

Acetal-Induced Strength Increases and Lower Resin Content of MUF and Other Polycondensation Adhesives

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ABSTRACT: Acetals such as methylal and ethylal are shown to be particularly effective additives in improving the strength of wood boards bonded with melamine-urea-formaldehyde (MUF) resins, although they show some appreciable but lesser effect on other resins too, particularly phenol-formaldehyde resins. They equally allow a considerable decrease in resin loading, and thus, in melamine content, on the bonded wood panel and at parity of performance. Their development as additives is then primarily, but not only, targeted at the MUF adhesive resins. One-third decreases in MUF adhesives loading at parity of performance or equally internal bond (IB) strength increases approximately up to 50% by addition of methylal are shown to be possible by laboratory particleboard as well as by thermomechanical analysis (TMA). The reasons for methylal and ethylal behavior were studied by a variety of techniques, including liquid- and solid-phase ¹³C-NMR and could be mostly ascribed to the increased effectiveness and participation of the melamine to resin crosslinking due to its now preferentially homogeneous rather than heterogeneous reactions, consequences of the increased solubility in water afforded by the acetal cosolvents. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2561–2571, 2002

Key words: acetals; methylal; melamine resins; phenol resins; urea resins; performance improvement; adhesives; wood panels

INTRODUCTION

The wood board and resin-impregnated paperboard industries heavily rely on the use of synthetic resins and adhesives: in short, without adhesives and resins, these industries would not exist.¹ The use of panels and their respective adhesives increased 13% just in western Europe during the last 4 years and 30% in the last 10 years. The adhesives used for these panels in 1998 (data from the European Panels Federation) were 3.2 million tons of resin solids, with 2.6

million being urea-formaldehyde (UF) resins, 350,000 being melamine-urea-formaldehyde (MUF) resins, to which one can add 220,000 tons for paper impregnation, for a total of 570,000 tons of melamine-based resins and 260,000 tons of phenol-formaldehyde (PF) resins.

These applications rely on polycondensation resins, namely, MUF, UF, and PF resins. As performance standards were established throughout the world for wood composite boards and resin-impregnated paperboards, the percentages of wood adhesives/resins used for the manufacture of these products to satisfy the requirements of such standards, if not completely at a constant percentage, at least vary little around the typical percentage values characteristic for each type of

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resin and process used. The resin binder, which constitutes the more expensive materials cost component (generally is responsible for between 40 and 60% of the total cost of the finished product, the board), is then one of the parameters of which it is not possible to change markedly the percentage, as this will cause a very marked decrease in performance and hence will fail to satisfy the relevant standard specifications. Changing to stronger and more performant resins generally improves the composite strength but fails badly on some other characteristics: for instance, when the formaldehyde molar ratio of the resin is increased, better strength performance is obtained, but often the composite fails on an allowed level of formaldehyde emission. Use of greater amounts of adhesive almost automatically disqualifies the composite because of a too high formaldehyde emission and its higher cost, hence, the lack of easy movement in cost structure and environmental acceptability of most of the present-day wood composites.

Attempts to change this situation have led to several different approaches been proposed in the past, most of them based on resin engineering modifications during resin manufacture. When devised by the adhesive's producers, these modifications have generally been implemented, but often with increases in performance also accompanied by increases in resin price denying any great advantage either to the resin or to the panel manufacturers. Among the other types of approaches proposed some did not work well, whereas others did work well but were not economically viable. There were, however, systems proposed that, notwithstanding their excellent performance and their economic viability, have not yet been implemented.²⁻⁶ The problem of a few of these has always been (1) the lack of existing industrial production of the additive needed or the difficulty in implementing the resin modification needed; (2) the very natural unwillingness of the adhesive producers to promote the manufacture of some material that could potentially cut their resin sales; and (3) the technical/technological difficulties experienced by the wood industry in introducing by themselves any new but more complex adhesive formulation.

This situation clearly indicates that any additive that is capable of markedly decreasing the percentages of adhesive needed must be economically very viable, but most important of all, (1) must be already produced and easily available commercially for other purposes in very sizable quantities and sold at a reasonably low price; (2)

must be extremely easy to use by the wood industry, for instance, just by addition to a glue-mix without any technical investment, or other hindering sophistication; and/or (3) must be able to be easily added to its finished adhesive by an adhesive manufacturer without any subsequent problems of adhesive storage or others.

This article then deals with the development of novel low-cost additives capable of decreasing between one-fourth and one-third of the consumption of traditional wood adhesives (MUF, PF, and UF) in the wood-panel products industry, or otherwise be capable of increasing at resin load parity their present-day internal bond (IB) strength performance in a panel between 25 and 50% and this with existing commercial adhesives, without in principle any modification to their formulations. The work described was primarily, but not only, targeted at MUF adhesive resins to decrease by this approach not only resin content but also to decrease total melamine content on the board while maintaining the same board performance. PF and UF adhesives were also examined. As regards environment and toxicity, this development (1) implied the possibility of lowering adhesive content of the board, implying then even lower formaldehyde emission values from panels bonded with modern UF and MUF resins, even if today these do not strictly need it anymore; and (2) implied a considerable lowering of raw materials' toxicity because the toxicity limits of the most available additive proposed here is quoted by the U.S. Environmental Protection Agency (EPA) at 1000 ppm in air against a limit of 0.1 ppm for formaldehyde under the same conditions, meaning that the additive is 10,000 times less toxic than formaldehyde (hence, its qualification as nontoxic by the EPA).

