Low Addition of Melamine Salts for Improved Melamine–Urea–Formaldehyde Adhesive Water Resistance

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ABSTRACT: The addition of melamine acetate salts to an adhesive glue mix can allow the use of melamine–urea–formaldehyde (MUF) resins of lower melamine contents (rather than just urea–formaldehyde resins) and lower total amounts of melamine. Performances can be obtained that are characteristic of the top-of-the-line, generally higher melamine content MUF adhesive resins for the preparation of wood particleboard panels. Improvements in the panel internal-bond strength of greater than 30% can be obtained by the addition of melamine acetate salts to top-of-the-line MUF resins. The approach to the concept of increased melamine solubility with a melamine salt is compatible with the approach of increasing melamine solubility with solvents such as acetals (e.g., methylal). However, the synergy advantage of using the two approaches jointly is not very marked. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 287–292, 2003

Key words: resins; strength; adhesives

INTRODUCTION

The main drawback of urea–formaldehyde (UF) resins is their sensitivity to water attack and, therefore, their lack of exterior durability.[1,2] Attempts to improve the water resistance of UF adhesives have led to the development of melamine–urea–formaldehyde (MUF) copolymer resins, in which melamine, urea, and formaldehyde need to be prereacted in a reaction vessel to prepare the MUF resin, a resin that is generally of greater manufacturing sophistication than UF resin systems. Such MUF resins have led to considerable improvements in the water resistance of UF adhesives. However, the levels of urea substitution by melamine needed to obtain an MUF resin of good performance are rather high (typically between 30% mass substitution for the cheaper resins and 50% mass substitution for the best performing, top-of-the-line MUF resins). This is relatively serious, as the cost of melamine is rather high.

Recently, a system for improving the waterproofing of UF plywood adhesives by the addition to the glue mix, as hardeners, of small amounts of melamine acid salts of lower ambient solubility but greater solubility at higher temperatures has been reported.[3–5] Melamine that copolymerized during UF hardening, directly during the hot-pressing cycle, yielded at an M : U mass ratio of 10 : 90 the equivalent waterproofing performance of prepolymerized MUF resins of an M : U mass ratio of 30–40 : 70–60.[3–5] This was at least

shown to be valid for plywood applications, in which the particular construction of the panel helps in such a performance.[3–5] One of the known reasons for this improvement is the elimination of one of the more evident problems in MUF resin preparation: the waste of melamine effectiveness due to its prereaction with formaldehyde before grafting onto the UF polymer.[3–5] In the preparation of precopolymerized MUF resins and, therefore, of today's normal, commercial MUF resins, during the high-temperature preparation reaction, the melamine also reacts with formaldehyde to form short melamine–formaldehyde (MF) chains, which are then bound to the more abundant UF chains. The hardening of MUF resins has been proven to occur almost exclusively by crosslinking through —CH$_2$— bridges connecting two melamines[6,7] because, on account of its much lower reactivity, urea is not greatly involved. The use of melamine salts at ambient temperature in the glue mix instead ensures that only single melamine molecules are singly and separately grafted onto the UF resin chain:

$$—U—CH_2—M—CH_2—M—CH_2—M$$
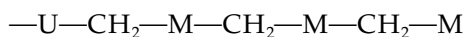
$$\text{against } —U—CH_2—M$$

For the crosslinking of MUF resins, only a very small number of melamine molecules for each UF chain are needed. The traditional MUF preparation systems, with the addition of melamine to a UF reaction mixture rich in free formaldehyde, do form MF oligomers first. Only when the great majority of the free formaldehyde has reacted to form these MF oligomers do these latter ones react and link to the UF resin by reacting with the methylol groups on the UF resin.

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This causes a standard MUF resin to have several melamine molecules linked as MF chains in the MUF resin structure. This does not improve the bond strength because either (1) only one of the melamines in the chain will react to form crosslinks with a melamine in another chain, the rest of the melamine not participating much, if at all, in the final crosslinking, or (2) even if all the melamines of the MF chain react in the same space zone of the network, the highly localized position on the vicinal sites in the network with a high density of crosslinks might well render the resin far too rigid and far too brittle (which is the case for most melamine-based resins). It is then clear that at least two-thirds of the melamine presently used in MUF resins is actually wasted and does not contribute much to the final results, other than in a damaging manner, this being unavoidable as a result of the system of preparation used.

