

Use of alkyl ketene dimer (AKD) for surface modification of particleboard chips

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Abstract The study objective was to impart urea-formaldehyde (UF) bonded particleboards higher and longer-lasting hydrophobicity than that resulting from conventionally used paraffin. Alkyl ketene dimer (AKD) is a paper sizing agent that can theoretically esterify wood compounds and result in a surface modification. Particles were 1) impregnated with an aqueous AKD-solution and cured at 130 °C prior to gluing, or 2) sprayed with a mixture of AKD-solution and UF-resin in a single step. Boards with and without paraffin wax were used as controls. Thickness swelling after 2, 24, and 48 h immersion was decreased by 90, 62, and 59% when the chips were impregnated with AKD in comparison to untreated control boards. Water uptake after 2, 24, and 48 h was reduced by 91, 75, and 60%. AKD-impregnation with subsequent curing decreased the internal bond strength by 53%, indicating that AKD impedes the adhesion. The mixture of AKD and UF-glue did not result in considerable hydrophobicity. Increased methyl/methylene and carbonyl bands in FTIR-spectra after toluene-extraction suggest that AKD partially formed ester bonds at the wood surface.

Die Verwendung von Alkylketendimer (AKD) zur Oberflächenmodifizierung von Spänen für die Herstellung von Spanplatten

Zusammenfassung Das Ziel der Untersuchung bestand darin, Harnstoff-Formaldehyd (UF) gebundene Spanplatten stärker und dauerhafter zu hydrophobieren als es mit kon-

ventionell verwendeten Paraffinprodukten möglich ist. Alkylketendimer (AKD) wird in der Papierindustrie als Masseleimungsmittel eingesetzt und kann theoretisch mit Zellwandbestandteilen Esterbindungen eingehen. Holzspäne wurden 1) mit einer wässrigen AKD Lösung imprägniert und bei 130 °C getrocknet oder 2) mit einer AKD/UF-Harz Lösung besprüht. Platten mit und ohne Paraffinbehandlung dienten als Referenzen. Im Vergleich zu Platten ohne Hydrophobierungsmittel wiesen Platten aus AKD-imprägnierten Spänen nach 2-, 24- und 48-stündiger Wasserlagerung eine um 90, 62 und 59% verminderte Dickenquellung auf. Die Wasseraufnahme wurde um 91, 75 und 60% reduziert. Die AKD Imprägnierung führte zu einer Verringerung der Querkzugfestigkeit um 53%. Dies deutet darauf hin, dass AKD die Verklebbarkeit negativ beeinflusst. Die Anwendung von AKD im Untermischverfahren führte nur zu geringer Hydrophobierung. FTIR Messungen an Furnierstreifen vor und nach einer Toluolextraktion wiesen darauf hin, dass ein Teil des AKD über Esterbindungen auf der Holzoberfläche fixiert ist.

1 Introduction

The crucial application restrictions of wood-based panels are ascribed to their poor dimensional stability in changing climates and in contact with liquid water. While the swelling and shrinking behavior of boards parallel to the plane complies with that of solid wood parallel to the fiber, the values perpendicular to the plane are significantly greater (Amthor 1972). Swelling and shrinkage of wood particles and hydrolysis of the adhesives limit the application to low humidity conditions. The dimensional stability is influenced by board density, wood species, resin type, resin level, pressing conditions, particle geometry, and hy-

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drophobic agents (Haaligan 1970). To date, paraffin wax emulsions are usually added to improve moisture resistance. The typical amount of wax ranges from 0.3–1% based on the oven-dry weight of the particles (Youngquist 1999). Higher additions show only marginal hydrophobic effect and cause reductions in bonding strength (Müller 1962, Amthor and Böttcher 1984); however, the major problem of paraffin is that it decelerates the uptake of liquid water and the swelling but cannot impart durable hydrophobicity (Youngquist 1999).

