Composites Based on Renewable Materials: Polyurethane-Type Matrices from Forest Byproduct/Vegetable Oil and Reinforced with Lignocellulosic Fibers

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ABSTRACT: The use of products and byproducts from the agro-industry and forest biorefinery is essential for the development of value-added and low environmental-impact materials. In this study, polyurethanes were prepared using sodium lignosulfonate (NaLS) and castor oil (CO) as reagents and were used to prepare composites reinforced with lignocellulosic fibers, namely, curaua and coir fibers (30 wt %, 3 cm length, and randomly oriented). The SEM images of fractured surfaces of the composites revealed excellent adhesion at the fiber/matrix interface of both coir and curaua composites, which probably resulted from the favorable interactions between polar groups, as well as amid low polarity domains that are present in both the matrix and the reinforcements. The composites exhibited different impact/flexural and strength/flexural moduli (NaLS/CO/Curaua = 465 Jm^{-1}/44 MPa/2 GPa; NaLS/CO/Coir = 180 Jm^{-1}/25 MPa/1 GPa). The higher tensile strength/aspect ratio of the curaua fibers (485 MPa/259) compared with that of the coir fibers (120 MPa/130) most likely contributes to the enhanced performance of its composite. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2224–2233, 2013
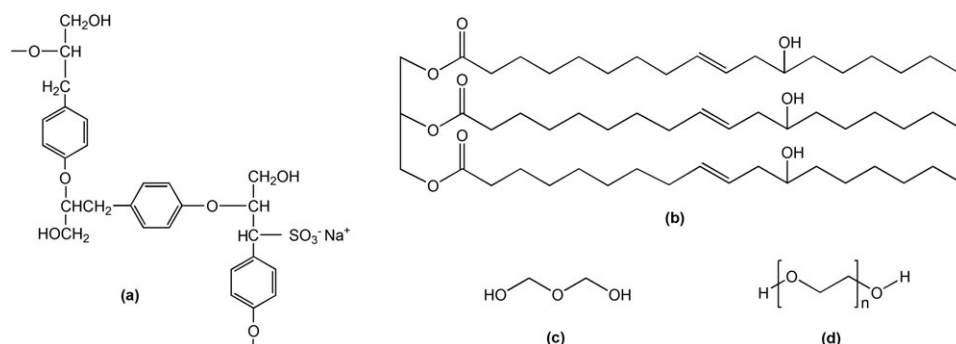
INTRODUCTION

In recent years, many efforts have focused on the development of lignin-based polymeric materials to find new alternatives to the petrochemicals products and their derivatives.[1] The use of renewable raw material (biomass) to produce chemical substances, materials and energy is an interesting topic, both in basic and applied research. Currently, the use of lignin is even more important because lignin is a by-product of biorefineries that produce ethanol from cellulose found in wood and lignocellulosic fibers.[2–4]

Lignosulfonate (NaLS) is an important lignin derivative that is obtained as a by-product of the sulfite pulping process of wood that generates cellulosic pulp. Lignin and lignosulfonate were already used as a substitute for phenol in the production of phenolic resins due to the presence of phenolic functionalities in their structures [Figure 1(a)]. This substitution reduces the demand for fossil resources and provides a safer alternative to phenol, which is a toxic petrochemical.[5] In previous studies, an organosolv lignin obtained from sugarcane bagasse was used to prepare formaldehyde-phenolic-type resins. Paiva et al.[6] and Tita et al.[7] prepared lignophenolic resins (lignin–phenol–

formaldehyde) that were used to develop composites reinforced with sugarcane bagasse. Similarly, Paiva et al.[8] prepared composites reinforced with sisal fiber using lignophenolic resin (lignin–phenol–formaldehyde) as the matrix. Ramires et al.[2] used sugarcane lignin to prepare phenolic-type resins (lignin–formaldehyde), which were also used as the matrix in the preparation of composites reinforced with sisal fibers. In addition, Silva et al.[9] prepared glutaraldehyde–lignosulfonate resins, which were used to prepare composites reinforced with sisal fibers. All of the studies demonstrated an improvement in the mechanical properties of the prepared composites compared with those of the traditional phenol–formaldehyde composites.

Lignins and lignosulfonates can also be used as polyols in the production of polyurethane (PU) due to the presence of hydroxyl groups in their structures [Figure 1(a)]. This potential was explored in this study.

PUs are a large class of polymers that have only one thing in common: the presence of the urethane group in the main chain.[10] The urethane group is formed due to the reaction between an isocyanate group (—N=C=O) and polyols. PUs are industrially important due to the variety of groups that can be

Figure 1. Structural representation of (a) Sodium lignosulfonate (NaLS); (b) ricinoleic acid, the main component of castor oil (CO); (c) diethylene glycol (DEG); and (d) polyethylene glycol (PEG).

introduced between the urethane bonds, resulting in different products, such as elastomers, plastics, adhesives, and foams that are used in the medical, automotive, construction, and industrial fields.[11,12]

Several studies regarding the use of lignins and lignosulfonates as polyols in the preparation of PUs have been reported in the literature. Evtuguin et al.[13] prepared crosslinked elastomeric PUs using oxygen–organosolv lignins isolated from spent liquors after the delignification of wood in different acidic organic solvent–water mixtures. Asano et al.[14] prepared rigid PU using sodium lignosulfonate (NaLS) and observed that with increasing NaLS content, the glass transition temperature (T_g) of PU increased whereas the degradation temperature decreased. Hatakeyama et al.[15] prepared semirigid PU foams using lignin (kraft and lignosulfonate), molasses, PEG polyols and observed that the apparent density of PU foams increased with increasing lignin content. Bonini et al.[16] used lignin obtained by steam explosion from straw to prepare PU, which demonstrated the potential to be used in coatings and in the formulation of wood adhesives. Nevertheless, to our knowledge, PUs based on lignin and/or lignosulfonates have not been used as the matrix in the composites, particularly in natural fiber-reinforced composites, such as in lignocellulosic fibers composites.