This reason is only one of the causes of the effectiveness of the addition of melamine salts to UF resins, the other being the increased solubility at higher temperatures of the salt.[4,8–10]

The formation of an MUF adhesive by the addition, in the glue mix, of a melamine salt to a UF resin, although it works rather well, suffers one drawback.[3–5] The performance improves only up to additions of 15% melamine in the UF adhesive. The addition to a UF glue mix of 15% melamine as a melamine salt yields resins with M : U weight ratios of 15 : 85. These resins have equal performances of reactor-prepolymerized MUF resins with M : U weight ratios between 30 : 70 and 35 : 65 and, therefore, much higher melamine contents. This means that larger additions to UF resins of melamine in the form of melamine salt would not allow us to improve the resin performance to the same level as that of the top-performing MUF resins of higher melamine contents (M : U = 40 : 60 and 50 : 50 w/w).

This study addressed this problem first by applying the melamine salt addition concept to MUF resins of low prereacted melamine contents rather than to just UF resins. This was done to determine if the system could allow the use of lower melamine contents also for obtaining performances characteristic of top-of-the-line, generally higher melamine content MUF resins. Second, the concept of increased melamine solubility was used, but with an approach different from that of just using a melamine salt. Third, these concepts were tested in the preparation of wood particleboard panels in which the construction of the panel protects much less than in plywood the glue line from water and weather attack.

EXPERIMENTAL

Preparation of MUF resins

MUF resins with (M+U) : F molar ratios of 1 : 1.9 and 1 : 1.2, M : U weight ratios of 47 : 53, 40 : 60, 30 : 70, and 20 : 80, and a UF molar ratio of 1 : 1.5 were prepared according to known sequential manufacturing procedures.[2] All these resins were prepared according to the example for a resin with a 1 : 1.5 molar ratio (M : U = 30 : 70), which follows. To 269.6 parts of formurea (a precondensate that was 23% urea, 54% formaldehyde, and 23% water) were added 57.9 parts of urea and 71.1 parts of water. The pH was set at 10–10.4, and the temperature was brought to 92–93°C under mechanical stirring. The pH was then lowered to 7.8, and the reaction was continued at the same temperature, with the pH allowed to fall by itself over a period of 1.5 h to 6.5–7 (the pH never could fall below 5). For the pH to be brought to 9.5 or higher, a 22% NaOH solution was added, and then 71.1 parts of melamine were premixed with 37.2 parts of water. Two parts of dimethylformamide were then added to the reaction mixture, which was kept at 93°C. The water tolerance was checked every 10 min, whereas the pH was allowed to fall by itself. When the water tolerance reached 180–200% (the pH was ca. 7.2), 35.5 parts of urea were added, and the pH was again brought up to 9.5. The reaction was continued until the water tolerance was lower than 150% (the pH was 7.7 at this stage). The pH was then corrected to 10.0–10.2 by the addition of a solution of NaOH, and the resin was cooled and stored.

Preparation of melamine salt (melamine acetate)

The preparation procedures for the preparation of melamine monoacetate of Cremonini and Pizzi,[4] modified according to Weinstabl et al.[10] and further modified according to Cremonini and Pizzi, were used for the preparation of melamine monoacetate.

Melamine (50 g) was suspended in 1 L of water and heated to 100°C under continuous mechanical stirring in a reactor equipped with a reflux condenser. Acetic acid was added in a stoichiometric amount to obtain melamine monoacetate over a period of 5 min, and the mixture was refluxed for 10 min before cooling to ambient temperature. The precipitate that formed on cooling was filtered but was not washed after we found that a purer and more stable salt was obtained through oven drying at 75°C for 72 h at ambient pressure; it was then cooled and stored. Neither during nor after this procedure was the salt dried *in vacuo*. The purity of the salt was checked by cross-polarity/magic-angle spinning (CP-MAS) ^{13}C-NMR: therefore, in Figures 1 and 2 are shown the spectra of impure and purified melamine monoacetate.

