Wood Sci Technol (2011) 45:359–368
DOI 10.1007/s00226-010-0327-5

ORIGINAL

Improved bondability of wax-treated wood following plasma treatment

Georg Avramidis · Gunthard Scholz · Evelyn Nothnick · Holger Militz · Wolfgang Viöl · Arndt Wolkenhauer

Received: 9 June 2009 / Published online: 9 April 2010

Abstract In this study, the impact of a plasma treatment using dielectric barrier discharge at atmospheric pressure on wax-treated beech was investigated by surface energy determination and adhesion tests. Measurements of the surface energy revealed a strong increase in surface polarity along with increased surface energy as a result of the plasma treatment, pointing to increased adhesion properties. To evaluate the adhesion properties of a polyvinyl acetate (PVAc) adhesive on beech treated with montan ester wax and synthetic Fischer–Tropsch wax, a special peel test was applied. This peel test provided evidence of increased adhesion of the PVAc after plasma treatment of both materials investigated.

Introduction

Increasing the durability of wood products, especially in outdoor applications, is a constant objective in wood processing and can be achieved by equipping the wood with water-repellent characteristics. Treatment with water-repellent agents meets this objective by increasing the wood hydrophobicity and reducing its moisture content. To render the wood more hydrophobic, chemicals, such as oils, silanes, silicones or waxes, have been used and applied to solid wood and wood-based

G. Avramidis · E. Nothnick · W. Viöl · A. Wolkenhauer
Faculty of Natural Sciences and Technology, University of Applied Sciences and Arts,
Von-Ossietzky-Strasse 99, 37085 Göttingen, Germany

G. Scholz · H. Militz
Department of Wood Biology and Wood Products, Georg-August-University of Göttingen,
Büsgenweg 4, 37077 Göttingen, Germany

W. Viöl (✉)
Laser-Laboratorium Göttingen e.V., Hans-Adolf-Krebs-Weg 1, 37077 Göttingen, Germany
e-mail: vioel@llg-ev.de

materials, e.g., fibre board and particle board, to reduce their water uptake and improve dimensional stability (Mai and Militz 2004; Donath et al. 2006a, b; Donath et al. 2007; Militz et al. 2008). Resin/wax treatment of wood results in reduced capillary water flow and improves dimensional stability of wood exposed to wet conditions (Banks 1973). Today, a great variety of different types of wax for wood treatment are available. Besides the natural waxes, such as beeswax, palm wax or fossil waxes, new synthetic waxes have been developed, such as the Fischer–Tropsch waxes, together with wax-like compounds derived from plastics. There are many applications for these waxes, like for example form releasing and hydrophobic agents, in plastic- and wood-based industries but also for cosmetic and culinary products (Illmann et al. 1983). The waxes vary in their specific properties such as viscosity, polarity or hardness as well as their costs and availability. All these waxes, however, are hydrophobic and render the wood and the wood surface hydrophobic. This is a positive effect since it results in reduced water uptake, the purpose of the treatment. However, for processing of the treated wood, e.g., gluing or painting, the hydrophobic surface is a drawback. The low surface energies of the waxes impede wetting of adhesives. This causes practical problems during bonding processes because of the common use of water-based adhesives. Because of the low polarity of the waxes, water-based adhesives are prevented from spreading on the wood surface, a requirement for sound bonding. For this reason, many techniques have been utilised to overcome this drawback and make the surface less hydrophobic, for example using bio-products such as enzymes (xylanases), chemicals such as tris (polyoxyethylene) sorbitan monooleate (Christiansen 1990), sodium hydroxide (NaOH), calcium hydroxide, nitric acid, hydrogen peroxide, borax (Sernek 2002) and hydroxymethylated resorcinol (HMR) (Kurt et al. 2008). Another possible way to improve the bonding properties of wax-treated wood is plasma treatment. Plasmas are widely used in polymer processing to improve surface properties, such as dye uptake, printability and bondability (Kogelschatz 2003; Hippler et al. 2004). They are well known for their ability to generate functional groups, e.g., C–OH, C=O, O=C–OH, whereby the polar character of the surface increases and consequently its surface energy (Chan 1994; Strobel et al. 1994). In recent years, research interest in the plasma treatment of wood and wood-based materials has grown, and similar effects and beneficial changes were found after plasma treatment on these materials (Wolkenhauer 2009). Plasma treatment results in a modification of the near-surface region without changing the desirable bulk properties of the material (Kogelschatz 2003). In this way, plasma treatment can alter the adhesion properties of wax-treated beech without compromising its performance during application. This study addresses this issue, and the potential increase in adhesion properties of wax-treated beech by plasma treatment is investigated. Wax-treated beech is plasma-treated by a dielectric barrier discharge at atmospheric pressure. To assess the impact of the plasma treatment on wax-treated beech surfaces, the surface energy was determined by contact angle measurements. In order to detect changes in adhesion of a PVAc adhesive after plasma treatment, a special peel test was applied. For this peel test, a cotton tissue was directly glued to the wood samples and, after drying of the adhesive, removed by a tensile testing machine. Each specimen possessed adjacent untreated and plasma-treated areas so that direct comparison was possible. This peel test has already been successfully applied on particle boards and fibre boards, yielding conclusive and unambiguous results (Wolkenhauer et al. 2008a).