EXPERIMENTAL

Resins Used

A commercial UF resin of 63% resin solids content and molar ratio $U : F = 1 : 1.5$, Seleform U4246 (Chimica Pomponesco, Italy), was used. Also used was a commercial UF resin of molar ratio $U : F = 1 : 1.3$ (Elf Atochem, France). For the MUF resins, both an industrial MUF resin of $(M+U) : F$ molar ratio $1 : 1.5$ and $M : U = 47 : 53$ mass ratio (Sadepan, Italy) and a sequential MUF having the same characteristics (molar ratio $1 : 1.5$ and mass ratio $47 : 53$) made in the laboratory according to an already reported procedure⁷ were used.

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

Acetal Type	Percentage Hydrolysis at		
	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

The MUF with a molar ratio of 1 : 1.2 and an equal mass ratio as the others was prepared according to the same reported sequential procedure.⁷ The PF resin used was prepared at F : P molar ratios of 1 : 1.7, also according to already reported procedures.⁸ The preparation procedure used is exemplified as follows: 1.0 mole phenol is mixed with 0.35 mol NaOH as a 30% water solution and 1.2 mol formaldehyde (as a 37% formalin solution) in a reactor equipped with mechanical stirring, heating facilities, and reflux condenser. After stirring for 10 min at 30°C, the temperature is slowly increased to reflux (94°C) over a period of 30 min, under continuous mechanical stirring, and kept at reflux for a further 30 min. Formaldehyde (0.5 mol as a 37% formalin solution) is then added. The reaction mix is now at pH 11 and the reaction is continued at reflux until the resin achieves a viscosity (measured at 25°C) of between 0.5 and 0.8 Pa s. The resin is then cooled and stored. Resin characteristics are then pH 11; resin solids content is 50 ± 1%.

Acetals Hydrolysis

The hydrolysis of methylal, ethylal, and 1,3-dioxolane over a period of 5 h at 20°C was followed and determined by ¹H-NMR. The acid solutions at pHs 0, 1, and 2 were prepared by using D₂SO₄ 97% in D₂O 99.5%. All three acetals concentrations were 5% by weight. For propylal and butylal, their concentrations were 2% by weight and contained C₂D₅OD as a cosolvent, and because of their lower solubility, the hydrolysis was followed for 5 h and 15 days, respectively. The percentage of hydrolysis results are shown in Table I.

Thermomechanical Analysis (TMA)

The resins above, used alone as controls, and after addition of 3, 10, and 20% acetal, respectively

(with addition of 1.5% ammonium chloride hardener, solids on resin solids, added as a 20% water solution in the case of the MUF and UF resins), were tested dynamically by TMA on a Mettler apparatus. The acetals tested were methylal for all resins, ethylal for most of the resins, and for some resins (as indicated in Tables II and III) also, propylal, butylal, and dioxolane were tested. Triplicate samples of beech wood alone, and of two beech-wood plys each 0.6 mm thick bonded with each system, for a total samples dimensions of 21 × 6 × 1.2 mm, were tested in nonisothermal mode between 40 and 220°C at a heating rate of 10°C/min with a Mettler 40 TMA apparatus in three points bending on a span of 18 mm exercising a force cycle of 0.1/0.5N on the specimens with each force cycle of 12s (6 s/6 s), according to already established procedures.^{9–11}

The classical mechanics relation between force and deflection $E = [L^3/(4bh^3)][\Delta F/(\Delta f)]$ allows the calculation of the Young's modulus E for each case tested, and this was done for the maximum value of the modulus as well as to follow the increase of modulus (MOE) as a function of temperature and time. The results are shown in Tables II and III.

¹³C-NMR Spectrum

The liquid ¹³C-NMR spectrum of all the resins used, the warmed-up and recooled mixes of just melamine + methylal and urea + methylal, and *ortho*-hydroxybenzyl alcohol (saligenin) and *para*-hydroxybenzyl alcohol, as simple model compounds of the PF resin after mixing and warming up with methylal were obtained on a Brüker MSL 300 FT-NMR spectrometer. Chemical shifts were calculated relative to (CH₃)₃Si(CH₂)₃SO₃Na dissolved in D₂O for NMR shifts control.^{12,13} The spectra were done at 62.90 MHz for a number of transients of approximately 1000. All the spectra

Table II Maximum MOE Values Obtained by Thermomechanical Analysis (TMA) by Curing *In Situ* in the Wood Joint a MUF Resin with Acetals Added in the Glue Mix

Resin: Molar Ratio: Additive Added	Maximum MOE (in MPa) for				
	MUF 1 : 1.5	MUF 1 : 1.2	PF 1 : 1.7	UF 1 : 1.5	UF 1 : 1.2
Resin alone, control	2995	2223	2126	1675	1936
+3% Methylal	3026	2523	2156	2286	1821
+10% Methylal	4059	3581	2632	2316	1862
+20% Methylal	5231	3733	3250	1889	1903
+3% Ethylal	3207	2744	—	2102	2079
+10% Ethylal	3963	4200	—	2164	1742
+20% Ethylal	4859	3206	—	2390	1617
+3% Dioxolane	3564	2442	—	—	—
+10% Dioxolane	2823	2842	—	—	—
+20% Dioxolane	2893	2831	—	—	—

were run with a relaxation delay of 5 s and chemical shifts were accurate to 1 ppm.

