

Procedural influence on the properties of particleboards made from AKD modified chips

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Abstract Wood chips were treated with alkyl ketene dimer (AKD) using three different processes to impart water resistance to particleboards. In the first process, AKD was blended with UF resin. Thickness swelling and water uptake after a 24 h immersion period (20 and 69%) were lower than in the control boards (28 and 81%) but were higher than in the paraffin references (10 and 22%). In process 2, AKD and UF resin were sprayed separately on the chips resulting in a greater reduction of thickness swelling (15%) and water uptake (49%) than in process 1. Paraffin references revealed a thickness swelling and water uptake of 7 and 25%, respectively. An extension of the pressing time in processes 1 and 2 did not increase water repellence. In process 3, particleboards were made from AKD-treated chips that were cured at 130 °C (24 h) prior to gluing. They showed a thickness swelling of 7% and a water uptake of 25%, whereas particleboards with paraffin exhibited levels of 8 and 29%. The thickness swelling and water uptake of boards with AKD increased when the curing time was reduced from 24 to 12 to 6 h (130 °C). Changing the curing temperature from 130 to 100 °C (12 h) had no effect on board properties. The IB of boards made from pre-cured chips with AKD (24 h/130 °C) was 44% lower than in controls and 35% lower than in paraffin references. This indicates that AKD impedes the adhesion.

Prozesseinflüsse auf die Eigenschaften von Spanplatten aus AKD behandelten Spänen

Zusammenfassung Holzspäne wurden in drei unterschiedlichen Prozessen mit AKD behandelt, um die Dimensionsstabilität der daraus gefertigten Platten zu erhöhen. Im ersten Prozess wurde die AKD Dispersion im Untermischverfahren mit der UF Leimflotte auf die Späne aufgebracht. Die Dickenquellung und Wasseraufnahme nach 24 h (20 und 69%) war niedriger als die der Kontrollplatten (28 und 81%), aber höher als jene der Paraffinreferenzen (10 und 22%). Im 2. Prozess wurden erst das AKD und anschließend die Leimflotte aufgesprüht. Im Vergleich zur AKD-Behandlung im Prozess 1 zeigten diese Platten eine geringere Dickenquellung (15%) und Wasseraufnahme (49%). Die Paraffinreferenzen des Prozesses 2 wiesen eine Dickenquellung und Wasseraufnahme von 7 und 25% auf. Eine Verlängerung der Presszeiten in Prozess 1 und 2 führte zu keiner erhöhten Feuchtebeständigkeit der Platten. Im 3. Prozess wurden die Späne jeweils mit AKD und Paraffin besprüht und vor der Beileimung bei 130 °C für 24 h getrocknet. Die Dickenquellung und Wasseraufnahme der Platten aus AKD behandelten Spänen lag bei 7 und 25%, jene von Paraffinreferenzen bei 8 und 29%. Die Verkürzung der Trocknungszeiten bei 130 °C von 24 auf 12 und 6 h führte zu erhöhten Dickenquellungen und Wasseraufnahmen von Platten mit AKD. Die Verringerung der Trocknungstemperatur von 130 auf 100 °C (12 h) hatte keinen Einfluss auf die Platteneigenschaften. Die Querzugfestigkeiten von Platten aus AKD vorbehandelten Spänen (130 °C/24 h) waren im Vergleich zu Kontrollplatten und Paraffinreferenzen um

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44 und 35% reduziert. Dies weist daraufhin, dass AKD die Verklebung mit UF Harz beeinträchtigt.

1 Introduction

Wood-based panels have become increasingly specialized and have been used in a wide range of applications in recent years. Their application in moist conditions has, however, been very limited due to their susceptibility to liquid and vaporous water. The moisture content essentially determines the different characteristics of the products. The uptake and release of liquid and vaporous water result in swelling and shrinking, which are most pronounced in the direction perpendicular to the plane. Thickness swelling is explained by a swelling of the wood itself and recovery from compression stress imparted during pressing. While the first is reversible, the latter is not. The uptake of moisture can, consequently, cause destruction of the adhesive-wood bonds and result in significant strength loss (Klauditz 1954, Neusser et al. 1965, Gatchell et al. 1966, Ernst 1967).

The dimensional stability of panels is dependent on a number of process variables, e.g., resin level, board density, wood species, particle geometry, blending quality, and pressing conditions (Neusser et al. 1965, Haaligan 1970, Schneider et al. 1982). But even if these parameters are optimized, the use of a hydrophobic agent – most commonly paraffin wax – is still required. The disadvantage of paraffin, however, is that it only decelerates water uptake and does not offer permanent protection against water damage (Roffael and Schneider 1981).

There has been extensive research done on wood modification to produce panels with high dimensional stability. These can be divided into active and passive methods depending on whether the cell wall polymers are changed or not. Furthermore, a distinction has been made between bulk and surface modification. The former implies that the modification reagent is distributed throughout the entire cell wall, the latter that the chemical alteration is confined to the wood surface (Hill 2006).

