This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Lourençon, Tainise V.; Santilli, Beatriz V.; Magalhães, Washington L.E.; Muniz, Graciela I.B.
Thermal Stabilization of Wood/Polypropylene Composites Through Addition of Unmodified, Low-Cost Kraft Lignin

Published in:
Waste and Biomass Valorization

DOI:
[10.1007/s12649-018-0484-6](https://doi.org/10.1007/s12649-018-0484-6)

Published: 30/10/2018

Document Version
Peer reviewed version

Published under the following license:
Unspecified

Please cite the original version:
Lourençon, T. V., Santilli, B. V., Magalhães, W. L. E., & Muniz, G. I. B. (2018). Thermal Stabilization of Wood/Polypropylene Composites Through Addition of Unmodified, Low-Cost Kraft Lignin. *Waste and Biomass Valorization*, 11(4). <https://doi.org/10.1007/s12649-018-0484-6>

Thermal stabilization of wood/polypropylene composites through addition of unmodified, low-cost kraft lignin

Tainise V. Lourençon^{1,4}, Beatriz V. Santilli², Washington L. E. Magalhães³, Graciela I. B. Muniz¹

¹Wood and Forestry Science Center (PPGEF), Federal University of Paraná, Lothário Meissner 900, 80210-170 Curitiba, Brazil

²Federal University of Amazonas, General Rodrigo Octávio 6200, Coroado I, 69080-900 Manaus, Brazil

³Embrapa Florestas, Estrada da Ribeira, km 111 PO Box 319 Colombo, PR, Brazil

⁴Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16300, 00076, Finland

Abstract: Wood/polymer composites are elegant strategies to produce materials with good performance and reduced cost. However, the addition of a lignocellulosic fiber is often responsible for the decreased thermal stability, decreasing their appeal as building materials. Here, we aimed to improve the thermal stability of wood/polypropylene composites through addition of unmodified, low-cost, abundant, ready-to-use kraft lignin. Besides thermal behavior, the composites were analyzed concerning to water relationships, colorimetric parameters, mechanical properties, and morphological features. The wood/propylene composites with and without lignin showed a very similar morphology with good interaction between matrix and biomasses. Thickness swelling decreased as function of lignin increment. The composites with 4, 12 and 20 wt% of lignin content had temperatures at 10% mass loss shifted toward higher temperatures (332, 350 and 362 °C, respectively) compared to wood/polypropylene (326 °C). Flexural strength of wood/propylene composite was preserved (42 MPa) at 4 wt% of lignin addition and tensile strength was kept unaltered in all ratios of lignin/wood (14-19 MPa).

29 **Statement of Novelty**

30 This work brings the use of a large available residual lignin into value-added product.

31 The considerations made here are transferable to the valorization of other wastes or

32 biomasses.

33

34 **Keywords:** thermal properties; water absorption; lignocellulosic; bio-based polymer

1. Introduction

Nowadays, polymeric composites prepared by incorporating natural fibers or particles in polypropylene matrices turned in key-materials that have been widely applied as automobile components and packing [1, 2]. By selecting lignocellulosic fillers instead of inorganics, it could be possible to obtain cheaper and greener materials. Besides that, biomass materials are renewable, biodegradable, abundantly and they present high strength-to-density ratio [2–5].

The incorporation of such biomass-derived fillers often result in decreased thermal stability of the resultant composite, which could be a limitation not only when manufacturing is considered, but also in promising potential applications as fire retardant [6], building and construction [7]. At this stage, if not properly coupled, the incorporated particles or fibers may lead to excessive nucleation of the polymer chain, decreasing its degree of polymerization and crystallinity index. As a consequence, the thermal energy demanded to melt it is in parallel decreased. Some good strategies to overcome this have been addressed by incorporation low loads of inorganic fillers or phosphorous derivatives [8–12]. However, fortunately, nature provides lignin, the most abundant source of aromatic compounds built up of phenylpropane structures [13]. Due to its aromatic chemical structure, this could be an excellent choice as thermal stabilizer [6]. Also, it is well-known that lignin is the responsible for charcoal formation of wood-derived materials during thermal stress [14, 15], which can indirectly provide thermal stabilization.

