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# OPTIMIZING OF STABILIZATION AND CARBONIZATION PROCESSES FOR SUSTAINABLE LIGNIN-DERIVED CARBON FIBER PRODUCTION

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**Abstract**

Carbon fibers, renowned for their exceptional strength-to-weight ratio and versatile applications, have long been pivotal in various industries. As interest grows in sustainable and cost-effective carbon fiber production, lignin emerges as a promising precursor due to its abundance from the paper and pulp industry, offering an eco-friendly alternative to petroleum-based sources. This research focuses on the crucial stabilization process for carbon fiber production. Phthalic anhydride is used as a cross-linker on extruded fibers, demonstrating effective chemical modification. Continuous research and optimization of thermal process parameters are essential for emulating a semi-continuous stabilization process, thus contributing to the efficient utilization of industrial waste streams and aligning with circular economy principles.

## 1. Introduction

Carbon fibers, renowned for their exceptional strength-to-weight ratio and versatile applications, have long been an integral component of advanced materials in various industries. In recent years, there has been a growing interest in exploring sustainable and cost-effective sources for carbon fiber production. Carbon fibers derived from lignin offer a pathway for sustainable and cost-effective manufacturing, leveraging the surplus of lignin derived from the paper and pulp industry [1]. The utilization of lignin as a precursor for carbon provides an eco-friendly alternative to traditional petroleum-based precursors [2]. This research contributes to the efficient utilization of industrial waste streams and aligns with the principles of a circular economy. Lignin's properties, such as its extent of hydrolytic degradation, chemical functionalities, and molecular weight, are intricately tied to processing conditions and the biomass source's characteristics [3]. Lignin's structure is notably complex, primarily comprising three main monomers: coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol [4]. This structural complexity presents challenges in the extrusion process and subsequent stabilization and carbonization stages necessary for carbon fiber formation. To facilitate extrusion, it is common to create blends with materials like polyamides. Stabilization is a crucial step involving the gradual oxidation and cross-linking of the material to elevate or eliminate its thermal transition points. This process prevents the fibers from melting during carbonization. Although lignin lacks a distinct melting point, its glass transition temperature (Tg) significantly impacts its mobility and thermal behaviour [5]. Both lignin and most carbon fiber precursors have Tg values lower than their thermal decomposition temperatures. Thus, the initial processing step involves thermally stabilizing the material to prevent fiber softening and fusion before carbonization. Chemical pretreatment can enhance thermosetting by promoting material cross-linking. Phthalic anhydride, for instance, has been successfully used in lignin treatments before extrusion. In our study, phthalic anhydride was chosen for post-extrusion treatment, aligning with sustainability principles as it can be derived from lignin oxidation.

## 2. Materials and methods

### 2.1. Materials

The fiber used in this study is composed of 40% lignin (Hardwood) and 60% PA11. The fibers were provided by Centelbex and consist of 24 filaments. Phthalic anhydride used for the chemical pre-treatment of the fiber was purchased from Chembiotin. Additionally, acetonitrile used for the fiber pre-treatment was acquired from Sigma Aldrich.

### 2.2. Methods

#### 2.2.1. Chemical treatment of the fiber

The fiber underwent a chemical treatment using phthalic anhydride to act as a cross-linker within the fiber structure [6]. Phthalic anhydride was dissolved in acetonitrile to form a solution. The fibers were then immersed in the solution at a ratio of fiber to phthalic anhydride of 1:2 [7]. The immersed fibers were maintained at 75°C for 4 hours. Subsequently, three cycles of washing with acetonitrile were conducted, followed by drying the fibers at 50°C overnight.

#### 2.2.2. Thermal treatment of the fiber

The fiber was subjected to thermal treatment using a tubular furnace, with a weight of 2 g applied to simulate tension [8]. The thermal process was conducted in ambient air. Initially, the sample was isothermally treated at 180°C for 2 hours, following a heating ramp from room temperature to 180°C at a rate of 3°C/min. Subsequently, the samples underwent natural cooling before being heated to 220°C

at a rate of 3°C/min and maintained at this temperature for 1 hour. Finally, a temperature boost to 240°C was applied for 30 minutes. Natural cooling was again employed after the thermal treatment.

#### 2.2.3. Characterization of the fiber

##### 2.2.3.1. Optical microscopy

Images of the fibers were obtained with the Olympus BX53M microscope using a brightfield observation method, with a camera resolution of 5760 x 3600 pixels. The Olympus Stream Motion software was used for capturing and analysing images.

