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FULL PAPER

Purification and Characterization of Colophony Extracted of *Pinus elliottii* (Engelm, var. *elliottii*)

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Abstract

This study reports the purification and characterization of the colophony. The method involves the step of water washing and solubilization of the extracted resin of *Pinus elliottii* Emgelm*, elliottii* variety on ethanol to the filtration for removal of solid residues (sand, leaves, pieces of the branch, etc.). After purification, the colophony and turpentine were separated using a soxhlet extractor. The thermal decomposition of colophony was investigated using thermogravimetric analysis-differential thermogravimetric-differential scanning calorimetry (TG-DTG-DSC). The resin was also characterized using the technique of infrared spectroscopy (ATR-FTIR). The TG curves revealed three decomposition steps, in which a total degradation occurred after 500 °C, indicating a good thermic stability. The FTIR spectrum showed bands in 1694 cm^{-1}, (stretch C=O) and 3362 cm^{-1} (stretch O-H) indicating the presence of carboxylic acid, have also been found bands corresponding to the aromatic ring. The presence of resinous acids can be confirmed.

Keywords: pine resin; turpentine; extraction; thermal decomposition

1. Introduction

Pinus is a fast growing, coniferous tree that is resistant to low temperatures and can grow on soil that is poor in nutrients and a great source of resin [1]. Pinus resin is a yellow/brown flammable viscous liquid with a strong odor. This material is produced by the living plant, is a viscous material, opaque, due to the presence of moisture and contains a certain amount of forest debris. Pinus resin is produced as a defense mechanism of the tree against herbivores and pathogens due to toxicity and adherent function [2].

The drainage involves a preparation of the tree, composed by a cut in the stem of the tree, application of a chemical compound to stimulate and maintain the flow of the resin and a material to collect the material. The depth of cut and stimulant component varies across countries. The drainage methods used in Brazil do not negatively affect the trunk quality, whose pine wood can be used while the resin process is stopped [3].

The resin is composed of a solid fraction, called a pitch or gum colophony, and a volatile part, known as turpentine. Colophony consists of diterpene monocarboxylic acids, the main one being abietic acid [2,3,4]. Turpentine is the volatile fraction of the pine resin and it is responsible for the characteristic smell of the same. It is widely used as a solvent for commercial paints. The problem then arises from the toxicity of organic solvents applied to paints that contribute to atmospheric pollution, affect the health of the painter, but also reduce the quality of the air present inside the building, damaging the health of users [5].

But there are countries that have been worrying about it for some time. Environmental protection agencies in the US, Canada, and the European Union have already put restrictions on the maximum volume of volatile organic

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compounds used to prevent environmental impact. These restrictions have had a major influence on product innovation in the ink industries, including in Brazil [5].

In the past, colophony was used with linseed oil to produce coatings that were used to varnish objects prior to the introduction of synthetic varnishes in the mid-1900 [6]. In particular, they were used to protect and decorate musical instruments in the 16th-18th centuries [7,8]. But it has also been used in furniture coatings for trestle and decorative arts [9, 10].

The main applications of colophony are in the production of synthetic rubber, adhesives, varnishes, paints, glue, tires, chewing gum, depilatory waxes, detergents, soaps, among others. Several papers related to the composition of colophony are found in the literature, however, despite the wide application, there are few thermal degradation studies found [1,2].

Currently, papers found in the literature show several applications of colophony such as the preparation of functionalized porous nano-γ-Al_2O_3 powders using colophony extract [6], as well as studies aimed at evaluating the influence of preparation processes on application properties of the flaxseed oil blend with colophony [11].

Thus, the objective of this work is to present a route of cleaning and purification of colophony, to use the vibrational spectroscopy technique to identify the main functional groups found in colophony and to present the study of the thermal behavior. The aim of this study is to understand the thermal behavior of the studied material, to improve its applications and know its properties

2. Material and Methods

2.1. Purification of Pinus resin and Extraction of Turpentine

The resin Pinus *elliottii* var. *elliottii* was provided *in natural* by producers from the Guarapuava region. To stimulate the tree to produce and excrete the resin, the producers usually apply a paste of H_2SO_4 in the cuts made in the stem of the trees, through which the resinous material is collected. Therefore, to remove this acid a rinse with distilled water under stirring was carried out. The wash water was changed until the solution reached pH 7. After the removal of all water, the resin was solubilized in fuel ethanol and thereafter vacuum filtered for the removal of impurities. Thereafter, the solvent was recovered through a rotary evaporation system.

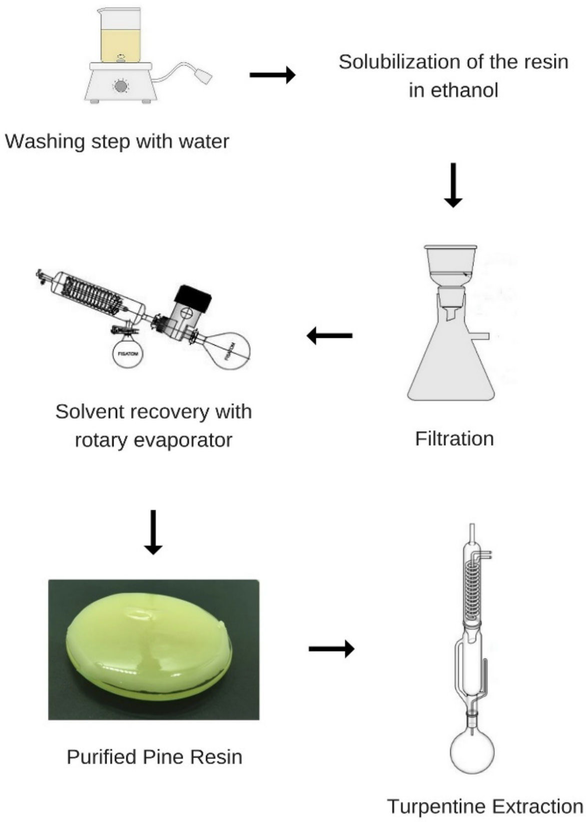

Figure 1. The scheme used to purify the pine resin and extract the turpentine.