CP-MAS ¹³C-NMR

Hardened samples of the 1 : 1.5 MUF resin hardened by addition of 1.5% ammonium chloride on resin solids in the absence and presence of 20% methylal, as well as hardened samples of the 1 : 1.7 PF resin in the absence and presence of 20% methylal and the precipitate of melamine + methylal mixes were examined by solid-state CP-MAS ¹³C-NMR under the following conditions: spectra were obtained on a Bruker MSL 300 FT-NMR spectrometer. The solid-state CP-MAS ¹³C-NMR spectra were obtained at a frequency of 75.45 MHz and at a sample spin of 3.5 kHz. Chemical shifts were calculated relative to TMS

Table III Maximum MOE Values Obtained by Thermomechanical Analysis (TMA) by Curing *In Situ* in the Wood Joint a MUF Resin with Acetals Added in the Glue-Mix

Resin: Molar Ratio:	MUF 1 : 1.5
Additive	Maximum MOE (MPa)
Resin alone, control	2382
+3% Propylal	2890
+10% Propylal	2695
+20% Propylal	2486
+3% Butylal	2473
+3% Butylal	2302
+3% Butylal	2013

for NMR control. Acquisition time was 0.026 s with a number of transients of about 1000. The spectra were accurate to 1 ppm. The spinning sidebands present are indicated on the spectra figures (SSB). Typical spin–lattice relaxation times for the types of compounds analyzed as well as peak interpretation for melamine and PF and MUF resins were taken from the literature.^{8,14–20}

Wood Particleboard Preparation

Duplicate one-layer laboratory particleboard with dimensions of 350 × 310 × 14 mm were then produced by adding on to dry wood particle 10% resin, 10% resin + 1% methylal, 8% resin + 0.8% methylal, and 6% resin + 0.6% methylal and using the 1 : 1.5 MUF resin, pressed at a maximum pressure of 28 kg/cm², followed by a descending pressing cycle, at 190–195°C, for pressing times of 3 min (12.8 s/mm). All the panels had densities comprised between 0.695 and 0.704 g/cm³. The panels, after light surface sanding, were tested for dry IB strength, for IB strength after 2 h boiling, and after 16 h drying at 105°C, tested dried. The results obtained are shown in Table IV.

DISCUSSION

The approach, which has shown considerable promise in markedly decreasing the percentage of adhesive solids on a board, and hence, in markedly decreasing melamine content too in MUF resins, is based on the addition to polycondensation resins used as wood adhesives of acetals used as additives, in particular, methylal and ethylal.

Table IV MUF-Bonded Laboratory Particleboard Results When Adding Methylal Directly in the Glue-Mix

	Adhesive Load (%)	IB Strength Dry (MPa)	IB Strength 2 h boil (MPa)
MUF control	10.0	1.01	0.40
MUF + 10% additive	10.0	1.34	0.39
MUF + 10% additive	8.0	1.03	0.30
MUF + 10% additive	6.0	0.83	0.18

Methylal and ethylal are the two more apt due to their cost to performance ratio,^{19,21} and because they do not release formaldehyde at pHs higher than 1 (Table I). This indicates that these acetals do not contribute to MUF and UF resin formaldehyde emission, as these resins are hardened at pHs not lower than between 3 and 4 to avoid to any great extent acid degradation of the lignocellulosic substrate. According to results reported by the EPA, methylal has an LD₅₀ value of 10,000 against 100 in the case of formaldehyde and is thus classified as nontoxic.²¹

In Table II are reported the TMA results of the increase in maximum modulus values reached in beech-wood joints bonded with different MUF, PF, and UF resins to which different amounts of methylal and ethylal have been added. A few examples for some of the more important cases are reported in Figures 1–3. The results in Table I

indicate that the strength results increase considerably with the progressive increase in the amount of acetal content of the resin. The increase in strength of the bonded joint is evident for all resins with the exception of the low molar ratio (1 : 1.2) UF resin, where the only MOE increase occurs at 3% ethylal addition and is only 7%. It is then evident that the system does not work for low molar ratio UF resins. Other low molar ratio UF resins, both industrial and laboratory-made, were also tested but the results was always the same: the acetals did not appear to improve the strength of joints bonded with lower molar ratio UFs. What is worse is that an explanation for such an apparently anomalous behavior is not even evident at this stage.

