

Special Edition

Influence of lignin type on the characterization of natural fiber polymer composites

Influência do tipo de lignina na caracterização de compósitos poliméricos com fibra natural

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ABSTRACT

The use of recycled raw materials and renewable sources are necessary for economical, social, environmental and technological development. In this context, this work aims to study the influence of two lignin types, one derived from pine (Lig I) and the other one from eucalyptus, (Lig II) on polymer composites properties of recycled low density polyethylene (r-LDPE-Al) and *Pinus Elliotti* wood flour (WF), in the proportion 70% and 30% matrix/reinforcement in weight, respectively. The r-LDPE-Al is from Tetra Pak post-consumer packaging. The composites were processed by extrusion in a laboratory co-rotation twin-screw extruder. The composites obtained were evaluated through tests of melt flow index (MFI), tensile strength, Charpy impact strength, density and heat deflection temperature (HDT). The MFI results indicated that both lignin showed potential use as a flow agent for r-LDPE-AL/WF composites, with an increase of 41% and 13% for Lig I and Lig II, respectively, when compared with composite reference 0 (without lignin). Mechanical test results showed that the lignin origin influences the composites' properties where Lig I, is derived from pine (the same source as wood flour) had the best performance, indicating a potential use as a coupling agent. The results were favorable for a more noble reuse for post-consumer packaging and the lignin by-product.

Keywords: Lignin; Natural fibers; Post-consumer packaging

RESUMO

O uso de matérias-primas recicladas e de fontes renováveis faz-se necessário tanto para o desenvolvimento econômico, social, ambiental quanto tecnológico. Nesse sentido, esse trabalho consiste no estudo da influência de 2 tipos de ligninas (uma derivada de pinus e denominada como Lig I e outra de eucalipto, denominada Lig II) na caracterização de compósitos poliméricos com polietileno de

baixa densidade reciclado (r-PEBD-Al) e farinha de madeira (FM), da espécie *Pinus Elliotti*, na proporção 70% e 30% em massa de matriz/reforço, respectivamente. O r-PEBD-Al é oriundo das embalagens pós-consumo Longa vida. Os compósitos foram processados em extrusora de laboratório dupla rosca co-rotante. Os compósitos obtidos foram avaliados através dos ensaios de índice de fluidez (IF), tração, resistência ao impacto *Charpy*, densidade e temperatura de deflexão térmica (HDT). Os resultados de IF indicaram que ambas as ligninas apresentaram potencial uso como agente de fluxo para os compósitos de r-PEBD-Al/FM, com 41% e 13% de aumento para Lig I e Lig II, respectivamente, em relação ao compósito 0 sem lignina (referência). As propriedades mecânicas evidenciaram que a origem da lignina influencia no desempenho dos compósitos, sendo que a Lig I, que é derivada de pinus, mesma fonte que a farinha de madeira apresentou uso potencial como agente de acoplamento. Os resultados se mostraram favoráveis para um reaproveitamento mais nobre para as embalagens pós-consumo e o subproduto lignina.

Palavras-chave: Lignina; Fibras naturais; Embalagens pós-consumo

1 INTRODUCTION

The accelerated development of industries and the integration of economies across the planet allowed a significant increase in the movement of people and goods, promoting the intensive and unsustainable use of natural resources. The Covid-19 pandemic emerges as a sanitary and humanitarian crisis, bringing to light several problems, mainly those of an environmental, social and economic nature (LIMA, *et al.*, 2020; LEE, TRIMI, 2021). Due to the current global context of economic instability, companies have been focusing their efforts on containing expenses, reducing costs and generating new business. The changes are taking place at scales and speeds unseen before. Therefore, sustainable development and innovation play an important role in overcoming these difficulties, since many natural resources will be limited in the future (ANUGWON, *et al.*, 2019; LEE, TRIMI, 2021). The integration of the circular economy in order to promote the intelligent use of resources and the elimination of waste is one of the challenges nowadays and one of the demands of sustainability. Optimizing environmental systems to reduce inequality is essential for sustainable development (MA, 2018; PLATNIEKS, *et al.*, 2020; POZO, 2020). The use of vegetable fibers as reinforcement materials in polymeric composites has been growing due to its low cost, lower density per weight of raw material, low environmental impact, besides involving important

socioenvironmental aspects when compared to synthetic fibers. The possibility of replacing, even if partial, fossil derivatives by materials from renewable sources represents a new approach in the development of materials, and today it is a viable alternative due to the growing interest in products with less environmental impact. Nevertheless, natural fibers of plant origin have some disadvantages such as low chemical interaction between the fiber-polymer interfaces, low dimensional stability, lower mechanical and thermal properties compared to synthetic fibers (CESARIANO, *et al.*, 2019; GUILHEN, *et al.*; 2017; KORDKHEILI, PIZZI, 2020; LEMOS, *et al.*; 2017).