Besides its ability to form charcoal, lignin presents chemical anisotropy in its three dimensional matrix [16]. It is not expected that pure unmodified lignin could act as a compatibilizer for wood-polymer composites; however, the hydrophobic and hydrophilic moieties in its composition may help to obtain composites with very good homogeneous

characteristics that is often disregarded. The ability of lignin to interphase hydrophobic and hydrophilic compounds have been widely addressed for emulsions for instance [17], which can draw a parallel to this study once wood polymer composites are sort of solid emulsion. As a matter of fact, considering the thermal stabilization as the main goal, it would be even better if the inserted filler did not bring any side effect in other important properties of these materials, such as mechanical and water absorption characteristics. Recent efforts have showed the positive effect that lignin can bring to polymer composites. Some good examples involve the addition of lignin in multiphase polymeric materials for improved mechanical properties [18, 19], butylated lignin for thermal stabilization [20], lignin in polymeric matrix as compatibilizer [5] and as antioxidant agent [21]. In general, the lignin is first chemically modified and then inserted in the composites; however, here we showed how pure and unmodified kraft lignin – replacing wood flour in different ratios - can be used to prepare low-cost bio-based composites. By doing so, it will be possible not only to prepare high-quality wood-polymer composites but also to benefit a by-product from pulp and paper industry. Currently, 70 million tonnes of lignin are produced annually in the world and only 5% is used in commercial applications, while 95% is burned for energy production [22]. The kraft process is the main method applied for pulping. In addition, lignin from the kraft process is a realistic prospective to produce high value-added products from biomass [23]. Taking into consideration a bio-economy perspective, there is an increased demand to use renewable sources for energy supply. At this scenario, residual lignin could be applied in new, up-coming, end uses while renewable energy is integrated to the pulping process [24]. At this stage, any attempt to develop high-added value products from lignin can be considered a starting point toward profitable, more sustainable process and materials, bringing up important fundamentals of circular economy. Thus, this study is looking at

the potential of the unmodified kraft lignin as a low-cost, abundant, ready-to-use agent to improve the thermal stability of wood-polypropylene composites. Here, we also study the effect of the lignin incorporation in other important technical properties, as mechanical and water relationships.

2. Material and Methods

2.1 Raw material and preparation of composites

The Polypropylene (P) PP H103, supplied by Braskem (Brazil), has a density of 0.905 g cm⁻³ and melt flow rate of 40 g/10 min. The lignin (L), supplied by Suzano Pulp and Paper, is a byproduct from hardwood kraft pulping process, recovered from the black liquor by CO₂ precipitation. Fast-growing *E. benthamii* wood flour (W) was collected from sawing process at Embrapa Florestas (Brazil). The material was oven dried at 60 ± 5 °C until constant mass, and then sifted between 40 - 60 mesh [25] to composite preparation. The composition of the above-mentioned materials is described in Table 1.

Table 1. Number average molecular weight (Mn), weight average molecular weight (Mw) and chemical composition of lignin, wood flour and polypropylene

	Mn	Mw	Lignin (%)	Ash (%)	Holocellulose (%)	Extractives (%)
P	49	236	-	-	-	-
L	903	1995	91.4	1.4	nq	nq
W	-	-	24.0	0.6	70.9	1.6

^{nq} not quantified

The polymer ratio of the composites was fixed at 60%, in order to investigate only the effect of lignin-to-wood flour ratio. Besides, this matrix/biomass ratio represents the range already commercialized in the market [26]. Four composites were prepared using the following mass percent combination, described in the subscript numbers: P₆₀W₄₀,

P₆₀W₃₆L₄, P₆₀W₂₈L₁₂, and P₆₀W₂₀L₂₀. A thermo-kinetic high-shear homogenizer (MH Equipamentos Ltda), operating at 3000 rpm, was used to mix 90 g of each composition. Then, the mixtures were individually thermo-molded using a Marconi MA098/A electrically heated hydraulic press with homogenous distribution of pressure (9 ton) for 10 min, carried out at 175 ± 2 °C. The nominal size of the composites was 140 mm x 140 mm x 4 mm after the cooling process. Additives and coupling agents were not used in the molding process of the composites.

2.2 Visual aspects and micro morphological features

The colorimetric evaluation of the composites was assessed by a Konica Minolta CM-5 spectrophotometer. The equipment was configured to use a D65 light source and observation angle of 10° (CIE-Lab standard). Three measurements of each composite were taken in order to obtain the colorimetric parameters: lightness (L^*), green-red chromaticity coordinate (a^*) and blue-yellow chromaticity coordinate (b^*). Then, C^* (chroma) and h^* (hue angle) were measured according to Konica Minolta Manual (2007). The fractured cross-section of the P₆₀W₂₀L₂₀ and P₆₀W₄₀ composites were coated with a 3 nm layer gold and further evaluated in a benchtop scanning electron microscope-FEI Phenom.

