



## TRATAMENTO POR DBD PLASMA DE NITROGÊNIO PARA AUMENTAR A ADESÃO DE PISOS DE MADEIRA

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**RESUMO:** Tratamento por plasma caracteriza-se como eficiente e como uma alternativa econômica e limpa para modificar a superfície da madeira. O presente estudo objetivou aumentar a adesão de peças de piso de madeira por plasma a frio. Para o tratamento dos pisos de madeira, utilizou-se um reator a plasma admitindo-se uma mistura de argônio e nitrogênio entre os eletrodos durante 10 minutos em baixa pressão. Configurou-se o reator para três níveis de potência – 50, 100 e 150 W e uma frequência de 13.5 MHz. O fluxo de gás de argônio e nitrogênio foi estipulado em 10 e 100 sccm, respectivamente. As modificações na adesão foram investigados por meio de um goniômetro para a mensuração do ângulo de contato e a energia livre superficial. Para cada amostra, três gotículas (9.6 µl) foram dispensadas na superfície da madeira. Os principais resultados encontrados mostraram que o ângulo de contato das amostras modificadas por plasma foram ~2 vezes menor em relação ao ângulo de contato mensurado nas amostras não tratadas. A energia livre superficial da madeira modificada por plasma aumentou significativamente. O ângulo de contato e a energia livre superficial das amostras tratadas em diferentes potências foram estatisticamente iguais. Portanto, os tratamentos de plasma modificou significativamente a superfície da madeira em diferentes níveis de potência, o que resultou no aumento da adesão.

**Palavras Chave:** molhabilidade, energia superficial, tratamento de superfície, plasma a frio.

## NITROGEN DBD PLASMA TREATMENT TO ENHANCE ADHESION OF WOOD FLOORING

**ABSTRACT:** Plasma treatment is characterised as efficient, clean and economic alternative to modify wood surface. This study aimed to increase adhesion of wood flooring using cold plasma surface treatment. Cold plasma reactor was used and a mixture of argon and nitrogen was admitted between the electrodes for 10 minutes at reduced pressure to treat wood flooring surfaces. Three levels of power – 50, 100 and 150 W – and 13.5 MHz frequency were used. Mass flow of argon and nitrogen was set to 10 and 100 sccm, respectively. Changes on adhesion were investigated using a goniometer to measure the contact angle and the surface energy. Three droplets (9.6 µl) per sample were disposed on wood surface. The main findings showed that contact angle of treated samples was ~2 times lower than contact angle measured in untreated samples. Surface free energy of wood modified samples increased significantly. Contact angle and surface free energy of wood samples treated with different values of power was statistically equal. Therefore, plasma treatments significantly changed the wood surface for all the power applied, which resulted in an increase of adhesion.

**Keywords:** wettability, surface energy, surface treatment, cold plasma.

## 1. INTRODUCTION

Wood is widely required by building sector and for aesthetic uses, which result, in most of the cases, in products with high value-added. Nevertheless, some of these products present limitations related to the adhesion of surface in their processing due to natural characteristics such as presence of extractives. Therefore, finishing process with the application of chemical products and coating films cannot present a desirable behaviour. Likewise, according to Jie-Rong et al. (1999), process such as printing, adhesion, spray and dyeing are highly related to the surface wettability of polymeric materials.

New techniques have been developed to use wood and wood-based products in better conditions. Among these techniques, impregnation and deposition of eco-friendly liquid or gaseous substances from natural or synthetic sources, such as enzymatic and plasma treatments should be emphasized.

One of the most promise alternatives is the plasma treatment, which presents recent studies about their advantages for modification of materials' surface using different types of gases. Utilisation of plasma enables the modification of surface properties of polymers, such as wettability and adhesion, without changes in bulk properties of the material (PODGORSKI et al., 2000).

Performance of plasma occurs in the surface of materials, in which the main objective is the modification of chemical and physical properties (INAGAKI, 1996). Surface changes depend on some factors such as substrate composition and gas used, which can be nitrogen, argon, helium, methane and ammonia (FINSON et al. 1995). On the other hand, improvement of plasma treatment can be performed modifying parameters of process such as pressure, time of discharge and gas flow (ROSSEL, 2007). Plasma treatment can be performed in two ways: at reduced pressure or at atmospheric pressure (BOENIG, 1982; UEHARA, 1999; KOGELSCHATZ, 2003).

According to Sarmadi et al. (1995), cold plasma presents many advantages, such as most of phenolic volatile compounds can be used as monomeric material; process of coating can be performed in only one-step of reaction; only a small quantity of material is necessary to implementation of the technique; and not present a high-energy consumption.

