

Effect of chemical modification of wood on the mechanical and adhesion properties of wood fiber/polypropylene fiber and polypropylene/veneer composites

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The effect of acetic, maleic or succinic anhydride modifications of wood fiber on the mechanical properties and dimensional stability of differently bonded fiber boards was studied. The binders for the fiber boards used in this work were: powdered phenol formaldehyde resin of the novolak type (PF), polypropylene (PP) and a combination of the two. In the second part of the research, birch veneers modified with succinic or phthalic anhydride were laminated with PP films and the effect of the modifications on the interfacial bond between the two materials was studied. Significant improvement in the mechanical properties of the PP-bonded boards was generally observed as a result of the anhydride modifications. Modification of wood fibers with maleic anhydride resulted in a reduction in the modulus of rupture of the PF- and PF/PP-bonded boards, whereas acetylation and modification with succinic anhydride did not cause any significant changes in the modulus of rupture of the boards. The anhydride modifications improved the internal bond strength of the fiber boards regardless of the binder type used. Dimensional stability of the fiber boards was observed to increase significantly as result of the modifications. Adhesion between the PP films and wood veneer showed an increasing trend as function of the degree of modification. In addition, SEM micrographs of the fiber boards and PP-coated veneer revealed improved interaction between the two components due to the anhydride modifications.

Einfluß chemischer Modifikation des Holzes auf die mechanischen und Haften-schaften von Holz- und Polypropylen-Fascerplatten sowie Polypropylen/furnier-Werkstoffe

Der Einfluß der Modifikation von Holzfasern mit Essig-, Malein- und Bernsteinsäureanhydrid auf die mechanischen Eigenschaften und die Dimensionsstabilität von unterschiedlich gebundenen Faserplatten wurde untersucht. Als Bindemittel wurden verwendet: Phenol-Formaldehydharz (Pulver) vom Novolak-Typ (PF), Polypropylen (PP) sowie eine Kombination der beiden. Weiterhin wurde Birkenfurnier mit Bernstein- und Phthaldäureanhydrid modifiziert und mit PP-Filmen beschichtet. Der Einfluß der Modifikation auf die Bindung zwischen den beiden Materialien wurde untersucht. Allgemein konnten signifikante Verbesserungen der mechanischen Eigenschaften der PP-gebundenen Platten durch die Reaktion mit den Anhydriden erreicht werden. Die Modifikation der Holzfasern mit Maleinanhydrid führte zu einer Verringerung des MOR der PF- und PF/PP-gebundenen Platten. Dagegen blieb der MOR nach Acetylierung oder Modifikation mit Bernsteinsäureanhydrid weitgehend unverändert. Alle Modifikationen mit den Anhydriden verbesserten die Querkzugfestigkeit der Faserplatten unabhängig vom Bindemittel. Die Dimensionsstabilität der Faserplatten stieg aufgrund der Modifikation ebenfalls deutlich an. Die Haftung zwischen den PP-Schichten und dem Furnier verbesserte sich parallel zum Ausmaß der Modifikation. Zusätzlich konnte anhand von REM-Aufnahmen von Faserplatten und PP-beschichtetem Furnier die verbesserte Wechselwirkung der beiden Komponenten von Faserplatten und PP-beschichtetem Furnier nach der Modifikation aufgezeigt werden.

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1 Introduction

In recent years, increasing interest has focused on thermoplastic composites reinforced with wood fiber or with other lignocellulosic and cellulosic based materials (Krzysik and Youngquist 1991, Maldas and Kokta 1993, Sanadi et al. 1994, Sanadi et al. 1995). Lignocellulosics are favored as new generation reinforcing materials in thermoplastics since they represent renewable natural resources. Secondly, the increasing concern about our environment promotes recyclable raw materials and products, emphasizing the demand for lignocellulosic-thermoplastic composites. Furthermore, lignocellulosic fibers, due to the strong cellulose backbone structure, possess good strength properties and the favorable

