

TREATMENT OF PARTICLEBOARD CHIPS WITH ALKENYL SUCCINIC ANHYDRIDE

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ABSTRACT

Wood chips were first sprayed with pure alkenyl succinic anhydride (3 % wt/wt) and then cured ($130^{\circ}\text{C} \cdot \text{h}^{-1}$) with the objective to impart water repellency to UF-bonded particleboards. Unlike conventionally used paraffin wax, the anhydride can be covalently anchored to the chip surface by esterifying wood hydroxyl groups; however, the treatment resulted in increased thickness swelling (67 %) after 2 h water submersion and decreased internal bond strength (IB; 0.10 N mm^{-2}) as compared to controls (21 % and 0.95 N mm^{-2}). Wettability studies revealed that the surface polarity was increased after the anhydride treatment. FTIR analyses before and after extraction of non-bonded anhydrides showed that esterification did not occur during the curing step. Viscosity measurements indicated that the non-bonded anhydride on the chip surface was hydrolyzed to a dicarboxylic acid by the aqueous glue, which in turn induced premature condensation before pressing and affected bonding.

Investigations on veneer strips suggested that an esterification requires a solvent to provide the anhydride certain mobility for orientation. The hydrophobicity of pure alkenyl succinic anhydride seems to impair the attachment to wood hydroxyl groups and the spreading over the polar chip surface.

KEY WORDS: alkenyl succinic anhydride, esterification, hydrophobic agent, particleboard, surface modification

INTRODUCTION

Paraffin wax emulsions are generally used to provide particleboards with repellence to liquid water. Its addition gives good protection against short accidental wetting during subsequent process steps, construction, and service life. Paraffin does not, however, impart sufficient dimensional stability under severe climate conditions and extensive wetting. In contrast to paraffin, alkenyl succinic anhydride (ASA) can chemically react with wood hydroxyl groups. This grafting is assumed to enhance the moisture-related properties of wood-based panels and improve their applicability in Use Class 3 according to EN 335-1.

ASA has become the most important internal sizing agent for papermaking besides alkyl ketene dimer (AKD) since its introduction in the 1960s (Wurzberg and Mazzarella 1963). The economical success of these synthetic products is understood by the change in papermaking from acid to neutral/alkaline conditions that made a substitution of rosin acids necessary (Neimo 1999; Gess and Rende 2005). The purpose of sizing is to impart hydrophobicity against spreading of water and other liquids through the native fiber network. ASA's effect is generally attributed to a chemical reaction with the hydroxyl groups of fibers (Fig. 1). The molecule has an amphipathic character because of its polar anhydride group and the non-polar hydrocarbon chain with lengths of C₁₄₋₂₀. While the partially positively charged carbonyl C-atoms can undergo an esterification with a hydroxyl group and anchors the molecule to the fiber surface, the hydrophobic entity points outwards and provides water repellency (Hubbe 2006).

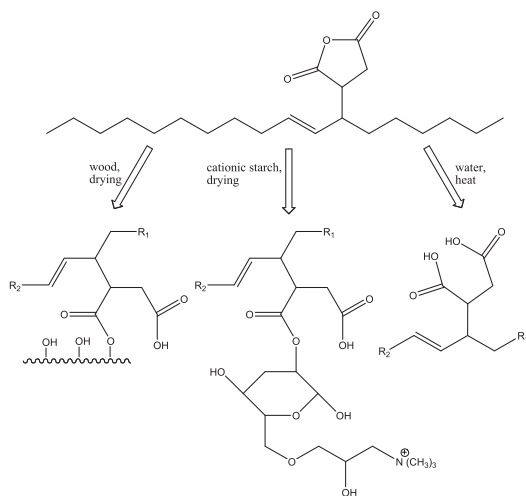


Fig. 1: Reaction pathways of AKD with wood compounds, cationic starch, and water

The molecule is formed by reacting maleic anhydride with an isomerized mixture of linear alkenes. ASA shows a comparatively higher reactivity than AKD does. It has been suggested that this is related to the ring strain of the cyclic anhydride group (Davis 1983). In addition, the adjacency of unsaturated groups to the anhydride group has been shown to determine the reactivity (Rossall 1975).

Both ASA and AKD are emulsified with a protective colloid – mostly cationic starch – in order to restrict hydrolysis. While AKD is supplied as an aqueous ready-to-use solution, ASA is usually emulsified on-site in the paper mill due to its higher reactivity. The hydrolysis depends strongly on the pH and the temperature. The optimum pH for ASA sizing ranges between 7.5 and 8.4 (Savolainen 1966).