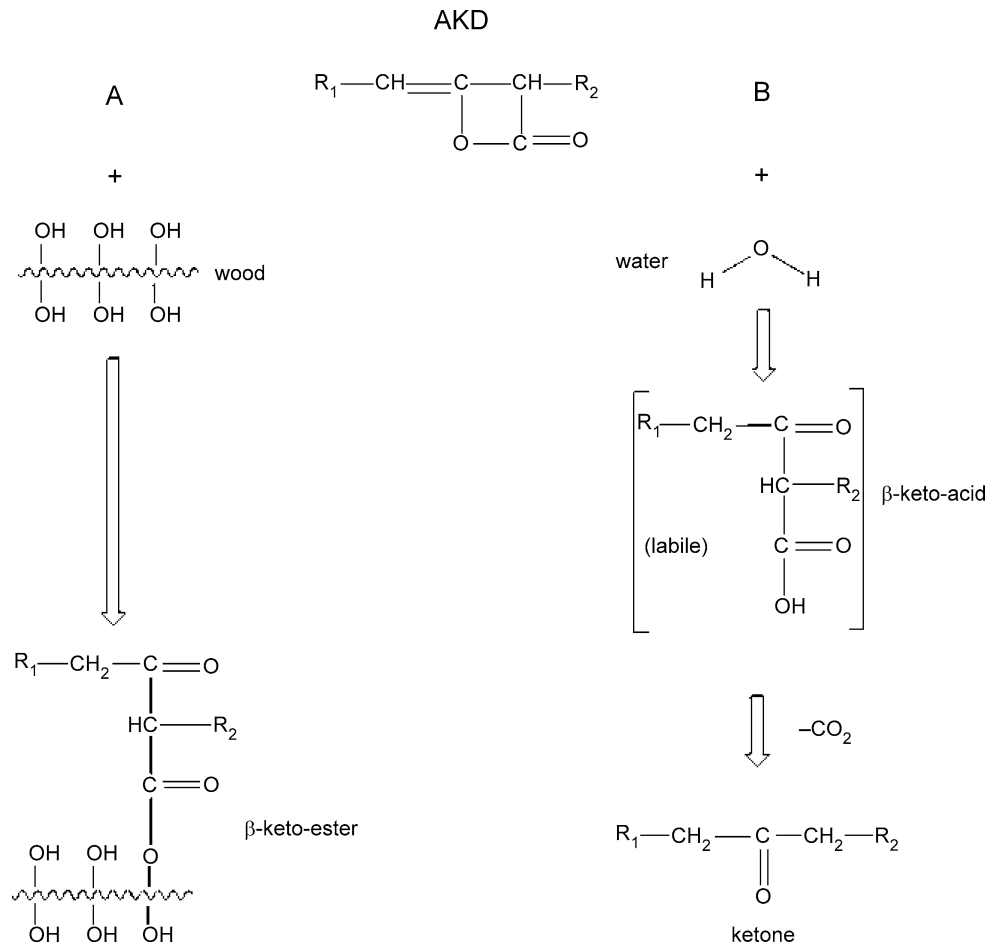
Besides the use of paraffin as a hydrophobic agent, a variety of treatments have proved as effective means to increase the water repellency of particleboards. Filcock and Vinden (2000) investigated the use of isocyanate resin to add water repellency to particleboards. Isocyanate-impregnated, not edge-sealed panels showed a thickness swelling of approx. 5% after 24 h as compared to control boards that revealed 17%. Several researchers reported that heat-treatment of particles leads to enhanced dimensional stability (Tomek 1966, Tomimura and Matsuda 1986, Boonstra et al. 2006). In addition, numerous studies on chemical modification have demonstrated that an

alteration of the wood cell wall structure can strongly increase the water resistance of particleboards. Kajita and Imamura (1991) studied the board properties made from chips that were treated with a low-molecular-weight phenol-formaldehyde resin. Particleboards at 20% WPG swelled less than 8%, while control boards swelled nearly 30% during two-hour boiling. Subiyanto et al. (1989) reported that boards made from acetylated chips bonded with isocyanate and phenol-formaldehyde swelled only 4% during 30 days of water immersion, whereas the control boards swelled over 20 and 30%, respectively. Further studies corroborating the dimension stabilizing effect by acetylation were carried out by Okino et al. (2004), Youngquist and Rowell (1986), and Rowell et al. (1986). Papadopoulos and Gkaraveli (2003) examined the performance of one-layer particleboards made from chips modified with propionic anhydride. The thickness swelling after 24 h was reduced by 46% as compared to controls.

Cell wall modification methods can strongly improve water-related properties but are expensive and difficult to implement in production processes of boards. The present

Fig. 1 Reaction mechanisms of AKD with wood hydroxyl groups **a** and water **b**. R_1 and $R_2 =$ C16–22

Abb. 1 Reaktionsschema von AKD mit Hydroxylgruppen des Holzes **a** und mit Wasser **b**. R_1 und $R_2 =$ C16–22



study, therefore, investigates the surface modification by alkyl ketene dimer (AKD), a widely used paper sizing agent. It is assumed that a superficial change of particles, fibers, or flakes in reconstituted wood products might impart a high and particularly permanent hydrophobicity in combination with the binder.

