Cross-linked lignin coatings produced by UV light and SF$_6$ plasma treatments

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ABSTRACT

Lignin is one of the most abundant macromolecules in vascular plants and has been studied for many years due to its high availability and low cost, regarding that lignin is the main by-product of the paper pulping process, and also typically burned as fuel. Despite that, lignin has only a few industrial applications. In this study, we found a simple method for preparing well-defined lignin surfaces. Lignin was extracted from sugar cane bagasse by Soda pulping and its coatings were prepared using solutions with different solvents on various substrates (silicon wafers, paper, steel and glass) by spin-coating. Two methods were tested in order to promote cross-linking on the surface of lignin coatings: SF$_6$ plasma treatment and ultra-violet radiation. Both treatments reduced the amount of hydroxyl groups on the surface leading to more stable, cross-linked coatings as observed by FTIR and thermal analysis. Ultra-violet light radiation turned lignin coatings hydrophilic while stable super-hydrophobic lignin coatings were obtained using SF$_6$ plasma.

INTRODUCTION

Lignin is a complex phenolic polymer that confers resistance and flexibility to the plants. It plays a fundamental role in water transport and creates a barrier against pathogens [1]. Although lignin is the most abundant natural polymer on earth after cellulose and the main renewable aromatic source, this macromolecule is wasted in papermaking and sugar production processes, due to technical and economic reasons. Less than 2% of lignin is used for market product, whereas the residual is burned as fuel and used as an energy source needed for the pulping process itself. It is known that the conversion of lignin into higher value-added products will surely offset any associated cost increases [2].

The two main methods employed industrially for obtaining lignin are Kraft and Soda pulping. Kraft pulping leads to the formation of lignosulfonates that are hydrophilic and dissolve in water while, lignin originating from Soda pulping are hydrophobic and do not dissolve in water [3,4] as soda pulping process cleaves aryl ether linkages through small formations of phenolic hydroxyls and loss of primary phenolic OH groups [5,6].

Intensive efforts, devoted to make lignin a useful polymeric material in the production of coatings, have been explored in different ways for many years [7–11]. Another way to increase polymeric materials industrial applications is by promoting cross-linking between molecules, ceasing molecular chain mobility [12]. Lignin has a complex high degree of non-branched and branched chains and finding ways of reticulating them might result in a cross-linked three-dimensional rigid structure. Therefore, different properties might arise, including better mechanical properties and chemical stability.

Lignin reactivity is essentially limited by the lack of free ortho positions in the aromatic rings. Researches have been increasing its reactivity by chemical modification, such as ethereification, phenolation, esterification, oxidation and reduction for many years [5–8]. This kind of alterations usually affects the hydroxyl groups. Lignin has phenolic hydroxyl – more susceptible to chemical modification – and aliphatic hydroxyl groups. Exposure to high-energy radiation can break the hydrogen bonds in the phenol hydroxyl groups and produce free radicals that react, generating bonds between the molecules. Ultra-violet curing is one of the most widely used methods in order to create polymer crosslinking. UV interaction with wood was extensively studied and radiations from 200 to 400 nm possess sufficiently energy to break chemical bonds, where lignin is the main UV absorber. UV induces wood degradation mainly related to lignin decomposition through the formation of phenoxy free radicals [13–16]. Plasma technology represents an efficient, clean and economical alternative for modifying the characteristics functional properties of most organic surfaces [17–19]. According to Carrino et al. [18] the interaction between a polymeric surface and a cold plasma flow of an electronegative gas, such as SF$_6$, induces surface reactions between plasma species and the
surface of the polymer, increasing the density of cross-links or three-dimensional structures [20]. During plasma treatment, ionization of the SF6 gas occurs forming F* and SFx species. The fluoride radical can be incorporated into the material surface through the formation of C–F bonds and, under specific conditions, can cause its hydrophobization.

In this work, lignin was extracted from sugar cane by Soda pulping method and plasma and UV radiation were used in order to cross-link lignin coatings produced by spin-coating. Coatings were characterized by solubility tests, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-Ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), swelling rate test in toluene and contact angle measurements.