Numerous studies have shown that thermally induced changes of the macromolecular components result in improved water repellency of wood-based panels (Tomek 1966, Burmester and Deppe 1973, Tomimura and Matsuda 1986, Boonstra et al. 2006, Paul et al. 2007). Chemical bulk modifications induced by various organic reagents have been successful in increasing the dimensional stability of boards (Youngquist and Rowell 1986, Fujimoto et al. 1988, 1991, Korai 2001, Papadopoulos and Gkaraveli 2003, Yildiz et al. 2005).

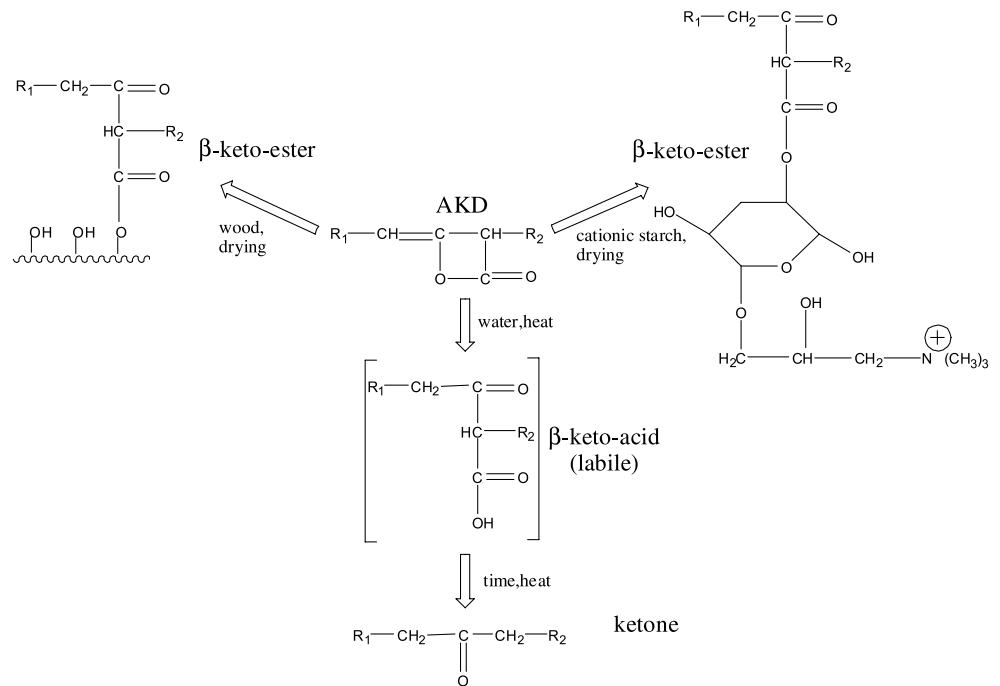
In contrast to chemical and heat modification, the so-called impregnation modification method is considered to be one of the passive procedures. Such processes include an

impregnation step using a solution of low molecular weight that diffuses into the cell wall and subsequently polymerizes. This leads to a condition where the reagent is locked without covalently reacting with cell wall compounds (Hill 2006). Phenol-formaldehyde resins were used for impregnating OSB strands (Wan and Kim 2006) and particles (Kajita and Imamura 1991); the boards displayed strongly reduced swelling following water submersion as compared to controls. Isocyanate-bonded waferboards which exhibited high dimensional stability were produced from DMDHEU-treated chips (Yusuf et al. 1995).

Bulk modification methods are based on the premise that the reagents gain access to the interior of the wood cell wall. Solute exclusion measurements have shown that the maximum diameters of the cell wall micropores are within the range of 2–4 nm in fully swollen wood (Hill et al. 2004). To insure that penetration occurs throughout the cell wall in solid wood treatments, vacuum/pressure is usually applied prior to curing. This impregnation process is, however, time-consuming and costly and is therefore not suited for manufacturing wood panels. It is necessary to consider whether bulk modification is adequate for products used in certain applications that do not exceed Use Class 3 (formerly Hazard Class) according to EN 335, e.g., particleboards as claddings or MDF boards in exterior doors. A surface modification of particles, fibers, or flakes in reconstituted wood products might be sufficient in combination with the adhesive to impart high and particularly durable water repellency.

Alkyl ketene dimer (AKD) has been shown to improve dimensional stability of particleboards (Hundhausen et al. 2008). Contact angle and drop extension measurements on AKD-treated veneer strips have revealed strongly reduced surface wettability. Hydrophobicity has been primarily attributed to the formation of β -keto-esters (Fig. 1), although extraction studies using FTIR-spectroscopy have indicated that only a small amount of the total AKD applied actually esterified wood hydroxyl groups. Besides esterification of wood hydroxyls, AKD may undergo other reactions, such as esterification with cationic starch (emulsifier) or hydrolysis with water. It is also noteworthy that the formed β -keto-ester may be thermally cleaved during hot-pressing of the wood chips.