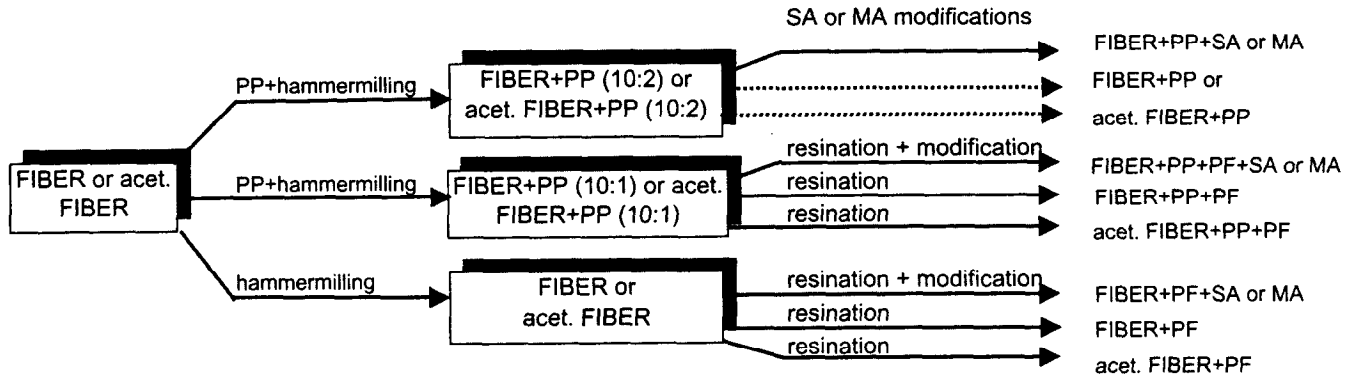


Fig. 1. Schematic presentation of the treatments carried out for MDF fibers

Bild 1. Schema der chemischen und mechanischen Behandlung

strength/weight-ratio of the fibers are an advantage compared with many conventional reinforcing materials.

However, the highly hydrophobic nature of certain thermoplastics, such as polyolefins, causes compatibility problems with the hydrophilic reinforcing materials. Since mechanical properties of the composites are related to the compatibility and interaction between the components, improvement of the interface and interphase interactions in polypropylene/wood composites is essential. Approaches to improve the interaction and thereby the stress transfer between lignocellulosics and polypropylene include, for instance, the use of coupling agents and compatibilizers of various kinds (Kolosick et al. 1990, Oksman and Clemons 1997, Westerlind and Berg 1988). Coating of wood filler with thermoset resin has also been proved to enhance the mechanical properties of wood/polypropylene composites (Sain and Kokta 1993). Recently, the use of chemical modifiers of wood has drawn attention as adhesion-promoting treatments for the composites in question. Thermoplasticization of wood with adequate modifiers and modification rates has been proved to facilitate blending and improve compatibility of the wood material with plastics (Hon and Chao 1993, Rowell et al. 1994a).

The objective of this study was to determine the effect of different organic anhydrides as wood modifiers on the mechanical properties of fiber-boards bonded either with polypropylene (PP) or phenol formaldehyde resin (PF) or a combination of both. In the present work, we also introduce a procedure to make modified fiber boards without an additional step for fiber modification. In the second part of the research, the effect of chemical modification on the adhesion properties between birch veneers and PP films was studied. Chemicals used for modification treatments of the fibers were acetic, maleic and succinic anhydrides and those for the veneers succinic and phthalic anhydrides.

2 Experimental

2.1 Materials

The fibers used in the first part of the study were of soft-wood origin and normally used to make medium density

fiber boards (MDF). The fiber material was provided by Kronospan. The moisture content of the fiber was 7%. Polypropylene fiber (PP), powdered phenol formaldehyde resin (PF) of the novolak type or a combination of both were used as binders for the fiber boards. The polypropylene fiber provided by Neste Chemicals (Finland) was 2.2 denier and 25 mm long. The powdered phenol resin was Peracit 888412 and supplied by Perstorp Chemitech SA, France. Maleic anhydride (Fluka Chemie AG) or succinic anhydride (Merck) was used as modification chemicals for the wood fiber. In addition, Kronospan fiber modified with acetic anhydride by BP Chemicals (U.K.) was used as raw material for board making. The degree of acetylation of the fiber was approx. 20% based on the dry weight of the fiber.

For the adhesion study of polypropylene film and modified wood surface, two-layered polypropylene-polyamide films supplied by Walki Pack Valkeakoski (Finland) were used. One of the films tested consisted of a polypropylene (PP) layer of 50 μm and a polyamide (PA) layer of 30 μm in thickness. The respective thickness values for the second PP/PA film were 70 and 20 μm , for the third film 100 and 60 μm . The reinforcement of the PP film with a PA layer made the films suitable for determination of the adhesion by means of a peel test. Sliced birch (*Betula pendula*) veneers of 1.2 mm in nominal thickness (radial direction) and 200 mm \times 200 mm in surface area were used as substrates for the PP/PA films. Prior to the chemical treatments with succinic or phthalic anhydride (both supplied by Merck), the veneer surfaces were smoothed by sanding with a sand paper of 150 grid and conditioned at 65% relative humidity (RH).