**MATERIAL AND METHODS**

**Lignin films preparation**

Soda lignin, obtained from sugar cane, was dispersed in acetone and water (9:1). Lignin films were then prepared from those solutions by spin-coating on different substrates (silica, glass, paper, AISI 1020 steel). Coatings of thickness between 1 and 2 μm were easily made by variations in the spinning rate or in the lignin concentration, as measured with the help of a Dektak II profilometer.

After production, lignin films were distributed in four groups with three samples in each: an untreated control group, two groups treated with SF6 plasma (15 and 30 min exposure) and two groups treated with UV light (15 and 30 min of exposure).

SF6 plasma treatment was performed in a plasma reactor working at 100 W power and 2.0 × 10−1 mbar pressure. The plasma reactor was homemade and composed by a glass tube with 6 cm of diameter, 100 cm in length and 0.5 cm of width. Primary vacuum was achieved using a mechanical pump connected to the upper part of the reactor. Gas was introduced by a needle valve connected to the lower part of the glass tube. Samples were put inside the reactor, always in the same position, with the faces exposed to the plasma.

Lignin coatings were also treated in a UV oven manufactured in LABCURA, using a 100 W/in power. This chamber consists of eight fluorescent lamps (model TKL 40 w/05) which emit ultra-violet radiation in the 200–460 nm region. Samples were placed at the center of the oven, with the face exposed to the UV lamp.

The optimum pH for lignin recovering was found to be 2. This was the pH at which the largest lignin mass was recovered in a lower filtration time and with a reasonable acid consumption.
CHARACTERIZATION

Morphology (SEM and AFM)

The coated surface was characterized by Scanning Electron Microscopy (SEM - JEOL JSM 6460-LV, USA) operated at 20 kV with magnifications of 1000x and 3000x. Lignin was spin-coated on silicon substrates and mounted on aluminum stubs using double sided tape. Then, the coating was covered by a 15 nm layer of gold to increase the resolution of the images.

Atomic Force Microscope (AFM) (WITEC Alpha 300, Germany) was used to investigate the surface topography of lignin coatings. Samples images were obtained in dynamic mode using a Micromasch probe with 5 N/m of elastic modulus. Phase contrast and topography images are showed without background correction. AFM nanoindentation was performed for determining Young modulus values of lignin coatings as well.

Chemical analysis (FTIR and XPS)

Chemical characterization of all lignin samples was performed by Fourier Transform Infrared Spectroscopy (FTIR) in a Nicolet Spectrometer model 6700 (Thermo Scientific) in ATR mode and all spectra were acquired in absorbance mode in the 600-4000 cm\(^{-1}\) range, 64 scans, 1 cm\(^{-1}\) step and resolution 4 cm\(^{-1}\). The coatings were scraped from the substrates and five spectra were taken for each condition in different points of the samples.

In addition to FTIR, chemical characterization of the lignin samples was performed using an ultra-high vacuum (UHV) X-ray photoelectron spectroscopy (XPS), Omicron Nanotechnology, Escaplus P model, with a monochromatic Al X-ray source (K\(_\alpha = 1486.7\) eV) operated at 300 W power. Survey XPS spectra were obtained with analyzer pass energy of 160 eV and step size of 1 eV. High resolution spectra of C 1 s, F 1 s and O 1 s regions were obtained with analyzer pass energy of 30 eV and 0.05 eV, 0.08 eV and 0.1 eV energy steps, respectively. The charge neutralizer was turned on during analysis, operating at 1 μA emission current and 1 eV voltage, to avoid binding energy shift in the collected spectra, so, no correction in the binding energy scale was needed. The peak fitting was performed using Casa XPS software.