##### 2.2.3.2. FTIR

Fourier-transform infrared (FT-IR) spectroscopy was conducted with an Agilent Cary 630 spectrometer FT-IR from 550 $cm^{-1}$ to 4000 $cm^{-1}$.

##### 2.2.3.3 Thermal analysis

The thermal stability was studied by thermal gravimetric analysis (TGA) through a Jupiter STA 449 F5 instrument (Jupiter, Germany). To this end, samples of fibers were heated in alumina crucibles at 10 °C $min^{-1}$ from 25 to 700 °C under nitrogen atmosphere (50 mL/min). The analysis was performed in accordance with ISO 11358.

The thermal behaviour of the fiber was assessed by using a Mettler DSC-822 apparatus. DSC analyses were carried out by heating about 10 mg of sample from 25 °C to 250 °C at a rate of 10 °C/min; the glass transition temperature ($T_g$) was taken by applying the first derivative method. Calibration was performed using indium as standard ($T_m$ = 156.4 °C; $\Delta H_m$ = 28.15 J/g).

## 3. Results

### 3.1. Optical microscopy

In the optical microscopy analysis of the precursor material composed of 40% lignin and 60% PA11, several observations were made. In the untreated precursor Figure 1.a, variations in fiber diameters were evident both between individual fibers and within the same fiber. The diameters range between 70 to 120 µm, likely due to the production process, particularly during extrusion where swelling may occur. The uneven diameters within filaments can create challenges during the stabilization process. Variations in diameter can lead to non-uniform heat transfer and diffusion rates during stabilization, potentially resulting in inconsistent reactions and properties across the material. Additionally, the rough surface observed on the fibers can amplify these issues by providing more surface area for reaction, further complicating the stabilization process.

Upon chemical and thermal stabilization treatments, the treated fibers exhibited reduced diameters of about 20-30% as can be seen in Figure 1.b. This reduction in diameter is a common phenomenon observed during stabilization processes. The heat treatments facilitate the removal of volatile components and induce structural rearrangements, leading to shrinkage and densification of the precursor material. Therefore, it is expected to observe a decrease in fiber diameter after stabilization treatments.

Comparatively, precursors for carbon fibers derived from PAN (polyacrylonitrile) typically have smaller diameters of about a quarter of the diameter of the fiber considered for this work. Decrease in fiber diameter is known to increase the mechanical properties of carbon fibers [9]. This variation can be attributed to the differences in molecular structure and processing conditions between lignin-based and PAN-based precursors. PAN precursors offer advantages such as higher carbon yield and better mechanical properties due to their more uniform and controlled molecular structure. However, extruding precursors containing lignin presents challenges, as lignin is more complex and prone to degradation at high temperatures, making it difficult to reduce extrusion hole diameters. This technical limitation in reducing extrusion hole diameters imposes constraints on lignin-based precursor production and contributes to the observed differences in fiber diameters compared to PAN-based precursors.

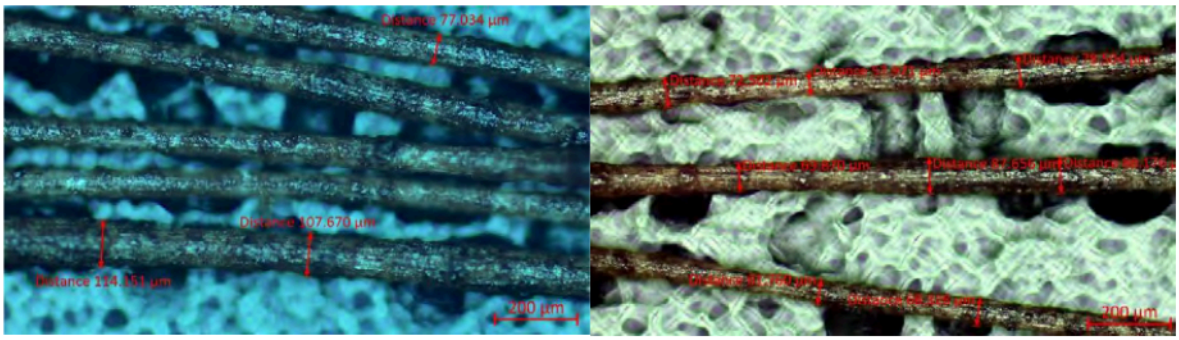


*Figure 1. Optical microscopy images: a) Pristine fiber; b) Fiber treated with chemical and thermal process.*