Water resistance equal to that of paraffin treated references was attained when chips were impregnated and cured at 130 °C for 24 h prior to board production (Hundhausen et al. 2008). In comparison, the admixture of AKD to UF glue did not have any great effect. This was most likely due to the hydrolysis of AKD by water vapor during pressing; however, there is a possibility that the pressing time (4 min) was too short to induce an esterification between AKD and hydroxyl groups of wood. An extension of the pressing time could cause the reaction during pressing and thereby supersede an extra curing step prior to panel manufacturing.

Fig. 1 Possible reaction pathways of AKD**Abb. 1** Mögliche Reaktionen von AKD

The hypothesis that the formation of β -keto-esters plays a major role in achieving hydrophobicity coincides with many results obtained from studies on AKD in paper sciences. It is widely accepted that the esterification between AKD and wood hydroxyl groups is the primary mechanism for paper sizing (Lindström and Söderberg 1986, Nahm 1986, Neimo 1999, Hubbe 2006).

2 Materials and methods

2.1 Materials

The wood chips were supplied by Pfeleiderer Holzwerkstoffe (Gütersloh, Germany). The AKD dispersions Hydrores 150M and 452N (KEMIRA, Leverkusen, Germany) have a solid content (s.c.) of 12 and 21%. Both products contain 10% active AKD and 2% cationic starch (based on s.c.). UF resin Kaurit 350 (BASF, Ludwigshafen, Germany) was used as a control (s.c. = 66.5%). HydroWax 138 (SASOL, Hamburg, Germany) served as a paraffin reference (s.c. = 50%).

2.2 Methods

2.2.1 AKD application and process variables

The experiment was designed to test and compare three processes (Fig. 2). In the first process, AKD (1% based on oven-dry weight of chips) was mixed with UF resin and sprayed on wood chips. In the second case, AKD and UF

resin were applied separately and in the third, the wood chips sprayed with AKD were cured in a high temperature dryer prior to gluing and pressing. In processes 1 and 2, three different pressing times at 200 °C (12, 30, and 60 s mm^{-1}) were employed to investigate whether a curing can be implemented in the pressing step. In process 3a the impact of three different curing times at 130 °C (6, 12, and 24 h) on the particleboard properties were examined. In process 3b the curing temperature was 100 °C (12 h).

2.2.2 Panel manufacturing and testing

A series of 81 particleboards was produced at a target density of 700 $kg\ m^{-3}$. Each treatment was represented by 3 panels ($450 \times 450 \times 20\ mm^3$) that were trimmed and sanded to $410 \times 410 \times 19\ mm^3$. The resin content was 7% for the core layer chips and 9% for the face layer chips. An amount of ammonium sulphate (3.5% based on resin solid weight) was used as a hardener and mixed with the liquid UF resin for the core layer. The glue was applied in a rotary drum with an internal spray nozzle. The resinated chips were, then, spread by hand into a mat using a wooden frame. They were subsequently pre-pressed to reduce the mat thickness, and finally hot-pressed in a platen press (HP-S 200, Joos, Pfalzgrafenweiler, Germany).

Before testing, samples were conditioned at 20 °C and 65% RH and until they reached equilibrium moisture content. All panels were tested for internal bond strength (IB; $n = 30$), modulus of rupture (MOR; $n = 9$), thickness swelling ($n = 30$), and water uptake ($n = 30$). Analysis of

