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Rambutan peel: An unconventional source of lignin and its potential applications in polymer science

Casca de rambutan: Uma fonte não convencional de lignina e suas potenciais aplicações em ciência de polímeros

Corteza del rambután: Una fuente no convencionale de lignina y sus posibles aplicaciones en la ciencia de los polímeros

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Emanoel Igor da Silva Oliveira
ORCID: https://orcid.org/0000-0003-0228-6279
Federal Institute of Education, Science and Technology of Bahia, Brazil
E-mail: emanoeloliveira@ifba.edu.br
Jean Brito Santos
ORCID: https://orcid.org/0000-0002-0813-8560
Federal University of Bahia, Brazil
E-mail: jean10brito@hotmail.com
Silvana Mattedi
ORCID: https://orcid.org/0000-0003-4816-7494
Federal University of Bahia, Brazil
E-mail: silvana@ufba.br
Nadia Mamede José
ORCID: https://orcid.org/0000-0001-8490-0337
Federal University of Bahia, Brazil
E-mail: nadia@ufba.br

Abstract
This study aimed to evaluate the properties of soda lignin obtained from an unconventional and abundant waste - the rambutan peel - since lignin has been shown as the most promising natural organic feedstock alternative to petroleum for polymer science. FTIR analysis and pH measurements have confirmed the acidic form of lignin, which has shown solubility in a wide range of polarities and so many solvents, making its insertion easy on polymeric matrices. While the ability to absorb UV-light was higher than commercial lignin tested as reference, the morphology and size distribution at microscopic level were less regular than that. When added to a starch-based film, the lignin decreases its natural affinity for water, improving the barrier properties, as well as increasing its thermal resistance. Microorganisms could be developed easily on starch-based films containing this kind of lignin. This material, still underreported for technological applications, points towards as promisor to be a component or additive in polymeric matrices.
Keywords: Lignin; Rambutan; *Nephelium lappaceum*; Polymer; Additive.

Resumo
O objetivo deste trabalho foi avaliar as propriedades da lignina soda obtida a partir de um resíduo abundante e não convencional - a casca do rambutan - uma vez que a lignina tem se mostrado como a mais importante fonte de matéria orgânica alternativa ao petróleo para ser usada em ciência de polímeros. Análises de FTIR e medidas de pH confirmaram a natureza ácida dessa lignina, mostrando-se solúvel em solventes de polaridades variadas, o que facilita sua adição a matrizes poliméricas. Enquanto a capacidade de absorção de luz ultravioleta foi maior em comparação à lignina comercial testada como referência, a morfologia e distribuição de tamanho no nível microscópico foram menos regulares. Quando adicionada a um filme de amido, a lignina diminui sua afinidade natural por água, melhorando tanto suas propriedades de barreira quanto sua resistência térmica. Micro-organismos se desenvolveram facilmente em filmes desse tipo que continham a lignina de rambutan. Esse material ainda pouco explorado em aplicações tecnológicas apresenta potencial para ser usado como componente ou aditivo em matrizes poliméricas.
Palavras-chave: Lignina; Rambutan; *Nephelium lappaceum;* Polímero; Aditivo.

Resumen
El objetivo de este trabajo fue evaluar las propiedades de la lignina soda obtenida de un residuo abundante y no convencionale - la corteza de rambután - ya que la lignina se ha presentado como la fuente más importante de materia orgánica alternativa al petróleo para ser utilizada en la ciencia de los polímeros. Las medidas del pH y FTIR han

confirmado el carácter ácido de esta lignina, soluble en distintos disolventes y polaridad, lo que facilita su adición a matrices poliméricas. Si bien la capacidad de absorción de luz ultravioleta fue mayor en comparación con la lignina comercial probada como referencia, la morfología y la distribución del tamaño fueron menos regulares. Cuando se agrega a una película de almidón, la lignina disminuye su afinidad natural por el agua, mejorando tanto sus propiedades de barrera como su resistencia térmica. Los microorganismos se desarrollan fácilmente en películas de este tipo que contienen lignina de rambután. Aunque los reportes de sus aplicaciones tecnológicas sean muy raros, esa lignina tiene potencial como componente o aditivo en matrices poliméricas.

Palabras clave: Lignina; Rambután; *Nephelium lappaceum;* Polímero; Aditivo.

1. Introduction

Nowadays, bio-based materials have been searched as eco-friendly alternatives to replace petroleum-based materials. Industries, organizations and research groups around the world have been studied biopolymers aiming to improve their performance and to make economic and technologically viable their commercial utilization in large scale (Iffand et al., 2015; InnProBio, 2017). Due the relative worldwide abundance, natural occurrence, relative low-cost, renewability and biodegradability, the lignocellulosic biomass has been highly evaluated as feedstock of biopolymers (Silva et al., 2009). Then, the currently global demand for performance and low environmental impacts look forwards that the materials developed must to be, always as possible, in accordance with the green chemistry principles for a sustainable use.