Besides its usability for papermaking, ASA's applicability for wood modification has been investigated. The dimensional stability of Scots pine (*Pinus sylvestris* L.) sapwood that was modified with 2-octen-1-yl succinic anhydride (OSA) and succinic anhydride (SA) in pyridine was studied (Hill and Mallon 1998). Water-soak/oven-dry cycles revealed that the volumetric swelling coefficient in cycle one was larger in OSA-treated wood than in unmodified wood;

the coefficient was less in subsequent cycles. As compared, SA-treated samples exhibited low volumetric swelling coefficients after all cycles. Weight loss data indicated that the esters in SA-treated wood are more susceptible to hydrolyses than those in OSA-treated wood. It was inferred that OSA's alkyl chain rearranges within the cell wall during the first cycles and protects the ester bond against hydrolysis.

The durability of Scots pine sapwood treated with heptadecenylsuccinic anhydride in a soil block test (12 weeks) was examined (Codd et al. 1992). The treatment improved resistance against the brown rot fungi *Coniophora puteana* and *Gloeophyllum trabeum*. The effective threshold was assessed to be at a WPG of approx. 30 %.

Suttie et al. (1998) investigated the resistance against brown, white, and soft rot of ASA-treated Scots pine sapwood. The samples were reacted without catalyst to a WPG of 10 %. ASA did not affect moisture uptake and it was therefore concluded that ASA does not penetrate the cell wall. Although ASA reduced the weight loss as compared to the controls by 41 % (*G. trabeum*), 46 % (*C. versicolor*), 39 % (*C. puteana*), 45 % (*P. placenta*), it conferred little or no resistance according to the threshold of 3 % weight loss.

The resistance of ASA-modified stakes (*Pinus nigra*) in unsterile soil in a fungal cellar (20 months) was verified (Forster et al. 1998). Resistance increased up to a WPG of 10 % where the stakes showed a weight loss of approx. 12 %; above 10 %, no further improvement was observed.

ASA has also been investigated for compatibilizing wood and polypropylene (PP). Qillin et al. (1992) treated 100 % cellulose and 70/30 wt. % cellulose/PP composite sheets in solution and emulsion form. It was found that the treatment had little beneficial effect on mechanical properties.

Previous investigations revealed that cell wall modification with succinic anhydride (SA) results in increased dimensional stability of wood towards liquid water (Matsuda 1985; Hill and Mallon 1998). The crucial problem of up-scaling wood modification processes with SA depends on the solid state of the reagent at moderate temperatures (melting point at 117-119°C). Therefore, an even distribution over and inside the wood requires a sufficient organic solvent. The use of water is not possible due to hydrolysis. Most other chemicals that solve SA are problematic regarding their low swelling effect on wood, e. g., acetone (Shiraishi et al. 1973, Mantanis et al. 1994, Yildiz et al. 2005), their recovery due to a high boiling point, e. g., dimethylsulfoxide (Shiraishi et al. 1973, Matsuda 1985, Mantanis et al. 1994), and their harmfulness towards human health and environment, e.g., dimethylformamide, pyridine, and xylene (Evans 1998, Hill and Mallon 1998, Suttie et al. 1998, Marchetti et al. 2000).

ASA proves advantageous over SA for particleboard manufacture due to its fluidity as an oily liquid. This allows spraying it in its pure form onto chips at room temperature. The reaction is, however, assumed to be limited to the wood surface without using a wood swelling solvent since the molecule size of ASA is much greater as compared to SA. The present study investigated whether ASA bonds to the surfaces of particleboard chips and, thereby, increases the water repellency as compared to conventionally used paraffin.

MATERIAL AND METHODS

Panel manufacturing and testing

Industrial core layer chips (Pfleiderer Holzwerkstoffe, Gütersloh, Germany) were dried to 1 % MC in a rotating reactor (70°C, 1 h, 150 mbar, and 12 rpm). Afterwards, ASA (Hydrores AS 1000, Kemira, Krems, Austria) was sprayed onto the chips in a gluing drum (3 % based on

oven-dry wood). The wetted chips were then put into the reactor again (130°C, 1h, 1013 mbar, and 12 rpm).