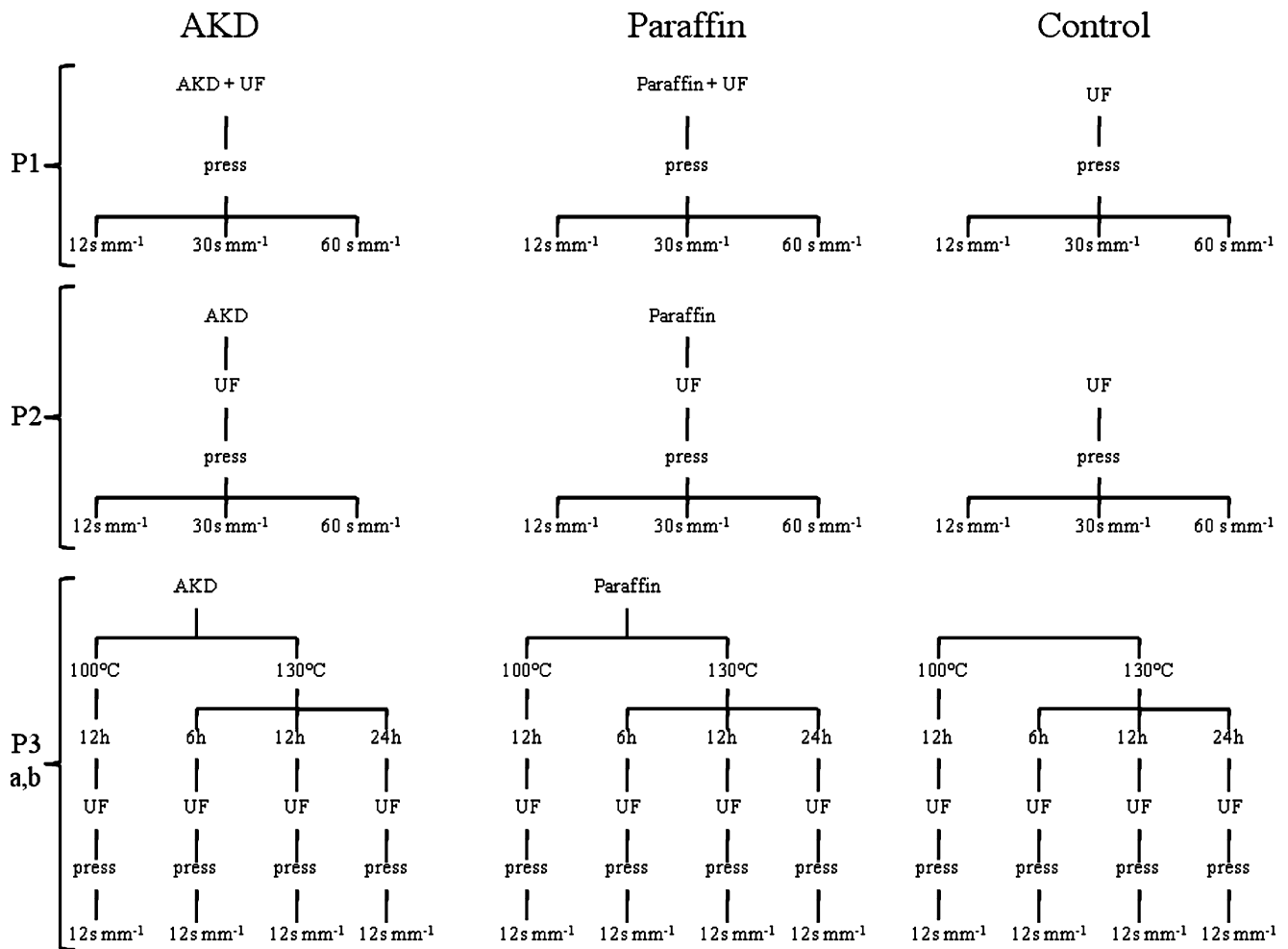


Fig. 2 Overview of process 1 (P1), process 2 (P2), and process 3 with 100 and 130 °C (P3a and b)

Abb. 2 Überblick über die Prozesse 1 (P1), 2 (P2) und 3 bei 100 und 130 °C (P3a und b)

variance (ANOVA) was performed to compare the means of each particleboard test ($p < 0.05$). All data were checked for normality according to Shapiro-Wilk ($p < 0.05$).

2.2.3 Assessment of IB failure

The fracture surfaces of IB samples from process 3a (130 °C/24 h) were sprayed with a solution of *p*-dimethylaminocinnamaldehyde (DACA) in ethanol and half concentrated hydrochloric acid (5 : 2 V/V) in order to stain UF resin red (Schriever 1981, Künniger 2008). Each treatment was represented by 10 samples. After spraying, the samples were stored in a drying cabinet at 105 °C (20 min); subsequently, the surfaces were digitized at a resolution of 1200 dpi with a color calibrated scanner (Epson Expression 10000 XL, Meerbusch, Germany). The red color percentages of the total areas were analyzed using the software ImageJ (Version 1.4.3.67). Areas of bark pieces were not taken into account. The red stain was defined by a threshold in a HSB color space that was applied for all measurements.

3 Results and discussion

3.1 Thickness swelling and water uptake

3.1.1 Process 1

In the first process (12 s mm⁻¹) the admixture of AKD to UF resin decreased thickness swelling by 28% as compared to controls (Table 1, P1). In comparison, the use of paraffin reduced swelling by 65%. Water uptake followed the overall trend of thickness swelling.

The results coincided with previous findings that indicated a low hydrophobic effect of AKD when it was applied after being mixed with UF resin (Hundhausen et al. 2008). Four potential reasons have been proposed. 1) AKD is hydrolyzed before it can react with hydroxyl groups on the particle surface. 2) A physical hindrance caused by the UF resin impedes spreading of the AKD on the particles during spraying. 3) The pressing conditions (temperature and time) are insufficient for esterification and orientation. 4) Esteri-

Table 1 Mean thickness swelling and water uptake values with standard deviations of controls (CO), paraffin references (PAR), and boards from AKD-treated chips (AKD) after 24 h submersion. P1 = process 1, P2 = process 2, P3 = process 3, a = curing temperature of 130 °C, b = curing temperature of 100 °C**Tabelle 1** Mittelwerte mit Standardabweichungen der Dickenquellungen und Wasseraufnahmen von Kontrollen (CO), Paraffinreferenzen und Platten mit AKD (AKD) nach 24 h Wasserlagerung. P1 = Prozess 1, P2 = Prozess 2, P3 = Prozess 3, a = Trocknungstemperatur von 130 °C, b = Trocknungstemperatur von 100 °C

