



## **Natural origin precursors for carbon fiber production**

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## Abstract

Carbon fibers are bundles of flexible, lightweight and thin filaments composed mostly by carbon atoms, high in tensile strength, that can be used in a wide range of high performance applications, such as in the aerospace and automotive industry, textiles and modern sports equipment.

Carbon fibers' raw materials are denominated precursors, being polyacrylonitrile (PAN) the most used one. Most carbon fiber precursors have fossil origin and due to oil price oscillations, environmental problems, and precursor cost, carbon fibers are considered expensive materials.

In the present work, to reduce the above-mentioned problems and, consequently, the cost of carbon fibers, a natural and sustainable source material, cardanol, was used in the production of two different compounds, a polymer (polycardanol) and a prepolymer (cardanol-based vinyl ester resin), which were investigated as precursors to produce more economically sustainable and more eco-friendly carbon fibers.

Both polycardanol and cardanol-based vinyl ester (VE) resin were characterized using several methods: Attenuated Total Reflectance – Fourier Transformed Infrared Spectroscopy (ATR-FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR), Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC).

Through these methods, it was possible to conclude that the synthesis of polycardanol was not as efficient as that of the prepolymer, making the latter a more promising material as a future carbon fiber precursor.

**Keywords:** carbon fibers; precursors; bioderived; PAN; cardanol; eco-friendly.



## Resumo

As fibras de carbono são feixes de filamentos flexíveis, leves e finos, compostos, principalmente, por átomos de carbono, com elevada resistência à tração, podendo ser utilizadas numa vasta gama de aplicações de elevado desempenho, como nas indústrias aeroespacial e automóvel, têxteis e equipamento desportivo.

A matéria-prima utilizada na sua produção é denominada precursor, sendo o poliácrlonitrilo (PAN) o mais utilizado. A maioria dos precursores de fibras de carbono são de origem fóssil e, devido a oscilações do preço do petróleo, problemas ambientais e custos dos precursores, as fibras de carbono são consideradas materiais dispendiosos.

Neste trabalho, de modo a reduzir os problemas supramencionados e, conseqüentemente, o custo das fibras de carbono, utilizou-se um material de origem natural e sustentável, o cardanol, na produção de dois compostos distintos, um polímero (policardanol) e um pré-polímero (resina vinil éster à base de cardanol), que foram estudados como potenciais precursores para produzir fibras de carbono mais sustentáveis e *eco-friendly*.

Tanto o policardanol como a resina foram caracterizados recorrendo a diversos métodos: Reflectância Total Atenuada – Espectroscopia de Infravermelho com Transformada de Fourier (ATR-FTIR), Espectroscopia por Ressonância Magnética Nuclear (RMN), Termogravimetria (TGA), Análise Térmica Diferencial (DTA) e Calorimetria Diferencial de Varrimento (DSC).

Através destes métodos, foi possível concluir que a síntese de policardanol não foi tão eficiente quanto a do pré-polímero, pelo que este último pode ser considerado como um material mais promissor como futuro precursor de fibra de carbono.

**Palavras-chave:** fibras de carbono; precursores; origem natural; PAN; cardanol; ecológico.





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## List of Acronyms

**AA** – Acrylic acid

**AN** – Acrylonitrile

**ATR** – Attenuated Total Reflectance

**BPA** – Bisphenol A

**CAGR** – Compound Annual Growth Rate

**CSNL** – Cashew nutshell liquid

**DGEBA** – Diglycidyl ether of bisphenol A

**DEPT** – Distortionless Enhancement of Polarization Transfer

**DSC** – Differential scanning calorimetry

**DTA** – Differential thermal analysis

**FTIR** – Fourier-Transformed Infrared Spectroscopy

**NMR** – Nuclear Magnetic Resonance Spectroscopy

**PAN** – Polyacrylonitrile

**RT** – Rotary evaporator

**T<sub>g</sub>** – Glass transition temperature

**TGA** – Thermogravimetric analysis

**TPP** – Triphenylphosphine

**VE** – Vinyl ester





# 1. Introduction

## 1.1 Thesis Scope and Motivation

FISIPE, S.A., is an European company that produces acrylic fibers and more recently carbon fiber precursors, and belongs, since 2012, to the German SGL Group, the largest European producer of carbon fibers [1].

Nowadays, almost everything is polymer-based. Polymers have a wide applicability range, from materials to produce clothing, cars or houses, to more sophisticated ends, such as medical supplies, electronic devices, etc. Most polymers are petrochemical products and, therefore, they suffer from the same problems that all petrochemical industries are subjected, namely the constant changes in oil prices and environmental problems.

Carbon fibers are polymers containing at least 92 wt. % carbon in their composition [2]. They are a flexible, lightweight and strong material used in a numerous specialized applications such as engineering materials, aerospace, high-performance vehicles, textiles, sporting equipment, etc, as presented in Figure 1 [3][4][5]. Their raw materials are organic polymers, known as precursors, which are, basically, composed by bundles of filaments. Each filament consists of long molecular chains held by carbon atoms [6]. The most common precursor used presently is polyacrylonitrile (PAN), which corresponds to around 90 % of the overall worldwide production of carbon fibers. It leads to the best quality carbon fibers. The other 10 % are related to the use of other precursors such as rayon (regenerated cellulose), pitch (petroleum or coal based) and more recently polyolefins (polyethylene and polypropylene), with known drawbacks [4][6].

