

New Adhesive System for Improved Exterior-Grade Wood Panels

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Abstract

Melamine was used to modify urea-formaldehyde resins and bond wood-based panels of improved weather resistance. Different methods of incorporating the melamine in resin production were tried in order to minimize the quantity required to achieve acceptable properties. The resins produced were tested for reactivity and molecular weight distribution. It was evident from the results that the way of addition of melamine substantially affects both properties. The difference in the chemical nature of the resins was confirmed by near-infrared measurements. The performance of the adhesive can also be enhanced by using a crosslinker or a special hardener. The production of weather resistant oriented strandboard complying with European Standard EN300, class 3 and 4 requires further modification of the resin by co-condensation with phenol. Addition of a non-toxic boron-based wood preservative to the glue mix during board production, before blending, can enhance long-term durability even more by imparting biological resistance to the boards.

Introduction

The vast majority of wood-based panels are bonded with urea-formaldehyde (UF) adhesives. Concerns about the effect of formaldehyde on health 20 years ago spurred much research to reduce the formaldehyde content of the adhesives and consequently the formaldehyde emission levels of the boards (1). The reduction of the free formaldehyde in the resin has actually provided a solution to the problem but has severely impaired the already vulnerable properties of the boards, in particular their water resistance. Alternative adhesive systems

proposed to solve the problems of health risk, high production cost, and impaired board performance had only limited commercial success. In parallel, another problem of wood itself as well as wood-based panels has always been their poor resistance to biological attack (2,3). The importance of improving weather and biological resistance of panel products in order to promote their use in structural/building applications as well as the significance of the building sector for the competitiveness of the panel industry, particularly in Europe, has been recently highlighted in two publications (4,5).

The low wet resistance of urea-formaldehyde (UF) resins has been attributed not only to the poor hydrolytic stability of such resins but also to their lack of elasticity due to their crystalline structure (6). Fortification of such resins with the addition of melamine is the most common way of improving their wet resistance (7,8). Melamine is hexafunctional and has a rigid triazid skeleton. Therefore it significantly increases the crosslink density of the cured product. Further improvements can be achieved by the addition of other crosslinkers and special hardeners. One should preferably use crosslinkers or hardeners with a dual function. Such chemicals can increase the durability by simply increasing the crosslink density, and simultaneously increase the elasticity by changing the secondary and tertiary structure of the resulting polymer network (9). Boron compounds are known to increase long-term durability of wood and panel products by increasing their biological resistance toward fungi.

Based on these concepts, an adhesive system was recently developed that uses a combination of an

aminoplastic resin, a special hardener, and a wood preservative. The boards produced have increased weather resistance while the level of formaldehyde emission is kept very low. Furthermore, by coupling a wood preservative with the adhesive, the durability is also improved in terms of biological resistance. This allows the use of the panels for new exterior applications, in particular those where ground contact is required. The use of the new adhesive systems significantly improves the weather/biological resistance of the final product extending several fold its service life under adverse conditions, thus contributing to raw material conservation and promoting the idea of sustainable development.

Materials and Methods

Formurea (precondensate with a composition of 61.4% formaldehyde and 24.65% urea) donated by Woodchem Europe S.A. was used for resin synthesis. Melamine was purchased from DSM (Belgium). All chemicals were used as received.

Viscosity measurements were performed with a Brookfield viscometer at 25°C using a small sample adapter. Solids contents were calculated by weighing resin samples before and after drying in the oven (120°C, 2 hrs.). The reported gel times were measured at 100°C (boiling water). All hardener levels reported are calculated on a percentage basis on resin solids. Buffer capacity corresponds to the ml of 0.1N H₂SO₄ needed to bring the pH of 200 ml 10 percent (w/v) of resin in isopropanol/water 2/3 mixture to the value of 4.0.

Free formaldehyde was measured with the perforator method (EN120). Internal bond (IB) values were measured with a Zwick tensiometer. The 2-hr. and 24-hr. swelling was calculated by measuring the thickness of board samples before and after immersion in water (20°C) for 2 hours or 24 hours, respectively. VI00 was measured with a Zwick tensiometer after immersion of the board samples in boiling water (100°C) for 2 hours.