2.3 Evaluation of the thermal behavior of the composites

Thermal properties of the composites were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The result for each sample is the average of two runs. DSC was performed to acquire the temperature of crystallization (T_c), melting temperature (T_m), heat of fusion (ΔH_f) and percentage of crystallinity (X_c) (Equation 1), which were calculated according to previous studies in the literature [28–

30]. The equipment used for this experiment was a Shimadzu DSC-60A set to operate under a nitrogen atmosphere at 20 mL min⁻¹. The T_m was determined by heating the samples from 30 to 180 °C and maintaining at this temperature for 5 min. The samples were then cooled to 30 °C at a rate of 5 °C/min to determine T_c .

$$X_c = (\Delta H_f / \Delta H_f^0) * (100/W) \quad (\text{Equation 1})$$

where ΔH_f is the heat of crystallization, W is the mass fraction of P in the composite and $\Delta H_f^0 = 190$ J/g, was taken for 100% crystalline isotactic P.

TGA was carried out in a Setsys Evolution (Setaram, France) instrument, under an argonium atmosphere at 20 mL min⁻¹. In this case, the samples were heated from 30 °C up to 600 °C at 10 °C min⁻¹.

2.4 Water-composites relationships

Five samples of each composite were used to evaluate water absorption (WA) and thickness swelling (TS), according to ASTM D 570-98. The samples were oven dried at 103 ± 5 °C to constant weight and then immersed in water. Weight and thickness of dry and immersed samples (2 and 24 h) were measured.

Measurements of the composites wettability were performed using a Crüss DSA25E goniometer, using the sessile droplet method. The contact angle was determined by the placement of a deionized water droplet (5 µl) on six distinct points (randomly selected) of each composite in different times, after 5, 20, 35, 50 and 65 s. The contact angle for neat polypropylene was demonstrated at 20s.

2.5 Mechanical properties

Five samples of each composite were tested related to mechanical properties by flexural strength (ISO 178) and tensile strength at break (ISO 527). All the tests were performed in an EMIC DL30000 universal machine.

2.6 Data analysis

The normal distribution and analysis of variance (ANOVA) of physical and mechanical data were evaluated at 95% of significance by F-test. When the null hypothesis ($p < 0.05$) was rejected, the average values were compared using Tukey test at 5% of probability of error, in which different letters reflected statistical significance.

3. Results and discussion

3.1 Visual appearance and morphological features

As can be seen in Table 2, the chromaticity coordinates a^* and b^* decreased with lignin increment, indicating a color changing direction from red to green and yellow to blue, respectively. From lightness (L^*) is possible to observe that all composites are in the dark range, especially in the presence of lignin. Chroma (C^*) parameter means saturation of color. In this sense, there is a clear decrease in C^* with lignin addition, indicating a greyish direction. Furthermore, the relationship between C^* and L^* and C^* and hue angle (h^*), can be interpreted as a darkening tendency in the composites as a function of lignin increment [27].

Table 2. Colorimetric parameters

Sample	L^*	a^*	b^*	h^*	C^*
P ₆₀ W ₄₀	18.23 ± 0.96	4.29 ± 0.09	6.09 ± 0.34	0.96 ± 0.03	7.45 ± 0.29
P ₆₀ W ₃₆ L ₄	17.22 ± 2.87	1.74 ± 0.46	2.08 ± 0.71	0.86 ± 0.05	2.72 ± 0.83

$P_{60}W_{28}L_{12}$	12.54 ± 0.85	2.91 ± 0.51	2.79 ± 0.59	0.76 ± 0.04	4.04 ± 0.76
$P_{60}W_{20}L_{20}$	15.37 ± 1.44	1.27 ± 0.49	0.78 ± 0.62	0.48 ± 0.18	1.52 ± 0.74

From scanning electron microscopy (Fig. 1) it was possible to observe that lignin at 20 wt% coated the wood fibers, decreasing the volume of voids at the wood/polypropylene interface (Fig. 1f - marked by circle). In addition, only a few lignin particles were observed in the micrographs (as marked by arrows), showing a good dispersion of lignin in the whole matrix. These lignin particles could be considered as excess of material that tended to agglomerate as spheres.

Besides the assumed good interaction, some gaps and cavities still can be seen in the morphology of both fractured $P_{60}W_{40}$ and $P_{60}W_{20}L_{20}$ composites. These features are mostly associated to a physical phenomenon of shrink during composite polymerization. Lignin addition was not able to suppress cavity/gap formation; moreover, lignin was not expected to be total miscible with the polymer due the presence of polar functional groups which seem interact stronger with each other than with the matrix polymer [31]. Even though, from the microscopy analysis it was possible to infer that wood-polypropylene as well as wood-polypropylene-lignin mixtures presented a similar morphology with good interaction between matrix and biomasses.