For the extraction of turpentine a soxhlet was used, for each sample fraction, 200.0 mL of extraction solvent was added. The turpentine was extracted for a period of 6 hours and the percentage of turpentine collected on the resin was approximately 18% (m / m).

2.2. Characterization

FTIR spectra were obtained on an Alpha of Bruker equipped with a crystal ZnSe. An average of 32 scans with a resolution of 2 cm^{-1} over the range 4000-650 cm^{-1} was used to obtain the final spectrum. Universal attenuated total reflectance (uATR-FTIR) mode was used for a colophony. Thermal analysis curves (thermogravimetry, TG; differential thermogravimetry, DTG; and differential scanning calorimetry, DSC) for colophony were conducted on a simultaneous thermal analyzer NETZSCH. The samples were heated up from room temperature to 1000 °C at 10 °C.min^{-1}, under the N_2 atmosphere, with a flow rate of 50 mL.min^{-1}.

3. Results and Discussion

The colophony sample, after the purification process, showed solid material characteristics, the staining was like that of the sample before being purified. Turpentine, extracted from the *Pinus* resin, presented an oily, colorless appearance. Therefore, the route of cleaning and purification of rosin was an efficient alternative.

3.1. FTIR Analysis

In the infrared spectrum of the colophony (Figure 2) a band at 1694 cm^{-1} can be observed, a characteristic of bonding of carboxylic acids (νC=O) [11,12]. Another band pertaining to the functional group (-COOH) is found at 3362 cm^{-1} and refers to the stretching bond (νO-H). Also in all spectra are bands at 2928 and 2870 cm^{-1} of aliphatic C-H elongation [13,14]. In this way, the presence of diterpene carboxylic acids can be identified. Between 1100 and 600 cm^{-1}, there are bands of binding stretches (νC-C) related to the hydrocarbon chain of colophony.

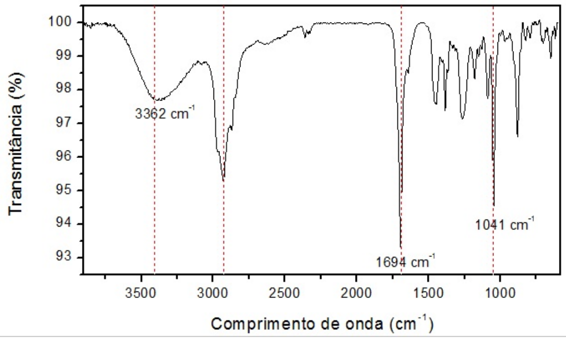

Figure 2. FTIR spectrum of colophony.

3.2. Study of thermal decomposition of colophony (TG/DSC)

Figure 3 shows the thermal degradation curves for resin. In the DTG curve is possible to observe an event three mass loss events, the first occurs between 25 °C and 150 °C, indicating a mass loss of 18.0% referring to the presence of water in the sample. At the peak at 120 °C located on the DSC curve, it can be stated that this event is endothermic and is related to the sample fusion. The second event started at 150 °C, extending up to 350 °C with a loss of mass of 70.0% and related to the decomposition of the organic material, characterized by an endothermic stage that could be observed in the DSC curve. At the end, from 350 °C, an event with mass loss of 12.0% occurred, characterizing as an endothermic stage, according to the DSC curve.

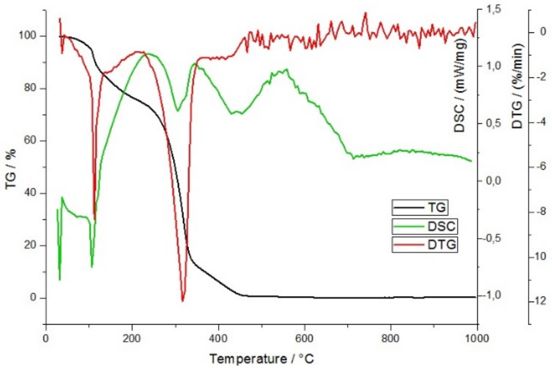

Figure 3. Thermal decomposition curves of colophony.

4. Conclusions

From the FTIR spectrum, it was possible to identify the functionality of resin, being composed of resinous acids, where the main ones are abietic acid and its derivatives, which are used in several sectors of the chemical and pharmaceutical industry, therefore, the purification and extraction methods were efficient. The thermal curves of the colophony showed good thermal stability, the total decomposition of the material is identified at approximately 450 °C, and the decomposition of the organic material starts after 150 °C. Three mass loss events were observed in the DTG curve, the first one referring to the loss of water from the material, while the latter two are related to the decomposition of the organic material. Both steps are described in the DSC curve as endothermic.

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