MOLHABILIDADE DA MADEIRA FURFURILADA DE PINUS APÓS TRATAMENTO POR PLASMA

[1]**Pedro Henrique G. de Cademartori** (pedrocademartori@gmail.com), [2]**Bruno D. Mattos** (brunodufaumattos@gmail.com), [3]**André L. Missio** (andreluizmissio@gmail.com), [1]**Graciela Ines B. de Muniz** (gbmunize@ufpr.br), [4]**Washington Luiz E. Magalhães** (washington.magalhaes@embrapa.br)

[1]**Federal University of Paraná**
Wood and Forestry Science Center, Lothário Meissner 900, ZIP code: 80210-170, Curitiba, Brazil.

[2]**Federal University of Paraná**
Integrate program in Engineering & Materials Science (PIPE), P.O Box: 19011, ZIP code 81531-990, Curitiba, Brazil.

[3]**Federal University of Santa Maria**
Forestry Engineering, Forest Products Laborator, P.O. Box 221, ZIP code 97105-900. Santa Maria, Brazil.

[4]**Embrapa Forestry**
Estrada da Ribeira, Km 111 – P.O Box: 319, ZIP code: 83411-000, Colombo, Brazil.

RESUMO: Este estudo objetivou investigar o efeito do tratamento por plasma na molhabilidade da madeira furfurilada de pinus por meio da técnica de ângulo de contato. Amostras de *Pinus taeda* livres de defeitos foram imersas em pressão atmosférica em duas soluções de álcool furfurílico com o intuito de obter-se dois níveis de ganho percentual de massa, 15 e 40%. A superfície das amostras controle e furfuriladas foi modificada com tratamento por plasma em um reator alimentado por radiofrequência (RF). O tratamento por plasma de argônio foi realizado em baixa pressão com uma potência de 80 W durante 120 s. Os parâmetros de molhabilidade foram mensurados pela técnica não-destrutiva de ângulo de contato, utilizando-se o método de gota séssil. As mensurações foram realizadas após 1, 4, 8, 12 e 20 dias do tratamento por plasma. Determinou-se o ângulo de contato aparente, o trabalho de adesão e a energia livre de superfície. Tanto a molhabilidade da madeira não tratada como a molhabilidade da madeira furfurilada aumentaram após o tratamento por plasma. O ângulo de contato aparente diminuiu e a superfície da madeira de pinus tornou-se mais molhável. O tratamento por plasma converteu a superfície hidrofóbica da madeira furfurilada de pinus em uma superfície hidrofílica. A madeira furfurilada de pinus recuperou parcialmente a sua hidrofobicidade natural ao longo dos dias de exposição. No entanto, mesmo com os efeitos da exposição prolongada, o alto nível de molhabilidade obtido após o tratamento por plasma pode ser um importante fator para futuras aplicações em processos industriais.

Palavras Chave: descarga luminescente, furfurilação, ângulo de contato, superfície da madeira, tecnologia da madeira.

WETTABILITY OF PLASMA TREATED FURFURYLATED SOLID PINE WOOD

ABSTRACT: This study aimed to investigate the effect of plasma treatment on wettability of furfurylated pine wood using contact angle technique. Free-defect Loblolly pine samples were immersed at atmospheric pressure in two different furfuryl alcohol solutions to obtain two levels of weight percent gain, 15 and 40%. Surface of untreated and furfurylated wood samples were modified by plasma treatment in a RF cold-plasma reactor. The argon plasma treatment were performed in low-pressure at 80 W for 120 s. Wettability parameters were measured by non-destructive sessile drop type contact angle at 1, 4, 8, 12 and 20 days after the plasma treatment. Apparent contact angle, work of adhesion and surface free energy were determined. The wettability of untreated and furfurylated wood was enhanced significantly. Apparent contact angle decreased and the pine wood surface became highly wetted. The plasma treatment converts the hydrophobic furfurylated wood surface into a hydrophilic surface. Furfurylated wood partially recovered their natural hydrophobicity after aging. Nevertheless, even after the aging effects, the high degree of wettability may be important for future applications in industrial processes.

