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Draft Manuscript for Review

**Mechanical characterisation of adhesives in particle boards
by means of nanoindentation
(Mechanische Charakterisierung von Klebstoffen in
Spanplatten mittels Nanoindentation)**

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1 **Mechanical characterisation of adhesives in**
2 **particle boards by means of nanoindentation**

3
4 **Mechanische Charakterisierung von**
5 **Klebstoffen in Spanplatten mittels**
6 **Nanoindentation**

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21 Abstract

22 Cured urea formaldehyde (UF) and melamine urea formaldehyde (MUF)
23 adhesives present in core and surface layers of particle boards were mechanically
24 characterised in-situ by means of nanoindentation. Comparing results between
25 investigated adhesives showed differences in micro-mechanical properties
26 particularly in the core layers, while mechanical properties in surface layers did
27 not differ significantly from each other. The method presented in this study
28 demonstrates that in-situ characterisation of adhesives within a particle board
29 cross section is feasible.

30
31

32 Zusammenfassung

33 Mittels Nanoindentation wurden mechanische Eigenschaften von ausgehärteten
34 Harnstoff-Formaldehyd (UF) und Melamin-Harnstoff-Formaldehyd Klebstoffen
35 (MUF) aus Deck- und Mittelschichten von Spanplatten charakterisiert. Ein
36 Vergleich der Ergebnisse der untersuchten Klebstoffe zeigte besonders in den
37 Mittelschichten Unterschiede in den mechanischen Eigenschaften. Der Vergleich
38 der Ergebnisse aus den Deckschichten ergab hingegen keine signifikanten
39 Unterschiede der Klebstoffeigenschaften. Die in der vorliegenden Studie
40 präsentierte Methode zeigt, dass eine in-situ Charakterisierung von Klebstoffen
41 innerhalb von Spanplatten möglich ist.

42 Introduction

43 The performance of particleboards results from a complex interaction between
44 processing and material parameters. By altering different parameters in particle
45 board production a wide range of product properties can be achieved. Among
46 others the choice of adhesive has a large influence on the performance of the
47 composite. From the literature the influence of the chemical properties of
48 adhesives (Dunky and Niemz 2002), wettability (Scheikl and Dunky 1998; Lee et
49 al. 2007), adhesive distribution (Kamke et al. 1996; Loxton et al. 2003; Grigsby et
50 al. 2005; Pakdel et al. 2008) and adhesive penetration (Kamke and Lee 2007) on
51 the composite performance is known. Due to a lack of suitable testing methods the
52 mechanical properties of cured adhesives within particle boards have not been in
53 the focus of research so far. With regard to solid wood bonds numerous studies on
54 the relationship between mechanical adhesive properties and bond stability were
55 performed in the last years (Serrano 2004; Gindl et al. 2005; Müller et al. 2005;
56 Serrano and Enquist 2005; Gindl and Müller 2006; Konnerth et al. 2006b, 2007a).
57 These studies showed a clear effect of adhesive mechanical behaviour on bond
58 performance. In analogy to solid wood bonding, it is assumed that also in wood
59 composites like particle boards the mechanical properties of the adhesive should
60 have a significant influence on the macroscopic behaviour of the composite.
61 Nanoindentation (NI) is a method to determine mechanical properties of very
62 small volumes on the microscopic scale. Originally developed for testing thin
63 metal films NI also was used in numerous studies on polymers (VanLandingham
64 et al. 2001) and on natural materials like wood cell walls (Wimmer et al. 1997;

Gindl et al. 2004; Konnerth and Gindl 2006) to obtain their mechanical properties. The mechanical properties of adhesives in solid wood bonds (Konnerth et al. 2006a; 2007b) as well as in cured adhesive films have already been investigated by means of NI and it was found to be a suitable testing method for this application. Based on the facts outlined above the objective of the present work was to study the feasibility of NI for characterizing the mechanical properties of cured adhesive present in particle boards.

Materials and Methods

Specimen preparation

Three layered particle boards were manufactured under laboratory conditions using three different commercial (melamine) urea formaldehyde adhesives (MUF / UF) with varying melamine content from 0 % to 23 % (Table 1) and with molar ratios (F/(NH₂)₂) between 1.07 and 1.09. The boards were produced with a size of 450 x 450 x 16 mm³ using standard industrial particles for core and surface layers in a mass ratio of 65 % to 35 %. The adhesive solid content in the different layers corresponds to industrial standards (app. 8-10%). Ammonium sulphate was used as adhesive hardener. The adhesive was applied to the particles in a rotating drum to achieve uniform adhesive distribution. Thereafter, the particles were pressed to boards in a displacement controlled hot press with a temperature of 220 °C for 128 s (8 s/mm thickness) resulting in a board density of app. 675 kg/m³. Prior to further processing the boards were stored in standard climate (20 °C, 65 % rel. humidity) until equilibrium moisture content was reached. The internal bond strength (IB) as well as thickness swelling (TS) (24h in water) of the particle boards were tested according to EN 319:1993 and EN 317:1993. On the microscopic level mechanical properties of the cured adhesive present in the particle board (Fig. 1) were evaluated by means of Nanoindentation (NI). For this purpose small samples (approx. 2 x 2 x 3 mm³) were taken from both face and core layers of each type of particle board. The samples were embedded in low viscosity epoxy resin (Agar Scientific Ltd.) and plane surfaces were created by using a Leica Ultracut microtome (Leica Microsystems) equipped with a Diatome diamond knife according to the procedure described in detail elsewhere (Konnerth et al. 2008).

