



Synthesis and Processing of Melt Spun Materials from Esterified Lignin with Lactic Acid

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Abstract: In this study, the carbon fiber manufacturing process is investigated, using high-density polyethylene (HDPE) and esterified lignin either with lactic acid (LA) or with poly(lactic acid) (PLA) as precursors. More specifically, lignin was modified using either LA or PLA in order to increase its chemical affinity with HDPE. The modified compounds were continuously melt spun to fibrous materials by blending with HDPE in order to fabricate a carbon fiber precursor. The obtained products were characterized with respect to their morphology, as well as their structure and chemical composition. Moreover, an assessment of both physical and structural transformations after modification of lignin with LA and PLA was performed in order to evaluate the spinning ability of the composite fibers, as well as the thermal processing to carbon fibers. This bottom–up approach seems to be able to provide a viable route considering large scale production in order to transform lignin in value-added product. Tensile tests revealed that the chemical lignin modification allowed an enhancement in its spinning ability due to its compatibility improvement with the commercial low-cost and thermoplastic HDPE polymer. Finally, stabilization and carbonization thermal processing was performed in order to obtain carbon fibers.

Keywords: carbon fibers; lignin; melt spinning; carbonization; Raman; micro-CT

1. Introduction

Carbon fibers are constantly being investigated considering their potential of high prospect technological application such as in the airspace or car industry, which require high performance and long-serving advanced materials for construction. Carbon fibers of exceptional mechanical properties have already been produced; however, new low-cost precursors are under investigation. At present, the need to reduce the cost of the carbon fibers for technological applications is of paramount importance and provides the opportunity to broaden their market. As a consequence, eco-friendly, renewable, and low-cost precursors of lignin have attracted major interest in order to be incorporated in the synthesis of the carbon fibers, considering both high carbon content and dense aromatic structure [1–3].

Synthesis of carbon fibers consists of several processing paths, such as chemical synthesis of the precursor polymer, fiber spinning (dry, wet, melt), stabilization in oxidative atmosphere to induce crosslinking and thermal resistance, and carbonization in inert atmosphere to induce graphitic planes in fiber structure. Regarding the chemical synthesis step, it should be mentioned that it requires careful selection and design of the reaction mechanism of the reagents in order to improve the linearity of molecular chains and reduce the polar character induced by lignin hydroxyls [4].

A potential low-cost precursor that could be used for carbon fiber production is Softwood Kraft Lignin (SKL). However, this precursor has several particularities due to the fact that it consists of



a complex three-dimensional network, while it becomes brittle upon thermal processing. Therefore, in order for lignin to be used for structural carbon–fiber production, it has to be modified so that the high-extent reactive C–O bonds in interunit lignin linkages, such as b-O-aryl ether, can be reduced [4]. On the other hand, lignin provides a low-cost and widely available alternative that could be utilized in industries, assuming that a viable modification route is established to enhance process ability and compounding to form fibers with enhanced mechanical properties and behavior overall. In general, lignin composites with epoxy resins, derivatives, and blends have already been investigated [5–8], but there is no sufficient reference to their spinning ability, while Zhou et al. overviewed the research done on plant fiber composites [9]. Moreover, Megiatto et al. investigated chemical modification of Sisal (a Mexican agave) with lignin and the effect of phenolic composite properties on fibers. It was concluded that phenolic functional groups enhance fiber properties.

In other works considering biopolymers similar to lignin, cellulose was studied as a binder in green composites [10,11], whereas application of plant fibers, composites, and their life cycle assessment was also reported [12–18]. Additionally, the properties of elastomeric composites coming from widely used commercial polymers are already known, as well as the effect of lignin enrichment in foams, composites, and fibers [19–21]. Furthermore, high-tech grafting of carbon nanotubes on lignin structures to manufacture fibers with advanced electrical or mechanical properties has been performed [22–24].