Experimental

Materials

Samples (380 × 110 × 10 mm^3) of beech (*Fagus sylvatica*) were dried at 100°C and subsequently fully impregnated at 120°C with two types of wax. A synthetic Fischer–Tropsch wax (Sasolwax C80®, Sasol, Germany) and a montan ester wax (Licowax E®, Clariant, Germany) were used (Table 1). The impregnation was carried out via vacuum-pressure treatment. A low-pressure impregnation step of 1 h at 10 kPa was followed by a high-pressure impregnation step for 1 h at 1.2 MPa.

After wax treatment, the samples were planed and stored for 1 week at 20°C and 50% relative humidity prior to investigation. For the peel test, a commercial PVAc adhesive was used (Ponal Super3, Henkel KGaA, Düsseldorf, Germany).

Plasma treatment

Figure 1 depicts the dielectric barrier discharge (DBD) setup used. The specimen is positioned on an insulated (rubber) grounded electrode (aluminium). An alternating high-voltage pulse generator with a pulse duration of 2 μs and a frequency of 17 kHz is connected to the upper electrode (Al_2O_3, 300 × 50 × 50 mm^3). In this unsealed setup, ambient air at room temperature is blown through the discharge gap, 2 mm wide, between the specimen and the high-voltage ($\approx$30 kV) electrode with a velocity of approximately 1 m s^{-1}. To minimise thermal impact during plasma treatment, 2 s of plasma treatment is followed by a break of 2 s so that the gas temperature did not exceed 40°C.

Surface energy determination

In recent years, plasma techniques have attracted interest for their wood modification effects and have been applied to wood and wood-based materials to

Table 1 Characteristics of the waxes used

Properties	Unit	Sasolwax C80®	Licowax E®
Density	g cm^{-3}	0.9	1.02
Viscosity at 100°C	mPa s	9.4	30
Drop point	°C	88	82
Acid value	mg KOH g^{-1}	–	17
Saponification value	mg KOH g^{-1}	–	145