Figure 1. Scanning microscopy of fractured composites $P_{60}W_{40}$ (a, b, c) and $P_{60}W_{20}L_{20}$ (d, e, f). The magnification of samples (a, d) x300 (b, e) x800 and (c, f) x4000.

3.2 Thermal behavior studies

TGA curves of the composites stated the onset temperatures increasing as lignin was added (Fig. 2a). It was previously showed that the incorporation of lignocellulosic materials leads to early thermal degradation of polypropylene [1]. However, the composites with higher content of lignin ($P_{60}W_{28}L_{12}$ and $P_{60}W_{20}L_{20}$) had temperatures at 10% mass loss shifted toward higher temperatures, reaching higher values than neat polymer (Table 3). These results indicate that lignin can be considered a barrier against thermal degradation [18], which rationale is based on its aromatic phenyl structures that are thermal stable due the overlapping of *p*-orbital [5].

Table 3. Temperatures at 5% mass loss ($T_{5\%}$), 10% mass loss ($T_{10\%}$) and residual mass at 600 °C of the studied materials

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Residual mass at 600 °C (%)
W	42	91	12
L	146	273	54
P	325	350	0
P ₆₀ W ₄₀	285	326	31
P ₆₀ W ₂₈ L ₄	290	332	24
P ₆₀ W ₂₈ L ₁₂	312	350	35
P ₆₀ W ₂₀ L ₂₀	321	362	41

Figure 2. Thermal gravimetric curves (a) and their first derivative (b) for the neat polypropylene, kraft lignin, wood flour and composites.

Three main peaks were observed in the dW/dt curves for all composites (Fig.2b). The first one at *ca.* 275 °C, was associated to the hemicellulose degradation [1, 2, 32]. The hemicellulose peak shoulder is more pronounced for the wood material than for pure lignin, and it can be tracked in the composites according to the amount of wood. The second peak at *ca.* 360 °C showed up slightly more intense than the hemicellulose peak among all composites and is attributed to cellulose [33]. These two peaks were not

observed in the composite P₆₀W₂₀L₂₀ in which the proportion of lignin reached 50% of biomass fraction. Here it seems that thermal degradation had been driving by lignin structure.

The third degradation peak (400-500 °C) showed the highest intensity for all composites and is associate to polypropylene degradation. The peak of thermal degradation for the neat polypropylene occurred at *ca.* 425 °C and this peak shifted toward higher temperatures (*ca.* 460 °C) influenced by incorporation of the biomasses, especially after incorporation of lignin. Lignin degrades in a broad temperature range; at around 235 °C occurs the degradation of lignin-carbohydrate complexes [34] and from *ca.* 300 °C, aliphatic side chains start to break down, up to cleavage of more stable carbon-carbon bonds, which arises at 370-400 °C [35]. Moreover, according to Magalhães et al. [1], the improvement of thermal stability can also be reached if there is good compatibility between biomass and polymer.

Figure 3. DSC thermograms of wood-polymer composites with different loads of lignin, (a) melting and (b) crystallization temperatures.

As can be seen in the DSC analysis the composites showed differences between the melting (Fig. 3a) and crystallization (Fig. 3b) temperatures. Table 4 summarizes these results. The glass transition temperature (T_g) of kraft lignin was observed to be at around 70 °C (Fig. 3a). The T_g is directly associated to the lignin molecular weight and to its chemical functionalities. Hardwood lignins usually present low T_g , which infers good mobility of the lignin molecules upon thermal stress [36]. The melting temperature (T_m) of lignin, in general, is reported to be near or higher of its T_g , making the determination of T_m analytically difficult to assess and often inaccurate.

T_m in the composites increased after addition of 12 and 20 wt% of lignin, stating that higher lignin amounts provided higher thermal stability for the obtained composites and according to Liu et al. [37] it can indicate a positive influence in inhibiting T_m of composites. In contrast, T_m of the polymer reduced in those composites with 0 and 4 wt% of lignin, suggesting that wood flour presence improved the mobility of polymer over thermal stress. These same composites had their crystallization temperature (T_c) shifted to higher temperatures when compared to neat polypropylene. The higher T_c was observed for P₆₀W₄₀ where there was higher amount of cellulose. Such shift has been reported in the literature [1, 2]. Indeed, the increment of lignocellulosic material acts as a nucleating agent [28] promoting an heterogeneous nucleation for the polypropylene. The higher number of nucleating agents toward crystallization promoted by lignocellulosic material can also be seen from crystallization index (X_c).

On the other hand, higher replacements of wood by lignin (P₆₀W₂₈L₁₂ and P₆₀W₂₀L₂₀) kept T_c temperatures similar to neat polypropylene which indicates that lignin could decrease the excessive nucleation sites, also confirmed from higher T_m observed for these composites.