		Thickness swelling [%]			Water uptake [%]		
		CO	PAR	AKD	CO	PAR	AKD
P3 ^b	12 h	23.5 (1.4)	7.1 (0.6)	11.8 (1.6)	76.4 (4.0)	30.2 (2.9)	35.1 (2.2)
P3 ^a	6 h	23.9 (1.5)	6.7 (0.5)	12.9 (2.3)	80.2 (6.0)	25.9 (2.2)	37.9 (5.8)
	12 h	22.8 (1.6)	7.1 (0.7)	11.1 (2.0)	81.0 (5.1)	30.1 (3.0)	34.7 (3.7)
	24 h	22.4 (1.3)	7.6 (0.9)	7.3 (1.5)	78.3 (4.8)	29.1 (3.6)	24.7 (1.5)
P2	12 s	27.8 (1.6)	6.8 (0.5)	15.0 (1.8)	80.9 (7.9)	25.4 (2.0)	48.5 (8.3)
	30 s	28.7 (2.4)	10.8 (2.0)	15.3 (2.3)	88.0 (6.5)	31.7 (2.2)	42.5 (5.2)
	60 s	26.4 (2.4)	10.6 (1.1)	12.0 (2.1)	82.6 (7.0)	31.1 (2.2)	40.4 (3.9)
P1	12 s	27.8 (1.6)	9.7 (2.1)	19.9 (1.7)	80.9 (7.9)	22.2 (2.4)	68.6 (6.7)
	30 s	28.7 (2.4)	6.7 (0.9)	19.0 (3.2)	88.0 (6.5)	26.5 (1.9)	63.3 (5.4)
	60 s	26.4 (2.4)	11.6 (2.2)	19.6 (1.8)	82.6 (7.0)	38.3 (3.3)	57.5 (7.1)

ification is not required for hydrophobicity, but the pressing time is too short for a physically based orientation.

The results do not point to a significant contribution to the hydrophobicity of unreacted AKD and hydrolyzed AKD in the form of ketones. Depending on their chain lengths, AKDs and ketones have melting points of 50–53 °C and 79–85 °C, respectively, and should therefore cover the chips' surfaces during pressing (Neimo 1999, Karademir 2002, Wei et al. 2002). The amphipathic character of AKD might also enable orientation through purely physical mechanisms. Elevated temperatures, which allow AKD to spread, may promote polar carbonyl groups to orient themselves towards the wood surface while the non-polar alkyl chains are directed outwards (Christiansen 1990). Such orientation should, however, also be possible with regard to ketones but most investigations in paper science have been unsuccessful in their attempts to impart hydrophobicity to fibers through ketones (Karademir et al. 2004) or unreacted AKD (Karademir and Hoyland 2003). Seppänen (2007) has proposed that unanchored molecules are mobile and may turn over exposing their polar part.

Amthor (1972) reported that the hardening of the UF resin hampers the spreading of paraffin when both are applied in a mixture. Microscopic analysis showed that nearly all glue droplets contained emulsified paraffin particles. Assuming that a patchwork-like pattern is formed on the chip surface, Hundhausen et al. (2008) have proposed that a similar mechanism occurs when AKD is mixed with UF resin. It was implied that pressing times over 12 s mm⁻¹ make the esterification of AKD possible which is located between the dried adhesive.

However, boards with AKD that were pressed for 30 and 60 s mm⁻¹ displayed thickness swelling (19 and 23%) similar to boards that were pressed for 12 s mm⁻¹ (20%). Thus, an extension of the pressing time could not induce an ester-

ification indicating that AKD was either hydrolyzed in the water-born UF glue or by water vapor during pressing.

3.1.2 Process 2

Boards were produced with chips that were sprayed separately with AKD and UF resin to validate whether AKD hydrolyzed prior to pressing in process 1. The back-to-back application of AKD and UF resin reduced swelling by 46% (12 s mm⁻¹) as compared to controls (Table 1, P2). In comparison, paraffin caused a decrease of 76%. The increased hydrophobicity displayed in process 2 as compared to process 1 indicates that separate spraying resulted in enlarged coverage of the chip surfaces by paraffin and AKD.

The extension of the pressing time from 12 to 30 s mm⁻¹ did not reduce thickness swelling of boards made from AKD treated chips (15 and 15%), whereas boards manufactured at 60 s mm⁻¹ showed a swelling of only 12%. In contrast to controls and paraffin references, the water uptake of boards made from AKD-treated chips decreased with increasing pressing time (49, 43, and 40%). The results, however, were not explicit enough to make it possible to conclude that an esterification occurred during extended pressing. It was, therefore, inferred that hydrolysis of AKD most likely took place during pressing and not within the adhesive system.

