

Surface properties of wood and MDF after ultrasonic-assisted cutting

GERHARD SINN, HERWIG MAYER*

Institute of Physics and Materials Science, BOKU, Peter-Jordan-Str. 82, A-1190 Vienna, Austria

E-mail: herwig.mayer@boku.ac.at

STEFANIE STANZL-TSCHEGG

Institute of Physics and Materials Science, BOKU, Peter-Jordan-Str. 82, A-1190 Vienna, Austria; Christian Doppler—Laboratory for Fundamentals of Wood Machining, BOKU, Peter-Jordan-Str. 82, A-1190 Vienna, Austria

Surfaces created by ultrasonic-assisted cutting (UC) of beech and spruce and of medium density fibreboard (MDF) are compared to surfaces obtained by conventional linear cutting (CC) using a sharp tool. Topography is evaluated performing roughness measurements and scanning electron microscopy. No effect of UC procedure on mean roughness is found. The surface of MDF and large areas of the surfaces of the woods appear similar after UC and CC, whereas other regions show impact marks and microscopic reels produced by the periodic oscillation of the tool in UC. The wettability of surfaces produced with both wood processing techniques is similar. Surface free energy measurements indicate accelerated ageing caused by UC, probably due to heating. © 2005 Springer Science + Business Media, Inc.

1. Introduction

Ultrasonic-assisted cutting is a promising material processing technology. With this method, the cutting tool is excited to ultrasonic vibrations at amplitudes of several micrometers and frequencies in the range of 20 kHz. Beneficial influences on the cutting process are the reduction of cutting forces as reported for cutting metals [1] and metal matrix composites [2] and improved surface finish which is observed in processing metals [3, 4], optical plastics [5] and glasses [6].

Few investigations exist on ultrasonic-assisted cutting of wood. Kato [7] found reduced cutting forces caused by ultrasonic excitation of the cutting knife in experiments with Hinoki (*Chamecyparis obtusa* ENDL.) and Buna (*Fagus crenata* Blume) wood. Fujiwara [8] showed that the kinetic friction coefficient could be reduced by 80% superimposing ultrasonic vibrations on the movement of the cutting tool. Our investigations performed with spruce (*Picea abies* (L.) Karst.) confirm the positive influence of ultrasonic vibrations on the cutting process. Superimposing oscillations of 8 μm to the linear movement of the knife reduced the cutting forces necessary to produce chips with thickness 100 μm by approximately 33% [9].

One of the most important factors in processing wood is the quality of the obtained surfaces. A new machining process should be able to create better or at least sim-

ilar surface quality to existing systems. No systematic investigation, however, on wood surfaces produced by ultrasonic-assisted cutting is found in the literature. Surface properties influence the subsequent technological steps, i.e., large surface roughness often makes additional sanding necessary; better wetting behaviour improves penetration and adhesion of coatings [10] and adhesive bonds may be weakened by layers of compressed and crushed wood cells [11–13].

The obtained wood surfaces after processing may be considered as a complex combination of the biological structure [14], the influence of the separation process to produce the surface [15] and time dependent organic chemical processes on the newly created surface [16]. In order to study the influence of ultrasonic-assisted cutting on surfaces of wood based materials (beech, spruce and MDF), resultant surfaces were analysed and compared to those obtained for the same materials and cutting geometry without superimposed vibration (conventional cutting). The investigated materials are commonly used in the furniture industry where high quality of surfaces is required. Scanning electron microscopy (SEM) and surface roughness measurements were performed to analyse the surface topography after conventional and ultrasonic-assisted cutting procedures. Wettability measurements and contact angle investigations served to quantify chemical modifications.

*Author to whom all correspondence should be addressed.

2. Materials and methods

2.1. Materials

Ultrasonic-assisted cutting (UC) and conventional cutting (CC) experiments were performed with softwood Norway spruce (*Picea abies* (L.) Karst.), with measured raw density of $415.4 \pm 23.2 \text{ kg/m}^3$ and with hardwood, beech (*Fagus sylvatica* L.) with density of $722.0 \pm 38.7 \text{ kg/m}^3$. Coated medium density fibre board (MDF) in moulding quality from MDF Hallein GmbH, Austria with raw density of $828.2 \pm 5.5 \text{ kg/m}^3$ served as representative for wood composites. MDF is an artificial product based on wood fibres with adhesive content of maximum 12% [17].

Both woods were cut in the longitudinal direction and parallel to the fibres creating an LR-plane [18]. The length of samples was 100 mm and the width was 10 mm (spruce and beech) and 19 mm (MDF), respectively. All specimens were stored in a climate chamber with standard climate of 20°C and 65% relative humidity until equilibrium moisture content was reached.