97 **Nanoindentation (NI)**

98 The indenter device used in the present study (Triboindenter, Hysitron Inc.) is
 99 capable of performing in situ scanning probe microscopy (SPM) imaging scans
 100 (Fig. 2) by using the indenter tip (Berkovich type) as probe. In the SPM mode
 101 positions intended to be tested by NI were marked and the indent was performed
 102 out of this mode with high positioning accuracy. Indents were performed in cured
 103 adhesive present in tracheid lumina (Fig. 2). According to Fischer-Cripps
 104 (Fischer-Cripps 2000) a general rule of thumb is to indent no more than 10 % of
 105 the material thickness in case of thin films to avoid influence of substrate material
 106 on measurements. By performing indents in adhesive filled cell lumina it was
 107 assumed that sufficient material was present below the indent. Furthermore, a
 108 relatively low indentation peak force of 200 μN was used in order to achieve
 109 indentation depths of no more than 150 nm in the case of UF and MUF. Thus a
 110 small deformation volume was achieved which should also avoid probable
 111 influence of surrounding wood cell walls or the embedding material. Indents were
 112 performed by using a three-segmented load-controlled ramp with load application
 113 within 3 s, a holding time of 20 s, and an unload segment of 3 s. Parameters
 114 evaluated were hardness (H) and reduced modulus of elasticity (E_r) according to
 115 the Oliver and Pharr method (Oliver and Pharr 1992) by using the load-
 116 displacement data from the NI tests.

117 For determining H , the peak load of the NI experiment ($P_{\max}$) was divided by the
 118 contact area of the indenter at the end of the holding segment (A). E_r was
 119 calculated by Equation 1 where S represents the unloading stiffness which is
 120 determined by the initial slope of the unloading curve.

$$121 \quad E_r = \frac{1}{2} \sqrt{\pi} \frac{S}{\sqrt{A}}, \quad (1)$$

122 Reduced modulus of elasticity is calculated according to Equation 2 and takes into
 123 account the compliance of the indenter tip.

$$124 \quad \frac{1}{E_r} = \left(\frac{1-\nu_m^2}{E_m} \right)_{\text{material}} + \left(\frac{1-\nu_i^2}{E_i} \right)_{\text{indenter}} \quad (2)$$

125 Since the modulus of elasticity of the diamond indenter tip (E_i 1140 GPa, Poisson
 126 ratio ν_i 0.07) is very high compared to the tested cured adhesives, the effect of
 127 indenter tip compliance on results is negligibly small. Furthermore, the Poisson

ratio v_m of the tested material is not known. Therefore, no corrections according to Equation 2 were performed, and E_r was used for further considerations.

Results and Discussion

Macroscopic testing

The results of standardized tests of internal bond strength (IB) and thickness swelling are shown in Fig. 3. UF1 as well as MUF1 adhesive bonded particle boards showed comparable results for both internal bond strength and thickness swelling. Specimens from particle boards bonded with high melamine content adhesive (MUF2, 23 % melamine) showed significantly better performance regarding both thickness swelling and internal bond strength. As the adhesives differ primarily in melamine content, the improved bond performance of MUF2 bonded boards was attributed to the high melamine content, which agrees well with data found in literature (Oh 1999; No and Kim 2007; Hse et al. 2008). However, the low melamine content in MUF1 of 7.5 % shows no significant improvement of macroscopic properties in this study. As no density profiles of specimens were measured, internal bond strength variations may also be affected by density variations.

Nanoindentation

Results from micromechanical measurements concentrate on the behaviour of cured adhesive present in particle board surface and core layers. In Fig. 4, results for reduced elastic modulus (E_r) as well as hardness are displayed. In the surface layer, the reduced elastic moduli are in the range of 12-13 GPa and show very similar magnitude for all three tested adhesives. Also for hardness no significant differences between the tested adhesives was found. In great contrast to the surface layer, the adhesives characterised in the core layer do show significant differences. E_r of UF1 is significantly lower in the core than the corresponding value from the surface, whereas MUF2 with increased melamine content performed similar to the surface layer adhesive. For both adhesives hardness values are lower in the core layer. Contrary to the adhesives described above the MUF1 bonded core layer with moderate melamine content performed better with regard to both reduced elastic modulus and hardness. From the results presented

in Fig. 4, it seems difficult to derive a systematic relation between the mechanical properties and the chemical variations within the set of adhesives. What can be said is that substantial variability in micromechanical properties was found in the core layer, whereas adhesive performance was very homogeneous in the surface layer. Temperature during hot-pressing in core layers is in general lower than in surface layers. The resin in core does not have time to achieve full curing. This probably makes adhesive in this area more sensitive to chemical modification. For example, by concentrating on UF1 and MUF2, a slight trend between core layer properties and melamine content could be found. Apparently the increased melamine content of MUF2 has helped the adhesive located in core layers to cure more completely and thus develop higher mechanical performance.

