Acetals-Induced Strength Increase of Melamine–Urea–Formaldehyde (MUF) Polycondensation Adhesives. II. Solubility and Colloidal State Disruption

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ABSTRACT: The strength improvement induced by addition of acetals such as methylal and ethylal in melamine–urea–formaldehyde (MUF) resins could be mostly ascribed to the increased effectiveness and participation of the melamine to resin cross-linking. This phenomenon has been shown here, by matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectroscopy, resin aging time stability, and mainly by laser light scattering, to be due to the following: (i) the increased solubility in water afforded by the acetals cosolvents of both the unreacted melamine and of the normally very much lower solubility, higher molecular weight, lower methylolated oligomers fraction, this leading to preferentially homogeneous and hence more effective reaction rather than heterogeneous reactions; and (ii) the effect that such acetals have on the size distribution of the resin colloidal particles, with the presence of acetals such as methylals markedly decreasing the average colloidal particles diameter of the resin. This latter effect appears to be due to the disruption of the molecular clustering of the MUF resin colloidal particles, but rearrangements in the size of the colloidal particles due to the decrease in surface tension of the system, which has also been noted, cannot be excluded. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1855–1862, 2002

Key words: acetals; methylal; ethylal; polycondensation; melamine resins; performance improvement; strength improvement; adhesives; wood panels; paper; colloidal state; size distribution

INTRODUCTION

The wood-board and resin impregnated paper-board industries rely heavily on the use of synthetic resins and adhesives: in short, without adhesives and resins these industries would not exist.[1] These applications rely on polycondensation resins; a major type among these resins for this application is melamine resins, in particular melamine–urea–formaldehyde (MUF) resins. Recently, acetals, such as methylal and ethylal, were used as novel low-cost additives capable of decreasing by $\frac{1}{4}-\frac{1}{3}$ the consumption of traditional wood adhesives, in particular of MUF resins, in the wood panel products industry.[2] Also, they were shown capable of increasing at resin load parity the panels internal bond (IB) strength performance between 25 and 50%, with existing commercial adhesives and without, in principle, any modification to the resins formulations.[2] Such an improvement in performance appeared to be due to the acetals excellent solvent and cosolvent action on melamine itself. All circumstantial evidence indicated this solvent/cosolvent action to be one of the main causes, although the point was not actually proven.[2]

Melamine is notoriously difficult to bring in water solution and in the manufacture of resins this occurs only after a fairly long time at ≥90 °C and after that abundant reaction with formaldehyde has introduced a high number of methylol groups on the melamine triazine ring. Even in water/dimethylformamide (DMF), DMF being the best industrial cosolvent known to date for melamine, without the solubilizing reaction with formaldehyde, melamine remains largely insoluble. Recently,[3–6] work on solubilizing melamine by the formation of its organic salts has shown that such an improvement in solubility yields resins of much improved performance. This result was shown to be due to the improvement in reaction yield consequent to the melamine–formaldehyde reaction occurring in homogeneous rather than heterogeneous phase, and to some consequent effects on resin structure. In short, in the traditional manufacturing approach to melamine resins, even after reaction with formaldehyde, there is a high proportion (as much as ⅔) of melamine in the resin that is wasted.[3] As a better solvent is found, the effectiveness of the reaction in-

creases considerably and as the proportion of melamine that contributes to cross-linking increases, so does the resultant strength of the hardened network and the strength of the bonded joint.

This paper deals then with the identification of the causes of the improved performance induced by acetals on formaldehyde-based melamine and MUF resins and with the extent of the respective contributions to this major effect.

EXPERIMENTAL

Resins used

The MUF resins used for laser light scattering were prepared according to commercial sequential procedures and formulations already reported.[7] Two resins of the same type were prepared with the characteristic molar ratio of 1:1.9 and mass ratios of melamine (M) to formaldehyde (F) M:F of 47:53 and 40:60, respectively. These resins were made in the laboratory according to a previously reported procedure.[3]

The melamine resins prepared for paper impregnation and for aging time stability were MUF resins with a (M+U):F molar ratio of 1:1.5 and a M:U weight ratio of 47:53 inclusive of an uron-inducing acid step[4] in the UF part of the reaction prepared according to the following procedure, all of which was conducted with continuous mechanical stirring: 77.6 parts by weight of paraformaldehyde in 77.6 parts water are heated at 80°C for 2 h with mechanical stirring in a glass reactor equipped with a reflux condenser. After all the paraformaldehyde grains disappear, the mix is cooled to <30°C and, after adding 21.6 parts of diethylene glycol, enough HCl 36% is added to reach a pH of 1.5. Next, 30.6 parts of urea are added, and the reaction is carried out for 1 h at 98°C until the reaction mix is clear. The reaction mix is then cooled to <30°C and enough NaOH 20% water solution added to reach a pH in the 9–10 range. Then, 64.6 parts of melamine are added, and the reaction mix is heated to 85°C for 90 min or longer if a resin of greater condensation level is required. The resin is then cooled to < 30°C and stored after checking that the pH is still in the 9–10 range.