Keywords: glow discharge, furfurylation, contact angle, wood surface, wood technology.

1. INTRODUCTION

In the last decades, many alternatives have been developed to improve wood properties, especially related to mechanical strength, dimensional stability and decay resistance. Nevertheless, some of these alternatives could inactivate wood surface, which is undesirable for coating and adhesion aspects. In situ polymerization (MATTOS *et al.* 2015; VENAS and RINNAN, 2008), heat treatment (CADEMARTORI *et al.* 2013; MISSIO *et al.* 2015) and wax impregnation (SCHOLZ *et al.* 2010) are examples of treatments that improve wood properties – especially hydrophobicity - but could inactive wood surface. This phenomenon of surface inactivation reduces the materials' surface free energy, resulting in liquid poor wettability (NUSSBAUM, 1999). According to CHRISTIANSEN (1991), some mechanisms of attractive reduction on wood surface influencing wood inactivation, such as migration of wood extractives to surface, micropores closure, surface oxidation and reorientation of molecular surface.

Regarding the surface inactivation, changes on wood surface are interesting to increase wettability and adhesion without modify their bulk structure. Plasma technique is a high-tech alternative to improve the performance of materials' surface. Among the applications in forest sector, plasma has been widely used to increase surface adhesion of wood-based panels (Cademartori et al. 2015), solid wood (ACDA *et al.* 2012; ASANDULESA *et al.* 2012) and natural fibers (XIAO *et al.* 2015).

One of the most simple and efficient tools to evaluate plasma changes on materials' surface is the non-destructive contact angle. This technique has been commonly applied in recent studies of plasma treated wood-based products (MAGALHÃES and SOUZA, 2002; AYDIN and DEMIRKIR 2010; LIU *et al.* 2010; POATY et al. 2013; CADEMARTORI *et al.* 2015).

Contact angle of polar and nonpolar solvents could infers changes on surface free energy, which is in relation to coating characteristics of wood and wood-based products (Pétrissans et al. 2003). Nevertheless, determination of contact angle should considers both chemical nature and roughness of surface (ADAMSOM, 1990). Among the methods for non-destructive contact angle measurement, sessile drop is commonly applied to evaluate surface of wood and wood-based products. Sessile drop directly measures a droplet of a liquid resting on a flat surface of a solid (ADAMSOM, 1990).

In this study, pine wood was treated with furfuryl alcohol to create a hydrophobicity surface with poor wettability. The effect of argon plasma treatment on wettability of furfurylated wood was evaluated. Plasma-treated furfurylated wood samples were stored at room environment for 20 days and the effect of aging was evaluated by contact angle technique.

2. MATERIAL AND METHODS

2.1 Raw material

Free-defect Loblolly pine (*Pinus taeda*) wood was cut into small pieces of 50 x 50 x 25 mm (length, width and thickness, respectively). All the samples' surface were sanded and kept in a climatic chamber (20°C and 65% of relative humidity) to reach the equilibrium moisture content.

2.2 Furfurylation

Loblolly pine samples were kept immersed at atmospheric pressure in two different furfuryl alcohol solutions. Wood samples were impregnated with furfuryl alcohol (Aldrich, 98% purity) for 4 and 72 hours to obtain two levels of weight percent gain, 15 and 40%. Citric acid at 4% w/v was used as the catalyst of the polymerization.