Gel permeation chromatography (GPC) measurements were effected using a Shimadzu LC-9A liquid chromatograph with a Rheodyne injection loop. Two Plgel columns (Polymer Labs) with pore diameters 100Å and 500Å, respectively, were used. Dimethylformamide (DMF) containing 0.5 percent LiCl was used as eluent. Detection was effected by a Shimadzu RID-6A differential refractometer. Calibration was done using polyethylene glycol standards (Polymer Labs). Correction of the molecular weights of the resins for the incorporation of solvent molecules was considered necessary. Resin samples were dissolved in dimethylsulphoxide (DMSO) and the solutions (approx. 0.5%) were introduced to the injection loop of the liquid chromatograph after filtration through a 0.45 µ filter. The temperature of the columns was kept at 70°C and the flow rate was 1 ml/min.

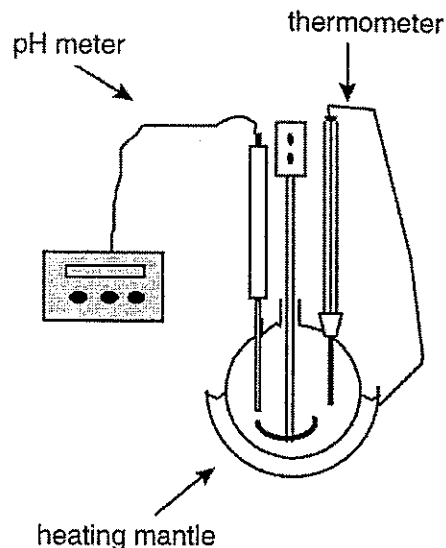


Figure 1.—Reactor used in resin synthesis.

Differential scanning calorimetry (DSC) measurements were performed with a Shimadzu TA-50WSI calorimeter. Sealed aluminum cells were used. Measurements were done under a nitrogen atmosphere. The samples were heated up at a rate of 10°C/min.

Near-infrared spectra were acquired with a Bruker Vector 22N FT-NIR spectrometer in a fiber-optic data acquisition mode. Spectra were collected at 8 cm⁻¹ optical resolution and represent typically averages of 100 scans. The acquisition time was 1 minute. A 1-mm quartz fiber was used. Data analysis was based on sub-routines available in the Bruker-OPUS software.

Resin Synthesis

A typical procedure for the synthesis of a UF or urea-melamine-formaldehyde (UMF) resin is as follows.

A 6-Lt, 4-neck round-bottom flask equipped with a mechanical stirrer, a thermometer, and a pH meter (Fig. 1) is charged with formurea solution and water. The temperature is controlled with a heating mantle connected with the thermometer that is immersed in the solution. The pH of the solution is adjusted around 8.5 and urea (or melamine) is added to the desired molar ratio (usually F/U 1.8:1 to 2.5:1) for the polymerization. The solution is heated to a standard temperature (85° to 95°C), and the pH is adjusted again by addition of acid (5.0 to 5.5). After a certain period of time (1 to 2 hr.), or when the viscosity has reached a certain value (700 to 1,000 cp), the polymerization is terminated by addition of a base and a second amount of urea (or mixture of urea and melamine) to achieve the desired final molar ratio.

Particleboard Preparation

Laboratory boards were produced in a lab press provided by DE METZ N.V. with platens of 60 by 60 cm size. The wood chips (mix of 60% pine, 20 % birch, and 20% poplar) were blended with the glue mix in a blender provided by Lödige. Press conditions and design parameters used are presented in Table 1.

Two boards were made for each press time investigated. For the determination of internal bond (IB) and swelling each board was cut into 15 pieces (5 by 5 by 1.6 cm), ten of which were randomly taken for IB test and 5 for swelling. The values reported are averages of all measurements.

Results and Discussion

Wet Resistance

Incorporation of Melamine into UF Resins.—Melamine is one of the most effective additives to UF resins in improving the wet resistance of the boards. Melamine-urea-formaldehyde (MUF) resins are very popular in Europe as they can give boards with good properties without suffering the limitations of phenolics (e.g., dark color). Cost factors, however, restrict the amount of melamine that can be added to UF resins to impart to them the desirable performance. Several methods of melamine addition have been investigated in our laboratory in order to minimize the amount of melamine used and in parallel optimize the performance of the MUF resin produced.