The large-scale use of composites reinforced with lignocellulosic fibers can contribute to sustainable economic development by reducing the cost relative to composites reinforced with synthetic fibers,[17] in addition to increasing the environmental sustainability.[18] Lignocellulosic fibers can be obtained from agricultural by-products, and are biodegradable, lightweight (low density), abundant, low cost, and are not dangerous to health. In addition, their application can provide a solution to the accumulation of these materials in the environment because new applications are found for the surplus raw material.[19–22] Natural fibers also have high electrical resistance and hollow cell structure that provides good sound-insulating properties. Moreover, the availability of these fibers nearly anywhere in the world is an additional advantage.[23–25]

Different types of fibers have been used as reinforcement materials in composites, such as jute and bamboo,[26] sugarcane bagasse,[6] sisal,[27] and banana,[28] as well as others. Curaua fibers are obtained from the curaua plant (*Ananas erictifolius*), which is cultivated in the Amazon region of Brazil.[29,30] Curaua fibers have been used as reinforcement in composites: Trindade et al.[29] prepared thermoset phenolic composites reinforced with curaua fibers unmodified and chemically modified by oxidation with chlorine dioxide followed by grafting with furfuryl alcohol. The modification improved the fiber/matrix interactions at the interface of the composites but also caused some fiber degradation that affected the mechanical properties and resulted in a decreased in the mechanical resistance of the composites. Trindade et al.[31] also prepared phenolic composites reinforced with curaua fibers treated with ionized air. The results showed that up to 7 h of treatment of the fibers, the composites exhibited increased impact strength and decreased water absorption capacity. Castro et al.[32] prepared composites of high-density biopolyethylene matrix reinforced with curaua fibers. The author also used hydroxyl-terminated polybutadiene (LHPB) as the compatibilizer. The results showed that the presence of curaua fibers enhanced the flexural strength and storage modulus of the composites; in addition, the use of LHPB improved the adhesion of the fiber/matrix at the interface, increasing the impact strength of the composites. Currently, the main application of curaua is in the automotive industry as reinforcement in polymer matrices as substitute for glass fiber.[33] The use of natural fibers in the automotive industry reduces the weight of vehicle, and thus provides improved fuel economy.[34,35]

Coir fibers are obtained from the husk (mesocarp) of the coconut, the fruit of the coconut palm (*Cocus nucifera*).[36,37] These fibers are characterized by hardness and durability, which is attributed to the higher lignin content than other natural fibers.[38,39] The processing of coconut, green, or ripe generates a significant amount of waste. The husks of ripe coconuts are often used as boiler fuel or processed to manufacture ropes, rugs, mats, and many other products. The development of alternative use of coconut husk allows for the reduction of solid waste disposal in landfills and provides a new income source for the production sites.[40] Coconut fibers have been used as reinforcement in composites.[41,42] Barbosa et al.[43] prepared composites using tannin-phenolic (tannin–phenol–formaldehyde) matrix reinforced with coir fibers. The authors observed that the use of coir fibers increased the impact strength and storage modulus of the composites; in addition, the composites demonstrated significant adhesion at the fiber/matrix interface. Coir fibers have also been used in interior automotive parts.[44]

In this study, bio-based composites were prepared predominantly from renewable sources, i.e., the PU matrix was based on NaLS and reinforced with curaua and coir lignocellulosic fibers. In addition, castor oil (CO), a vegetable oil obtained from the seed of the castor bean, contains ricinoleic acid [Figure 1(b)] as its main component and has been extensively used in the preparation of PU.[45–48]

METHODS

Materials

Coir fibers (supplied by POEMATEC, Sustainable Technology for the Amazon, Ananindeua, Para, Brazil) and curaua fiber (supplied by PEMATEC Triangel, São Bernardo do Campo, São Paulo, Brazil) were Soxhlet extracted with cyclohexane/ethanol (1 : 1, v/v) for 50 h to remove extractives such as waxes, terpenes, and fatty acids. Next, they were washed with distilled water to remove salts and low molecular weight sugars, and then dried in an air-circulated oven at 105°C until a constant weight was obtained.

NaLS [Figure 1(a)] Vixilex SD type was supplied by Lignin Products LignoTech Brazil (Cambará do Sul, Rio Grande do Sul, Brazil). This by-product is obtained from the sulfite pulping process of *Pinus taeda* wood. SL [$M_w \sim 6000$ g mol^{-1}, 5.5% of sulfur, 1.7% of magnesium, 0.2% of calcium, 0.9% of sugars, according to the supplier] was used to prepare lignopolyurethane matrices. The average molar mass of the C9 unit of NaLS was 220.89 g mol^{-1},[49] and the content of phenolic and alcoholic hydroxyl groups was 0.7 mol per C9 unit.[50]

The diphenylmethane diisocyanate (MDI) was supplied by BASF PUs (Mauá, Sao Paulo, Brazil). Diethylene glycol [DEG, Figure 1(c)] and polyethylene glycol (PEG, $M_n = 300$ g mol^{-1}, Figure 1(d)], were purchased from Synth. CO (hydroxyl index of 155 mg KOH g^{-1} and $M_n \cong 980$ g mol^{-1}), whose main component is ricinoleic acid [Figure 1(b)], was purchased from Azevedo Indústria e Comércio de Óleos (Itupeva, Sao Paulo, Brazil).