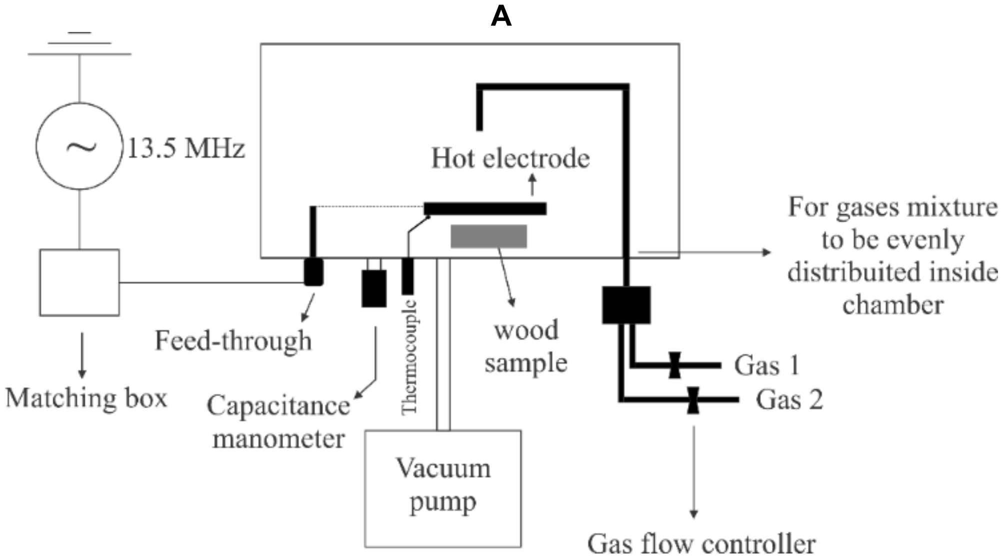
After the impregnation, wood samples were kept wrapped in aluminum foil and were oven-dried at 90±2ºC for 24 hours. These steps are based on the methodology described by MAGALHÃES and SILVA (2004).

2.3 Plasma treatment

Plasma treatment was performed in a cold plasma stainless steel cylindrical reactor previously described in CADEMARTORI *et al.* (2015). This reactor was developed in Embrapa Forestry and works at low-pressure in a RF (radio frequency, 13.5 MHz) system (Figure 1A).

Before the plasma treatment, argon was introduced inside the reactor to remove contaminants. Subsequently, glow discharge (Figure 1B) was performed at ~0.3 torr pressure with a gas flow of 20 sccm. Power applied was 80 W and time of discharge was 120 seconds. After plasma treatment, all the wood samples were kept in a desiccator to avoid contact with air humidity.

A



B

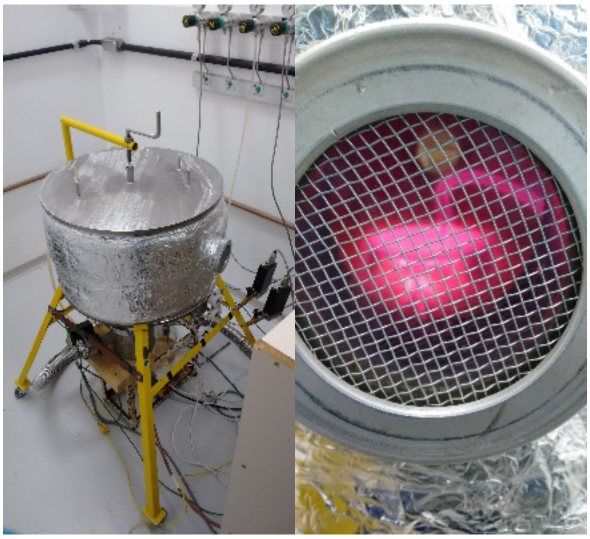


Figure 1. Schematic of cold-plasma reactor (A); Glow discharge applied in the furfurylated pine wood (B).

2.4 Wettability

The sessile drop type contact angle technique was used to measure changes on wettability of plasma treated pine wood. Apparent contact angle, work of adhesion and surface free energy parameters were determined in a goniometer Krüss DSA25 as a function of the time of droplet deposition. The first measurement was twenty-four hours after the plasma treatments by depositing three droplets of deionized water (surface tension of 72.80 mN m-1) with 5 µl volume on the surface of each sample. The apparent contact angle was measured after 5 s and 15 s of droplet deposition on samples' surface.

Aging effects on untreated and plasma-treated furfurylated wood surface were evaluated after storage in a room at 20±5ºC and 65±5% of relative humidity for 20 days. Wettability parameters were measured after 1, 4, 8, 12, 20 and 20 days of storage.