A comparison of the results obtained with particle board adhesives in the present study with conventional wood adhesives for structural purposes revealed another interesting aspect. Structural adhesives (Konnerth et al. 2006a) did show values for reduced elastic modulus in the range of 2.7 GPa for polyurethane up to 8.7 GPa for melamine-urea formaldehyde adhesive, and hardness values from 0.14 to 0.58 GPa, respectively. In contrast adhesives for particle boards tested in the present study showed elastic moduli above 12 GPa. Furthermore, hardness values measured (0.8 to 1.1 GPa) were much higher than known values for conventional adhesives.

Thus, the possible range of mechanical properties of adhesives seems to be very wide and their effect on the mechanical performance of the bond and consequently on the finished product is very probably quite substantial. However, as shown in the present study, straightforward correlations between chemical variability and micro mechanical performance of the adhesives as well as the macro mechanical performance of the particle board specimen are not easily found.

Conclusion

In the present study it is demonstrated that a direct characterisation of mechanical properties of cured adhesive within a particle board cross section is feasible. In-situ nanoindentation measurements of cured UF and MUF particle board adhesives showed differences in micro-mechanical properties particularly in the core layers, while mechanical properties in surface layers did not differ

192 significantly from each other. Due to the complexity of influences affecting the
193 curing of adhesive in particleboards the differences could not be clearly attributed
194 to single factors.

195 **Acknowledgement**

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198 Table 1 Amino resins used for bonding particle boards

199 Tabelle 1 Für die Spanplattenherstellung verwendete Aminoharze

Code	Melamine Content
UF1	0 %
MUF1	7,5 %
MUF2	23 %

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Fig. 1 Incident light microscopy image of an epoxy embedded particle board specimen. Typical positions selected for nanoindentation in lumen filled with adhesive are indicated by arrows in the amplified detail.

Abb. 1 Auflichtmikroskopiebild einer in Epoxid eingebetteten Spanplattenprobe. Positionen für Nanoindentation in mit Klebstoff gefüllten Zelllumina sind im vergrößerten Bereich mit Pfeilen gekennzeichnet.

Image Scan Size: 30.000 µm

Image Scan Size: 30.000 µm

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Fig. 2 In-situ scanning probe microscopy image of a spruce tracheid filled with UF adhesive prior to (left) and after nanoindentation (right) with remaining indents marked by arrows.

210

Abb. 2 In-situ Scan einer mit Klebstoff gefüllten Fichtentracheide vor (links) und nach (rechts) der

211

Nanoindentation mit verbleibenden Indent-Abdrücken

Fig. 3 Internal Bond Strength (IB) and Thickness Swelling (TS) after 24 h in water of particle board samples bonded with different adhesives: UF1 urea-formaldehyde, MUF1 melamine-urea-formaldehyde adhesive with low melamine content and MUF2 with high melamine content. n is the number of samples tested.

Abb. 3 Querzug (IB) und Dickenquellung nach 24 stündiger Lagerung in Wasser (TS) von mit unterschiedlichen Klebstoffen hergestellten Spanplattenproben: UF1 – Harnstoff-Formaldehyd, MUF1 – Melamin-Harnstoff-Formaldehyd mit niedrigem Melaminanteil und MUF2 mit hohem Melaminanteil. n entspricht der Prüfkörperanzahl

Fig. 4 Indentation Hardness and Reduced Elastic Modulus (E_r) of cured adhesives present in surface and core layers of particle boards. UF1 urea-formaldehyde, MUF1 melamine-urea-formaldehyde adhesive with low melamine content and MUF2 with high melamine content. n is the number of samples tested.

Abb. 4 Härte und reduzierter Elastizitätsmodul (E_r) aus Nanoindentation an Klebstoffen, die sich innerhalb von Deck- und Mittelschichten von Spanplatten befinden. UF1 - Harnstoff-Formaldehyd, MUF1 – Melamin-Harnstoff-Formaldehyd mit niedrigem Melaminanteil und MUF2 mit hohem Melaminanteil. n entspricht der Prüfkörperanzahl

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 231 senkrecht zur Plattenebene, DIN Deutsches Institut für Normung e. V.
 232 EN 317 (1993) Spanplatten und Faserplatten; Bestimmung der Dickenquellung
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