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Influence of the adhesive formulation on the mechanical properties and bonding performance of polyurethane prepolymers

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Abstract

Only small amounts of additives are needed to formulate one-component polyurethane (1C PUR) adhesives for various applications. The current study illuminates the effects of the formulation on the mechanical properties of pure adhesives, on the one hand, and their performance in bonded wood joints on the other. Tensile shear tests on bonded wood joints, tensile tests on adhesive films, and nanoindentation measurements in the interphase region of the bond were performed. Analyses by means of infrared, atomic force, and electron microscopy provided the explanatory basis for the results obtained. Additionally to laboratory made 1C PUR, unmodified commercial 1C PUR, melamine-urea-formaldehyde (MUF), and phenol-resorcinol-formaldehyde (PRF) were tested for comparison. The results obtained confirm that the mechanical properties of 1C PUR adhesives are significantly affected by their prepolymer composition. The adhesive formulation by means of additives, on the other hand, does not affect the mechanical properties but is to a large extent responsible for the bonding performance.

Keywords: 1C PUR; adhesives for wood; AFM; ATR; ESEM; FTIR; film; lap-shear; mechanical properties; nanoindentation; polyurethane; prepolymer.

Introduction

Adhesives for modern timber engineering should have a broad range of properties, fitting to variations of wood species, process conditions, and application requirements.

The rheological and kinetic properties of the adhesive have to be adjusted to the anatomical features of wood as an anisotropic biocomposite. The penetration in longitudinal direction, for example, is usually higher than that perpendicular to the grain (Siau 1984). Softwood and hardwood properties vary considerably; significant variations also exist between single species (Kamke and Lee 2007). Species with a higher density reveal lower penetration due to a smaller lumen size, which results in limited interlocking of the adhesive. A higher density also causes greater dimensional changes (swelling and shrinking), which are leading to higher internal stresses (Suomi-Lindberg et al. 2002). In addition, wood extractives may reduce the wettability of the surface as well as the flow and penetration of the adhesive (Hse and Kuo 1988). Mechanical wood properties vary also considerably between species and change under environmental influences, such as moisture and temperature (Niemz 1993).

The fabrication of finger joints, straight and bent glulam beams, cross-laminated timber, or of other structural wood products needs adhesives that are tailor-made in terms of their open time, pressing time, and rheology. The conditions in which the wooden joints are used also differ. Adhesives for load-bearing timber constructions, for example, must generally resist high static and dynamic mechanical loads, as well as high stresses due to the swelling or shrinking of wood resulting in increased elastic and even plastic deformations.

Polyurethane-based adhesives (PUR) and sealants have been known for a long time as versatile tools in wood industry. 1C PUR adhesives have good strength, are ductile, resistant to moisture, and cause little emission. The cross-linking reaction of the isocyanate groups (-NCO) occurs under the influence of water derived from the moisture content (MC) of the wood or from the humidity in the ambient air. This reaction leads under CO₂ formation to thermally stable urea-type structural groups, which build up strong hard segments. Under dry conditions, high temperatures, influence of filling material, various undesired structures – such as allophanates, biurets, uretdiones or carbodiimides – can be formed (Ionescu 2005). These reactions may influence the cross-link density of the polyurethane network (Woods 1990) and possibly also the mechanical properties of the cured adhesive.

PUR adhesives are still matter of basic research focusing on their properties along the wood bond line and penetration into the wood (Gindl et al. 2005; Müller et al. 2005). Widsten et al. (2006) investigated the factors influencing timber gluability with 1C PUR on nine Australian timber species. The penetration of adhesives into wood, including PUR res-

ins, was in focus of the paper of Konnerth et al. (2008). The wetting of modified wood with adhesives, including PUR, was tested by Bryne and Wålinder (2010).

The properties of 1C PUR adhesives are also in focus of the present paper because of the large importance of this type of adhesives. Their production takes place in a two-stage process: (1) In the first stage, an exothermic polyaddition reaction of polyol with an excess of polyisocyanate leads to urethane prepolymers with a defined amount of free monomeric polyisocyanate, which acts as a solvent for the prepolymer. (2) In the second stage, the prepolymer is mixed with different additives to generate the final product. The properties of the final product can largely be controlled by varying not only by the molar ratio of the components but also by additives. Several details are not well known in this regard.