Internal sizing agents are used in the paper industry to accomplish resistance against fluids, improving paper properties like wet strength and printability. During the 1980s, the commonly-used rosin in combination with alum was increasingly substituted by cellulose-reactive systems, particularly based on AKD and alkenyl succinic anhydride (ASA) (Neimo 1999). Today, AKD is the most common internal sizing agent in Europe's papermaking industry. Typical addition lies between 0.05 and 0.2%, based on dry mass of fiber (Davis et al. 1956, Neimo 1999). ASA's and AKD's hydrophobic effect is predominantly ascribed to an esterification with the wood fiber's hydroxyl groups, as illustrated in Fig. 1 (Hubbe 2006, Seppänen 2007). The main difference between both sizing agents is the lower reactivity and hydrolysability of AKD. Thus, it is pre-emulsified by the AKD-manufacturer and shipped as a ready-to-use dispersion with maximum solid contents of 20–25% to the papermaker whereas ASA must be emulsified on-site at the paper mill. Both materials need to be stabilized to prevent hydrolysis and coalescing of the particles. Cationic starch is most commonly used as emulsifier. It is assumed that its quaternary nitrogen facilitates the attachment of the droplets to the negatively charged fiber surfaces. The ratio of AKD to starch is usually in the range of 1.5 : 1 to 4 : 1 whereas the ratio of ASA to starch is 1 : 2 to 1 : 4 (Neimo 1999). The lower starch content in AKD-dispersions can be presumably considered as advantageous for the use in particleboards since the hydrophilic nature of an emulsifier works counteractive to the aspired hydrophobicity (Amthor 1972).

While AKD has been extensively investigated in paper sciences (Lindström and Söderberg 1986, Quillin et al. 1992, Neimo 1999, Karademir 2002, Wei et al. 2002, Hubbe 2006, Seppänen 2007), there has been only one study found dealing with it in wood modification. Suttie et al. (1998) reported that AKD-treated samples with a WPG of 8.3% displayed high resistance against *Gloeophyllum trabeum*, *Coriolus versicolor*, and *Poria placenta*, but failed to prevent attack against *Coniophora puteana* in an EN 113 fungi test.

AKD emulsion particles show an average size of 1 µm (Neimo 1999). They can therefore not penetrate and modify the cell wall that has micropores in the region of 2–4 nm (Fengel and Wegener 1984). This makes it rather unsuitable for solid wood modification methods (Hill 2006), but interesting for wood-based panels where a surface modification in combination with a proper adhesion might yield improved properties.

2 Experimental

2.1 Wood and chemicals

The raw material for the particleboards came from Pfeleiderer Holzwerkstoffe (Gütersloh, Germany). Kaurit 350 (BASF, Ludwigshafen, Germany) was used as UF-resin (solid content of 66.5%). The AKD-dispersion Hydrores 157YC (Kemira, Leverkusen, Germany) is a commodity paper sizing product with a solid content of 16%, containing 10% active AKD, 2% cationic starch, and 4% cationic polymers as stabilizers. HydroWax 138 (Sasol, Hamburg, Germany) served as a paraffin reference (solid content of 50%). Knife-cut spruce veneer were obtained from Danzer Furnierwerke (Kehl, Germany).

2.2 Board production

Two different AKD-application processes were compared: In process 1, the AKD-dispersion was applied under vacuum/pressure and subsequently cured. In process 2, the AKD-dispersion was mixed with the glue and sprayed on the particles prior to pressing.

In process 1, the particles were filled into pillow cases to facilitate a better handling. Afterwards, they were submerged in a 1% (wt/wt) AKD-solution and subjected to vacuum (60 min/80 mbar) and pressure (120 min/12 bar) in order to accomplish a maximum penetration into the cell lumina (AKD im). After impregnation, the cases were centrifuged in a spin dryer to separate the bulk of non-absorbed solution. The particles were then put into a drying cabinet at 130 °C (24 h) to induce the reaction between AKD and wood. After curing, the weight percent gain (WPG) was determined as follows:

$$WPG[\%] = \frac{m_2 - m_1}{m_1} \times 100 \quad (1)$$

where m_2 [g] is the particle mass after curing and m_1 [g] is the dry particle mass before impregnation.

The control boards were made from particles that were water- (CO im) or paraffin- (PAR im) impregnated (1% solid content based on dry particle mass) and subsequently cured. Impregnation and curing parameters complied with those of the AKD-treatment.

In process 2, 1% AKD- or paraffin-dispersion (solid content based on oven-dry weight of particles) was blended with the UF-glue, respectively, and both were sprayed in a gluing drum on the particles (AKD bl, PAR bl). In addition to the paraffin references, boards without any hydrophobic agent served as controls (CO).