Lignopolyurethane Synthesis and Composites Preparation

In the synthesis of lignopolyurethane, the NCO/OH ratio was 1 and 30% of the OH groups were derived from NaLS and 70% were derived from DEG, PEG, or CO. This calculation was performed using the average molar mass and functionality of each polyol.

Curaua or coir fibers (30 wt %, 3 cm in length and randomly oriented in the composites) and NaLS were previously dried in an air-circulated stove at 105°C for 4 h. Subsequently, these materials, DEG and MDI were weighed and placed in the fridge for 20 min. Approximately half of the NaLS was mixed with MDI and the other half was mixed with the second polyol. The fibers were slowly impregnated into the NaLS/MDI mixture and then into NaLS/(DEG, PEG, or CO). Finally, to improve the impregnation of the fibers in the mixture, the assembly (fibers/mixture) was subjected to mechanical stirring for 10 min (20 rpm) using a JVJ mixer (Pardinho, Sao Paulo, Brazil), which consisted of a mixing chamber with a rotating steel drum and steel forks. Compression molding was performed in molds (300 × 140 × 5 mm) under pressure using the following cure cycle: 60°C/60 min/10 ton; 85°C/60 min/14 ton; 120°C/60 min/16 ton; 150°C/60 min/16 ton.

Lignopolyurethane Without Reinforcement of Fibers

Isocyanate and polyols were mixed in the absence of fibers, and the same cure cycle was used as for the composites.

Characterization

Curaua and Coir Fibers. The moisture content was determined according to ABNT NBR9656 (Brazilian Technical Standards Association) by calculating the percentage difference between the initial sample weight and the weight observed after 4 h of drying at 105°C.

The ash content was determined by calculating the difference in the weight of the dried fiber samples (free of moisture) and the sample obtained after calcination for 4 h at 800°C.

Klason lignin content was determined by the isolation of lignin after the hydrolysis of polysaccharides (cellulose and hemicellulose) with concentrated sulfuric acid (72%).

Holocellulose (hemicellulose + cellulose) content was determined according to the TAPPI T19m-54 by the selective sodium hypochlorite degradation of lignin at 70°C. The cellulose content was determined by selective sodium hydroxide degradation of the hemicellulose at room temperature. The hemicellulose content was obtained by calculating the difference between the holocellulose and cellulose contents.

For all the previously mentioned analyses (with the exception of moisture content), the samples were previously dried for 4 h in an air-circulated oven at 105°C to remove moisture. A minimum of three samples were tested.

The crystallinity index, I_c, was determined by X-ray diffraction using the RIGAKU Rotaflex model Ru-200B diffractometer operating at 40 kV, 20 mA, and λ (Cu Kα) = 1.5406 Å. The crystallinity index was calculated using the Buschle–Diller and Zeronian equation: $I_c = (1 - I_1/I_2) \times 100$, where I_1 is the intensity at the minimum of the crystalline peak ($18° < 2\theta < 19°$) and I_2 is the intensity at its maximum ($22° < 2\theta < 23°$).

Lignopolyurethanes and Composites. Izod impact strength was assessed according to ASTM D256 using an Izod impact CEAST Resil 25 equipment. The impact tests were carried out at room temperature with an impact speed of 4 m s^{-1} and incident energy of 5.5 J, using 20 un-notched samples with the following dimensions: 63.5 mm length × 12.7 mm width × 4.5 mm thickness.

Flexural strength test was performed according to ASTM D 790, using an INSTRON universal machine, model 5569. As determined by the standard, the L/d ratio was 16 and with the following dimensions: 127 mm length × 12.7 mm width × 3.2 mm thickness.

SEM images were obtained using a Zeiss-Leica apparatus, model 440, with an electron acceleration of 20 kV. Fractured samples were covered with a thin layer of gold using a sputter-coating system before analysis.