Table 4. Thermal properties of the composites and neat polypropylene

Sample	T_c	T_m	ΔH_f (J/g)	X_c
P	116.26	166.13	94.71	49.85
P ₆₀ W ₄₀	126.96	164.7	62.47	54.8
P ₆₀ W ₃₆ L ₄	121.96	164.77	59.58	52.26
P ₆₀ W ₂₈ L ₁₂	115.65	167.04	55.19	48.41
P ₆₀ W ₂₀ L ₂₀	117.59	167.56	60.74	53.28

The heat of crystallization (ΔH_f) of all composites decreased compared to neat polypropylene, and all composites in the presence of lignin also had lower ΔH_f when compared to P₆₀W₄₀ (Table 4). The increment of lignin in up to 20 wt% seemed assisting cellulose to act as a diluent in the P matrix [28].

3.3 Water-composites relationships at bulk and surface level

Differences in thickness swelling (TS) and water absorption (WA) were observed among the composites. The TS (Fig. 4b) was lower after 4 wt% of lignin incorporation evaluated at 2 and 24 h. In general wood is more hygroscopic than lignin [5]; therefore, it would be expected that TS decreased as wood flour was replaced by lignin (Fig. 4a). Decreasing in WA as function of lignin addition was not as evident as in TS. At 24 h, the composites presented no statistical differences in WA. In the first 2 h underwater though, the WA of the composites containing higher amounts of lignin was decreased.

Figure 4. Water absorption and thickness swelling of the composites, after 2 and 24 h.

Average values followed by the same letter are not statistically different, according to the Tukey test at 95% of significance. The times (2 and 24 h) were evaluated separately and differ by upper and lowercase letters. WA at 2 h presented F ratio= 10.7; WA at 24 h presented F ratio= 0.63; TS at 2 h presented F ratio= 4.3; TS at 24 h presented F ratio= 4.7.

The water absorption and thickness swelling were very low, in the magnitude of 0.6% and 3%, respectively. These results could be considered desirable characteristics for building applications, since absorption of water would lead to biodegradation, dimensional instability and reduced performance at long-term [38].

Table 5. Kinetics of contact angle

Sample	Time (s)				
	5	20	35	50	65
Contact Angle (°)					
Neat P		86 ± 4			
P ₆₀ W ₄₀	98 ± 5	97 ± 8	98 ± 8	96 ± 6	98 ± 11
P ₆₀ W ₃₆ L ₄	100 ± 14	98 ± 11	98 ± 14	96 ± 11	96 ± 11
P ₆₀ W ₂₈ L ₁₂	87 ± 11	82 ± 13	82 ± 12	80 ± 10	79 ± 12
P ₆₀ W ₂₀ L ₂₀	96 ± 13	93 ± 14	93 ± 12	90 ± 10	92 ± 11
F ratio	1.06 ^{ns}	1.10 ^{ns}	1.47 ^{ns}	1.57 ^{ns}	1.57 ^{ns}

^{ns} not significant

It is already established that polypropylene presents low surface energy and homogeneous but rough surface. Furthermore, its resultant contact angle usually reported in the literature is around 90° [30, 39], which fits perfectly with the measured contact angle of neat P at 20s (86°) (Table 5). Although hydrophilic components were added to the composites, it was observed no significant change in their wettability, for both lignin content and time variables. The standard deviation of the contact angles measurements were high, what can be explained by the chemical non-uniformity and roughness of the composites surface [40]. Overall, it can be inferred that lignin addition in the composites provided not only thermal stability and water resistance but also maintenance of wettability behavior.

3.4 Mechanical properties

All mechanical properties of the composites presented statistical differences when compared to neat polypropylene (Table 6). In this context, modulus of elasticity (MOE) increased both with wood flour and lignin incorporation. According to Luo et al. [5] the presence of lignocellulosic material in polymeric matrixes tends to reduce the mobility of the polymer chains, causing increase in the MOE. Likewise, flexural strength and tensile strength of the composites were lower than neat polypropylene, as commonly reported [5, 41]. Similar tensile strength was observed for all composites, regardless the presence or not of lignin. On the other hand, flexural strength showed a linear decreasing after 4wt% of lignin incorporation. Based on the mechanical analysis it was possible to observe that with any addition of lignin the tensile strength kept unaltered, while a slightly decrease was observed for the other tested mechanical stresses. Even though, the mechanical behavior of the composites after incorporation of lignin was predictable

(linear tendency), thus making easier to project and design new building or materials components using these composites.