The long life packages are widely used around the world due to the convenience of preserving fresh food, shelf-stable and without losing properties. Although, recycling this type of packaging is complex and requires special processing plants, due to its composition: cardboard (75%), low-density polyethylene (20%) and aluminum (5%). The cardboard is separated from the polyethylene and aluminum and each material can be reused into different applications (PLATNIEKS, *et al.*, 2020; ROBERTSON, 2021). According to the company Tetra Pak, in 2019, more than 190 billion long life packages were supplied to more than 160 countries, of which only approximately 26% of these packages were recycled by Tetra Pak (GEORGIOPOULOU, *et al.*, 2021). The rest of the packaging has garbage as its final destination, resulting in serious problems of wasted resources and environmental pollution. Thus, the integration of these wastes in the circular chain of raw materials is of significant importance for the economy of cities as well as for the environment (MA, 2018; PLATNIEKS, *et al.*, 2020).

According to Kordkheili and Pizzi (2020), the pulp and paper industry generates more than 50 million tons/year of lignin. Lignin is a compound from renewable resource, considered as the second most abundant natural polymer, but a large part is still treated as waste or as a source of energy produced by the paper industry (ANUGWON, *et al.*, 2019; KORDKHEILI, PIZZI, 2020; SAKAI, *et al.*, 2018; YAN, *et al.*, 2021). Due to its complex structure, which contains polar and non-polar

groups, several studies have been investigating more noble applications for lignin, such as use in biomaterials, adhesives and as coupling agent in wood-polymer composite or flow agent in blends with polypropylene/lignin and polyethylene/lignin (ALEXY, *et al.*, 2000; KORDKHEILI, PIZZI, 2020).

Thus, aiming to reuse available resources more effectively through circular economy, sustainable development and innovation, the main objective of this study was to evaluate the influence of two lignin types in the characterization of recycled low-density polyethylene composites with wood flour. The composites with lignin were compared with a referenced composite (without addition of lignin) and evaluated through the melt index, tensile, Charpy impact strength, density and heat deflection temperature tests.

2 MATERIALS AND METHOD

2.1 Materials

Wood flour (WF), from *Pinus Elliottii*, with 35 to 325 mesh granulometry, with a higher concentration (72%) in the range of 35 and 60 mesh granulometry and 7% humidity was used as reinforcement. WF originates from agro-industry.

Recycled low density polyethylene-aluminum (r-LDPE-Al) from post-consumer long life packaging containing about 80 wt% polyethylene and 20 wt% aluminum according to the literature dates PLATNIEKS, *et al.*, 2020 and ROBERTSON, 2021. This PE was used as matrix.

Two types of lignin which were used in this study are by-products of the pulp and paper industry. Both were obtained from the kraft process, one derived from pine, here called type I lignin (Lig I) and the other derived from eucalyptus, called type II lignin (Lig II). Both lignin samples did not receive any pre-processing, being used as received, in powder form.

2.2 Processing

The r-LDPE-Al/WF composites were processed by extrusion in co-rotation twin screw extruder (model CDR 22 and L/D = 40). All composites were prepared with 30 wt% of the WF. The composites were denominated according to the addition of lignin: 0 (reference without lignin), Lig I (5 wt% lignin type I) and Lig II (5 wt% lignin type II). Table 1, shows the identification of composites and their respective compositions. The temperature extruder profile used was 70°C, 100°C, 120°C, 140°C, 150°C and 160°C (from feed to flat die) with screws rotation of 55 to 65 RPM. The composites were processed in tape shape and then, molded by thermal compression in a press (Hidraumak), using a 20 x 20 cm metal mold, being preheated for 1 min (160°C) followed by 20 s of pressing (pressure of 50 kgf/cm²). Subsequently, the materials were cooled in a press (Eletrovale) at room temperature and pressure of 5 kgf/cm² for 20 s.

Table 1 – r-LDPE-Al/WF composites and their composition

Composites	Components			
	WF (%)	r-LDPE-Al (%)	Lig I (%)	Lig II (%)
0	30.0	70.0	-	-
Lig I	28.5	66.5	5.0	-
Lig II	28.5	66.5	-	5.0

Source: Authors, 2021

2.3 Characterization

Composites were characterized according to the following rheological, mechanical and physical tests.

The melt flow index (MFI) was performed on the Ceast Melt Flow Junior equipment, according to ASTM D1238:2020 standard. The conditions of 190°C/2.16 kg were used in the heating cylinder and load, in that order, with preheating and cut times of 300 s and 15 s, respectively. The test was performed in triplicate.