A series of 1-layered particleboards was pressed at a target density of 700 kg m⁻³, consisting of 3 boards with ASA, 3 boards with paraffin, 3 boards made from chips that were cured in the reactor, and 3 boards from untreated chips. Urea-formaldehyde (UF) resin (Kaurit 350, BASF, Ludwigshafen, Germany, 9 % solid resin based on oven-dried wood) with an amount of 2 % potassium carbonate (based on solid resin weight) was used as binder. Paraffin served as reference (HydroWax 138, Sasol, Hamburg, Germany) that was blended with the UF resin (1 % solid paraffin based on oven-dried wood). The chips were resinated in a rotating gluing drum (target MC of 10 %) and subsequently formed to a mat using a wooden mould (450 x 450 mm²). Boards were pressed to a thickness of 20 mm for 12 s mm⁻¹, at 200 bar, and 200°C. Distance was controlled by using steel spacing strips. After pressing, the boards were trimmed and sanded to 410 x 410 x 19 mm³. Samples were conditioned (20°C / 65 %) and tested for thickness swelling (EN 317; n = 30), water uptake (n = 30), IB (EN 319; n = 30), and MOR (DIN 52362; n = 9).

Mesh analysis

The size distribution of chips was determined by using a sieve shaker (KS 1000, Retsch, Haan, Germany, speed = 90 rpm, t = 9 min). The analysis comprised 6 fractions with mesh sizes of 4, 2, 1.6, 1, 0.5, and 0 mm.

Viscometry

Viscosities of UF resin (Kaurit 350, BASF, Ludwigshafen, Germany) with different additions of ASA (10, 20, 30, and 50 wt. % on solid resin) were determined using a coaxial measure system (Rheolab MC1, Physika; Osterfildern, Germany). The test was carried out according to EN ISO 3129. The shear rate was 500 s⁻¹. The torque was automatically recorded at 40 measure points during a test period of 600 s.

Surface wettability

Wettability was determined on core layer chips and spruce veneer strips (40 x 40 x 0.7 mm³) according to the drop extension method described by Hundhausen et al. (2009). The drops (10 µl) were stained with picric aniline (5 % in distilled water). All samples were conditioned (20°C/65 % RH) prior to measuring.

Two droplets were randomly placed on 5 chips per treatment (CO and ASA). The picture rate was 5 s during a total measurement period of 15 s. Veneers were treated with ASA using 3 different procedures: 1) Two veneers were submersed in pure ASA in a glass reactor that was thermo-oil-regulated (130°C, 1 h). 2) Two veneers were sprayed, using an aerosol can, with an ASA/dimethylsulfoxide (DMSO) solution (10 % by volume) and cured in an oven (130°C, 1 h). 3) Two veneers were sprayed with an ASA/ethylacetate solution (10 % by volume) and cured in an oven (130°C, 1 h). The extension of 5 droplets per veneer was recorded by taking pictures every 5 s during a total duration of 15 s.

FTIR analyses

FTIR measurements were taken with a spectrometer (Vector 22, Bruker, Bremen, Germany) equipped with an ATR unit (DuraSampIRII, SensIR Technologies, Danbury, USA). Chips and veneers were characterized before and after extraction (10 h) with a mixture of toluene:ethanol:acetone (4:1:1 by volume) in a Soxhlet apparatus.

RESULTS AND DISCUSSION

Particleboards

The average thickness swelling of particleboards made from ASA-treated chips was already 67 % after 2 h water submersion (Fig. 2 A); in comparison, those of controls were at 21 % (CO) and 23 % (COtr). Boards with paraffin showed only 6 % swelling. Results of water uptake exhibited the same relationship between treatments. Measurements after 24 h were not carried out due to the poor stability of the ASA samples.

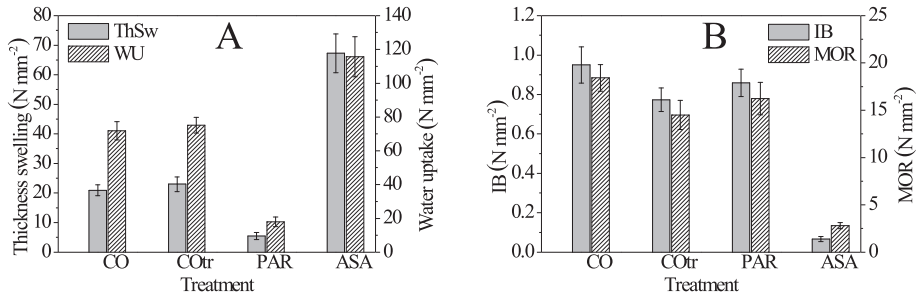


Fig. 2: Thickness swelling and water uptake after 2 h water submersion (A), and IB and MOR (B) of controls (CO), controls from cured chips (COtr), paraffin references (PAR), and boards with ASA (ASA)