Table 6. Mechanical properties of P and composites

Sample	Modulus of elasticity (MPa) $\pm$ SD	Flexural Strength (MPa) $\pm$ SD	Tensile Strength (MPa) $\pm$ SD
P	1530 $\pm$ 85 <i>a</i>	69 $\pm$ 6 <i>f</i>	46 $\pm$ 3 <i>c</i>
P ₆₀ W ₄₀	2867 $\pm$ 207 <i>d</i>	44 $\pm$ 1 <i>de</i>	17 $\pm$ 3 <i>ab</i>
P ₆₀ W ₃₆ L ₄	2489 $\pm$ 54 <i>c</i>	42 $\pm$ 2 <i>cd</i>	19 $\pm$ 1 <i>b</i>
P ₆₀ W ₂₈ L ₁₂	2345 $\pm$ 88 <i>bc</i>	38 $\pm$ 2 <i>bc</i>	16 $\pm$ 1 <i>ab</i>
P ₆₀ W ₂₀ L ₂₀	2140 $\pm$ 84 <i>b</i>	30 $\pm$ 2 <i>a</i>	14 $\pm$ 1 <i>a</i>
F ratio	72.1 *	181.0 *	171.6 *

*Average values followed by the same letter are not statistically different, according to the Tukey test at 95% of significance

4. Conclusion

Flat pressed wood/polypropylene composites were successfully prepared with the incorporation of different lignin fractions. Thermal behavior and other important properties of the composites without and with addition of unmodified, low-cost kraft lignin were investigated.

The parameter related to saturation of color (C^*) decreased from 7.5 to 1.5 with lignin addition. The relationship between C^* and L^* and C^* and hue angle (h^*), indicated a darkening tendency in the composites as a function of lignin increment. The composites with and without lignin showed a very similar morphology with good interaction between matrix and biomasses.

Overall, water resistance of composites after 2 and 24 h of submersion, increased with lignin incorporation. Furthermore, all composites containing lignin had temperatures at 5

and 10% mass loss shifted toward higher temperatures compared to wood/polypropylene. MOE of wood/polypropylene decreased from 2867 to 2140 MPa with 20 wt% of lignin increment. Flexural strength of wood/propylene composite was preserved (42 MPa) at 4 wt% of lignin addition and tensile strength was kept unaltered in all ratios of lignin/wood (14-19 MPa).

Acknowledgments

The authors would like to thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (National Counsel of Technological and Scientific Development) for supporting this work.

5. References

1. Magalhães, W.L.E., Pianaro, S.A., Granado, C.J.F., Satyanarayana, K.G.: Preparation and characterization of polypropylene/heart-of-peach palm sheath composite. *J. Appl. Polym. Sci.* 127, 1285–1294 (2013). doi:10.1002/app.37633
2. Mattos, B.D., Misso, A.L., De Cademartori, P.H.G., De Lima, E.A., Magalhães, W.L.E., Gatto, D.A.: Properties of polypropylene composites filled with a mixture of household waste of mate-tea and wood particles. *Constr. Build. Mater.* 61, 60–68 (2014). doi:10.1016/j.conbuildmat.2014.02.022
3. Jakab, E., Várhegyi, G., Faix, O.: Thermal decomposition of polypropylene in the presence of wood-derived materials. *J. Anal. Appl. Pyrolysis.* 56, 273–285 (2000). doi:10.1016/S0165-2370(00)00101-7
4. Bao, F.C., Jiang, Z.H., Jiang, X.M., Lu, X.X., Luo, X.Q., Zhang, S.Y.: Differences in wood properties between juvenile wood and mature wood in 10 species grown in China. *Wood Sci. Technol.* 35, 363–375 (2001). doi:10.1007/s002260100099
5. Luo, S., Cao, J., Sun, W.: Evaluation of Kraft lignin as natural compatibilizer in wood flour/polypropylene composites. *Polym. Compos.* n/a-n/a (2015). doi:10.1002/pc.23821
6. De Chirico, A., Armanini, M., Chini, P., Cioccolo, G., Provasoli, F., Audisio, G.: Flame retardants for polypropylene based on lignin. *Polym. Degrad. Stab.* 79, 139–145 (2003). doi:10.1016/S0141-3910(02)00266-5
7. Faruk, O., Bledzki, A.K., Fink, H.-P., Sain, M.: Progress Report on Natural Fiber Reinforced Composites. *Macromol. Mater. Eng.* 299, 9–26 (2014). doi:10.1002/mame.201300008
8. García, M., Hidalgo, J., Garmendia, I.: Composites : Part A Wood – plastics

composites with better fire retardancy and durability performance. *Compos. Part A*. 40, 1772–1776 (2009). doi:10.1016/j.compositesa.2009.08.010