Water contact angle

Contact angles of 2 μl distilled water droplets on the coatings were measured using a Ramé-Hart goniometer, USA, 500. Three measurements on different positions of the film surface were made and the average was determined.
Thermal analysis (TGA)

Pure and plasma or UV treated lignin samples, mass of 10 mg, were subjected to TGA analysis in a TGA Pyris 1, Perkin-Elmer apparatus in a nitrogen atmosphere with flow rates of 60 ml min$^{-1}$, heating rate of 10 °C min$^{-1}$, from room temperature up to 800 °C. The analyses were performed in duplicate. The nitrogen atmosphere was used to avoid the occurrence of any oxidation reaction that could affect our data - since the purpose of the TGA measurement was to investigate only the processes of heat degradation.

Stability test (stability to organic solvents and swelling test)

To investigate the stability of the spin-coated lignin, the coatings were immersed in different organic solvents (alcohol, acetone and water) under magnetic stirring for different time.

Another parameter that can be used to compare the effectiveness of “cure” by UV light in relation to SF$_6$ plasma is the swelling rate. The degree of cross-linking was determined from the swelling of lignin coatings in toluene. The samples were weighted before and after being immersed in toluene for 24 h. Samples were then dried for 24 h at room temperature and weighed again, until the stabilization of mass. We have used the following formula to determine the rate of swelling:

$$SR (\%) = \left( \frac{M_s}{M_i} \right) \times 100$$  \hspace{1cm} (1)

At where: $SR =$ swelling rate; $M_s =$ mass of the lignin sample after the second drying; $M_i =$ initial mass of the lignin sample.

RESULTS AND DISCUSSION

Morphology (SEM and AFM)

The morphology of the films was analyzed by SEM and the images are presented in Fig. 1. Secondary electron images of untreated lignin, Fig. 1 a, and UV 30 min treated lignin, Fig. 1 b, are smooth and homogeneous while SF$_6$ plasma treated films for 15 and 30 min, Fig. 1 c and d, respectively, show high roughness. The formation of a three-dimensional structure, with wrinkles and voids creation, indicates that a material rearrangement occurred after plasma treatment. This re-arrangement can be related to strong cross-linking between molecules [21] as will be shown in the chemical analysis section. After 15 min of SF$_6$ plasma treatment, lignin degradation probably occurs due to the more fragmented structure, as observed by SEM image.
Images obtained by AFM confirm the morphology previously observed by SEM images. Topography and phase contrast images of the coatings, as prepared and after UV treatment, are presented in Fig. 2. The formation of nanometric structures can be observed for both films, before (Fig. 2a and c) and after UV treatment for 15 min (Fig. 2b and d). After UV treatment, a more compact, reticulated surface structure is observed, Fig. 2b. Besides that, phase contrast image of UV treated lignin, Fig. 2d, indicates the formation of a tridimensional network where the nanometric structure appears darker, indicating that it is composed by a harder phase [22].

Fig. 3 shows the evident changes undergone by the material after SF$_6$ plasma. Comparing the morphology of the produced material, there was the formation of nanostructures that can be related to the cross-linking of polymeric chains. A huge increase in surface roughness can be observed by AFM images. SF$_6$ plasma for 15 min induced a
homo- geneous roughness in all lignin surfaces while 30 min exposure induced a flatter surface in some regions, as observed in the right side of Fig. 3b. The roughness features were attributed to aggregation of polymeric chains (induced by cross-linking). The flatter surface can be related to the ion damage or deposition of sputtered materials that takes place during plasma treatment [22].

AFM was also used to evaluate the hardening of the lignin coating surface after the different treatments. Fig. 4. shows the samples elasticity modulus. All treatments induced surface hardening, but SF₆ plasma treated samples presented better mechanical properties than UV treated ones. This reinforces the idea that both, UV light as well as SF₆ plasma, are leading to cross-linking between lignin chains [21,23]. Besides, the hardening was higher in samples treated for 15 min than 30 min of SF₆ plasma, corroborating the idea that plasma may be degrading the lignin surface after 30 min exposure, as already observed by SEM and AFM images.

**Chemical analysis (XPS and FTIR)**

Fig. 5 and Tab. S1 (see Support information section) shows the C1 s XPS spectra analysis of all samples. Sample surfaces were analyzed as well as SF₆ plasma treated sample after being scrapped from the substrate. It can be observed by survey spectra quantification that a high.