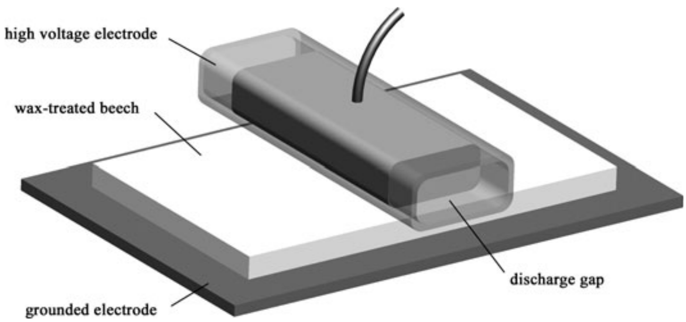

Fig. 1 Schematic sketch of the plasma treatment setup

improve surface characteristics such as wettability and bondability (Podgorski et al. 2000; Rehn et al. 2003; Klarhöfer et al. 2005; Topala and Dumitrascu 2007; Evans et al. 2007; Odrášková et al. 2008; Wolkenhauer et al. 2008b; Lecoq et al. 2008; Custódio et al. 2009). These investigations showed that plasma treatment positively affects wood surface characteristics by increasing the surface energy. In this study, the surface energy was determined by means of contact angle measurements using the Owens–Wendt approach on the basis of Young's equation (Owens and Wendt 1969):

$$\gamma_{\mathrm{S}} = \gamma_{\mathrm{SL}} + \gamma_{\mathrm{L}} \cos\theta, \tag{1}$$

where γ_{S} is the surface energy of the solid in mN·m^{-1}, γ_{SL} is the interfacial energy between solid and liquid, γ_{L} is the surface tension of the liquid, and θ is the contact angle. This approach divides the total surface energy (γ^{tot}) into a polar component (γ^{P}) and a disperse component (γ^{D}):

$$\gamma^{\mathrm{tot}} = \gamma^{\mathrm{D}} + \gamma^{\mathrm{P}}. \tag{2}$$

In order to determine disperse and polar components of the surface energy, at least two test liquids are required, but the more liquids are used, the more reliable are the results obtained. Therefore, five test liquids are used to determine surface energy: distilled water ($\gamma^P = 51$ mN·m^{-1}, $\gamma^D = 21.8$ mN·m^{-1}), glycerol ($\gamma^P = 30$ mN·m^{-1}, $\gamma^D = 34$ mN·m^{-1}), ethylene glycol ($\gamma^P = 19$ mN·m^{-1}, $\gamma^D = 29$ mN·m^{-1}), diiodomethane ($\gamma^P = 0$ mN·m^{-1}, $\gamma^D = 50.8$ mN·m^{-1}) and formamide ($\gamma^P = 19$ mN·m^{-1}, $\gamma^D = 39$ mN·m^{-1}).

Contact angles were measured directly after plasma treatment with the static sessile drop method 3 s after droplet deposition using the G 10 measuring system (Krüss GmbH, Hamburg, Germany) and the corresponding software DSA 1. The surface energy was calculated using the average contact angle data of 10 droplets (droplet volume = 10 µl).

Peel test

Figure 2 depicts a schematic sketch of the peel test. The cotton tissue is glued to the wax-treated beech samples and removed by a tensile testing machine (Z010, Zwick

GmbH & Co. KG, Ulm, Germany) with a traverse speed of 20 mm min^{-1} and a force data acquisition rate of 10 μm in order to measure the peel force versus the peel length. To ensure good adhesion and to avoid adhesive failure between cotton tissue and PVAc adhesive, plasma treatment (30 s) of the cotton tissue was also necessary for the peel test. The wax-treated samples are only partially plasma-treated so that a plasma-treated surface of 50 mm width is formed between two untreated areas. In this way, two transitions (untreated/plasma-treated and plasma-treated/untreated) are obtained during the peel test and a change in peel force should be detectable. After plasma treatment of the wood samples, the cotton tissue is glued on with the PVAc adhesive, pressed (1 N mm^{-2}) for one hour and stored for 7 days in a climate chamber at 20°C and 50% relative humidity. Subsequently, the samples were sawn into five specimens 20 × 180 mm^2 for the peel test. With this method, adjacent untreated and plasma-treated areas can be investigated with one specimen so that scattering of results can be minimised.