Three representative ways of preparing MUF resins containing 15 percent (w/w) melamine are describe:

1. By mixing UF resin with MF resin. This is the oldest and simplest way of preparing an MUF resin of any melamine content. The production of MF resin can be regarded as a way of bringing the insoluble melamine into solution. UF and MF resins are miscible with each other while both resin types' hardening is catalyzed by acids.
2. By mixing UMF resin with MF resin. In this case, a small amount of melamine is added during the synthesis of the UF resin. The resin thus produced, having low amounts of melamine content, is usually called UMF and is used in industry to achieve good mechanical properties in combination with very low free-formaldehyde emissions. By mixing UMF with MF, one retains some flexibility to produce resins of various melamine contents on site.
3. By introducing all the melamine during the UF synthesis. The resin thus produced will be hereafter called single-stage MUF resin. It is argued that addition of the melamine during resin synthesis allows the co-condensation of melamine

Table 1.—*Press conditions and board parameters.*

Pressure (kg/cm ²)	35
Press temperature (°C)	200
Press time (sec./mm)	9.0 to 11.0
Board density (kg/m ³)	680
Resin load (%)	12.0
Hardener (%)	3.0
Board dimensions (cm)	35 by 35 by 1.6

with urea and can result in better networks than in case 1 above.

All resins were characterized by the standard methods (viscosity, % solids, gel time, buffer capacity) as well as by modern analytical techniques (DSC, GPC, and FT-NIR) in order to evaluate their differences both in macroscopic and microscopic characteristics. The results are summarized in Tables 2 and 3.

The gel times obtained indicate that the MUF resin that was prepared in a single-stage is more reactive. This can be partially attributed to its lower buffer capacity, which results in a lower pH of the glue mix. To examine whether the results of the standard gel time stem from inherent differences in the resins and the mechanism of curing or just from the difference in buffer capacities, reactivity curves were drawn (by measuring the gel time of each resin at various hardener contents). The results are shown in Figure 2.

From these reactivity curves we can conclude that the difference in reactivity between the single-stage resin and the mix is not just because of the buffer capacity differences since in both of the cases of the mixes the gel time levels off at approximately 5 percent hardener and at this point it is considerably higher than the gel point of the single-stage resin even with 3 percent hardener.

Therefore the method of melamine addition clearly affects the reactivity of melamine-containing resins. Differential scanning calorimetry (DSC) measurements also show that the total heat released during resin curing is not the same for these three resins, further confirming that the three resins have a different number or type of reactive groups available for hardening.

DSC measurements were performed both with and without the addition of hardener and the results are summarized in Table 3.

The results from the DSC thermograms in the presence of hardener do not directly correlate to the gel time measurements. However, they still indicate that the curing is faster in the case of the single-stage MUF resin since the peak of the exotherm comes faster (at a lower temperature). The exotherm of the mix of UF and MF is much broader, and this is the reason for obtaining the peak of curing at higher temperature. The onset of cur-

Table 2.—Characteristics of resin mixes containing 15% melamine.

Resin	Viscosity (cp)	Solids (%)	Gel time ^a		Buffer capacity (ml 1N H ₂ SO ₄)
			Gel time of glue mix ^b (sec.)		
UF + MF	265	65.5	80	104	29.5
UMF + MF	280	65.7	78	100	26.4
MUF (single stage)	350	65.4	68	87	23.2

^a Standard gel time measured at 100°C with 3% (s/s) ammonium chloride as hardener.

^b Gel time of the glue mix used in board production with 5% (s/s) ammonium chloride.

Table 3.—Results from DSC analysis of MUF resins containing 15% melamine.

Resin	Gel time (sec.)	With 3% hardener		Without hardener	
		Peak, °C	Heat, J/g	Peak, °C	Heat, J/g
UF + MF	80	105.3	51	160.3	59
UMF + MF	78	106.0	57	164.4	51
MUF (single stage)	68	102.0	75	164.1	68

ing in all cases is approximately at the same temperature. Furthermore, it is observed that the total heat released per gram of resin is greater in the latter case. Since the solids contents of the resins are practically the same, the higher amount of heat released could indicate either that there is a larger number of reactions taking place during curing of the MUF single-stage resin, or that all the reactions that take place are not of exactly the same nature. The picture is completely different in the case of the exotherms obtained in the absence of hardener. This clearly indicates the different effects of catalysis to the three types of resins. Extensive kinetic studies of the curing behavior should be performed in order to deduce safe conclusions.