### 3.2. FT-IR

The Figure 2 show the FT-IR analysis performed on three samples. One spectrum is related to the untreated fiber, one to the fiber chemically treated with phthalic anhydride, and one to the fiber treated both chemically and thermally (as previously described). The spectroscopic pattern remained consistent across the samples, except for a notable peak rising at 800 $cm^{-1}$ in the spectrum of the chemically treated fiber, which became more pronounced in the spectrum of the fiber treated both chemically and thermally. This rising of a peak at 800 $cm^{-1}$ was due to the ortho substitution of aromatic compounds (indicating aromatic out-of-plane $\delta_{C\text{-}R}$), corresponding to the esterification of functionalities of lignin during the reaction with the phthalic anhydride [10]. Consequently, the lignin component act as an anchoring point within the fiber matrix, contributing to its stabilization through the formation of esteric linkages promoted by both the temperature and the oxidative atmosphere used.

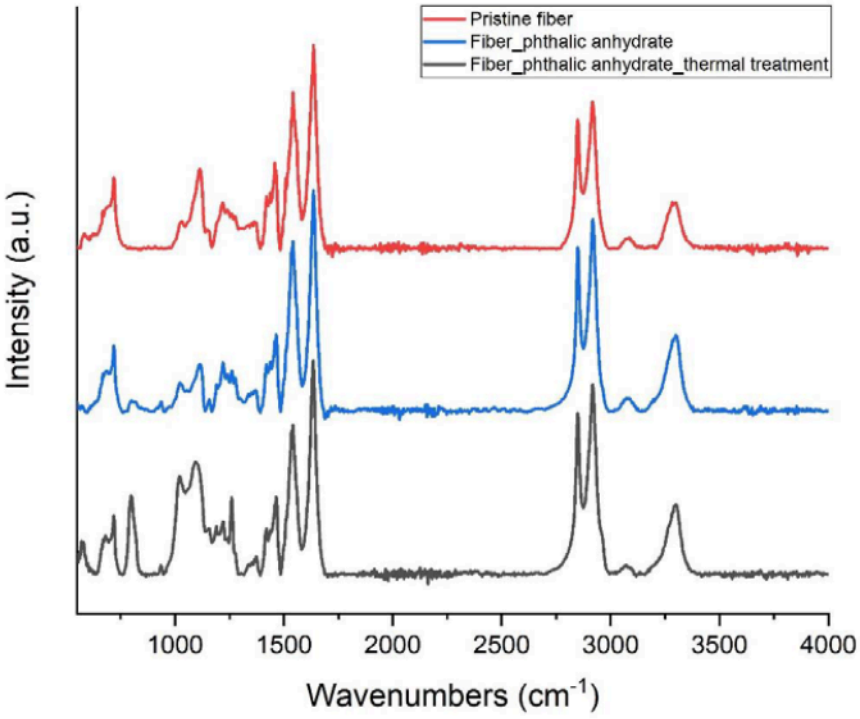


*Figure 2. FT-IR spectra of the fiber at each phase of the process.*

### 3.3. Thermal analysis

In the thermogravimetric analysis (TGA) showed in Figure 3 and Figure 4, two distinct weight loss profiles were observed for the untreated and chemically treated fibers. In the TGA curve of the untreated fiber, three mass losses were detected. The first onset at 247.8°C, accounting for about 7% mass loss, corresponds to the decomposition of labile functional groups, which could include aliphatic groups. These aliphatic groups may be present as side chains or as part of the polymer backbone and are susceptible to thermal degradation at relatively low temperatures. The second mass loss onset at 350°C, also contributing to about 7% of the total mass loss, may correspond to the degradation of additional aliphatic groups or other labile components. This further decomposition process could involve the breaking of weaker bonds within the polymer structure, leading to the release of volatile components and subsequent weight loss. The major weight loss, with an onset at 383.8°C and constituting 67.41% of the total mass loss, likely reflects the decomposition of polyamide (PA11) and the aromatic portion of lignin. Polyamide decomposition typically occurs at elevated temperatures, where the polymer chains break down into smaller molecular fragments. Similarly, the aromatic components of lignin are thermally stable but can undergo degradation at elevated temperatures, leading to the release of volatile by-products and carbonaceous residues. This significant loss reflects the decomposition of the polymer matrix, where the breaking of one bond may lead to the collapse of the entire structure.