The gluing step took place in a rotary drum with two spraying nozzles that assured uniform distribution of the resins. Afterwards, the moisture content was measured

which enabled the calculation of the necessary particle mass for a target density of 700 kg m^{-3} . The resin content was 7% in the middle layer chips and 9% in the top layer chips based on the weight of dry resin solids and oven-dry weight of the particles. In the middle layer, the UF-resin contained 3.5% ammonium sulfate (based on solid resin weight) as hardener. The particles were spread by hand to a mat in a mould and cold-pressed with a deck to reduce mat thickness. Afterwards, the mat was pressed for 12 s mm^{-1} at 200°C in an electrical platen press (HP-S 200, Joos, Pfalzgrafeweiler, Germany). The board thickness was adjusted to 20 mm by steel bars. Three boards ($450 \times 450 \times 20 \text{ mm}^3$) per treatment were produced and eventually trimmed and sanded to $410 \times 410 \times 19 \text{ mm}^3$. The samples were tested for thickness swelling ($n = 30$), water uptake ($n = 30$), internal bond strength ($n = 30$), and bending strength ($n = 9$).

2.3 Veneer treatment

Five knife-cut spruce veneer strips ($50 \times 50 \times 0.7 \text{ mm}^3$) that showed radial orientation were immersed for 90 min in a 1% (wt/wt) AKD-solution and subsequently dried at 130°C for 24 h (AKD). Five untreated veneer strips served as controls (CO). Five veneer strips that were either treated with water (CO tr) or with a 1% (wt/wt) aqueous paraffin dispersion (PAR) before curing were used as references. All samples were conditioned at 20°C and 65% RH prior to measuring the surface wettability.

2.4 Determination of surface wettability

The drop extension method is based on the determination of the cumulative area increase of a deionized $5 \mu\text{l}$ water drop. Each treatment was represented by 2 veneers where 10 drops were randomly placed on. The water was stained with 5% aniline blue in order to enhance the contrast between drop and veneer. The extension was vertically observed through a reflected light microscope (S8AP0, Leica, Wetzlar, Germany) with a magnification factor of 10 equipped with a digital camera (DXM 1200, Nikon, Düsseldorf, Germany) that was interfaced with a computer. The software Lucia Image (Version 4.82) automatically took pictures every 10 s during the total measurement period of 120 s. The area extension was analyzed by using the software ImageJ (Version 1.4.3.67). The area at t_0 was set as 0% and the cumulative enlargement plotted against the measurement time.

Contact angles were captured and analyzed as constant wetting rate angle values (cwra) taking 1 picture/0.04 s during a total duration of 15 s by a goniometer (G 10 and DSA 1 software, Krüss, Hamburg, Germany). The dropping rate was $250 \mu\text{l min}^{-1}$. Each treatment was represented by 5 veneers. Five $10 \mu\text{l}$ droplets of deionized water were randomly applied on each veneer.

2.5 Extraction and FTIR-spectroscopy

The same AKD- and untreated veneers that were used for wettability studies were analyzed by a FTIR-spectrometer (Vector 22, Bruker, Bremen, Germany) with an ATR-unit (DuraSamplIRII, SensIR Technologies, Danbury, USA) operating on 32 scans and at 4 cm^{-1} resolution. Three measurements at randomly chosen spots were taken on each veneer. The spectra were base-line corrected and normalized to the lignin peak at approx. 1505 cm^{-1} . The point of measurement was marked on each veneer by redrawing the ATR-stamp. Subsequently, the strips were extracted with toluene in Soxhlet extractors for 10 h and FTIR-spectra were taken again.

2.6 Statistical analysis

Analysis of variance (ANOVA) was conducted to assess the differences between treatments in all tests. The confidence level was defined at the 0.05 probability level. Prior to the ANOVA, the Shapiro–Wilk test was used to determine whether or not the variables follow a normal distribution ($p < 0.05$). The computation of the drop extension method comprised values at 30, 60, and 120 s. The model for contact angle measurements included values after 15 s.

3 Results and discussion

3.1 WPG

Top layer particles that had been treated with AKD and paraffin revealed a negative WPG of -2.8 and -2.7% , respectively, whereas the water-impregnated particles of the control boards showed a WPG of -3.9% . In comparison, AKD- and paraffin-treated middle layer particles exhibited a WPG of -1.3% and -1.4% , the water-treated ones -2.4% . The overall mass loss is ascribed to the leaching of extractable wood compounds during the impregnation step. The differences in WPG of approx. 1% between controls and AKD-/paraffin-treated particles are attributed to the uptake of AKD and paraffin, respectively. Furthermore, it is assumed that more extractives were removed by the treatment solution from top layer particles than middle layer particles due to the smaller size of the former.