The high thickness swelling of boards produced from ASA-treated chips is primarily attributed to impaired bonding. The treatment with ASA reduced IB by 93 % as compared to controls (CO, Fig. 2B). In addition, boards with ASA showed a thickness of approx. 21 mm instead of 20 mm after pressing. This springback clearly indicates insufficient bonding. As a consequence, the average density of boards with ASA showed merely 630 kg m⁻³. Although UF-resin is a very brittle adhesive (Zeppenfeld and Grunwald 2005), the considerable reduction in IB indicate that the strength loss is not only due to a mechanical destruction of UF bonds by stress concentration, which is induced by exceedingly high swelling of ASA-treated chips. It is rather assumed that non-bonded anhydride remained on the chip surface after curing; this was hydrolyzed to alkenyl succinic acids in the aqueous UF resin, which in turn initiated condensation before pressing and affected the bond strength. This hypothesis is confirmed by the viscometry measurements, which show that additions of ASA to UF resin increased the torque (Fig. 3).

Control boards made from untreated chips (CO) showed higher IB and MOR than those made from chips that were dried in the reactor (COtr). The loss in IB might be explained by hornification (Fengel and Wegener 1984, Newman and Hemmingson 1997, Gruber and Weigert 1998, Hakkou et al. 2005) and migration of extractives to the chip surface (Christiansen 1990) that affect the adhesion between UF resin and chip surface.

The lower MOR of COtr is probably based on two reasons: 1) A comparison with the IB suggests that the affected bonding had also a negative influence on the MOR. 2) The mesh analysis revealed that the agitator caused a decrease of the fractions 2-4 and > 4 mm due to shear strain during pre-drying and curing (Fig. 4). The reduced lengths resulted consequently in decreased bending strength.

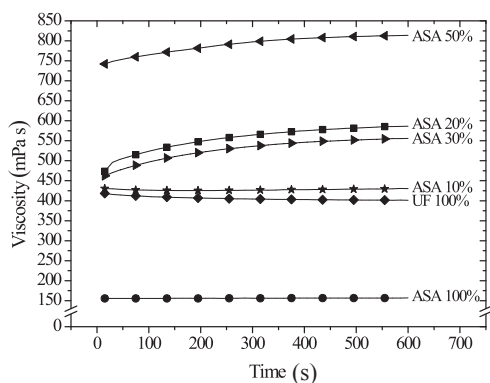


Fig. 3: Viscosities of UF resin over time dependent on ASA additions [% wt based on solid resin]

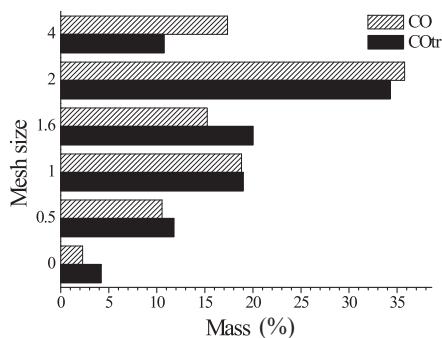


Fig. 4: Mesh size distribution of untreated chips (CO) and chips that were dried in the agitator reactor (COtr)

The surface wettability on ASA-treated wood chips was significantly greater than on controls (Fig. 5). ASA's effectiveness is generally assigned to a covalent anchorage by esterifying hydroxyl groups on fibers by most researchers in paper science (McCarthy and Stratton 1987, Neimo 1999, Gliese 2003, Hubbe 2006). If this applies, the hydrophilicity indicates that no ASA or only minor amounts were covalently bonded to the chips.

One explanation is that ASA did neither react with wood hydroxyl groups nor with water. The other explanation is that the surface was covered with hydrolyzed ASA (alkenyl succinic acid), which is strongly hydrophilic due to its two carboxylic groups. It remains, however, unclear at which point of time the hydrolysis should have occurred. The chips had been dried to 0.8 % MC right before ASA was applied in the rotary drum. After spaying, the chips were directly transferred into the reactor.