Plasma treatment is one of the most interesting and promising technique in forestry sector for modification the properties of wood fibres used for production of composites (LIU et al., 2010; HAN et al., 2011; MOGHADAMZADEH et al., 2011). Furthermore, can be used as protective layer in solid wood pieces and to improve many characteristics, such as adhesion and dimensional stability (ACDA et al., 2012; JAMALI and EVANS, 2011; MAGALHÃES and SOUZA, 2002), mainly when structural properties of the material are desirables. Therefore, plasma treatment is feasible when the main objective is improve the properties related to wettability and adhesion of surface of solid wood and wood-based products (PODGORSKI et al., 2000; REHN et al., 2003; ACDA et al., 2012).

In this context, the present study aimed to increase the surface adhesion of *Dialium guianense* solid wood flooring using cold plasma treatment (nitrogen DBD treatment).

## 2. MATERIAL AND METHODS

Material used in this study was collected in a Brazilian wood flooring industry. Samples of *Dialium guianense* (tamarindo) solid wood flooring measuring 2.5 x 2.5 x 10 cm were prepared and dried at 103°C in an oven without force air circulation to obtain moisture content of ~0%, which was the initial point of the plasma treatments.

Plasma treatments were performed in a cylindrical stainless reactor (Figure 1) developed in Embrapa Forestry. The reactor is equipped with a vacuum system and a butterfly valve for controlling the level of pressure inside the chamber; a capacitance manometer performs determination of this pressure. Dielectric barrier discharge (DBD) is performed using a system of capacitive stainless plates measuring 30 cm diameter, which is connected to a system of power generation at high frequency (13.5 MHz). Admission of gases is controlled

by a gas flow system and dispersion of gases inside the chamber is performed using a homogenous spatter around the reactor.



**Figure 1. Plasma reactor (left) and luminescent discharge inside the cold plasma reactor (right).**

Dielectric barrier discharges admitting a gas mixture of argon and nitrogen inside the reactor at reduced pressure (0.08 torr) were performed. Gas flow of argon and nitrogen was 10 and 100 sccm, respectively. The effect of power in DBD plasma treatments were investigated. To achieve this, three levels of power was considered: 50, 100 and 150 W. Time of discharge was set in 10 minutes.

Changes on adhesion of surface of wood flooring were evaluated using a goniometer. Contact angle was measured for each untreated and plasma treated samples. Three droplets with 9.6  $\mu\text{l}$  was put on the surface of samples based on the sessile droplet method. Consequently, surface free energy (SFE) was determined by EOS (Equation of State) method.

The data collected was analysed using descriptive statistics and analysis of variance considering the power as the factor for the contact angle and the surface free energy variation. If the null hypothesis was rejected, the average values were compared using Tukey Test at 5% of probability of error.

### 3. RESULTS AND DISCUSSION

Analysis of variance of contact angle (Tab. 1) showed that this property varied significantly as a function of plasma treatment, i.e., contact angle changed as a function of power applied. In the same context, surface free energy also was influenced by the power applied (Tab. 2), which infers that power used in dielectric barrier discharge is an important factor to define the level of surface adhesion of solid wood flooring.

**Table 1. Analysis of variance of contact angle as a function of plasma treatments.**

Source	SS	Df	MS	F	p
Between groups	21553,5	3	7184,5	41,28	0,0000
Within groups	6787,12	39	174,029		
Total (Corr.)	28340,6	42			

**Table 2. Analysis of variance of surface energy as a function of plasma treatments.**

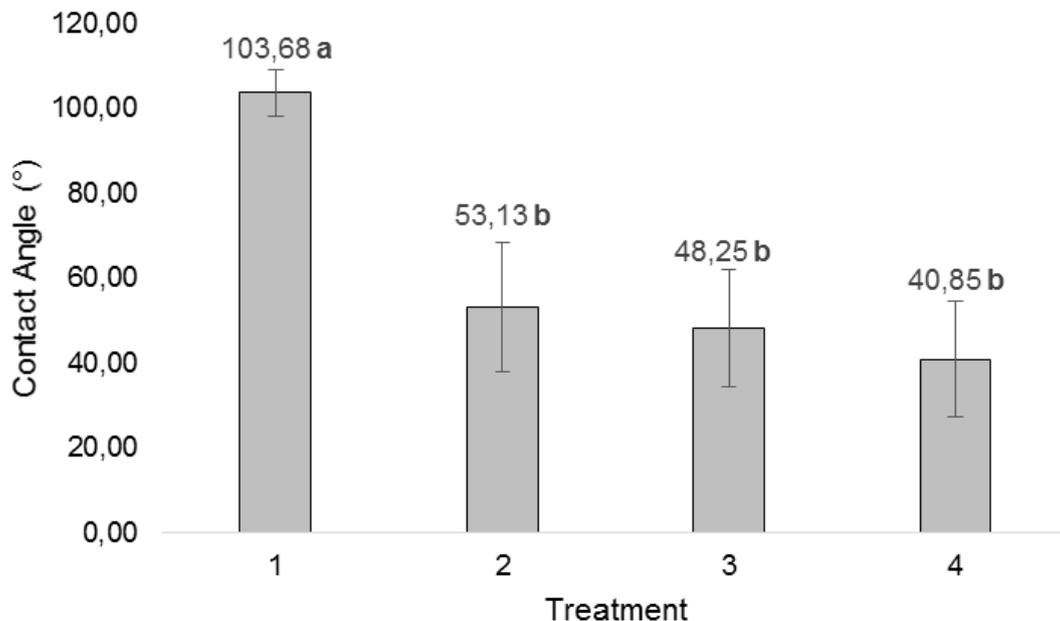
Source	SS	Df	MS	F	p
Between groups	2955,3	3	985,099	24,94	0,0000
Within groups	434,489	11	39,499		
Total (Corr.)	3389,79	14			

