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Particleboards from Acetylated Wood Flakes

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Summary. Particleboards from acetylated wood flakes with various resins were pressed and compared with untreated control boards with respect to their weathering resistance and mechanical strength. The industrially used melamine, urea, and phenol resins showed a poor adhesion behavior to the acetylated flakes resulting in a high decrease of the mechanical strength of the particleboards. A novel type of apolar resin based on methylmelamines was developed and characterized. Using this resin particleboards with good mechanical strength and weathering stability could be produced.

Keywords. Acetylation; Isopropenylacetate; Methylmelamine resin; Particleboard; Wood.

Introduction

A common method to achieve a substantial improvement in particleboard properties like weather resistance or durability is an acetylation of the wood components [1, 2]. Here the free hydroxyl groups react with an acetylating agent to an acetic ester thus decreasing polarity. Usually, this reaction is performed with acetic anhydride with the undesired by-product acetic acid, which is difficult to remove from the wood flakes. If the product is not washed properly, the wood flakes have a unpleasant vinegar smell. Thus typically 10–15 hot steam treatments are necessary to achieve odor-free products [3]. By using a novel synthesis route based on isopropenyl-acetate, which yields acetone as by-product, this problem could be solved [4].

As known from previous studies [5, 6] the side effect of acetylation is a decrease in the mechanical properties of the particleboards made of acetylated wood flakes. A possible explanation is an adhesion problem between the industrially used hydrophilic water soluble urea formaldehyde (*UF*) and melamine urea formaldehyde (*MUF*) resins and the hydrophobic acetylated flakes [7]. To verify this assumption different types of commercially available resins and also a novel type of a specially designed hydrophobic melamine resin were applied.

Results and Discussion

The wood flakes consisted of a mixture of 90% spruce and 10% pine wood. The acetylation with isopropenyl acetate was performed in technical scale at 100°C for 2 h. A mesh analysis of the material before and after the reaction showed that there was no mechanical degradation due to the process conditions (Table 1).

The commercially available resins from Dynea and BASF are *MUF*, phenol formaldehyde (*PF*), and melamine urea phenol formaldehyde (*MUPF*) types typically used in the particleboard industry. Table 2 shows a classification of the resins used in this study.

A test series of particleboards made from wood flakes with an increasing degree of acetylation but

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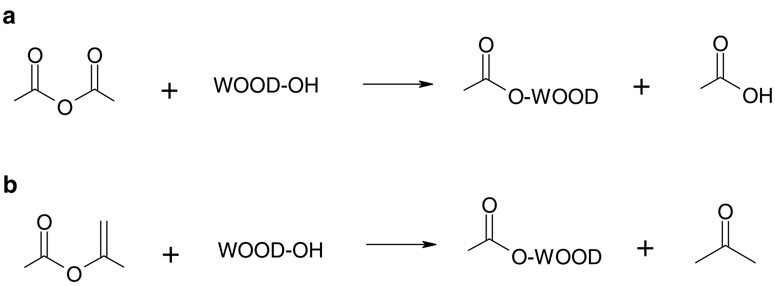

Scheme 1. Reactions of hydroxyl containing wood components with a) acetic anhydride and b) isopropenyl acetate

Table 1. Particle size distribution measured by mesh analyses of the used wood flakes before and after the acetylation process

Mesh size/μm	Mass% acetylated flakes	Mass% untreated flakes
<125	6.8	5.7
125	2.6	3.1
180	3.8	4.9
250	10.7	11.2
355	16.9	15.3
500	20.9	21.6
710	19.2	19.0
1000	18.7	18.5
2000	0.5	0.7

Table 2. Types of commercial resins used in this study

Trade name	Manufacturer	Resin type	Comment
Prefere 10H119	Dynea	*MUF*	67% in water
Prefere 10G119	Dynea	*MUF*	67% in water
Prefere 14J330	Dynea	*PF*	44% in water
Prefere 10J227	Dynea	*PF*	60% in water
Prefere 10J414	Dynea	*PF*	50% in water
Kaurit 541	BASF	*MUPF*	65% in water

the same resin as the binder showed, that there is a linear relationship between the 24 h thickness swelling test and the weight percentage gain (*WPG*), an indicator of the degree of acetylation, of the material (Fig. 1). The gradient and ordinate intercept depend on the used resin and also vary slightly with the properties of the wood flakes (wood species, particle size distribution). With a commercial *MUF* resin a *WPG* of 18 is needed to reach values under 9% in the 24 h thickness swelling test to qualify for high quality particleboard classes according to EN 321-5 (P5) and EN 321-7 (P7).