Typical bands in FTIR spectra of non-hydrolyzed ASA are at approx. 2921 and 2847 cm^{-1} that originate from methyl and methylene groups of the alkyl chain (Fig. 6). Characteristic bands of ASA's carbonyl groups appear at 1858 and 1781 cm^{-1} . In comparison, hydrolyzed ASA reveals only one dominant carbonyl peak at approx. 1707 cm^{-1} , which represents the

carboxyl group. The methyl/methylene bands coincide with those of non-hydrolyzed ASA. Other characteristic bands in the fingerprint range are difficult to identify in modified material because of a superimposition with bands of unmodified wood.

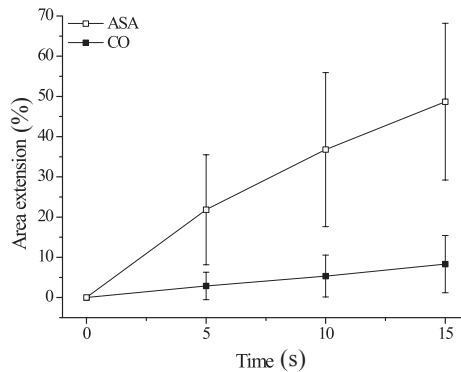


Fig. 5: Cumulative drop extension of droplets on untreated (CO) and ASA-treated (ASA) core layer chips

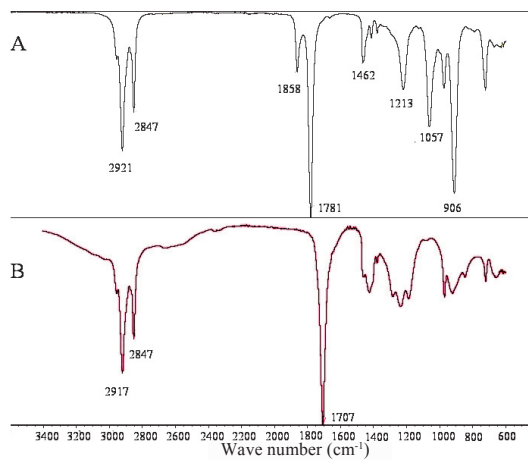


Fig. 6: FTIR transmission spectra of non-hydrolyzed ASA (A) and 100 % hydrolyzed ASA (B) (Kemira 2008)

Treated wood chips exhibited absorption bands at approx. 2921, 2847, and 1781 cm^{-1} that indicate the presence of ASA (Fig. 7 A). The absorption shoulder between 1735 and 1750 cm^{-1} found in wood chips before extraction indicates new formed ester groups (McCarthy and Stratton 1987); however, the highest absorption in the region of carbonyl resonance frequency was observed at approx. 1707 cm^{-1} that refers to carboxyl groups of alkenyl succinic acid (Fig. 6). It is therefore assumed that both hydrolyzed and non-hydrolyzed ASA was located on the chip surface after curing in the reactor.

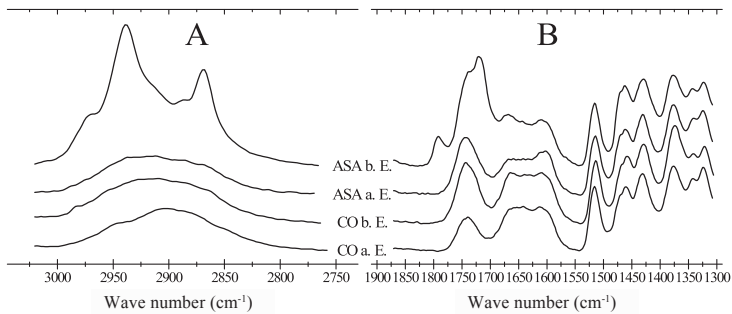


Fig. 7: FTIR spectra of ASA-treated chips (ASA) and controls (CO) before (b.) and after (a.) extraction (E.)

FTIR measurements after Soxhlet extraction did not show any signals for the presence of ASA (Fig. 7 B). This suggests that none of the applied ASA did esterify wood hydroxyl groups and was therefore removed by the solvents during extraction in the Soxhlet apparatus.