Lignin, one of the main constituents of lignocellulosic biomass, is the generic term for a large group of aromatic polymers resulting from the oxidative combinatorial coupling of 4-hydroxyphenylpropanoids (Vanholme et al., 2010) by biosynthesis. It has a big and complex chemical structure that offers some difficulty in its elucidation mainly due modifications occurring over its extraction from lignocellulosic matrices (Sakakibara, 1980). The processes for lignin extraction are carried out under conditions in which lignin is progressively broken down to lower molecular weight fragments (Mousavioun and Doherty, 2010) beyond chemical composition modifications (oxidations or hydrolytic processes, for example), resulting in changes to its properties. More easily, the native lignin can be understood generically as an amorphous and branched macromolecular structure where aromatic rings with different substituents (hydroxyl, carboxyl, methoxyl and others) are linked for ether bonds able to be broken under specific conditions (Saliba et al., 2001). Lignin can be present in both wood and non-wood biomass, largely available in the planet, providing several functions as mechanical resistance, waterproofing and protection against microbial attack (Fengel and Wegener, 1984). In the native form, it is mixed with carbohydrates and other components, so to utilize it as a raw material to produce value-added products is needed to remove it from that complex structure using chemical and/or physical methods (Brunow, 2005). The dissolution in alkaline medium occur by the cleavage of some α-aryl and β-aryl ether bonds, producing smaller soluble-fragments (Wang et al., 2013) which, when precipitated by a pH decreasing, is named as soda lignin (Vishtal and Kraslawski, 2011).

Many kinds of lignin are being studied as organic feedstock to yield added-value products, as polymers and fuels. Despite their promisor use, generally the Kraft kind is the one explored due its big availability (Vishtal and Kraslawski, 2011). Soda lignin can be used as raw material for dispersants (Nadif et al., 2002) and animal nutrition (Baurhooa et al., 2008) but restrictedly works were found for composites (Botros et al., 2005; Zhu et al., 2014). The potential opportunities to add value and provide end-use to lignin was already discussed before (Zakzeski et al., 2010). Concerning the application in the composite field, it is important to highlight that they were and are still a much-explored kind of materials since they offer design flexibility and the opportunity to improve on the inherent limitations of traditional materials (Markgraaff, 1999). Composites and polymeric blends can include on its formulation extra-constituents to modulate the required properties, as compatibilizers, antioxidants, dyes, UV-light absorbers, conservators and biodegradation aids (Lahimera et al., 2017). Some of these uses were reported already for lignin, as plasticizer (Miranda et al., 2015), mechanical reinforcement (Nitz et al., 2001) and antioxidant (Bhat et al., 2013). When mixed with polymers in some adequate proportions, partial or until completely biodegradable materials can be produced

(Schorra et al., 2014; Stewart, 2008).

Rambutan fruit (*Nephelium lappaceum*) is an exotic tropical fruit from Asia, whose cultivation has occurred in other parts of the world as Brazil, but mainly in countries like Malaysia and Thailand where, to obtain juice, jams, jellies and marmalades, it is industrially processed. Only in Thailand, the production reached around 0.6-0.7 million tons a year and the exportation around 10-15 million US dollars. The fruit composition is around 40% of edible portion and 60% of peel and seed (Lestari et al., 2014; Sirisompong et al., 2011). Despite its consumption has increased in recent years due to the softness, sweet flavor of its edible portion and its nutritional composition rich in antioxidant compounds (Lestari et al., 2014), few technological applications of its peel were found, just as coal (Ahmad and Alrozi, 2011) or antioxidant source (Gusman and Tsai, 2015). The high content of lignin in rambutan peel, close to that found on piassava (d'Almeida et al., 2006) and other richest lignin content fibers, make it an abundant and interesting unconventional waste-source to be valued. In a previous work (Oliveira et al., 2016), our research group has reported the extraction of soda lignin from rambutan peel, and to the best of our knowledge studies with this lignin remains today underreported.

Some important properties of rambutan's soda lignin and its potential use in polymer science has discussed by this work through solubility measurements, UV-light absorption (UV-Vis DRS), microscopic morphology (SEM), molecular structures and their interactions (FTIR), thermal behavior (TGA/DTA), water vapor permeability (WVP) and enzymatic browning inhibition (EBI) of apples.

2. Methodology

2.1 Production and Characterization of Lignin

Lignin Kraft with low sulfonate content (LIG$_{ref}$) was chosen as a reference sample. It was purchased from Sigma-Aldrich and used as received. The solubility tests were carried out in a large range of P.A. solvents, used without further purification: n-hexane (Vetec), toluene (Vetec), chloroform (Synth), ethyl acetate (CRQ), acetone (Synth), dimethyl sulfoxide (Merck), ethanol (Dinâmica), acetic acid (Synth) and prepared dilute alkali solution (NaOH, Vetec). Potassium bromide (KBr) spectroscopic grade, previously dried and purchased from Sigma-Aldrich, was used to prepare tablets for FTIR analysis.