The mechanical tensile test was performed according to ISO 527-1:2019 standard recommendations, using a universal testing machine EMIC, model DL 500 BF with a load cell of 500 kgf and 50 mm/min rate. Charpy impact determination were based on ISO 179:2010 standard, using a Ceast Resil 5.5 impact machine with 0.5 J hammer and 3.60 m/s speed. For each mechanical tests, 7 specimens were tested.

The apparent density was realized in triplicate and determined by Archimedes principle using a precision balance and distilled water, as recommended by ASTM D 792:2020 standard.

Heat deflection temperature (HDT) was performed in Ceast Vicat/HDT Junior model 6910 equipment, based on ISO 75:2020 standard, using 1.8 MPa load, heating rate of 120°C/hour and distance between supports of 100 mm. In this case, 7 specimens were tested.

Statistical analysis of variance (ANOVA) were performed on all results obtained and complemented by Tukey's test, using the free software PAST, version 4.06b.

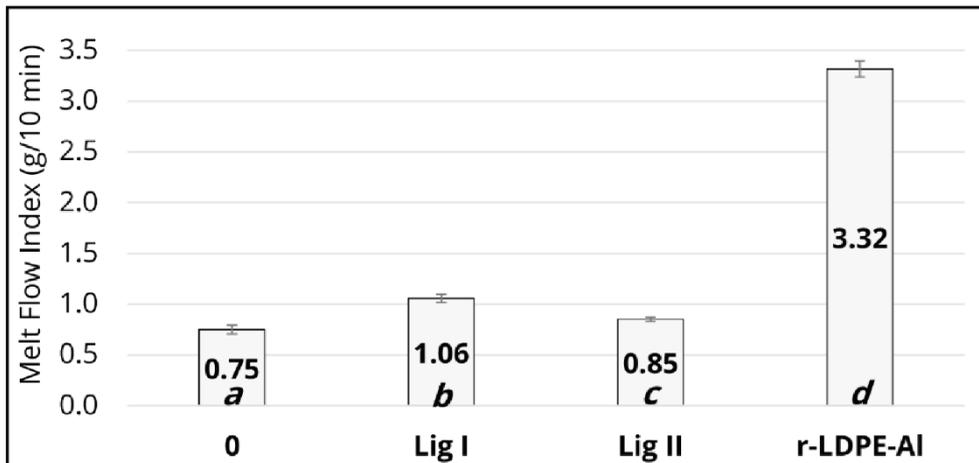
3 RESULTS AND DISCUSSION

3.1 Melt Flow Index

Figure 1 shows the results of melt flow index (MFI) of r-LDPE-Al and of the r-LDPE-Al/WF composites without and with lignin. The r-LDPE-Al showed higher MFI when compared to composites 0, Lig I and Lig II, the result were expected, since the incorporation of WF changes the rheological behavior of the material, hindering the movement of polymer chains and reducing the flow capacity of composites (CARVALHO, *et al.*, 2020; CERQUEIRA, 2006). Also, according to Figure 1, it can be seen that the composite with Lig I was the one with the highest MFI (41% in relation to composite 0) followed by composite with Lig II (13% in relation to composite 0).

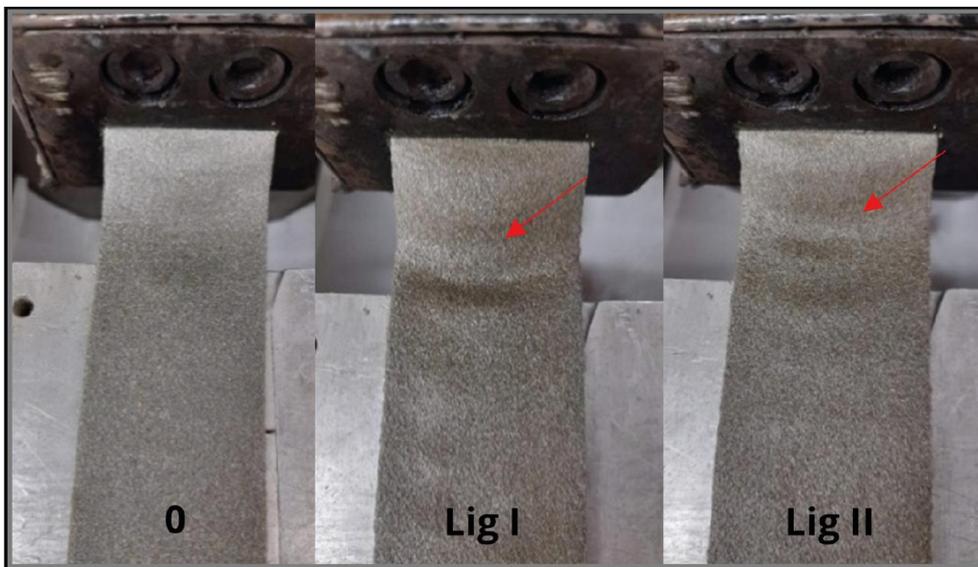
This result confirms that the presence of lignin influences the increase in the fluidity of the composite, indicating that it may be acting as a flow agent, according to Alexy *et al.* (2000). Italicized letter in each column of the graph represent the Tukey test¹.