3. RESULTS AND DISCUSSION

Before the plasma treatment, apparent contact angle (CA) at 5s of droplet deposition of untreated wood was similar to CA of furfurylated wood. Nevertheless, CA of furfurylated wood showed a stabilization after 15s on wood surface, while CA of untreated wood decreased around 14%. This confirms the efficiency of treatment with furfuryl alcohol to improve hydrophobicity of wood surface.

Table 1. Apparent contact angle of untreated and furfurylated wood before the plasma treatment.

Treatment	Contact Angle (°)	
	After 5 s	After 15 s
Untreated	95.18 ± 17.13	82.48 ± 16.36
15% load level (15% FA)	107.54 ± 9.66	105.28 ± 8.16
40% load level (40% FA)	101.28 ± 6.67	99.33 ± 5.55

Plasma treatment affected significantly wood surface of untreated and furfurylated wood. Plasma treatment converts hydrophobic furfurylated wood into a hydrophilic material, especially 15% FA samples (CA reduction of ~93%). Wood samples with 40% FA were less susceptible to the plasma treatment, wherein CA reduction was ~68% in the first day after the surface activation (Fig. 2A).

Work of adhesion (WoA) and surface free energy (SFE) presented an inverse behavior of CA (Fig. 2B and 2C). Activation of surface reduces apparent contact angle, which results in higher wood surface reactivity. Thus, efficiency of finishing steps – coating and bonding – should be better. Previous studies infer this CA decrease to introduction or formation of oxygen-containing functional groups on materials' surface (DE GEYTER *et al.* 2007; LIU *et al.* 2013; CADEMARTORI *et al.* 2015).

