NOTE

Low-Volatility Acetals To Upgrade the Performance of Melamine–Urea–Formaldehyde Wood Adhesive Resins

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ABSTRACT: 1,1,2,2-Tetramethoxyethane (TME), a high boiling point acetal derived from glyoxol, lhas been shown to upgrade the performance of melamine-urea-formaldehyde (MUF) and some UF resins used for wood adhesives. This affords the possibility of decreasing the percentage of resin used in the preparation of wood panels without volatilizing the TME acetal used.

Key words: acetals; resins; adhesives; performance improvement

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 for this application being melamine resins, particularly melamine–urea–formaldehyde (MUF) resins. Recently, acetals such as methylal and ethylal have been used as novel low-cost additives capable of reducing, by one-fourth to one-third, the consumption of traditional wood adhesives, particularly MUF resins, in the wood-panel-product industry.[2] Moreover, they are capable of increasing, at resin load parity, the internal-bond (IB) strength performance of panels by 25–50% with existing commercial adhesives, without any modification to the resin formulations, in principle.[2] However, the lower molecular weight acetals that have been used, methylal and ethylal, have relatively low evaporation temperatures of 42 and 88°C, respectively. Laboratory trials in which an adhesive, dosed with the acetals, was applied to wood particles at ambient temperature yielded excellent results. However, the application of methylal to wood chips in a full-scale plant trial yielded only a relatively mild improvement in the thickness swelling of the board.[3] This was due to the wood particles reaching a temperature of 45–65°C in the industrial glue blenders.[3] The use of higher boiling point, and more expensive, ethylal should solve, at least partially, such a problem. Acetals with much higher boiling points do exist. One of these acetals, which also presents the same improvement effect on the performance of MUF and urea–formaldehyde (UF) adhesives, could completely eliminate the aforementioned problem at the industrial level.

1,1,2,2-Tetramethoxyethane (TME) is a diacetal derived from glyoxal

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$$CH_3OCHOCH_3$$
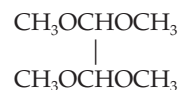
with a boiling point of 165°C. This article concerns identifying the improvement of the performance of MUF resins when this acetal is used and the extent of this effect.

EXPERIMENTAL

MUF resins were prepared according to procedures already reported.[4] Two resins were prepared, an MUF resin with an (M + U)/F molar ratio of 1:1.2 and a weight ratio of M/U = 30:70 and an MUF resin with an (M + U)/F molar ratio of 1:1.2 and a weight ratio of M/U = 47:53 (where M is melamine, U is urea, and F is formaldehyde). The UF resins were commercial ones from Dynea (Krems, Austria). One was a pure UF resin with a U/F molar ratio of 1:1.2, and the second one, containing 4 wt % melamine on the resin solids, coreacted with the UF resin. All these resins were used with the addition of 3 wt % ammonium sulfate hardener to the MUF resin solids, the ammonium sulfate being applied as a 30% solution in water. In addition, 10% and 20 wt % TME was added to the resin solids.

The MUF resin glue mixes were tested on beech wood by thermomechanical analysis (TMA) at a constant heating rate of 10°C/min according to procedures already described.[2,4] The UF resins were tested with laboratory wood particleboard as follows. One-layer laboratory particleboard samples (350 mm × 310 mm × 14 mm), which were 70 wt %
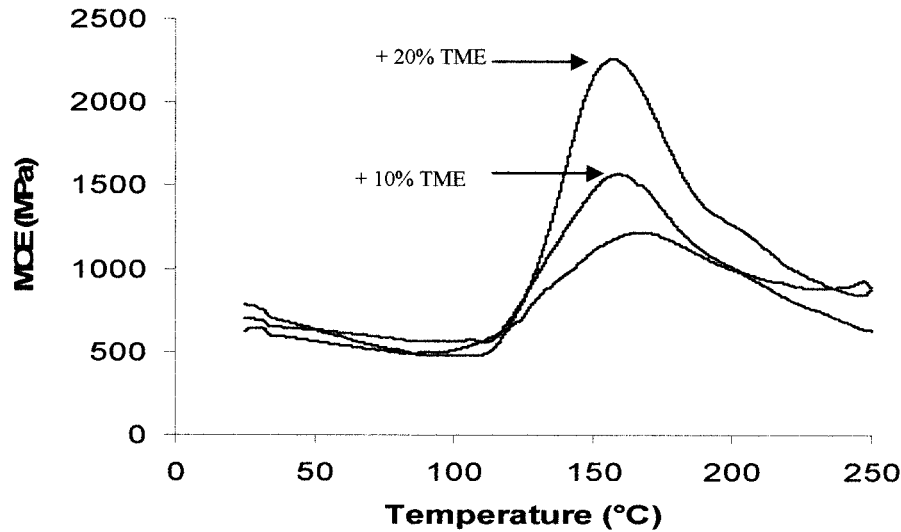
Figure 1 MOE variation as a function of temperature obtained by TMA of beech joints during the hardening of an MUF resin, with an (M + U)/F molar ratio of 1:1.2 and an M/U weight ratio of 30:70, containing 3% ammonium sulfate hardener on resin solids, without TME and with 10 or 20 wt % TME added on resin solids.