It is also evident from Table II that the two MUF resins were the ones more positively affected, with the MUF resin of (M+U) : F 1 : 1.5

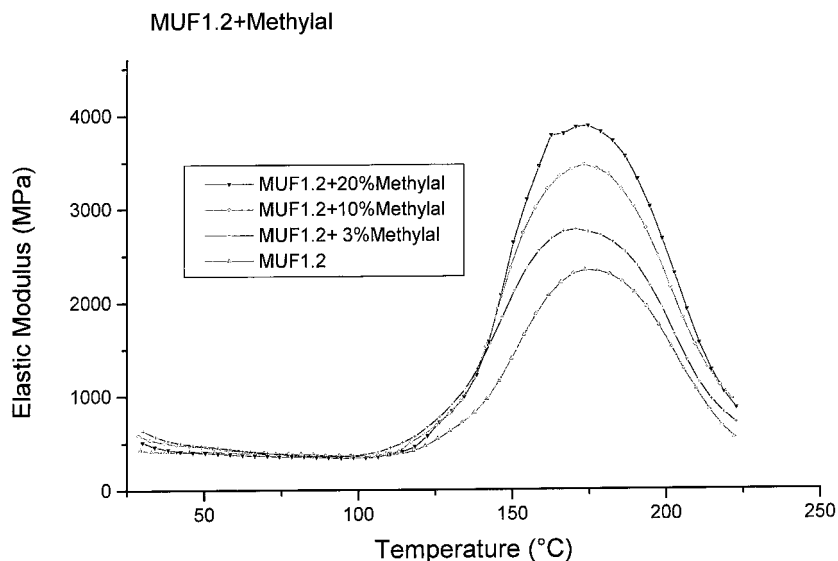


Figure 1 Curve of increase of hardening as a function of temperature and at a constant heating rate of 10°C/min of the modulus of beech-wood joints bonded with a MUF resin of (M+U) : F 1 : 1.2 molar ratio (+1.5% NH₄Cl) without and with addition of 3, 10, and 20% methylal on resin solids.

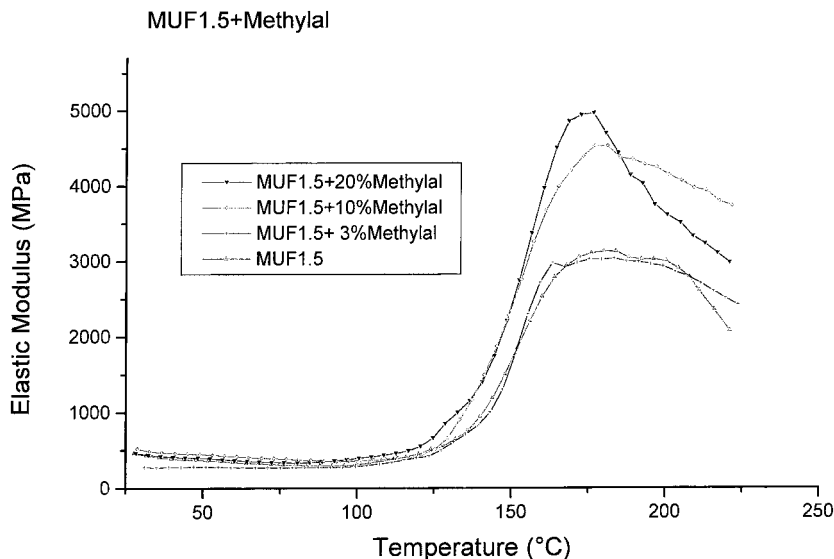


Figure 2 Curve of increase of hardening as a function of temperature and at a constant heating rate of 10°C/min of the modulus of beech-wood joints bonded with a MUF resin of (M+U) : F 1 : 1.5 molar ratio (+1.5% NH₄Cl) without and with addition of 3, 10, and 20% methylal on resin solids.

molar ratio increasing the joint's strength by 1, 35, and 75% for the addition of 3, 10, and 20%, respectively, of methylal on resin solids. The equivalent ethylal-induced increases for the same resin were 7, 32, and 62%, respectively. For the MUF resin of (M+U) : F 1 : 1.2 molar ratio, the corresponding percentage increases were 13, 61,

and 68% for methylal addition, and 23, 89, and 44% (one of these two values appearing to be anomalous) for ethylal addition, hence, a very different behavior than the other low molar ratio aminoplastic resin, namely, the UF 1 : 1.3.

The MUF maximum modulus results obtained for wood joints by methylal addition compare very

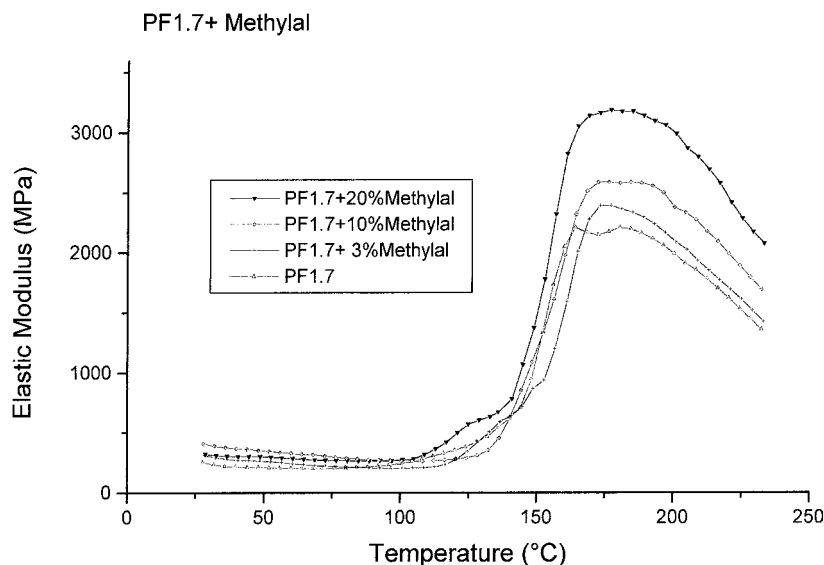


Figure 3 Curve of increase of hardening as a function of temperature and at a constant heating rate of 10°C/min of the modulus of beech-wood joints bonded with a PF resin of P : F 1 : 1.7 molar ratio without and with addition of 3, 10, and 20% methylal on resin solids.