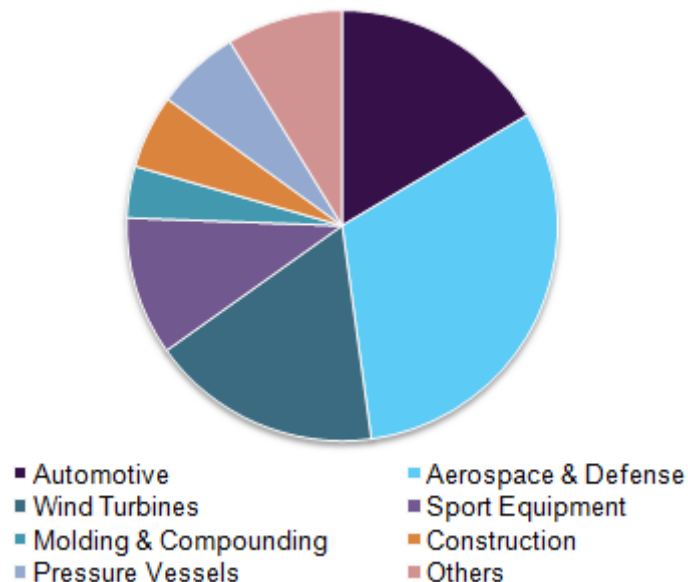
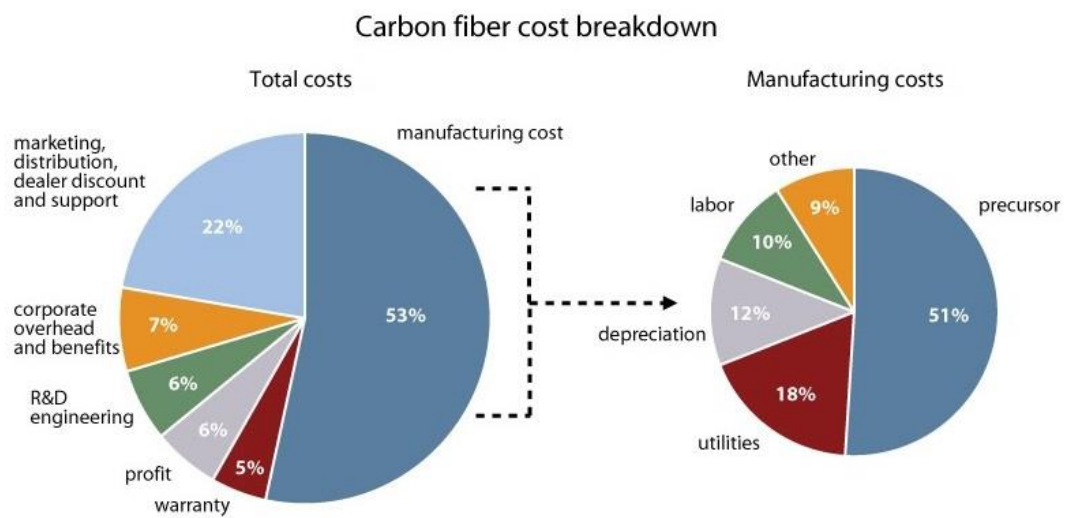


Figure 1 – Global carbon fiber market volume share by application, in percentage, in 2016 [5].

Presently, there is a trend towards increasing the use of carbon fibers in various industries, such as the automobile, aerospace and construction, replacing more traditional materials, due to some intrinsic advantages such as an excellent combination of superior mechanical properties, low density and high stability lightness, performance and superior strengths [7]. In 2015, the value of the global

carbon fiber market was USD 2.25 billion, and it is expected to grow at a compound annual growth rate (CAGR) of 10.9% from 2017 until 2025. The increasing use of carbon fibers, in Europe, North America and Asia, is directly related to the growth of industries, such as aerospace, wind energy and automobile, due to, not only the growth of these industries, but also due to the rapid economic development and industrialization in Asia, and due to the existence of some strict environmental regulations that emphasize the use of carbon-based composites [5][8].

Despite the expected growth, the high cost associated with the production (precursors cost represents 51 % of the manufacturing cost (Figure 2)), and the consequent market value of carbon fiber presents itself as a barrier to the spread of its use and to its larger scale production.



**Figure 2 – Carbon fiber cost breakdown (Adapted from [9]).**

As mentioned, due to oil price oscillations, environmental problems and precursor cost, carbon fibers are considered expensive materials, typically only used in specific and high-performance, high-added value materials. To reduce these problems and consequently the cost of carbon fibers, researchers have been trying to replace the fossil (petroleum-based) raw materials by natural, sustainable and renewable ones. These alternative precursors include lignin, glycerol, lignocellulosic sugars, etc.

This new generation of carbon fibers, produced with renewable and more eco-friendly precursors, will enable the reduction of the price of the fibers, making them accessible, in an economically sustainable way, for application in various industries, thus opening doors to new products and applications in several areas, while allows the reduction of the environmental (and sustainability) problems associated with the use of petroleum-based products.

## 1.2 Objectives

The overall goal of the present work is to develop new bio-derived materials and study their feasibility to produce carbon fiber precursors from natural resources. To achieve this main goal, a polymer and a prepolymer derived from cashew nut shell liquid waste will be synthesized, characterized and its potential as carbon fiber precursors evaluated.

### **1.3 Thesis Outline**

There are six main chapters in this thesis. In chapter 1, the main problems associated with carbon fibers production are discussed, as well as the reasons behind the move from petroleum derived precursors to those of natural origin.

In chapter 2, a literature review about carbon fibers and its precursors is presented. First, an overall contextualization is made concerning the carbon fibers, namely related to the different manufacturing processes, as well as the properties that carbon fibers possess. Then, the main carbon fiber precursors are presented, as well as the main solutions for carbon fiber precursors, based on natural bio-resources as substitutes for petroleum-based precursors. Since the main objective of this thesis is the development (feasibility study) of precursors of sustainable and renewable origin, a briefing about cardanol-based prepolymers and polymers, as well as their potential use as precursors, is carried out. Finally, the polymerization techniques used in this work are explained.

Chapter 3 consists of the description of the materials and experimental methods employed in this thesis, which includes a brief introduction about each characterization method used.

The results obtained on the achieved samples of polycardanol and cardanol-based vinyl ester (VE) resin, are reported and discussed in chapter 4.

Finally, in chapters 5 and 6, the main conclusions and some guidelines for future work are presented, respectively.



## **2. Literature Review**

### **2.1 Carbon fiber**

Carbon fibers are composed by bundles of thin, strong crystalline filaments of carbon and they are typically used as reinforcement materials in high added-value applications. They are thinner than a filament of human hair, have higher stiffness, tensile strength and chemical resistance, lower weight to strength ratio and lower thermal expansion [10]. Besides these characteristics, carbon fibers are tolerant to excessive heat [10] and they are around 70 % lighter than steel (used in car components) [11] and around 40 % lighter than aluminum [11]. By using carbon fibers (normally in the form of fiber reinforced polymer matrix composites), it would be possible to reduce passenger car weight by 50 %, which would reduce the gas emissions, improving fuel efficiency in 35 % [10].

The invention of carbon fibers is attributed to Thomas Edison, in 1879, when he used cotton threads and, later, bamboo strips, cellulose-based materials (natural polymer), as filaments for the first incandescent light bulbs. These natural materials were shaped and then heated at high temperatures in a controlled atmosphere (pyrolysis) obtaining, therefore, an exact sized and shaped material, with the same chemical composition of the original material. Edison verified that this resulting filament was fire resistant and capable of withstanding the intense heat required for incandescence. Despite these characteristics, the carbon filaments in electric lightbulbs were considered inefficient and later replaced by tungsten wire [3][12].