Thermogravimetric analysis (TGA) was carried out using a Shimadzu instrument, model TGA-50. The samples (8–10 mg) were placed in platinum pans and heated from 25 to 800°C at 10°C min^{-1}, under an atmosphere of synthetic air with a flow rate of 20 mL min^{-1}.
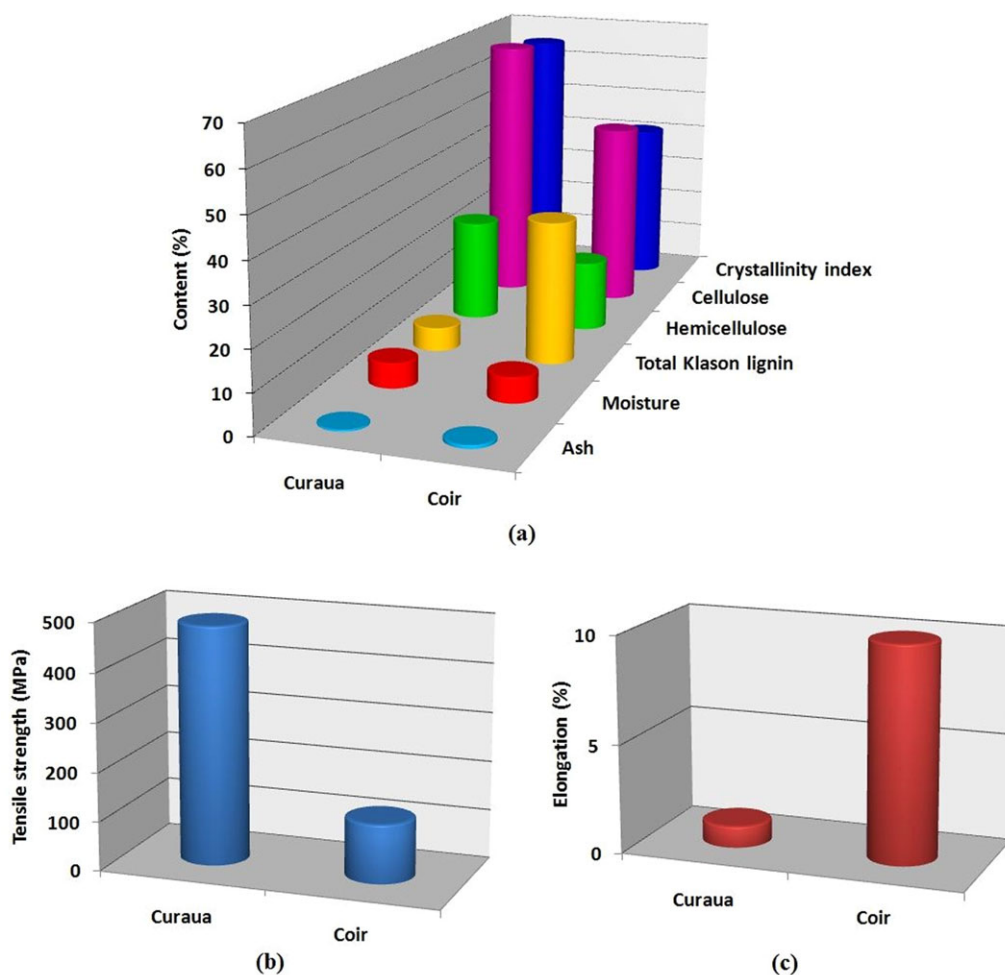
Figure 2. Composition and properties of curaua and coir fibers. Standard deviation following the order curaua and coir fibers: ±42 and ±8 MPa for tensile strength, ±0.1 and ±1.2% for elongation, ±0.1 and 0.1% for ash, ±0.2 and ±0.2% for moisture, ±0.3 and ±0.5% for total Klason lignin, ±0.4 and ±0.3% for hemicellulose, ±1.0 and ±0.5% for cellulose.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Characterization of Curaua and Coir Fibers

Natural fibers have some nonuniformity in the properties because plant age, origin, climatic factors, extraction, and purification processes can influence the structure of the fiber and its chemical composition.[51,52] Figure 2 provides the average results for the characterization of curaua and coir lignocellulosic fibers, which were used as reinforcement agents in the composites.

The values for the cellulose, hemicellulose, and lignin content obtained for curaua and coir fibers in this study are in agreement with literature values. Correa et al.[53] characterized curaua fibers and obtained values of 70.2% of cellulose, 18.3% of hemicellulose, and 9.3% of lignin, whereas Trindade et al.[29] observed values of 73.6% of cellulose, 9.9% of hemicellulose, and 7.5% of lignin. Malkapuram et al.[54] characterized coir fibers and found values of 36–43% of cellulose, 41–45% of lignin, and 10–20% of hemicellulose. These fibers have a low ash content, which corresponds to the inorganic components (calcium, sodium, potassium, and silica) that are attached to the fibers in the form of salts.[55]

The coir fiber exhibited a low crystallinity index [41%, Figure 2(a)], mainly due to the presence of 35.7% of lignin and 20.4% of hemicellulose [Figure 2(a)] in the noncrystalline regions of this fiber. Curaua fiber exhibited a higher crystallinity index [65%, Figure 2(a)] due to the higher cellulose content [67.7%, Figure 2(a)] in the crystalline regions of the curaua fiber. Trindade et al.[29] obtained a value of 67% for the crystallinity index of the curaua fibers, and Barbosa et al.[43] obtained a value of 44% for the crystallinity index of the coir fibers, which are very similar to the values obtained for the fibers used in this study. The higher crystallinity (65%) and cellulose content (67.7%) of the curaua fiber are responsible for its higher tensile strength [485 MPa, Figure 2(b)] compared to that of the coir fibers [120 MPa, Figure 2(b)]. The coir fiber exhibited a 10-fold increase in elongation at break in tension, in comparison with the curaua fibers. The lower crystallinity of the coir may contribute to this result, as the coir contained spiraled microfibrils that have a greater possibility of promoting rearrangements and elongation toward the noncrystalline regions before fracture.[17]
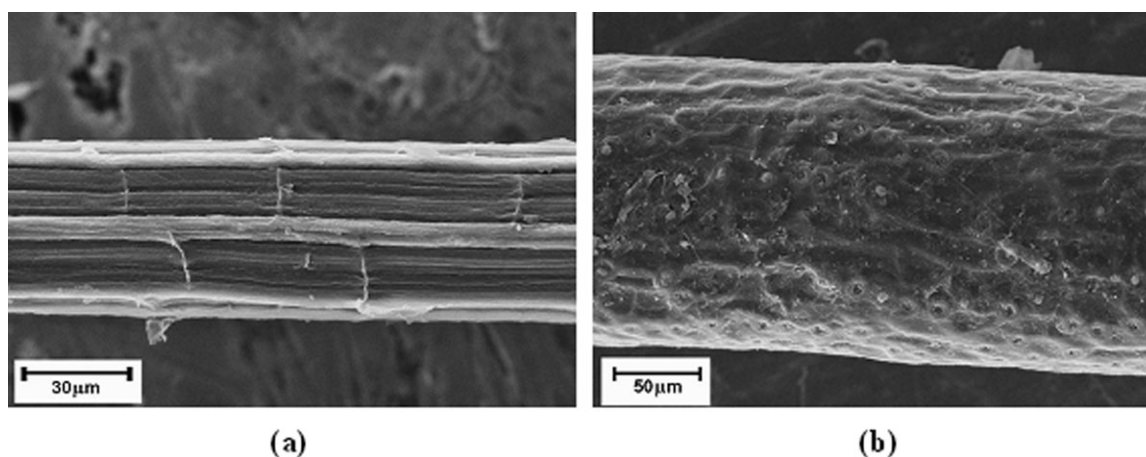
Figure 3. SEM images of curaua (a) and coir (b) fibers.