Thus the objective of this study is to investigate the influence of the adhesive formulation on the mechanical properties of the cured adhesive. Of particular interest are effects caused by the addition of amin catalyst and additives such as pyrogenic silica and defoamers. This study is aimed at clarifying whether a catalyst accelerates side-reactions that might have negative effects on the mechanical properties. The question should also be answered whether the adjustment of viscosity leads to agglomerations of the pyrogenic silica within the prepolymer matrix. Furthermore, the influence of softening effects by surfactants (defoamers) should be investigated.

Material and methods

Three prepolymers were produced by Bayer MaterialScience (Leverkusen, Germany) based on the reaction of isocyanates and polyols. The isocyanates used were mixtures of methylene diphenyl diisocyanate (MDI) monomer and polymeric MDI. Since polymeric MDI contains more than two isocyanate groups per molecule, the resulting overall functionality of the prepolymers is >2 . The polyols used resulted from a base-catalyzed reaction of 1,2-propylene glycol with propylene oxide. The water-free polyol component was mixed with the isocyanate components at 50–70°C under continuous stirring, until the desired NCO content was reached and remained constant. Three different functionality adjustments were chosen, each having an NCO content of about 16% (Table 1).

These prepolymers formed the basis for the formulation of adhesives by adding and dispersing identical amounts of defoamer, pyrogenic silica and amine catalyst by the adhesive producer Purbond (Sempach-Station, Switzerland). A similar reactivity of the adhesives was achieved, measured as open time in the range of 60–90 min. Additionally, commercially available adhesives for structural wood bonding – phenol-resorcinol-formaldehyde (PRF), melamine-urea-formaldehyde (MUF), and 1C PUR – were included into the study for comparison [for tensile shear results of these and further adhesives see Clauß et al. (2011c)]. The adhesive performances were tested by: (1) Longitudinal tensile shear strength according to (DIN EN 302-1 2004). (2) Tensile properties of adhesive films according to ISO 527-1 (2010). (3) Micro-mechanical properties by means of nanoindentation.

In accordance with DIN EN 302-1, beech (*Fagus sylvatica* L.) was selected as substrate because of (1) its low content of extractives and (2) its higher strength compared with spruce, which is common in timber engineering. The raw density of the beech was $735 \pm 34 \text{ kg m}^{-3}$ at an equilibrium moisture content of $12 \pm 1\%$. Pressure of about 0.8 MPa was applied for specimen preparation and subsequent curing under standard climatic conditions (20°C/65% RH) was performed at least for 7 days. The specific bonding parameters for the different adhesives are listed in Table 2.

The bonds were tested under tensile shear load (standard climatic conditions, Zwick/Roell Z010 universal testing machine), which implies a position-controlled measurement of the load-displacement curves of adhesively bonded lap joints until failure. The strain measurement was performed by means of a clip-on displacement transducer. The wood failure percentage (WFP) was estimated visually in steps of 10%.

Cubes with an edge length of about 10 mm were cut from the climatically conditioned joints for nanoindentation. The bond line of the specimens was oriented in the middle. Subsequently, a gently sloping apex was microtomed on the surface of the unembedded specimens. Afterwards, a tip was sliced off the apex with a diamond knife microtome similar to the preparation method described in detail by Jakes et al. (2008).

A Hysitron Tribolindenter (Hysitron, Minneapolis, MN) equipped with a three-faceted diamond pyramid (Berkovich) indenter tip was used for the measurements. The machine compliance was determined by a series of indents in the center of a fused silica standard with loads ranging from 0.05 to 10.00 mN. From the load-depth graph, hardness and Young's modulus were calculated according to Oliver and Pharr (1992). Data of Young's modulus were not corrected (Gindl et al. 2004). The deformation energy was determined as the integral of load vs. displacement as previously described (Konnerth et al. 2007a; Stanzl-Tschegg et al. 2009).

Table 1 Chemical and physical parameters of laboratory polyurethane prepolymers and adhesives.