Laser light scattering

The measures of granulometry of MUF resins of (M+U):F molar ratio = 47:53 and of M:U weight ratios of 47:53 and 40:60, respectively, were carried out with an 18-mm diameter Malvern laser and helium/neon source, with the detector positioned at 90° to the light beam and the area scanned being 50 μm. The different resins were dispersed in water in proportion by volume of 1:1. The translational diffusion coefficient was obtained by 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.

Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF-MS)

The spectra were recorded on a KRATOS Kompact MALDI 4 instrument. The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity, positive; flight path, linear; mass, high (20 kV acceleration voltage); and 100–150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200–800 ns.

MALDI-TOF sample preparation

The samples were dissolved in water (4 mg/mL). The sample solutions were mixed with an acetone solution (10 mg/mL acetone) of the matrix. Because the matrix dithranol was used, NaCl was not added to the matrix. The solutions of the sample and the matrix were mixed in equal amounts and 0.5–1 μL of the resulting solution were placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer. The mass peaks correspond to M+Na (from natural abundance) and M+H attached cations.

Stability of resins to aging and surface tension

The melamine resins prepared for paper impregnation and for aging time stability were MUF resins with a (M+U):F molar ratio of 1:1.5 and M:U weight ratio of 47:53 . The resin was maintained at ambient temperature (25 °C) in a sealed clear glass container, and its percentage water tolerance (WT) was checked daily and recorded. The water tolerance was determined by adding to 10 mL of the finished liquid resin the amount of water needed to have resin precipitation. The WT is measured in percentage of milliliters of water added on the milliliters of liquid resin used and is a direct measure of the advancement and age of the resin. The viscosity was checked at 25°C with a Brookfield RVL viscometer. The surface tension measures were made with a Wilhelmy balance with immersion depth of 3 mm and measure range of 50 μm.

RESULTS AND DISCUSSION

Melamine is notoriously difficult to bring into water solution and, in the manufacture of resins, this solubility occurs only after a fairly long time at ≥90°C and after abundant reaction with formaldehyde has introduced a high number of methylol groups on the melamine triazine ring. Even in water/dimethylform-

TABLE I
Percentage Acetals Hydrolysis Obtained by Standardized Methods under Controlled pH and Temperature (20°C) Conditions

	Percentage hydrolysis at		
Acetal type	pH = 0	pH = 1.0	pH = 2.0
Methylal (after 5 h)	52	4	0.0
Ethylal (after 5 h)	33	22	0.0
Propylal (after 5 h)	0	0	0.0
Propylal (after 15 days)	66	0	0.0
Butylal (after 5 h)	0	0	0.0
Butylal (after 15 days)	20	0	0.0
Dioxolane (after 5 h)	9	0	0.0

TABLE II
Solubility of Melamine in Acetals and Acetals/Water Mixtures[a]

	Solubility in g/L at 20°C	
Acetals/water mixture	Melamine analytical grade	Melamine technical grade
H_2O 100%, control	3.46	3.20
Methylal 100% control	0.0	0.0
Ethylal 100% control	0.0	0.0
Dioxolane 100% control	0.0	0.0
Ethylal 5/95	3.98	4.45
Methylal 5/95	4.17	3.98
Methylal 10/90	4.95	5.02
Methylal 20/80	6.00	5.81
Methylal 30/70	7.06	6.61
Dioxolane 5/95	4.28	4.79
Dioxolane 10/90	5.52	5.29
Dioxolane 20/80	7.45	8.22
Dioxolane 30/70	10.15	10.35
Dioxolane 50/50	13.78	14.07
Dioxolane 70/30	9.48	9.86
Dioxolane 90/10	2.98	3.17

[a] Proportions by weight.