The procedures to deal with rambutan peel and lignin extraction from it (LIG$_{ramb}$) is already described in literature (Oliveira et al., 2016). Both samples were evaluated by FTIR equipment from Shimadzu, model IR Prestige-21, spectral range 4000 to 800 cm^{-1} in transmittance mode and no normalization was needed to the acquired raw data. The solubility tests were carried out in test tubes using 0.1 g of each lignin for 3 ml of each solvent by manual stirring. The UV-light absorption was carried out with the dried and powdered lignins dispersed in a sample port with a quartz window and measured on an equipment model UV-2450 from Shimadzu, with a DRS accessory of spectral range 200 to 800 nm in absorbance mode. Morphology studies were carried out with the same samples, coated by gold powder in a coater model IC-50 linked to a scanning electron microscopy model SSX 550 from Shimadzu. The experimental parameters for all these analyses were chosen based on common parameters described in literature.

2.2 Production and Characterization of Films

Sodium bromide (NaBr) and Silica were purchased from Synth and dried on a laboratory-oven overnight prior to the analysis. Apples were purchased at a local supermarket.

A series of three films was prepared through the solvent casting method as described by Miranda et al. (2015), using starch as matrix, glycerol as plasticizer, cellulose nanocrystals and lignin as modifiers and distilled water as solvent. The filmogenic solutions were prepared in a water bath at 70-80 ºC under mechanical stirring, by mixture of all constituents in the same order, until the point of starch gelatinization. The solutions were placed in a nonstick tray, on an air-circulation laboratory-oven for 18 hours until complete drying. The films produced were stored in aluminum bags inside of a polystyrene box prior to the analysis. The films were named using the letter "S" to starch, "G" to glycerol, "L" to lignin and "05" to 0.5% wt. cellulose nanowhiskers in the ratio shown in Table 1:

Table 1. Compositions (%wt.) used to produce the filmogenic solutions.

Film	**Starch**	**Glycerol**	**Lignin**	**Nanocrystals**	**Water**
FSG	5.0	2.5	0.0	0.0	92.5
FSLG	5.0	1.5	1.0	0.0	92.5
FSLG05	5.0	1.5	1.0	0.5	92.0

Source: Authors (2021).

Average film thickness was measured by a digital caliper rule with uncertainty 0.01 mm in five different points of each film. Gramature average was measured gravimetrically in triplicate by weighing film squares with 2.0 cm of side in an analytical balance. Molecular structures and their possible interactions were accessed by spectroscopy (FTIR): Film samples were fixed to tablets made with KBr on equipment from Shimadzu, model IR Prestige-21, spectral range of 4000 to 800 cm^{-1}, in transmittance mode and no normalization was needed to the acquired raw data. In the same way, their thermal behavior was determined using over 10 mg of each sample, from 25 to 800 ºC, at 20 ºC min^{-1}, in an equipment TGA/DTA EXXTAR 6000 from Seiko (TGA/DTA). The experimental parameters for all these analyses were chosen based on common parameters described in literature.

Barrier properties were evaluated by water vapor permeability (WVP) according to ASTM E96/E96M-05. Films were stored in a desiccator at 58% (R.U.) filled with saturated NaBr aqueous solution for 48 h prior to the analysis. Another one was filled with water to maintain 100% (R.U.). Each permeation cell was filled with 20 g of silica to maintain 0% (R.U.), covered with the films and then placed in the desiccator with 100% (R.U.). The mass gain was monitored each 30 min by an analytical balance for 7 h, in duplicate. The WVP was calculated by Eq. (1), where "w" is the mass gain in the cell, "t" is the time of evaluation, "A" is the area exposed to water permeation, "ΔP" is the pressure difference between the two sides of the film (measured by water vapor pressure at 25 ºC) and "ε" is the thickness:

$$WVP = (w/(t\ A))/\Delta P\ \ \varepsilon \qquad (1)$$

Finally the microbiological susceptibility could be simply and qualitatively revealed by a test of enzymatic browning inhibition (EBI), using a modified procedure described by Oliveira et al. (2008). Selected apples with similar diameters of 5.5 cm were covered by the films, attached by metallic pins and exposed to the air. The appearance was monitored daily and after 15 days to verify the influence of lignin on the undesirable process of browning.

3. Results and Discussion

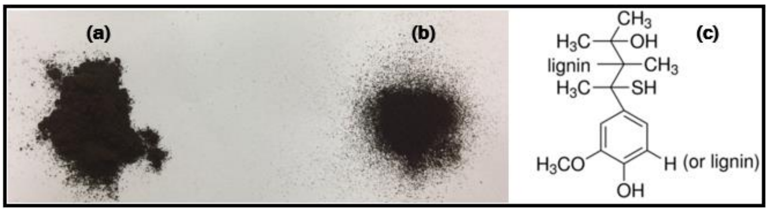
3.1 Lignin

3.1.1 General Aspects

Fig. 1 shows a comparison of the visual characteristics between LIG_{ramb} and LIG_{ref}. Both present a similar intense brown color, however LIG_{ramb} has obtained as a very fine powder similar to the talc texture, while LIG_{ref} looks like very small granules.