CP-MAS ^{13}C-NMR of salts

The pure melamine monoacetate could not be examined by liquid ^{13}C-NMR because it was insoluble at ambient temperature and dissociated in acetic acid and melamine at higher temperatures. The pure melamine monoacetate
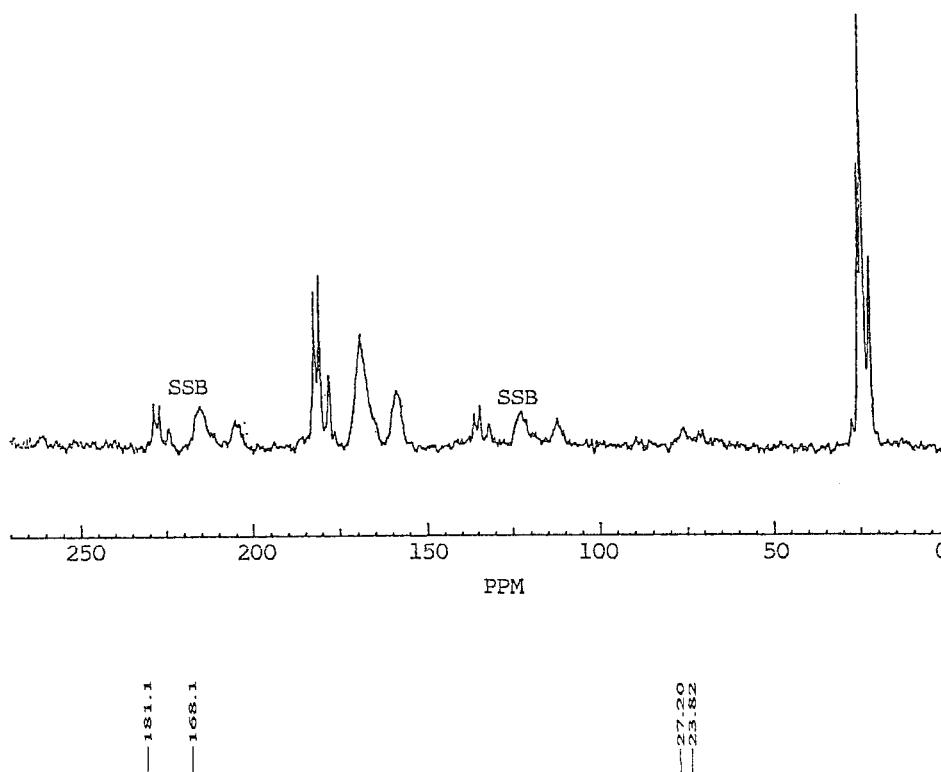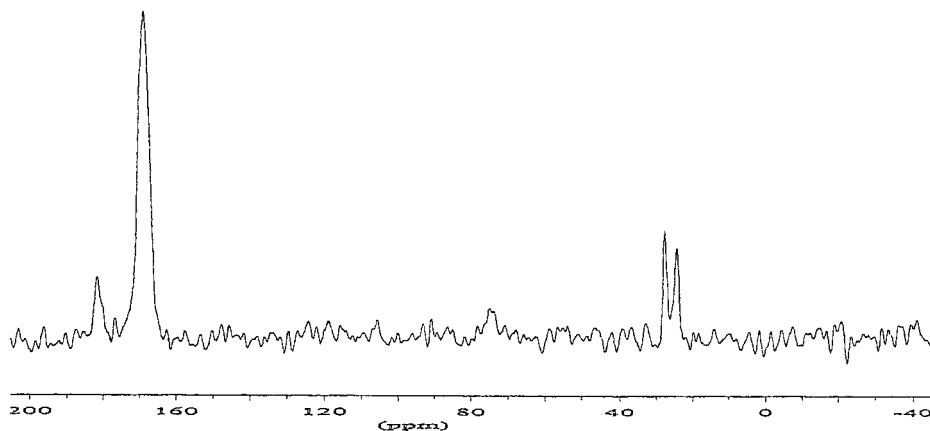
Figure 1 Solid-state CP-MAS ^{13}C-NMR of impure melamine monoacetate (the reaction of melamine and acetic acid in molar proportions of 1:1).