favorably then with the MOE increases for PF resins, also shown in Table II. Thus, to equivalent methylal additions to a PF resin of P : F 1 : 1.7 molar ratio corresponds an increase in MOE of 1, 24, and 53%, respectively, on the control. The strength increases are then almost as good as in the case of MUF adhesive resins.

For the higher molar ratio UF (U : F = 1 : 1.5), the relative MOE increases reported in Table II are 36, 38, and 13% for methylal addition, and 25, 29, and 43% for ethylal addition. It is evident, even in this more favorable UF case, that improvement is obtained with a very small addition of acetal, but that a subsequent increase in the proportion of acetal most often does not appear to yield further MOE improvements. This is opposite to what can be observed in the case of the MUF and PF adhesives, where there appears to be some direct relationship between the amount of acetal and the improvement in joint performance obtained (Table II).

Of the other acetals used (propylal and butylal), some improvement is obtained in the case of propylal, yet again with the advantage acquired at low levels of addition decreasing in intensity as one increases the relative proportion of propylal (Table III). The addition of butylal instead does not appear to yield any improvement (Table III); this can be explained by the lack of solubility of butylal in water (relative solubilities in water methylal = 32.3%; ethylal = 6.33%; propylal = 0.4%; and butylal = insoluble),²² an important consideration, as it indicates that the effects/reactions which yield the strength improvement must occur in homogeneous phase, in water solution.

The TMA diagrams of an increase in modulus with an increase of the temperature at a constant heating rate shown in Figures 1–3 indicate that the addition of the acetals does not only lead to an increase in the maximum value of the joint MOE, but that the MOE curves increase more rapidly and earlier with increasing relative proportion of acetal added. This indicates that either (1) the acetal has a catalytic curing acceleration effect; this cannot be the case, as the gel points for the curves on each graph are just about the same (around 115°C for Fig. 1, for example); or (2) the acetal has a curing accelerating effect on resin network formation due to the apparent or effective increased functionality of one of the reagents; or (3) the acetals react with the resin and its reaction starts as early as any of the other crosslinking reactions. The possible improvement in the viscoelastic dissipation of energy in the

joint then starts to be noticed immediately as resin networking starts and progressively increases with the progress in hardening of the system.

Transacetalization reactions could be one cause or a contributory factor of the observed strength improvement of the hardened resin and consequent joint strength improvement. If they occurred, they could be observed by solid-phase CP-MAS ¹³C-NMR. The CP-MAS ¹³C-NMR spectra of the 1 : 1.5 MUF resin hardened alone and in presence of methylal are shown in Figures 4 and 5. Here, the only differences are the existence of the shoulder at 60–65 ppm and the increase in relative intensity of the 54–57 ppm band in the MUF + methylal-hardened resin. The NMR bands pertaining to the —CH₂—O— and CH₃—O— groups in pure methylal spectra appear at 99 and 57–58 ppm, respectively. This means that the increase of the bands at 54–57 ppm in Figure 5 correspond to CH₃—O— bands of free, or still unreacted, methylal which has been added and is still present in the system. The shoulders at 60–65 ppm correspond instead to the unreacted MUF methylol groups,^{14–20} —CH₂—OH, the methylene ether bridges,^{14–20} —CH₂—O—CH₂— which are formed in the hardened network of a MUF resins and possibly even to the —CH₂—O—CH₂—O—CH₂— bridges obtained by transacetalization. It is clear, however, that even if these latter ones do form (and of this one cannot be sure from the spectrum), their proportion is clearly so small not to be a contributing factor, to any extent, of the increase in joint strength noted. The other peaks present in both spectra are the two peaks at 165–167 and 160 ppm pertaining to the partially substituted melamine triazine carbons and to the carbonyl group of urea in the MUF resin,^{15–20} respectively, and the peaks centering in the very narrow range around the one at 49 ppm belonging to the methylene bridges, —NH—CH₂—NH—, linking melamine to melamine, melamine to urea, and urea to urea, which are always present in this type of resins.^{14–20}

The spectra done on PF resins (not reported here) hardened in the presence of methylal show the same lack of transacetalization noted for the MUF resins. Equally, liquid-phase NMR spectra (not shown here) done on the reaction at a variety of pHs of *ortho*- and *para*-hydroxybenzyl alcohols as simple model compounds of a PF resin with methylal did not show anything else than mixtures of the phenolic alcohol and the unreacted acetal.

