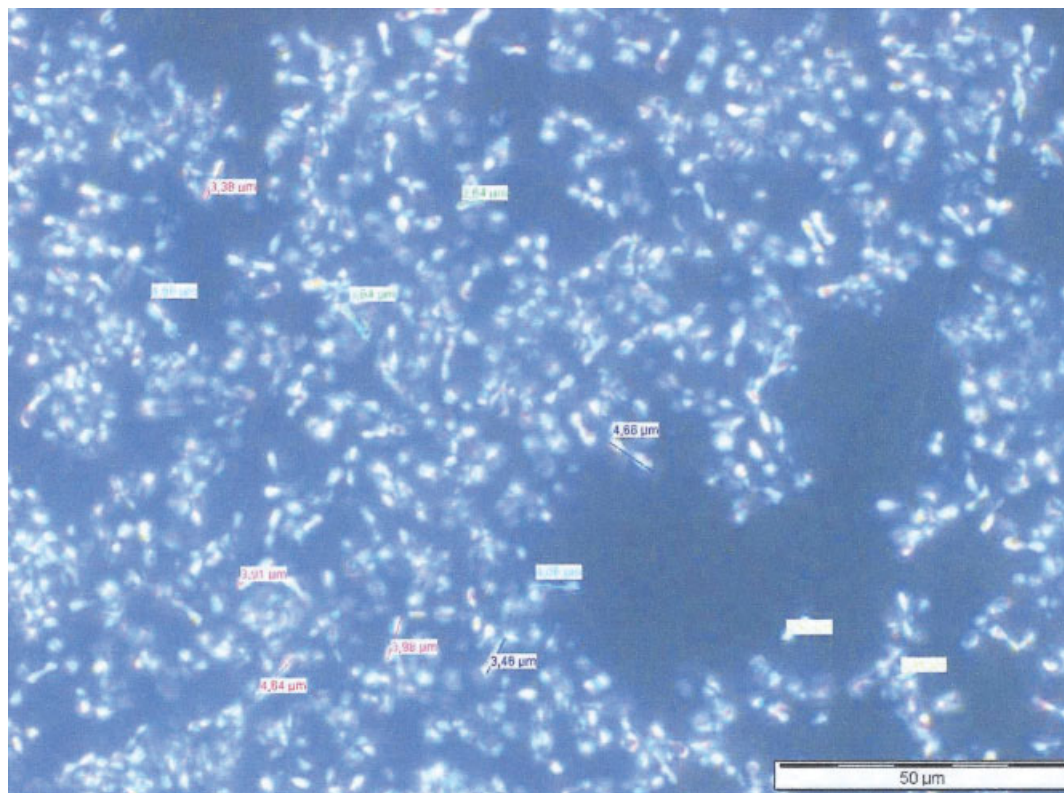


Figure 5 Polarizing light optical microscope micrograph of the very diffuse superclusters of colloidal particles in a whitened, sequential MUF resin. Resin is 2 months old. Note that the size of particles is around 3.0–5.0 μm . Note that the great majority of the resin is in colloidal cluster form.

ing to be completely devoid of colloidal particles (the black background). The average dimension of each individual particle was around $1.2\text{--}1.7 \times 0.3\text{--}0.8 \mu\text{m}$, the shape of the particles being approximately rodlike. The length and width of a melamine molecule are approximately 5 nm, and the M_n from Figure 1(a,b) shows that the number average degree of polymerization of the resin is approximately 3–4. Thus, the dimensions of the smaller observable particles indicate that even the smaller particles observable can only be and are already cluster aggregates. The dimensions of the superaggregate in Figure 4 are approximately $73 \times 40 \mu\text{m}$, this aggregate being an unusually big one. Much smaller superaggregates are observed in the same micrograph, of diameter roughly around 8–9 μm . This indicates that the dimensions obtained by LALLS and reported in Figure 2 for the nonsequential resin refer to the dimensions of the colloidal particle itself rather than to the rare aggregates present in Figure 4.