had to be examined by solid-state CP-MAS ^{13}C-NMR under the following conditions. Salt spectra were obtained with a Bruker MSL 300 FT-NMR spectrometer (Germany). The solid-state CP-MAS ^{13}C-NMR spectra of the solid melamine acetates were obtained at a frequency of 75.45 MHz and at a sample spin of 3.5 kHz. Chemical shifts were calculated relative to tetramethylsilane for NMR control. The acquisition time was 0.026 s, with the number of transients at about 1000. The spectra were accurate to 1 ppm. Typical spin–lattice relaxation times for the types of compounds analyzed and peak

interpretations for melamine and for UF resins were taken from the literature.[3,11–30]

Glue mixes and wood particleboard preparation and testing

The glue mixes were prepared by the addition, to an MUF resin, of enough melamine monoacetate to bring the total melamine content up to those of resins of a higher category. Therefore, to an MUF resin of M : U = 30 : 70, enough salt was added in the glue mix to

Figure 2 Solid-state CP-MAS ^{13}C-NMR of melamine monoacetate purified by evaporation at 75°C for 72 h (the reaction of melamine and acetic acid in molar proportions of 1:1).
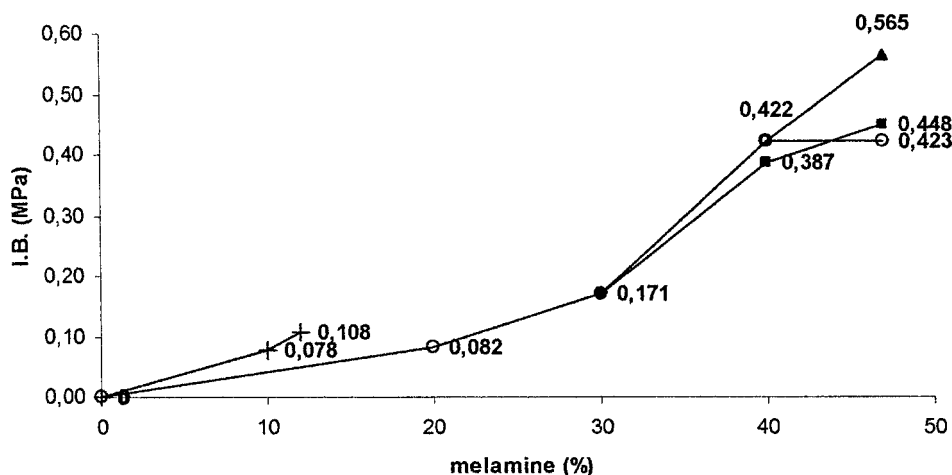
Figure 3 Wood particleboard IB strength after 2 h of boiling in water as a function of the melamine content (M : U weight ratio) for (○) prereacted MUF resins alone, (■) MUF (M : U = 30:70 w/w) with and without the addition of melamine acetate (to reach M : U = 40:60 and 47:53), (▲) MUF (M : U = 40:60 w/w) with the addition of melamine acetate (to reach M : U = 47:53), and (+) UF with the addition of melamine acetate.

obtain M : U ratios of 40 : 60 and 47 : 53. The melamine balance in these resins was 30 melamine coming from the original MUF and 10 and 17 coming from the ambient-temperature mixing of melamine monoacetate, the balance being urea in the MUF resin. As the amount of formaldehyde remained the same, that is, only the formaldehyde that originated from the original MUF resin, the (M+U) : F molar ratio decreased from the original 1 : 1.9 to 1 : 1.73 and 1 : 1.6 for the latter two glue mixes. Furthermore, to an MUF of M : U = 40:60, enough salt was added in the glue mix to obtain an M : U ratio of 47 : 53 (therefore, 40 melamine coming from the MUF resin and 7 from the melamine acetate added at ambient temperature), with the (M+U) : F molar ratio decreasing to 1 : 1.76. For the UF resin, 10 and 13% melamine in the form of melamine monoacetate was added.