2.2 Modifications and preparation of specimens

2.2.1 Fiber boards

Prior to modifications of the fiber material, PP fibers were mixed with wood fiber in ratios 1:10 and 2:10 (based on the dry weight of the wood fiber), respectively. Mixing by means of a hammer mill was observed to result in a mixture in which the wood and PP fibers were distributed relatively evenly. A third batch of fibers were put through

the mill without an addition of PP. Fibers from the former batches were then used for all the boards where PP acted as binder (mixture with the fiber ratio 2:10) or as one of the binders (mixture with the fiber ratio 1:10). The fibers of the third batch were used for the rest of the boards, i.e., for the control and modified boards to be bonded only with the powdered PF resin.

Modifications with maleic and succinic anhydride were carried out by mixing the solid anhydride with the wood fiber (with or without PP) in a resination drum. The amount of the anhydrides added to the fiber was 15% based on the dry weight of the fiber. Powdered PF resin was added simultaneously with the anhydride to the fiber batches which were to be used for PF-bonded or PP + PF-bonded boards (for the control boards no anhydride added). Although the acetylated fiber had already gone through the modification stage (by BP Chemicals) and was rather loose, hammer-milling was needed in order to blend PP fibers with the acetylated material (in ratios 1:10 and 2:10, respectively). The blend with the higher portion of PP was used as such for board making. The blend with the lower portion of PP was mixed with PF resin in a resination drum (the ratio of PF to the dry weight of wood fibers 1:10), after which board making took place. For comparative reasons, acetylated fiber was put through a hammer mill as such (without an addition of PP) and resinated with PF powder, after which the blend was used for board making. Fig. 1 shows a schematic presentation of the different treatment phases carried out on the fiber material before the board making.

From the different fiber batches, fiber mats of 400 mm × 400 mm in surface area were made by brushing the fiber blends through a mesh. The mats were then pressed into boards using the following parameters: target density 750 kg/m³ and 1000 kg/m³, press temperature 180 °C, pressing time 60 s/mm, target thickness 4 mm. After the boards were released from the press, they were kept in an oven at 170 °C for 2 hours in order to assure a thorough reaction of the chemical throughout the whole board. The heat treatment was also carried out on the unmodified boards in order to eliminate interference of the heat treatment in the results.

2.2.2

Coating of veneer samples

Modification solutions for the veneer samples were prepared by diluting succinic or phthalic anhydride with acetone to a concentration of 10% (w/v). Application of the modification chemicals on the veneer samples took place by spraying and the procedure was regulated so that the spreading rates of approximately 20, 40 and 60 g/m² were achieved for the chemicals. After application of the succinic or phthalic anhydride solution, the veneer samples were air-dried. The preparation of the veneer samples was proceeded by pressing a PP/PA film (PP layer facing the wood surface) on the modified veneer surface using the following parameters: pressure 0.3 MPa or 0.9 MPa depending on film type, temperature 165 °C, pressing time 120 s followed by cooling down to

120 °C under pressure. Two replica veneer composites were made for each modification rate and film type.

2.3

Methods

2.3.1

Strength, dimensional stability and adhesion tests of the composites

The European Standard EN 310 was used to measure the modulus of rupture (MOR) and the modulus of elasticity (MOE) in bending of the fiber boards. The determinations were carried out by applying a load to the center of test specimens (150 × 50 × 4 mm) supported at two points. The distance between the supports was 100 mm and the rate of loading was adjusted so that the maximum load was reached within (60 ± 30) s. The bending strength of the specimens was given as the ratio of the bending moment (at the maximum load) to the moment of its cross-section. The modulus of elasticity was calculated from the linear region of the load-deflection curve. The internal bond (IB) strength of the test boards were determined according to the European Standard EN 319. The plane surfaces of square test specimens with a side length of 50 mm were glued to metal loading blocks using a two component epoxy glue. The metal blocks were attached with the grips of the test device (Fiskars) and the specimens were subjected to tensile force perpendicular to the board surfaces until rupture occurred. The maximum load was reached within (60 ± 30) s. For the determinations of the mechanical properties, six specimens (three specimens from two individual boards) for each density level and combination of binders and modifiers were used. Prior to the mechanical tests, the boards were conditioned at 65% relative humidity (RH) and 20 °C. The results of the boards with the lower target density were interpolated to the density of 750 kg/m³ and those of the boards with the higher target density to the density of 1000 kg/m³.

Determination of the dimensional stability of the fiber boards was carried out in accordance with the European Standard EN 317. In this method, the dimensional stability of square test specimens with a nominal side length of 50 mm (conditioned at 65% RH and 20 °C) was determined by measuring the increase in thickness of the specimens after immersion in water (20 °C, pH 7) for 24 hours. The specimens were placed in the water bath with their faces in vertical position. The data of the mechanical and the dimensional stability tests were subjected to statistical data handling through an ANOVA variance analysis and a Tukey's difference test in order to evaluate the significance of the modifications on the board properties. The statistical analyses were carried out separately for both density levels.