Figure 1 – MFI of r-LDPE-Al and composites



Source: Authors, 2021

Figure 2 – Composite tapes at extruder die



Source: Authors, 2021

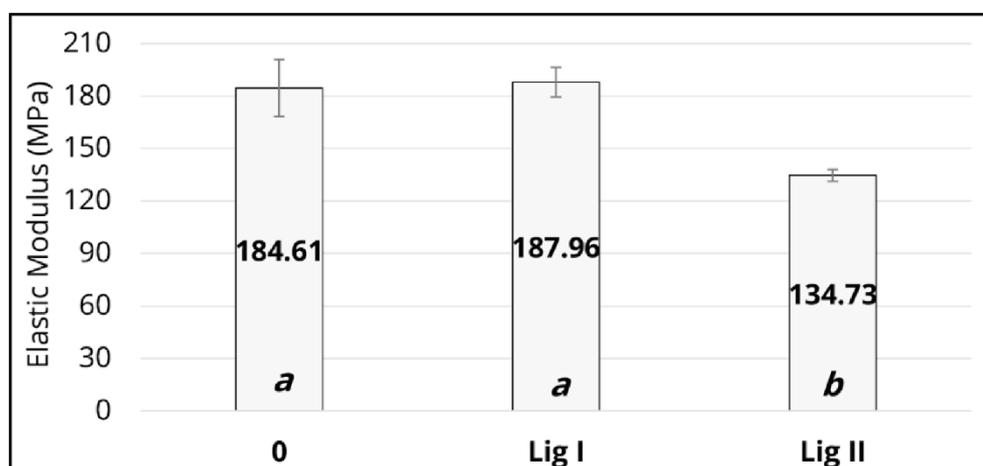
¹ Different letters mean that the values are statistically different from each other, at a significance level of 5% by Tukey's test.

Figure 2 shows photographic images of the composite tapes at the extruder die and, as it can be seen, the Lig I and Lig II composites show greater fluency due to the presence of "wrinkles" on the tapes when compared to composite 0, results which corroborate with the highest MFI values found. In addition to a slight yellowing when compared to the composite without lignin is observed. Statistical analysis showed that the MFI values of all composites showed significant differences from each other.

3.2 Tensile Properties

In Figure 3, the results of the elastic modulus of the composites are presented, where it is possible to observe that the composites 0 and Lig I did not present significant differences between them, while there is a decrease of 27.02% in the elastic modulus for Lig II in relation to composite 0.

Figure 3 – Elastic modulus of composites obtained by tensile test

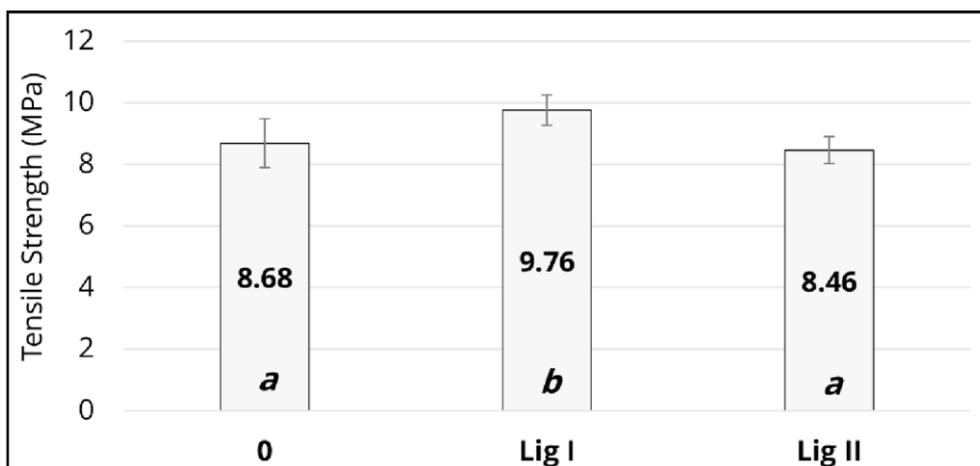


Source: Authors, 2021

Figure 4 shows the tensile strength at break of the evaluated composites. The Lig I composite showed a significant difference compared to the 0 composite. The Lig II composite did not show a significant difference compared to the 0. According to Miléo (2015), the tensile strength is strongly dependent on the compatibility between the fiber and the matrix, while the modulus of elasticity is more influenced