3.2 Thickness swelling and water uptake

Control boards made of untreated particles (CO) revealed highest thickness swelling and water uptake for all 3 dipping times (Table 1). In comparison, controls produced from water-impregnated and cured particles (CO im) showed slightly reduced values; this is mainly attributed to minor

Table 1 Mean values with standard deviations (in parentheses) of thickness swelling, water uptake, internal bond, and bending strength (CO = control; PAR = paraffin; AKD = AKD; bl = blended in UF resin; im = impregnated and cured). Different letters within a row indicate significant differences ($p = 0.05$) between treatments

Table 1 Mittelwerte mit Standardabweichungen (in Klammern) der Dickenquellung, Wasseraufnahme, Querzugfestigkeit und Biegefestigkeit (CO = Kontrollen; PAR = Paraffin; AKD = AKD; bl = Untermischverfahren; im = imprägniert und getrocknet). Unterschiedliche Buchstaben innerhalb einer Zeile bedeuten, dass die Behandlungen sich signifikant ($p = 0,05$) unterscheiden

		AKD bl	AKD im	PAR bl	PAR im	CO	CO im
Thickness	2h	9.3 (1.3) a	2.0 (0.5) b	1.5 (0.4) b	2.1 (0.8) b	19.7 (1.4) c	13.3 (0.4) d
Swelling [%]	24h	23.3 (1.4) a	10.4 (0.6) b	10.2 (0.5) b	10.7 (0.5) b	27.7 (1.6) c	23.1 (1.1) a
	48h	25.3 (0.9) a	12.3 (0.5) b	14.1 (0.5) b	13.7 (1.1) c	30.4 (1.5) d	25.4 (1.1) a
Water	2h	42.3 (6.8) a	6.6 (0.5) b	7.9 (0.6) c	4.2 (0.4) d	69.2 (5.0) e	60.4 (3.7) f
Uptake [%]	24h	72.5 (5.3) a	20.1 (0.9) b	24.8 (1.9) c	17.6 (2.4) d	80.9 (7.9) e	81.8 (3.2) e
	48h	82.2 (5.9) a	36.1 (1.0) b	43.4 (3.1) c	38.9 (2.2) d	89.8 (6.2) e	89.8 (2.9) e
Internal Bond [N mm ⁻¹]		0.53 (0.1) a	0.33 (0.1) b	0.64 (0.1) c	0.48 (0.1) d	0.70 (0.1) e	0.58 (0.1) f
Bending Strength [N mm ⁻¹]		10.1 (0.5) a	7.6 (0.3) b	10.9 (0.6) c	9.7 (0.7) a	11.3 (0.4) c	9.6 (1.0) a

structural cell wall changes that are known to occur at temperatures of 130 °C (Kollmann and Fengel 1965, Hill 2006). Specimens containing paraffin displayed strongly decreased swelling irrespective of the application method (PAR bl, PAR im). AKD imparted hydrophobicity comparable to the effect of paraffin when it was applied by impregnation followed by a curing step (AKD im). The swelling of AKD-specimens was even slightly lower after 48 h immersion (AKD im = 12.3%) than that of paraffin-specimens (PAR im = 13.7%, PAR bl = 14.1%). In contrast, the admixture of AKD to the resin caused only little hydrophobicity. The difference in effect of AKD can be attributed to at least 4 potential reasons:

1. The AKD is hydrolyzed before it can react with hydroxyl groups on the particle surface.
2. The pressing conditions (temperature and time) are insufficient for an esterification.
3. The hydrophobicity is based upon an orientation of the alkyl chains regardless whether it is anchored by an esterification. The pressing time is not sufficient for an orientation.
4. A physical hindrance by the UF-resin impedes a spreading of the AKD on the particle surfaces during spraying.

It is widely accepted, yet still debated, in the field of paper research that an esterification of the AKD is mandatory for the sizing effect (Neimo 1999, Hubbe 2006). The low amounts of AKD in the paper process, however, make a detection of covalent bonds and their quantification problematic (Karademir 2002). If it was assumed that the observed hydrophobicity in particleboards is also based upon an esterification, a hydrolysis of the ketene would impede a reaction with the hydroxyl groups on the particle surfaces. Nevertheless, a rapid hydrolysis in the aqueous glue before

pressing appears unlikely because the AKD-dispersion has a storage time of 4 weeks at 25–30 °C and the laboratory temperatures were approx. 18 °C during the production of the boards. Also a damage of the AKD-dispersion due to the pH-value of the glue is improbable because the AKD-dispersion has a pH of 2.5–4.5 at 20 °C and is stable until pH 8–9. The measured pH-value of the UF-glue, however, was 7–8. Even if the temperature and shear forces during mixing are assumed to be sufficient to cause pronounced hydrolysis, the question arises why this did not occur during the vacuum-pressure pre-treatment of the particles. Against this background, a hydrolysis caused by water vapor during pressing seems more probable.