The motivation of the present work is the synthesis of carbon fibers using low-cost and eco-friendly precursors. Therefore, the aim in the present research is to follow a relatively simple and low-cost procedure to reach a carbon fiber production. Lignin was esterified with lactic acid (LA) and poly(lactic acid) (PLA) in order to improve its chemical affinity with high-density polyethylene (HDPE) and pave the way for the preparation of a blend that could be melt spun and then produce carbon fibers. The aforementioned organic acids were implemented in the precursor lignin-enriched fiber production via chlorination with thionyl chloride (SOCl₂) and esterification with lignin. Evaluations of esterification reaction, spinning process, as well as stabilization and carbonization procedures were conducted. The originality and novelty of the present study lies in the fact that a melt-spun lignin conjugation with high molecular weight commercial spinnable polymers was accomplished, using esterification after a chlorination reaction, so as to enhance the intermolecular bonds between the compounds. Finally, it could be mentioned that the added value of our work resides in the fact that the chemical synthesis that was conducted in this study provided thermal process ability to the precursor fiber without the use of plasticization.

2. Materials and Methods

2.1. Materials

Analytical reagent grade chemicals were used. Lactic acid (LA, Fisher Chemicals, Waltham, MA, USA), high-density polyethylene (HDPE, Sigma Aldrich, St. Louis, MO, USA, Mw~125,000), poly(lactic acid) (PLA, Sigma Aldrich, St. Louis, MO, USA, Mw~125,000), hydrochloric acid (HCl 37%, Fisher Chemicals, Waltham, MA, USA), thionyl chloride (SOCl₂, Acros Organics, Geel, Belgium), chloroform (CHCl₃, Fisher Chemicals, Waltham, MA, USA), and pyridine (Fisher Chemicals, Waltham, MA, USA) were used as received without further purification. Softwood kraft lignin (SKL, Westvaco Corp., Indulin AT, MWV, Norcross, GA, USA) was washed with HCl 0.1 M before being used in the blends. All blends intended for melt spinning were placed in a vacuum oven before the extrusion took place and were left there overnight.

2.2. Synthesis of Fibers

In a 1000 mL three-neck round bottom flask, 100 mL of LA was dissolved in 230 mL of CHCl₃, under vigorous stirring at room temperature for 1 h. Then, 100 mL of SOCl₂ was added to the mixture, dripping slowly and in small amounts in order to perform the chlorination reaction. As the SOCl₂ was

added to the flask, vapors of SO_2 were released from the chemical system according to the reaction in Figure 1 [25]. According to this reaction, a nucleophilic substitution pathway occurs, in which the carboxylic acid is first converted into a chlorosulfite intermediate. Then, the chlorosulfite reacts with a nucleophilic chloride ion in order lactic acid chloride (LCl) to be synthesized.



Figure 1. Chemical reaction of the chlorination process.

The released vapors indicate that the chlorination reaction has progressed. After partial evaporation of the solvent (CHCl₃), the solution was added to 250 mL of pyridine. Then, 100 g of washed SKL was added to the mixture, and the blend was left under vigorous stirring at room temperature for 1 h. The temperature was then elevated at 120 °C, and a reflux condenser was adapted onto the flask. The esterification reaction duration was 5 h at the aforementioned conditions; the mechanism of the corresponding esterification reaction (alcoholysis) between the hydroxyl groups of SKL and lactic chloride is depicted in Figure 2 [26]. According to the esterification process, an addition of oxygen (nucleophile) to the carbonyl group occurs, yielding a tetrahedral intermediate. Then, an electron pair from oxygen displaces the chloride (leaving group), generating a new carbonyl compound as a product. After the completion of the reaction, the solvent (pyridine) was evaporated. The solid product (SKL esterified with lactic chloride, SKL–LA) was oven-dried overnight at 70 °C.



Figure 2. Esterification reaction between Softwood Kraft Lignin (SKL) and lactic acid chloride (LCl).