by the impregnation of fibers in the matrix. Thus, lignin I in addition to being a flow agent, may have helped in the fiber/matrix interaction of the Lig I composite, as observed by Anugwom *et al.* (2019), where the presence of lignin proved to be promising in replacing the compatibilizer agent, presenting higher values of tensile strength in composites of PLA with wood flour. The same did not happen with Lig II, which presented a value of tensile strength statistically equal to the composite without lignin (composite 0) and lower modulus of elasticity than the other composites. It is believed that these results were influenced by lignin sources, since lignin I is derived from pine as well as WF, showing a better interaction than lignin II which is derived from eucalyptus.

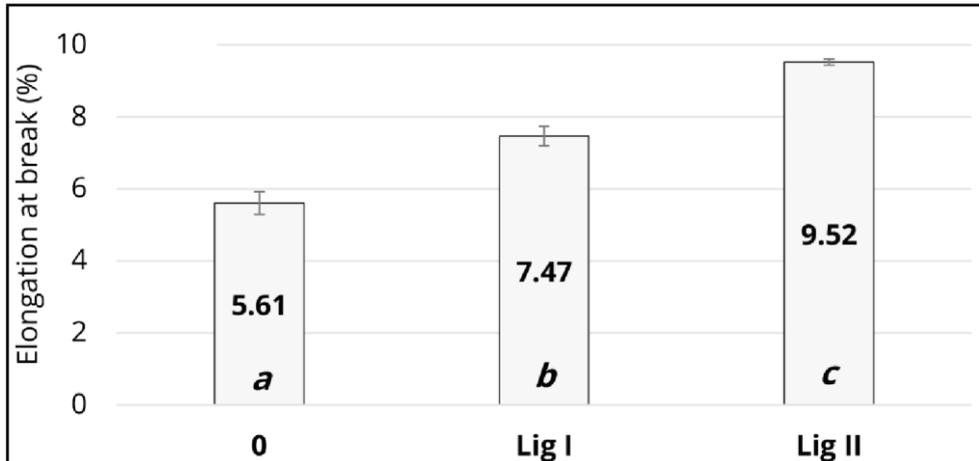
Figure 4 – Tensile strength at break of composites obtained by tensile test



Source: Authors, 2021

Figure 5 shows the elongation at break of the evaluated composites. Composites with Lig I and Lig II had higher values than composite 0. The results found for elongation of composites are consistent with the values found in the literature, where composites with higher modulus of elasticity have lower elongation values at break (JESUS, *et al.*, 2015; PETROUDY, 2016). Thus, the Lig II composite was the one with the highest elongation value, as expected, since it was the one with the lowest elastic modulus.

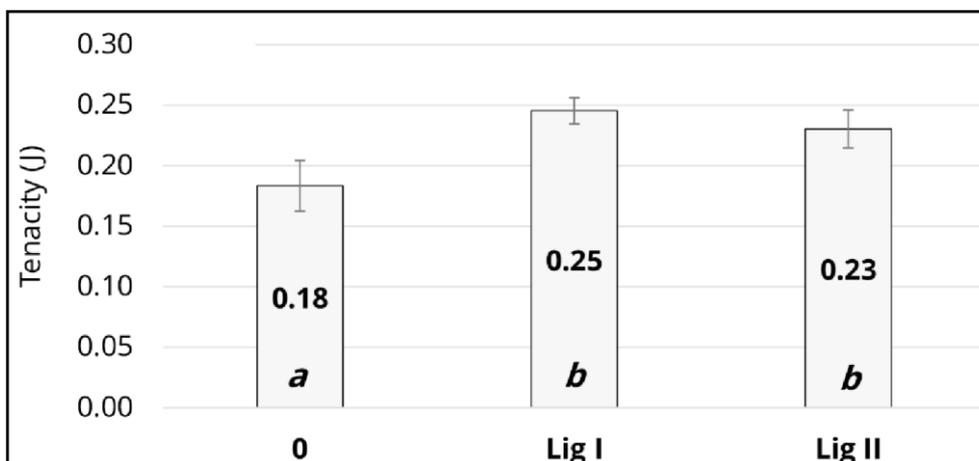
Figure 5 – Elongation at break of composites obtained by tensile test



Source: Authors, 2021

Figure 6 shows the tenacity results of the studied composites. Composite 0 showed a significant difference in relation to Lig I and Lig II. The composites Lig I and Lig II did not show significant differences between them and showed higher values than composite 0. According to Cândido *et al.* (2012) the energy absorption capacity and tenacity of the composite are optimized by the mechanisms of wettability and fiber/matrix adhesion. Thus, the increase of approximately 38% and 27% in tenacity for Lig I and Lig II, respectively, in relation to 0 could indicate an improvement in fiber/matrix adhesion in these composites caused by lignin that could be acting as a coupling agent.