2.2. Ultrasonic-assisted cutting

The arrangement used in the cutting experiments is shown in Fig. 1. The sharp cutting knife (steel blade) with wedge angle, β of 45° is fixed by soldering at the tip of the tool holder. The tool holder is rigid in order to minimise undesirable movement of the knife due to forces acting during the cutting experiments. The clearance angle of the cutting knife, α is 10° . The device is mounted on an instrumented microtome to cut slices at constant cutting speed 170 mm/s and constant thickness of the uncut chip of $100 \mu\text{m}$.

The whole device comprising the ultrasonic transducer to generate ultrasonic vibrations, components to mount the equipment and the cutting tool with the attached steel knife is mounted at an angle δ of 30° with respect to the specimen's surfaces. Longitudinal ultrasonic vibrations at vibration amplitude of $8 \mu\text{m}$ at the place of the steel knife are generated at the frequency of approximately 20 kHz, which is the resonance frequency of the mechanical system. In ultrasonic-assisted cutting experiments, the movement of the steel blade may thus be considered as the superposition of the harmonic vibration in direction 30° with respect to the specimen surface and of the linear movement of the load train with constant cutting speed parallel to the specimen surface.

2.3. Surface topography analysis

Surface roughness is one of the most considered factors regarding surface quality. Within this work 4 roughness parameters were evaluated using stylus type system, the Mahr surface Perthometer M2. Surface roughness of the cut surface was measured in cutting direction (growth direction of the wood) with cut-off length 2.5 mm. Three roughness height parameters were evaluated: The average deviation of the profile from the mean line, R_a , the root mean square roughness, R_q , and the average of 5 peak-to-valley heights, R_z [19, 20] according to norm ISO 4287. To include one roughness spacing pa-

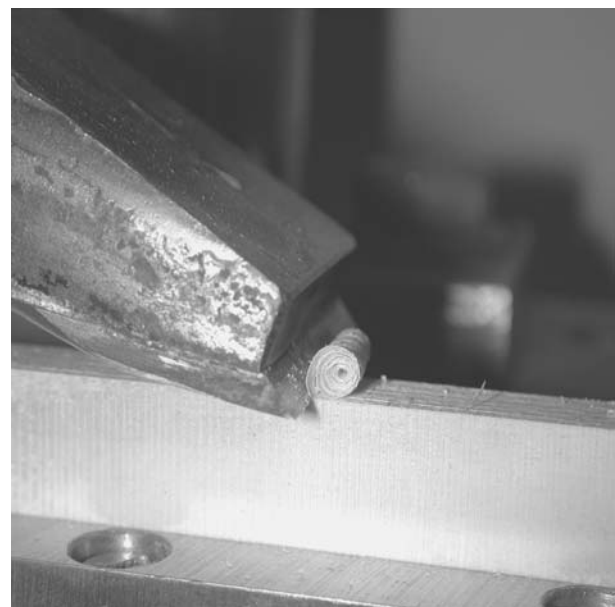
rameter in the evaluation, the mean spacing of profile irregularities, R_{Sm} (ISO 4287) was evaluated.

The roughness height and spacing parameters served to evaluate potential differences of surface profiles obtained by conventional and ultrasonic-assisted cutting. Additionally, cut specimens of the three materials have been analysed by scanning electron microscopy to compare surfaces obtained with both techniques.

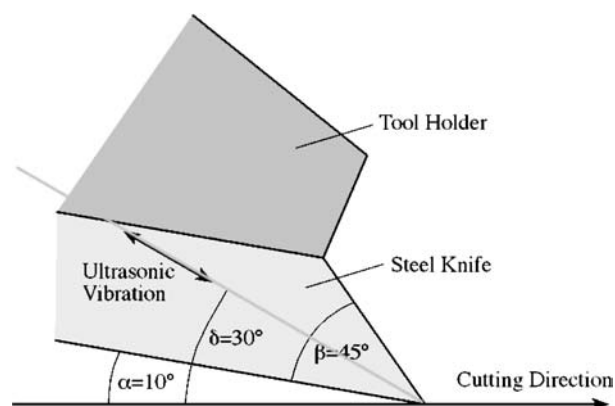
2.4. Contact angle measurements

Semiautomatic measuring equipment—Digidrop from GBX Company—was used to perform contact angle measurements. All experiments were performed within five hours after cutting in order to avoid substantial surface inactivation. Two kinds of experiments were performed with beech:

The first series of experiments served to analyse the time-dependent wettability of water droplets placed on the different surfaces. Drops of specified volume are dosed automatically by an auto syringe and are picked up by the specimen lying on a movable sample table



(a)



(b)

Figure 1 Geometric arrangement of ultrasonic-assisted cutting and conventional cutting experiments. (a), the tool tip and attached knife while cutting spruce. (b), involved angles, i.e., clearance angle α , wedge angle β and angle of vibration axis δ with respect to the cutting surface.