*Fig. 3. AFM images, where: a) topography and c) phase contrast image images of lignin coatings after SF₆ plasma treatment for 15 min, and b) topography and d) phase contrast image after SF₆ plasma treatment for 30 min.*
Amount of fluoride (48 at%) was incorporated to the film and that fluoride is strongly located at the film surface, however it is present throughout the whole film thickness, since after scraping the surface, fluorine-carbon chemical bonds content decreased, but it is still significant (~24 at%). Carbon and oxygen content decreased after the fluorine incorporation. C1 s deconvolution spectra show that C=C and C≡C bonds decreased after SF$_6$ treatment, as observed in a previous work where wood fibers were treated by SF$_6$ plasma [24]. This decay was attributed to the breakage in lignin bonds and replacement by fluorine, according with changes observed in the XPS C1 s spectra. The reduction in the percentage of the first two components (C≡C and C–C) after treatment is comparable with the percentage of total number of carbon atoms covalently bonded to fluorine (C–CF, CF–CF$_2$, CF$_3$), Tab. S1 (see Tab. S1 in Support information section).

Concerning oxidized carbon functional groups, the main change observed through the comparison between untreated lignin sample and SF$_6$ treated ones, was the percentage of carboxyl groups, that increases from 3 to 4 times after treatment. These carboxyl groups are formed during the plasma treatment by consumption of the oxygen atoms ripped from the material or from humidity or O$_2$ trapped inside the lignin [25]. Another possibility is that acyl fluoride groups (F–C=O), formed during the treatment, react with hydroxyl groups from humidity generating carboxylic groups [26].

On the other hand, C1 s XPS spectra of UV treated lignin sample presented a decrease in oxygenated groups on the surface. C=C double bond content increases with UV treatment for both treated samples: UV-15 and UV-30. Concerning the other carbon functional groups, UV-15 sample showed a significant decrease in all of them (C=C, C–OH, C=O and O=C–OH) while the sample UV-30 showed a decrease only in the oxygenated carbon groups (C–OH, C=O and O=C–OH).

FTIR spectrum obtained for all films are presented in Fig. 6. It can be observed the decrease in intensity of the strong broad OH stretching (3300–4000 cm$^{-1}$) for all treatments. The decrease is more accentuated for SF$_6$ plasma treated samples. Peaks related to the
CeH stretching in methyl and methylene groups (2800–3000 cm\(^{-1}\)) are more prominent after all treatments, indicating that both treatments may be promoting lignin cross-linking \[27\]. For the sake of evaluating if the treatment time was too high, films were also treated with SF\(_6\) for 5 min. By SEM images analysis, cross-linking was observed only on the lignin surface after SF\(_6\) 5 min treatment (Fig. SI 3a), where the surface morphology presented a similar pattern to the one observed for higher treatment times. By the other side, lignin sample SEM image, after 5 min of UV treatment, shows a smooth and homogeneous surface, similar to untreated one (Fig. SI 3b). FTIR for both samples (Fig. SI 3c) shows a strong carbonyl band in 1720 cm\(^{-1}\) region, corresponding to aromatic carbonyl stretching, formed during the plasma or UV treatment, indicating the start of the degradation process. However, in the case of SF\(_6\) treated lignin, the acyl fluoride groups (F–C=O) in 1763 cm\(^{-1}\) are not evident after 5 min plasma exposure, indicating that this small time of treatment can promote only a superficial degradation. Besides that, both 5 min treated samples still showed the broad OH stretching (3300–4000 cm\(^{-1}\)) indicating that this time was not enough for reticulation of the whole thickness of the sample, as observed in the supplementary material data.

The presence of bands around 1598 cm\(^{-1}\), 1510 cm\(^{-1}\) and 1460 cm\(^{-1}\), characteristics of the aromatic lignin skeleton was also observed by FTIR. A shoulder can be seen in the region of 1270 cm\(^{-1}\), and can be attributed to guaiacyl. In addition, a signal around 1330 cm\(^{-1}\), characteristic of the syringyl, and around 880 cm\(^{-1}\) of p-hydroxyphenyl were observed \[27–29\]. SF\(_6\) plasma treatment leads to the suppression of the \(\beta\)-hydroxyphenyl band and the appearance of C=O bands (1730 cm\(^{-1}\)), as observed by XPS results.