On the other hand, no linear relationship between *WPG* and modulus of rupture (*MOR*) could be found.

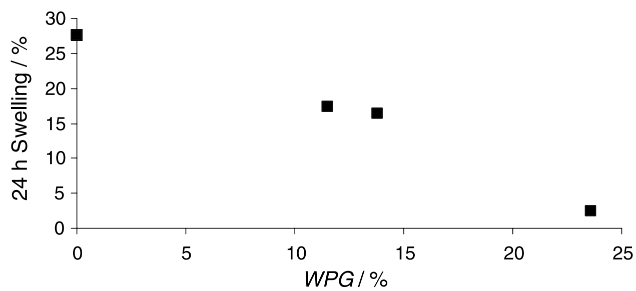

Fig. 1. Improvement of the 24 h water swelling properties with increasing degree of acetylation of the wood flakes; particleboards bonded with 8% Prefere 10H119

Even a low degree of acetylation results in a high decrease of the mechanical strength of the board. All commercial resins used for acetylated boards showed a much lower *MOR* compared to untreated control samples with untreated wood. Besides maybe a small contribution due to chemical degradation of the wood itself a feasible explanation could be an adhesion problem between the rather polar resins and the apolar acetylated wood flakes, which was confirmed by penetration measurements. A drop of a Rhodamin B colored resin was applied to samples of untreated and acetylated wood flakes. After the same residence time of 30 minutes each sample was cut in the middle of the resin drop and examined by reflected light microscope measurements. The *MUPF* resin penetrated 4–5 times deeper in untreated wood compared to the acetylated one (*WPG* 18) (Fig. 2).

A novel type of *MF* resin was produced from 2,4,6-trimethylmelamine. In contrast to the free amino and imino groups of a conventional melamine resin, most functionalities are now *N*-methyl groups, which results in a dramatically decreased polarity (Fig. 3a) [8]. The structure of the methylmelamine resin was elucidated with mass spectrometry [9], as shown in Fig. 3b. It consists of mainly dimers

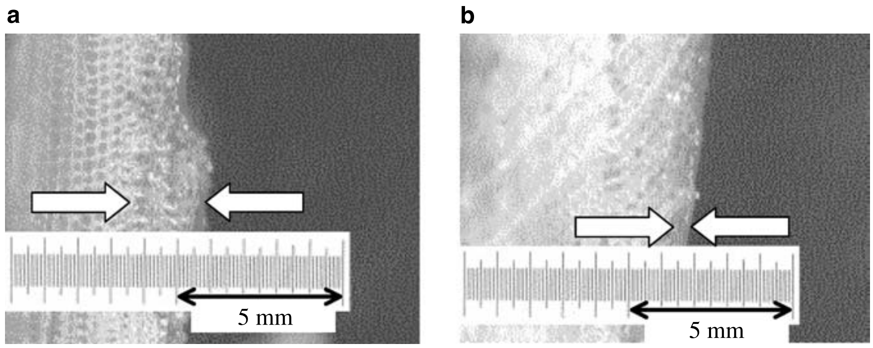

Fig. 2. Penetration measurements of a Rhodamin B coloured *MUPF* resin (Kaurit 541) with a) untreated and b) acetylated wood