Figure 3 provides the SEM images of the curaua and coir fibers. The curaua fiber is composed of linked bundles of microfibrils and contains some fragments on the surface of the fiber, most likely due to the parenchyma cell residues. The average diameter of the curaua fibers is 116 ± 24 μm (determined using digital image analysis, ImageJ). The coir fiber has a rough surface with salience and re-entrance in circular shapes. The average diameter of the coir fibers is 230 ± 51 μm (also determined using ImageJ).

Characterization of the Lignopolyurethane Composites
Thermogravimetry provides information about the thermal stability of the materials, which is a very important property that defines the application range of the material. Figure 4 shows the dTG curves of the curaua and coir fibers and lignopolyurethane composites reinforced with curaua. Lignopolyurethane composites reinforced with coir fiber demonstrated behavior similar to that of curaua fiber reinforced composites, so the dTG curves of this material are not shown. Up to 100°C, the mass loss of the curaua and coir fiber samples (4.8 and 2.9%, respectively) (figure not shown) is related to the loss of water relative to the

moisture absorbed (or adsorbed) to the fibers. This event is related to the peak with a maximum at ~ 60°C in the dTG curves [Figure 4(a)]. Although the samples were previously dried in an air-circulated oven, the complete elimination of water is not possible due to the hydrophilic character of the fibers, which have water molecules bound to their structure. Water molecules were mainly bound to the hemicellulose groups in the noncrystalline regions of the fibers. Curaua and coir fibers exhibited excellent thermal stability until 250°C because mass loss was only related to the water evaporation (moisture) and not fiber decomposition.

Above 300°C, the fiber samples exhibited a significant mass loss due to the thermal decomposition of cellulose.[56,57] This event was responsible for an intense peak with maximum at ~ 330–345°C in the dTG curves [Figure 4(a)]. The shoulder observed at a lower temperature (300–310°C) is attributed to the decomposition of hemicellulose. The maximum decomposition temperature of cellulose in coir fibers was observed at a lower temperature (330°C) than that of curaua fibers (345°C). This is likely because the cellulose chains were mainly in noncrystalline
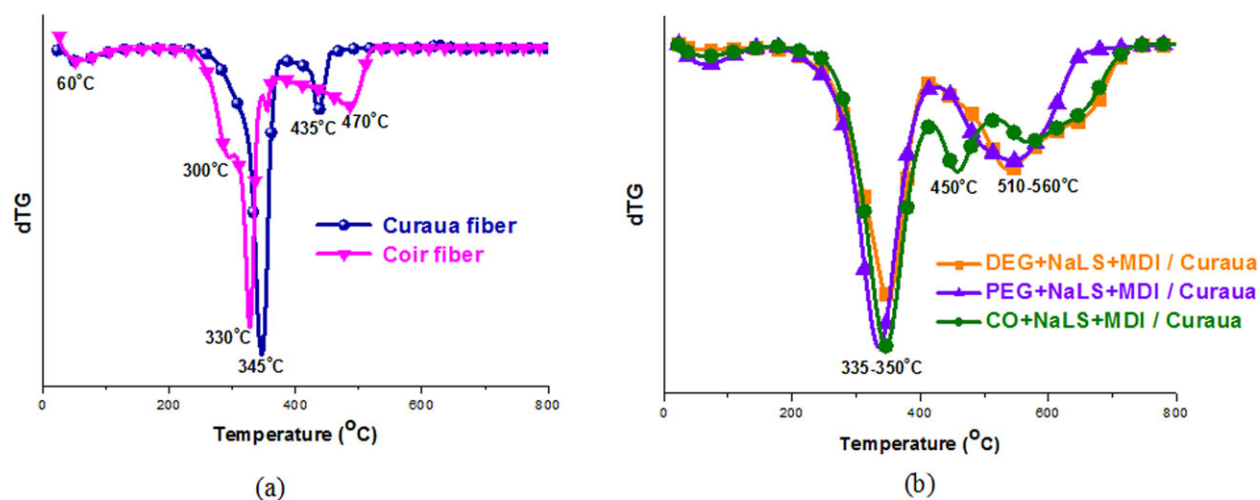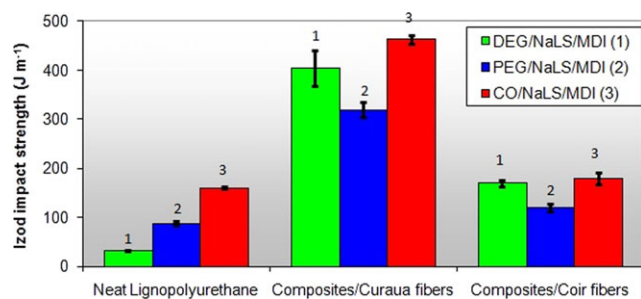

Figure 4. dTG curves of curaua and coir fibers (a); lignopolyurethane composites reinforced with curaua fibers (b), in an atmosphere of synthetic air (20 mL min^{-1}) and a heating rate of 10°C min^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

