

## NOTE

# Variation of Acetal Effect on Performance of Phenol–Formaldehyde Resin Adhesives

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### INTRODUCTION

Recently, acetals such as methylal and ethylal have been used as novel, low-cost additives capable of decreasing between a fourth and a third of the consumption of traditional wood adhesives, particularly of melamine–urea–formaldehyde (MUF) resins, in the wood panel products industry.<sup>1,2</sup> They have also been shown to be capable, at resin load parity, of increasing the internal bond (IB) strength performance of the panels by between 25% and 50%, using the existing commercial adhesives, without principal modification of the resins formulations.<sup>1,2</sup> Such an improvement in performance appears to be due to several effects of the acetals,<sup>1–3</sup> including (i) the increased solubility of the unreacted melamine chemical, although this is the less determinant effect, (ii) the increased solubility of the normally less soluble or insoluble higher molecular weight oligomer fraction in the liquid resin, likely a more important effect, (iii) the disruption of the molecular clustering of the resin colloidal particles,<sup>2,4</sup> and (iv) other, less well-defined structural effects of the acetal.<sup>3</sup> Effects (ii) and (iii) appear to be the two that are likely to contribute most to the improvement in MUF resin performance. The last effect was shown to occur by the variation in size distribution of resin colloidal particles upon addition of an acetal such as methylal.

While acetals such as methylal and ethylal were shown to be particularly effective additives in improving the strength of wood boards bonded with MUF resins, they also showed some appreciable but lesser effect on other resins too, particularly phenol–formaldehyde (PF) resins.<sup>1</sup> The reason they work on PF resins, however, is not clear. Effect (i) above cannot be operative because there are no problems of solubility of phenol in water or water/methanol. Effect (ii) above cannot really be operative because PF resins usually contain relatively high percentages of methanol (as high as 20–30% of the solvent used). Methanol is also a good solvent for the less soluble, higher molecular weight oligomer fraction in the liquid resin. Effect (iii) might be present, but this needs to be verified. The presence of methanol in the resin appears to indicate that this effect might be minor, as methanol is

capable of the same disruption in the size distribution of resin colloidal particles.

This article examines whether the effect of an acetal such as methylal exists and to what an extent, whether effect (iii) above contributes to the improvement in resin performance, and what other contributing effects might be present in the acetal/PF resin system.

### EXPERIMENTAL

#### Preparation of PF resins

A 500 mL flat-bottomed flask equipped with a condenser, thermometer and a magnetic stirrer bar was charged with 94 parts by mass phenol, 40 parts (20/80) methanol/water solution (or water only for methanol-free resins) and 55 parts by mass 96% paraformaldehyde. After stirring for 30 min at 40°C, the temperature was slowly, over the period of 30 min, increased to reflux (94°C). A total of 20 parts by mass of 33% sodium hydroxide solution was added in four equal parts at 15-min intervals. The mixture was refluxed for 30 to 60 min and then cooled in an ice bath to yield a pale yellow, transparent resin of 300 mPa s for 59% solids content.

#### Laser light scattering

The measures of granulometry for the three PF resins of molar ratio P:F of 1 : 1.76 were carried out with an 18 mm diameter Malvern laser and a helium/neon source, with the detector positioned at 90° relative to the light beam, and a scanned area of 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  $\eta$  is the viscosity.

#### Thermomechanical analysis

The resins above were tested dynamically by thermomechanical analysis (TMA) on a Mettler apparatus. Triplicate samples of beech wood alone, and with two beech wood plys, each 0.6 mm thick, bonded to each system, for a total sample dimension of 21 × 6 × 1.2 mm, were tested in

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**TABLE I**  
Maximum Value of MOE Obtained by TMA for Beech Wood Joints Bonded with Methanol-Free PF Resin with and without Addition of Methylal

	MOE max (MPa)	Peak temperature (°C)
PF, control	3729 ± 167	167
PF + 10% methylal	4652 ± 164	164
PF + 20% methylal	4391 ± 163	163