beech and 30 wt % spruce, were produced with an industrial wood-chip furnish through the addition of 10% total MUF or UF resin solid to the dry wood particles. The panels were pressed at a maximum pressure of 28 kg/cm² (2 min from platen contact to the high pressure and maintenance of the high pressure), and this was followed by a descending pressing cycle of 1 min at 12–14 kg/cm² and 2 min at 5–7 kg/cm², at 190–195°C, for a total pressing time of 5 min. The resinated chip moisture content was 12%. All the panels had densities of 0.695–0.704 g/cm³. The panels, after light surface sanding, were tested exclusively for the dry IB strength.

Low-angle laser light scattering (LALLS) measurements of the granulometry of the MUF resins without (control) and with 5 or 10% additions of TME to the liquid resin were carried out with a Malvern 18-mm-diameter laser (Switzerland) and a helium–neon source, with the detector positioned at 90° to the light beam and the area scanned being 50 μm. The different resin mixes were dispersed in water in a 1:1 (v/v) ratio. The translational diffusion coefficient was obtained with the Stokes–Enstein equation, $d(H) = KT/(3\eta\pi D)$, where $d(H)$ is the hydrodynamic radius, D is the diffusion coefficient, K is the Bolt-
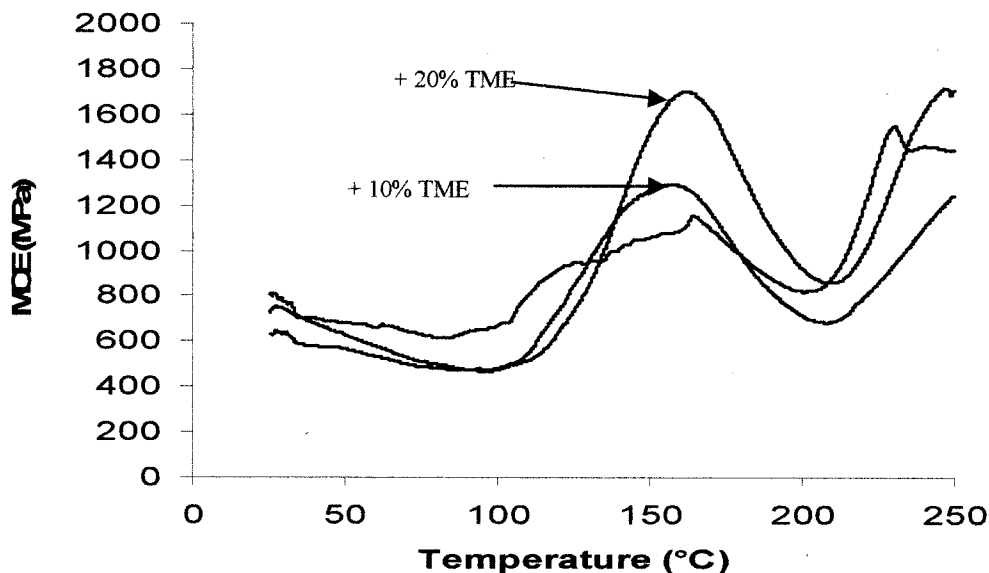