3.1.3 Process 3

AKD imparted higher hydrophobicity to particleboards in process 3 (130 °C) than in processes 1 and 2 (Table 1, P3). Boards showed thickness swelling of 13, 11, and 7% and water uptake of 38, 35, and 25% after curing for 6, 12, and 24 h, respectively. The fact that the effectiveness of AKD in processes 1 and 2 differ in comparison to process 3 supports

the theory that esterification is crucial for achieving a high level of water repellence. While AKD was apparently hydrolyzed during pressing in processes 1 and 2, esterification took place during pre-curing in process 3. The decrease in thickness swelling and water uptake with increasing curing time is a further indication that covalent bonding occurred. Esterification might be facilitated through the effect of temperature over longer time periods. It is also imaginable that anchored AKD molecules function as templates for non-esterified AKD molecules causing them to orientate their alkyl chains outwards. This alignment might stem from hydrophobic interactions between alkyl chains of bonded and unbonded molecules. Similar patterning by hydrophobic interactions is, for instance, known to occur among alkanes.

However, the reduction of the curing temperature from 130 to 100 °C (12 h) did not result in significantly different thickness swelling. Thus, 100 °C were sufficient to obtain esterification and orientation. This seems possible considering that temperatures typically range between 100 and 130 °C at the end of a drying section in a paper machine (Baumann and Herberg-Liedtke 1994).

Most studies in paper science state that AKD is partially anchored by esterification to the fiber (Neimo 1999, Hubbe 2006). AKD's mode of function is not explicitly explained because the small amounts used in paper manufacture make an assessment of the covalently bonded portion difficult (Karademir 2002). Analytic detection can apparently be simplified by applying more AKD to wood; however, the bulkiness of the emulsion particles impedes the access into the cell wall and limits the reaction to hydroxyl bonds on the wood surface. This is also reflected in the board properties made from chips that were treated differently prior to curing. Vacuum pressure impregnation (Hundhausen et al. 2008) led to thickness swelling and water uptake (10 and 20%) which were similar to spraying (7 and 25%).

FTIR analyses before and after toluene extraction on veneer strips treated with AKD and cured (130 °C/24 h) indicated that a minor fraction of AKD reacted with wood hydroxyl groups under the curing conditions applied (Hundhausen et al. 2008). In addition, Lindström and Söderberg (1986) have reported that only 0.008 to 0.038% of bonded AKD is sufficient for paper sizing. They speculated that the area of action of AKD is greater than the area that is occupied by the molecule itself. This could be explained by the two alkyl chains orientating outwards from the fiber surface.

3.1.4 Long-term water immersion

All three board types in process 3 showed continuous thickness swelling and water uptake for more than 12 d (Fig. 3). The relationship between swelling and water uptake was similar for controls and paraffin references. In contrast, water uptake and swelling of AKD-treated specimens revealed

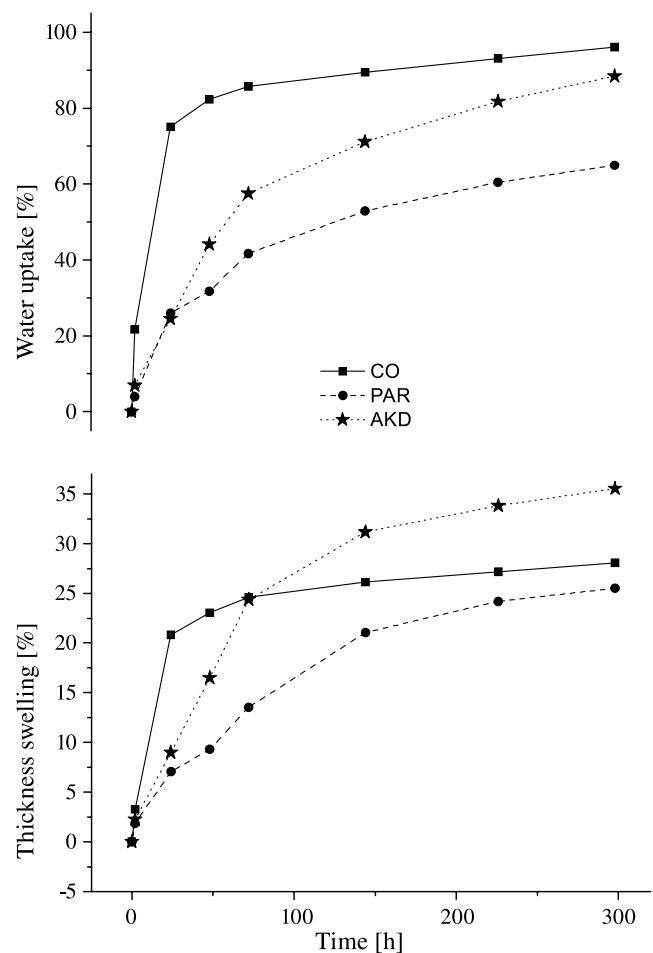


Fig. 3 Long-term (2, 24, 48, 72, 144, 226, and 298 h) thickness swelling and water uptake of controls (CO), paraffin references (PAR), and AKD-treated (AKD) specimens of process 3a (curing: 130 °C/24 h)

Abb. 3 Langzeit- (2, 24, 48, 72, 144, 226 und 298 h) Dickenquellung und Wasseraufnahme von Kontrollen (CO) Paraffinreferenzen (PAR) und Platten mit AKD (AKD) des Prozesses 3a (Vortrocknung: 130 °C/24 h)

different trends. While swelling of AKD samples exceeded that of paraffin references after 24 h and even that of controls after 3 d, water uptake kept below that of controls. Despite their high thickness swelling and water uptake, AKD treated specimens floated longer on the water surface than the paraffin references and the controls did.