In the TGA of the untreated fiber, the observed weight loss profiles can be attributed to various chemical processes occurring within the precursor material. The single mass loss peak observed with an onset at a higher temperature (417.8°C), accounting for an 81.55% mass loss, indicates significant thermal stability imparted by the cross-linking reaction. The cross-linking process involves the formation of covalent bonds between functional groups of lignin and PA11, resulting in the creation of branching points within the polymer matrix. The enhancement of cross-links improved the mechanical properties of the fiber by increasing its structural integrity and resistance to thermal degradation.

Furthermore, the absence of weight loss at 210°C indicates the successful removal of adsorbed phthalic anhydride, confirming the completion of the cross-linking reaction. This thorough washing ensures that any residual chemical species are effectively removed, leaving behind a stable cross-linked structure.

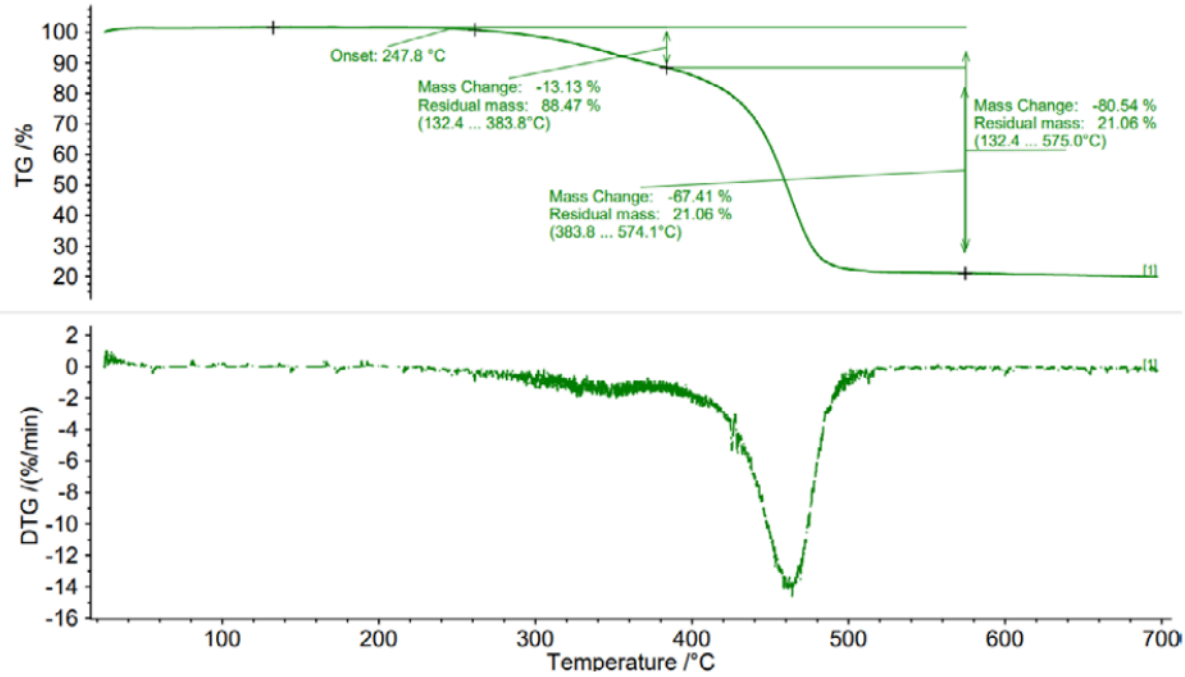


*Figure 3. TGA/DTG pristine fiber.*

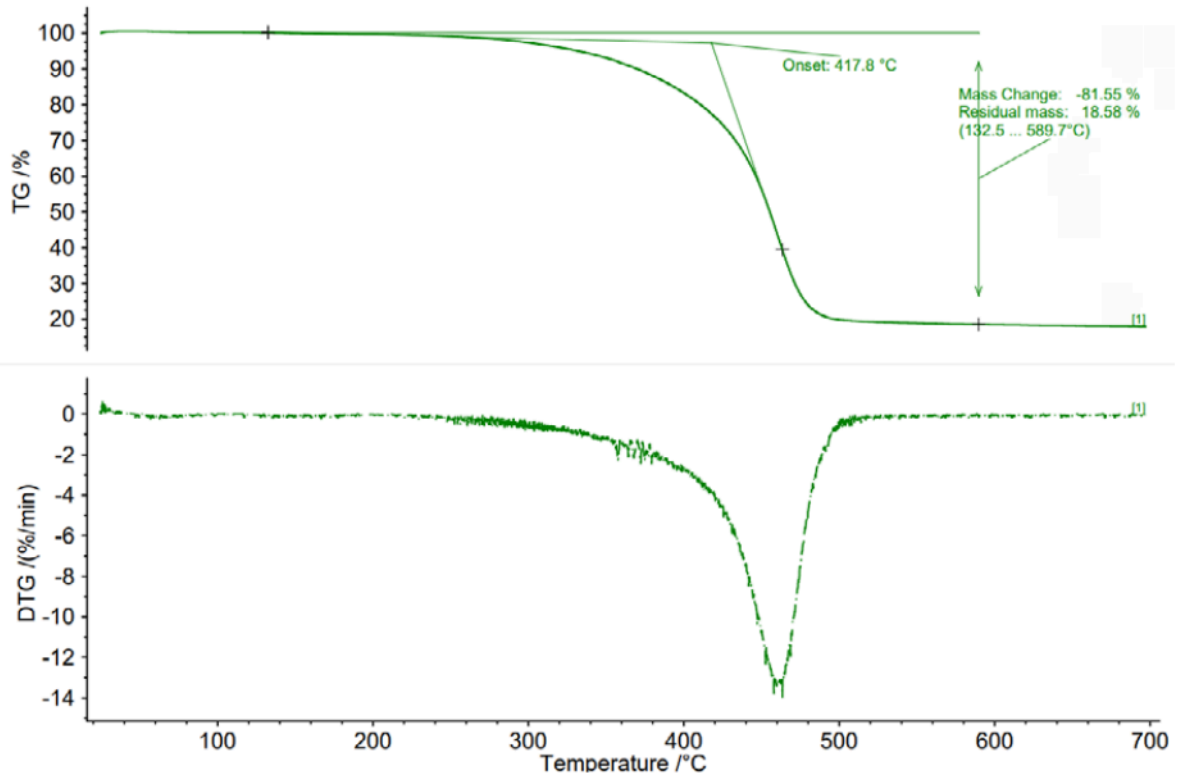


*Figure 4. TGA/DTG fiber treated with phthalic anhydrate.*

In the differential scanning calorimetry (DSC) analysis, the chemical and thermal treatments on the fibers were evaluated to understand their effect on thermal stabilization. In the untreated fiber, a low

glass transition temperature (Tg) around 37°C and a double melting peak were observed. The presence of two endothermic peaks is commonly reported for polyamide materials such as PA11 [11] and PA12 [12]. The onset of the first peak at 180°C and the second at 188°C corresponds to the melting of different crystalline phases of PA11. The smaller, less intense peak is attributed to the melting of less stable crystals formed during cold crystallization or the transformation of α-PA11 to γ-PA11, while the more intense peak corresponds to the melting of crystals in the γ phase.