amide, without the solubilizing reaction with formaldehyde, melamine remains largely insoluble. In Table I and Figure 1 are shown the results of solubility of melamine in water and in different proportions by weight of methylal/water, ethylal/water, and dioxolane and water. First of all, by themselves, none of them dissolves melamine. They are effective only when coupled with water, hence only as cosolvents. Secondly, notwithstanding the fact that all the three acetals do improve the performance of melamine resins in the order of effectiveness methylal $\geq$ ethylal $>>$ dioxolane, the order of improvement obtained does not follow their respective effectiveness as cosolvents in dissolving melamine. Thus, the most effective melamine cosolvent, namely dioxolane, is the acetal that improves less the strength results of the resin, with methylal and ethylal performing approximately the same as strength improvement additives but with methylal being the better cosolvent of the two for some melamine grades and vice versa (Table I). It is then evident that the acetals influence in improving the solubility of melamine is only one effect, and definitely not the main aspect of the improved performance imparted to MUF resins. To this effect, the impressive percentage increases in melamine solubility (up to 400% for dioxolane and up to 200% for methylal) shown in the results Table II mask in reality a small absolute increase in the weight of melamine
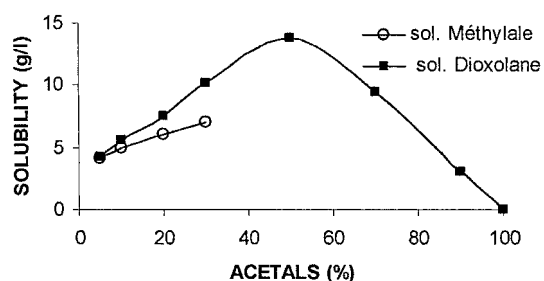

Figure 1 Variation of the solubility of pure melamine in acetal/water solutions as a function of different percentages acetal. Key: (○) methylal/water; (■) dioxolane/water.

that is really brought into solution. Thus, to improve the solubility of melamine from 3.46 to 7.06 g/L in the best case for methylal and up to 13.78 g/L for dioxolane is a rather dismal performance when it is realized that the concentration of melamine in a MUF resin is ~300–500 g/L of liquid. Such improvement can justify the improvement in performance observed in resins of low melamine level,[3–6] where the melamine concentration is perhaps up to 50 or even 100g/L, but does not explain by itself the improvement observed in top of the range MUF resins of high melamine content.[2] In short, as effective as any acetal can be in dissolving melamine during reaction and hardening, as effective the addition of an acetal can be in retrieving to the reaction the undissolved melamine in a MUF resin in hardening, it is quite clear by comparing the above concentrations that the effect of acetals on the solubility of the unreacted melamine chemical, although a well-defined contributory effect, cannot be the main contributor to the improved strength effect which is noticed.

The concept to which the results just presented then appears to lead is that the solubility connected effect must apply to well-defined higher molecular weight fractions of the MUF resin itself rather than only just to the unreacted melamine chemical in the system. It is known for instance that the progressive whitening of MUF resins on aging is due to the appearance of colloidal clusters and to higher molecular weight fractions that appear in the resin as the reaction slowly proceeds on aging.[8] This is clearly inferred for instance by the results of aging stability of MUF resins
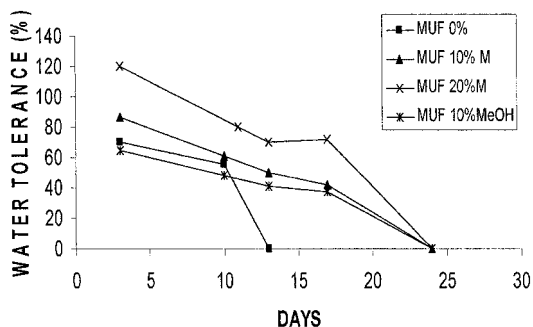
Figure 2 Variation of the percentage water tolerance of a paper impregnation MUF resin of molar ratio $(M+U):F = 1:1.5$ and weight ratio $M:U = 47:53$, as a function of number of days aging at ambient temperature. Key: (■) MUF resin alone; (▲) MUF resin + 10% methylal; (×) MUF resin + 20% methylal; (*) MUF + 10% methanol.