TABLE I Surface energy components (in mJ/m^2) of the test liquids used in this work [26]

Test liquid	γ	γ^{LW}	γ^{ab}	γ^+	γ^-
Diiodomethane (CH_2I_2)	50.80	50.80	0.00	0.00	0.00
Formamide (CH_3NO)	58.00	39.00	19.00	2.28	39.60
Water	72.80	21.80	51.00	25.50	25.50

[21]. The two-dimensional shape of the droplet as observed from the tangential direction was recorded in a movie file with 15.5 pictures per second, and left and right contact angles were evaluated. 42 experiments have been performed for both CC and UC surfaces of beech.

The second experimental series comprised advancing contact angle measurements, which served to determine the surface free energy by using the acid-base approach [22–25]. Contact angles of expanding droplets, i.e., advancing contact angles of test liquids were measured on the cut surfaces as observed from the tangential direction. For these experiments, the syringe stays in the droplet continuously adding fluid from the top. This enables the performance of measurements in dynamic equilibrium where the three-phase boundary moves on the surface. Thus, the size of the droplet increases and continuously wets new areas of the surface. In advancing contact angle measurements experimental difficulties due to penetration of fluid into the wood can be overcome. Diiodomethane, formamide and water with surface energy parameters taken from Ref. [26] and shown in Table I were used to evaluate the measurements. A total of 25 contact angles were evaluated for CC and UC surfaces, respectively.

3. Results

Results of roughness measurements (mean values and standard deviation) are summarized in Table II. For beech and MDF mean roughness height parameters of UC surfaces were slightly lower than for CC surfaces, whereas the opposite was found for spruce. Considering standard deviations of the measured values, however, scatter ranges of roughness parameters measured on CC and UC surfaces overlap.

In order to statistically analyse the measured data in more detail, two sided T -Tests ($P = 5\%$) were performed. The hypothesis for these T -Tests is that for the same material the mean surface roughness produced with UC and CC are equal. Table III shows the results of these T -tests. The hypothesis could not be rejected in all cases, which means that mean values of R_a , R_q ,

R_z and R_{Sm} were not significantly different for UC and CC surfaces.

Single sided F -Tests ($P = 5\%$) served to compare variances of roughness parameters measured on UC and on CC surfaces for the same material. Two hypotheses were tested, i.e., the variance measured in UC tests is larger than the respective value measured in CC tests, and the variance in CC tests is smaller than in UC tests. Table IV shows that both hypotheses were rejected for MDF. This means that variances of surface roughness parameters were similar for both cutting procedures. Similarly, no influence of the cutting procedure on roughness parameter R_{Sm} was found for spruce and beech. Variance of the other roughness parameters R_a , R_q and R_z , however, may be larger (spruce) or smaller (beech), respectively, for UC than for CC.

Scanning electron microscope investigations have been used to detect possible differences in the appearance of surfaces produced by UC and CC cutting. In spruce and beech, the cut surface shows longitudinal cells oriented in the cutting direction, partially sliced with visible middle lamellae and open cell lumina. In large areas, the surfaces produced with both cutting techniques do not show any differences. In other regions, however, specific features could be found on UC surfaces but not on CC surfaces. Periodic impact marks produced by the ultrasonically vibrating knife are visible in some areas of the cut surface of beech (Fig. 2a) and spruce (Fig. 2b). Other features are microscopically small reels with diameter 10–20 μm and length in the order of 50 μm , which could be occasionally found on UC surfaces. Fig. 3 shows such reels on the cut surface of beech (Fig. 3a) and spruce (Fig. 3b).

In contrast to wood, the structure of medium density fibreboard consists of irregularly oriented wood fibres embedded in the matrix. The cut surface shown in Fig. 4 reflects this structure, and cells oriented approximately normal as well as parallel to the cutting direction are visible. No reels or impact marks are found, and the surfaces produced by UC and CC do not show obvious differences. Conventional and ultrasonic-assisted cutting of MDF produces particles and some debris, which are visible on the cut surfaces. In both woods continuous chips are produced in CC as well as UC experiments.