The effect of the chemical modifications on the adhesion properties of the PP films to veneer surfaces was studied by means of a 90° peel test. The test was performed according to the standard test of ASTM D 3167-76, which was slightly modified. The alteration of the standard concerned the width of the specimens: instead of specimens 12.7 mm in width, specimens 24.5 mm wide were used.

2.3.2

Scanning electron microscope (SEM)

Interfacial regions between the thermoplastic and wood in the fiber and veneer composites were studied by means of a JEOL JSM-820 scanning electron microscope using the back scattered electron detector (BSE). Prior to the SEM-studies, fiber board and veneer composite samples were conditioned at 65% RH after which a freezing microtome was used to smoothen the cross section surfaces of the samples. All the SEM-samples were vacuum-coated by evaporation with carbon. The accelerating voltage used to study the sample surfaces was 10 kV.

3

Results

3.1

Mechanical properties of the fiber boards

Table 1 presents the modulus of rupture of the fiber boards bonded with PF resin, polypropylene or both. The statistical analysis proved that no significant changes (at a confidence level of 95%) due to acetylation or succinic anhydride modification took place in the modulus of rupture of the boards bonded with PF resin or with the combination of PF resin and polypropylene. However, treatment of the fibers with maleic anhydride resulted in a significant decrease in the MOR values of the boards bonded with PF resin or with the combination of PF and polypropylene. The bending strength values of the modified boards bonded with polypropylene were 24 to 42% (the higher density level) or 70 to 120% (the lower density level) higher than the respective values of the control boards. The improvements were statistically significant at both density levels. The most improvement in the bending strength was observed for PP-bonded boards treated with succinic anhydride.

The effect of the different chemical modifications on the modulus of elasticity in bending of the fiber boards is presented in Table 1 at the two density levels. The MOE values of all the acetylated boards regardless of the binder type did not show any significant difference from those of the control boards. However, modification with maleic anhydride caused an increase of statistical significance in the MOE values of all the fiber boards. Modification with succinic anhydride significantly increased the MOE values of the boards bonded with PP or with the combination of PF and PP. The observations apply to both density levels. A significant increase in the internal bond strength of the fiber boards due to the succinic and maleic anhydride modifications was recorded (Table 1). The trend was recorded for all the binder types. Acetylation also seemed to cause an increase in the IB values of the boards, but the change from the control boards was statistically significant only in the case of the boards bonded with the combination of PF and PP.

The mechanical properties of the untreated and treated boards bonded with polypropylene were significantly inferior to those of the boards produced with PF or with the combination of PF and PP. The binder mixture of PF and PP resulted in boards (treated and untreated) with mechanical properties similar to those of the respective PF-bonded boards.

The dimensional stability test for the fiber boards was comprised of a 24 h water-soaking of the samples. The measurements of thickness swelling of the boards proved the modified boards had superior dimensional stability compared with the control ones (Table 1). The thickness swelling of all the modified boards did not exceed 10%, whereas the swelling of the control boards varied from 20 (PF + PP-bonded) to 47% (PP-bonded). Again, the effect of the modifications was most pronounced for the boards bonded with polypropylene. The changes in thickness swelling due to the modifications showed statistical significance.

Table 1. The effect of binder type and modification on the modulus of rupture, modulus of elasticity, internal bonding strength and thickness swelling of the fiber boards

Tabelle 1. Einfluß der Art des Bindemittels and der Modifikation auf MOR, MOE, Querkzugfestigkeit and Dickenquellung von Faserplatten

Treatment	Binder	Modulus of rupture MPa		Modulus of elasticity MPa		Internal bond strength MPa		Thickness swelling (%) 750–1000 kg/m ³
		Density level (kg/m ³)		Density level (kg/m ³)		Density level (kg/m ³)		
		750	1000	750	1000	750	1000	
Untreated	PF ¹	35.6	59.3	3022	5321	0.97	1.82	26.1
Acetylated		37.7	61.3	2895	5194	1.13	2.40	2.5
MA		29.6	53.2	3685	5985	1.91	2.69	5.6
SA		38.5	62.1	3265	5564	2.30	3.30	4.5
Untreated	PF+PP ²	35.8	59.5	2845	5144	1.02	1.91	19.5
Acetylated		35.7	59.4	2458	4758	1.56	2.53	1.8
MA		27.8	51.3	3153	5453	1.65	2.43	4.8
SA		34.2	57.9	2956	5256	2.13	2.94	5.2
Untreated	PP ³	12.3	35.9	1730	4029	0.37	1.22	47.3
Acetylated		20.9	44.6	2146	4446	0.45	1.67	5.7
MA		21.3	45.0	2482	4782	1.07	1.86	6.9
SA		27.1	50.8	2345	4644	1.56	2.22	6.7