for paper impregnation reported in Figures 2 and 3. In paper impregnation of MUF resins, the maintenance of a totally clear resin is a requisite. Also, the longer the resin is capable of remaining clear at parity of performance, to avoid whitening, the more valuable is the resin for this application. In Figures 2 and 3 is shown first of all that the water tolerance of a MUF resin increases on addition of methylal. This result becomes more evident on resin aging to the point that the stability to whitening on aging of the raw MUF resin of 13 days (Figure 2), improves by 85% to 24 days on addition of 10 and 20%. Similarly, water tolerance at 2.5 days of aging improves from 70 to 85% and to 120%, respectively (Figure 2). Of equal importance in paper impregnation resins is the value of the surface tension of the resin, which determines the ease of resin loading and at parity of conditions the level of resin loading in the paper. This level is influenced by the surface tension characteristic of the resin. The substantial decrease in the value of this parameter for a MUF resin for addition of increasing percentages of methylal, values which can never be achieved by addition of water due to precipitation and whitening of the resin are shown in Figure 3 (compare water tolerance in Figure 2). Equally indicative in Figure 4 is the decrease
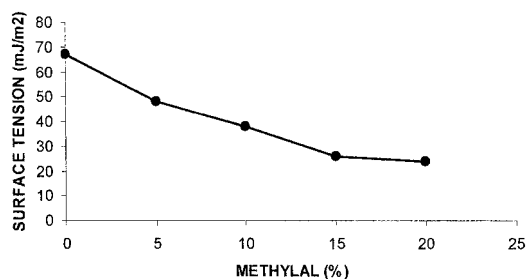
in viscosity of the resin on the addition of increasing percentages of methylal.

More supporting evidence comes from MALDI-TOF-MS[9–15] of the MUF resin control and of the same resin to which either 10% water or 10% methylal has been added (Figures 5 and 6). In these figures, the series of peaks 127–157–187–217 Da are those of, respectively, unreacted melamine (M), monomethylol melamine (MF), dimethylol melamine (MF_2), and trimethylol melamine (MF_3). The series 139–169–199 Da is composed of, respectively, $M—CH_2^+$ or $M=CH_2$ or $HOCH_2—M—CH_2+$, whereas the 199 Da peak can be either $M—CH_2—$urea or $CH_2=M—(CH_2OH)_2$. The series of peaks 152–181–210–242–272 Da corresponds therefore to the signals of $CH_2=M—CH_2+$, $CH_2=M(—CH_2OH)—CH_2+$, $M—CH_2—$urea$—CH_2^-$ fragment, $HOCH_2—M—CH_2—$urea$—CH_2^-$, and $(HOCH_2)_2—M—CH_2—$urea$—CH_2^-$, or urea$—CH_2—$$M—CH_2—$urea, with the first one of these two being more likely. Similarly, the two peaks at 226 and 299 Da are due to $HOCH_2—M—CH_2—$urea (theoretical 229 Da) and to $HOCH_2—M—(CH_2—$urea$—)_2$ (theoretical 299 Da). Some interesting conclusions can be drawn on the basis of the particular presence and intensity of this last peak: The 299 Da peak is a very pronounced peak in the MUF + 10% methylal (Figure 5), whereas it is practically nonexistent in the pure MUF and in the MUF + H_2O resins spectra (Figure 6). This result indicates methylal is beneficial in helping to dissolve the resin oligomers fractions that are relatively poorer in methylol groups ($—CH_2OH$). Thus, the 299 Da peak is very intense only in the MUF + 10% methylal (Figure 5) case, whereas, for example, the 272 Da peak $(HOCH_2)_2—M—CH_2—$urea$—CH_2^-$, which presents less urea residues but relatively more methylol groups, is clearly in solution in all three resins (Figures 5 and 6). This situation is confirmed in the extended spectra shown in Figures 7 and 8 in the 520–1900 Da range. In these figures, the series of peaks 674–898–
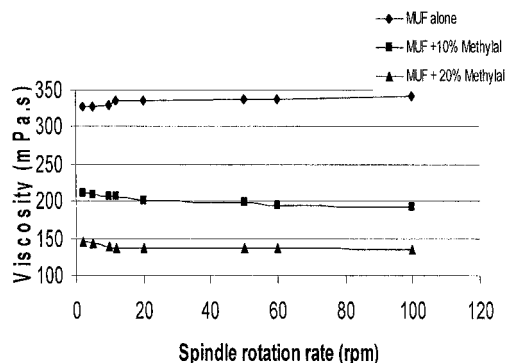

Figure 3 Variation of the surface tension of a paper impregnation MUF resin of molar ratio $(M+U):F = 1:1.5$ and weight ratio $M:U = 47:53$, as a function of the percentage of methylal added on resin solids.