FTIR spectrum of the UV treated sample also shows the appearance of the band related to C=O as observed by XPS. UV light absorption yields significant intensity changes in the IR spectrum of lignin. The characteristic aromatic lignin band at 1510 cm\(^{-1}\) decreased compared to original value. Moreover, the lignin decay is combined with strong formation of new carbonyl absorption in the region below 1700 cm\(^{-1}\) (conjugated and aromatic carbonyls) and in the 1700-1750 cm\(^{-1}\) region (non-conjugated aliphatic carbonyls). The formation of carbonyl bands proves the photoinduced oxidation of lignin coatings, which can be related to the increase in surface hydrophilicity. As far as the results from XPS can be compared with FTIR, the decrease in the total oxygen content observed by XPS is probably related to the suppression of –OH groups as observed in FTIR spectra. The band at 1650 cm\(^{-1}\) is related to C=C in the presence of absorbed water and is bleached after either treatment. For UV radiation, it is substituted to bands close to 1605 cm\(^{-1}\) that are related to aryl ring symmetric stretch, characteristic of stronger wood \[27–29\].
Fig. 5. High resolution XPS spectra of carbon peaks from untreated, UV and SF$_6$ treated lignin samples, where: a) C1s of untreated lignin, b) C1s peak of lignin treated with 15 min of UV radiation (UV 15 min), c) C1s peak of lignin treated with 30 min of UV radiation (UV 30 min), d) C1s peak of lignin treated with 15 min of SF$_6$ plasma (SF$_6$ 15 min), e) C1s peak of lignin treated with 30 min of SF$_6$ plasma (SF$_6$ 30 min) and f) C1s peak of lignin treated with 30 min of SF$_6$ plasma (SF$_6$ 30 min scrapped) after scraping of the surface.

Fig. 6. FTIR spectra of lignin, UV-treated samples for 15 and 30 min and SF$_6$ plasma treated samples for 15 and 30 min. The peaks marked with * correspond to the lignin peak assignment, such as: 3450 cm$^{-1}$(ν$_{OH}$), 2920 cm$^{-1}$(ν$_{asCH2}$, guaiacyl and siringyl), 2840 cm$^{-1}$(ν$_{sCH2}$, guaiacyl and siringyl), 1730 cm$^{-1}$(ν$_{C=O}$ non conjugated ketone and aromatic ester), 1658 cm$^{-1}$(ν$_{C=O}$ aryl ketone p-substituted, guaiacyl), 1510 cm$^{-1}$ and 1425 cm$^{-1}$(ν$_{C=C}$ aromatic ring, guaiacyl and siringyl), 1325 cm$^{-1}$(ν$_{s}$ siringyl ring),1275 cm$^{-1}$(ν$_{s}$ guaiacyl ring, ν$_{asC-O-C}$),1220 cm$^{-1}$(ν$_{s}$ siringyl ring),1030 cm$^{-1}$(δ$_{C-H}$ guaiacyl aromatic ring and δ$_{C-OH}$ primary alcohol), and 860 cm$^{-1}$(γ$_{=CH}$ aromatic ring, guaiacyl-siringyl) (Lisperguer, Perez, & Urizar, 2009; Popescu et al., 2007) [27,28].

Also, acyl halide chemical bonds were observed by FTIR in both SF$_6$ treated samples. The acyl fluoride band appeared as a strong peak in 1765 cm$^{-1}$. Other two C–F peaks appeared in 1100 cm$^{-1}$ and 1345 cm$^{-1}$ that can be assigned as C–F stretching vibration [29] and CF$_3$CF$_2$ groups, in agreement with XPS peak assignment showed previously [24].