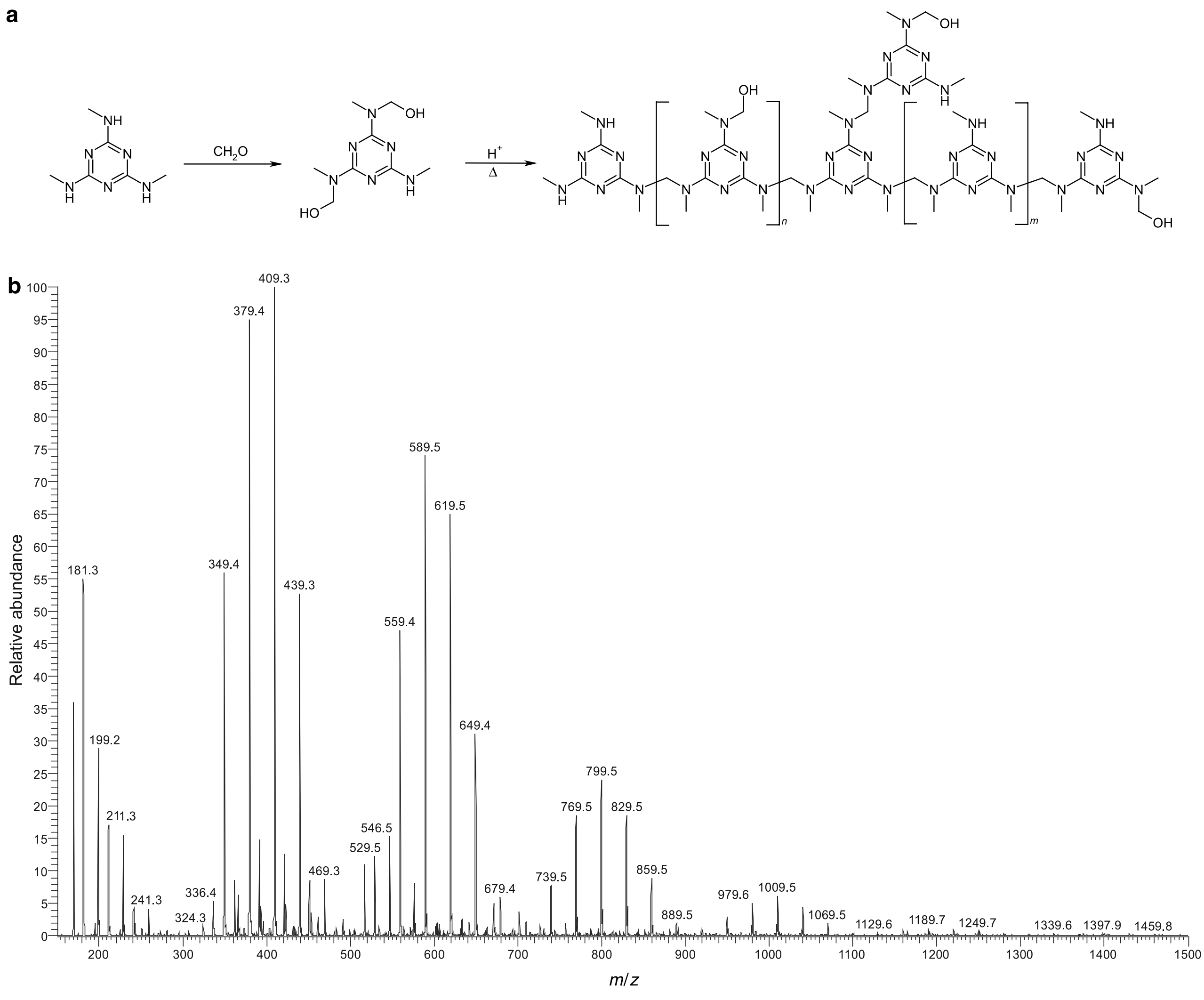

Fig. 3. Structure and ESI-MS of the methylmelamine resin

($m/z = 349$–469) and trimers ($m/z = 529$–679) with an average of about 1.5 methylol groups per melamine unit.

Using the methylmelamine resin for particleboards with acetylated wood, it was possible to improve the mechanical values dramatically. Not only

Table 3. Mechanical and water resistance properties of the particleboards made from acetylated and untreated wood

Resin	Wood	Density of board/g cm^{-3}	24 h Swelling^{i}/%	*MOR*^{ii}/MPa	*E* modulus^{iii}/ MPa	n^{iv}
Methylmelamine	acetylated *WPG* 23.5	0.857	2.7 (0.3)^{v}	11.4 (1.1)^{v}	2173 (169)^{v}	6
Prefere 10H119	acetylated *WPG* 22	0.598	2.7 (0.3)	6.6 (0.7)	992 (170)	5
Prefere 10G119	acetylated *WPG* 21.5	0.662	4.7 (0.8)	8.2 (0.5)	1103 (48)	5
Prefere 14J330	acetylated *WPG* 14.5	0.788	–	14.9 (0.3)	1214 (54)	4
Kaurit 541	acetylated *WPG* 14.5	0.660	–	2.3 (0.4)	207 (31)	4
Prefere 10J227	acetylated *WPG* 14.5	0.740	–	11.9 (1.7)	982 (133)	5
Prefere 10J414	acetylated *WPG* 14.5	0.753	–	9.9 (0.9)	709 (67)	5
Methylmelamine	untreated	0.760	11.3 (0.9)	12.7 (0.9)	2184 (146)	5
Prefere 10H119	untreated	0.712	27.5 (0.1)	10.9 (0.4)	1221 (44)	5
Prefere 10G119	untreated	0.709	29.5 (0.6)	12.4 (0.5)	1217 (90)	6
Prefere 14J330	untreated	0.938	–	25.0 (1,5)	2154 (85)	4
Kaurit 541	untreated	0.823	–	4.0 (0.6)	336 (30)	6
Prefere 10J227	untreated	0.916	–	23.6 (1.4)	1842 (13)	5
Prefere 10J414	untreated	0.916	–	24.1 (1.6)	1791 (91)	5