Figure 4 Variation of the viscosity as a function of viscometer spindle rotation rate of a paper impregnation MUF resin of molar ratio $(M+U):F = 1:1.5$ and weight ratio $M:U = 47:53$ for (♦) MUF resin alone, (■)MUF resin + 10% methylal, and (▲) MUF resin + 2% methylal.
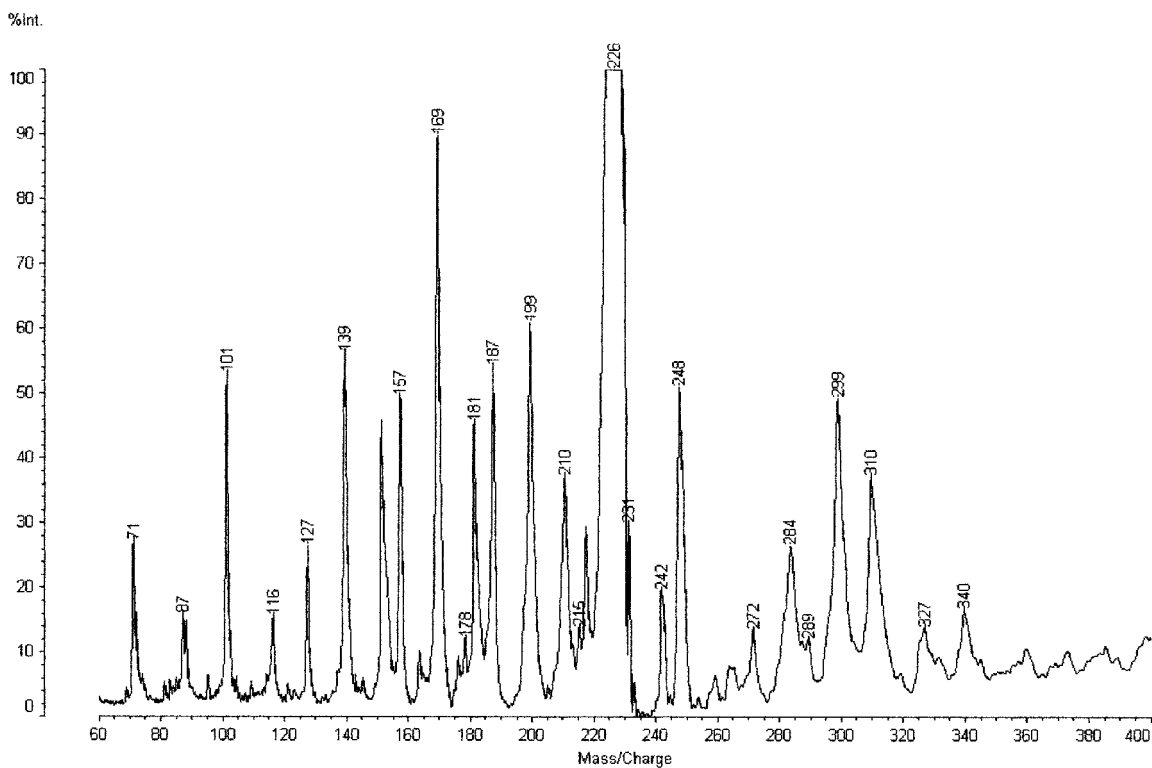
Figure 5 MALDI mass spectrum of MUF resin + 10% methylal. Details of the 60–400 Da range. Note the presence of the 299 Da peak. MUF adhesive resin of molar ratio (M+U):F = 1:1.9 and weight ratio M:U = 47:53.
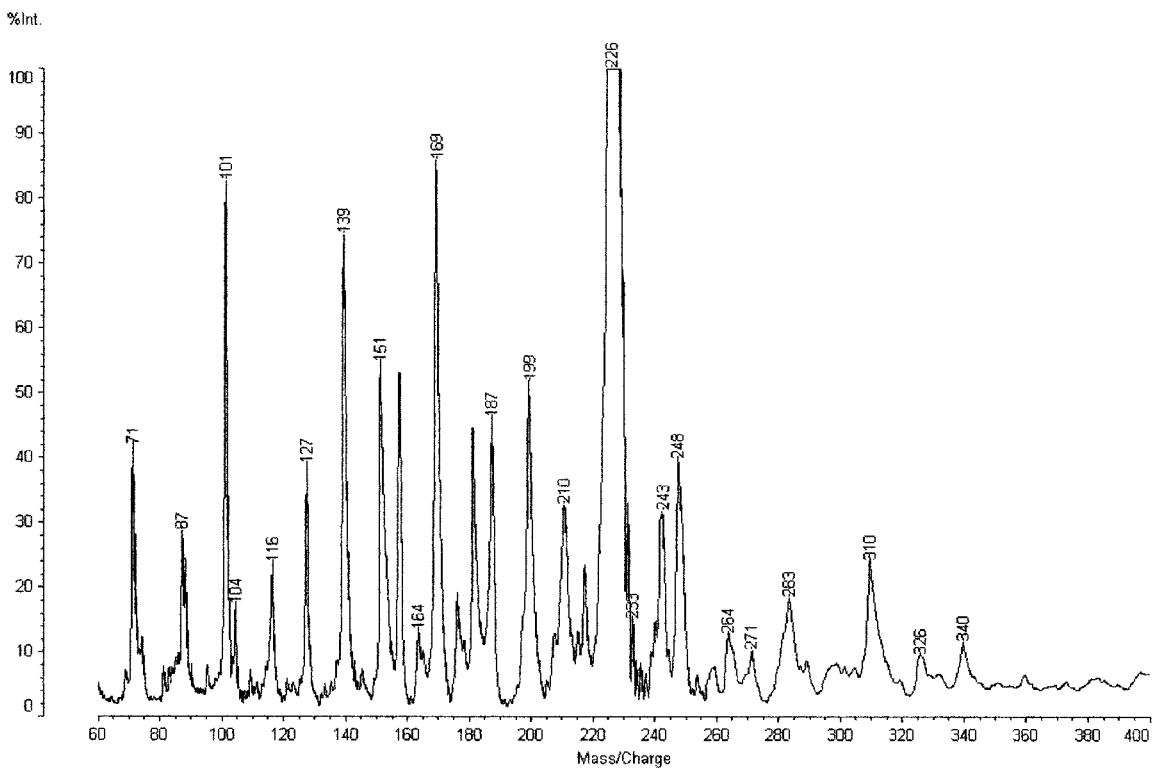