Another main difference verified is regarding the pH in 3% wt. water: LIG_{ramb} has shown pH 1, i.e., was yielded in an acidic form, while LIG_{ref} has pH 10.5. These differences on pH reflect directly the differences on their structures, mainly due acid functional groups which are absent on LIG_{ref} structure (Fig. 1c). Concerning the challenges and difficulties to determine the complex lignin structure as reported previously (Sakakibara, 1980), it's possible to use the chemical structure and other data available for LIG_{ref} as references to know indirectly about LIG_{ramb} chemical structure. According to the data available, LIG_{ref} has high sodium content in its composition, pointing therefore to a salt form.

Figure 1. Lignin samples: (a) LIG_{ramb} ; (b) LIG_{ref} ; (c) LIG_{ref} chemical structure.

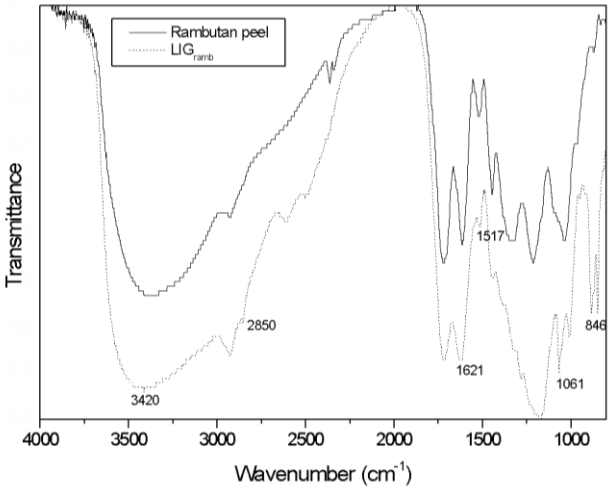


Source: Authors (2021).

3.1.2 Spectroscopy (FTIR)

The IR spectra of LIG_{ramb} was compared with the spectra from rambutan peel (Fig. 2). The signals were attributed based on a previous report about soda lignin obtained from sugarcane bagasse (Li and Ge, 2011), since the spectra registered in this work was similar to that. The band of hydroxyl groups at 3420 cm^{-1} appears more intense and broad than that for rambutan peel, suggesting an increase in the hydroxyl content as well the hydrogen-bonding network. The bands from organic general content (methyl and methylene groups) were ignored for a more focused analysis, i.e., only those bands of lignin present in rambutan peel spectra that appear modified in LIG_{ramb} spectra were evaluated. These bands are 2850 cm^{-1}, attributed to methoxyl groups; 1621, 1517 and 846 cm^{-1} attributed to aromatic rings and 1061 cm^{-1} absent to rambutan peel and isn´t reported for lignin. The band at 1517 cm^{-1} appears less intense to LIG_{ramb}, which suggests changes in the aromatic ring pattern, while 1061 cm^{-1} may be associated with the sulfur content due the sulfuric acid precipitation.

Figure 2. FTIR spectra of LIG_{ramb} and its source.

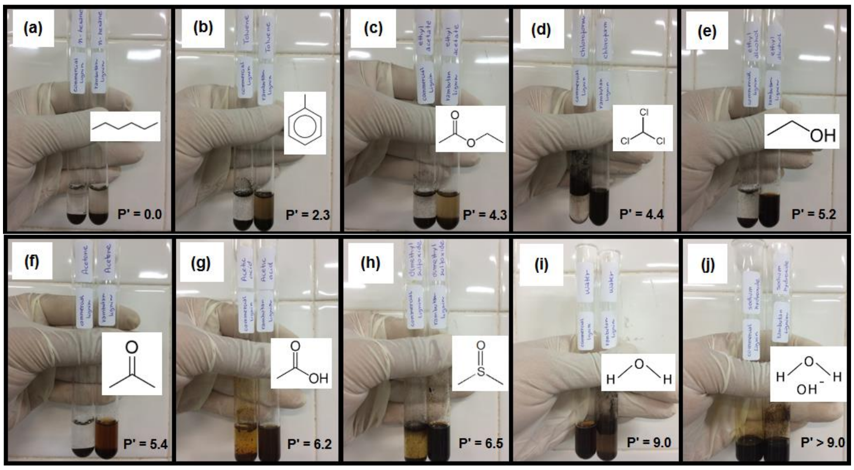


Source: Authors (2021).

3.1.3 Solubility

The solubility of LIG_{ramb} and LIG_{ref} is shown on Fig. 3. The tests were carried out in a broad range of polarities according to the Polarity Index (P'), defined by Snyder (1974) as "the ability of the solvent to interact with various polar test solutes", so were evaluated nonpolar solvents till polar ones. The results are presented in ascending order of solvent polarity to facilitate the systematization of relations between solvent structure and lignin solubility in each one of them.

Figure 3. Solubility of LIG_{ref} (left) and LIG_{ramb} (right) in some solvents: (a) n-hexane; (b) toluene; (c) ethyl acetate; (d) chloroform; (e) ethanol; (f) acetone; (g) acetic acid; (h) DMSO; (i) water and (j) alkali solution.