In a 1000 mL glass beaker, 45 g of poly(lactic acid) (PLA) was dissolved in 600 mL of chloroform under vigorous mechanical stirring. The blend was left under stirring overnight in order to ensure complete dissolution. Afterwards, 100 mL of SOCl₂ was added dripping in the solution under mechanical stirring. The SOCl₂ reacted with the hydroxyl groups of PLA and produced poly(lactic acid) chloride (PLCl) according to the reaction in Figure 3 [25]. During the SOCl₂ addition, there was a release of SO₂ vapors that indicated the reaction progress. After completion of the reaction, the obtained product (PLCl) was dried and pulverized. Then, 25 g of the synthesized PLCl was dissolved in 270 mL of pyridine in a 500 mL three-neck round bottom spherical flask and was left

under vigorous stirring overnight at room temperature. In the next step, 40 g of SKL was added, and the mixture was left to react at 120 °C for 5 h under vigorous stirring. After that, the solvent was evaporated, and the solid collected product of SKL–PLA (SKL esterified with PLA) was dried at 80 °C. The chemical reaction of the esterification process (alcoholysis) is illustrated in Figure 4 [26].



Figure 3. Chemical reaction of the poly(lactic acid) (PLA) chlorination process.



Figure 4. Esterification reaction between SKL and PLCl.

The abovementioned materials were mixed with HDPE, and the resulting blends were loaded in an extruder line, optimizing spinning parameters of extruder temperature, roller distance from the extruder, and extrusion speed for each precursor blend. The parameters and conditions for the optimization process for the HDPE spinning for the production of HDPE/SKL–LA (80:20) and HDPE/SKL–PLA (80:20) fibers are tabulated in Tables A1 and A2. The best results concerning the spinning ability of the blends were obtained for the conditions that are presented in Table 1. The blend mass ratio of the HDPE/esterified lignin was 80/20 by weight (HDPE/SKL–LA (80:20), HDPE/SKL–PLA (80:20)).

Table 1. Tabulated parameters and conditions of melt spinning process.

Blend	Stage 1	Stage 2	Extrusion Speed	Roller
	Temperature (°C)	Temperature (°C)	(% rpm)	Distance (cm)
HDPE/SKL–LA	226	230	100	23
HDPE/SKL–PLA	222	225	85	25

The extruded precursor HDPE/SKL–PLA fibers were fixed in bundles and were thermally treated following four different thermal stages. Firstly, they were subjected to a 1 h long pre-stabilization step at 150 °C, followed by a second stage at 220 °C for 3 h and finally at 300 °C for 10 min to maximize crosslinking. This thermal procedure enhanced crosslinking through oxidation and prepared the structure to withstand carbonization. Carbonization was performed at 800 °C, under nitrogen atmosphere with a residence time of 5 min. The thermal treatment effect is presented in Table 2.

Sample	150 °C, 1 h	220 °C, 3 h	300 °C, 10 min	Proceeded to Carbonization	Successful Carbonization
HDPE/SKL-LA	sustained	sustained	sustained	Yes	need for optimization
HDPE/SKL-PLA	sustained (fiber shrinkage)	sustained	sustained	Yes	Yes

Table 2. Tabulated thermal treatment results.

The carbonization of the fibers was conducted via a high-temperature furnace (Protherm—PTF Series, Single-Zone tube furnace, Maximum Temperature: 1200 °C) under nitrogen atmosphere at 800 °C for 5 min.

The melt spinning experiments were carried out on a Dynisco extruder. The Dynisco LME (Laboratory Mixing Extruder) is a laboratory tool developed to produce fibers continuously derived from thermoplastic polymers. The specimen is conveyed in a cooled hopper right after exiting the hot surface of the cylindrical rotor, against the inclined surface of the stationary scroll, and moves toward the outlet die.

2.3. Characterization

The fibers composition and their morphology were determined with a Hitachi Electron Microscope TM3030 coupled with an Ultra-High Resolution Scanning Electron Microscope (UHR-SEM) using NOVA NANOSEM 230 (FEI Company, Hillsboro, United States, 2009) and with an Energy Dispersive X-ray Spectrophotometer (EDS) (QUANTAX 70, BRUKER, Billerica, Massachusettes, United States, 2016). The Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (FTIR) instrument Cary 630 spectrometer (Agilent, Santa Clara, California, United States, 2016) was used to analyze the FTIR spectra of the fibers. This instrument has a resolution of 4 cm⁻¹ and an operating wavelength range of 4000–400 cm⁻¹.