	Prepolymers			Formulated adhesives		
PUR code	P1	P2	P3	A1	A2	A3
NCO content (% w/w)	16.0	16.0	16.0	16.0	16.0	16.0
Cross-link density (mol kg^{-1})	0.22	0.87	1.25	0.22	0.87	1.25
Urea group content (mol kg^{-1})	2	2	2	2	2	2
Urethane group content (mol kg^{-1})	0.58	0.77	0.58	0.58	0.77	0.58
Viscosity (23°C) (mPa s^{-1})	1310	8920	5460	2500	19 000	14 000
Film drying time (min)	960	660	720	180	160	180
Defoamer ¹	–	–	–	Yes	Yes	Yes
Pyrogenic silica ¹	–	–	–	Yes	Yes	Yes
Amine catalyst ¹	–	–	–	Yes	Yes	Yes

¹Identical amounts of defoamer, pyrogenic silica and catalyst for all adhesives.

Table 2 Bonding parameters of the tested adhesives and prepolymers.

Adhesive	Adhesive/ hardener ratio ^a	EMC ^b [%]	Pressure ^a [MPa]	Pressing time [h]	Application side	Spread per side [g m ⁻²]
MUF	100/35	≈ 12	0.8–1.2	4	2 sides	200
PRF	100/20	≈ 12	0.8–1.2	5	2 sides	180
1C PUR commercial	–	≥ 8	0.6–1.0	3	1 side	200
1C PUR prepolymer	–	–	–	12	1 side	200
1C PUR adhesive	–	–	–	6	1 side	200

^aApplied in liquid state.^bEquilibrium moisture content as recommended by adhesive producer.

The indents (10 indents spaced 5 μm apart) were placed along the bond line according to Figure 3a. Under these circumstances an interaction between the indents can be disregarded (Jakes et al. 2008). The experiments were performed in load-controlled mode (test speed 1.7 Ns^{-1} , peak force 400 μN) resulting in indent depths of about 450 nm for the cured adhesive and 200 nm for the secondary cell wall, respectively. At peak load, a hold period of 5 s was included in order to determine the viscoelastic performance.

For the preparation of the adhesive films for the tensile tests, the liquid adhesives were applied to a plastic sheet. The typical foaming effect of polyurethanes could be minimized by applying a film thickness of only about 0.25 mm in a 50% RH environment. The films were peeled from the plastic sheet and stored for a minimum of 3 days under standard climatic conditions. Specimens of shape type 1B according to ISO 527-3 (2003) were prepared from these films.

The tensile properties of the adhesives were obtained according to ISO 527-1 (2010) (standard climatic conditions, Zwick/Roell Z100 universal testing machine, 500 N load cell, test speed 5 mm min^{-1}). The strain was measured optically by a video extensometer.

Thereby tensile and transverse deformation was recorded; Young's modulus, strength and strain at maximal load, and the Poisson's ratio were calculated from the load displacement curves. The mean values presented in Table 3 are a series of at least six specimens.

FTIR spectra of the cured adhesives were recorded on a ThermoFinnigan Continuum FTIR Microscope in transmission mode using thin sections taken from the interface region of the bond line sliced with a microtome knife. Spectra were taken from an area of a size of an adhesively filled vessel. The bonds had been stored for one month under standard climatic conditions and the spectra were recorded directly after the thin sections had been prepared. The measurements were repeated on the same specimens after 1 and 4 weeks. As a reference, spectra were also recorded from the adhesives in a liquid state by attenuated total reflectance (ATR) spectroscopy. The ratio between the NCO band at 2278 cm^{-1} and the stable aromatic C-H band at 3030 cm^{-1} , which remains constant during the reaction, was calculated and taken as a measure for free NCO groups.

For a qualitative analysis of the bond line and interphase region, micrographs were taken by means of a Dual Beam Scanning Elec-

Table 3 Summary of the results determined by tensile test on films, nanoindentation and tensile shear test on bonded wood joints.