Based on the XPS and FTIR results, a mechanism of lignin induced cross-linking can be proposed. It was shown in Fig.7. the cross-linking reaction for guayacyl and p-hydroxyphenyl
lignin subunits. Plasma energy can create a radical oxygen group in the hydroxyl from phenyl group. This electron, by resonance, will occupy both ortho positions in relation to oxygen and para position, i.e., the same position as the continuation of the chain. The electron moves across the ring and the radical, certainly, will be present in these positions.

Probably the least hindered position, from the steric point of view, will react. However, since the free radical only stays in the ortho and para positions due to resonance, p-hydroxyphenyl units have two ortho positions free to react while guayacyl groups have only one available ortho position. For syringyl units, there are no ortho positions available, so the oxygen from phenyl groups probably reacts with a guayacyl or p-hydroxyphenyl subunits to crosslink. Beyond that, other combinations of the three lignin subunits are probable if there are no steric hindrance effects.

**Fig. 7.** Proposed mechanism of the reaction between OH groups with lignin chain formed radical that is able to create cross-linking between aromatic rings.

Water contact angle

In order to evaluate the surface wettability changes, contact angle of water with lignin was measured as a function of time, Fig. 8. For the untreated coating of lignin, the initial equilibrium contact angle was 90°. The contact angle was relatively stable during data acquisition. However, its value decreased slightly until 88° close to 30 min. This implies that the coating is relatively non-swelling and nonporous. As the water evaporates, the contact angle decreases. Therefore, it is reasonable to assume that soda lignin have a higher prevalence of nonpolar groups. This result is in agreement with previous works [9,20,22].
We see an increase of the water affinity when lignin was treated by UV light. The water contact angle values were $60^\circ$ for UV 5 min treated lignin sample (Fig. S 3d,f), and for both samples, UV 15 min and UV 30 min, the initial contact angle was $58^\circ$ and decreased to $42^\circ$ during few minutes. By the other side, after SF$_6$ plasma treatment, lignin coatings exhibit a superhydrophobic behavior. Contact angle was $150^\circ$ for SF$_6$ 5 min sample (Fig. S 3e,f) and after 15 min, the contact angle did not depend on the plasma treatment time - both SF$_6$ treated surfaces (SF$_6$ 15 min and SF$_6$ 30 min) presented values higher than $160^\circ$ and zero hysteresis, thus, confirming their superhydrophobic behavior.

The superhydrophobicity achieved by plasma treatment and, consequently, the increase in the contact angle with water may be explained by the two factors: the chemical factor that is promoted by the fluorine incorporation, modifying the surface properties, and by the increasing of the micro and nanoroughness patterns generated by the ion plasma bombardment. Superhydrophobicity, characterized by contact angles above $150^\circ$, is known to be an effect enhanced by surface roughness. This roughness creates air trap areas over which the water droplets roll – Lottus effect. The Supplementary Video 1 shows a lignin coating treated with SF$_6$ plasma and its extreme water repellence (.avi file).

Fig. 8. Images of contact angle of water with lignin measurements, where: a) untreated lignin, b) SF$_6$ treated lignin for 15 min, c) UV treated lignin for 30 min and d) SF$_6$ plasma treated lignin for 30 min, e) contact angle stability as a function of time plot.
Thermal analysis

Coating stability could also be analyzed by TGA, as presented in Fig. 9. While pure lignin presented a loss of 10% of mass from the ambient temperature up to 100 °C, due to the adsorbed water on its surface, SF₆ plasma-modified lignin presented, up to 100 °C, a mass loss of 5% and 4%, respectively. In pure lignin, there were two more degradation events. One occurred in the range of 190 °C–300 °C (loss of 11% mass) and the other of 300 °C until the end of the analysis (loss of 54% mass). The maximum degradation rate occurred at 398 °C. At 800 °C, the residual mass corresponded to 21%.

The wide range of thermal degradation of lignin can be justified by the different oxygenated functional groups in their structure, which provides different thermal stabilities [30]. This difference is reasonable since the modified lignin have less free hydroxyls, which makes the affinity with water lower. The thermal degradation of lignin generally occurs in three main steps: 0–120 °C, related to the evaporation of absorbed water, 180–350 °C related to the degradation of carbohydrates which are converted into volatile gases, such as CO, CO₂ and CH₄ and above 350 °C related to the degradation of lignin-derived products together with the removal of produced gases [30].