As the melamine salt so obtained did not contain enough acid to function as a hardener when alone, as remarked previously,[4] 1.5% $(NH_4)_2SO_4$ (based on the total resin solid content), as a 20% solution in water, was added to the glue mix as a hardener.

Duplicate one-layer laboratory particleboard (350 mm × 310 mm × 14 mm) was then produced from industrial wood chips consisting of 70 wt % beech and 30 wt % spruce by the addition of 10% total MUF and salt resin solid content to the dry wood particles. The panels were pressed at a maximum pressure of 28 kg/cm^2 (2 min from platen contact to high pressure and maintenance of the high pressure), and this was followed by a descending pressing cycle of 1 min at 12–14 kg/cm^2 and 2 min at 5–7 kg/cm^2, 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/cm^3. The panels, after light surface sanding, were tested exclusively for internal-bond (IB) strength after 2 h of boiling and 16 h of drying at 105°C. The results are shown in Figures 3 and 4.

DISCUSSION

The first results of interest are obtained by the interpretation of the ^{13}C-NMR spectra in Figures 1 and 2 of the impure and pure melamine monoacetate, respectively. It is interesting to note the variations in the integrated areas of the peaks at 182 and 180 ppm (two forms of $CH_3\underline{C}OO^-$), 178 ppm ($CH_3\underline{C}OOH$), 168 ppm (triazine ring of melamine monoacetate), 165 ppm (triazine rings of melamine diacetate and triacetate), and 158 ppm (triazine rings of melamine acetates in the —C=NH form)[3,4] and of the peaks at 27 ppm (methyl carbon of free $\underline{C}H_3COO^-$), 25 ppm ($\underline{C}H_3COOH$ not ionized), and 23 ppm ($\underline{C}H_3COO^-$ M—C=NH_2^+). For the stoichiometrically reacted melamine/acetic acid used to form impure melamine monoacetate (Fig. 1), it is possible to see the 168 ppm peak of monoacetate salt, although the 165 ppm peak of the diacetates and triacetates is still present. The 158 ppm peak is also noticeable in Figure 1, indicating that the CH_3COO^- M—C=NH_2^+ is the favorite form of all the acetates (i.e., the equilibrium is shifted toward the ionized form of melamine).[3,4] Of the three types of methyl group signals present, the CH_3COOH signal (25 ppm) is the predominant one in Figure 1. Free CH_3COO^- and CH_3COO^- M—C=NH_2^+ are in the majority over the nonionized CH_3COOH for high stoichiometric proportions of acid added to melamine to form the salt, as determined previously.[4] It is also evident that for the impure compound monoacetate is a spurious label, as in reality both monoacetates and diacetates are always present (it is not possible to distinguish from the ^{13}C-NMR solid-phase spectra between real diacetate and triacetate).