Results and discussion

Surface energy

To ascertain the impact of plasma treatment on wax-treated wood and to investigate the influence of the duration of the plasma treatment, the surface energy was determined as a function of the treatment time as shown in Figs. 3 and 4. In the untreated state, both synthetic wax-treated beech and montan ester wax-treated beech possess a non-polar surface character. Thus, the total surface energy is only determined by the disperse component of the surface energy. This lack of surface polarity prevents the formation of attractive polar forces and thereby impairs

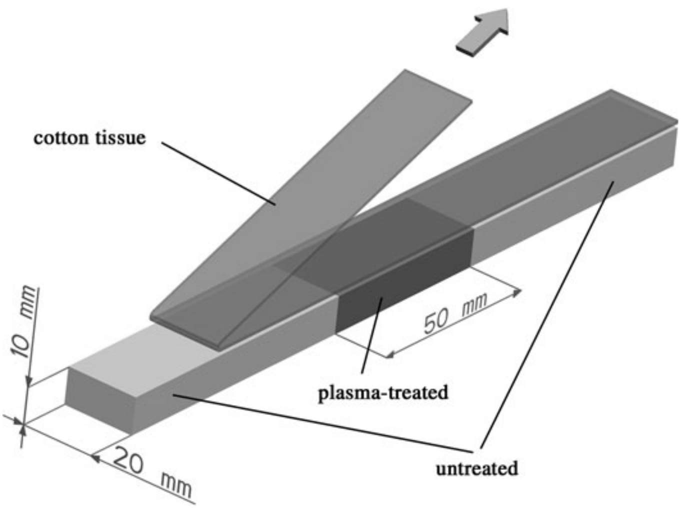

Fig. 2 Schematic sketch of the peel test

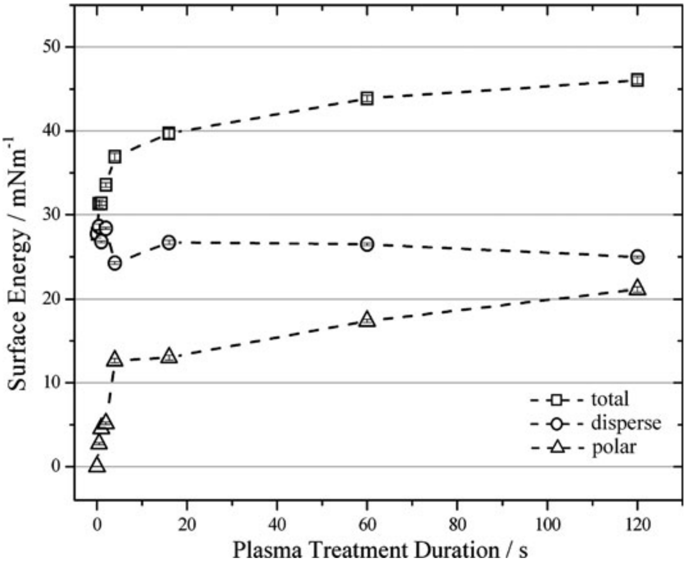

Fig. 3 Surface energy of synthetic wax-treated beech as a function of the duration of plasma treatment