Contact angle measurements were performed with beech. In experiments with MDF and spruce, the testing fluid rapidly penetrated into the surface, which made evaluations impossible. Wettability tests with testing liquid water served to evaluate the surface reactivity of beech. The results for surfaces produced by CC are shown in Fig. 5a and b for UC. The measured data show

TABLE II Mean values and standard deviations (in μm) of roughness parameters R_a , R_q , R_z and R_{Sm}

Specimen	Repetitions	R_a	R_q	R_z	R_{Sm}
Beech CC	15	5.16 ± 2.25	6.95 ± 2.97	32.4 ± 12.8	591 ± 166
Beech UC	15	4.98 ± 1.24	6.85 ± 1.63	30.6 ± 5.0	624 ± 137
Spruce CC	15	4.63 ± 1.31	6.10 ± 1.73	28.4 ± 6.8	721 ± 163
Spruce UC	14	5.36 ± 2.77	6.99 ± 3.40	31.9 ± 14.5	645 ± 149
MDF CC	15	6.63 ± 1.78	9.07 ± 2.45	52.7 ± 13.0	273 ± 44
MDF UC	15	6.20 ± 1.81	8.45 ± 2.43	49.1 ± 12.0	276 ± 51

TABLE III Results of *T*-Tests of significance of two unknown means, μ with unknown standard deviations, σ

	R_a	R_q	R_z	R_{Sm}
Beech	Yes	Yes	Yes	Yes
Spruce	Yes	Yes	Yes	Yes
MDF	Yes	Yes	Yes	Yes

“Yes” means that the hypothesis $H_0: \mu(CC) = \mu(UC), P = 5\%$ cannot be rejected.

pronounced scatter, mainly due to the inhomogeneous structure of wood. Thick lines represent mean curves, which are similar for UC and CC. This means that the wettability is not influenced by the cutting procedure, within the ranges of scatter.

Surface energy measurements and evaluations were performed using the acid-base approach. In Fig. 6, the surface energy components evaluated for CC and

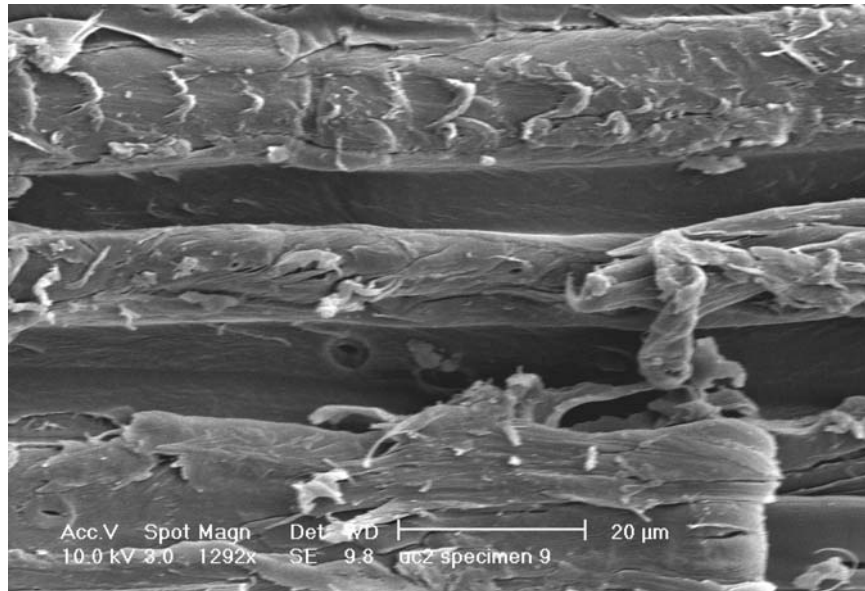
TABLE IV Results of *F*-Tests of significance of the hypotheses $H_0: \sigma^2(CC) > \sigma^2(UC)$ and $H_0: \sigma^2(CC) < \sigma^2(UC), P = 5\%$

	R_a	R_q	R_z	R_{Sm}
Beech	CC > USC	CC > USC	CC > USC	–
Spruce	USC > CC	USC > CC	USC > CC	–
MDF	–	–	–	–

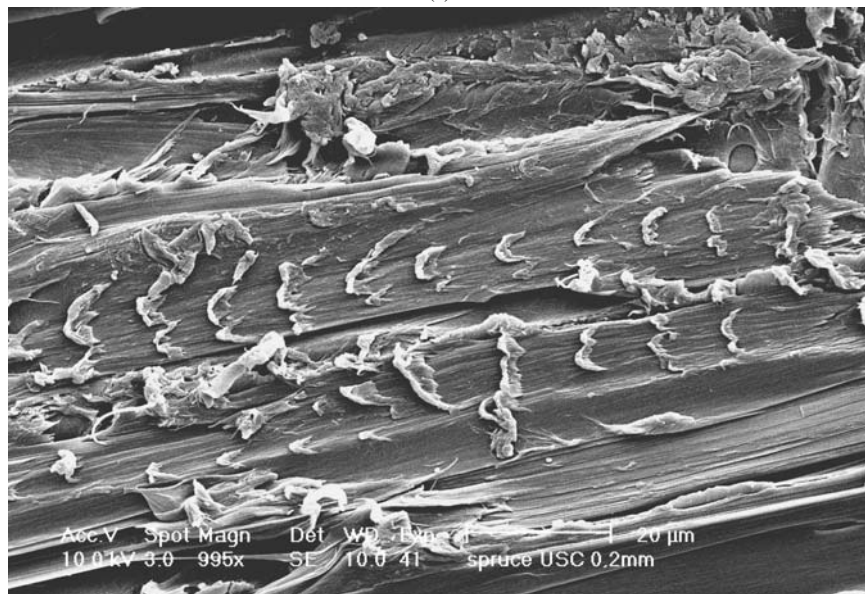
“CC > USC” means that hypothesis $\sigma^2(CC) > \sigma^2(UC)$ cannot be rejected and “CC < USC” means that hypothesis $\sigma^2(CC) < \sigma^2(UC)$ cannot be rejected.