It seems that the hydrophobicity of pure ASA makes an attachment to the polar chip surface difficult and, hence, impedes an esterification of the wood hydroxyl groups. Normally, cationic starch is used as a stabilizer in ASA dispersions, protecting the anhydride from hydrolysis (Neimo 1999). But it also helps to attach the droplet to the negatively charged fiber surfaces (Isogai et al. 1996). Best performance of ASA protected by cationic starch was found at emulsion particle diameters of approx. 1 μm (Chen and Woodward 1986). The use of water and cationic starch for panel manufacture would, however, increase the particle size and further decrease the penetration ability of the already bulky ASA molecule. In addition, the high ratio of cationic starch to ASA (3-5:1) might be also problematic since the polar character of the starch increases the hydrophilicity of boards.

Veneers

The investigations on wood chips showed that esterification is not induced when pure ASA is applied. For this reason, different applications of ASA were investigated in order to find an appropriate method for particleboard production.

The wettability study on veneers revealed that none of the applications with ASA could increase water repellency as compared to the respective controls (Fig. 8). Veneers that were reacted in pure ASA at 130°C for 1 h (ASA) showed a higher wettability than those that were sprayed with an ASA/ethylacetate solution (ASAea). This was ascribed to the lower WPG of the latter (Tab. 1). ASA/DMSO-treated veneers, however, showed only a WPG of 12 % but highest wettability. This is attributed to remaining DMSO which can be clearly seen by the WPG of the controls (COdms). The WPG proves that DMSO did not completely evaporate during curing. In comparison, controls that were only cured at 130°C for 1 h (CO) and controls that were sprayed with pure ethylacetate (COea) showed no WPG.

Tab. 1: Masses of veneers before (b.) and after (a.) modification (M.) with the corresponding WPG

Treatment	Abbreviation	m b.M. (g)	m a.M. (g)	WPG (%)
Control	CO	0.4703	0.4696	0
Control with ethylacetate	COea	0.4684	0.4693	0
Control with DMSO	COdmsO	0.4409	0.4668	6
ASA 100%	ASA	0.4324	0.5195	20
ASA in ethylacetate	ASAea	0.4572	0.4873	7
ASA in DMSO	ASAdmsO	0.4450	0.4977	12

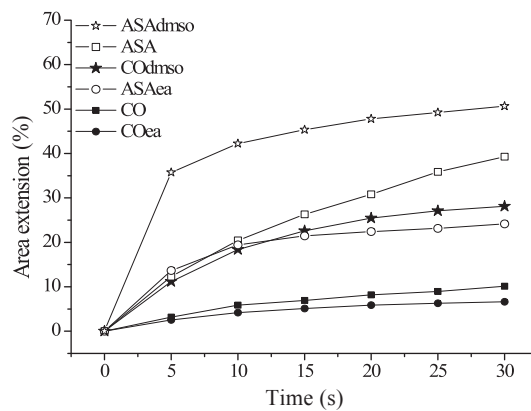


Fig. 8: Cumulative area extension of water droplets on veneers

Veneers that were treated with pure ASA in a glass reactor showed high absorption bands of non-hydrolyzed ASA at approx. 2921, 2847, 1858, 1781, 1462, 1213, 1057, 981, and 916 cm^{-1} after modification and before extraction (Fig. 9a). Same bands became evident in treatments with ethylacetate and DMSO (Fig. 9 c and e). The comparatively low absorption at veneers treated with a 10 % ASA/DMSO solution is probably explained by the poor solvability of the hydrophobic ASA in the rather hydrophilic DMSO. The chemicals dissolved in the aerosol can; hence, only a small amount of ASA was applied on the veneer surfaces.

The comparison of spectra taken before and after extraction reveals that ASA was completely removed when it was applied purely or in ethylacetate. In contrast, the use of DMSO caused an esterification, provided that only covalently bound ASA cannot be extracted. The spectrum after extraction showed increased absorption bands at 2921 and 2847 cm^{-1} in comparison to untreated veneers (Fig. 9e). These can also originate from methyl groups of remaining DMSO; however, reference measurements of pure DMSO revealed that the sulfur-oxygen double bond in DMSO absorbs at 1640 cm^{-1} . This band was not detected. Instead, bands between 1735 and 1750 cm^{-1} can be attributed to the formation of new ester bonds (Silverstein et al. 2005). The absence of a peak at 1707 cm^{-1} gives indication that hydrolyzed ASA was not present (McCarthy and Stratton

1987). The typical absorption band of ASA at 1858 cm^{-1} (Fig. 6A) were not obtained in treatments with DMSO. This band is characteristic for the anhydride group but disappears after reaction with hydroxyl groups or water.