Another reason for the different effects of AKD in processes 1 and 2 might be that the water-repellency is strongly related to a time-dependent orientation of the alkyl chains, regardless whether an esterification occurs or not. This might imply that the pressing time of 4 min in process 2 was insufficient for an alignment. The majority of researchers in paper science, by all means, believe that solely the combination of an esterification and a subsequent orientation plays a central role in achieving sizing (Neimo 1999, Hubbe 2006).

Moreover, unreacted AKD and hydrolyzed AKD in the form of ketones may contribute to hydrophobicity. AKD's and ketones have melting points of 50–53 °C and 79–85 °C, respectively (Neimo 1999, Karademir 2002, Wei et al. 2002), which are clearly exceeded during pressing at 200 °C. Most investigations, however, failed at making fibers hydrophobic by ketones or unreacted AKD (Hubbe 2006). One explanation could be that unanchored molecules are mobile and turn over, exposing their polar part (Seppänen 2007).

Furthermore, it appears likely that the UF-resin hampers physically the spreading of AKD considering the findings

Amthor (1972) reported for paraffin dispersions. His investigations revealed that almost each glue droplet contains evenly distributed emulsified paraffin particles. When the melting point is reached in the press, the paraffin droplets coalesce and form a paraffin film. The hardening of the UF-resin, however, countervails and impedes the spreading of the paraffin. It seems probable that the same mechanism occurs when AKD and UF-resin are mixed together. Yet, studies showed that the typical amounts of resin do not suffice a complete coverage of the particle surface (Wilson and Kraemer 1976, Scott 2001). This implies that AKD is located between the glue dots and, therefore, might react with wood hydroxyl groups when pressing times are extended to more than 12 s mm^{-1} .

3.3 Strength properties

All the treatments resulted in reduced internal bond and bending strengths (Table 1). Control boards produced from water-impregnated and cured particles (CO im) showed lower values than those made from untreated particles (CO). This can be explained by the formation of formic and acetic acid during the curing step (Roffael 1989). The acidity leads to the decomposition of carbohydrates, thus, to shear strength reduction (Boonstra et al. 2006) and promotes the hydrolysis of the UF-resin (Myers 1983).

In comparison to controls (CO), the addition of paraffin (PAR bl) and AKD (AKD bl) to the glue reduced the internal bond strength by 9 and 24%, respectively. Boards made from impregnated and cured particles exhibited the same trend but lower values for all treatments. In comparison to water-treated boards, the pre-curing with paraffin (PAR im) and AKD (AKD im) decreased the internal bond strengths by 17 and 43%. The findings arise the question why the gluability was considerably stronger affected by AKD than by paraffin although both agents resulted in comparable reduction in water uptake and thickness swelling.

The hydrophobicity of AKD and paraffin is basically determined by their alkyl chains of similar lengths. This suggests that the orientation of the chains is mainly responsible for the different bonding. It is hypothesized that those of paraffin rather arrange plane-parallel to the wood surface and provide numerous and evenly distributed interactions across the interface with the UF-resin, e.g., in form of van der Waals bonds (Schultz and Nardin 2003). In contrast, the hydrophobic entities of AKD turn out from the surface as the esterification proceeds onwards and enable a formation of fewer bonds to the UF-resin. In addition, it is well-known that the polycondensated resin provides strengths through a mechanical interlock by intertwining into the interspaces of wood (Packham 2003, Rowell 2005). It is assumed that glue and hydrophobic agent form a patchwork on the sur-

face. The accessibility of glue to the wood's microvoids might be more confined by AKD than by paraffin. This would be explained by the hypothesis of Lindström and Söderberg (1986) that AKD's region of action is far greater than the area which is actually occupied by the molecule itself in an anchored state.

3.4 Wettability of veneers

The wettability on veneer surfaces was determined to assess the hydrophobic effect of AKD and paraffin without the influence of adhesive and production parameters. The advantage to use veneers instead of particles is their homogeneous texture. Other influences than the hydrophobicity on the wettability, e.g., differences in surface roughness, knots, fiber deflection, were therefore considered as insignificant.