Figure 6 – Tenacity of composites obtained by tensile test

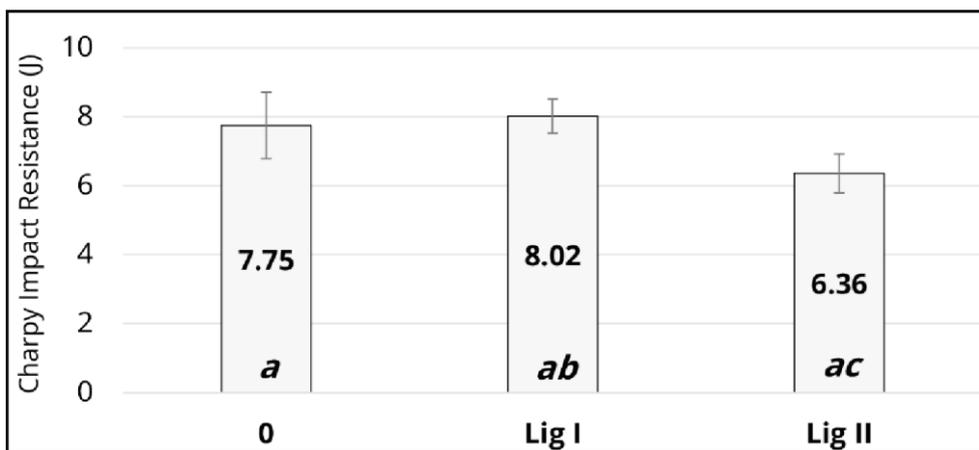


Source: Authors, 2021

3.3 Impact resistance

In Figure 7 it can be seen that, in relation to the result of Charpy impact resistance, composite 0 did not present a statistically significant difference in relation to Lig I and Lig II composites. However, comparing the impact resistance between Lig I and Lig II, it was found that Lig II composite was inferior in relation to Lig I. According to Carvalho *et al.* (2020), the poor distribution of the reinforcement phase in the matrix can cause agglomerates that act as stress concentrators, forming cracks which reduce the energy absorbed in the impact test.

Figure 7 – Charpy impact resistance of composites evaluated

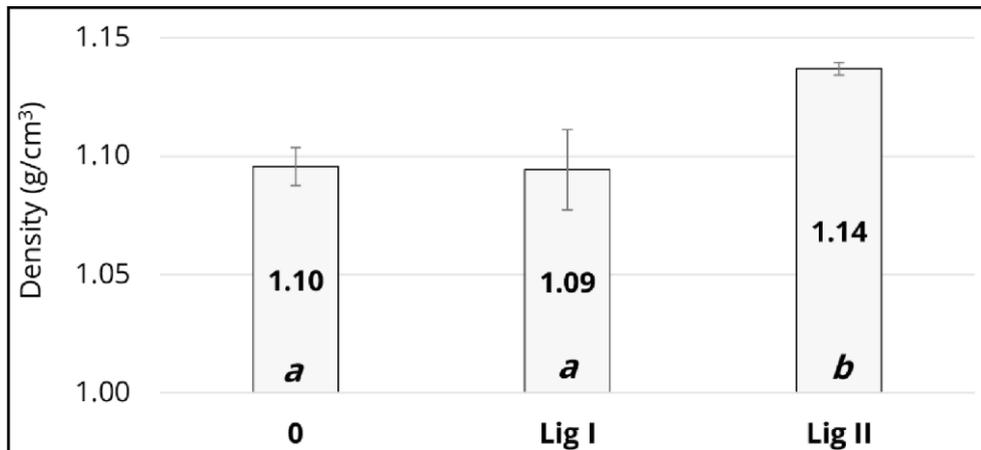


Source: Authors, 2021

3.4 Density

In Figure 8, the density results of the evaluated composites are presented. Based on the density value found for the composites, it appears that Lig II was the one with the highest density, which could probably be related to heterogeneous specimens. Still, it appears that composites 0 and Lig I did not show statistically different values from each other.