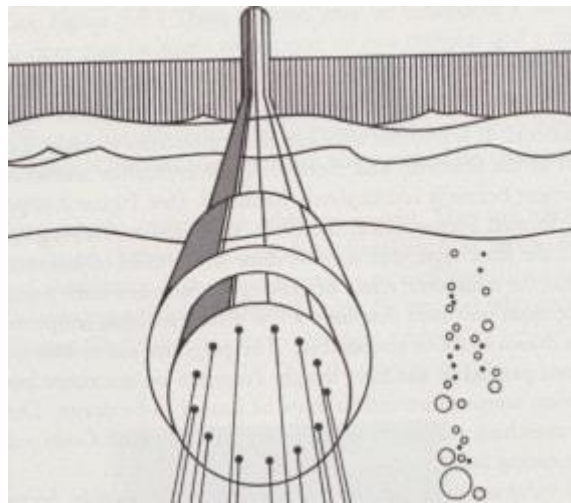
Later, in 1959 and 1962, two manufacturing processes using rayon and PAN as precursors were developed. In 1963, the pitch-based carbon fiber was invented [3]. Since the 1960s until today many precursor materials to produce carbon fibers, such as biomass-based precursors, have been investigated. By 1980, the overall carbon fiber demand grew due mainly to the aerospace industry and, until that time, pitch was the preferred raw material, because of its price and higher char yield, when compared to the other precursors. In the 1980s, PAN started to become the most used precursor for carbon fibers due to the higher processing costs that producing a spinnable pitch requires. Rayon, despite having a lower cost as a raw material, was and still is not as widely used as PAN or pitch. This is mainly due to its inferior properties and low char yield (20 – 25 %) after carbonization which result in a higher overall cost [13].

#### **2.1.1 Carbon fiber synthesis**

Even though different precursors produce carbon fibers with different properties and require different processing conditions, the general production process is similar. First, the precursor is thermally stabilized (oxidation in air) at 200 – 400 °C, being this step critical to obtain a high-quality carbon fiber. Long residence times (1 to 2 hours) are required to ensure conversion without runaway reactions and filaments fusion or breakage. These stabilized fibers are then carbonized in two steps, being subjected to a treatment at high temperatures (around 1000 °C in low temperature carbonization and ~2000 °C in high temperature carbonization) carried out in an inert atmosphere to remove non-carbon elements, such as oxygen or hydrogen. The carbonized fibers can be graphitized at higher temperatures (around 3000 °C) to improve the properties of the fibers, in particular to achieve a higher carbon content and a higher Young's modulus. These high modulus carbon fibers (also called graphite fibers) are speciality

products for aerospace applications. The last step before spooling and packaging is the surface treatment, where the carbon fiber surfaces are electrochemically treated to increase the chemical compatibility with the composite matrix and ultimately increase the composite mechanical properties [3][14].

To synthesize a fiber, first it is necessary to convert the precursor (polymer) into a liquid or semiliquid state, either by being heated until molten or by being dissolved in a solvent [15]. The resulting liquid (viscous liquid) is then extruded using a spinneret (Figure 3). This device has a set of small holes, through which the liquid passes and then emerges, being converted into solid filaments. The process of extrusion and the filament formation is called spinning. There are several spinning techniques to produce fibers, such as solution (wet or dry) spinning, melt spinning, dry-jet spinning and emulsion spinning [16].



**Figure 3 – Spinneret [17].**

The solution spinning process (Figure 4) is, usually, used when the polymers are thermosets (e.g. non-thermoplastic cellulose) and it includes the wet and the dry spinning. It started to be used industrially in the 19<sup>th</sup> century, being this the oldest fiber production method [17].

During the wet spinning process, the spinneret is generally submerged in the spin bath, into which the filaments are extruded. The solvent diffuses out of the extrudate into the bath, and a non-solvent (usually water) diffuses from the bath into the extrudate. The polymer precipitates and the filaments are formed [16][17]. This is the technique currently employed at FISIFE. In the dry spinning method, the polymer is dissolved in a solvent and the resulting solution passes through the spinneret, allowing the fibers to be extruded. As the fibers emerge through the spinneret, the solvent is evaporated with hot air. With the wet spinning, it is possible to spin a large number of fiber filaments at a time, because a single spinneret may have thousands of holes. The emerging fibers can be spun at rates slow enough to turn possible the use of larger processing equipment, such as the spin bath. On the other side, the dry spinning process has a much higher spinning rate, but less fibers are extruded at a time, in order to achieve an adequate solvent removal and drying of the fibers. For these reasons, wet spinning has a higher productivity and is highly economical, when compared to dry spinning. The latter is only being used for the production of special fibers that cannot be spun using a different method, such as spandex [16].

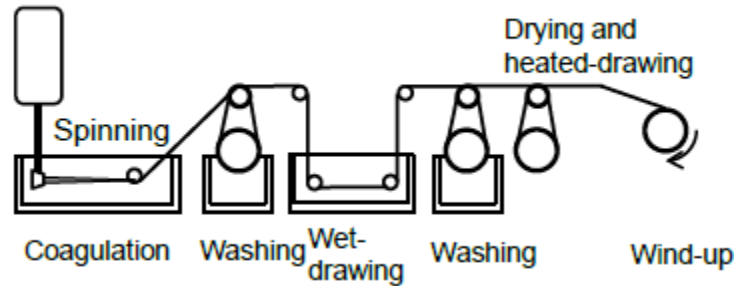


Figure 4 – Solution spinning process (Adapted from [18]).

The melt spinning process (Figure 5) is used when the polymers are thermoplastic synthetics (polymers that get soft and melt when heated), such as nylon or polyester [17]. In this process, the polymer granules are melted and then extruded through a spinneret into a spinning tower, where the molten polymer is going to be solidified using cold air. When compared to the other spinning methods, the melt spinning one is the most economical, due to the nonexistence of solvent to recover and because the spinning rates are higher [16].

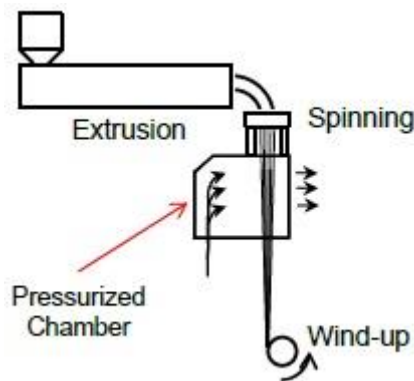


Figure 5 – Melt spinning process (Adapted from [18]).