Variation of contact angle as a function of plasma treatment can be observed in Fig. 2. It is notable that power applied influenced significantly the values of contact angle.

Treatment 1 (untreated samples) presented average value of 103.68°. Application of 50 W in plasma treatment was sufficient to decrease significantly the contact angle in ~49%. Likewise, treatment 3 (100W) and treatment 4 (150 W) was ~53% and ~61% lower than treatment 1, respectively.

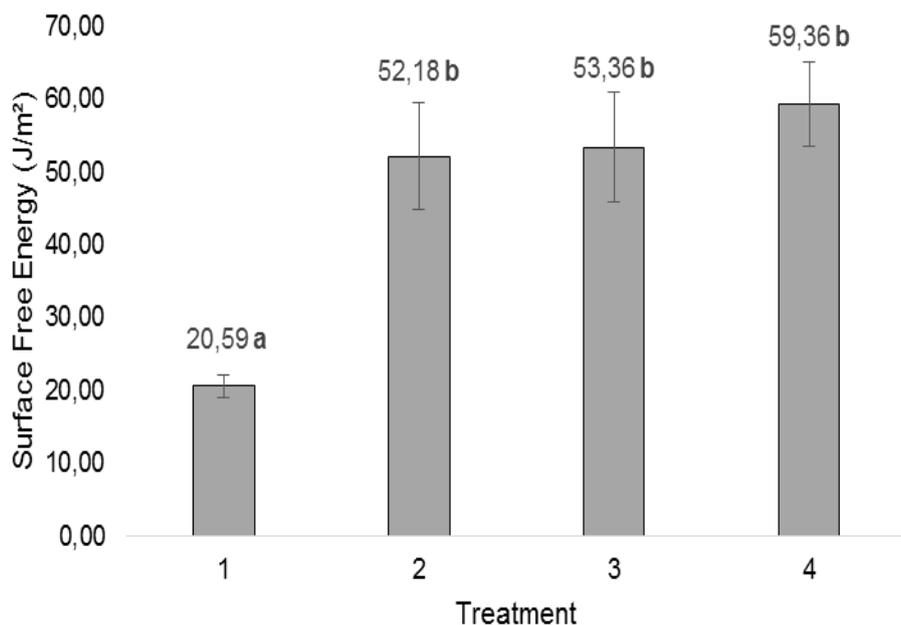
Nevertheless, it is possible to observe that average values of treatments 2, 3 and 4, when compared between powers applied, not varied significantly. This behaviour can be related to the time of discharge applied in the present study, which can reduced the influence of application of a higher power. Furthermore, an increase in spreading contact area of the samples treated using nitrogen DBD plasma was observed, which resulted in higher adhesion of surface. It is important emphasizing that decrease of contact angle and, consequently, increase of surface adhesion of wood flooring is related to changes on spreading contact area, since formation of contact angle is negatively influenced due to the higher absorption of water on the surface of samples.

The results obtained in the present study are similar to those found in previous studies, which proved the increase of surface wettability after application of dielectric barrier discharges at atmospheric pressure (AVRAMIDIS et al., 2012), reduced pressure and admission of oxygen (ACDA et al., 2012) and admission of helium (ASANDULESA et al., 2010).



**Figure 2. Average values of contact angle as a function of plasma treatments.**

Variation of surface free energy, which was determined by EOS method (Fig. 3), confirmed the significant increase of surface adhesion of wood flooring after nitrogen DBD plasma treatments. Surface free energy increased significantly after plasma treatments; however, application of different levels of power not significantly changed this property.