Hundhausen et al. (2008) conducted surface wettability studies on veneer strips which had been either impregnated with AKD or paraffin and then cured. The results displayed contact angles and drop extension rates for both treatments which were statistically similar. It thus follows that the high level of thickness swelling of AKD specimens can primarily be explained by the failure of the glue bonds at the interface between resin and wood. The high water uptake of AKD treated samples can be ascribed to water filling interspaces between chips rather than to water that penetrated into cell

Table 2 Mean IB and MOR values with standard deviations (in parentheses) of controls (CO), paraffin references (PAR), and boards from AKD-treated chips (AKD). P1 = process 1, P2 = process 2, P3 = process 3, a = curing temperature of 130 °C, b = curing temperature of 100 °C
Tabelle 2 Mittelwerte der Querkzugfestigkeiten (IB) und Biegefestigkeiten (MOR) von Kontrollen (CO), Paraffinreferenzen (PAR) und Platten mit AKD (AKD). P1 = Prozess 1, P2 = Prozess 2, P3 = Prozess 3, a = Trocknungstemperatur von 130 °C, b = Trocknungstemperatur von 100 °C

		IB [N mm ⁻²]			MOR [N mm ⁻²]		
		CO	PAR	AKD	CO	PAR	AKD
P3 ^b	12 h	0.57 (0.05)	0.47 (0.05)	0.36 (0.03)	14.2 (1.6)	11.7 (1.3)	10.6 (1.0)
P3 ^a	6 h	0.58 (0.06)	0.43 (0.04)	0.37 (0.04)	13.6 (1.2)	12.1 (1.3)	10.2 (0.8)
	12 h	0.57 (0.07)	0.47 (0.05)	0.37 (0.04)	13.5 (0.9)	11.8 (1.1)	11.3 (1.0)
	24 h	0.59 (0.04)	0.51 (0.06)	0.33 (0.03)	13.1 (0.6)	11.7 (1.4)	10.9 (0.9)
P2	12 s	0.68 (0.04)	0.62 (0.06)	0.55 (0.11)	15.1 (0.3)	15.0 (1.4)	13.2 (1.9)
	30 s	0.57 (0.06)	0.61 (0.07)	0.58 (0.12)	15.4 (2.7)	14.2 (1.5)	12.9 (1.3)
	60 s	0.61 (0.08)	0.54 (0.05)	0.49 (0.05)	13.1 (1.6)	11.5 (1.5)	10.7 (0.5)
P1	12 s	0.68 (0.04)	0.62 (0.03)	0.58 (0.05)	15.1 (0.3)	12.1 (0.2)	13.5 (2.1)
	30 s	0.57 (0.06)	0.69 (0.06)	0.60 (0.04)	15.4 (2.7)	13.8 (1.7)	12.6 (1.3)
	60 s	0.61 (0.08)	0.56 (0.06)	0.51 (0.04)	13.1 (1.6)	10.2 (0.8)	10.8 (0.8)

walls. The influence of hydrolysis at 20 °C was regarded as negligible (Zeppenfeld and Grunwald 2005) although it might have had a minor influence considering the length of water submersion.

3.2 Strength properties

3.2.1 Process 1

Boards pressed with AKD for 12 and 30 s mm⁻¹ revealed slightly increased IB (0.58 N mm⁻², 0.60 N mm⁻²) in comparison to boards pressed for 60 s mm⁻¹ (0.51 N mm⁻²) (Table 2, P1). Similar results were obtained from boards with paraffin (0.62 N mm⁻² (12 s mm⁻¹), 0.69 N mm⁻² (30 s mm⁻¹), and 0.56 N mm⁻² (60 s mm⁻¹). IB of controls made at 60 s mm⁻¹ (0.61 N mm⁻²) and 30 s mm⁻¹ (0.57 N mm⁻²) were lower than those made at 12 s mm⁻¹ (0.68 N mm⁻²). The strength losses indicated at 60 s mm⁻¹ were also reflected in MOR. The hydrolysis of UF resin was probably facilitated by increased temperatures in the core layer during extended pressing times. In addition, elevated temperatures intensified the formation of acids that, in turn, further increased hydrolysis (Poblete and Roffael 1985, Roffael 1989).