Figure 6 MALDI mass spectrum of MUF resin + 10% water. Details of the 60–400 Da range. Note the absence of the 299 Da peak. MUF adhesive resin of molar ratio (M+U):F = 1:1.9 and weight ratio M:U = 47:53.
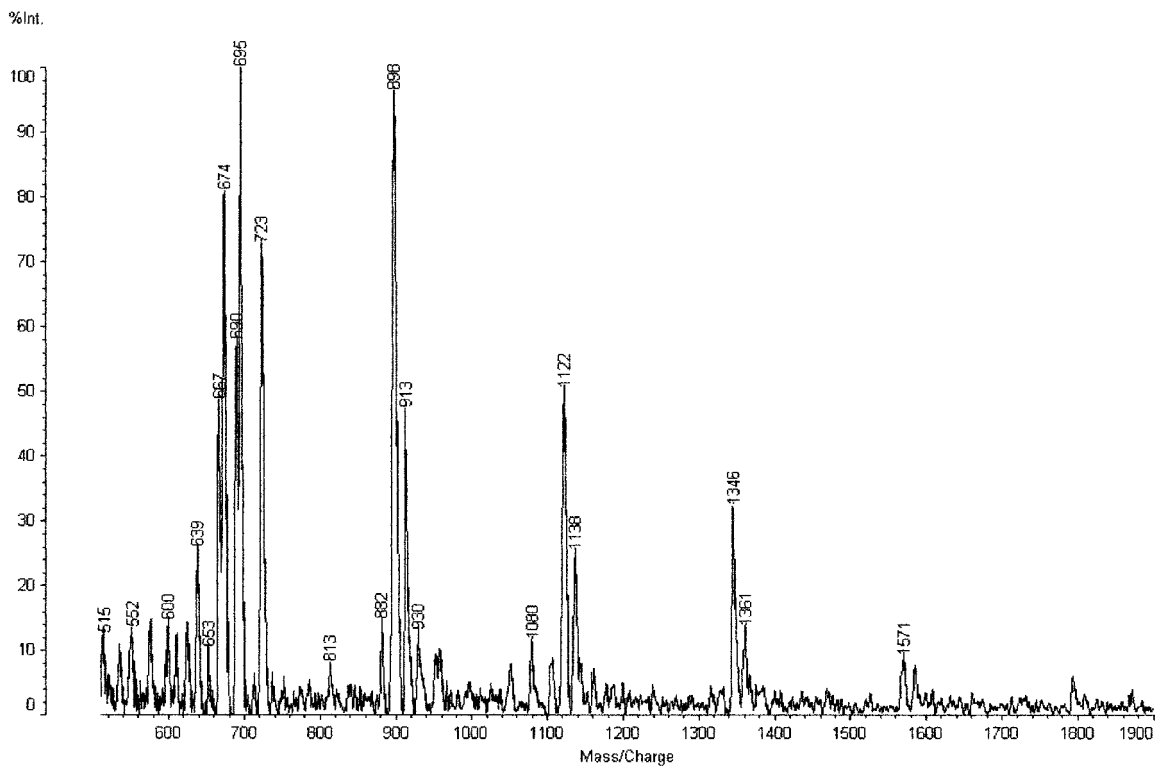
Figure 7   MALDI mass spectrum of MUF resin + 10% methylal in the 500–1900 Da range. MUF adhesive resin of molar ratio (M+U):F = 1:1.9 and weight ratio M:U = 47:53.
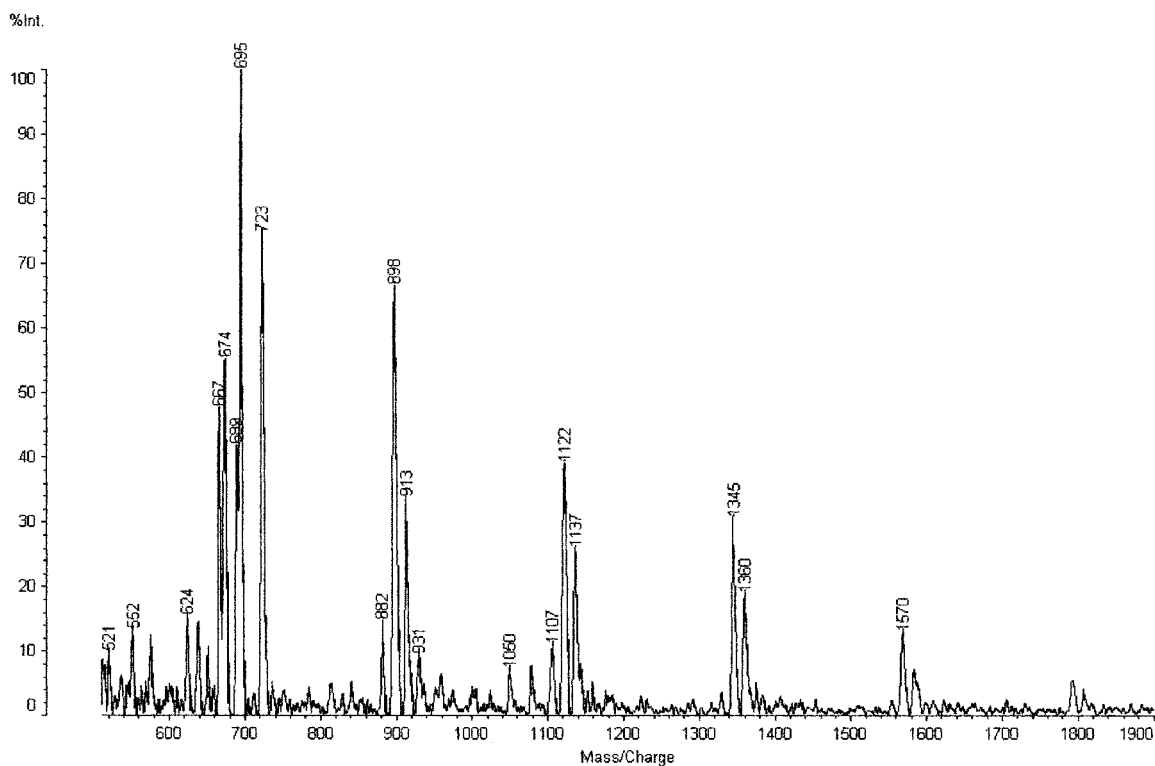