**Figure 3. Average values of surface energy as a function of plasma treatment.**

Treatment 2 (50 W) resulted in an increase of ~60%, while treatments 3 and 4 resulted in an increase of ~61% and ~65%, respectively. Tang et al. (2012) also related increase of surface free energy in a study with poplar wood veneer treated with cold oxygen for 1-9 minutes. In the same context, Novák et al. (2011) identified an increase of surface free energy of oak wood modified by DCSBD (diffuse coplanar surface barrier discharge) for 25 seconds using oxygen and power of 300 W.

#### 4. CONCLUSIONS

Nitrogen DBD plasma treatment increased significantly the surface adhesion of *Dialium guianense* solid wood flooring.

In general, the contact angle of plasma treated samples was ~2 times lower than the contact angle verified in untreated samples. Surface free energy increased at least ~2.5 times.

Utilisation of three levels of power was not efficient to increase significantly the adhesion of surface, probably due to the high time of discharge used.

#### 5. ACKNOWLEDGMENTS

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#### 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, n. 0, 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.

- AVRAMIDIS, G.; MILITZ, H.; AVAR, I.; VIÖL, W.; WOLKENHAUER, A. Improved absorption characteristics of thermally modified beech veneer produced by plasma treatment. **European Journal of Wood and Wood Products**, v. 70, n. 5, p. 545-549, 2012.
- BOENIG, H.V. **Plasma Science and Technology**. USA: Cornell University Press, 1982.
- FINSON, E., KAPLAN, S., WOOD, L., Plasma treatment of webs and films. In: 38<sup>th</sup> TECHNICAL PROCEEDING OF SOCIETY OF VACUUM COATERS, 1995, Chicago, Anais... Chicago: 1995. p. 52-58.
- HAN, Y.; MANOLACH, S. O.; DENES, F.; ROWELL, R. M. Cold plasma treatment on starch foam reinforced with wood fiber for its surface hydrophobicity. **Carbohydrate Polymers**, v. 86, n. 2, p. 1031-1037, 2011.
- INAGAKI, N. **Plasma Surface Modification and Plasma Polymerization**. USA: CRC Press, 1996.
- JAMALI, A.; EVANS, P. Etching of wood surfaces by glow discharge plasma. **Wood Science and Technology**, v. 45, n. 1, p. 169-182, 2011.
- JIE-RONG, C; XUE-YAN, W.; TOMIJI, W. Wettability of Poly(ethylene Terephthalate) Film Treated with Low-Temperature Plasma and Their Surface Analysis by ESCA. **Journal of Applied Polymer Science**, v. 72, n. 10, p. 1327-1333, 1999.
- KOGELSCHATZ, U. Dielectric-barrier discharges: Their history, discharge physics, and industrial applications. **Plasma Chemistry and Plasma Processing**, v. 23, n. 1, p. 1-46, 2003.
- 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.
- MAGALHÃES, W. L.E.; SOUZA, M.F. Solid softwood coated with plasma-polymer for water repellence. **Surface and Coatings Technology**, v. 155, n. 1, p. 11-15, 2002.
- MOGHADAMZADEH, H.; RAHIMI, H.; ASADOLLAHZADEH, M.; HEMMATI, A. R. Surface treatment of wood polymer composites for adhesive bonding. **International Journal of Adhesion and Adhesives**, v. 31, n. 8, p. 816-821, 2011.
- NOVÁK, I.; POPELKA, A.; VANKO, V.; PRETO, J.; SEDLIACK, J.; CHODÁK, I.; KLEINOVA, A.; POLLÁK, V. Modification of wood by low-temperature atmospheric discharge plasma. **Annals of Warsaw University of Life Sciences (Forestry and Wood Technology Series)**, n. 75, p. 135-141, 2011.
- PODGORSKI, L.; CHEVET, B.; ONIC, L.; MERLIN, A. Modification of wood wettability by plasma and corona treatments. **International Journal of Adhesion and Adhesives**, v. 20, n. 2, p. 103-111, 2000.
- REHN, P.; WOLKENHAUER, A.; BENTE, M.; FÖRSTER, S.; VIÖL, W. Wood surface modification in dielectric barrier discharges at atmospheric pressure. **Surface and Coatings Technology**, v. 174-175, n. 0, p. 515-518, 2003.
- ROSSELL, T. N. **Plasma modification of carbon black surface: From reactor design to final application**. Tese (Doutorado) - Universitat Ramon Llull, Barcelona, Espanha, 2007.

SARMADI, A. M.; YING, T. H.; DENES, F. HMDSO-plasma modification of polypropylene fabrics. **European Polymer Journal**, v. 31, n. 9, p. 847-857, 1995.

UEHARA, T. Corona discharge treatment of polymers. In: K. L. Mittal and A. Pizzi (Eds). **Adhesion Promotion Techniques: Technological Applications**. New York: CRC Press, 1999. pp. 139–174.

## **7. NOTA DE RESPONSABILIDADE**

Os autores são os únicos responsáveis pelo que está contido neste trabalho.