UV treated lignin had two thermal events of degradation, the first in the range of 100 °C–230 °C (mass loss of 11.7%) and the second in the range of 230 °C until the end of the analysis (mass loss of 66.5%). The maximum rate of degradation was also found at 398 °C – similar to untreated samples - and the final residue at 800 °C was 25%.

SF₆ plasma treated lignin samples presented a degradation event at temperatures in the range of 400–560 °C (loss of mass of 6.1%) and most of the mass was degraded above 560 °C, until the end of the analysis (loss of mass of 64.5%). The maximum degradation rate was achieved at 644 °C and the residual mass at 800 °C was 29.6%. TGA plot, Fig. 9, do not evidence any difference of thermal stability when we compare the two treated by SF₆ plasma samples. A reason for that is the degradation seen by TGA refers only to a thermal degradation while SF₆ ion bombardment promotes crosslinking between the lignin subunits.
chains (as it can be seen by FTIR and illustrated in the mechanism in the Fig. 7), which also increase the thermal stability of the two samples. The temperature range in which degradation occurs, i.e., maximum mass loss, \( T_{\text{max}} \), was different for all four samples, suggesting that the events of degradation were displaced to higher temperatures, mainly for SF\(_6\) plasma treated samples. This result corroborates the evidence of occurrence of plasma-induced reticulation, as more energy is needed to break cross-linked chemical bounds [31,32]. UV treated samples has Fig. 10. Stability of the coatings in alcohol solution. lower maximum temperature of mass loss than SF\(_6\) treated ones because lower reticulation happen in this case, despite that, higher than untreated ones.

**Stability test (stability to organic solvents and swelling test)**

The stability of the lignin coatings was improved after plasma treatment, probably due to the treatment induced cross-linking. When the untreated surfaces were exposed to a pH 11 aqueous solution, the phenolic groups in the lignin structure were dissociated and the film deteriorated. The film also deteriorated when it was exposed to acetone and alcohol, which is already expected, since the pure lignin could be dissolved in these solutions. However, the treated coatings seemed very stable in all these solvents. Even the UV treated coating has increased its stability in the same solutions. In Fig. 10, the change in the coating weight in relation to exposure time in alcohol is presented. As we see, after plasma treatment the weight of coatings did not have a significant change. The UV treated sample had a significant weight change in the first 30 min of exposure, but after this time the weight seemed stable. The untreated coating started to deteriorate as soon as put in contact with the solvent and, after few minutes, we could not see the coating. Tab. 3 shows the values determined for the swelling rate of the samples. It is observed that the swelling rate was influenced by the type of treatment performed on the lignin. The order observed in the swelling test was: untreated > UV treated > SF\(_6\) treated lignin. This result can be related to the degree of cross-linking where the SF\(_6\) treated lignin was higher than UV treated lignin and untreated one.

**CONCLUSION**

Super-hydrophobic surfaces have been developed with the potential of being applied in self-cleaning, oil-water separation, anti-fouling, anti-icing and especially anti-corrosion applications. Stable super-hydrophobic lignin coatings produced in this work will provide corrosion resistance for many metals, including steel. UV light and SF\(_6\) plasma were successfully used to reticulate lignin, producing hydrophilic and super-hydrophobic stable coatings, respectively. After UV light exposure, the lignin films were only affected locally, as smooth coatings
were formed. UV irradiation led to OH suppression and the creation of \( \text{C} \text{O} \) and \( \text{CH}_x \) bonds, providing a hydrophilic character to the surface in the UV treated lignin films. By the other side, \( \text{SF}_6 \) plasma treated ones, let to a major surface restructuring. Surface became rougher, with a strong incorporation of \( \text{CF}_x \) and \( \text{CH}_x \) groups. \( \text{C} \text{O} \) groups were also formed, but not in an extension to prevent the formation of a perfect, superhydrophobic surface.

## AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors. All.

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