The inability to directly correlate the gel time measurements with the peak temperature obtained by DSC has been observed before and has been occasionally attributed to the dry out effect, hence to a diffusional hindrance effect. DSC tests are obtained under pressure whereas the resins lose their water during the gel time test. Another significant difference between the DSC and gel time tests is that the DSC test is performed under steadily increasing temperature at a rate precisely monitored. On the other hand, gel time measurements are supposedly performed at a constant temperature. However, it is usually the temperature of the water bath inside which the test is performed that is monitored and not the actual temperature of the glue mix that hardens. Since the hardening reaction is exothermic, the temperature of the glue mix may actually be higher than the bath temperature. The actual temperature of the glue mix will therefore depend on the heat released by the curing of the resin and the rate of heat release.

In order to examine further the differences among the three resins that lead to different reactivities, the

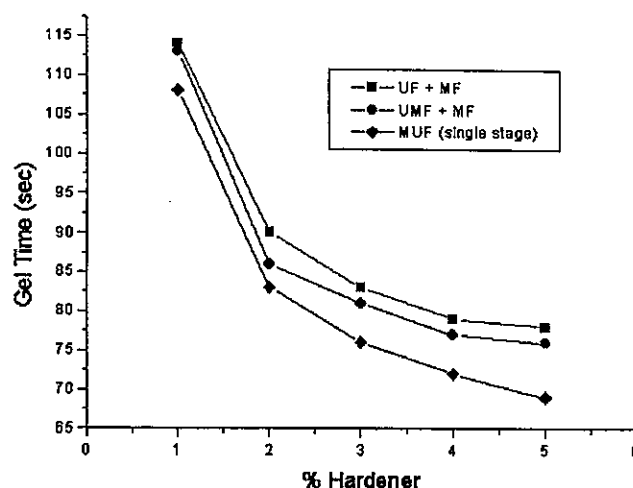


Figure 2.—Reactivity curves of the three MUF resins containing 15% melamine.

molecular weights and molecular weight distribution of the resins were obtained with GPC measurements. The results of the GPC analysis are given in Table 4. In the same Table are the results from the analysis of the MF, UF, and UMF resins that were used in order to obtain the mixes.

The GPC chromatograms of the three resins are overlaid in Figure 3. It can be seen from this Figure that the resin produced by mixing UF with MF lacks the high molecular weight part at retention volume lower than 11 ml. This high molecular weight region develops in UMF and MUF resins during the last stages of the polymerization. The mixture of UF and MF has practically the same viscosity with the mixture of UMF and MF but very different molecular weight distribution. This is due to the difference in the molecular weight distributions between the UF and UMF resins

Table 4.—GPC analysis of resins.

Resins	M_n	M_w	PDI
MF	195	290	1.5
UF	205	465	2.3
UF + MF	207	437	2.1
UMF	204	897	4.4
UMF + MF	211	807	3.8
MUF (single stage)	213	657	3.1

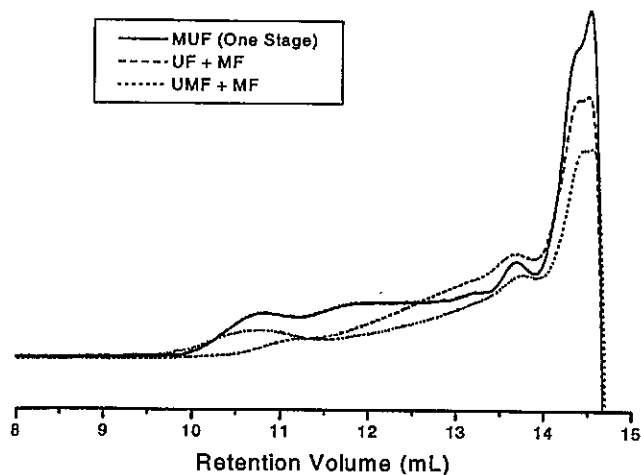


Figure 3.—GPC chromatograms of the three MUF resins containing 15% melamine.

used in the mixes. Comparing the molecular weight distributions of the single-stage MUF with the mix of UMF and MF, we could say that the first contains a larger percentage of low molecular weight molecules. This abundance of relatively small molecules could be one reason contributing to the higher reactivity of the resin due to their higher mobility.