The spectrum of the monoacetate after a drying time extended to 72 h at 75°C is shown in Figure 2. It is quite evident that only one form of CH_3COO^-, that forming the CH_3COO^- M—C=NH_2^+ salt, is present.
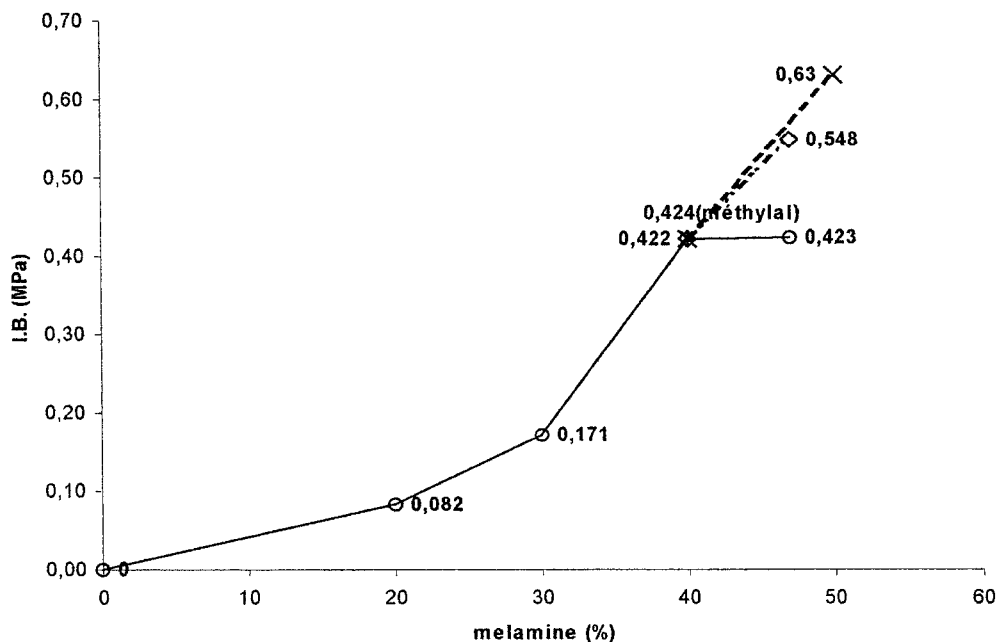
Figure 4 Wood particleboard IB strength after 2 h of boiling in water as a function of the melamine content (M : U weight ratio) for (○) prereacted MUF resins alone; (*) MUF (M : U = 40:60) and 10% methylal only; (×) MUF (M : U = 40:60), melamine acetate (M+M$_{ac}$:U = 40+10:50), and 10% methylal; and (◇) MUF (M : U = 40:60), melamine (M+M : U = 40+7:53), and 10% methylal.

Therefore, only the peaks at 182 ppm, a very small peak at 180 ppm of free CH$_3$$\underline{C}OO^-$, the major peak of monosubstituted triazine at 168 ppm, a very low 27 ppm peak of free $\underline{C}$H$_3$COO$^-$ confirming the very small amount of this species observed from the 180 ppm band, and the 23 ppm band of the $\underline{C}$H$_3$COO$^-$ M—C≡NH$_2^+$ salt exist in Figure 2. Therefore, the peaks of diacetates and triacetates, as in the impure compound in Figure 1, are not found anymore in the pure compound in Figure 2. Therefore, not only are just traces of free acetic acid in any form found in the sample, but an almost pure monoacetate of melamine is also left after the greatest part of the excess of acetic acid is driven off by a long enough period of drying. The very low level of residual acetic acid results in a much longer pot life of an MUF glue mix but introduces the need to use a standard MUF hardener such as an ammonium salt in the system to obtain fast enough curing at higher temperatures.

In Figure 3 are reported the results of the IB strength, after 2 h in boiling water, of particleboard made with premanufactured MUF resins with M : U weight ratios of 20 : 80, 30 : 70, 40 : 60, and 47 : 53. These are compared to the same MUF resins to which melamine monoacetate (M$_{ac}$) is added in different amounts to obtain MUF glue mixes with (M+M$_{ac}$) : U = (30+10) : 60, (30+17) : 53, and (40+7) : 53. The results show that at a parity of panel density, there appears to be only a small difference between an MUF of M : U = 40 : 60 and one of (M+M$_{ac}$) : U = (30+10) : 60, with the IB of the former at 0.42 MPa being still a bit higher than value of the 0.39 MPa obtained by the