The other two methods are only used in specific cases, such as when the solutions have a very high solid content (dry-jet spinning) or if it is a non-melting or insoluble polymer [16].

### 2.1.2 Carbon fiber properties

The properties of the carbon fibers depend on the structure of the fibers. In general, carbon fibers have low density, high tensile modulus and strength, low thermal expansion coefficient, thermal stability in the absence of oxygen over 3000 °C, excellent creep resistance, chemical stability (particularly in strong acids), biocompatibility, high thermal conductivity and low electrical resistivity [2].

According to their mechanical properties, carbon fibers can be classified into different types: ultra-high modulus (UHM) (>500 GPa), high modulus (HM) (>300 GPa), intermediate modulus (IM) (>200 GPa) and high tensile strength type (HT) (>4 GPa) [3][19].

## 2.2 Carbon fiber precursors

### 2.2.1 PAN – based precursors

As mentioned before, PAN is the most used precursor to produce carbon fibers. It is obtained through the addition polymerization process of acrylonitrile (AN), either using the solution or suspension polymerization [10]. To produce carbon fibers from PAN-based precursor, the steps presented in Figure 6 are the typical ones, being the usual carbon yield around 50-60 wt. % [3]. The manufacturing process of carbon fibers from PAN-based precursors in FISIFE is demonstrated in Figure 7 and the precursors development set-up in Figure 8. Although being possible to polymerize AN, and making fibers from it, according to the several processes explained before (Section 2.1.1), PAN-based copolymers are currently employed for facilitating the process and obtaining better quality fibers. Solution and suspension polymerizations are currently the most used to prepare PAN-based copolymers [20].

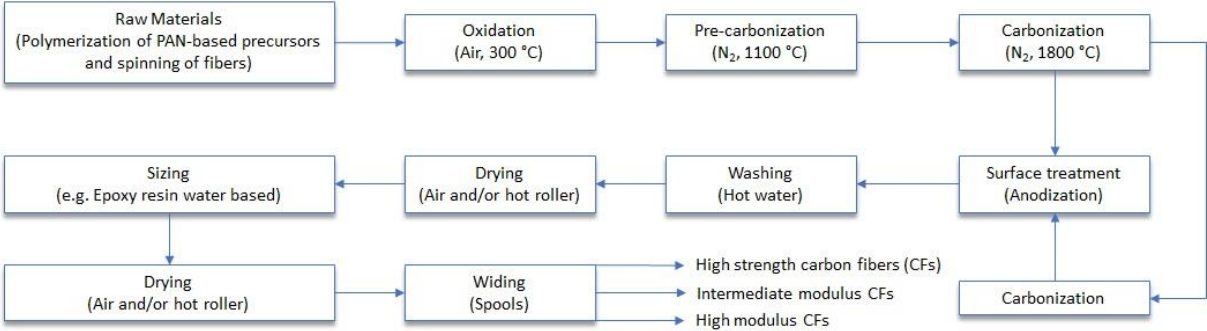
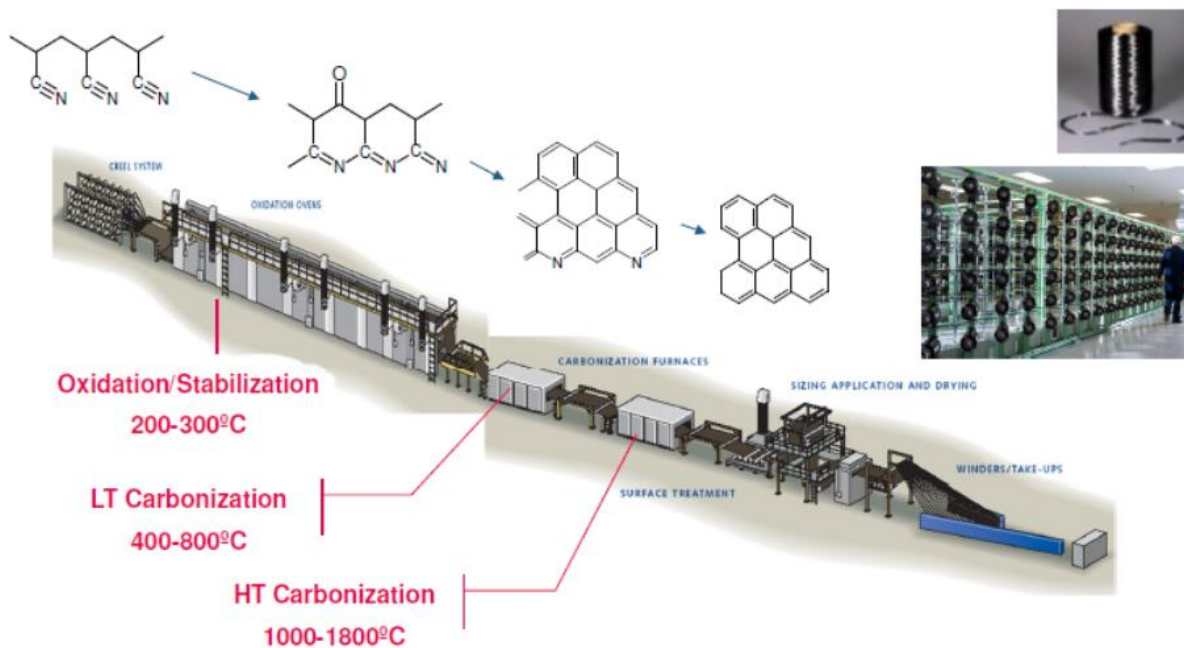


Figure 6 – Manufacturing process of carbon fibers from PAN-based precursor (Adapted from [3]).



Figure 7 – FISIFE's manufacturing process of carbon fibers from PAN-based precursor [21].