The resins were further analyzed with NIR spectroscopy. Typical NIR absorption spectra (10,000 to 4,250 cm^{-1}) of the three resins are presented in Figure 4. Three spectra from each different resin are overlaid in this Figure in order to depict the reproducibility of the method.

The first observation is a frequency independent background absorption. This must be originating from light scattering by particles with sizes of the order of the wavelength of the NIR light (0.8 to 2.5 μm). Therefore, NIR can provide a tool for quantifying the development of such particles. However, we have not concluded yet in a relation between the cloudiness and the performance of the resins.

Some basic assignments of the bands observed have been achieved based on on-line observations during resin synthesis and on spectra of starting materials and model compounds. Since most bands are broad and

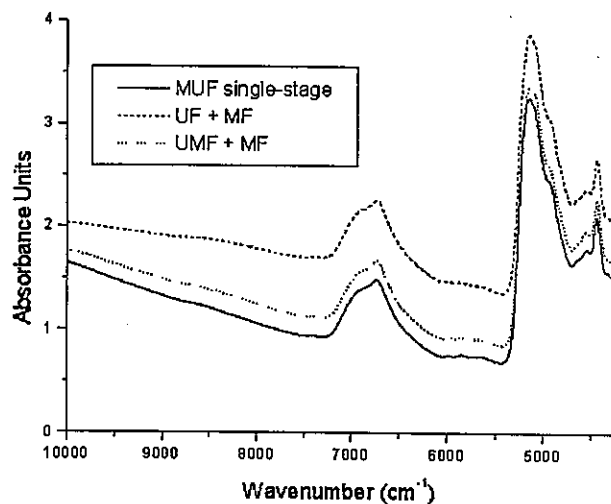


Figure 4.—FT-NIR spectra of MUF resins.

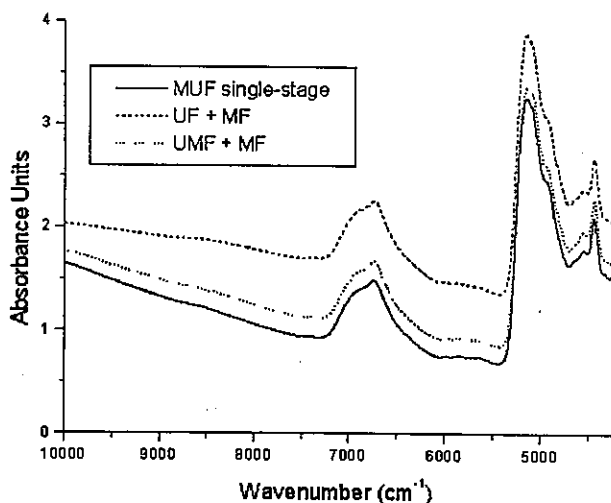


Figure 5.—Second derivatives of FT-NIR spectra of MUF resins.

overlapping (due to strong hydrogen bonding), the various component bands are better resolved in the 2nd derivative spectra (Fig. 5). Starting from the low frequency end, the absorption band at approximately 4,400 cm^{-1} is due to a CH_2 combination mode.

The two adjacent overlapping features at approximately 4,550 and 4,640 cm^{-1} are tentatively attributed to a combination mode of C-N-H and N-H vibrations. These bands are also observed in aqueous urea solutions and are decreasing in intensity during the methylation of urea. At higher frequencies, a strong and broad band is observed at approximately 4,930 cm^{-1} and has been attributed to the 2nd overtone of the carbonyl stretch.