Source: Authors (2021).

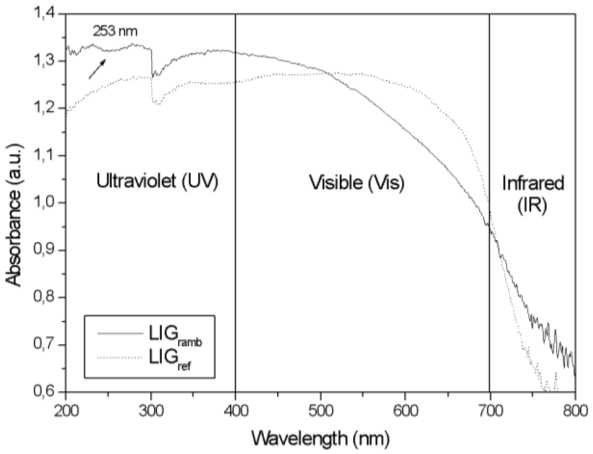
According the Fig. 3 is possible to observe that LIG_{ref} have presented some solubility just on polar solvents from acetone, increasing it to aqueous mediums, while LIG_{ramb} have presented some solubility in almost fully solvent range, except to nonpolar solvents and water. According Evstigneev (2011), the solubility of lignin in aqueous alkali solutions is determined by the ratio of the number of phenolic hydroxyls to the number of phenylpropane units in the macromolecule. Then, it is reasonable to propose that in LIG_{ramb}, water-insoluble, this ratio is low to dissolve lignin in the water, but sufficient to dissolve in the alkali solution since the hydroxyl groups will be deprotonated. According to Biermann (1996), in acidic conditions the phenolic groups are not in the salt form that contributes to water solubility, and it was verified on the LIG_{ramb} spectra by the increasing of the hydroxyl band intensity. LIG_{ref} is water-soluble since it is on the salt form, the good interaction ion-dipole between phenolate oxygen charged negatively and the water dipole contributes to its dissolution. According to Jablonský et al. (2015), it is well known when lignin is precipitated from Kraft black liquor, the carboxyl and phenolic hydroxyl contents increase. Decreasing the pH of the black liquor using different agents (organic or mineral acids, CO_2), phenolic hydroxyl groups in lignin are protonated.

Since that LIG_{ref} has a high molecular weight (Mw ~10.000) and has presented low solubility in several solvents, it indicates that LIG_{ramb} was yield in a lower Mw than LIG_{ref}, contributing to its higher solubility once small particles and fragments from native lignin on the rambutan peel present different chemical structures, allowing be dissolved in a larger range of mediums. The high solubility of LIG_{ramb} in several solvents makes easy its insertion on different polymeric matrices to produce composites and blends; furthermore, its low affinity for water makes it a good component to hydrophobic applications.

3.1.4 Spectroscopy (UV-Vis DRS)

The ability of lignin to absorb UV-light has been already reported in literature (Jablonský et al., 2015; Lee et al., 2013). The higher absorption for both samples (Fig. 4) occurred on UV range and its decrease to visible and infrared range. Since the spectroscopic study at 210-350 nm can be used to verify the purity of the precipitated lignin, then the high absorbance for LIG_{ramb} in this range reveals that lignin was yield in high concentration and a good purity level (The decreasing on signal intensity at 300 nm is just due the change of the lamp in the equipment). It is possible to observe a shoulder at 253 nm for LIG_{ramb} which is absent for LIG_{ref}. This band was observed also (Jablonský et al., 2015) for a series of lignins precipitate from black liquor using several acids. The effect of alkali treatment on UV-Vis lignin absorption has been summarized (Lemon, 1947) and is possible to conclude that the shoulder at 253 nm is due electronic transitions from p-hydroxybenzoic acid groups formed in the acidic precipitation. This data is in concordance with the acid structure proposed for LIG_{ramb} based on the solubility tests and pH measure. Another point to highlight is that UV absorption to LIG_{ref} trends to decrease at wavelengths below 200 nm, while to LIG_{ramb} that absorbance remains. It was observed a hyperchromic effect, increasing around 11% in the LIG_{ramb} UV absorption in comparison to LIG_{ref}. This result can be attributed to the extraction process where lignin is precipitated with concentrated sulfuric acid, a strong oxidizer agent that promotes the formation of chromophore groups that absorb more intensely the light, as well some residual antioxidant phenolic compounds from rambutan peel which can remain mixed with lignin. It is a desirable aspect considering the potential application of lignin as an UV-light absorber and/or antioxidant.