The situation is different in Figure 5, which shows a polarized light micrograph of the sequential MUF resin. In Figure 5, both the dimensions of the colloidal particles themselves are bigger, mainly longer, between 3 and 5 μm in length, the shape of the particles in this case being more clearly and in the greater majority rodlike. The predominantly elongated, rodlike structure of the particles, with the increase of the

average particle length but with very little difference in its width (Fig. 5), suggests not only that on ageing polymerization continues and the MUF chain length continues slowly to increase mostly linearly and without much branching,¹⁵ but that this “linearity” somehow also influences the direction of growth of the smaller visible colloidal particles (that can only be aggregates). In the case of Figure 5, not only big clusters are present, but even the clusters appear to have started clustering between themselves. The LALLS in this “crowded” situation will be able to detect only these big “superclusters,” hence the dimensions observed for the sequential resins in Figure 2. Furthermore, it is evident in Figure 5 that the great majority of the resin is present in colloidal form (the dark areas are very much less or even absent).

The formation of these superclusters is even more evident in Figure 6, a micrograph of the sequential MUF resin to which monoethanolamine has been added, the optical observation confirming the very high aggregates dimension obtained by LALLS in Figure 2. The phenomenon of physical gelation as described by other authors⁷ appears then to be just the terminal part of the clustering process described above. In short, physical gelation starts at the onset of extensive colloidal clustering, namely, what has been called above superclustering, as shown in Figures 5