Figure 2 MOE variation as a function of temperature obtained by TMA of beech joints during the hardening of an MUF resin with an (M + U)/F molar ratio of 1:1.2 and an M/U weight ratio of 47:53, containing 3% ammonium sulfate hardener on resin solids, without TME and with 10 or 20 wt % TME added on resin solids.
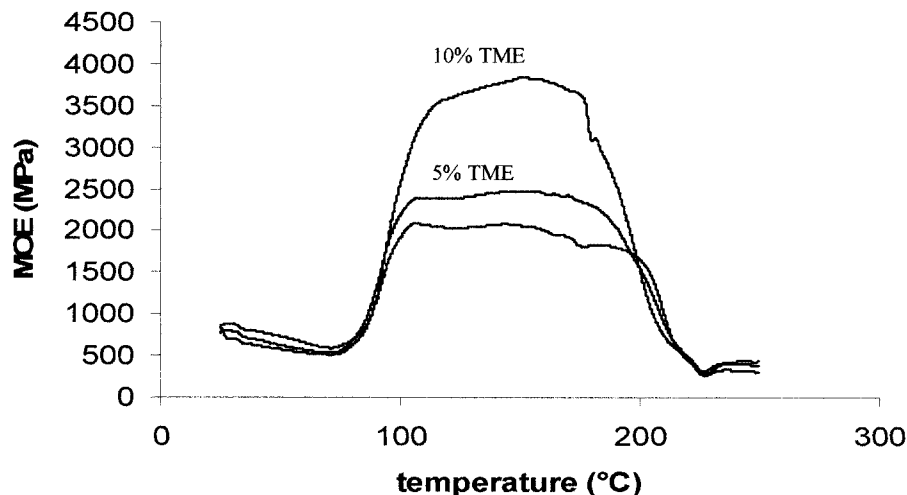
Figure 3 MOE variation as a function of temperature obtained by TMA of beech joints during the hardening of a commercial UF resin with a U/F molar ratio of 1:1.2, containing 3% ammonium sulfate hardener on resin solids, without TME and with 10 or 20 wt % TME added on resin solids.

zmann constant, T is the absolute temperature, and η is the viscosity.

DISCUSSION

The comparative curves of the modulus of elasticity (MOE) as a function of the time and temperature, obtained by TMA, for two MUF resins containing the diacetal in different proportions are shown in Figures 1 and 2. These indicate that high-boiling-point TME was also capable of markedly improving the performance of MUF resins of higher and lower melamine contents. Figure 1 shows, for an MUF resin with an (M + U)/F molar ratio of 1:1.2 and an M/U weight ratio of 30:70, improvements in the maximum value of MOE of 28 and 84% with the addition of 10 and 20% TME to the resin solids, respectively. Figure 2 shows, for a resin with a higher melamine content, an equivalent trend, with the maximum value of MOE increasing 13 and 48% with the addition of 10 and 20% TME to the resin solids, respectively. The same trend can be observed in Figure 3 for a commercial UF resin with a U/F molar ratio of 1:1.2. The maximum value of MOE improved 15 and 85% with the addition of 5 and 20% TME to the resin solids, respectively.

Tables I and II provide the IB strength results obtained

with laboratory particleboard bonded to a UF resin and a UF resin reinforced with 4 wt % melamine with respect to the resin solid weight. TME was added according to the combinations shown in Table I. The wood particles to which TME was added were heated to 50°C before the addition of the glue mix and were maintained at this temperature during the application of the glue mix. The results indicated that the IB strength of the boards increased 13 and 14%, respectively, when 10% diacetal (with respect to the resin solids) was added to the two resins. These values were in the same range but somewhat lower than the differences in the MOE values observed with TMA. This difference was expected because it is known that comparative TMA tends to exaggerate differences in performance.[2] These results confirm that TME can withstand higher wood particle temperatures in a plant and that the effect can be maintained at an industrial level when this diacetal is used.

The influence of acetals on MUF resins has been proved[4] to be due not only to the increased solubility in water afforded by the acetal cosolvents of both the unreacted melamine and the higher molecular weight and lower methylolated oligomer fraction (normally with a very much lower solubility), this leading to a preferentially homogeneous and, therefore, more effective reaction rather than heterogeneous reactions.[4] It has also been shown to be due to the effect that acetals have on the size distribution of the

TABLE I
Glue Mixes of Pure UF Resins and UF Resins Fortified with 4% Melamine with and Without the Addition of TME

	Glue mix			
	1	2	3	4
Dry wood	1000	1000	1000	1000
UF resin + 4% melamine	100	100		
UF resin			100	100
TME		10		10

TABLE II
IB Strengths of Wood Particleboard Bonded with Pure UF Resins and UF Resins Fortified with 4% Melamine with and Without the Addition of TME