The strongest band envelope at approximately 5,200 cm^{-1} (Fig. 5) clearly consists of a number of component bands, which can be attributed to combination modes

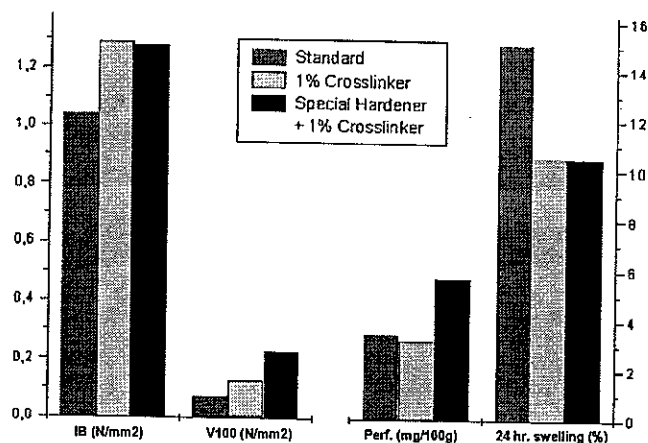


Figure 6.—Effect of crosslinker and special catalyst use. From laboratory particleboard production with MUF resin containing 23% melamine; press time: 7.5 sec./mm; catalyst: 5% $(\text{NH}_4)_2\text{SO}_4$ on resin solids. V20 designates dry IB and V100 wet IB after the boil test.

of water, as well as hydroxyl and $-\text{NH}_2$ terminal groups, in close interaction to each other (hydrogen bonding).

The band at approximately $4,815 \text{ cm}^{-1}$ is not present in UF resins. It is interesting that it appears with different intensities in the UF + MF mix and UMF + MF mix and it is absent in the case of the single-stage MUF resin. In the case of MF resins a broader band is observed at $4,790 \text{ cm}^{-1}$.

Finally, the performance of the three resins was evaluated by lab scale particleboard production. There is no significant difference in the performance of the MUF single-stage resin with that of the mix of UMF and MF while the mix of UF and MF seems to be inferior in weather resistance.

In summary, we can say that the method of melamine addition affects both the chemical nature and the performance of the resulting resin. A new method is being developed in our lab for the on-line monitoring of resin production and the chemical characterization of the final products with FT-NIR.

Use of a Crosslinker or Hardener

It is well known that free formaldehyde in the resin acts as a crosslinker during the polymerization reaction. Resins with high formaldehyde to urea (F/U) molar ratios show higher resistance to hydrolysis and give panels with improved weather resistance. Various alternative crosslinkers have been tested which can compensate for the lack of free formaldehyde in modern low F/U molar ratio resins and can significantly improve the weather resistance of composite panels. The crosslinkers used are added *in situ* to the glue mix. Depending on the crosslinker used, the moisture resistance properties of the boards (EN1087-1, boil test)

Table 5.—Laboratory boards prepared by using 13% MUPF resin. Properties were measured according to European standards EN322, EN323, EN317, EN319, EN1087-1, and EN120.

Property	19-mm board	36-mm board
Thickness (mm)	19.44	36.7
Density (kg/m^3)	664	570
MOR (N/mm^2)	24.0	15.2
Internal bond (N/mm^2) ^a		
V20	1.01	0.61
V100	0.28	0.17
Acid test	0.27	0.14
24-hr. swelling (%)	5.23	8.50
Water absorption (%)	32.4	66.9
Perforator (mg FF/100 g)	4.0	3.2
Moisture (%)	10.3	10.0

^a V20 = dry IB, V100 = wet IB after boil test; acid test values are after treatment at a pH of 2 before the boil test.

were improved up to 40 percent. A special catalyst can be used along with the crosslinker to accelerate resin curing and allow enhanced board properties at reduced press cycles. This leads to both product improvement as well as increased productivity.

The use of an additive *in situ* to the glue mix has several advantages as well as limitations. The major advantage is that one can adjust the level of additive depending on the quality of the boards that are produced. However, several panel producers do not want to add an extra component to their formulations and prefer to have a resin of improved performance. The incorporation of a crosslinker to the resin on the other hand may affect good stability. The development of crosslinkers that do not impair the stability of the resins is a very challenging task.

Figure 6 shows the results from a successful combination of a special catalyst and a crosslinker in laboratory-scale particleboard production. Swelling values and wet properties of the boards can be dramatically improved with very low levels of crosslinker addition.