latter. The situation, however, changes more markedly when we aim to obtain a performance similar to that of the MUF resin with M : U = 47 : 53. If we use an approach of (M+M$_{ac}$) : U = (30+17) : 53, the IB strength that results after 2 h in boiling water is higher at 0.45 MPa than the value of 0.42 MPa obtained with the pre-engineered MUF resin. If we instead use the approach of (M+M$_{ac}$) : U = (40+7) : 53, the improvement obtained is very marked, yielding panels with an average IB strength of 0.57 MPa, which is much more than 30% higher than the value of 0.42 MPa obtained with the pre-engineered MUF resin. These results are all the more remarkable if we consider that, the lower the relative amount is of formaldehyde in the (M : U) : F molar ratio of an MUF resin, the lower the IB strength is of a panel. Results that are much better or just better than the premanufactured MUF 47 : 53 resin are obtained for (M+M$_{ac}$) : U = (40+7) : 53 when the molar ratio has decreased from 1 : 1.9 to 1 : 1.76. This is a consequence of the addition of melamine acetate and (M+M$_{ac}$) : U = (30+17) : 53 at a molar ratio of only 1 : 1.6. In Figure 3, it is also shown that the addition of 13% melamine as melamine monoacetate to a UF resin improves the wet IB strength of the particleboard to the same extent as that which would be given by a premanufactured MUF with an M : U weight ratio of 25 : 75. Whenever an increased IB strength result is obtained by M$_{ac}$ salt addition, the choice exists to have panels of greater performance [e.g., in Fig. 3, the resin with (M+M$_{ac}$) : U = (40+7) : 53 performs almost the same as a pure and very expensive MF resin would] or

to reduce the amount of resin but retain a performance equal to that of premanufactured resins.

It must be clearly noted here that the gel times of the resins are slow and are not accelerated at all by any great proportion of acetic acid. Controls with only acetic acid accelerate the gel time, whereas resins in which pure melamine monoacetate has been used need additional hardeners such as 1.5% $(NH_4)_2SO_4$ (see the Experimental section) to be able to gel fast enough, as has been clearly demonstrated before.[3,4] Furthermore, panels in which MUF resins harden with acetic acid have already clearly been shown to give very poor results, worse than an MUF control.[3,4] Even more indicative is the already well proven fact that the addition of melamine only or of melamine and acetic acid in the glue mix yields much poorer bonded joint results than the addition of melamine monoacetate.[31]

A different approach to improving MUF performance results, also based, as in the case of the melamine salts, on the increased solubility of melamine, can also be taken. Recently, the use of methylal, ethylal, and other acetals to improve the solubility of melamine and higher molecular weights MUF fractions was described.[32,33] In Figure 4 are shown the results of adding to an MUF with an M : U weight ratio of 40:60 an amount of melamine so that $(M+M_{ac}):U = (40+7):53$ is reached by either (1) the addition of melamine acetate in methylal or (2) the addition of just pure melamine in methylal. The results show that the biggest contribution to the improvement of strength is the increased solubility of melamine and its greater availability for reaction in the homogeneous phase. Therefore, the addition of melamine in methylal brings the IB strength after 2 h of boiling to 0.55 MPa (Fig. 4) from the value of 0.42 MPa of the control with MUF alone. The addition of melamine acetate alone yields instead 0.57 MPa (Fig. 3). The addition of both melamine acetate and methylal yields 0.59 MPa [Fig. 4; 0.63 MPa is not directly comparable because it corresponds to a higher amount of melamine acetate to yield $(M+M_{ac}):U = (40+10):50$]. Synergy between the two approaches exists, but the advantage that can be obtained by their combined use is not very marked.

CONCLUSIONS

The addition of melamine acetate salts can allow the use of MUF resins of lower melamine contents, rather than just UF resins, and of lower total amounts of melamine also for obtaining performances characteristic of top-of-the-line, generally higher melamine content MUF resins. This is valid also for the preparation of wood particleboard panels in which the construction of the panel does not protect the glue line from water and weather attack.

The approach to the concept of increased melamine solubility with a melamine salt has been shown to be compatible with the approach of increasing melamine solubility by solubilization with acetals such as methylal, although the synergy advantage of using the two approaches jointly is not very marked.