Adhesive	E_{film} [GPa]	σ_{film} [MPa]	ε [%]	μ [-]	E_{indent} [GPa]	H [GPa]	W [pJ]	τ [MPa]	WFP [%]
Wood/S2	$\bar{x}$	–	–	–	16.72	0.38	30.2	13.97	–
	v [%]	–	–	–	12	18	14	29	–
PRF	$\bar{x}$	3.63	29.50	0.86	–	7.78	0.45	18.5	14.72
	v [%]	22	17	14	–	5	4	5	14
MUF	$\bar{x}$	3.13	26.65	1.09	–	7.63	0.46	20.5	12.25
	v [%]	25	11	22	–	10	3	4	20
PUR	$\bar{x}$	0.33	11.50	18.83	0.45	3.03	0.16	40.0	12.15
	v [%]	20	15	13	18	14	12	6	8
P1	$\bar{x}$	0.80	18.64	6.28	0.48	1.88	0.09	53.2	6.93
	v [%]	5	1	4	10	20	27	13	16
P2	$\bar{x}$	2.09	40.03	3.47	0.4	3.83	0.20	34.7	8.28
	v [%]	17	10	7	18	3	4	3	15
P3	$\bar{x}$	1.88	36.17	3.54	0.42	3.38	0.18	36.7	6.73
	v [%]	10	5	13	16	7	5	4	12
A1	$\bar{x}$	0.73	17.84	6.57	0.45	1.94	0.09	53.8	11.29
	v [%]	3	2	3	5	13	16	8	17
A2	$\bar{x}$	1.84	33.55	2.76	0.43	3.45	0.19	34.5	10.46
	v [%]	11	5	8	14	18	9	3	13
A3	$\bar{x}$	1.79	33.19	3.16	0.38	3.58	0.19	35.8	10.07
	v [%]	7	2	12	21	4	4	4	12

(E_{film}) Young's modulus measured by tensile test, (σ_{film}) tensile strength, (ε) strain at failure, (μ) Poisson ratio, (E_{indent}) Young's modulus measured by nanoindentation, (H) hardness, (W) deformation energy, (τ) tensile shear strength, (WFP) wood failure percentage, ($\bar{x}$) mean value, (v) coefficient of variation.

tron Microscope (Quanta 200 3D, FEI) in low vacuum mode. Additional AFM imaging was performed in tapping mode by means of the Atomic Force Microscope (Digital Instruments D3000, Bruker) providing phase contrast images of the polymer structure.

Results and discussion

Tensile shear strength of bonded wood joints

The tensile shear test on bonded wood joints revealed significant differences between the tested prepolymers and the formulated adhesives (Figure 1a). Each type of adhesive reached, on average, 40% higher values than the basic prepolymer. Due to the higher strength of the formulated adhesives, wood failure partially occurred. The mean WFP for all 1C PUR adhesives was below 50% (Figure 1c). The prepolymers, however, showed no wood failure at all, irrespective of their cross-link density.

The tensile shear strength with the commercial 1C PUR adhesive was on average about 15% higher than with the

laboratory formulations; the WFP was about 40%. PRF reached significantly higher values than all the other adhesives and its strength was comparable with that of beech wood. MUF and the commercial 1C PUR exhibited similar values within the interquartile range of wood strength; however, the WFP of PUR was considerably lower. Both polycondensation resins showed wood failure but not cohesive adhesive failure.

Tensile properties of adhesive films

The tensile strengths (Figure 1b) and the Young's moduli (Figure 1d) were significantly different between the adhesive types and within the particular groups of prepolymers and formulated adhesives. The prepolymers with medium (P2) and high cross-link density (P3) reached tensile strengths and Young's moduli that were about twice as high as those of the prepolymer with low cross-link density (P1).

The adhesives formulated from these prepolymers resulted in nearly the same tensile strengths and Young's moduli of the formed films as the respective prepolymers. The mean

Figure 1 Mechanical properties of (a, c) bonded wood joints and (b, d) films: (a) tensile shear strength, (b) tensile strength, (c) wood failure percentage and (d) Young's modulus. For explanation of the abbreviations on the x-axis (see Table 1).

values of the groups (prepolymer and formulated adhesive) did not differ significantly, as shown by the Welch two-sample *t*-test ($\alpha=0.05$). The difference between the commercial products and the laboratory formulations is also significant. The commercial 1C PUR adhesive had the lowest tensile strength (11.5 MPa) and also the lowest Young's modulus (329 MPa) of all tested films.