The Thermogravimetric/Differential Scanning Calorimetry (TGA/DSC) instrument STA 449 F5 Jupiter (NETZSCH-Gerätebau GmbH, Selb, Germany, 2017) was used for the thermal analysis of the fibers. The system consists of a SiC furnace with an operation temperature varying between 25 and 1550 °C. The maximum heating rate is 50 K/min. The gas used was nitrogen at a volumetric rate of 50 mL/min and at a heating rate of 20 °C/min.

A Renishaw inVia spectrometer was used to perform micro-Raman measurements coupled with a green diode laser with emission at 532 nm (Renishaw plc, Gloucestershire, United Kingdom, 2013). The backscattering configuration was used. A beam spot size of 1 micrometer for a 1 mW beam at 1% intensity was used. The MATLAB 8.0 and Statistics Toolbox 8.1 (The MathWorks, Inc., Natick, Massachusetts, United States, 2012) was used for fitting the Raman signal to calculate the integrals of D and G peaks and quantify ID/IG ratio.

The structure of the fibers was observed and collected by the instrument SkyScan 1272, a 3D X-ray scan system (BRUKER, Billerica, Massachusettes, United States, 2017). The system disposes an X-ray source which operates at 20–100 kV and 10 W ($<5 \mu$ m spot size @ 4W), an X-ray detector with a maximum resolution of 11 Mp (4032 × 2688 pixels), and a CCD fiber of 14 bits, cooled and optically joined to a scintillator. During the observation, the specimens were fixed on a rotational stage, the distance between the rotation axis and the radiation source is set from 6 to 12 mm, and the pixel resolution is set to 2016 × 1344 in order to obtain reliable images. Several stacked images were used for rendering, calculations, and image analysis for each sample.

The tensile strength at the breaking point of the fiber was determined according to the scale of the dynamometer of the MPM-10 tensile test machine, based on the standards ISO 11566:1996 and ASTM D 3379-89.

3. Results and Discussion

3.1. Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

Taking into account the SEM images of the fibers HDPE/SKL–LA, HDPE/SKL–PLA (precursor) and HDPE/SKL–PLA (carbonized) (Figures 5–7, respectively), it can be observed that the diameter of the fibrous materials ranges from 158 to 170 μ m (Table 3). It should be stated that the SEM characterization of the fibers in respect of their diameter (Table 3) includes the measurement of 10 fibers of each sample. Moreover, two measurements were conducted in each fiber.



Figure 5. SEM image of high-density polyethylene (HDPE)/SKL-LA fiber.



Figure 6. SEM image of HDPE/SKL-PLA (precursor) fiber.



Figure 7. SEM image of HDPE/SKL–PLA carbonized fiber.

Table 3. Tabulated SEM analysis results of the produced fibers.

Sample	Min. Diameter (µm)	Max. Diameter (µm)	Average Diameter (µm)
HDPE/SKL-LA	158	165	161.5
HDPE/SKL–PLA (precursor)	155	164	159.5
HDPE/SKL-PLA (carbon fiber)	168.5	170.1	169.3

Although the typical diameter of a PAN-based precursor fiber is only 15 μ m, materials with a bigger diameter than that were produced because of the low elasticity of the HDPE and the use of a 1.8 mm spinneret. Additionally, the addition of lignin reduces the tension capacity of the material [27]. The thermal behavior of HDPE/SKL-LA fibers was not proper to withstand carbonization, due to the formation of agglomerates and heterogeneity on the extruded fiber. On the other hand, HDPE/SKL-PLA fibers were carbonized due to the fact that SKL–PLA presents enhanced mixing ability with HDPE blends. Furthermore, it should be mentioned that HDPE/SKL-PLA carbon fiber shrunk in length about 6% compared to the precursor, owing to densification and the increase of sturdiness after carbonization treatment [28]. Due to the same fact, the diameter of the fiber is increased. Furthermore, combined SEM-EDS analysis was conducted on the produced samples in order to provide information of the chemical composition, with the percentage of each chemical element in the fibers, as well as to support the chlorination mechanism of LA and PLA reaction and to confirm the successful synthesis of modified lignin by the corroboration of the absence of Cl element in the observed specimens. Table 4 presents the tabulated values of wt.% elemental composition of the produced HDPE/SKL-PLA fibers prior to and after carbonization process. Regarding the obtained results, it should be remarked that the percentage of chlorine in the samples was practically zero for both the HDPE/SKL–PLA precursor and carbon fiber specimens.