Figure 8   MALDI mass spectrum of MUF resin + 10% water in the 500–1900 Da range. MUF adhesive resin of molar ratio (M+U):F = 1:1.9 and weight ratio M:U = 47:53.

1122–1345–1570 Da is particularly prominent. This series is one of higher molecular weight fractions corresponding, respectively, to HOCH$_2$—M—CH$_2$—(—urea—CH$_2^-$)$_7^-$, and—(—CH$_2$—M—CH$_2$—urea—CH$_2$—)$_n$—(HOCH$_2$—)M—CH$_2$—(—urea—CH$_2^-$)$_7^-$, where **n** varies between 1 and 4. These are all compounds of lower solubility, but the results in Table III start to indicate to what extent the presence of 10% methylal increases their solubility. In Table III as the molecular weight does increase the difference in amount of the fraction detectable when methylal is absent or present decreases, with no differences appearing by the time one reaches the peak at 1570 Da. This result means that the molecular weight is so high that methylal cannot contribute any more to added solubility. However, the relative difference in solubility is very marked for still very high molecular weight oligomers in the range 674–1122 Da. This result indicates clearly that methylal and other acetals not only favor the solubility of unreacted melamine but, even more importantly, they favor the solubility and hence the effectiveness of participation in any further reaction during hardening of the less soluble higher molecular weight fractions of the MUF resin.

Finally, laser light scattering of MUF + 10% methylal resins and of MUF and MUF + H$_2$O 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 rather advanced MUF resin with a (M+U):F molar ratio = 1:1.9 and M:U weight ratios of, respectively, 47:53 and 40:60, to which has been added 10% methylal, have yielded average colloidal particles diameters of, respectively, 588 nm (M:U = 47:53) and of 387 nm (M:U = 40:60), whereas the same resins present average particle diameters of 3109 nm (a wide peak 3001–3218 nm) in absence of methylal (Figure 9) for both types of resin. Furthermore, the size distribution is wider in absence of methylal (2798–3451 nm) than when methylal is present (564–636 nm for the M:U = 47:53; 350–428 nm for the M:U = 40:60 resin), indicating a much narrower polydispersity range. This result means that the acetals are capable of either (i) disrupting the molecular clustering of the resin colloidal particles, or (ii) rearranging the size of the colloidal particles because of the decrease in surface tension of the
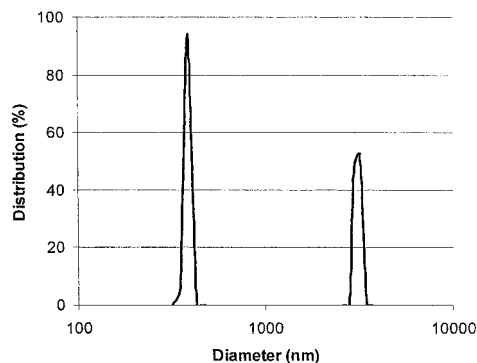

Figure 9 Colloidal particles diameter distribution by low angle laser light scattering (LALLS) obtained for MUF adhesive resins of molar ratio (M+U):F = 1:1.9 and weight ratio M:U = 40:60 (at 3100 nm, MUF resin alone; at 387 nm, MUF resin + 10% methylal).

system, or both. Because the methylal is added to the MUF resin much after its preparation, the former explanation appears to be the most likely, especially in light of the recent observation that the progressive whitening of MUF resins on aging is due to the appearance of colloidal clusters and to higher molecular weight fractions that appear in the resin as the reaction slowly proceeds on aging.[8] However, the data do not allow elimination of the second explanation, which might be valid too. The picture that appears then is one of effectiveness of cross-linking between the lower diameter component colloidal particles leading to a better cross-linked network when methylal is added, and the cross-linked 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.

In conclusion, it is evident that adding acetals to a MUF resin involves several effects: (i) The least determinant effect is increased solubility of the unreacted melamine chemical. (ii) Perhaps the most important effect is the increased solubility of the normally less soluble or insoluble higher molecular weight oligomers fraction in the liquid resin. This effect is correlated to the proportion of methylol groups on the oligomer, with the lower the methylolation level, the more noticeable the effect of acetal addition. (iii) The third effect is either the disruption of the molecular clustering of the resin colloidal particles or the rearranging of the size of the colloidal particles due to the decrease in surface tension of the system, or both. The latter two effects are likely to contribute most to the improvement in MUF and other polycondensation resins performance that have already been reported.[2]

TABLE III
Relative Peak Intensity of MALDI Peaks of Higher Molecular Weight Resin Oligomers

Peak (Da)	MUF alone (%)	MUF + 10% methylal (%)
674	55	80
898	67	96
1122	41	52
1345	33	34
1570	14	14

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