9. Stark, N.M., White, R.H., Mueller, S.A., Osswald, T.A.: Evaluation of various fire retardants for use in wood flour/polyethylene composites. *Polym. Degrad. Stab.* 95, 1903–1910 (2010).

doi:10.1016/j.polymdegradstab.2010.04.014

10. Deka, B.K., Maji, T.K.: Effect of Silica Nanopowder on the Properties of Wood Flour / Polymer Composite. *Polym. Eng. Sci.* (2012). doi:10.1002/pen

11. Deka, B.K., Maji, T.K.: Effect of SiO₂ and nanoclay on the properties of wood polymer nanocomposite. *Polym. Bull.* 403–417 (2013). doi:10.1007/s00289-012-0799-6

12. Toldy, A., Niedermann, P., Rapi, Z., Szolnoki, B.: Flame retardancy of glucofuranoside based bioepoxy and carbon fibre reinforced composites made thereof. *Polym. Degrad. Stab.* 142, 62–68 (2017).

doi:10.1016/j.polymdegradstab.2017.05.024

13. Chakar, F.S., Ragauskas, A.J.: Review of current and future softwood kraft lignin process chemistry. *Ind. Crops Prod.* 20, 131–141 (2004).

doi:10.1016/j.indcrop.2004.04.016

14. Shu-lai, W.: Formation of Charcoal from Biomass in a Sealed Reactor. *Ind. Eng. Chem. Res.* 1162–1166 (1992)

15. Antal, M.J.: The Art, Science, and Technology of Charcoal Production †. *Ind. Eng. Chem. Res.* 1619–1640 (2003)

16. Nyman, V., Rose, G., Ralston, J.: The colloidal behaviour of kraft lignin and lignosulfonates. *Colloids and Surfaces.* 21, 125–147 (1986). doi:10.1016/0166-6622(86)80087-7

- 407 17. Ago, M., Huan, S., Borghei, M., Raula, J., Kauppinen, E.I., Rojas, O.J.: High-
 408 Throughput Synthesis of Lignin Particles (~ 30 nm to ~ 2 μ m) via Aerosol Flow
 409 Reactor: Size Fractionation and Utilization in Pickering Emulsions. *ACS Appl.*
 410 *Mater. Interfaces*. 8, 23302–23310 (2016). doi:10.1021/acsami.6b07900
- 411 18. Lee, H.J., Lee, H.K., Lim, E., Song, Y.S.: Synergistic effect of
 412 lignin/polypropylene as a compatibilizer in multiphase eco-composites. *Compos.*
 413 *Sci. Technol.* 118, 193–197 (2015). doi:10.1016/j.compscitech.2015.08.018
- 414 19. Toriz, G., Denes, F., Young, R.A.: Lignin-polypropylene composites. Part 1:
 415 Composites from unmodified lignin and polypropylene. *Polym. Compos.* 23,
 416 806–813 (2002). doi:10.1002/pc.10478
- 417 20. Ye, D., Li, S., Lu, X., Zhang, X., Rojas, O.J.: Antioxidant and Thermal
 418 Stabilization of Polypropylene by Addition of Butylated Lignin at Low Loadings.
 419 *ACS Sustain. Chem. Eng.* (2016). doi:10.1021/acssuschemeng.6b01241
- 420 21. Sailaja, R.R.N., Deepthi, M. V: Mechanical and thermal properties of
 421 compatibilized composites of polyethylene and esterified lignin. *Mater. Des.* 31,
 422 4369–4379 (2010). doi:10.1016/j.matdes.2010.03.046
- 423 22. Laurichesse, S., Avérous, L.: Chemical modification of lignins: Towards
 424 biobased polymers. *Prog. Polym. Sci.* 39, 1266–1290 (2014).
 425 doi:10.1016/j.progpolymsci.2013.11.004
- 426 23. Schorr, D., Diouf, P.N., Stevanovic, T.: Evaluation of industrial lignins for
 427 biocomposites production. *Ind. Crops Prod.* 52, 65–73 (2014)
- 428 24. Irmer, J.: Lignin – a natural resource with huge potential,
 429 [https://www.biooekonomie-bw.de/en/articles/dossiers/lignin-a-natural-resource-](https://www.biooekonomie-bw.de/en/articles/dossiers/lignin-a-natural-resource-with-huge-potential/)
 430 [with-huge-potential/](https://www.biooekonomie-bw.de/en/articles/dossiers/lignin-a-natural-resource-with-huge-potential/), (2017). Accessed 10 July 2018
- 431 25. Missio, A.L., Mattos, B.D., de Cademartori, P.H., Berger, C., Magalhães, W.L.,