**Figure 8 – Carbon fiber precursors development in FISIFE [21].**

Usually, for the carbon fiber manufacture, PAN is used with a comonomer, because it is difficult to process the homopolymer (polymer composed of identical monomer units [22]) PAN into a carbon fiber, due to the rapid evolution of heat during the reaction process (exothermic reaction). The use of comonomers may lead to improvements in the stabilization process, because they will act as a plasticizer and they will break up the structure, reducing the intermolecular interactions, so that the polymer solubility in the spinning solvent improves, resulting in better orientation and better mechanical properties of the precursor and the resultant carbon fibers. These comonomers should be used in minimum quantities, due to the effect that they may cause in the cyclization step, in the production process of carbon fibers [3]. Usually, the PAN-based copolymers contain a maximum of 5 mol % of the comonomer [20]. There are several compounds that can be used as comonomers, being the most effective ones the itaconic, methacrylic and acrylic acids and acrylamide, due to the presence of carboxylic groups, which facilitate the cyclization reaction in the stabilization step [3][14]. In order to obtain high-performance fibers, with the properties wanted, the selection of the monomers, the composition of the precursor polymer, molecular weights, molecular-weight distribution and spinning, drawing, stabilization and carbonization parameters are really important aspects and must be taken into account [20].

The first PAN-based fibers were developed for use in the textile industry, in the 1940s, by DuPont Company. Since then, several studies have been carried out, e.g. those by Shindo, in 1959. He studied the carbonization and graphitization of the fibers, in particular the importance of an oxidative heat treatment step before the carbonization, so the processing time could be reduced and the carbon yield improved [3][23][24].

Since Shindo's work, several researchers have been studying the use of PAN as a carbon fiber precursor, and several changes have been made in the production processes, with the aim of obtaining

fibers with better properties, more sustainable and more economically viable, which have induced an evolution in this field.

## **2.2.2 Pitch – based precursors**

The natural pitches are obtained due to the refining of petroleum and destructive distillation of coal, being, these ones, the main pitches used as precursor for carbon fiber production [3]. The synthetic pitches are produced by pyrolysis of synthetic polymers, such as polyvinyl chloride (PVC) [3][19]. Comparing both coal and petroleum pitch, the latter is preferred despite being less aromatic, because coal pitch has a much higher benzene and quinoline-insoluble content, which usually means that the solid content is high. During the process of formation of the fiber, this solid content can accelerate coke formation, due to temperature change, which can lead to fiber breakage [19][2].

When compared to PAN, pitch has a lower material cost, higher char yield and higher degree of orientation, but the processing costs to achieve high-performance carbon fibers are higher, due mainly to pitch purification, mesophase formation and fiber spinning [3][14].

## **2.2.3 Rayon – based precursors**

Rayon is an artificial fiber composed by cellulose, mainly from natural sources, like cotton. It was originally created to substitute silk and may, therefore, be referred to as artificial silk [15]. It is denominated a semi-synthetic fiber, because it has a long chain polymer structure with natural origin and is only modified and degraded in part by chemical processes [25]. During the manufacture process of these carbon fibers, the cellulose is dissolved chemically (wet spinning process) and then is regenerated in an acid solution [26]. The cellulose fiber precursors used have high thermal conductivity, high purity, mechanical flexibility and low cost, allowing to form strong carbon fibers. Examples of these precursors are viscose, cuprammonium rayon and saponified cellulose acetate rayon [3]. Despite being originated from cellulose, which is a renewable resource and the most abundant natural one, the produced carbon fibers have inferior properties when compared with the ones produced using PAN or pitch [13], being this the main reason why rayon is not the main carbon fiber precursor used.

## **2.2.4 Natural bio-resources**

As mentioned throughout this thesis, the concern about the environment has been increasing, being necessary to explore new sustainable, economical and renewable alternatives to petroleum-based materials. Lignin has been the main alternative precursor studied, with the purpose of producing more eco-friendly carbon fibers.

### **2.2.4.1 Lignin – based precursor**

Lignin (Figure 9 and Figure 10), apart from cellulose, is the second most abundant renewable resource and it is usually obtained as a by-product from pulp and paper industries [27]. It is presented as a good substitute material for PAN, the main precursor of carbon fibers, since it has a high carbon content (60 %), due to its structure composed by phenyl propane groups, it exists in abundance in nature

and presents a low cost [28][29]. Despite all these advantages, lignin has several disadvantages, being the major one the fact that it is difficult to recover it in a clean, pure form [29].



Figure 9 – Raw lignin [30].

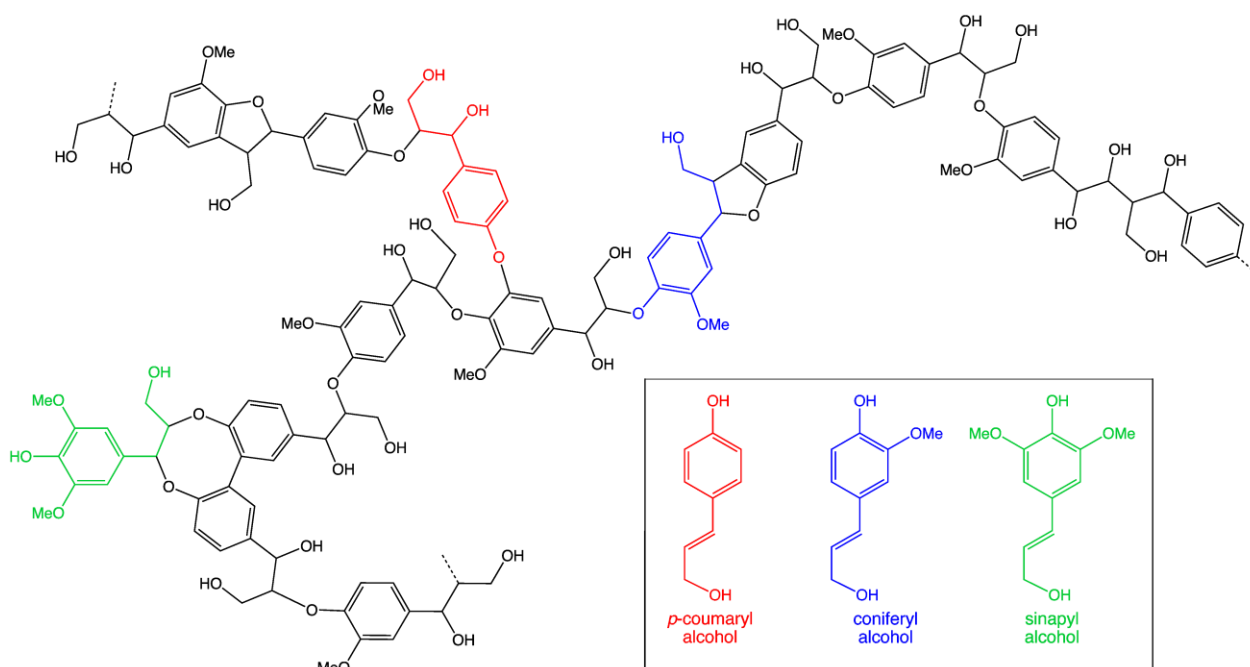


Figure 10 – Schematic representation of lignin's structure and its structural units [31].