“–” means that both hypotheses are rejected.

UC beech surfaces are presented. Data of the entire surface free energy, γ , the Lifshitz van der Waals component, γ^{LW} and the polar component, γ^{ab} with the constituents’ acid component, γ^+ and base component, γ^- are shown. Surface free energy, components and constituents are correlated according to



(a)

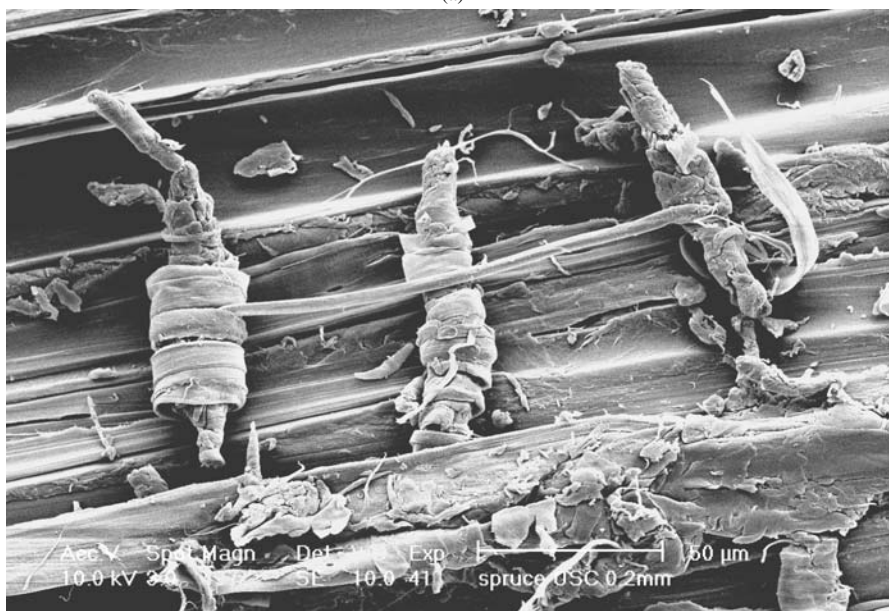


(b)

Figure 2 Periodic impact marks on the surface of beech (a) and spruce (b) created by ultrasonic-assisted cutting. Cutting direction is from right to left (a) and from left to right (b), respectively.



(a)



(b)

Figure 3 Surfaces produced by ultrasonic-assisted cutting of beech (a) and spruce (b). Microscopically small reels were formed. Cutting direction was from bottom to top (a) and from left to right (b), respectively.

Equation 1.

$$\gamma = \gamma^{LW} + \gamma^{ab} = \gamma^{LW} + 2\sqrt{\gamma^+ \gamma^-} \quad (1)$$

Entire surface free energies, Lifshitz van der Waals components and the polar components of beech surfaces produced by CC coincide with the respective values of surfaces produced by UC, within the ranges of scatter. The base component, γ^- , however, is larger for CC surfaces than for UC.

4. Discussion

In this study, the woods beech and spruce and the wood based fibre material MDF were cut with a sharp tool. In MDF, UC as well as CC produced small particles, whereas continuous chips were formed in both proce-

dures cutting wood in longitudinal direction. For this process and cutting direction it is known that a sharp tool produces reasonably good surfaces even for low cutting speeds, like 170 mm/s as used in this study [27].