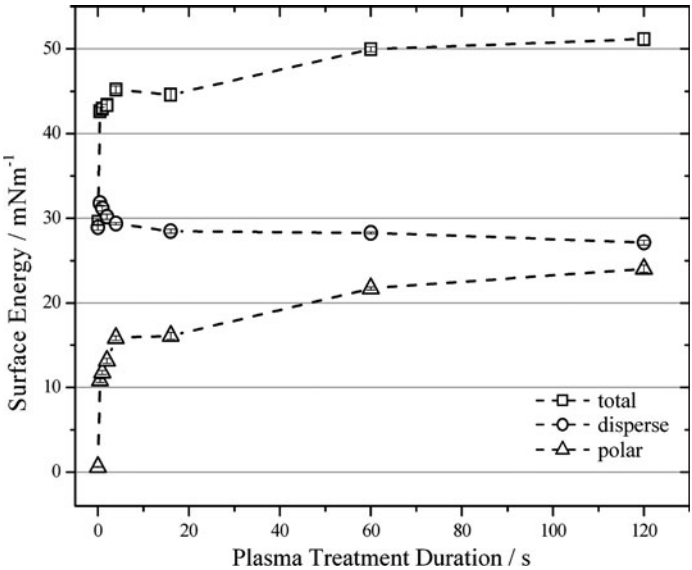

Fig. 4 Surface energy of montan ester wax-treated beech as a function of the duration of plasma treatment

wetting, and in consequence reduces adhesion. These results differ considerably from those of the unmodified beech (Wolkenhauer et al. 2008c, 2009) showing clearly the impact of the wax treatment on the surface energy characteristics.

Furthermore, both wax-treated beech samples exhibit similar surface energy characteristics.

To evaluate the influence of the plasma treatment duration on the wax-treated beech surfaces, seven different treatment durations (0.5, 1, 2, 4, 16, 60, 120 s) were investigated. With plasma treatment, a distinct increase in the polar component of the surface energy is evident. For both synthetic wax-treated beech and montan ester wax-treated beech, the most dramatic changes take place within the first 4 s of plasma treatment. In this period of time, the polar components of surface energy show a strong and continuous increase to 13 and 16 $mN \cdot m^{-1}$ for synthetic and montan ester wax-treated beech, respectively. The disperse component of the montan ester wax-treated beech shows, within the same period, a slight increase, followed by a decrease to its initial value. This effect cannot be observed clearly for the synthetic wax-treated beech. After this first stage, the disperse components show a continuous and slight decrease as the duration of the plasma treatment increases. The polar components, on the other hand, show a continuous but more pronounced increase up to 21 and 24 $mN \cdot m^{-1}$ for the synthetic wax and montan ester wax-treated beech, respectively, after 120 s of plasma treatment. In general, both wax-treated beech samples show similar responses to plasma treatment.

Peel test

The results of the surface energy determination, especially the observation of strong increases in the polar components, suggest improved adhesion after plasma treatment. To obtain the first evidence of increased bond strength of the PVAc adhesive, a force sensitive peel test was carried out. In order to detect changes in adhesion properties, the duration of the plasma treatment of the 50 mm wide surface was fixed at 120 s. Figures 5 and 6 show the peel force versus peel length for the synthetic wax-treated beech and montan ester wax-treated beech, respectively. The force progression line is the mean value of ten specimens (two plates, each with five specimens). A distinct increase and decrease in peel force is apparent when entering and leaving the plasma-treated surface. The average increase in peel force for synthetic wax-treated beech is about 60% and for montan ester wax-treated beech about 50%. The results of this peel test show conclusive and unambiguous differences in adhesion on untreated and plasma-treated surfaces and support increased adhesion of PVAc adhesive on wax-treated beech after plasma treatment.

Conclusion and outlook

This study has yielded the first evidence that adhesion of PVAc adhesive on wax-treated beech is positively affected by plasma treatment. A significant increase in the polar component of the surface energy was evident after plasma treatment, whereas the disperse component decreased slightly. This increase in surface energy suggests improved adhesion, which was confirmed by a force sensitive peel test. An increase in peel force of 60 and 50% was found after plasma treatment on synthetic wax-treated beech and montan ester wax-treated beech, respectively. Further studies