Studies of lignin as a carbon fiber precursor started in 1969, when Otani et al. described several methods of producing fibers from different types of lignin (hardwood Kraft lignin, softwood Kraft lignin and alkali softwood lignin) by using both dry-spinning and melt-spinning methods, and their conversion into carbon fiber, graphite fiber and activated carbon fiber [32][33]. The first commercial lignin-based carbon fibers, denominated Kayacarbon, were developed in the 1960s, in Japan. These fibers were obtained from thiolignin, alkali lignin and liginosulfonates, using polyvinyl alcohol as plasticizer and the dry-spinning method using sodium hydroxide aqueous solution as solvent. The poor mechanical properties and the fact that the other carbon fiber precursors developed more rapidly, at a lower cost and with better mechanical properties, made the project of the Kayacarbon fibers to be abandoned [32][33].

During the 1990s, some researchers developed several studies related to lignin-based carbon fibers, focusing their work on the melt spinning process, since it is simpler and cheaper than the wet or dry spinning processes. The melt spinning process requires that lignin has a certain rheology, being determined by the chemical structure and level of purity. Since lignin can come from different sources of biomass (hardwood, softwood and grasses) and different methods of extraction (Kraft, Organosolv, steam explosion), it is possible to find lignin with different levels of purity and various chemical structures. This means that different biomass sources will lead to lignin with different ratios of monomer units and therefore, depending on the extraction method, lignin will have different levels of fragmentation and degradation, which will affect molecular weight, functional groups, condensation, intermolecular linkages, types and ratios of monomers and, consequently, will lead to variations at the level of fiber precursor and resulting carbon fiber properties [33][34][35].

These initial studies served as base for several strategies that have been developed over the years to improve the use of lignin as a precursor, among which lignin purification and fractionation, chemical and thermal modifications of lignin, polymer blending and fillers [34].

### 2.3 Cardanol-based prepolymer and polymers

Cashew nut shell liquid (CNSL) is a by-product of the cashew nut industry, constituted mainly by phenolic compounds, with a long side chain substitution at the meta position, such as anacardic acid, cardol, cardanol and 2-methylcardol (Figure 11).

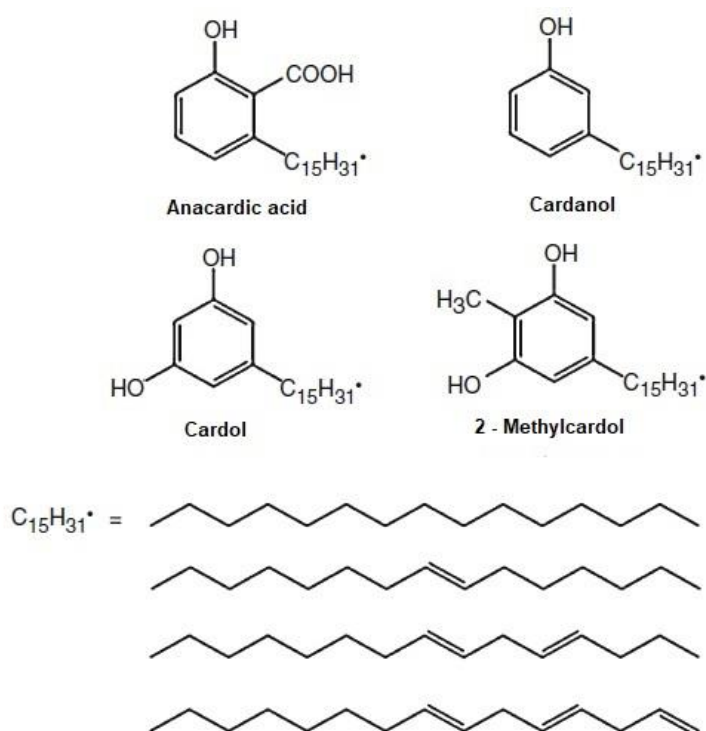


Figure 11 – CNSL main components (Adapted from [36]).

According to the Food and Agriculture Organization of the United Nations [37], between 1994 and 2014, the global production of cashew nut increased since 1,174,348 to 3,713,467 tonnes/year, corresponding to an increase of more than 300 %, as presented in Figure 12 [37], confirming that the

worldwide production of cashew nuts is growing. The major producers, between 1994 and 2014, were Vietnam, India, Nigeria, Côte d'Ivoire and Brazil, as visible in Figure 13 [37]. Due to being a cheap agricultural by-product of renewable resources and widely available, CNSL is a good substitute to petroleum derived phenols, and can be used as a raw material in a wide range of applications, for example, surface coatings, paints and primers, additives, resin synthesis and polymers [36][38][39].

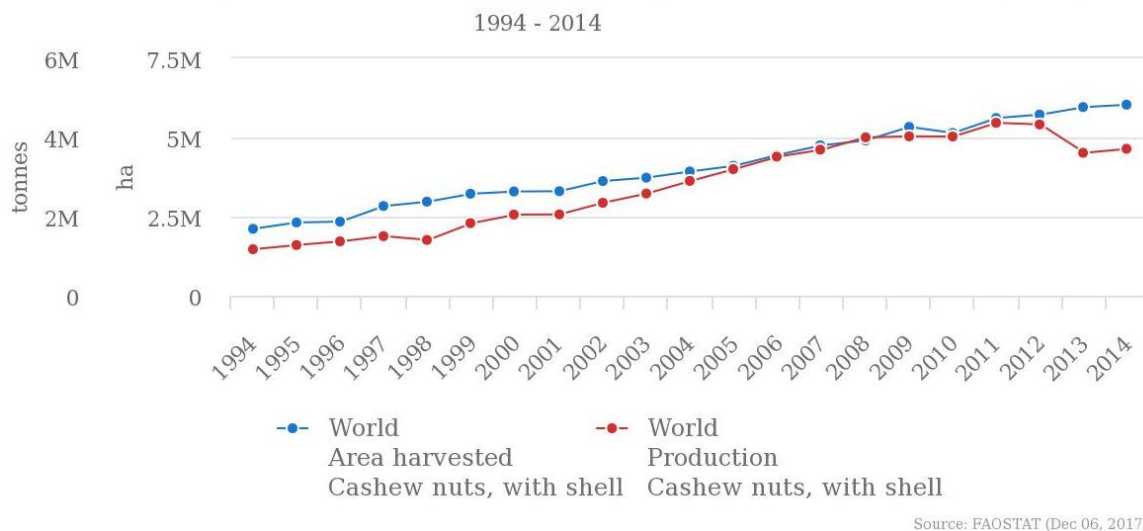


Figure 12 – World area harvested and production of cashew nuts, between 1994 and 2014 [37].