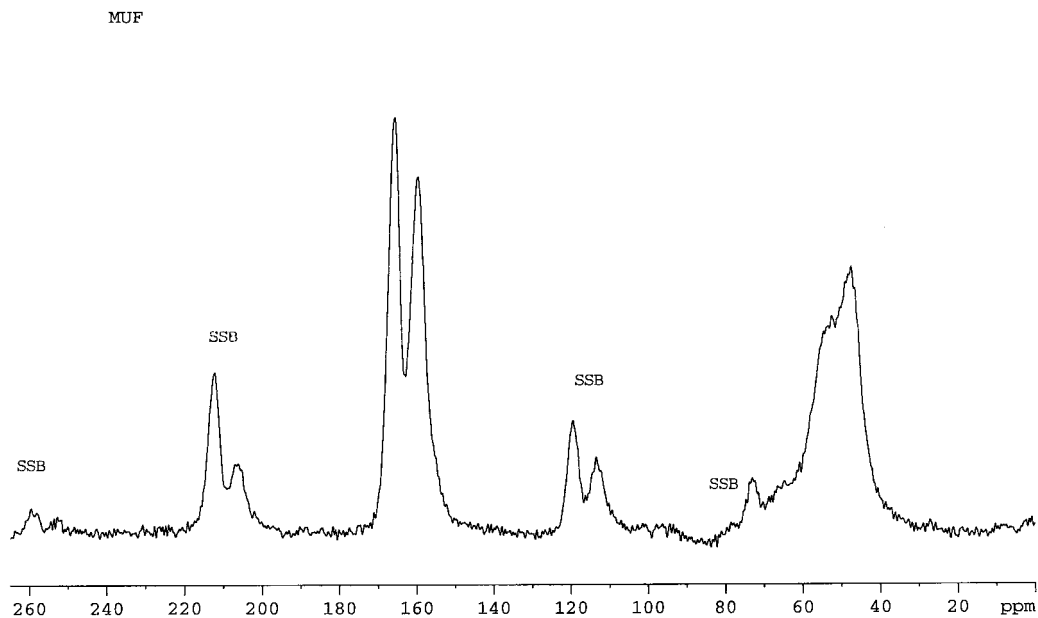


Figure 4 Solid-phase CP-MAS ^{13}C -NMR spectrum of a MUF resin of (M+U) : F 1 : 1.5 molar ratio hardened with +1.5% NH_4Cl . Spinning side bands (SSB) are indicated on the spectrum.

However, something totally different gave a lead as to what appears to be the main contributory cause of the strength increase effect. Although NMR spectra of melamine alone (not a resin) (Fig. 6), at pH 3 and 11, and urea alone with acetals, showed no reaction product other

than the original melamine, it was noted that addition of methylal and ethylal to melamine in water and to the reaction medium during the preparation of a MUF resin improved the solubility of melamine, considerably more than the well-known and widely used dimethylformamide cosol-

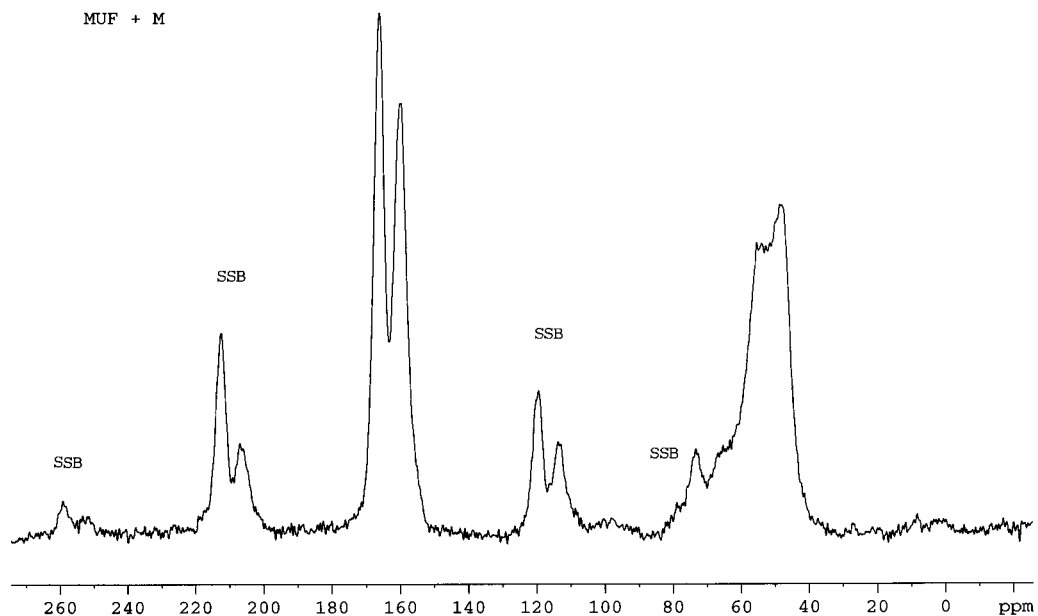


Figure 5 Solid-phase CP-MAS ^{13}C -NMR spectrum of a MUF resin of (M+U) : F 1 : 1.5 molar ratio hardened with +1.5% NH_4Cl after addition of 20% methylal on resin solids. Spinning side bands (SSB) are indicated on the spectrum.