Figure 5. Izod impact strength and standard deviation of the lignopolyurethane composites (DEG/NaLS/MDI, PEG/NaLS/MDI, and CO/NaLS/MDI) in the presence and absence of curaua and coir fibers (30% w/w, 3 cm length, and randomly oriented) (un-notched samples). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

domains in the coir fibers, where the intermolecular interactions are weaker in comparison with the crystalline domains, which may shift the maximum decomposition temperature to a lower value. In general, the thermolysis reactions of polysaccharides (cellulose and hemicellulose) occur by the cleavage of glycosidic bonds, C—H, C—O, C—C bonds, as well as by dehydration, decarboxylation, and decarbonylation.[58] At $\sim$ 435°C (curaua) and 470°C (coir), another peak was observed [Figure 4(a)] due to the decomposition of aromatic rings and the rupture of the C—C bonds present in lignin, and the release of water and CO_2, followed by structural rearrangements.[59,60]

The peaks with a maximum intensity between 320 and 345°C in the dTG curves of the composites reinforced with curaua [Figure 4(b)] and coir fibers (figure not shown) were related to the mass loss associated with the break-up of urethane bonds, i.e., the degradation of the hard segments in the PU matrix.[14,61] In addition, the moieties typical of NaLS present in the matrix began to decompose at this temperature, and the cellulose present in the fibers used as reinforcement also decomposes. The decomposition of the lignosulfonate occurs with the release of H_2O, CO_2, and SO_2. Some mercaptans can also be formed.[62]

Above 450°C, a new stage of mass loss took place with a maximum intensity peak at 510–560°C in dTG curves [Figure 4(b)], which corresponds to the decomposition of the soft segments of the PU matrix.[63] In lignopolyurethane composites with the CO/NaLS/MDI matrix, the peak degradation of the soft segments in PU was divided into two, with a maximum at a lower temperature of 450°C [Figure 4(b)]. This was most likely due to the higher structural complexity of the ricinoleic acid, the main component of CO, in comparison with DEG and PEG [Figure 1(b–d), respectively], generating soft segments that decomposed at a lower temperature.

Figure 5 provides the results of the Izod impact test. In neat lignopolyurethanes (nonreinforced), the Izod impact strength increased with increasing chain length of the polyol used: the lignopolyurethane prepared from CO [Figure 1(b)] exhibited higher impact strength than that of PEG [Figure 1(d)], which had higher impact strength than that of DEG [Figure 1(c)]. The use of polyols with longer chains may lead to a lower degree of

crosslinking and a material with more elastomeric characteristics and high molecular mobility, resulting in higher impact strength.[14]

The introduction of curaua fiber resulted in increased Izod impact strength compared with the neat lignopolyurethane (Figure 5). The energy required to break the samples was higher for the composites, confirming that lignocellulosic fibers acted as a reinforcement. The increase in the impact strength was mainly due to the high efficiency of the load transference from the matrix to the fibers, which distributed the applied load and consequently, increased the strength of the material.

The composites reinforced with curaua fibers exhibited superior impact strength in relation to composites reinforced with coir fibers. In fact, when considering the standard deviations, only the DEG/NaLS/MDI composite prepared with the coir fiber exhibited matrix reinforcement. For other coir materials, the neat polymer and the respective coir composites exhibited similar impact strength values (Figure 5). As previously mentioned, curaua fiber has a much higher tensile strength [485 MPa, Figure 2(b)] than the coir fiber [120 MPa, Figure 2(b)]. This higher tensile strength is associated with a higher cellulose content and higher crystallinity index of the curaua fibers [67.7 and 65%, respectively, Figure 2(a)] compared with those of the coir fibers [50 and 41%, respectively, Figure 2(a)]. The highest tensile strength of the curaua fiber contributed to the increased impact strength of the composite prepared with this fiber because it provided better support for the load that was transferred from the matrix to the fiber during the Izod impact strength test.

In addition, the aspect ratio (Length/diameter, L/d) of the fibers used as reinforcement in the composites also influenced the impact strength of the composites. The aspect ratios of the fibers were calculated by taking into account the average diameter of the curaua and coir fibers (116 and 230 μm, respectively) and their length (3 cm). The curaua fiber had an average aspect ratio of $\sim$ 259, whereas the coir fiber had an average aspect ratio of $\sim$ 130. In addition, the SEM images of the curaua composites [Figure 6(j)] showed that the curaua fiber bundles were disaggregated by the presence of the matrix, leading to a higher aspect ratio. Generally, fibers with high aspect ratios can act as a more efficient reinforcement in the composites, leading to a material with better mechanical properties. This improved performance results from the larger contact area of the fibers with a higher aspect ratio, allowing for greater interaction between the fiber and the matrix in the interface region. In turn, this enhanced interaction allows for the better transference of the applied load from the matrix to the fibers during the Izod impact test, generating composites with higher impact strength.[64]

The higher aspect ratio of the curaua fibers also explains the better impact strength of the composites reinforced with curaua fibers.