The strengths of both polycondensation resins were similar to the results of the laboratory 1C PUR adhesives, with PRF showing a slightly higher strength (29.5 MPa) compared with MUF (26.7 MPa). Due to the brittle behavior of the films, the fracture occurred spontaneously without developing a yield point; also the Young's modulus was considerably higher compared with the 1C PUR adhesives. PRF reached the highest Young's modulus with 3.6 GPa, followed by MUF with 3.1 GPa.

Nanoindentation

The prepolymers differed significantly regarding the parameters determined by nanoindentation. The prepolymer with the lowest cross-link density (P1) exhibited significantly lower hardness (Figure 2a) and Young's modulus (Figure 2c) than the prepolymers with medium (P2) and high (P3) cross-link density. A correlation between cross-link density and mechanical properties, however, could not be detected. In spite of the higher cross-link density, P3 resulted in a lower hardness and stiffness than P2. The deformation energy (Figure 2e) showed the opposite tendency. As expected, the prepolymer with the lowest cross-linking was able to absorb the most energy.

By means of nanoindentation it was possible to distinguish indents in phases of the bond line with preferably hard and soft segment-rich phases of the bond line. The hard segment domain of P1 showed significantly higher values for indent hardness and Young's modulus. The deformation energy in contrast was lower compared to the soft segment domain. The prepolymers with higher cross-link density did not show segregations in the polymer structure.

The formulated adhesives showed a similar picture; however, differences in hardness, Young's modulus, and deformation energy between the adhesives A3 (high cross-link density) and A2 (medium cross-link density) were not statistically significant, as this was also proven by means of an analysis of variance ($\alpha=0.05$).

The values for the commercial 1C PUR were in between the laboratory formulations with low and medium cross-link density. PRF and MUF showed no significant difference in hardness and stiffness; MUF was able to absorb more deformation energy than PRF. For both adhesives hardness and stiffness were clearly higher than for all 1C PUR adhesives.

The hardness of the cell wall of beech was slightly lower than for the amino- and phenoplastic resins; however, the variance for the wood samples was much higher than that of the two adhesives. The Young's modulus of beech was considerably higher than the values for the adhesives. The force-displacement curves in Figure 2b illustrate the amount of deformation energy absorbed, which is represented by the area below the curve. The curves for the polycondensation

resins were similar to those of the wood cell wall, whereas the PUR formulations are characterized by a minor slope and a significantly greater area below the curve. The creep deformation, which can be estimated by the displacement under constant maximum load, was also higher for PUR adhesives compared to the polycondensation resins and the cell wall.

Prepolymer composition

The variation in the prepolymer configuration is reflected by the tensile tests on films and nanoindentation results in the interphase region. A low cross-link density of the prepolymer resulted in lower stiffness, strength, and hardness. Caused by the minor cross-linking, the alternating hard and soft segments of the molecule chains could easily segregate to form hard segment domains in the soft segment matrix. By means of AFM phase contrast images (Figure 3b), it was possible to visualize these domains due to their differing micromechanical properties. Phase contrast imaging shows a brighter contrast of areas in the sample with higher elasticity and/or lower adhesive forces between the silicon tip of the AFM cantilever and the sample material. At higher cross-link density, the structure of the prepolymer was significantly more homogeneous.

The tensile shear strength of bonded wood joints is in contrast to the results of pure prepolymers not affected by their chemical composition, although it might be claimed that in the case of no wood failure the shear strength of the joint completely relies on the cohesive strength of the adhesive. The mechanical properties are negligible in case of a poor bond line formation of the prepolymers. This is clearly identifiable by comparison of ESEM micrographs showing bonds of beech wood with either prepolymer (Figure 3c) or formulated adhesive (Figure 3d). Vessels in a distance of more than 500 μm from the bond line were filled by the prepolymer and the bond line showed several imperfections. A quantification of the lower pore space saturation by means of synchrotron tomography confirmed a starved bond line (lacking of resin) in the case of PUR prepolymers (Haß et al. 2011). A satisfactory bond formation is hardly possible under these circumstances.