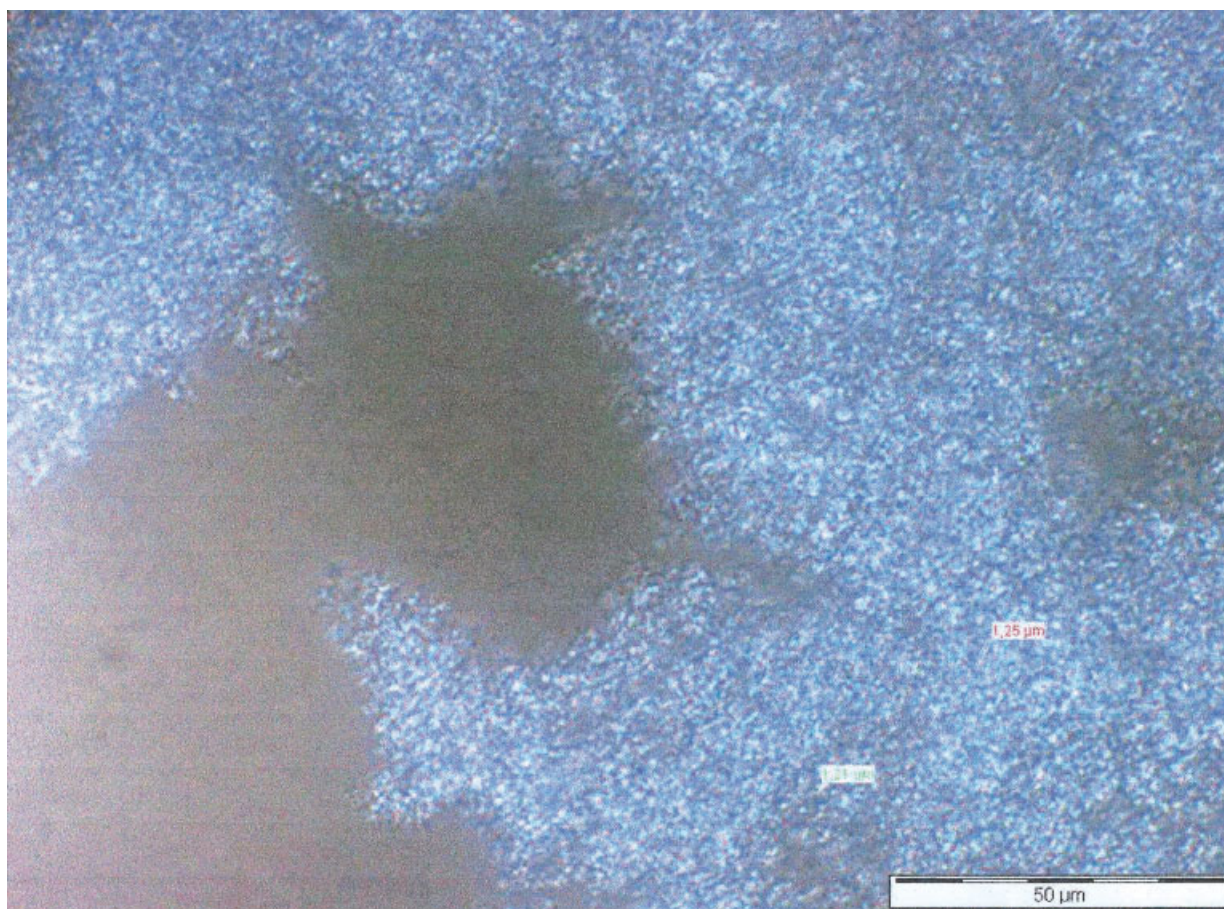


Figure 6 Polarizing light optical microscope micrograph of the very diffuse superclusters of colloidal particles in a whitened, nonsequential MUF resin+monoethanolamine. Resin is 2 months old. Note that the size of the particles has decreased to around 1.2–1.4 μm and that the great majority of the resin is in colloidal supercluster form.

and 6. The results in Table 2, obtained by averaging the results of 10 optical micrographs each for the cases illustrated in Figures 4–6, confirm numerically the progression of the extent of the resin that is present as colloidal clusters, with the nonsequential formulation presenting a much higher fraction which is either colloidal but not in supercluster form or in solution.

What described can also explain why nonsequential MUF resin formulations have a much longer shelf life than sequential MUF resins. The nonsequential MUF has been defined as mainly a MF resin drowned in

unreacted or underreacted urea.^{10–12} Free urea is very effective at disrupting the colloidal state of a number of polycondensation resins, and it is often used in a variety of applications just for this purpose.^{13,14,16} This explain the much longer shelf life of this resin and the very much longer period it maintains its transparency. What described also explains why the use of acetals, shown to strongly disrupt the colloidal state of sequential MUF resins,^{1,2} improve markedly their performance. All these additives allow a much higher level of homogeneous reaction, and final crosslinking, due to the resin being relatively freer of diffusional constraints as a consequence of the marked decrease of clustering.

The dimensions of the smaller visible colloidal particles, already aggregates, indicate that these are already at the approximate upper limit of what is defined as a colloidal particle, namely, approximately 1 μm . This means that the process observed in passing from Figure 4 to Figures 5 and 6 describes visually the stages of physical gelation⁷ of the resin. It indicates also quite clearly that resin whitening and storage stability are processes of physical gelation.⁷

TABLE II
Average Fractional Area with Dark Background
(No Visible Clusters) for MUF resins

Resin	Average fractional area (%) ^a
MUF nonsequential	88.9
MUF sequential	57.9
MUF sequential+monoethanolamine	49.1

^a Calculated from 10 light optical micrographs for each resin.

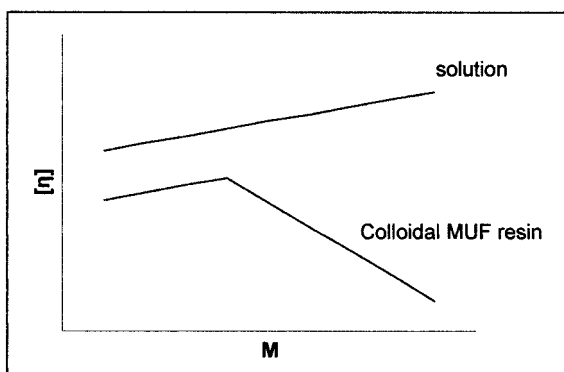


Figure 7 Schematic representation of the dependence of the intrinsic viscosity $[\eta]$ on molecular mass M in (a) thixotropic MUF resins presenting a whitened, colloidal superclustered structure and (b) transparent MUF resins presenting not-yet-visible colloidal clusters.