- 432 Haselein, C.R., Gatto, D.A., Petutschnigg, A., Tondi, G.: Impact of Tannin as
 433 Sustainable Compatibilizer for Wood-Polypropylene Composites. *Polym.*
 434 *Compos.* online version (2017). doi:<https://doi.org/10.1002/pc.24498>
- 435 26. Carus, M., Eder, A., Dammer, L., Korte, H., Scholz, L., Essel, R., Breitmayer, E.,
 436 Barth, M.: Wood-Plastic Composites (WPC) and Natural Fibre Composites (
 437 NFC): European and Global Markets 2012 and Future Trends in Automotive and
 438 Construction. *Plast. Addit. Compd.* 4, 18–21 (2015)
- 439 27. Minolta, K.: Precise color communication: color control from perception to
 440 instrumentation. (2007)
- 441 28. Amash, A., Zugenmaier, P.: Morphology and properties of isotropic and oriented
 442 samples of cellulose fibre–polypropylene composites. *Polymer (Guildf)*. 41,
 443 1589–1596 (2000). doi:10.1016/S0032-3861(99)00273-6
- 444 29. Beg, M.D.H., Pickering, K.L.: Reprocessing of wood fibre reinforced
 445 polypropylene composites. Part I: Effects on physical and mechanical properties.
 446 *Compos. Part A Appl. Sci. Manuf.* 39, 1091–1100 (2008).
 447 doi:10.1016/J.COMPOSITESA.2008.04.013
- 448 30. Cademartori, P.H.G. de, Claro, F.C., Marinho, N.P., Zanoni, P.R.S., Magalhães,
 449 W.L.E.: Co-production of thermoplastic composites with solid residue from
 450 enzymatic hydrolysis of recycled paper sludge. *J. Clean. Prod.* 162, 27–33
 451 (2017). doi:10.1016/J.JCLEPRO.2017.06.009
- 452 31. Kun, D., Pukánszky, B.: Polymer/lignin blends: Interactions, properties,
 453 applications. *Eur. Polym. J.* 93, 618–641 (2017).
 454 doi:10.1016/j.eurpolymj.2017.04.035
- 455 32. Saheb, D.N., Jog, J.P., others: Natural fiber polymer composites: a review. *Adv.*
 456 *Polym. Technol.* 18, 351–363 (1999)

- 457 33. Norgren, M., Edlund, H., Wågberg, L.: Aggregation of lignin derivatives under
 458 alkaline conditions. Kinetics and aggregate structure. *Langmuir*. 18, 2859–2865
 459 (2002). doi:10.1021/la011627d
- 460 34. Toledano, A., Serrano, L., Garcia, A., Mondragon, I., Labidi, J.: Comparative
 461 study of lignin fractionation by ultrafiltration and selective precipitation. *Chem.*
 462 *Eng. J.* 157, 93–99 (2010). doi:10.1016/j.cej.2009.10.056
- 463 35. Nassar, M., MacKay, G.: Mechanism of thermal decomposition of lignin. *Wood*
 464 *Fiber Sci.* 16, 441–453 (1984)
- 465 36. Doherty, W.O.S., Mousavioun, P., Fellows, C.M.: Value-adding to cellulosic
 466 ethanol: Lignin polymers. *Ind. Crops Prod.* 33, 259–276 (2011).
 467 doi:10.1016/j.indcrop.2010.10.022
- 468 37. Liu, R., Peng, Y., Cao, J., Chen, Y.: Comparison on properties of lignocellulosic
 469 flour/polymer composites by using wood, cellulose, and lignin flours as fillers.
 470 *Compos. Sci. Technol.* 103, 1–7 (2014). doi:10.1016/j.compscitech.2014.08.005
- 471 38. Bajwa, S.G., Bajwa, D.S., Holt, G., Coffelt, T., Nakayama, F.: Properties of
 472 thermoplastic composites with cotton and guayule biomass residues as fiber
 473 fillers. *Ind. Crops Prod.* 33, 747–755 (2011).
 474 doi:10.1016/J.INDCROP.2011.01.017
- 475 39. Long, J., Chen, P.: Surface characterization of hydrosilylated polypropylene:
 476 Contact angle measurement and atomic force microscopy. *Langmuir*. 17, 2965–
 477 2972 (2001). doi:10.1021/la001547u
- 478 40. Wenzel, R.N.: Resistance of solid surfaces to wetting by water. *Ind. Eng. Chem.*
 479 28, (1936)
- 480 41. Zhong, M., Dai, H., Yao, H., Dai, D.: Strong , flexible high-lignin polypropylene
 481 blends. *Soc. Plast. Eng.* 12, 2–4 (2011)