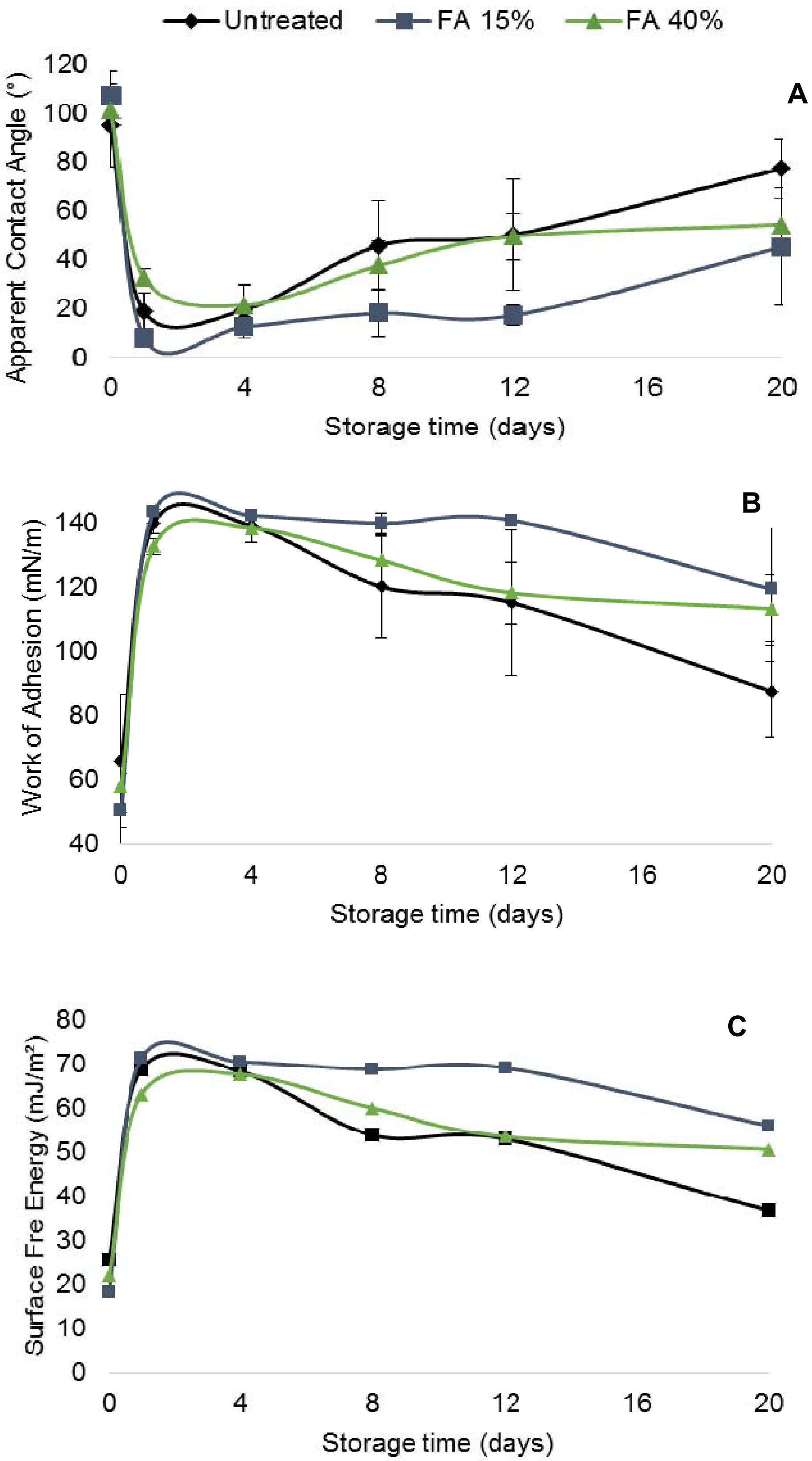


Figure 2. The effect of aging on apparent contact angle (CA), work of adhesion (WoA) and surface free energy (SFE) of untreated and furfurylated wood before (time=0) and after plasma treatment.

Figure 2A illustrates the aging effect on untreated and furfurylated wood surface after the plasma treatment. CA of both woods increased with increasing storage time. This loss of plasma effect during aging was described by previous studies with polypropylene (Yun et al. 2004), synthetic fibers (LIU *et al.* 2013) and solid wood (NOVÁK *et al.* 2015). Plasma treatment is not permanent, since species generated by plasma are high instable (SANCHIS *et al.* 2008). The same authors concluded partial hydrophobic recovery occurs due to the rearrangement of polar species on materials' surface.

The effect of aging is more intense in untreated samples, mainly after 8 storage days. After 20 storage days, furfurylated wood samples recovery part of their surface hydrophobicity. Nevertheless, CA average values are significant lower than CA measured before the plasma treatment. From industrial process point of view, this behavior is interesting, in the course of which the plasma treated wood samples remain with high surface reactivity for application of finishing products. This is also proved by the WoA behavior of plasma treated furfurylated wood after 20 storage days (Fig. 2B).

4. CONCLUSIONS

Wettability of untreated and furfurylated pine wood increased significantly after plasma treatment. Apparent contact angle, work of adhesion and surface free energy clearly showed loss of plasma effects during aging, wherein untreated and furfurylated wood recovery part of its hydrophobicity after 20 storage days. Surface of furfurylated wood was less susceptible to the plasma treatment due to its natural water repellence in comparison to untreated wood.

5. ACKNOWLEDGMENTS

This work was partially supported by the National Counsel of Technological and Scientific Development (CNPq), Coordination for the Improvement of Higher Education Personnel (CAPES), Araucaria Foundation and Embrapa Forestry.

6. REFERENCES

Acda, M.N.; Devera, E.E.; Cabangon, R.J.; Ramos, H.J. Effects of plasma modification on adhesion properties of wood. **International Journal of Adhesion and Adhesives**, v.32, p. 70-75, 2012.

Asandulesa, M.; Topala, I.; Dumitrascu, N. Effect of helium DBD plasma treatment on the surface of wood samples. **Holzforschung**, v.64, n.2, p.223-227, 2010.

Aydin, I.; Demirkir, C. Activation of Spruce Wood Surfaces by Plasma Treatment After Long Terms of Natural Surface Inactivation. **Plasma Chemistry and Plasma Processing**, v.30, n.5, p. 697-706, 2010.