Roughness parameters investigated here, i.e., three roughness height parameters, R_a , R_q and R_z and one spacing parameter, R_{Sm} delivered similar mean values for UC and CC surfaces. For homogeneous materials, these roughness parameters could be used reasonably well to characterise the influence of the processing technique on the obtained surfaces. In porous materials like woods, however, the measured roughness is influenced by both, the material's structure and the material's processing technique [27, 28]. There exists no generally accepted rule to divide structural roughness from roughness caused by processing. UC may influence the surface profile; however, the considered

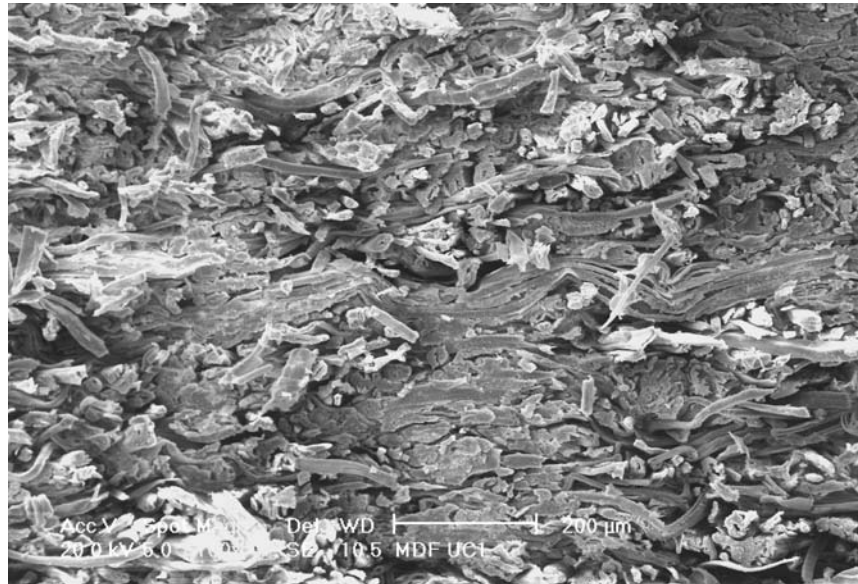
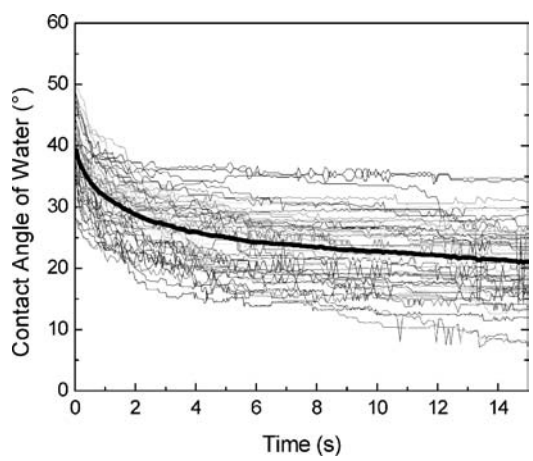
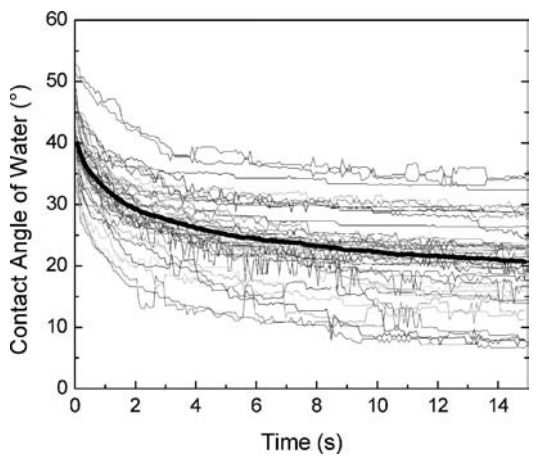


Figure 4 Surface of MDF produced by UC. Randomly oriented fibres embedded in adhesive are visible. Cutting direction is from left to right.



(a)



(b)

Figure 5 Contact angle of water measured on cut surfaces of beech as a function of time. Surfaces were produced by CC (a) and UC (b), respectively.

roughness parameters could be too insensitive to account for these variations.

Additional information on surface structure caused by UC is available from the SEM surface studies. Two surface features of wood, which were found only on

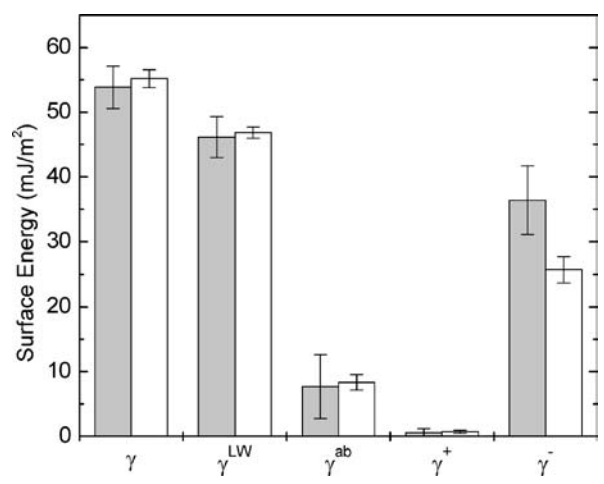


Figure 6 Surface energies on beech surfaces produced by CC (grey columns) and UC (white columns). γ is the entire surface free energy, γ^{LW} the Lifshitz van der Waals component, γ^{ab} the polar component, γ^+ the acid component, and γ^- the base component. Error bars indicate standard deviations.

