NOTE

Structure Effects of Additives in Performance Improvement of Aminoplastic Adhesive Resins

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INTRODUCTION

The wood panels industry relies on polycondensation resins, among them urea formaldehyde (UF) and melamine–urea formaldehyde (MUF) resins, as adhesives. Performance standards for these resins as wood adhesives have been established throughout the world.[1] Recently, several different approaches have been proposed to improve the performance of UF and MUF resins, the latter of which have much lower proportions of melamine. Most of these approaches are based on the use of additives during resin application. The techniques include: (1) The use of acetals, such as methylal, ethylal, tetramethoxy-1,1,2,2-ethane (TME) and others[2,3]; and (2) the use of additives to buffer the resin in the correct hardening pH range such as hexamine sulphate, ethanolamine, and others.[4,5] All of these additives function by addition to the end of the resin after preparation, or by addition to the glue-mix before resin application.

The action of these additives has been attributed to a variety of causes. The main ones are: (1) their use as more effective solvents for melamine and higher molecular weight melamine resin fractions; (2) their disruption of the colloidal state of UF and MUF resins, both of which function as facilitators of homogeneous phase reactions[3]; (3) their use as a buffer of the resin in the correct hardening pH range to ensure better uniform network formation.[4,5]

The similarity of the structures of these additives indicates, however, that part of the improvement observed might be due to an additional effect, one not yet defined. This effect might result from the characteristic structure of the additives themselves.

This article attempts to identify whether there exists some as yet undefined, underlying principle for this mechanism.

EXPERIMENTAL

Resins

An industrial MUF resin of (M + U) to F molar ratio of 1 : 1.5 and M : U mass ratio of 47 : 53 (Sadepan, Italy) was used.

The results were checked with laboratory made MUF resins of molar ratio 1 : 1.2 and 1 : 1.5 and mass ratio equal to the other prepared, according to reported sequential procedures.[1] Table I reports the highest modulus of elasticity (MOE) values obtained overall by thermomechanical analysis (TMA). In 90% of the cases, these values were obtained with the laboratory prepared MUF of molar ratio 1 : 1.5.

Thermomechanical analysis (TMA)

The resins above, used alone as controls, and after the respective addition of 3%, 10%, and 20% different additives (with the addition of 1.5% ammonium chloride hardener, solids on resin solids, added as a 20% water solution), were tested dynamically by thermomechanical analysis (TMA) on a Mettler apparatus. The additives tested were two acetals, namely methylal (Lambiotte, Belgium) and tetramethoxy-1,1,2,2-ethane (Clariant, France). The iminomethylene bases were produced by reacting hexamethylenetetramine and sulfuric acid according to procedures already reported.[4,5] The series of additives included: an industrial sample of hexamethoxymethyl melamine (Maprenal 900; Hoechst, Germany); acetaldehyde dimethylacetal; and *N,N*-dimethylformamide dimethylacetal (Aldrich, USA). Triplicate samples of beech wood alone, and of two beech wood plys, each 0.6 mm thick and bonded with each system gave a total sample dimension of 21 × 6 × 1.2 mm. These samples were tested in 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 on an 18 mm span and applied forces of 0.1 N and 0.5 N with each force cycle of 12 seconds (6s/6s), according to already established procedures.[6] 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 completed both to find the maximum value of the modulus and to follow the increase of the modulus (MOE) as a function of temperature and time. The results are shown in Tables I and II.