Adhesive formulation

Rheology, kinetics, and wettability are mainly influenced by the formulation of the adhesive. The penetration of the adhesives is considerably limited due to the adjustment of these properties. Since the prepolymers P2 and P3 had considerably higher viscosities than adhesive A1, a correlation between viscosity and shear strength cannot be established by the current results. Previous studies by Clauß et al. (2011b) and Haß et al. (2011) do not provide any evidence of this either. The notably different film drying times (Table 1) of prepolymers and adhesives quantify their different reaction rates. The faster reaction of the adhesive's NCO groups with water, accelerated by the addition of catalyst, also restricts the penetration and therefore promotes greater concentration of the adhesive in the bond line. However, it might also be possible that NCO groups of prepolymers do not fully react

Figure 2 Nanoindentation results of the bond line interphase region: (a) hardness, (b) force-displacement curves, (c) Young's modulus, (d) correlation between Young's modulus and hardness, (e) deformation energy by measured indent areas and (f) correlation between Young's modulus measured by means of nanoindentation and tensile test. Commercial adhesives: PRF, MUF, IC PUR. PUR prepolymers: P1, P2, P3. Laboratory formulated IC PUR adhesives: A1, A2, A2. (h) hard and (s) soft segment-rich phase. (S2) cell wall of beech wood. Error bars: standard deviation. Boxes: quartile of distribution. Whiskers: $1.5 \times$ interquartile range. Points: outliers.

Figure 3 AFM micrographs of formulated adhesive A1: (a) nano-indentations along the bond line and (b) dispersed pyrogenic silica inclusions, hard segment and soft segment-rich phases in the polymer matrix. ESEM micrographs of bond lines: interphases formed by penetration of (c) prepolymer P1 and (d) adhesive A1 into wood adjacent to the bond line.

with water and therefore the network of the prepolymer is less cross-linked compared with a catalyzed adhesive.

FTIR spectroscopy of the cured adhesives showed significant differences in the absorption peaks due to the NCO groups that appear as intense and sharp bands at about 2278 cm^{-1} in the ATR spectra (Figure 4a). After curing under standard climatic conditions, the NCO group absorption of all of the bonds was reduced drastically but did not disappear completely (Figure 4b). In the case of the formulated adhesive, the absorbance is comparatively low amounting to a free NCO content of 0.04%. A repeated measure of the same thin section after 6 days revealed that the peak disappeared. In the prepolymer, an NCO content of about 0.13% was measured; after one month only 0.06% of unreacted NCO was detected, compared with 16% NCO in the liquid state. It may therefore be assumed that the cross-link reaction was almost complete.

The formulation of the prepolymer to an adhesive led to the formation of a well-defined bond line thickness, resulting in significantly higher tensile shear strength of the formulated adhesives compared to the prepolymers. As the mechan-

ical properties measured by tension test and nanoindentation are nearly identical for prepolymers and formulated adhesives, one can conclude that the cohesion of the adhesive is almost completely governed by the prepolymer configuration. Negative side effects due to the addition of catalyst, defoamer, and pyrogenic silica could not be detected. Nonetheless, it cannot be ruled out that side reactions occur; NMR spectroscopy might provide objective evidence of this (Ni and Frazier 1998).

The Young's modulus obtained with the tension test on thin films was (for all tested adhesives) considerably lower compared to the values measured by nanoindentation (Figure 2f); similar findings were also reported by Lucas et al. (1998) and Konnerth et al. (2006). Several basic differences in the methods used have a strong influence on the test results. The three dimensional stress state below the indenter tip is affected by shear forces in comparison with the uniaxial tension test. The sample area can be considered to be different by several orders of magnitude, thus local imperfections (e.g., CO_2 blisters or pyrogenic silica) have a different impact on the results. Additionally, the contact depth, geometry of the

Figure 4 IR spectra: (a) recorded by attenuated total reflexion (ATR) spectroscopy of the liquid prepolymer P1 and (b) recorded by Fourier transform infrared (FTIR) spectroscopy in transmission mode from thin sections cut from the interphase region of the bond line of samples glued by prepolymer P1 and adhesive A1 (see Table 1).

indenter tip and unloading speed are important influencing factors of the nanoindentation method (VanLandingham et al. 2001). The results of the tension tests are influenced by the strain rate and the type (secant, regression) and range [$\sigma_1 - \sigma_2$, (ISO 527-1 2010)] of Young's modulus determination. The high linear correlation ($R^2=0.84$) between the two methods, however, confirms that the differentiation of the polymers is independent of the method used, since different methods and experimental parameters affect the absolute values, but scarcely the relation of the adhesives to each other.