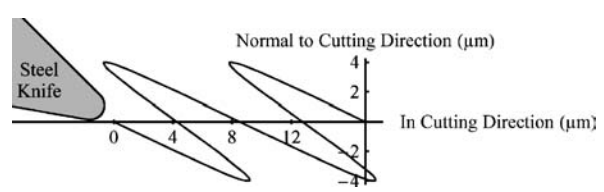


Figure 7 Movement of the knife at vibration amplitude $8 \mu\text{m}$, vibration frequency 20 kHz, cutting speed 170 mm/s and angle of vibration axis 30° .

surfaces produced by UC and not on those created by CC were periodic impact marks (Fig. 2) and microscopic reels (Fig. 3). Both microscopic features can be rationalised with the kinematics of the steel blade with respect to the cutting surface, as shown in Fig. 7. The steel blade vibrates at 20 kHz and vibration amplitude $8 \mu\text{m}$ and is inclined by 30° to the cutting surface. The whole system moves forward with constant speed in the cutting direction. Moving the blade with 170 mm/s for 50 ms (duration of one oscillation), the blade has

the same vertical position and moving direction within a periodic distance of 8.5 μm in cutting direction.

The sinusoidal movement of the steel blade means that the blade penetrates the material in a forward direction, creates new surfaces and then moves back and upward before it reverses and penetrates the material again. Periodic impact marks shown in Fig. 2 reflect the oscillation of the steel blade and distances between two marks are in the range 8.5 μm . Although sharp blades were used in the experiments, the cutting edge has certain roundness (the radius of the sharp blade is less than 1 μm and progressively increases with increasing in-service time). Besides material separation, the material below the blade is compressed and deformed and some adhesion of material may occur. Adhesion of loose material may lead to the microscopic reels, which are observed in some regions of the cutting surfaces of both woods (Fig. 3).

Changes in surface chemistry were evaluated by wettability tests and surface free energy measurements. Wettability tests performed on beech showed, that spreading and penetration of the water drops are similar on surfaces produced by UC and CC. The main parameter besides surface chemistry, which determines wettability, is the surface structure. Except for some specific features, which were found in certain areas of UC surfaces, surface appearance was similar after both cutting procedures and no influence on the measured mean roughness was found. Compression of cells and the creation of weak boundary layers of destroyed material [13] were rare in both cases since sharp tools have been used.

Surface energy is sensitive to variations of surface chemistry. Measurements performed on beech surfaces revealed similar values of entire surface free energy, the Lifshitz van der Waals component, the polar component and the acid component, within the ranges of scatter. The base component, however, was reduced by approximately 30% on UC surfaces compared with surfaces produced by CC. Investigations on microtomed beech samples showed reductions of the base component of aged wood [24, 29], and thermal loading accelerates ageing [30, 31]. Heat may be generated on the cutting surfaces in UC experiments due to the high frequency movement of the steel blade. This could explain accelerated ageing and thus the lowered base components on UC surfaces.

5. Conclusions

Cut surfaces of beech and spruce in longitudinal fibre direction and of MDF have been studied after conventional cutting (CC) and ultrasonic-assisted cutting (UC). UC experiments have been performed superimposing ultrasonic vibrations of 8 μm and frequency 20 kHz on to the linear movement of the cutting knife. The following conclusions may be drawn:

1. Mean roughness obtained after UC and CC were similar, whereas variances of the roughness parameters R_a , R_q and R_z were respectively larger (beech) or smaller (spruce) for conventionally cut surfaces.

2. Electron microscopy revealed similar cutting surfaces produced in MDF for UC and CC and reflect the structure of randomly oriented fibres embedded in adhesive. Large areas of the surfaces of both woods appear similar after both cutting procedures and show (partially sliced) cells. Compression of cells and the creation of weak boundary layers of destroyed material were rare since sharp tools were used. Periodic impact marks and microscopic reels were found only on UC surfaces.

3. Wettability of beech with water was similar after UC and CC.

4. Surface reactivity investigations of beech surfaces showed influences of cutting procedure on the base component of the surface free energy, which was lower for UC surfaces. Possible explanation is accelerated ageing due to thermal loading of the cutting surface.