Sample	Element	wt.%
	С	57.60
HDPE/SKL–PLA (precursor)	0	41.53
	Cl	0.87
	С	87.89
HDPE/SKL-PLA (carbon fiber)	0	11.60
	Cl	0.51

Table 4. Tabulated values of wt.% elemental composition of the produced HDPE/SKL-PLA fibers.

3.2. Thermogravimetric Analysis and Differential Scanning Calorimetry

The TGA and DSC diagrams of lignin compounds are illustrated in Figure 8. The gas used was nitrogen and the temperature ramp was 10 °C/min. Taking into consideration the TGA and DSC diagrams of the compounds SKL-LA (Figure 8b) and SKL-PLA (Figure 8c), it may be remarked that both compounds present an initial peak of thermal degradation at 280 °C, whereas their thermal degradation end temperature is located at 800 °C leaving a residue of approximately 22% and 35% mass, respectively (Table 5). The residual mass is attributed to the autocatalytic stabilization effect of lignin derived by high elemental composition in oxygen [29–32]. The PLCl is degraded almost quantitatively at 400 °C (Figure 8a). The DSC curve of PLCl presents two characteristic peaks, an endothermic at 340 °C and an exothermic at 480 °C, which correspond to its thermal degradation peak and crosslinking, respectively [33] (Figure 8a). As far as SKL-LA is concerned, the DSC graph presents a wide exothermic curve, which implies a steady rate and slow evolution of gases as crosslinking byproducts of the material, considering the mass loss as provided by TGA (Figure 8b). Finally the DSC graph for the SKL–PLA sample demonstrates a more intense exothermic peak ascribed to oxygen-derived autocatalytic crosslinking, generated at multiple starting points due to its size, but there is only a small endothermic peak at 700 °C, relating to its degradation and state transition from crystal-like to amorphous [34,35] (Figure 8c). Concerning the TGA/DSC graphs of the HDPE/SKL-PLA carbon fiber, it can be easily observed that the carbon residue after thermal treatment is about 85%, meaning that the whole procedure successfully produced a carbon fiber with desired thermal behavior, resistance, and adequate carbon yield. The wide exothermic DSC curve is ascribed to intramolecular bond forming reactions as well as to polycondensation and denitrification reactions (Figure 8d) [36].



Figure 8. TGA/DSC graphs of: (a) PLCl compound, (b) SKL–LA compound, (c) SKL–PLA compound, and (d) HDPE/SKL–PLA carbon fiber.

Sample	Onset Temperature of Thermal Degradation (°C)	Peak Temperature of Thermal Degradation (°C)	End Temperature of Thermal Degradation (°C)	Mass Change (wt.%)
PLCl	284.9	320.8	399.3	95
SKL-LA	205.1	277.9	740.0	75
SKL-PLA	236.1	285.7	781.8	69
HDPE/SKL–PLA (carbon fiber)	625.0	725	800.0	15

Table 5. Thermal analysis of the samples.

3.3. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

As evidenced in the aforementioned SEM/EDS micrographs as well as in the FTIR spectrogram in Figure 9, the chlorination reaction of PLA to PLCl was successful. The major differences in FTIR spectra after chlorination of PLA and LA are pointed out in the peaks at 1558 and 1640 cm⁻¹ [37] that are attributed to asymmetric CO_2^- stretching vibration, which is mainly reacted with SOCl₂ [38–41]. Further peaks are similar between PLA and PLCl, slightly more intense in case of PLCl. This is due to the –Cl group electronegativity and the use of SOCl₂ in the chlorination reaction [25,42]. The FTIR analysis results are presented in Table 6.