The drop extension measurements displayed that AKD- and paraffin-treatments reduced the wettability as compared to the controls (Fig. 2). The ANOVA-analysis for values after 30, 60, and 120 seconds did not indicate a significant difference between AKD- and paraffin-treated veneers at the 0.05 probability level. The areas slightly decreased which is accounted to evaporation and vertical penetration of the water into the veneer surface. The wettability of water-treated control veneers was also significantly lower than that of untreated veneers. This might be due to a hornification which was induced by the curing step. The phenomenon of hornification is well-known in pulp and paper sciences and has frequently been associated with the formation of irreversible or partially reversible hydrogen bonding caused by dry-

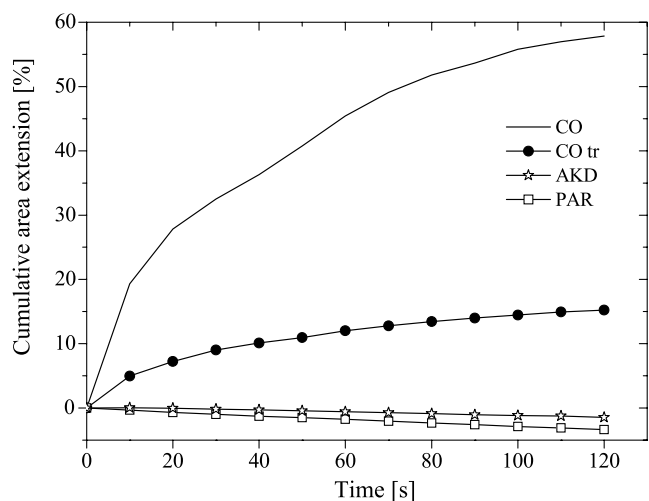


Fig. 2 Surface wettability determined by measuring the cumulative area extension [%] of drops on AKD- (AKD), paraffin- (PAR), water- (CO tr), and untreated (CO) veneer strips depending on time [s]

Abb. 2 Die Bestimmung der Oberflächenbenetzbarkeit mittels Messung der kumulativen Flächenvergrößerung [%] von Tropfen auf AKD- (AKD), paraffin- (PAR), wasser- (CO tr) und unbehandelten Furnierstreifen in Abhängigkeit der Zeit

ing (Newman and Hemmingson 1997, Gruber and Weigert 1998).

The results of the contact angle measurements mirrored the findings of the drop extension method (Fig. 3). The untreated control exhibited the most hydrophilic surface reflected by a constantly decreasing angle, whereas the AKD- and paraffin-treated veneers showed steady angles at approx. 120°. In contrast to the drop extension method, the ANOVA revealed that water-treatment resulted in similar wettability as AKD- and paraffin-treatment.

3.5 Extraction studies

The FTIR-analysis indicated that an esterification can occur at the applied curing conditions of 130 °C (Fig. 4). The spectra of the control sample before and after toluene extraction coincide. This suggests that toluene did not leach out significant amounts of wood extractives. The spectrum of the AKD-treated veneer before extraction exhibited absorption peaks at 1466, 1715, 2847, and 2913 cm⁻¹ that

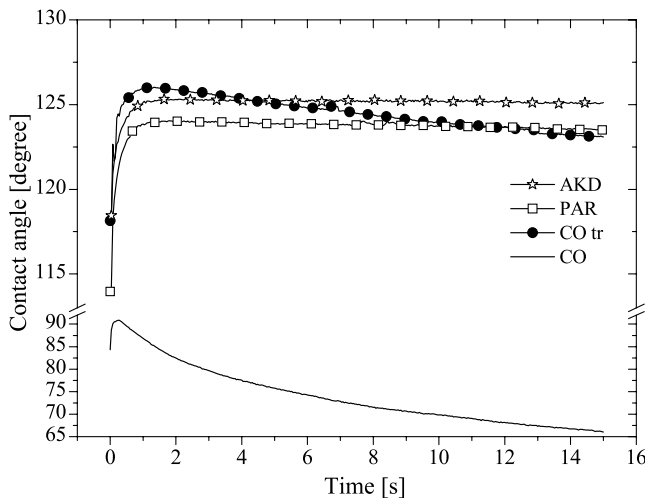


Fig. 3 Surface wettability determined by measuring contact angles [°] of deionized water droplets on AKD- (AKD), paraffin- (PAR), water- (CO tr), and untreated (CO) veneer strips depending on time [s]
Abb. 3 Die Bestimmung der Oberflächenbenetzbarkeit mittels Kontaktwinkelmethode anhand von AKD- (AKD), paraffin- (PAR), wasser- (CO tr) und unbehandelten Furnierstreifen in Abhängigkeit der Zeit

Table 2 Integral values [absorption units cm⁻¹] of control- (CO) and AKD- (AKD) spectra before (b.) and after (a.) extraction (E.) by toluene
Tabelle 2 Integrale [absorption units cm⁻¹] der FTIR Spektren von unbehandelten (CO) und AKD- (AKD) behandelten Furnierstreifen vor (b.) und nach (a.) Toluolextraktion (E.)