Figure 6 provides the SEM images of the fractured surfaces of the lignopolyurethane composites reinforced with 30% w/w of curaua and coir fibers following the Izod impact test. The SEM images of the composites exhibited good adhesion at the fiber/matrix interface in all composites (Figure 6). The matrices have
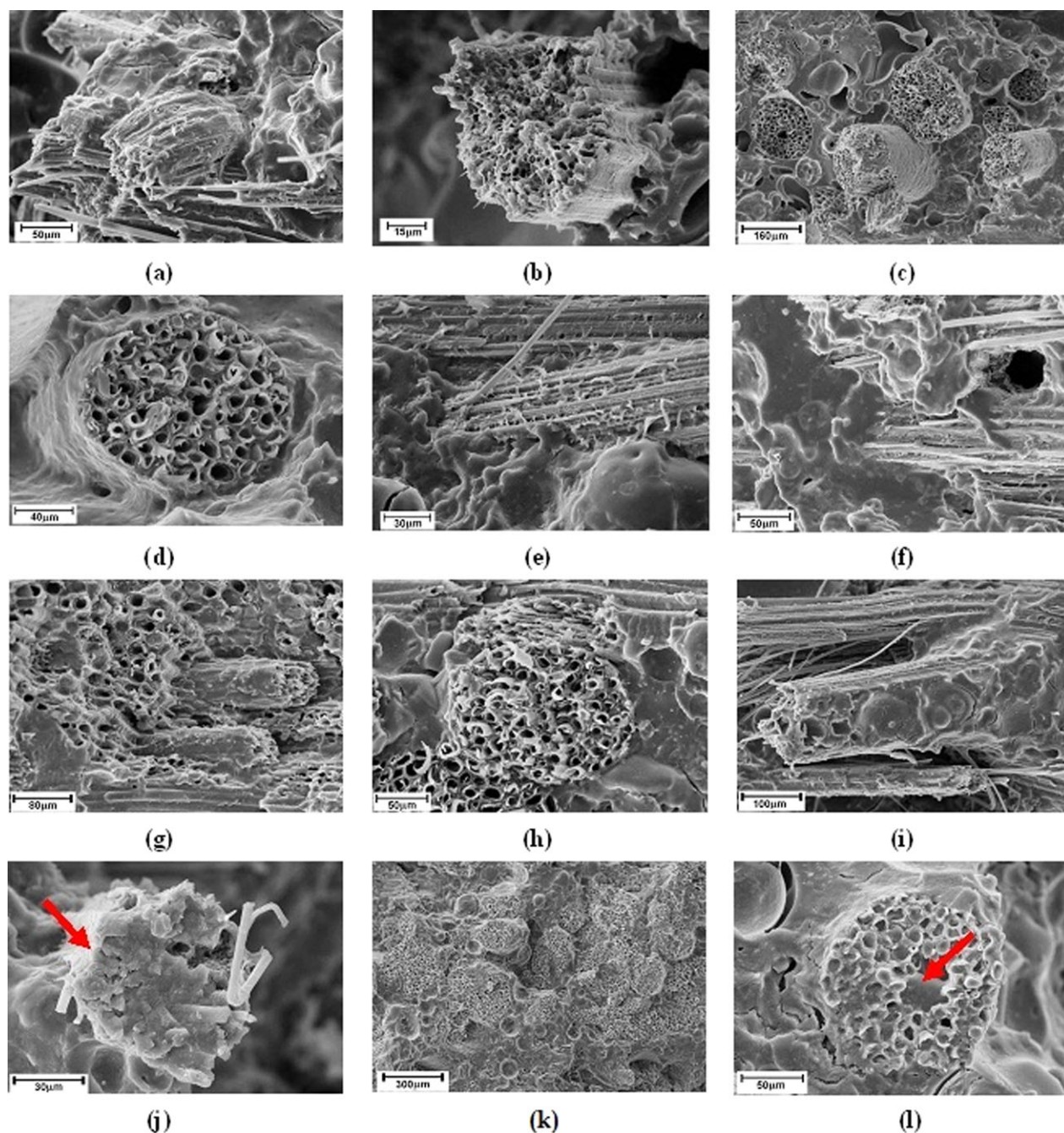
Figure 6. SEM images of fractured surfaces of lignopolyurethane composites DEG/NaLS/MDI reinforced with curaua fibers (a, b) and coir fibers (c, d); PEG/NaLS/MDI reinforced with curaua fibers (e, f) and coir fibers (g, h); and CO/NaLS/MDI reinforced with curaua fibers (i, j) and coir fibers (k, l). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

domains of low polarity in their structures as well as polar sites, which are also present in the components of the lignocellulosic fibers. These components favor the interactions at the fiber/matrix interface, leading to stronger adhesion. Additionally, the presence of typical lignin moieties in the matrices, due to the use of NaLS in their preparation, enhances the interaction between the matrices and the lignin present in the fibers.

The presence of hydroxyl groups on the surface of the fibers (in cellulose, hemicellulose, and lignin structures) enables their

reaction with the isocyanate groups, which takes place during the preparation of the composites and results in the formation of urethane-type covalent bonds between the fibers and the polymeric matrix.[65] This reaction may have also occurred in the present work, but the scope of this study did not include an extensive structural investigation to confirm that these bonds have been formed.