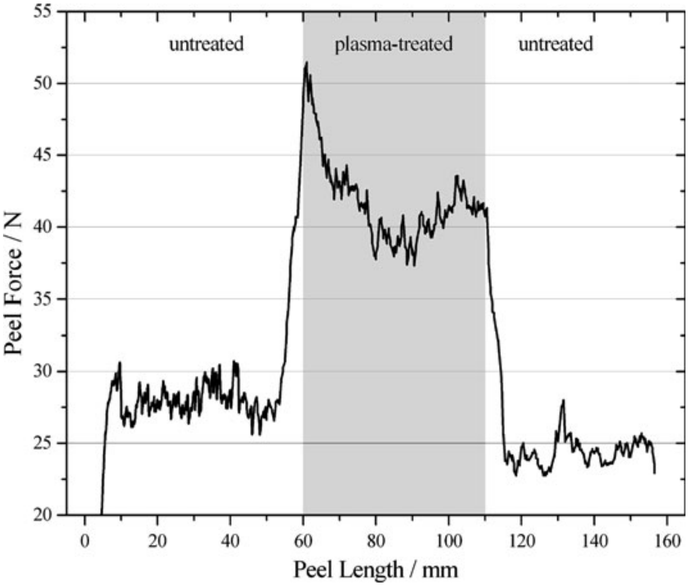

Fig. 5 Peel force on synthetic wax-treated beech versus peel length

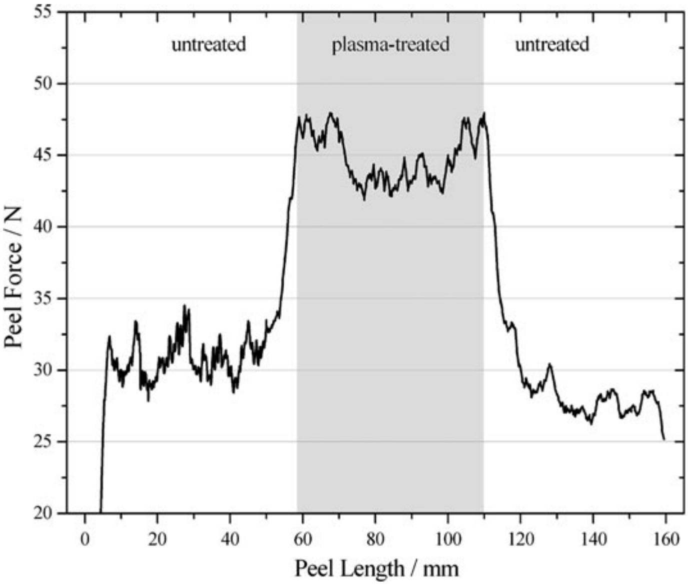

Fig. 6 Peel force on montan ester wax-treated beech versus peel length

are needed to confirm the increased adhesion of adhesives and paints after plasma treatment, and other testing methods are necessary in order to obtain comparable and quantitative results.

Acknowledgments Financial support from the German Research Foundation (DFG, VI 359/1-3) and the Federal Ministry of Education and Research (BMBF, 1708X08) is gratefully acknowledged.

References

Banks WB (1973) Water uptake by Scots pine sapwood and its restriction by the use of water repellents. Wood Sci Technol 7:271–284

Chan CM (1994) Polymer surface modification and characterization. Carl Hanser Verlag, Munich

Christiansen AW (1990) How overdrying wood reduces its bonding to phenol-formaldehyde adhesives: a critical review of the literature, part 1, physical response. Wood Fiber Sci 22:441–459

Custódio J, Broughton J, Cruz H, Winfield P (2009) Activation of timber surfaces by flame and corona treatments to improve adhesion. Int J Adhes Adhes 29:167–172

Donath S, Militz H, Mai C (2006a) Creating water repellent effects on wood by treatment with silanes. Holzforschung 60:40–46

Donath S, Militz H, Mai C (2006b) Treatment of wood with aminofunctional silanes for protection against wood destroying fungi. Holzforschung 60:210–216

Donath S, Militz H, Mai C (2007) Weathering of silane treated wood. Holz Roh Werkst 65:35–42

Evans PD, Ramos M, Senden T (2007) Modification of wood using a glow-discharge plasma derived from water. In: Hill CAS, Jones D, Militz H, Ormondroyd GA (eds) Proceedings of the third European conference on wood modification. Biocomposites Centre, University of Wales, Bangor, pp 123–132