Figure 4. UV-Vis spectra of LIG_{ramb} and LIG_{ref}

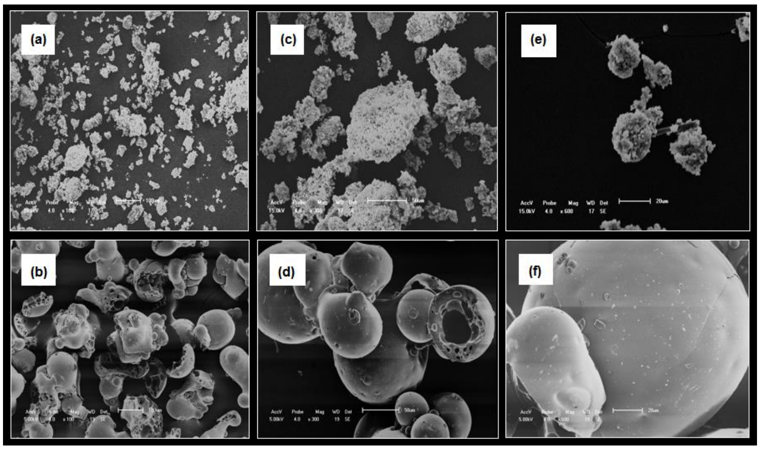


Source: Authors (2021).

3.1.5 Microscopy (SEM)

The Fig. 5 shows the microscopic appearance of LIG_{ramb} in comparison to LIG_{ref}. While LIG_{ref} has a spherical shape well defined, a smooth surface with some porous on bulk and a more regular size distribution, LIG_{ramb} has a not well-defined shape, and exhibits a granular aspect on its surface. Some spherical particles can be observed, but they aren´t the majority. The particles in LIG_{ramb} have presented some heterogeneity regarding their dimensions, with some particles very smaller than others. These results suggest that some fragmentation has occurred on the original lignin structure present on rambutan peel during the extraction process, which is according to the decreasing at 1517 cm^{-1} on FTIR spectra. The morphology presented however is according with other works before reported (Sun et al., 2014). According to Pua et al. (2011), the morphology and particle shape might be due to the concentration process of extracting lignin from black liquor.

Figure 5. SEM micrograph at magnifications (a,b) 100x, (c,d) 300x and (e,f) 600x of LIG_{ramb} (above) and LIG_{ref} (below).



Source: Authors (2021).

3.2 Films

3.2.1 General Aspects

The films showed a homogeneous aspect since lignin was added as a very fine powder. They were also slightly sticky due the starch affinity for water, but less for the films containing lignin. The control film containing only starch and glycerol (FLG) has no characteristic color, while the lignin provides a characteristic brown color. The films containing lignin (FLSG and FLG05) were harder than FLG. The Table 2 shows their thickness and gramature:

Table 2. Thickness and films gramature.

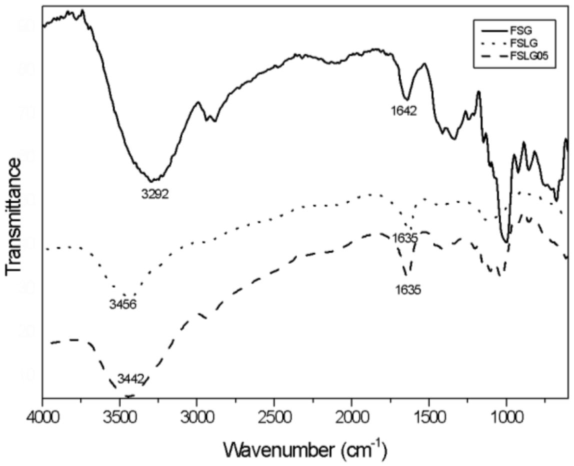
Film	Thickness (mm)	Gramature (g m^{-2})
FSG	0.09	440.25
FSLG	0.08	279.67
FSLG05	0.09	300.92

Source: Authors (2021).

3.2.2 Spectroscopy (FTIR)

Two bands were evaluated (Fig. 6): O-H Stretching (3292 cm^{-1}) and water angular deformation (1642 cm^{-1}). It was possible to observe a displacement of O-H band for higher wavenumbers in presence of lignin, indicating modification in the hydrogen bonds pattern (starch-lignin-glycerol interaction). Another important change is regarding the water angular deformation band, different from films containing lignin, suggesting a direct effect of its presence in the water affinity. Since one of the challenges to starch-based packaging is the high hydrophilicity, these results indicate potential to modulate.

Figure 6. FTIR spectra of the films.