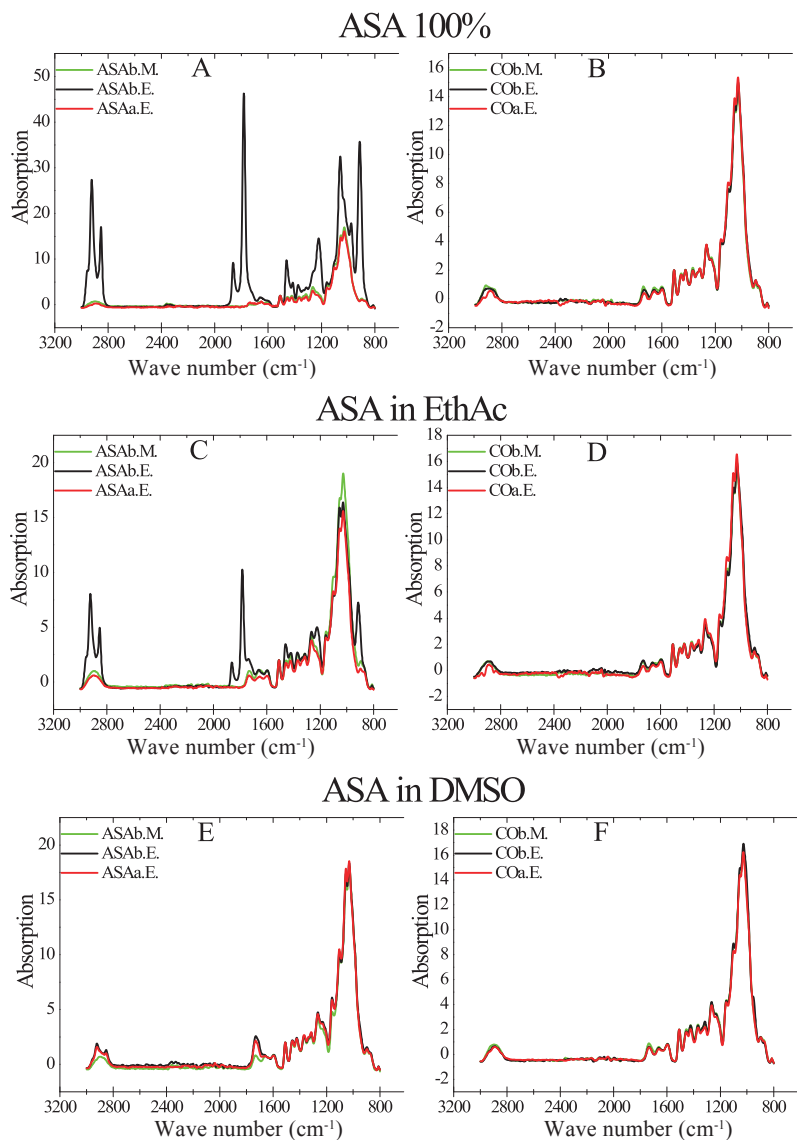


Fig. 9: FTIR spectra before modification (b. M.), before extraction (b. E.), and after extraction (a. E.)

The different FTIR results suggest that an esterification requires a certain mobility of the ASA molecule. DMSO was chosen due to its high boiling point that allows ASA to orientate

its carbonyl C-atoms towards the wood hydroxyl groups during curing. However, DMSO's high boiling point of 189°C and its poor miscibility with ASA are disadvantageous. Other solvents, such as xylenes, show better solvability with ASA and possess lower boiling points (135-145°C) than DMSO but are not useful because of their harmfulness to human health.

CONCLUSIONS

ASA does not increase the water resistance of particleboards when it is applied in its pure form. The FTIR analysis of chips showed that an anchorage on the surface by esterification does not occur. The chips were presumably covered with both non-hydrolyzed and hydrolyzed ASA. The high polarity of the surfaces led to increased wettability of ASA treated chips as compared to controls. Moreover, viscometry indicated that alkenyl succinic acids supply protons when UF resin is applied to the chips. This results in resin condensation before pressing and reduces the IB.

Tests on veneers suggest that an application of ASA in its pure form or in non-stabilized dispersions is not feasible for board manufacture. The use of stabilizers in water emulsions would, however, hamper ASA's penetration into the wood; moreover, it is assumed that the accumulation of stabilizers in boards would probably increase hydrophilicity.

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