3.2.2 Process 2

IB of paraffin and AKD-treated boards was slightly decreased compared to process 1 (Table 2, P2). MOR did not reveal significant differences between the first and the second process. Successive spraying of hydrophobic agent and resin led to higher repellency than did spraying with a mixture. It can therefore be assumed that the more evenly distributed paraffin and AKD on the chip surface therefore affected penetration and weakened the mechanical interlock between the binder and wood (Schultz and Nardin 2003). Paraffin, however, created higher water resis-

Table 3 DACA-stained UF resin on fracture surfaces of IB specimens
Tabelle 3 Mit DACA angefärbtes UF Harz auf Bruchflächen der Querkzugproben

Treatment	Mean (STDEV) [%]
CO	66 (13.7)
PAR	67 (9.1)
AKD	53 (10.1)

tance but slightly less reduction in bonding than did AKD in processes 1 and 2.

3.2.3 Process 3

Controls made of pre-cured chips (130 °C) exhibited a reduced IB of 15 (6 h), 16 (12 h), and 13% (24 h) in comparison to controls made from untreated chips in the first two processes (12 s mm⁻¹) (Table 2, P3). This reduction might be ascribed to a heat-induced decomposition of carbohydrates which results in increased brittleness and is also reflected in reduced MOR. Temperatures above 150 °C are generally considered to have a severe influence on wood composition and properties (Militz 2008) even though minor alterations in the cell wall structure can already occur at approx. 130 °C (Hill 2006). Yet, strength losses of controls made from chips cured only at 100 °C (12 h) point more to bonding failure than cell wall degradation. Organic acids were most likely formed during curing and facilitated the hydrolysis of the UF resin (Myers 1983, Roffael 1989). Adhesion might have also been affected by hornification (Fengel and Wegener 1984, Newman and Hemmingson 1997, Gruber and Weigert 1998, Hakkou et al. 2005) as well as migration of extractives to the chip surfaces (Christiansen 1990). Both mechanisms are known to reduce the wettability and could have consequently impeded the penetration of UF glue into the chips.

The IB of paraffin references (130 °C) decreased by 26 (6 h), 18 (12 h), and 14% (24 h) in comparison to controls. The strength losses due to AKD treatment (130 °C) were even greater: IB was reduced by 36 (6 h), 35 (12 h), and 44% (24 h). AKD imparted considerable hydrophobicity and at the same time reduced gluability only when chips were cured before pressing. This suggests that a heat- and time-induced orientation, probably based on esterification, is required to attain water repellency. In contrast, paraffin caused high water repellency in all three applications but affected adhesion much less than did AKD in process 3. Since both chemicals have alkyl chains of similar lengths, the alignment on the chip surface probably governs adhesion. It is known that the structure of *n*- and iso-alkanes influences hydrophobicity as well as physical-technological particleboard properties (Stegmann and Durst 1964, Roffael et al. 1982).

The staining of the IB samples with DACA displaced an evenly distribution of UF resin in control boards and paraffin references (Table 1). In contrast, boards made from chips that were AKD treated showed a smaller red-stained area and a spotty coverage by the UF resin. It is assumed that the higher IB of controls and references can be attributed to a stronger adhesion between UF resin and wood, which leads mainly to cohesion failures within the glue line. This caused that UF glue remained on both parts of the test specimen in nearly equal shares. In comparison, AKD decreased bonding and the IB samples showed numerous adhesion failures in the interface between resin and wood, thus, one part of the sample was red-colored and the counterpart was not. The spotty distribution indicates that AKD hampered a spreading of the resin. It is, however, unclear why paraffin did not affect the distribution of the UF glue to a similar extent as AKD did, since contact angles on paraffin and AKD-treated veneer strips revealed same surface wettabilities (Hundhausen et al. 2008).

4 Conclusion

The way in which AKD was applied to the wood chips processes 1, 2, and 3 had a major influence on particleboard hydrophobicity. Differences in thickness swelling and water uptake strengthen the hypothesis that esterification with subsequent orientation is a precondition for achieving water repellency. AKD's low efficacy in processes 1 and 2 can be mainly attributed to hydrolysis by water vapor during pressing. Esterification with the protective colloid (cationic starch) might also be an impairing factor. Thus, the extension of the pressing time did not result in water repellency and consequently the attempt to implement curing during the pressing step failed.

Boards treated in process 3 revealed that spraying AKD resulted in similar board properties as vacuum/pressure im-

pregnation (Hundhausen et al. 2008). In contrast to controls and paraffin references, prolonged curing significantly reduced the thickness swelling and water uptake of boards with AKD. Although the differences were small, they did indicate that hydrophobicity requires esterification. The reduction of the curing temperature from 130 to 100 °C did not significantly change board properties; therefore, 100 °C was regarded as sufficient for esterification.

AKD reduced IB more than did paraffin when wood chips were cured before board manufacture. This might be explained by an orientation of AKD's alkyl chains pointing outwards from the chip surface. Weak bonding led to high thickness swelling of boards submersed in water for more than 12 d.

AKD treatment holds little commercial viability as long as a pre-curing of the wood chips is unavoidable. In addition, the AKD treatment should impart clearly better properties, e.g., durability in outdoor applications, than paraffin does.

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