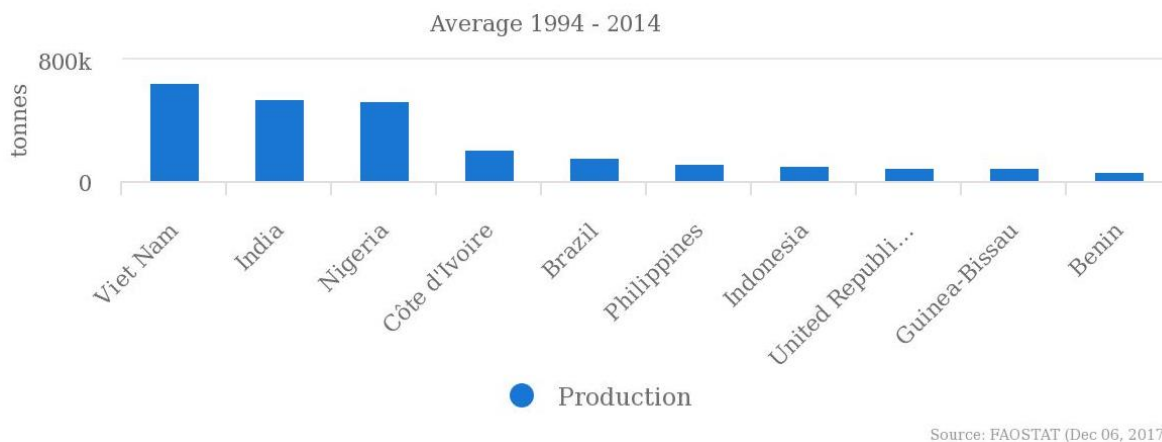
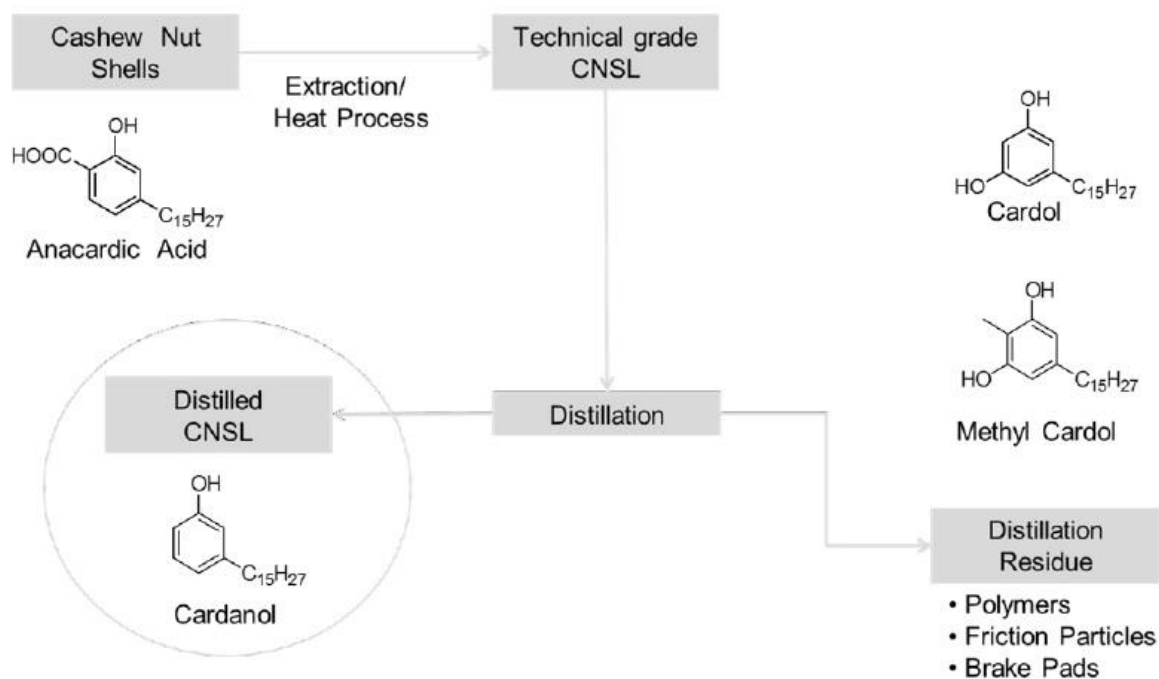


Figure 13 – Top 10 producers of cashew nuts, between 1994 and 2014 [37].

CNSL is heat treated, which induces the partial decarboxylation of anacardic acid, and then purified through distillation, resulting in an industrial grade cardanol, as shown in Figure 14 [40][41]. Cardanol can be used as a raw material for the production of polymers, either by using a step-growth polymerization mechanism (condensation), through the aromatic ring, or by using a chain polymerization mechanism (addition) through the unsaturations of the cardanol side chain ( $C_{15}H_{31}^*$ ). Cardanol's step-growth polymerization can be performed through reactions with OH groups, or with electrophiles, such as aldehydes (formaldehyde), while cardanol chain polymerization can be performed by ionic initiation opening double bond [42].



**Figure 14 – Cashew nut shell liquid technology (Adapted from [41]).**

As cardanol is the major component of CNSL, its use in resin production is of high interest. The cardanol-based resins can be epoxy, phenolic, vinyl, etc [36][40].

Epoxy resins are thermosetting materials (polymers that once cured cannot be melted or remolded, and that are resistant to solvents [43].) for which the precursors contain at least one epoxy function, that is highly reactive. At the present time, around 90 % of the world's production of epoxy resin is based on the reaction of Bisphenol A (BPA) with epichlorohydrin, obtaining DGEBA resin [44]. This type of resin can be used in a wide range of applications, due to its exceptional properties. However, there has been a growing concern related with the utilization of BPA in polymers, in addition to its increased cost, leading to a higher cost of the epoxy resin, which has been concerning the industry and the customers. Thus, the utilization of natural and renewable materials to synthesize epoxy resins is under development [45]. Cardanol-based epoxy resins can be used as protective coating materials, auto primers, linings for cans, drums and pipes, potting and encapsulation of electrical and electronic components, and in electrical laminates. These epoxy resins synthesized with cardanol were claimed to have superior characteristics than the regular ones [46].