Binder contents based on the dry weight of the wood fiber: ¹ 10%, ² 10%+10%, ³ 20%

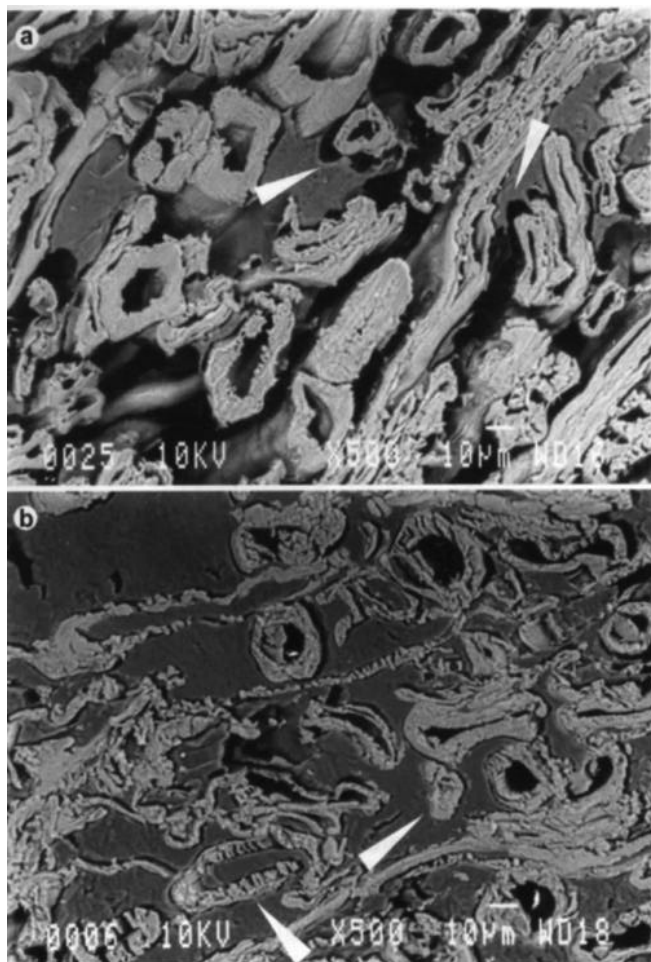


Fig. 2a, b. SEM micrographs showing detailed structure of (a) an unmodified and (b) a SA-modified fiber board bonded with polypropylene

Bild 2a, b. REM-Aufnahmen der Strukturen der PF-gebundenen Faserplatten aus: (a) unmodifizierten Fasern; (b) modifizierten Fasern mit Bernsteinsäureanhydrid

3.2

Morphology of the fiber boards

In the SEM studies, useful information on the interface/interphase between the wood fibers and polypropylene

was obtained (Fig. 2a, b). Wide gaps between the surfaces of wood and polypropylene seemed to occur frequently in the control boards (Fig. 2a arrows), whereas in the modified boards closer attachment between the two materials was often seen. Figure 2b shows a typical image of a SA-modified board showing evidence of the improved interaction between the wood material and polypropylene due to the modification (arrows). Overall scanning of the cross-sections of the fiber boards revealed that the polypropylene binder was more evenly distributed in the acetylated boards than in the control or SA- and MA-modified boards. Structural changes in the tracheids of wood, such as the collapse and delamination of cell walls as a consequence of the modification treatments, especially due to SA and MA treatment, were seen.

3.3

Adhesion studies of the coated veneer samples

The results of the PP-coated veneer samples subjected to the 90° peel test are presented in Table 2. Modification of the wood surface with phthalic or succinic anhydride increased the load needed to peel the PP/PA films off the wood surface. The increase in the peel strength values proceeded gradually with the increasing amount of the anhydride. At the higher anhydride levels, it was rather common that splitting of the two-layered films took place leading to a detachment of the upper layer (PA) from the PP layer attached firmly to the wood surface.

In addition to the increased peel strength values, the fracture of the modified specimens in peeling propagated differently compared with that of the reference specimens. Peeling a PP/PA film off an untreated wood surface resulted in a rather high wood failure ratio; in other words, small fragments of wood were pulled up from the untreated veneer surfaces with the plastic film. However, when the treated samples were subjected to the peel test, fragments of the PP layer were found sticking out from the wood surface after the test.