The FTIR spectra of SKL–LA and SKL–PLA in Figure 10 demonstrate similar peaks. The small band at about 3500 cm⁻¹ is attributed to the hydroxyl group of phenolic and aliphatic structures of lignin. This peak is more intense for SKL–LA due to the fact that the LA monomers which are esterified to the lignin hydroxyl groups have one hydroxyl group at a single end. The PLCl chains esterified to lignin (SKL–PLA) own only one hydroxyl group at the end of each chain. Therefore, the only signal that SKL–PLA presents at 3500 cm⁻¹ is ascribed almost completely on the lignin hydroxyls, because the contribution from the PLCl hydroxyls to this signal is negligible. Moreover, SKL–LA demonstrates

a peak of medium intensity at 2900 cm⁻¹, which is attributed to C–H stretches. The peaks at 2900 cm⁻¹ result from various C–H bonds due to the aromatic methoxy groups and the methyl/methylene side groups. The characteristic absorption bands for aromatic rings of lignin are at 1600, 1500, and 1410 cm⁻¹. The peak at 1600 cm⁻¹ also implies the presence of a conjugated structure. There is also a shoulder at 1750 cm⁻¹, corresponding to lignin's carbonyl groups [43–45]. The FTIR most important peaks are tabulated in Table 7.



Figure 9. FTIR spectra of PLA and PLCl.



Figure 10. FTIR spectra of SKL–LA and SKL–PLA materials.

Table 6. Identified FTIR peaks ascribed to the peaks of PLA and PLCl materials.

Wavenumber (cm ⁻¹)	Type of Bond Vibration
3294	-COOH (PLA)
2847	–COOH (PLA)
1750	C=O (both PLA and PLCl)
1640	asymmetric CO ₂ ⁻ stretching vibration (PLA)
1558	asymmetric CO_2^- stretching vibration (PLA)
1453	C–H (both PLA and PLCl)
1185	C–O (both PLA and PLCl)
1080	C–O (both PLA and PLCl)
750	C–H (both PLA and PLCl)

Wavenumber (cm ⁻¹)	Type of Bond
3500	O–H (both SKL–LA and SKL–PLA)
2900	C–H stretch
1750	C=O (both SKL–LA and SKL–PLA)
1600	aromatic lignin rings (conjugated structure)
1500	aromatic lignin rings
1410	aromatic lignin rings
1150-1185	C–O (both SKL–LA and SKL–PLA)
750	C–H bend (both SKL–LA and SKL–PLA)

Table 7. Identified First Deaks ascribed to the SNL-LA and SNL-FLA material	Table 7.	Identified	FTIR peak	s ascribed	to the SI	KL–LA and	SKL-PLA	materials
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3.4. Thermal Processing (Stabilization—Carbonization)

Taking into consideration Table 5, it may be remarked that the HDPE/SKL–PLA fibers present an enhanced thermal behavior compared to those of HDPE/SKL–LA, because they present a higher onset, peak, and end temperature of thermal degradation and considering the fact that HDPE has the same thermal behavior in both samples. Moreover, taking into consideration the two fibers, the HDPE/SKL–PLA precursor is expected to exhibit an extended linear-like polymeric chain and bigger molecular weight, in comparison with the much smaller HDPE/SKL–LA fibers, which were not successfully carbonized, due to the aforementioned reasons. The yield of the carbon fiber after carbonization of the HDPE/SKL–PLA fibers was 85%. Based on the higher end temperature and lower weight loss as given in Table 5, HDPE/SKL–PLA is more thermally stable compared to HDPE/SKL–LA. According to the literature, although the carbonization of PAN precursor fibers is carried out between 1000 and 1800 °C, in our study, the fibrous materials were carbonized at 800 °C for 5 min (in a horizontal furnace used for CVD), due to the different texture and thermal behavior of the materials.