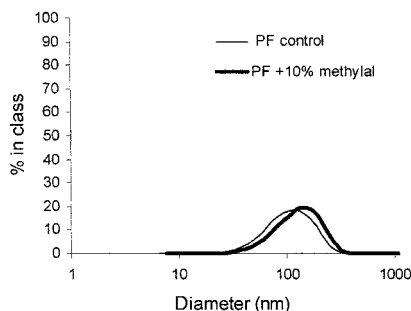
non-isothermal mode between 40°C and 220°C at a heating rate of 10°C/min with a Mettler 40 TMA apparatus in three points bending over a span of 18 mm exercising a force cycle of 0.1/0.5 N on the specimens with each force cycle of 12 s (6s/6s). The classical mechanics relation between force and deflection,  $E = [L^3/(4bt^3)][\Delta F/(\Delta f)]$ , allows the calculation of the Young's modulus ( $E$ ) for each case tested. As the deflections ( $\Delta f$ ) obtained were proven to be constant and reproducible,<sup>5,6</sup> and these are inversely related to the values of the modulus, we usually report the values of the deflection (in  $\mu\text{m}$ ) in the tables.

#### Wood particleboard preparation

Duplicate, single-layer laboratory particleboard of 350 × 310 × 14 mm were produced by adding 9% PF resin solids to dry wood particles, pressing at a maximum pressure of 28 kg/cm<sup>2</sup>, and then employing a descending pressing cycle, at 190–195°C, for pressing times indicated in the results tables. All of the panels had densities between 0.695 and 0.704 g/cm<sup>3</sup> unless otherwise indicated in the results tables. The panels, after light surface sanding, were tested for dry IB strength, for IB strength after 2 h of boiling and after 16 h of drying at 105°C.<sup>7</sup> Viscosity results were obtained with a Brookfield viscometer at 20°C. The results obtained are shown in the tables.

## RESULTS AND DISCUSSION

Table I shows the maximum values of the modulus of elasticity (MOE) of wood joints bonded with a PF resin prepared in absence of methanol without methylal and of those with 10% and 20% of methylal added. The improvement in MOE



**Figure 1** Colloidal particle size distribution of a methanol-free PF resin with and without the addition of 10% methylal.

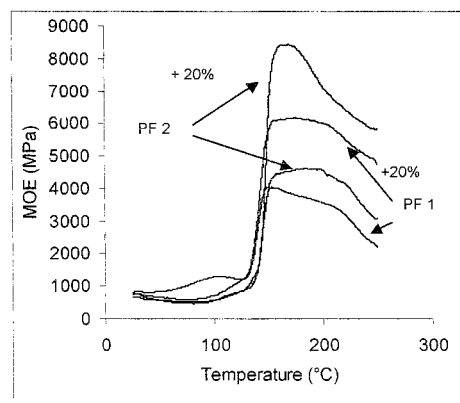
**TABLE II**  
Characteristics of Resins PF1 (Fresh) and PF2 (Aged) and Their Colloidal Particle Size Distribution with and without Methylal

	Methylal (%)	PF1	PF2
Viscosity at 20°C (mPa s)	0	300	8000
Viscosity at 20°C (mPa s)	20	120	640
Water tolerance (%)	0	690	715
Water tolerance (%)	20	774	903
LALLS average peak size (nm)	0	291.2	100.5
LALLS average peak size (nm)	20	304.5	99.8

value was considerable (25%) when passing from 0% to 10% methylal. The presence of acetal also slightly lowers the temperature at which the maximum MOE value is attained. There was no significant improvement between the 10% and the 20% addition cases. This PF resin was made in the absence of methanol to eliminate methanol interference, which indicates that the main improvement mechanisms for PF resins prepared in the absence of methanol is, as for MUF resins, (i) the increased solubility of the normally less soluble or insoluble higher molecular weight oligomer fraction in the liquid resin, which is perhaps the most important effect, (ii) the disruption of the molecular clustering of the resin colloidal particles, and/or (iii) the structural effects of the acetal, of an unknown nature, that have already been observed for MUF resins.<sup>3</sup>