Figure 8 - Density of composites evaluated

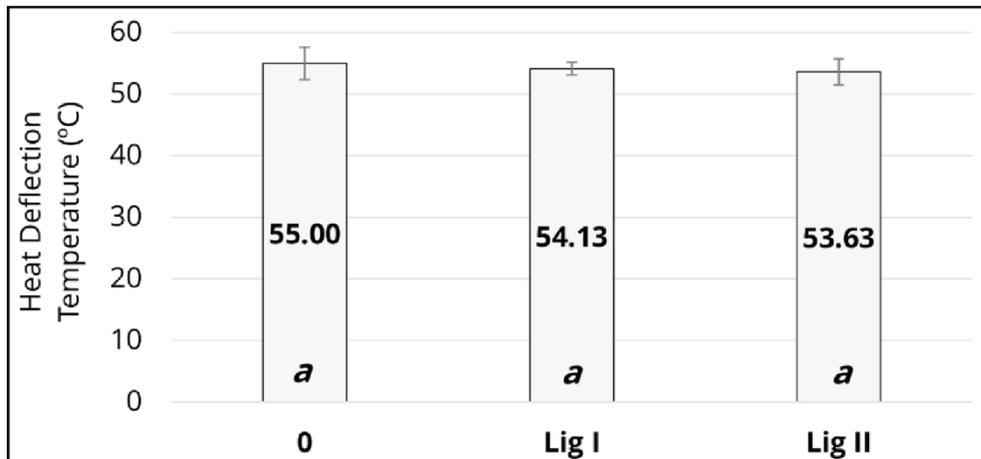


Source: Authors, 2021

3.5 Heat deflection temperature

Figure 9 shows the heat deflection temperature (HDT) results of the evaluated composites. According to Jesus *et al.* (2019), the HDT represents the maximum temperature which a material subjected to a given effort remains without deformation, and is therefore an important test in composites, as from it the maximum working temperature is delimited. Thus, according to the results of Figure 9 and the statistical analysis, it was found that the composites Lig I and Lig II did not present statistically significant differences when compared to each other and to the reference composite 0. Thus, the replacement of 3.5 wt% of a petrochemical source polymer by a natural polymer does not affect the thermal stability of the final composite.

Figure 9 – Heat deflection temperature of composites evaluated



Source: Authors, 2021

4 CONCLUSION

The samples of lignin I and II showed to be promising as rheological modifiers (flow agents) in r-LDPE-Al/WF composites (70/30 wt), as verified in the MFI results. Lignin I, in addition to acting as a flow agent, may also have acted as a coupling agent, enabling an improvement in fiber/matrix adhesion justified by the superior results of mechanical performance in the Lig I composite when compared to Lig II and 0 composites. It is probably due to its origin being the same as WF (pinus).

Considering the sustainability trends, it was possible to replace a portion of material from petrochemical sources, the same as those of recycled origin, by a residue from natural source and without significant loss of properties. In addition, r-LDPE-Al post-consumer packaging has its application restricted due to the presence of aluminum that acts as a filler, making the process difficult. The use of lignin as a flow agent could become an economical and sustainable alternative for a more efficient reuse of these post-consumer packaging, in addition to providing an opportunity for a more noble use for the lignin by-product.

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REFERENCES

ALEXY, P.; KOSÍKOVÁ, B.; PODSTRÁNSKA, G. The effect of blending lignin with polyethylene and polypropylene on physical properties. **Polymer**, v. 41, n., p. 4901-4908, 2000.

ANUGWON, I.; LAHTELA, V.; KALLIOINEN, M.; KÄRKI, T. Lignin as a functional additive in a biocomposite: Influence on mechanical properties of polylactic acid composites. **Industrial Crops & Products**, v. 140, n., p. 111704, 2019.

CÂNDIDO, G. M.; REZENDE, M. C.; DONADON, M. V.; ALMEIDA, S. F. M. de. Fractography of aeronautical composite structures submitted to mode I interlaminar fracture toughness characterization. **Polímeros**, v. 22, n. 1, p. 41-53, 2012.

CARVALHO, M. S. de; AZEVEDO, J. B.; BARBOSA, J. D. V. Effect of the melt flow index of an HDPE matrix on the properties of composites with wood particles. **Polymer Testing**, v., n., p. 106678, 2020. Disponível em: <https://doi.org/10.1016/j.polymertesting.2020.106678>.

CERQUEIRA, M. H. de. **Processamento do compósito LDPE/Al proveniente da reciclagem de embalagens cartonadas e desenvolvimento de suas modificações com fibras de madeira**. 2006. 96 p. Dissertação (Mestrado em Engenharia de Materiais) - Universidade de São Carlos, São Carlos, 2006.

CESARIANO, I.; DIAS, O. A. T.; NEGRÃO, D. R.; ROCHA, L. L. N.; LEÃO, A. L. High-density green polyethylene biocomposite reinforced with cellulose fibers and using lignin as antioxidant. **Journal of Composite Science**, v. 3, n. 24, p., 2019.