References

1. Dunky, M. In Polymer Materials Encyclopedia; Salamone, J. C., Ed.; CRC: Boca Raton, FL, 1996; Vol. 11.
2. Pizzi, A. Advanced Wood Adhesives Technology; Marcel Dekker: New York, 1994.
3. Prestifilippo, M.; Pizzi, A.; Norback, H.; Lavisci, P. Holz Roh Werkst 1996, 54, 393.
4. Cremonini, C.; Pizzi, A. Holzforsch Holzverwert 1997, 49(1), 11.
5. Cremonini, C.; Pizzi, A. Holz Roh Werkst 1999, 57, 318.
6. Higuchi, M.; Roh, J. K.; Tajima, T.; Irita, H.; Honda, T.; Sakata, I. Adhesives and Bonded Wood Symposium; Proceedings 4735; Forest Products Society: Lake Tahoe, CA, 1994; p 429.
7. Pizzi, A.; Panamgama, L. A. J Appl Polym Sci 1995, 58, 277.
8. Pizzi, A. Wood Adhesives 2000 Symposium Proceedings; Forest Products Society: Lake Tahoe, CA, 2000, p 219.
9. Pizzi, A. In Handbook of Adhesive Technology, 2nd ed.; Pizzi, A.; Mittal, K. L., Eds.; Marcel Dekker: New York, 2002; Chapter 32.
10. Weinstabl, A.; Binder, W. H.; Gruber, H.; Kantner, W. J Appl Polym Sci 2001, 81, 1654.
11. Breitmaier, E.; Voelter, W. Carbon-13 NMR Spectroscopy, 3rd ed.; VCH: Weinheim, 1987.
12. Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. Tables of Spectral Data for Structure Determination of Organic Compounds, 2nd ed.; Springer: Berlin, 1989.
13. Gu, J.; Higuchi, M.; Morita, M.; Hse, C.-Y. Mokuzai Gakkaishi 1995, 41, 1115.
14. Pizzi, A.; Lipschitz, L.; Valenzuela, J. Holzforschung 1994, 48, 254.
15. Tomita, B.; Hatono, S. J Polym Sci Polym Chem Ed 1978, 16, 2509.
16. Maciel, G. E.; Szevereyi, N. M.; Early, T. A.; Myers, G. E. Macromolecules 1983, 16, 598.
17. Ferg, E. E.; Pizzi, A.; Levendis, D. J Appl Polym Sci 1994, 50, 907.
18. Rammon, R. J Adhes 1986, 19, 115.
19. Soulard, C.; Kamoun, C.; Pizzi, A. J Appl Polym Sci 1999, 72, 277.
20. Ebdon, J. R.; Heaton, P. E. Polymer 1977, 18, 971.
21. Tomita, B.; Ono, H. J Polym Sci Polym Chem Ed 1979, 17, 3205.
22. Panamgama, L. A.; Pizzi, A. J Appl Polym Sci 1995, 55, 1007.
23. Tomita, B.; Hse, C.-Y. Mokuzai Gakkaishi 1993, 39, 1276.
24. Tomita, B.; Ohyama, M.; Itoh, A.; Doi, K.; Hse, C.-Y. Mokuzai Gakkaishi 1994, 40, 170.
25. Yoshida, Y.; Tomita, B.; Hse, C.-Y. Mokuzai Gakkaishi 1995, 41, 547.
26. Yoshida, Y.; Tomita, B.; Hse, C.-Y. Mokuzai Gakkaishi 1995, 41, 555.
27. Yoshida, Y.; Tomita, B.; Hse, C.-Y. Mokuzai Gakkaishi 1995, 41, 652.
28. Tomita, B.; Hse, C.-Y. J Polym Sci Part A: Polym Chem 1992, 30, 1615.
29. Mercer, T. A.; Pizzi, A. J Appl Polym Sci 1996, 61, 1687.
30. Mercer, T. A.; Pizzi, A. J Appl Polym Sci 1996, 61, 1697.
31. Kamoun, C.; Pizzi, A. Holz Roh Werkst 1998, 56, 86.
32. Pizzi, A.; Beaujean, M.; Zhao, C.; Properzi, M.; Huang, Z. J Appl Polym Sci, 2002, 84, 2561.
33. Zanetti, M.; Pizzi, A.; Beaujean, M.; Pasch, H.; Rode, K.; Dalet, P. J Appl Polym Sci, 2002, 86, 1855.