^{i} Mean of 2 values
^{ii} Modulus of rupture; relative to density
^{iii} Relative to density
^{iv} Number of samples tested
^{v} Mean deviation

that the *MOR* reached the same level as if untreated wood flakes were used, even the elasticity modulus (*E* modulus) was improved from about 850 MPa to over 1600 MPa for boards made from untreated wood flakes and for acetylated flakes even from about 700 MPa to almost 1900 MPa. The water resistance of the particleboards, determined as the 24 h thickness swelling, was improved drastically just by using the methylmelamine resin (Table 3). The best value reached for a particleboard made from acetylated wood chips and the methylmelamine resin was 2.7%. Figure 4 summarizes the *MOR*s of the acetylated boards with all types of resins compared to a standard board produced from untreated wood.

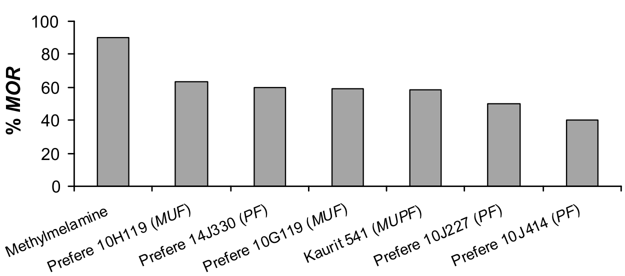

Fig. 4. Comparison of the mechanical properties of acetylated particleboards with different types of resin. % *MOR* is the retention of *MOR* compared to the particleboards with untreated wood flakes

Conclusion

It could be shown that the acetylation of wood flakes is a useful method for the production of particleboards, which have excellent stability against water. Unfortunately, the mechanical stability of these boards is lowered to about 60–70% of a conventional particleboard due to inferior impregnation of the apolar acetylated wood flakes with conventional resins. This problem was solved by using a novel type of methylmelamine resin. With this apolar resin the *MOR* was increased to the level of conventional particleboards and elasticity modulus and water resistance were even improved. With acetylated wood and the novel methylmelamine resin it is now possible to produce particleboards for the use in wet rooms according to EN 321-5 (P5) and EN 321-7 (P7).

Experimental

Acetylation of Wood Flakes

The acetylation of the wood flakes was performed in a 180 dm^3 steel reaction vessel with integrated filtration unit. 7 kg wood and 50 dm^3 isopropenyl acetate with 0.05 mol dm^{-3} *p*-toluoenesulfonic acid were heated up to 100°C (pressure raised to 1.5 bar). After 120 min reaction time the liquid reaction media was filtered. The wood flakes were washed directly in the reactor, once with methanol and acetone and 3–4 times with H_2O. Drying of the acetylated product was done at 90°C under reduced pressure (~100 mbar) overnight also in the reaction vessel.

Methylmelamine Resin

200 g 2,4,6-trimethylmelamine (1190 mmol) and 10 g ethylene glycol (161 mmol) were suspended in 315 cm^3 H_2O and heated up to 100°C. Then 175 cm^3 formaldehyde solution (37% in H_2O, 2140 mmol) were added and after 45 min the reaction mixture cooled to room temperature under stirring. The resin was separated from the surmounting aqueous solution and suspended in 1 dm^3 methanol before application to the wood flakes.

Particleboards

All particleboards were produced in a two-step pressing process, first cold pressing of a blank shape and finishing by hot pressing at 180°C for 2–3 min with a format of $38 \times 32 \times 1.1\ cm^3$. The density of the boards ranged from 0.65–0.75 $g\,cm^{-3}$. The resin content was 8% (wt/wt) based on the dry weight of the wood flakes and was inserted by spraying. With each type of resin one board was made from which 4–6 samples were cut for determination of mechanical values and 2 samples were used for the 24 h swelling test.

Characterization

The 24 h thickness swelling was determined according to EN 317 and the modulus of rupture (*MOR*) according to EN 310. Microscopic measurements were made with a Nikon Labophot 2A Light Microscope equipped with a Panasonic Digital Camera. Mass Spectra were recorded on a Thermo Finnigan LCQ Deca XP plus in $CHCl_3/MeOH$ (1/1) in ESI positive mode.

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