The adhesion at the fiber/matrix interface of the composites reinforced with the coir fibers was as good as that of composites
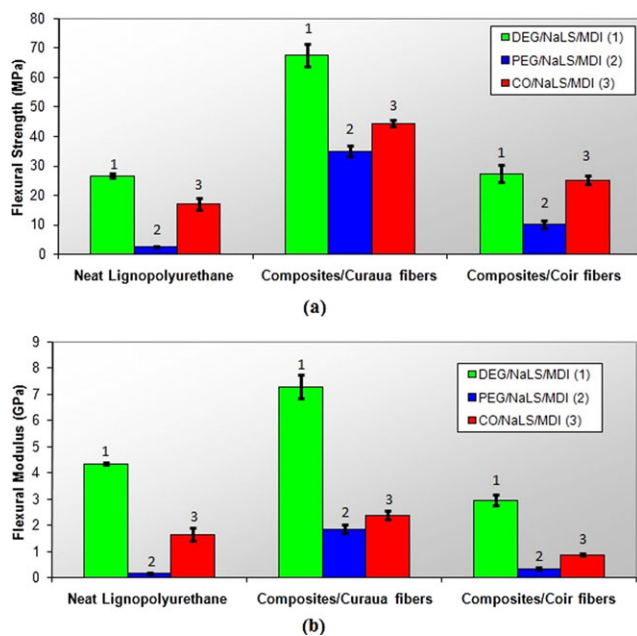
Figure 7. Flexural strength (a) and flexural modulus (b) with respective standard deviation of the neat lignopolyurethane (DEG/NaLS/MDI, PEG/NaLS/MDI, and CO/NaLS/MDI) and lignopolyurethane composites reinforced with curaua and coir fibers (30% w/w, 3 cm length, and randomly oriented). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reinforced with curaua fibers. As previously mentioned, the matrix has low polarity domains and polar sites that can interact with the components of the fibers with the same characteristics, favoring the interaction at the interface and resulting in strong adhesion. Moreover, hydrogen bonds between the hydroxyl groups of the fibers and the —NH of the urethane groups of the polymeric matrix could also be formed.[61] Therefore, as previously mentioned, the higher impact strength of the composites reinforced with curaua fibers is due to the higher tensile strength and aspect ratio of the curaua fiber itself compared with the coir fiber.

In the composites with CO/NaLS/MDI lignopolyurethane matrices, the tips of curaua and coir fibers were filled with the matrix [see arrows in Figure 6(j,l)]. This filling was of great importance because the unfilled fibers could act as tension concentrators and decrease the mechanical properties of the composite.[2] Therefore, this fill effect, as well as the higher strength of this polymeric matrix, is related to the higher impact strength of the composites with the lignopolyurethane matrix CO/NaLS/MDI.

The polymer matrices of the composites exhibited a rough surface and the formation of voids, which were most likely caused by the presence of residual moisture in the fibers used as reinforcement. Although the fibers and NaLS were dried before use, some residual moisture still remained in the fibers, leading to voids due to the release of CO_2 during the reaction between water and isocyanate.

Figure 7 provides the flexural strength and modulus of the neat lignopolyurethane and lignopolyurethane composites reinforced

with curaua and coir fibers. Both flexural strength and modulus of the composites demonstrated the same trend: neat lignopolyurethane prepared from DEG/NaLS/MDI exhibited the highest flexural strength and flexural modulus, followed by lignopolyurethane CO/NaLS/MDI and lignopolyurethane PEG/NaLS/MDI, which had the lowest flexural strength and modulus. DEG is a small polyol [Figure 1(c)] and, therefore, its use leads to a higher proportion of hard segments (due to urethane linkages) in the PU when compared with PEG [Figure 1(d)] and CO [Figure 1(b)], which are longer chain polyols that form longer soft segments in the PU. The increase in the proportion of hard segments in the lignopolyurethane DEG/NaLS/MDI leads to increased stiffness of the material and, consequently, an increase in the flexural modulus. The use of CO results in PU with double bonds in its soft segment, which increases the stiffness of the material compared to the PU prepared with PEG, which has a linear soft segment and no double bonds. Thus, the lignopolyurethane CO/NaLS/MDI is more rigid and, therefore, has higher flexural modulus compared with the less rigid lignopolyurethane PEG/NaLS/MDI.

In the flexural test, the surface properties of the samples are very important. In the surface of the composites, the matrix is usually the predominant component, so the flexural strength and flexural modulus are considerably influenced by the matrix properties. Thus, the composites demonstrated the same trends as the neat lignopolyurethanes. When the coir fibers were used in the PU composites, the reinforcement action was not really important, and the results of flexural strength and flexural modulus were mainly influenced by the matrix. Consequently, considering the standard deviations, the results for the lignopolyurethane composites exhibited no significant variation when compared with the neat PU [Figure 7(a,b)]. However, the introduction of curaua fibers significantly increased the flexural strength and flexural modulus of composites compared with neat lignopolyurethane [Figure 7(a,b)]. The superior mechanical property of the curaua fibers, in addition to their higher aspect ratio when compared with the coir fibers, resulted in a significant contribution of the reinforcement to the flexural properties of the composites.

CONCLUSIONS

NaLS was successfully used in the preparation of PU matrices, which were used in composites reinforced with lignocellulosic fibers. The SEM images of the fractured surfaces of both coir and curaua composites revealed excellent adhesion at the fiber/matrix interface, most likely due to the presence of hydrogen bonds between the urethane groups of the matrix and the hydroxyl groups of the fibers, as well as the interactions between the less polar domains present in the fibers and the matrix. It can also be mentioned the likely establishment of covalent bonds between the isocyanate and the hydroxyl groups of the fibers, which can be formed during the preparation of the composites, allowing the fiber to bond covalently with the matrix.

The use of curaua as the matrix-reinforcing agent resulted in improvements in the mechanical properties of composites, increasing their impact strength, flexural strength, and flexural

modulus. The lignopolyurethane composites reinforced with curaua fibers exhibited the best properties, due to both improved mechanical strength and aspect ratio of the curaua fibers compared with the coir fibers. However, the use of coir may be advantageous in some applications in which the mechanical properties are not criterion of choice because they lead to materials with lower density, lower cost, and higher content of raw materials coming from renewable sources, when compared with the neat PU-type polymer.

In general, the results are promising because biocomposites were successfully prepared using a high proportion of materials obtained from renewable sources, namely curaua fibers, NaLS, and CO.

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