3.5. Tensile Testing of Precursor Fibers

A tensile test was performed on the precursor fibers. Regarding the obtained results, the measured average tensile strength at the breaking point varied between the fibers. The fibers which presented the optimum properties were HDPE/SKL-PLA fibers, at 32.33 MPa demonstrating an average diameter of 159.5 µm, while the HDPE/SKL–LA demonstrated 25.12 MPa of tensile strength. The pure HDPE fibers showed a tensile strength of 19.87 MPa. All tests were conducted three times, and then the average value was calculated (3 fibers of each different type were used, 9 fibers in total, 27 measurements in total). The crosshead speed used for testing was 0.2 mm/min. According to the literature [46,47], as far as the orientation is concerned, it was not substantially modified after the tensile test, which was a promising indication for potential thermal treatment (stabilization, carbonization), because during these processes, the fibers tend to shrink and become thicker. Furthermore, these values are related and comply with the tensile properties of natural fiber composites [48], while the difference between the precursor fiber in tensile strength is ascribed to their slightly different microstructure, which is affected by extrusion speed, temperature, and residence time of the materials in the extrusion line and the size of the spinneret [49]. Further, the tensile deformation and damage of fibers are strongly affected by both defects and orientation [50], while the chemical bonding has a severe impact on stiffness and tensile strength of fiber network [51].

3.6. Micro-CT Analysis

The micro-CT analysis results are depicted in Table 8, and the volume rendering images of carbon fibers are presented in Figure 11. Concerning the X-ray tomography obtained results, micro-CT studies on inner geometry and morphology of carbon fiber tapes [52] demonstrated a similar morphology as the one obtained in the present work. Additionally, tomography performed on low-density carbon fiber materials and composites exhibits similar physical properties with home-grown carbon fibers [53,54]. Furthermore, investigation of carbon fiber failure and breakage via micro-CT modeling showed similar

values [55–57] and supports effective carbonization in the present study. The surface density is the mass per unit area (mm²). Linear density is the density that the material demonstrates in relation to its length [58]. In the presented work, it is the amount of mass per millimeter. The degree of anisotropy (DA) is an index that shows the alignment of the materials (fibers) into the total scanned volume [59], and in our study, it is a measure of the orientation of the fibers within the rectangles of the Figure 8.Fractal dimension is a measure showing the change in the detail of a specific object (fibers in this case) as the measuring scale changes [60]. The micro-CT is useful for the scope of the current research as it gives information about the porosity and the morphology of the final material. The innovation of the presented technique applied to the samples produced in this study is the demonstration of a porosity below 2%. This fact underlines the durability and the sturdiness of the synthesized materials.

Table 8. Micro-CT arithmetical values.

Parameters	HDPE/SKL-PLA Carbonized
Object Surface Density (mm ⁻¹)	17.19
Structure Linear Density (mm ⁻¹)	12.68
Degree of Anisotropy	1.599
Fractal Dimension	2.600
Total Porosity (%)	1.995



Figure 11. Micro-CT volume rendering images of the HDPE/SKL-PLA carbonized fiber.

3.7. Raman Spectroscopy

Raman spectroscopy measurements provided insight into the carbonization procedure (Figure 12). More specifically, taking into consideration that the presence of G-bands around 1650 cm⁻¹ is a straightforward indication of graphite planes formation, it should be mentioned that the I_D/I_G ratio of HDPE/SKL–PLA carbon fibers was 0.847, denoting a lower intensity of D-band at 1300 cm⁻¹ compared to G-band, denoting that the sp³ bonds are more than the sp² bonds.

Raman investigation of the produced carbon fibers was performed in order to characterize the structural transformation of the precursor fiber to carbon fiber; the formation of a graphite-like sp² plane is expected to be formed as a result of carbonization. Lignin-based carbon fibers presented a promising response to electromagnetic radiation in Raman characterization, with all D, G, and 2D peaks to appear. A trend of forming a sharper and of higher intensity G to D peak was recorded in Raman spectra, which seems to provoke a proper structure reorientation [61].

Looking at the envelope of fit reported in Figure 12, it can be clearly stated that D and G regions encompass four different Gaussian components. Two of them were used to fit the D peak and two of

them were used for the G peak. The D peak is described by two components centered at 1330 and 1360 cm⁻¹ which present low-intensity variation changing from LA to PLA. The G peak demonstrates a more stable component around 1590–1600 cm⁻¹ [62]. To obtain quantitative information by Raman spectroscopy, the ratio of the intensity of D to G peak (I_D/I_G) is measured, and I_D/I_G obtained a value of 0.847, indicating the strong presence of graphitic-like planes present in carbon fiber structure [63–65].