As revealed by Table 2, the initial peel strength along with the peel strength level reached by the modifications were dependent on the film type (film thickness), modification method and the parameters used to press the film

Table 2. The effect of modification of veneer with succinic and phthalic anhydride on the adhesion properties between polypropylene film and the wood surface

Tabelle 2. Einfluß der Modifikation des Furniers mit Bernstein- und Phthalsäureanhydrid auf die Modifikation Haft-eigenschaften zwischen PP-Film und Holzoberfläche

Treatment	Spreading rate (g/m ²)	Peel strength (N/mm)					
		Film 1 ¹		Film 2 ²		Film 3 ³	
		min.	max.	min.	max.	min.	max.
FA	0	0.29	0.35	0.16	0.24	0.23	0.31
	20	0.37	0.48	0.14	0.26	0.20	0.29
	40	0.44	0.53	0.22	0.31	0.31	0.47
	60	0.53	0.64	0.22	0.33	0.42	0.56
SA	0	0.38	0.47				
	20	0.42	0.45				
	40	0.52	0.63				

¹ PP layer 70 µm and PA layer 20 µm thick, pressure used 0.3 MPa

² PP layer 50 µm and PA layer 30 µm thick, pressure used 0.3 MPa

³ PP layer 100 µm and PA layer 60 µm thick, pressure used 0.9 MPa

on the wood surface. Modification with succinic anhydride appeared to lead to a better interaction between the PP/PA film and the wood surface than what was reached by means of phthalic anhydride.

3.4

SEM studies of the coated veneer samples

In the SEM studies of the veneer samples coated with PP/PA films, wide gaps between the unmodified wood substrate and the PP surface were observed along the interface

of the two materials, which is an indication of the poor adhesion of the film to the wood surface (Fig. 3a). Contrary to that, closer attachment of PP to the modified (phthalic anhydride, 20 g/m²) wood surfaces was observed (Fig. 3b). Further modification (40 g/m²) seemed to enhance interlocking (penetration) of the polypropylene film with the wood surface, as well as cause distortion and collapse of the wood cell structure (Fig. 3c).

4

Discussion

The surface quality of the fiber boards produced by pressing and modifying the boards simultaneously was not the best possible. Dark spots on the board surfaces, especially on the MA-treated boards, revealed that the distribution of the modification chemical and/or the PF resin was not even throughout the boards. Acetylated fibers were rather loose and did not form tight clumps. This may have been a reason for a satisfactory surface quality of the acetylated boards and for a better dispersion of the wood fibers with polypropylene (seen also in the SEM micrographs) than what was the case with the other modifications.

The modification treatments had a positive effect on the modulus of rupture and elasticity in bending as well as on the internal bond strength of the fiber boards bonded with polypropylene. Statistical analyses showed that these differences from the values of the control boards were statistically significant in the case of the boards treated with SA or MA, whereas the effect of acetylation was statistically significant on the MOR values only. In addition, the IB values of the boards bonded with PF or with PF + PP showed an increasing trend as a result of the modifications: the treatments with SA or MA caused an increase of statistical significance, the effect of acetylation was statistically significant only on the boards bonded with PF + PP. In general, significant impairment in the mechanical properties was only seen in the MOR values of the boards modified with MA and bonded with PF or PF + PP.

The acetylation procedure and the targeted degree of acetylation (20%) differed from those of the MA and SA