It is of interest to observe the effect that the formulation and the physical state of the resin have on the dependence of the intrinsic viscosity $[\eta]$ on molecular mass according to the Mark–Houwink equation:^{17–19} $[\eta] = KM^a$, where K and a are constants, M is the molecular mass, and $[\eta]$ is the intrinsic viscosity. The values of $[\eta]$ obtained for the two resins are shown in Table 1. First of all, the marked thixotropic effect of the sequential MUF resin must be noted. Its strong colloidal clustering appearance (Figs. 5 and 6) explains this. The extrapolated value of $[\eta]$ obtained is negative when the initial viscosity is used in the Mark–Houwink equation, the extent of its negative value decreasing as shear continued to be applied (Fig. 7). This means that in this resin, at the beginning of a shear force application, the equation has to be written as $[\eta] = -KM^a$. This means that graphs of $[\eta]$ as a function of M have a slope opposite to what is normally accepted, and that the slope reverts to normal once the process of colloidal “superaggregation” has been completely disrupted. This is shown in the scheme in Fig. 7. What is then observed at the beginning of shear is the effect of the supercluster on viscosity; and as the shear force applied disrupts its arrangement, the viscosity tends to settle down. This settling down is likely to be only apparent. This is so because the molecular size clusters, namely, the smaller visible particles, present aggregation that is either more difficult to disrupt or not possible to disrupt. What is of interest is the behavior of the transparent, nonsequential resin where only very few clusters are present, and the rest of the resin appears to be in solution, and where an obvious thixotropic effect is not present. The viscosity for this resin is stable, but this too yields a slightly negative value of $[\eta]$, this too responding then to the inverse equation $[\eta] = -KM^a$ and being a good measure of the low level of thixotropy and colloidal aggregation of the resin. The only reason why this is so is likely to be that the

thixotropic behaviour is small but present already, confirming that molecular clustering is already starting to occur, notwithstanding the fact that the clusters are still so small that they are not visible. This implies that all aminoplastic resins, and especially MUF resins, are always in a colloidal aggregation state, early from their preparation, even when they are still perfectly clear/transparent, and that it is only the advancement of their colloidal state to superclusters that whitens them and that triggers the start of physical gelation. As this state of the resin advances, liquid/superaggregate separation occurs (not liquid/liquid and not as yet liquid/solid, which occurs later). Thus, the ageing of the resin proceeds from (1) clear resin (molecular colloidal aggregation) to (2) superclusters of a whitened, heavily thixotropic resin, which is the beginning of physical gelation to (3) liquid/cluster separation, when water tolerance has practically become nonexistent, which is the terminal stage of physical gelation, to be finally followed by the initial stages of hardening.

CONCLUSIONS

In conclusion, colloidal particle formation followed by their clustering appears to be the normal way of ageing of aminoplastic resins, as has been shown for MUF resins, and possibly of other water-borne polycondensation 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 both of 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 is not even in colloidal state and even when the resin is still transparent. However, it eventually progresses to resins which are mostly in colloidal, clustered state, followed by a supercluster state much later. There appears to be clear correspondence between molecular mass increases as obtained by GPC, LALLS analysis and observation by polarizing optical microscopy. LALLS, however, appears to indicate the dimensions of the colloidal particles themselves when the level of colloidality is rather low, but it indicates the dimensions of the clusters once the resin is mostly colloidal. It is also interesting to note that the visible colloidal particles are mostly of an elongated, rodlike shape, the length of which grows much further than their width with resin advancement and ageing. As their dimensions indicate, these are already clusters; this implies that the mainly linear increase of the polycondensate chains influences also the simpler colloidal clusters growth direction, possibly explaining the resins’ lack of tridimensional hardening while still in storage. It also explains why molecules such as free urea and acetals, by disrupting these colloidal aggregation mechanisms, allow both a

much longer shelf life of the resin and its better performance in hardening. It also points out why MUF resins formulated in very different ways, with their formulation being based on a very different concept, present such differences in performance. The ageing of the resin appears then to proceed from (1) clear resin (molecular colloidal aggregation) to (2) superclusters of a whitened, heavily thixotropic resin, which is the beginning of physical gelation to (3) liquid/cluster separation, which is the terminal stage of physical gelation.

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