Band	Chemical group	CO b.E. [au cm ⁻¹]	CO a.E. [au cm ⁻¹]	AKD b.E. [au cm ⁻¹]	AKD a.E. [au cm ⁻¹]
2800–3000	methyl/methylene/methine	93	83	286	117
1750–1700	carbonyl	23	23	58	34

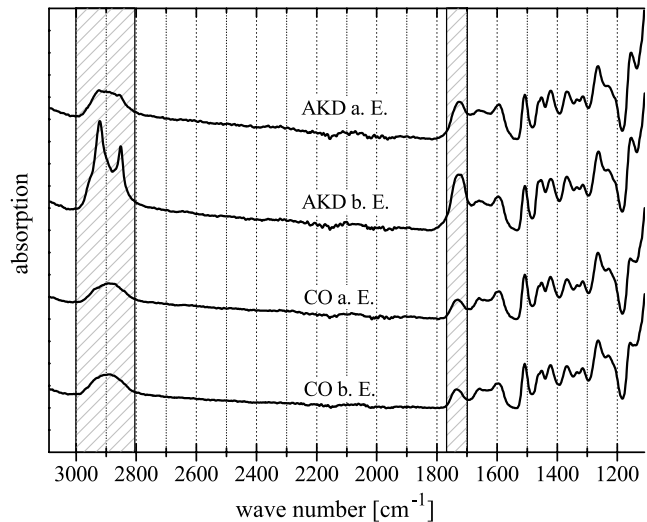


Fig. 4 FTIR-spectra of AKD-treated and untreated veneer strips before (b.) and after (a.) toluene extraction (E.)
Abb. 4 FTIR Spektren von AKD- und unbehandelten Furnierstreifen vor (b.) und nach (a.) Toluolextraktion (E.)

can be clearly assigned to AKD. Especially two bands are of greater interest: The one between 2800 and 3000 cm⁻¹ represents methyl and methylene groups of the alkyl chain in the AKD-molecule. The second band between 1700 and 1750 cm⁻¹ indicates carbonyl groups originating from both AKD (Fig. 1) and wood compounds, e.g., hemicelluloses and lignin (Hergert 1971). An esterification creates additional carbonyl groups (β -keto-ester) and counteracts the loss by non-bonded AKD due to extraction. A comparison of the AKD spectra and their integrals revealed that both absorption bands were strongly reduced after extraction but still exceeded those of control veneers (Table 2). Yet, the increase of the carbonyl band could be partially based on other ways in which AKD potentially reacts covalently. The adjacency of the protective colloid makes it likely that AKD preferably esterifies the cationic starch than the wood surface. Additionally, solvent extraction is theoretically able to remove non-bonded substances, e.g., ketones and unreacted AKD. But, it is less definite whether they also potentially extract oligomerized AKD and the polar products of cationic starch and AKD (Hubbe 2006).

Still, the comparison of FTIR-spectra before and after extraction gave strong indication that AKD is partially bonded to the wood although the reacted amount constituted a very small proportion of the total applied AKD. Several researchers applying spectroscopic and extraction methods have calculated the minimum fraction of bound AKD that sufficiently provides water-repellency on paper fibers. Lindström and Söderberg (1986) found that only 0.008 to 0.038% of esterified AKD, based on mass, are adequate. The lower level was assessed to comply with solely 4% of a monolayer of coverage. The water repellency was attributed to rotation and “wobbling” of esterified AKD-molecules, affecting a region significantly larger than it is taken by the molecule itself.

4 Conclusions

AKD reduced thickness swelling and water uptake of boards when the particles were previously impregnated and cured. The admixture of AKD to the UF-resin did not result in pronounced dimensional stability towards liquid water.

The water-repellency attained with AKD is predominantly ascribed to an esterification with wood hydroxyl groups and a subsequent orientation of the hydrocarbon chains. Though FTIR-spectroscopy indicated of ester formation, the strong absorption bands decreased after toluene extraction; this suggest that only a minor amount was covalently bonded. The contribution of esterification to hydrophobicity still remains unclear since it is possible that the reaction primarily takes place between AKD and its protective colloid (cationic starch) or wood.

A replacement of cationic starch by a colloid which is destroyed and evaporates during pressing would be desirable to reduce the hydrophilicity of panels.

Moreover, AKD affects the gluability more than paraffin does. This is explained by an orientation of AKD hydrocarbon chains that turn out from the particle surface.

With regard to the costly and time-consuming vacuum-pressure impregnation, it is of interest to investigate other application methods. One approach is to spray AKD separately to the glue on the particles.

The particle surface is presumably covered by a patchwork of glue and AKD. Extended pressing times could make a reaction of AKD possible, which is located between areas of glue. The implementation of the curing in the pressing step would supersede a pre-curing.

Further studies are in progress to investigate the influence of AKD-formulations on particleboard production.

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