However, the colloidal particle size distribution obtained by low angle laser light scattering (LALLS) analysis is comparable for the two resins, as shown in Figure 1. This indicates that for PF resins, even in the absence of methanol, and in contrast to MUF resins, disruption of the molecular clustering of the resin colloidal particles does not occur with the addition of acetals. This means that case (ii) above does not contribute to the improvement of performance of the resin.

Two resins containing methanol and prepared according to a standard PF formulation were then used for further LALLS analysis of the colloidal particle size distribution. The characteristic viscosity and water tolerance of the resins



**Figure 2** Variation of the average MOE of a fresh (PF1) and aged (PF2) phenolic resin containing methanol with and without the addition of 20% methylal.

**TABLE III**  
**Results of Wood Particleboard Bonded with PF1 Resin**  
**with and without Methylal Addition**

	PF Control	PF + 10% Methylal	PF + 20% Methylal
IB strength, dry (MPa)	0.27 ± 0.04	0.54 ± 0.15	0.52 ± 0.05
Board density (kg/m <sup>3</sup> )	694	716	708
IB strength, after 2 h boil (MPa)	0.07 ± 0.03	0.12 ± 0.03	0.13 ± 0.03
Board density (kg/m <sup>3</sup> )	710	717	689

before and after addition of methylal are shown in Table II. The increase in water tolerance observed is symptomatic of a solvent that improves solubility of the less soluble, higher molecular weight oligomer fraction in the liquid resin. This indicates that effect (i) observed for MUF resins is also operational for PF resins and contributes to the improvement in their performance. However, even in this case, as for the resins prepared without methanol, the differences in colloidal particles size distribution are insignificant. The two resins used were a freshly prepared one and an identical one aged at ambient temperature for several months. The results obtained are also shown in Table II. These indicate that, upon addition of either acetals, methanol, or both to PF resins, disruption of the molecular clustering of the resin colloidal particles does not appear to occur. This means that case (ii) above does not contribute to the improvement in performance of the resin in standard PF resins, which contain some methanol.

The two resins prepared with methanol, one freshly prepared and the same resin aged at ambient temperature for several months, were tested by TMA with and without the addition of 20% methylal. The results in Figure 2 show that, in both cases, the addition of 20% methylal considerably increases the maximum value of the MOE obtained for the two resins. The resin PF1 is the freshly prepared one and PF2 the aged one. For PF1 the improvement is 87%, and for PF2 it is 53%. Because TMA results sometimes exaggerate the differences among formulations, to determine to what extent the addition of an acetal really increases performance, wood particleboard was prepared and tested using the same two PF adhesives (Table III). The results in Table III indicate that, while the addition of 10% methylal already increases dry IB strength of the panel by 100%, no further improvement is

obtained with a 20% addition. PF resins are used as adhesives for exterior grade products; hence it is the IB strength after 2 h in boiling water that is the most important evaluation parameter. In Table III, this can be observed. The IB strength after 2 h boiling in water improved by 70% upon addition of 10% methylal and by 85% upon addition of 20% methylal. However, the wet IB strength difference between a 10% and a 20% addition is not significant (compare the values in Table III), and therefore there seems to be no advantage in using the higher percentage of acetal.

The results shown indicate that the improvement in performance of the PF resin on addition of an acetal such as methylal is only due to some of the mechanisms noted in MUF resin, and the others are inactive. In PF resins, the two effects that explain performance improvement are (i) the increased solubility of the less soluble, higher molecular weight oligomer fraction in the liquid resin and (ii) the structural effect of the acetal.<sup>3</sup> The disruption of the molecular clustering of the resin colloidal particles, an effect very important in MUF resins, appears to have no bearing on PF resins.

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