Bai, Y.; Gao, Z. The ambient aging of wood fiber and its effect on mechanical properties of MDF panels. **Wood Science Technology**, v.45, n.3, p.501-510, 2011.

Cademartori, P.H.G.; dos Santos, P.S.B.; Serrano, L.; Labidi, J.; Gatto, D.A. Effect of thermal treatment on physicochemical properties of Gympie messmate wood. **Industrial Crops and Products**, v. 45, p. 360-366, 2013.

Cademartori, P.H.G.; Muniz, G.I.B.; Magalhães, W.L.E. Changes of wettability of medium density fiberboard (MDF) treated with He-DBD plasma. **Holzforschung**, v. 69, n. 2, p. 187-192, 2015.

Christiansen, A.W. How overdrying wood reduces its bonding to phenol-formaldehyde adhesives : a critical review of the literature. Part II, Chemical reactions. **Wood and Fiber Science**, v. 23, n.1, p. 69-84, 1991.

De Geyter, N.; Morent, R.; Leys, C.; Gengembre, L.; Payen, E. Treatment of polymer films with a dielectric barrier discharge in air, helium and argon at medium pressure. **Surface and Coatings Technology**, v. 201, n. 16–17, p. 7066-7075, 2007.

Liu, Y.; Tao, Y.; Lv, X.; Zhang, Y.; Di, M. Study on the surface properties of wood/polyethylene composites treated under plasma. **Applied Surface Science**, v. 257, n. 3, p. 1112-1118, 2010.

Liu, Z.; Chen, P.; Han, D.; Lu, F.; Yu, Q.; Ding, Z. Atmospheric air plasma treated PBO fibers: Wettability, adhesion and aging behaviors. **Vacuum**, v. 92, p. 13-19, 2013.

Magalhães, W.L.E.; da Silva, R.R. Treatment of Caribbean pine by in situ polymerization of styrene and furfuryl alcohol. **Journal of Applied Polymer Science**, v. 91, n. 3, p. 1763-1769, 2001.

Magalhães, W.L.E.; Souza, M.F.d. Solid softwood coated with plasma-polymer for water repellence. **Surface and Coatings Technology**, v. 155, n. 1, p. 11-15, 2002.

Mattos, B.D.; Missio, A.L.; Cademartori, P.H.G.; Lourençon, T.V.; Gatto, D.A.; Magalhães, W.L.E. Pinewood Composite Prepared by In Situ Graft Polymerization of Epoxy Monomer. **Polymer Composites**, Online First, 2015.

Novák, I.; Popelka, A.; Špitalský, Z.; Mičušík, M.; Omastová, M.; Valentin, M., et al. Investigation of beech wood modified by radio-frequency discharge plasma. **Vacuum**, v. 119, p. 88-94, 2015.

Poaty, B.; Riedl, B.; Blanchet, P.; Blanchard, V.; Stafford, L. Improved water repellency of black spruce wood surfaces after treatment in carbon tetrafluoride plasmas. **Wood Science Technology**, v. 47, n.2, p. 411-422, 2013.

Sanchis, M.R.; Calvo, O.; Fenollar, O.; Garcia, D.; Balart, R. Characterization of the surface changes and the aging effects of low-pressure nitrogen plasma treatment in a polyurethane film. **Polymer Testing**, v. 27, n. 1, p. 75-83, 2008.

Scholz, G.; Militz, H.; Gascón-Garrido, P.; Ibiza-Palacios, M.S.; Oliver-Villanueva, J.V.; Peters, B.C., et al. Improved termite resistance of wood by wax impregnation. **International Biodeterioration & Biodegradation**, v. 64, n. 8, p. 688-693, 2010.

Yun, Y.I.; Kim, K.S.; Uhm, S.-J.; Khatua, B.B.; Cho, K.; Kim, J.K., et al. Aging behavior of oxygen plasma-treated polypropylene with different crystallinities. **Journal of Adhesion Science and Technology**, v. 18, n. 11, p. 1279-1291, 2004.

7. RESPONSIBILITY NOTE

The authors are responsible for the content of this manuscript.