Acknowledgments

This work was financed by the Austrian Federal Ministry of Transport, Innovation, and Technology (BMVIT), Subprogram "Factory of Tomorrow", which is gratefully acknowledged.

References

1. V. K. ASTASHEV and V. I. BABITSKY, *Ultrasonics* **36** (1998) 89.
2. C. S. LIU, B. ZHAO, G. F. GAO and F. JIAO, *J. Mater. Process. Technol.* **129** (2002) 196.
3. G. F. GAO, B. ZHAO, F. JIAO and C. S. LIU, *ibid.* **129** (2002) 66.
4. M. JIN and M. MURAKAWA, *ibid.* **113** (2001) 342.
5. J.-D. KIM and I.-H. CHOI, *ibid.* **68** (1997) 89.
6. M. ZHOU, X. J. WANG, B. K. A. NGOI and J. G. K. GAN, *ibid.* **121** (2002) 243.
7. K. KATO, K. TSUZUKI and I. ASANO, *Mokuzai Gakkaishi* **17** (1971) 57.
8. K. FUJIWARA, M. NOGUCHI and H. SUGHIHARA, *ibid.* **22** (1976) 76.
9. G. SINN, P. BEER, B. ZETTL and H. MAYER, in Proceedings of the 16th IWMS, Matsue, Japan, August 2003, edited by P. C. Tanaka (Organizing Committee of the 16 IWMS. Faculty of Science and Engineering, Shimane University, Matsue, Japan, 2003) p. 203.
10. M. DE MEIJER and H. MILITZ, *Progr. Org. Coat.* **38** (2000) 223.
11. M. STEHR, J. SELTMAN and I. JOHANSSON, *Holz-forschung* **53** (1999) 93.
12. M. STEHR, *ibid.* **53** (1999) 655.
13. M. STEHR and I. JOHANSSON, *J. Adhes. Sci. Technol.* **14** (2000) 1211.
14. H. A. CORE, W. A. CÔTÉ and A. C. DAY, in "Wood: Structure and Identification" edited by W. A. Côté, Syracuse Wood Science Series, 6 (Syracuse University Press, Syracuse, 1979).
15. E. MAGOSS and G. SITKEI, in 15th IWMS, Los Angeles, California, USA, 2001, edited by R. Szymani (Berkeley, CA) p. 437.
16. T. NGUYEN and W. E. JOHNS, *Wood Sci. Technol.* **13** (1979) 29.
17. M. DUNKY and P. NIEMZ, in "Holzwerkstoffe und Leime. Technologie und Einflussfaktoren" (Springer, Berlin Heidelberg, 2002) p. 135.
18. J. KOPAC and S. SALI, *J. Mater. Process. Technol.* **133** (2003) 134.
19. E. WESTKÄMPER and A. RIEGEL, *HolzRoh. Werk.* **50** (1992) 475.
20. L. MUMMERY and R. ROMETSCH, "Rauheitsmessung. Theorie und Praxis" (Hommelwerke, VS-Schwenningen, 1993) p. 24.

21. M. GINDL, G. SINN, A. REITERER and S. TSCHEGG, *Holzforschung* **55** (2001) 433.
22. M. GINDL, G. SINN, W. GINDL, A. REITERER and S. TSCHEGG, *Coll. Surf. A* **181** (2001) 279.
23. M. GINDL and S. TSCHEGG, *Langmuir* **18** (2002) 3209.
24. M. E. P. WÄLINDER, *Holzforschung* **56** (2002) 363.
25. M. DE MEIJER, S. HAEMERS, W. COBBEN and H. MILITZ, *Langmuir* **16** (2000) 9352.
26. R. GOOD J., "Contact Angle, Wettability and Adhesion" edited by K. L. Mittal (VSP, Utrecht, 1993) p. 3.
27. B. ETTTEL, "Sägen Fräsen Hobeln Bohren: Die Spannung von Holz und ihre Werkzeuge" (DRW-Verlag Weinbrenner GmbH & Co., Leinfelden-Echterdingen, 1997).
28. Y. FUJIWARA, Y. FUJII and S. OKUMURA, in Proceedings of the 16th IWMS, Matsue, Japan, August 2003, edited by P. C. Tanaka (Organizing Committee of the 16th IWMS. Faculty of Science and Engineering, Shimane University, Matsue, Japan, 2003) p. 359.
29. M. GINDL, A. REITERER, G. SINN and S. E. STANZL-TSCHEGG, *Holz Roh. Werk.* **62** (2004) 273.
30. A. W. CHRISTIANSEN, *Wood Fiber Sci.* **22** (1990) 441.
31. *Idem., ibid.* **23** (1991) 69.

*Received 25 February 2004
and accepted 16 February 2005*