Figure 12. Raman spectroscopy of HDPE/SKL–PLA carbon fiber. The different colored lines correspond to the Gaussian curves used for fitting the density plot of Raman signal via a MATLAB script. The integrals were used to determine I_D/I_G ratio.

3.8. Outcome Analysis

In the present research, a relatively low-cost procedure was followed to reach a carbon fiber production, including a comprehensive stage of organic synthesis, three stabilization stages, and one carbonization stage, with the precursor fiber containing 20 wt.% content of lignin. Moreover, the aim of this study is the industrial upscalability along with simplicity (high profit, high spinning speed and production rate, low cost, one pot reactions), a fact which seems feasible according to this study. According to the literature, despite the fact that chemical modifications of lignin have been investigated [24], there are no references of successful melt-spun lignin conjugation with high molecular weight commercial spinnable polymers, using esterification after a chlorination reaction, so as to enhance the intermolecular bonds between the compounds. The successful chemical synthesis, which was conducted in this study without the use of plasticization [66] and confirmed by characterization, provided thermal process ability to the precursor fiber. Anthracene-oil-derived pitches as precursors have led to green carbon fibers [67], but the diameter of the fibers varied depending on the winding speed, and overall, that method was more expensive than using lignin in the blends. Additionally, carbon fibers from low molecular weight polymers by solvent extraction [68] and from polyacrylonitrile combined with CNTs [69] showed good strength but lacked the low-cost synthesis. While cellulose has been used in the fabrication of carbon fibers [70], the potential of lignin has been acknowledged already [2], but its handling and treatment remained an issue. Finally, lignin, compared to cellulose, is more suitable as a precursor for carbon fiber due to its aromatic groups, which strengthen the material structure after carbonization (higher carbon yield) [71].

4. Conclusions

In the present study, lactic acid and poly(lactic acid) were modified by chlorination, in order to produce the corresponding organic chlorides. Then, these compounds were esterified with SKL. Subsequently, the obtained product was compounded and spun with HDPE thermoplastic polymer to form composite precursors suitable for carbon fiber production. Stabilization and carbonization were conducted, and the obtained HDPE/SKL–PLA fibers demonstrated lower I_D/I_G , by Raman characterization for carbonization at 800 °C, which was adopted as optimal thermal processing. The relative low I_D/I_G ratio, compared to carbon fibers reported in literature, indicates that graphitic sp² planes are substantially formed and oriented, and thus, it can be feasible to enhance the electrical properties of composites. The results from this work can constitute a solid basis for scaling up similar procedures.

Author Contributions: P.G., I.A.K., and C.A.C. conceived and designed the experiments. P.G. conducted the experiments. P.G., G.K., and I.A.K. performed the characterization and evaluation of the data. P.G., I.A.K., and C.A.C. discussed the data and wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Blend	Stage 1 Temperature (°C)	Stage 2 Temperature (°C)	Extrusion Speed (% rpm)	Roller Distance (cm)
	220 226	230	100	23
HDPE/SKL–LA	220	230 235	100	23
	220	230	80 100	23
	220	230	100	23 28
	226	230 235	100	23
	226	230	80 100	23
	226	230	100	23 28

Table A1. Tabulated parameters and conditions for the optimization process for the HDPE spinning(HDPE/SKL–LA (80:20)).

Table A2. Tabulated parameters and conditions for the optimization process for the HDPE spinning	5
(HDPE/SKL-PLA (80:20)).	

Blend	Stage 1 Temperature (°C)	Stage 2 Temperature (°C)	Extrusion Speed (% rpm)	Roller Distance (cm)
	215 222	225	85	25
HDPE/SKL–PLA	215	225 230	85	25
	215	225	65 85	25
	215	225	85	25 30
	222	225 230	85	25
	222	225	65 85	25
	222	225	85	25 30

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