Titrations and buffer action

The titration of the MUF resin with the different additives used 20 g of resin of 60% resin solids content and titrated with H_2SO_4 of 10% concentration in water. The results are

TABLE I
Effect of Different Additives on Maximum MOE of Wood Joints Bonded with MUF Resins

MUF + additive type	Additive (%)	Average value Max.MOE (MPa)
MUF control	-	2363
MUF + Methylal	3	2698
MUF + Methylal	10	3440
MUF + Methylal	20	4360
MUF + Tetramethoxy-1,1,2,2-ethane	10	3050
MUF + Tetramethoxy-1,1,2,2-ethane	20	4430
MUF + Diiminomethylene methane/Imino methylene bases	3	3109
MUF + Diiminomethylene methane/Imino methylene bases	6	3892
MUF + Methylamine	3	3370
MUF + Methylamine	10	3540
MUF + Methylamine	20	2874
MUF + hexamethoxymethyl melamine (Maprenal)	5	2567
MUF + hexamethoxymethyl melamine (Maprenal)	20	2473
MUF + Acetaldehyde dimethylacetal	3	2471
MUF + Acetaldehyde dimethylacetal	10	2743
MUF + Acetaldehyde dimethylacetal	20	2949
MUF + N,N-Dimethylformamide dimethylacetal	3	2717
MUF + N,N-Dimethylformamide dimethylacetal	10	2770
MUF + N,N-Dimethylformamide dimethylacetal	20	2908

Results obtained by thermochemical analyses (TMA).

given in the figures in milliliters of this solution that were needed to reach a given pH.

DISCUSSION

The structures of the additives investigated are shown in Tables I and II. Additives 1–3 in Tables I and II are in the early phases of commercialization, with a certain industrial interest being shown[2,3,7]. The rest of the compounds are models that were used for comparison because their structures showed some similarity to the first three. Table I reports the effects of the different additives, some of their physical characteristics, and the improvement in mechanical performance they induced on resins' bonding of wood joints, measured by TMA. The results in Table 1 indicate that the structures C—N—C and C—O—C appear to be repeated in all of these compounds. However, their degree of success in upgrading MUF resins' performance is rather different. The recognized causes of their performance are also due to a number of different effects. These are indicated in Table III as far as they could be ascertained, and they have already been reported for the different materials[2–5]. Table III indicates that there are at least three types of effects that clearly influence the performance of these additives. One is based

TABLE II
Structure of Additives Used with MUF and/or UF Resins and Maximum MOE Increase on Control Resin Observed by TMA

Additive Structure	MOE Increase (%)	
H_3C—O—CH_2—O—CH_3	± 90	b.p. = 42°C
H_3C—O—CH—O—CH_3 (with lower branch) H_3C—O—CH—O—CH_3	± 90	b.p. = 165°C
H_2C=N—CH_2—N=CH_2 (and H_2C=N—CH_2^+)	65	
H_3C—NH_2	50	b.p. = 48°C
H_3C—O—CH_2-N—C, C—N—CH_2-O—CH_3 N CH_3	31	m.p. = 31°C
H_3C—O—CH—O—CH_3	25	b.p. = 64°C
H_3C—O—CH—O—CH_3 N H_3C CH_3	23	

Additives listed in same order as Table I.

TABLE III
Reasons for Strength Performance Improvements with Different Additives[2–5,7]

Compound No.	1	2	3	4	5	6	7
Solubility effect	yes	yes	no	yes	no	no	no
Buffer effect	no	no	yes	yes	no	no	no
Colloidal disruption	yes	yes	no	no	no	no	no
Viscoelastic dissipation of energy	yes[a]	yes[a]	yes	yes	yes	no	no

[a] Only as an external, unlinked plasticizer.

on the reported buffer action of the additive, namely the pH interval within which the additive buffers and to what extent[4,5], which is the case for compounds 3 and 4 in Table III. The second one is based on the increased solubility of higher molecular weight, lower solubility oligomer fractions and the concomitant disruption of the colloidal characteristics of the resins[2,3], which is the case for compounds 1 and 2. The third is based on the more rapid reaction introduced in the resin due to resin methylol groups reacting on the additive more rapidly. This additive (additive 4) causes only linear growth in the polymer network and does not lead to increased crosslinking. The consequence is improved viscoelastic dissipation of energy in the hardened network and higher strength.[8] Methylamine is the main example, with a maximum of two methylol groups of the resin reacting rapidly with its amine functionality.