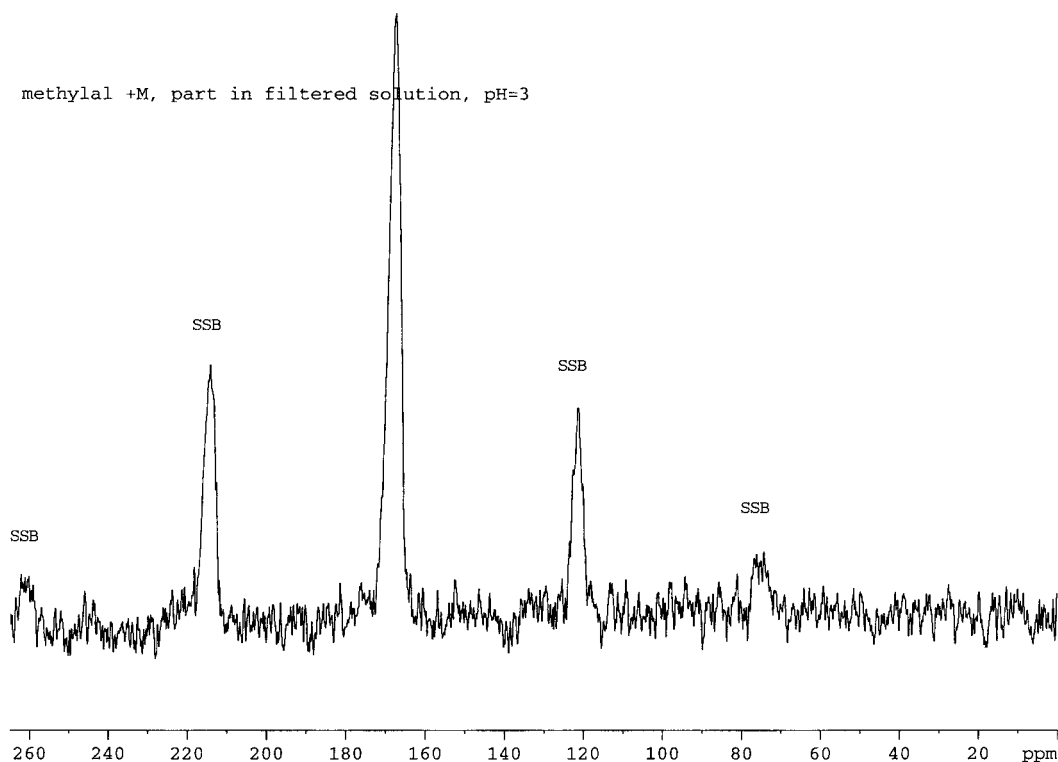


Figure 6 Typical solid-phase CP-MAS ^{13}C -NMR spectrum of filtered precipitate of melamine after addition and reaction of 20% methylal on resin solids. The identical pattern was observed in both filtered melamine + methylal solution and filtered solid precipitate, both at pH 3 and 11. Only the unsubstituted triazine carbons of melamine at 170 ppm are seen. Spinning side bands (SSB) are indicated on the spectrum.

vent. Melamine is notoriously difficult to bring in water solution and in the manufacture of resins this occurs only after a fairly long time at $\geq 90^\circ\text{C}$, and after abundant reaction with formaldehyde has introduced a high number of methylol groups on the melamine triazine ring. Even in water/dimethylformamide, without the solubilizing reaction with formaldehyde, melamine remains largely insoluble. Recently,²⁻⁵ 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 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 two-thirds) of melamine in the resin which is wasted.² As a better solvent is found, the effectiveness of the reaction increases considerably, and as the proportion of melamine that contributes to crosslink-

ing increases, so does the resultant strength of the hardened network and the strength of the bonded joint.

In conclusion, the main mechanism of some acetals improvement of melamine resins is their excellent solvent and water cosolvent action on melamine. The case of melamine salts referred to and the consequent loss of effectiveness due to wastage of melamine are applicable in this case also. Melamine, when added to a reacting mixture during resin manufacture, is not really soluble. It reacts then in heterogeneous phase with the other components of the resin, some of it being in a transient state in equilibrium between being in solution and being out of solution, and thus its effectiveness is partially, but noticeably, reduced. The introduction of an excellent solvent, none better than these known before, brings a greater proportion of the reaction in homogeneous phase with a consequent, noticeable improvement in both the effectiveness of reaction and the effectiveness in melamine utilization. Thus, it appears that the notion that addition of acetals through reactions of transacetalization be equivalent to

say that without any free formaldehyde and without any additional formaldehyde emission, one is able to increase the molar ratio of the resin to unheard of levels does not appear to be valid. Also invalid is that facile partial transacetalization reactions (thus not arriving to the crosslinking stage), and which are easily reversible equilibria, of the type $Melamine-NH-CH_2OH + CH_3-O-CH_2-O-CH_3 \Leftrightarrow Melamine-NH-CH_2-O-CH_2-O-R + CH_3OH$ (with $R = CH_3, H$) and $Melamine-NH_2 + CH_3-O-CH_3-O-CH_3 \Leftrightarrow Melamine-NH-O-CH_2-O-R + CH_3OH$ contribute to the considerably improved solubility of melamine, which leads to strength improvement. This would be an interesting possibility but it also does not occur, as can be seen as an example in Figure 6, as neither in the solid nor liquid phase spectra is there any trace of such transacetalization reactions having occurred.