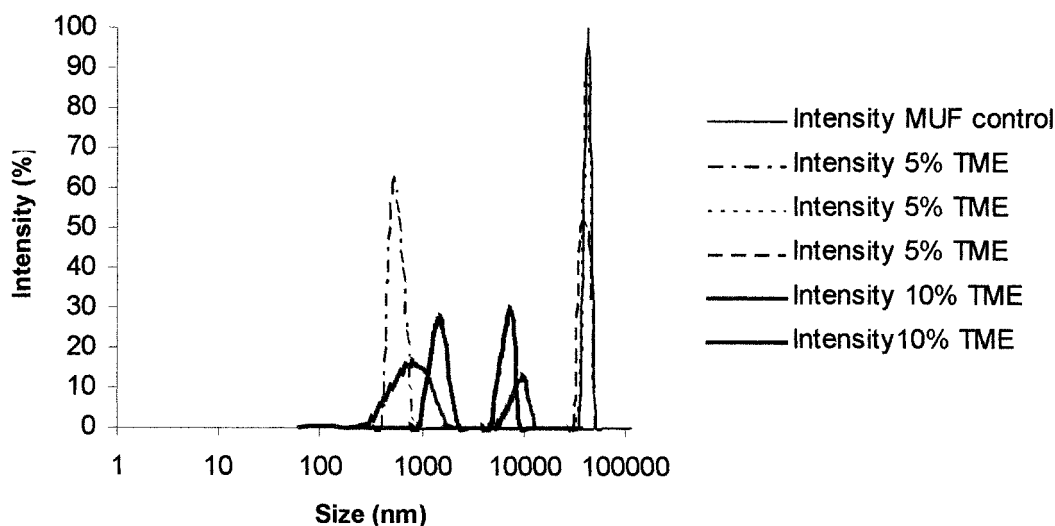| Glue mix and type	IB strength (MPa)
1. UF + 4% melamine control	0.858
2. UF + 4% melamine + 10% TME	0.966
3. UF control	1.077
4. UF + 10% TME	1.227

Figure 4 Colloidal particle diameter distributions from LALLS obtained for an MUF adhesive resin with an (M + U)/F molar ratio of 1.1.2 and an M/U weight ratio of 30:70. We can observe the following: at 70,000 nm, the MUF resin alone and two cases of the same MUF resin with 5% TME; at 800 nm, the only case of MUF with 5% TME showing a reduction of the colloidal particle size with a small addition of TME; at 1060 and 9000 nm, one case of an MUF resin with 10% TME; and at 950 and 9500 nm, a second case of an MUF resin with 10% TME.

resin colloidal particles, the presence of acetals such as methylals markedly decreasing the average colloidal particle diameter of the resin.[4,5] This latter effect appears to be due to the disruption of the molecular clustering of the MUF resin colloidal particles,[4,5] but rearrangements in the size of the colloidal particles due to the decrease in the surface tension of the system, which has also been reported, cannot be excluded.

To establish if at least the most important of these mechanisms was present for TME, we compared the size distribution of the colloidal particles constituting the resin once TME was added. This was done with LALLS. The results shown in Figure 4 indicate that the addition of TME reduced the size of the colloidal particles constituting the resin, confirming that this important mechanism of action of acetals was equally important for TME. Figure 4 also indicates that the addition of TME reduced the size of the colloidal particles constituting the resin, but the reduction was different each time. Thus, from approximately 70,000 nm of the pure resin (control), the addition of 5% TME yielded only a very slight decrease in the size

distribution or a decrease to 800 nm (the taller peak at 800 nm). This meant that the addition of only 5% TME did not always reduce the resin colloidal particle size and that some other factor played a role when it did. The addition of 10% TME instead always reduced the colloidal particle size distribution. Figure 4 shows that two peaks were always present, one at 1060 and 9000 nm and the other at 950 and 9500 nm.

References

1. Pizzi, A. Wood Adhesives Chemistry and Technology; Marcel Dekker: New York, 1983.
2. Pizzi, A.; Beaujean, M.; Zhao, C.; Properzi, M.; Huang, M. Z. J Appl Polym Sci 2001, 84, 2561
3. Zanetti, M.; Beaujean, M. Unpublished data on industrial trials, ENSTIB, Univ. of Nancy 1, 2001.
4. Zanetti, M.; Pizzi, A.; Beaujean, M.; Pasch, H.; Rode, K.; Dalet, P. J Appl Polym Sci 2002, 86, 1855
5. Zanetti, M.; Pizzi, A. J Appl Polym Sci, to appear.