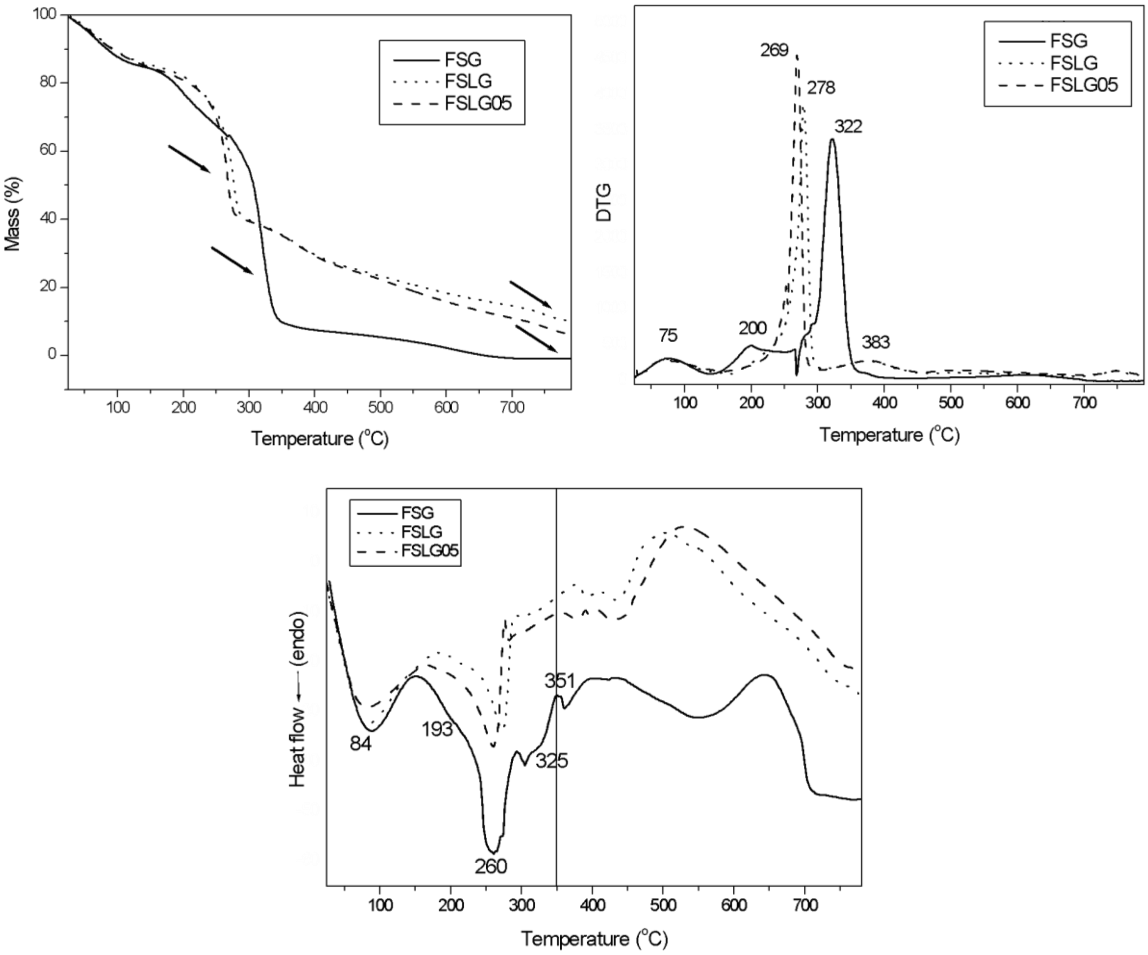


Source: Authors (2021).

3.2.3 Thermal behavior (TGA/DTA)

The thermal behavior of films containing lignin was different to the others (Fig. 7). There was observed a smaller mass loss rate in presence of lignin, producing a higher char amount at 800 ºC. There were observed three thermal events for each series: the first (50-100 ºC) due to moisture loss, the second (200-250 ºC) due to degradation of glycerol and the main, the third (300-350 ºC) due to degradation of starch. To films containing lignin, the mass loss occurs between 100 to 900 ºC, showing an event at 400 ºC corresponding mainly to the lignin pyrolysis stage (Nassar and MacKay, 1984). The event of starch degradation occurred at smaller temperatures, confirming the interaction between starch and lignin shown by FTIR, which provides improvement on stability of the starch.

Figure 7. Profiles of TG and DTG (above) and DTA (below).



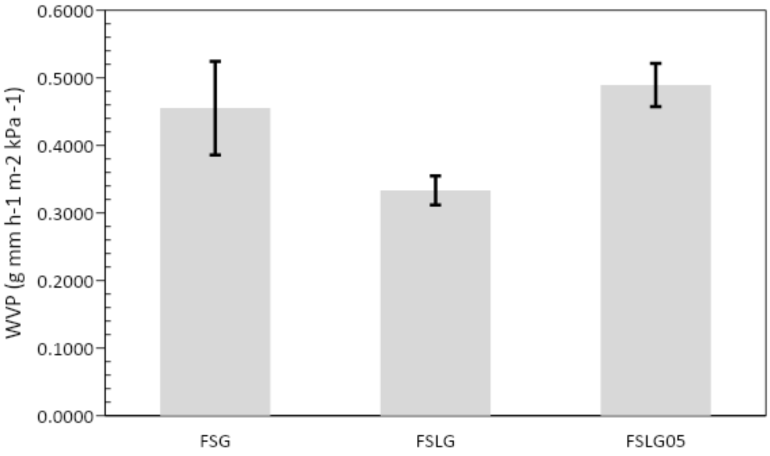
Source: Authors (2021).