The only major effect of the ones described above for which data for all of the additives listed in Tables I and II have not been gathered is the buffer effect. Figure 1 shows the comparative titration behavior of pure MUF resin and MUF resin with seven different additives, both of which were titrated with a 10% H_2SO_4 solution. Figure 1 shows
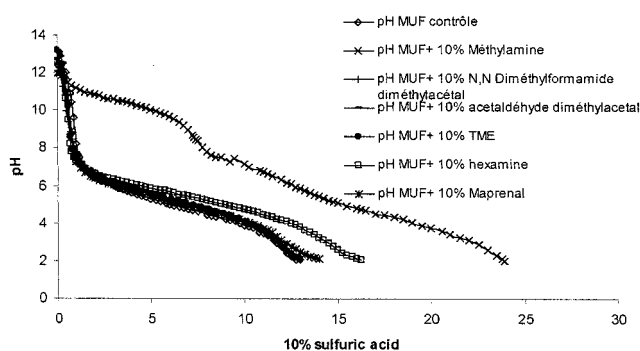
Figure 1 Titration curves of MUF resins with 10% H_2SO_4. The resin samples each weighed 20 g, were of 60% concentration, F/(M+U) molar ratio of 1.5 : 1, and M : U weight ratio of 47 : 53. They were combined with different additives: (◇) pure MUF control; (×) MUF + 10% methylamine; (—) MUF + 10% *N,N*-dimethylformamide dimethylacetal; (–) MUF + 10% acetaldehyde dimethylacetal; (●) MUF + 10% TME; (□) MUF + 10% hexamine; (*) MUF + 10% Maprenal.

that only additive 3 (obtained from the reaction of hexamine with sulfuric acid)[4,5] and additive 4 in Table II present well defined buffer actions. The other additives present none; their titration curves are almost indistinguishable from that of the MUF resin alone.

The combination of these three effects partially explains the scale of effectiveness of these additives, as shown in Table III. Examining the physical characteristics of the compounds, such as melting and boiling points, in conjunction with the data in Table I, reveals no trends that are obviously related to these physical properties. However, testing reveals that, in comparison with structures 1 and 2, structures 5, 6 and 7 do not have any major solubility/colloidal disruption effects. The increase in MOE value is approximately 90% for compounds 1 and 2, while it is approximately 23–31% for compounds 5, 6 and 7. There are no additional noteworthy buffer effects in these three latter cases (Fig.1), which could contribute to the improved MOE of the joint. The major reasons for the effectiveness of compounds 5, 6, and 7 are likely related to their similarity in structure to compounds 1 and 2. There must be some structural effect on the improvement of the MOE in compounds 5, 6 and 7. Around 25% of the effectiveness of compounds 1 and 2 can be attributed to the same structural effect; the remainder is due to the already proven contribution of the other two effects mentioned in Table III. Although it is not the main reason for the effectiveness of the additives, the similarities in structures do contribute to their behavior to a limited extent. The specific cause of this structural effect cannot be explained with the limited amount of data available.

REFERENCES

1. Pizzi, A. Wood Adhesives Chemistry and Technology; Marcel Dekker Inc.: New York, 1983.
2. Pizzi, A.; Beaujean, M.; Zhao, C.; Properzi, M.; Huang, M.Z. J Appl Polym Sci 2002, 84, 2561.
3. Zanetti, M.; Pizzi, A.; Beaujean, M.; Pasch, H.; Rode, K.; Dalet, P. J Appl Polym Sci 2002, 86, 1855.
4. Kamoun, C.; Pizzi, A.; Zanetti, M. J Appl Poly Sci, to appear.
5. Zanetti, M.; Pizzi, A. J Appl Polym Sci, to appear.
6. Garcia, R.; Pizzi, A. J Appl Polym Sci. 1998, 70, 1111.
7. Pizzi, A.; Lambiotte, G. Eur. Pat. app. EP 1 174 480 A1 (2002).
8. Ebewele, R. O.; Myers, G.; River, B. H.; Koutsky, J. A. J Appl Polym Sci 1991, 42, 2997.