Hippler R, Pfau S, Schmidt M, Schoenbach KH (2004) Low temperature plasma physics. Wiley-VCH, Berlin

Illmann G, Schmidt H, Brotz W, Michalczyk G, Payer W, Dietsche W, Hohner G, Wildgruber J (1983) Wachse. In: Ullmanns Enzyklopädie der technischen Chemie, 4th edn, vol 24, Wiley-VCH, Weinheim, pp 1–49

Klarhöfer L, Frerichs M, Maus-Friedrichs M, Kempter V, Viöl, W (2005) Investigation of pure and plasma treated spruce with surface analytical techniques. In: Proceedings of the second European conference on wood modification, Göttingen, Germany, pp 339–345

Kogelschatz U (2003) Dielectric-barrier discharges: their history, discharge physics and industrial applications. Plasma Chem Plasma Process 23:1–46

Kurt R, Krause A, Militz H, Mai C (2008) Hydroxymethylated resorcinol (HMR) priming agent for improved bondability of wax-treated wood. Holz Roh Werkst 66:333–338

Lecoq E, Clement F, Panousis E, Loiseau JF, Held B, Castetbon A, Guimon C (2008) Pinus pinaster surface treatment realized in spatial and temporal afterglow DBD conditions. Eur Phys J Appl Phys 42:47–53

Mai C, Militz H (2004) Modification of wood with silicon compounds. Inorganic silicon compounds and sol-gel systems: a review. Wood Sci Technol 37:339–348

Militz H, Mai C, Ghosh SC (2008) Combined effect of hydrophobation and durability improvement of wood treated with silicone emulsions. Cost action E37 final conference in Bordeaux. Socio-economic perspectives of treated wood for the common European market, pp 31–39

Odrášková M, Ráhel J, Zahoranová A, Tino R (2008) Plasma activation of wood surface by diffuse coplanar surface barrier discharge. Plasma Chem Plasma Process 28:203–211

Owens DK, Wendt RC (1969) Estimation of the surface free energy of polymers. J Appl Polym Sci 13:1741

Podgorski L, Chevet B, Onic L, Merlin A (2000) Modification of wood wettability by plasma and corona treatments. Int J Adhes Adhes 20:103–111

Rehn P, Wolkenhauer A, Bente M, Förster S, Viöl W (2003) Wood surface modification in dielectric barrier discharges at atmospheric pressure. Surf Coat Technol 174–175:515–518

Sernek M (2002) Comparative analysis of inactivated wood surfaces. PhD thesis, Virginia Polytechnic Institute and State University

Strobel M, Lyons CS, Mittal KL (1994) Plasma surface modification of polymers: relevance to adhesion. VSP, Utrecht

Topala I, Dumitrascu N (2007) Dynamics of the wetting process on dielectric barrier discharge (DBD)-treated wood surfaces. J Adhes Sci Technol 21:1089–1096

Wolkenhauer A, Militz H, Viöl W (2008a) Increased PVA-glue adhesion on particle board and fibre board by plasma treatment. Holz Roh Werkst 66:143–145

Wolkenhauer A, Avramidis G, Hauswald E, Militz H, Viöl W (2008b) Plasma treatment of wood-plastic composites to enhance their adhesion properties. J Adhes Sci Technol 22:2025–2037

Wolkenhauer A, Avramidis G, Militz H, Viöl W (2008c) Plasma treatment of heat treated beech wood—investigation on surface free energy. Holzforschung 62:472–474

Wolkenhauer A (2009) Plasma treatment of wood and wood-based materials by dielectric barrier discharge at atmospheric pressure. Sierke, Göttingen

Wolkenhauer A, Avramidis G, Hauswald E, Militz H, Viöl W (2009) Sanding vs. plasma treatment of aged wood: a comparison with respect to surface energy. Int J Adhes Adhes 29:18–22