The heat flow from the thermal events were evaluated by DTA analysis on Fig. 7c. Until 350 ºC, the FSG profile is similar for the others, modifying to higher temperatures. The signals attributions were made based on the work reported by Beninca et al. (2008). To FLG are signaled events for starch and glycerol: at 84 ºC, endothermic event due the moisture removal by evaporation; at 193 ºC, endothermic event due film fusion; at 260 ºC, vaporization of glycerol; from 256 until 351 ºC, starch degradation with amylose degradation in an endothermic event at 325 ºC and amylopectin exothermic event at 351 ºC. The events occurring at higher temperatures couldn´t be signaled for neither constituents. Comparing the same events for the films containing lignin, it is possible to observe that the first moisture event is slightly displaced to lower temperatures, suggesting a lower interaction between the water molecules and the film, which can be attributed to the hydrophobic effect of lignin. A displacement of the second event to higher temperatures suggests some increase in the melting temperature by influencing the lignin and lignin/nanocrystals association, which indicates a thermal reinforcement. Similar effect is shown for amylopectin decomposition, which occurs at higher temperatures for FLSG and FSLG05. The last event at 500 ºC is reported for lignin pyrolysis and due to high intensity, has been covered the last event non-identified for FLG.

3.2.4 Barrier properties (WVP)

The results (Fig. 8) showed that the composition directly affects the water affinity of films. By comparison between FSG and FSLG it is possible to observe that lignin decreases the water affinity, evidence that can be attributed to the big hydrophobic carbonic chain present on the lignin rings and the structural aspects discussed before. A similar effect was reported before (Baumberger, 1998), but for Kraft lignin. The film FSLG05 showed water affinity similar to the film control FLG, then the hydrophobic effect provided by lignin was offset by the hydrophilicity typical of the nanocrystals surface.

Figure 8. Water vapor permeability of the films.

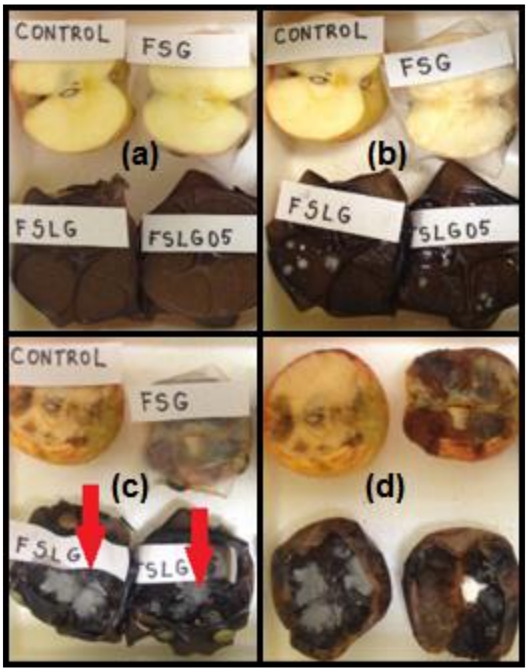


Source: Authors (2021).

3.2.5 Enzymatic Browning Inhibition (EBI)

The results (Fig. 9) showed that the lignin-based films were not good to maintain the apples' properties and inhibit the enzymatic browning, because on the 3rd day it is possible to observe formation of spots made of microorganisms, absent on the control apple as well in that covered by a film without lignin. These spots have increased until the 15st day. This biological susceptibility suggests an opportunity to explore this lignin as an additive to accelerate the biodegradation of some polymers that delay so many years to decompose on the environment (Shah et al., 2008). So, since one of the lignin´s properties is its hardness and mechanical strength to provide protection for biomass against mechanical impacts and microbial attack, a lignin which can be easily decomposed by ligninolytic microorganisms is interesting not only to preserve the nature but also another research fields, as fuels and chemicals produced from lignin (Naz et al., 2015; Kneževića et al., 2013). This behavior can be attributed to the partial fragmentation of lignin during the process extraction, as shown by FTIR and SEM analysis, making the film more susceptible to decomposition. Despite previous study about starch and lignin composites, biodegradation and water barrier properties weren´t explored (Wua et al., 2009).

Figure. 9. Enzymatic Browning in apples covered by the films produced: (a) 1st day; (b) 3rd day; (c) 15th day covered; (d) 15th day uncovered.



Source: Authors (2021).

As additional comments, Petersen et al. (1999) have summarized some characteristics desirable to a widely different kind of food packaging. Cheese and some milks require high water and light barrier properties as vital factors for maintaining the quality of these foods, mainly due the photoxidation processes and microbial growth, which contributes to decrease the lifetime. In this sense, despite LIG_{ramb} hasn´t been tested for this purpose, the WVP and UV-light absorption results presented here point to a potential application of LIG_{ramb} and another's soda lignin on milk and cheese packaging.

4. Conclusion

Soda lignin could be successfully yielded from an unconventional and abundant waste rich in lignin, the rambutan peel. This kind of lignin is soluble in many solvents, has a non-regular morphology and size distribution, beyond a higher ability to absorb UV-light than commercial one (Kraft). When lignin is associated with starch it decreases its hydrophilicity and improves the barrier property and thermal resistance. Since microorganisms could be developed easily, this material yet not reported point towards to be a promisor as component or additive in polymeric matrices. Finally, for a future perspective, we suggest some quantitative and comparative evaluation between LIG_{ramb} and other lignin types for a more accurate understanding of its real technological potential.

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