GEORGIPOULOU, I.; PAPPAS, G. D.; VOUYIOUKA, S. N.; MAGOULAS, K. Recycling of post-consumer multilayer Tetra Pak® packaging with the selective dissolution-precipitation process. **Resources, Conservation & Recycling**, v. 165, n., p. 105268, 2021.

GUILHEN, A.; GADIOLI, R.; FERNANDES, F. C.; WALDMAN, W. R.; DE PAOLI, M. A. High-density green polyethylene biocomposite reinforced with cellulose fibers and using lignin as antioxidant. **Journal of Applied Polymer**, v. 134, n., p. 45219, 2017.

- JESUS, L. C.; LUZ, S. M.; LEÃO, R. M.; ZATTERA, A. J.; AMICO, S. C. Propriedades mecânicas de compósitos de poliestireno reforçado com celulose de bagaço de cana. **Revista Interdisciplinar de Pesquisa em Engenharia**, v. 1, n. 1, p., 2015. Disponível em: <https://periodicos.unb.br/index.php/ripe/article/view/20721>.
- JESUS, L. C.; LUZ, S. M.; LEÃO, R. M.; ZATTERA, A. J.; AMICO, S. C. Comportamento térmico de compósitos de poliestireno reforçado com celulose de bagaço de cana. **Revista Matéria**, v. 23, n. 3, p., 2019.
- KORDKHEILI, H. Y.; PIZZI, A. Ionic liquid- modified lignin as a bio-coupling agent for natural fiber-recycled polypropylene composites. **Composites Part B**, v. 181, n., p. 107587, 2020.
- LEE, S.; TRIMI, S. Convergence innovation in the digital age and in the COVID-19 pandemic crisis. **Journal of Business Research**, v. 123, n., p. 14-22, 2021.
- LEMO, A. L. de; PIRES, P. G. P.; ALBUQUERQUE, M. L. de; BOTARO, V. R.; PAIVA, J. M. F. de; DOMINGUES JÚNIOR, N. S. Biocomposites reinforced with natural fibers: thermal, morphological and mechanical characterization. **Revista matéria**, v. 22, n. 2, p., 2017.
- LIMA, N. T.; BUSS, P. M.; SOUSA, R. P. A pandemia de Covid-19: uma crise sanitária e humanitária. **Cadernos de saúde pública**, v. 36, n.7, p., 2020. Disponível em: <https://doi.org/10.1590/0102-311X00177020>.
- MA, Y. Changing Tetra Pak: from waste to resource. **Science Progress**, v. 101, n. 2, p. 161-170, 2018.
- MILÉO, P. C. **Estudo do uso de ligninas como agente compatibilizante em compósitos de polipropileno reforçados com celulose de bagaço e palha de cana-de-açúcar**. 2015. 199p. Tese (Doutorado em Ciências) - Universidade de São Paulo, Lorena, 2015.
- PETROUDY, S. R. D. Physical and mechanical properties of natural fibers. *In*: FAN, M; FU, F. (ed.). *Advanced High Strength Natural Fibre Composites in Construction*. Editora Woodhead Publishing, 2016. p. 59-83.
- PLATNIEKS, O.; BARKANE, A.; IJUDINA, N.; GAIDUKOVA, G.; THAKUR, V. K.; GAIDUKOV, S. Sustainable tetra pak recycled cellulose / Poly(Butylene succinate) based woody-like composites for a circular economy. **Journal of Cleaner Production**, v. 207, n., p. 122321, 2020.
- POZO, C; GALÁN-MARTÍN, A.; CORTÉS-BORDA, D.; SALES-PARDO, M.; AZAPAGIC, A.; GUIMERÀ, R.; GOSÁLBEZ-GUILLÉN, G. Reducing global environmental inequality: determining regional quotas for environmental burdens through systems optimization. **Journal of Cleaner Production**, v. 270, n., p. 121828, 2020.

ROBERTSON, G. L. Recycling of Aseptic Beverage Cartons: A Review. **Recycling**, v. 6, n. 20, p., 2021.

SAKAI, H.; KURODA, K.; TSUKEGI, T.; OGOSHI, T.; NINOMIYA, K.; TAKAHASHI, K. Butylated lignin as a compatibilizing agent for polypropylene-based carbon fiber-reinforced plastics. **Polymer Journal**, v. 50, n., p. 997-1002, 2018.

YAN, Q.; ARANGO, R.; LI, J.; CAI, Z. Fabrication and characterization of carbon foams using 100% Kraft lignin. **Materials and Design**, v. 201, n., p. 109460, 2021.

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