Commercial adhesives

The commercial 1C PUR revealed good bond properties despite the low stiffness and strength of the pure adhesive,

which ranged below the values of the laboratory formulations. Obviously, suitable rheological and film formation properties are more important for good bond quality than the mechanical properties of the tested adhesives. The deviation from the high correlation between Young's moduli obtained by tensile test and nanoindentation (Figure 2f) suggests an underestimated Young's modulus calculated from the tensile test; however, other studies report very similar results for this adhesive (Konnerth et al. 2006). A possible reason could have been the fibrous filler material of the commercial PUR, which tended to agglomerate during the film formation and was also aligned in the direction of application. The filler material, however, is largely responsible for the better performance in the shear test (Clauß et al. 2011a).

In contrast to PUR, amino- and phenoplastic resins are characterized by high stiffness and brittle failure behavior; however, both adhesive types are able to reach high tensile shear strengths. The high WFP for PRF and MUF demonstrates that the wood strength is clearly exceeded by these adhesives, thus properties of the adherend determined the resulting values (Forest Products Laboratory 2000). It is known that PUR adhesives reach lower WFP at equal shear strength (Niemz and Allenspach 2009; Clauß et al. 2011c), in particular under wet conditions (Vick and Okkonen 1998). Possible reasons for this could be changes in wood properties due to inter- or intracellular adhesive penetration (Konnerth and Gindl 2006; Konnerth et al. 2007b; Stöckel et al. 2010) or gross penetration through the cellular network (Kamke and Lee 2007). The high gross penetration of the ductile polyurethane possibly contributes to delaying wood failure by reinforcing the wood. Furthermore, intracellular penetration of PRF or MUF in the interphase region could promote wood failure due to embrittlement of the cell wall. However, more experiments are needed to test this hypothesis.

Impact on the wood

The current nanoindentation measurements on wood cell walls do not allow conclusions about changes in their mechanical properties due to a possible penetration of the adhesive into the intercellular regions. If penetration still occurred, beech (in contrast to spruce tested in other publications) is most likely less affected as the Young's modulus obtained by indentation is significantly higher compared to the adhesives tested. The high variation in the values determined for wood can be explained (1) by specimens taken from varying samples and (2) indents in different cell types (fiber tracheids and vessels) with varying micro-fibril angles, which are highly correlated to the stiffness of the material (Gindl and Schöberl 2004; Tze et al. 2007; Donaldson 2008; Wu et al. 2009).

Young's modulus and hardness of the adhesives showed a high linear correlation ($R^2=0.97$) (Figure 2d) also documented by Shi et al. (2006). The cell wall of beech shows a similar trend but worse correlation ($R^2=0.29$); however, the moduli are higher by about 10 GPa compared to the various adhesive films. This shows again that beech exhibits in the

area of S2 cell wall layer a hardness in the range of PRF or MUF but with a considerably stiffer behavior.

Conclusions

- The mechanical properties of the 1C PUR adhesives are determined by the prepolymer compositions.
- The adjustment of viscosity and reactivity significantly enhanced the bonding performance of formulated adhesives in comparison with unformulated prepolymers.
- Negative side effects due to the addition of catalyst, pyrogenic silica, defoamer, etc., on the mechanical properties or the bonding performance could not be detected.
- Too low cross-linking of the polyurethane prepolymer can result in segregation into hard and soft segment-rich phases of the polymer with differing mechanical properties.
- 1C PUR adhesives are characterized by significantly lower stiffness and hardness compared to amino- and phenoplastic resins, but absorb much more deformation energy and show ductile failure behavior leading to lower wood failure.

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