Thus, for the reasons exposed initially, the correct one is (2): the acetal has a curing accelerating effect depending on the apparent or effective increased functionality of one of the reagents. The effective functionality of melamine in most polycondensation reactions is much lower than what it really should be due to these solubility problems. Thus, the case (2) above is the real cause of the improvement due to the improved acetal-induced solubility of melamine, which will lead to an increase in the effective functionality of melamine during resin preparation as well as in its crosslinking, hardening stage. As melamine is the molecule with the more problematic solubility, it is clear the effect is at its most noticeable in melamine resins.

This explains why acetals have very little effect on UF resins, as solubility of urea in water is rather good. This, however, does not explain why it still improves rather markedly the performance of PF resins. In PF resins, the problem is that a limit of solubility of the resin (not of phenol, which is well soluble in water) is reached easily and early on during preparation of the resin. The existence of a solvent which is able to extend the level of linear polymerization during curing without the resin precipitating will also contribute considerably to the improvement of the level of participation to crosslinking during hardening, and hence, the performance of the resin. This effect should also exist in melamine and urea resins and might account for the small but definite improvement of the strength of the UF resins with small amounts of acetals noticed for the 1 : 1.5 UF resin. The effect is small and thus in UF's a considerable increase in the amount of acetal

will not improve the result; however, a small addition will, as indeed can be noted in Table II.

As TMA-derived MOE of bonded wood joints have been shown to be in direct relation with the internal bond strength of particleboard,²³⁻²⁵ the final proof of the effectiveness of these additives, and the real extent of the improvement under wood panels operational conditions, was searched by applying them to the preparation of wood particleboard. The results are shown in Table IV. Decreases in MUF resin solids content of as much as 33%, while conserving the same performance are reported in the case of wood particleboard and appear to be possible using 20% methylal addition, as 10% methylal addition is capable of yielding the same performance with 20% less MUF resin (Table IV). Thus, in the case of MUF resins, the addition of 10% additive on resin solids yields laboratory particleboard in which one can decrease the percentage resin solids on the board of between 20 and 25% without any loss of performance (Table IV). Equally, from Table IV, at equal resin solids, the strength of a particleboard is 33% higher when 10% additive on resin solids is added to the glue-mix. Addition of 20% methylal on the board would yield, in the case of the same resin, the same strength with 31% less adhesive (and hence less melamine), or an increase of strength of approximately 50%.

The particleboard results shown in Table IV are only indicative: even better decrease in the amount of adhesive (as much as between 30 and 40% less adhesive) can be obtained by just adding 20% additive directly in the glue-mix. Furthermore, although this appears less interesting, one can maintain the same amount of resin while decreasing the percentage of melamine in it by using such an additive. This might be of interest but is less interesting than just decreasing markedly the adhesive while using a standard off-the-shelf MUF resin.

CONCLUSIONS

Acetals such as methylal and ethylal are particularly effective additives in improving strength of wood boards bonded with melamine-urea-formaldehyde (MUF) resins, although they show some appreciable but lesser effect on other resins too, particularly PF resins. They equally allow a considerable decrease in resin loading, and thus of melamine content, on the bonded wood panel and this at parity of performance. Their development as additives is primarily, but not only, targeted

then at the MUF adhesive resins. At one-third decrease of MUF adhesives for an addition of 10% additive (which costs about one-fifth of the resin) on adhesive resin solids this means a redundancy and a saving of up to approximately 80,000 tons of MUF adhesives solids per year in the Western European market alone indicating that economic prospects for such a simple technology appear to be rather good. As there is considerable scarcity of MUF resins for application in other fields, these materials will not negatively affect the resin producers, at least in the short term.

At present the ever more stringent environmental protection regulations in the field of wood-based composite panels are aimed at drastically limiting gas emission (formaldehyde) as well as further water discharge limitations (for phenol, for example) from bonded wood products. Considerable and excellent progress has already been made in the formulation of more environmentally friendly adhesives and panels. However, any further tightening of the regulations, tightening that might well still occur, might cause to wood panel manufacturers considerable problems both to meet tougher specifications, as well as in the supply of the type of materials which could be used by manufacturers to satisfy more severe and more limiting standards. In this context a drastic decrease of the percentage of adhesive used in the panel, without any loss of performance, will immediately improve to a considerable degree the capability of many wood panels manufacturers to meet tougher environmental emission and discharge standards by drastically limiting the problem at source. To roughly quantify this statement, it is sufficient to quote the U.S. Environmental Protection Agency (EPA) as regards the toxicity limits of the most available additive proposed which is based at 1000 ppm (parts per million) in air against a limit of 0.1 ppm for formaldehyde under the same conditions, meaning that the additive is 10,000 times less toxic than formaldehyde (hence its qualification as nontoxic by the EPA).²¹

The introduction of such additives is also likely to change the cost structure of the wood panel industry by markedly decreasing the cost of wood panels, which is strongly determined by the cost and percentage of adhesive used.

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