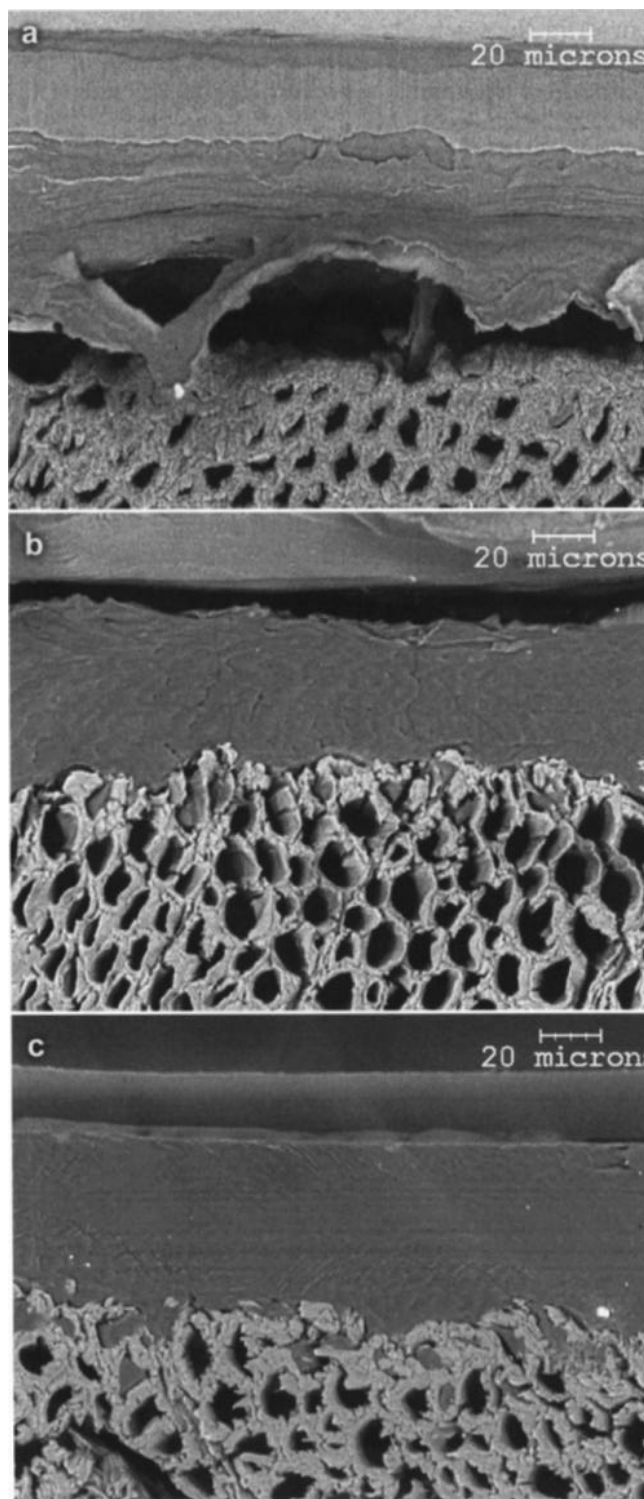


Fig. 3a, b, c. SEM micrographs of birch veneer coated with a PP/PA film (PP layer facing the wood surface): *a*) a view of a drastically poor interaction between the film and untreated wood surface, *b*) improved interactions between the two materials due to modification of the wood surface with phthalic anhydride (20 g/m²), penetration of PP and PA layers was often the result of the modification, *c*) improved interaction between the PP layer and the wood surface modified with phthalic anhydride (40 g/m²), penetration of PP to some of the wood cell lumens has taken place

Bild 3a, b, c. REM-Aufnahmen von Querschnitten durch Birkenfurniere mit PP/PA-Beschichtung (PP-Schicht an der Holzoberfläche): *a*) Blick auf eine äußerst schwache Wechselwirkung zwischen den beiden Materialien; *b*) verbesserte Haftung aufgrund der Modifikation der Holzoberfläche mit Phthalsäureanhydrid (20 g/m²); ein Spalt zwischen PP- und PA-Schicht war oft die Folge dieser Modifikation; *c*) verbesserte Haftung zwischen PP- und Holzoberfläche nach Modifikation mit Phthalsäureanhydrid (40 g/m²); PP ist an einigen Stellen in die Holzfasern eingedrungen

treatments (15%) which makes comparison between the modification chemicals inadequate. However, it is rather inconsistent that the MA and SA modifications showed very different effects on the MOR values of the thermoset-bonded boards. It is apparent that the carboxylic acid sites of MA and SA which remain unreacted with wood fibers cause a drastic drop in the pH of the boards. However, maleic anhydride is known to cause more acidic and hydrophilic conditions than succinic anhydride. Due to the acidity of the fiber material, phenol resin of the novolak type was particularly chosen as a binder since it is less susceptible to changes in pH than the resol type. Thus, the difference in the results of the two modifications is most likely due to the impaired surface quality of the MA-modified boards. Besides the uneven distribution of the chemicals and fiber, the impaired surface characteristics may result from partial degradation of the MA-treated board surfaces under the press by the combined effect of heat and acidity. Severe discoloration of the MA-treated boards supports this assumption.

The increase in the mechanical properties of the fiber boards due to chemical modification is an indication of improved interaction and stress transfer between the components. Some authors have reported that softening and increased thermoplasticity of wood fiber surface facilitates contact and dispersion of the fiber with thermoplastics (Maldas and Kokta 1993, Rowell and Clemons 1992). In addition, the esterification of wood with all the anhydrides studied, except acetic anhydride, has been shown to improve moldability of wood. The effect of the anhydrides on the moldability properties decreases in the following order: succinic>maleic>phthalic anhydride (Matsuda 1987, Rowell and Clemons 1992). The degree of thermoplasticity achieved by chemical modification depends on several factors: the type of the chemical, the degree of substitution, the method used and chemical composition of the fiber, just to mention a few. From the standpoint of reinforcing materials, it is essential that modification only takes place on the matrix of the fiber leaving the cellulose backbone unattacked (Rowell et al. 1994a).