Co-Condensation of Melamine, Urea, Phenol, and Formaldehyde

Typical systems currently used for weather-resistant oriented strandboard (OSB) (EN300, class 3 and 4) are phenol-formaldehyde or isocyanate-based resins. The development of MUF resin formulations to achieve colorless OSB complying with this standard was quite challenging. This has been finally achieved with the co-condensation of melamine, urea, phenol, and formaldehyde for the production of an MUPF resin. This resin has been recently certified for weather-resistant board production by the Deutsches Institut für Bau-

Table 6.—Addition of preservative in MUF resin with 23% melamine content (press time is 8.0 sec./mm, preservative level based on liquid resin).

Hardener	Preservative (%)	IB (N/mm ²)	V100	Density (kg/m ³)	HCHO (mg/100 g)	24-hr. swell (%)
(NH ₄) ₂ SO ₄	--	0.94	0.11	711	2.8	7.9
(NH ₄) ₂ SO ₄	8	0.98	0.11	718	3.8	7.5
Special hardener	--	1.10	0.25	722	5.8	6.2
Special hardener	8	1.00	0.28	712	5.3	7.0

Table 7.—Average percentage mass loss of unleached particleboard panels for different preservative levels.

Type	<i>Coniophora puteana</i>	<i>Gloeophyllum trabeum</i>	<i>Coriolus versicolor</i>
	----- (%) -----		
Virulence control	19.2	16.0	22.8
MUF (control)	13.4	9.9	18.9
MUF + 4% preservative	0.9	1.4	0.7
MUF + 8% preservative	0.5	1.2	0.7
MUF + 12% preservative	0.3	0.4	0.2

Table 8.—Average percentage mass loss of leached particleboard panels for different preservative levels.

Type	<i>Coniophora puteana</i>	<i>Gloeophyllum m trabeum</i>	<i>Coriolus versicolor</i>
	----- (%) -----		
Virulence control	22.5	17.6	27.7
MUF (control)	7.4	2.5	21.1
MUF + 4% preservative	5.8	0.7	11.8
MUF + 8% preservative	1.8	0.6	6.7
MUF + 12% preservative	0.8	0.3	3.1

technik (DIBt) in Germany. Laboratory boards using this resin were produced and tested at the Wilhelm-Klauditz-Institut (WKI) in Germany according to European Standards. Indicative results of such tests with particleboard are presented in Table 5.

Biological Resistance

Biologically resistant wood-based panels are usually made by impregnating a wood preservative to the panel itself or the wood material before resination (10-12). Common treatments (e.g., coating, dipping) require an extra process step and protect effectively mainly the surface layers unless vacuum is used. A method was developed for the addition of a non-toxic boron-based preservative to the glue mix formulation, before blending with wood, during the normal board production process. Fixation of the preservative is achieved by the resin itself without any additional fixating agents commonly used (13). Adding the preservative directly to the glue mix is a simple single-stage process eliminating the need for the costly and time consuming pre-treatment of the wood material or post-treatment of the board.

Boards prepared with addition of various amounts of wood preservative to the glue mix were first leached according to European Norm EN84 and then tested for biological resistance (EN113). Table 6 shows representative properties of boards made with and without preservative. Table 7 shows the average percentage

mass loss of unleached particleboard panels for different fungal species, while in Table 8 the respective figures for leached samples are presented. It was concluded that a level of 10 percent preservative addition (w/w on resin) is efficient in providing satisfactory biological resistance after leaching. The boards were also tested for their mechanical properties and weather resistance. The latter were found to be unaffected by the presence of the preservative. Evaluation of the preservative for other types of boards is underway.

Conclusions

Structural applications require exterior-grade panels with sufficient long-term durability. Such panels can be effectively produced by using an adhesive system based on an aminoplastic resin, a special hardener, and a boron-based wood preservative. Optimal use of melamine requires careful manipulation of the way of its incorporation during resins synthesis. Near infrared analysis has a potential for on-line resin production process monitoring and control.

Acknowledgments

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tests were carried by Mrs. M-F. Thévenon at ENSTIB/ University of Nancy 1. Resin synthesis and board manufacturing and testing were carried out by lab staff at A.R.I. Ltd.

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**Session 3B: Advances in
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