In the DSC curve of the chemically and thermally treated fiber, the Tg disappeared, indicating a successful chemical pre-treatment. This phenomenon can be attributed to the successful cross-linking induced by the chemical treatment, which creates branching points within the polymer matrix. These branching points, formed through the breaking of PA11 chains and the creation of bridges between fibers, enhance mechanical properties while maintaining elasticity. Although endothermic peaks are still present in the chemically and thermally treated fiber, notably the first peak is almost disappeared. This suggests progress in stabilization, as the disappearance of these endothermic peaks indicates complete thermal stabilization.

## 4. Conclusions

Despite facing significant challenges inherent to the precursor material, including non-uniform diameters, a small number of filaments of about 24, and complexities in processing, the study has demonstrated the effectiveness of the chemical treatment with phthalic anhydride. It is noteworthy that while phthalic anhydride is typically employed for cross-linking lignin prior to fiber extrusion, its application directly to the fiber precursor in our study yielded successful results. This was evident through comprehensive analyses including FTIR and TGA, which confirmed the desired chemical modifications and thermal stability achieved. However, the presence of residual endothermic peaks in the DSC suggests that complete stabilization has not yet been achieved, indicating the need for extended thermal treatment durations to allow for further structural modifications. Overall, the preliminary results are promising, but further optimization of thermal treatment times may be necessary to achieve complete stabilization.

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