In our SEM study, softening of some degree in the wood fiber due to SA and MA modifications was observed which appeared as increased distortion of the tracheids when pressed to boards. Based on the increase in the mechanical properties of the PP-bonded boards, it seems evident, however, that the fibers have not been subjected to any significant loss of strength and if so, compensation for the loss of strength by improved compatibility is taking place. According to the literature, the use of catalysts is needed in order to modify not only lignin and hemicellulose but cellulose as well (Rowell et al. 1994b). In the present study, no catalysts or solvents were used to carry out the SA and MA modifications, which supports the assumption of the limited effect of the modifications on the fiber strength. It is not excluded that in this study the improved interaction between the wood fibers and polypropylene is related to more similar surface energies and even to chemical bond formation between the components.

The enhancement of the mechanical and the adhesion Properties of the PP-bonded fiber boards due to modifi-

cation is in good agreement with the results of the PP-coated veneer samples. The pressing conditions of the veneer samples were such that no attachment of the PP film on the untreated wood surface was seen in the SEM micrographs or recorded by the peel test. Improved attachment of the two materials was evident due to the modifications. The SEM micrographs of the coated veneer samples often showed collapsed cell walls in the upper layers of the treated veneer surfaces indicating softening of the wood material by the modifications studied. Improved peel test values compared with control samples are partially attributed to a better anchoring of the PP coating in the wood structure through increased penetration depth. The absence of gaps between the PP layer and the veneer surface revealed by the SEM micrographs of the modified laminates also leads us to believe that the two materials are attracted to each other rather than repelling each other as was the case without a modification.

On the other hand, Boeglin et al. (1996) have reported that despite the lack of chemical compatibility between polyolefins and wood (unmodified), adequate mechanical adhesion between the materials can occur, leading to good mechanical properties of the composites. Evidence of the mechanical interlocking of the components in particleboards bonded with recycled polyethylene has been obtained by means of SEM micrographs which showed wood cell lumina filled with the plastic. Furthermore, particleboards bonded with recycled polyolefins have been proved to reach mechanical properties comparable to those of commercial particleboards (Boeglin et al. 1997, Pecina et al. 1998). Similarly, mechanical tests of composites composed of alternating layers of recycled paper and polyethylene sheets have shown that the bending properties of the composites do not differ much from those of commercial particleboards (Ellis et al. 1993). According to Gomez-Boeso et al. (1999), polyolefins perform well as binder materials for fiber boards but a slight improvement in the mechanical properties of the boards as a result of acetylation can be achieved. Furthermore, acetylation is explained to increase the surface free energy of wood fibers leading to improved wetting of the fiber surfaces with melting thermoplastics and thereby to improved interfacial shear strength between the materials (Liu et al. 1994).

The anhydrides studied here are known to form ester and hydrogen bonds with -OH groups of wood components (Rowell 1984). By reducing free -OH groups in wood, susceptibility of the wood material to water and thereby to swelling is reduced. Acetylation of fibers had been carried out on an industrial scale with controlled reaction times among other parameters which assures thorough modification throughout the whole fiber batch. Contrary to this, it was unclear to what extent the covalent ester bonding between the fibers and the powdered anhydrides (SA, MA) takes place during the short board pressing and post-treatment at 170 °C. However, the reduction in thickness swelling of the boards due to SA and MA modifications was considerable and did not differ from that of the acetylated boards, which leads us to conclude that the modification level in the wood fiber was sufficient to result in boards with good dimensional stability. Krzysik and

Youngquist (1991) have reported that by raising the PP binder level in non-woven web composites from 15% to 30%, the thickness swelling and water absorption of the composites halved. This was explained to be due to the encapsulation effect of the wood fibers by PP at the higher PP level. In this study, the relatively drastic thickness swelling of PP-bonded control boards (45%) reveals that the encapsulation effect of the wood fibers by PP hardly plays a role, and that the reduction in the swelling of the treated boards derives from the modifications.

5

Conclusions

Based on the results of the mechanical tests of the fiber boards, it can be stated that chemical modification of wood fiber by means of anhydrides was most beneficial for the fiber boards bonded with polypropylene, i.e., significant improvement in the mechanical properties and dimensional stability of the PP-bonded boards took place as a result of the modifications. The observations on the positive effects of the modifications on the compatibility between polypropylene and wood were supported by increased adhesion values between the polypropylene films and veneer surfaces due to different anhydride modifications. Additional information on the improved interaction between PP and wood due to the modifications was gained in the SEM studies of the fiber and veneer composites. In general, the modifications studied had a positive effect, although not always statistically significant, on the mechanical properties of fiber boards regardless of the binder used (PF, PP or both). Exceptionally, modification of wood fibers with maleic anhydride caused reduction in the modulus of rupture of PF- and PF/PP-bonded boards. Improved dimensional stability of the fiber boards due to the treatments was prominent in all the modification and binder types.

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