As for phenolic resins, they are typically prepared through the reaction of formaldehyde with phenol. These resins can be synthesized under both alkaline or acidic conditions. If it is an alkaline catalyst, the resin prepared is named Resol and has a formaldehyde/phenol ratio higher than 1. If, on the other hand, it is an acidic catalyst, the resin prepared is named Novolac and the formaldehyde/phenol ratio is between 0,75 and 0,85 [44][47][48]. With the purpose of increasing the eco-friendly profile of phenolic resins and to enhance their properties and performance, researchers have been studying the partial, and to some extent, total substitution of phenol by bio-based phenolic compounds, such as cardanol [47]. When compared with the regular phenolic resins, cardanol-based resins have better flexibility, due to the internal plasticizing effect of the long chain, which leads to a

better processing capacity. In addition, cardanol-based resins possess other valuable characteristics, such as the existence of the side chain, which provides the hydrophobic behavior to the resin, heat and electrical resistance, antimicrobial properties, high-resistance to acids and alkalis, etc. However, in some structural applications, cardanol-based resins have lower tensile strength than conventional phenolic resins, which is thought to be due to the steric hindrance, caused by the side chain, and due to the reduced intermolecular interactions between the main and side chains. To overcome these problems, natural fibers have been added to cardanol-based resins, such as ramie, flax or jute [44]. More recently, researchers have been reporting new studies with modified phenolic resins, with synthesis of phenolic resins using cardanol and a different compound (such as bismaleimide or maleic anhydride) or a different catalyst (for example, para-toluenesulfonic acid). All these modifications on the synthesis have resulted in improved mechanical properties of the phenolic resins [44][46].

Vinyl ester resins are one of the most important classes of thermosetting polymers, combining the chemical, mechanical and thermal properties of epoxy resins with the rapid cure of unsaturated polyester resins [49]. The conventional vinyl ester resins are prepared by the reaction of DGEBA epoxy resin with methacrylic acid, and are used in a wide number of applications, such as surface coatings, adhesives and composites. Cardanol is, among the renewable resources, used to prepare thermosetting polymers [50]. The use of cardanol or other renewable resource might reduce the use of harmful chemicals, such as styrene, during curing of the vinyl ester resins. Besides this fact, cardanol can improve the mechanical properties of the resin, producing more eco-friendly polymers, and lowering its cost [49].

As mentioned, the use of cardanol in resin production is of high interest, not only because of being a natural bio-resource, but also due to the improvement that causes in the mechanical properties of the resins. Because of these facts, it is believed that cardanol is a potential substitute for petroleum-based carbon fiber precursors.

So, in this thesis, cardanol is going to be explored as a functional bio-derived molecule, to produce a prepolymer (cardanol-based vinyl ester resin) and a polymer (polycardanol) dedicated to be carbon fiber precursors. While polycardanol could potentially be mixed with PAN to obtain carbon fiber, the cardanol-based vinyl ester resin, or prepolymer, is a kind of bio-based aromatic building block for further free radical polymerization with acrylonitrile, forming a co-polymer.

## **2.4 Polymerization techniques used**

Carbon fiber precursors are polymers, or more typically copolymers, most of the times of synthetic origin. According to the polymerization mechanism, synthesized polymers are classified into addition polymers (reaction between the monomers) or condensation polymers (reaction between two functional groups to form a different functional group, with loss of a small molecule) [51][52]. The condensation term has been replaced by step-growth (only one type of reaction is involved in the synthesis of the polymer and the reaction proceeds step by step) and the addition term by chain-growth (polymer is formed through a chain reaction, wherein growth proceeds only by reaction between the monomers and the reactive site of the polymer chain). With this new classification, it is possible to

include polymers that are synthesized according to a step-reaction mechanism without the elimination of small molecules (H<sub>2</sub>O, HCl, etc) [51][53].

During the 1940s and 1950s, researchers discovered an important new type of chain-growth polymerization, the free radical. Free radical polymerization includes three major steps: initiation (decomposition of initiator molecules, in order to form very active radicals, that can initiate a new polymer chain), propagation (addition reaction that creates the polymer chain through a series of fast steps of monomer addition over the propagating radical) and termination (combination of a polymer chain radical with the initiator radical or with another macro radical) [51][52].

In this thesis, both the prepolymer and the polycardanol were synthesized through a step-growth polymerization. Despite being the same type of polymerization, there are some differences. The major difference between both is that, for the synthesis of polycardanol, the monomer and the structural unit are identical (self-polymerization), with the polymerization being performed between OH groups, and in the other polymerization, the monomer reacts with acrylic acid, in the presence of an inhibitor, to prevent self-polymerization [50].



### 3. Materials and Experimental methods

#### 3.1 Materials

Cardanol NX-9001 and epoxidized cardanol NC-514 (EEW=490 g/eq [54]) were obtained from Cardolite Corporation and used as supplied. Sodium hydroxide (NaOH) (min. 99 %) was obtained from Riedel-de-Haën and used as received. Triphenylphosphine (TPP) (99 %) and hydroquinone ( $\geq 99$  %) were purchased from Sigma-Aldrich and used as supplied. Acrylic acid (AA), sodium chloride (NaCl) (min. 99.5 %) and potassium carbonate ( $K_2CO_3$ ) (min. 99 %) were obtained from Merck and used as received.

#### 3.2 Experimental methods

##### 3.2.1 Synthesis of prepolymer cardanol-based VE resin

The preparation method of the vinyl ester prepolymer resin was adapted from reference [55], being the reaction scheme for the synthesis represented in Figure 15. The experimental set-up is presented in Figure 16. Around 20 g (0,035 mol) of epoxidized cardanol were mixed with 11 g (0,15 mol) of AA, hydroquinone (0,25 % by weight of the resin) and TPP (1 % by weight of the resin) in a 3-neck round bottom flask at 80 °C and kept under mechanical stirring (175 rpm) for about 12 h. To remove the unreacted AA, the obtained prepolymer was dissolved in chloroform, treated with  $K_2CO_3$  and stirred for 2 h at 30 °C. The AA in the salt form was extracted with water (decantation) and the chloroform was evaporated under vacuum in a rotary evaporator at RT.

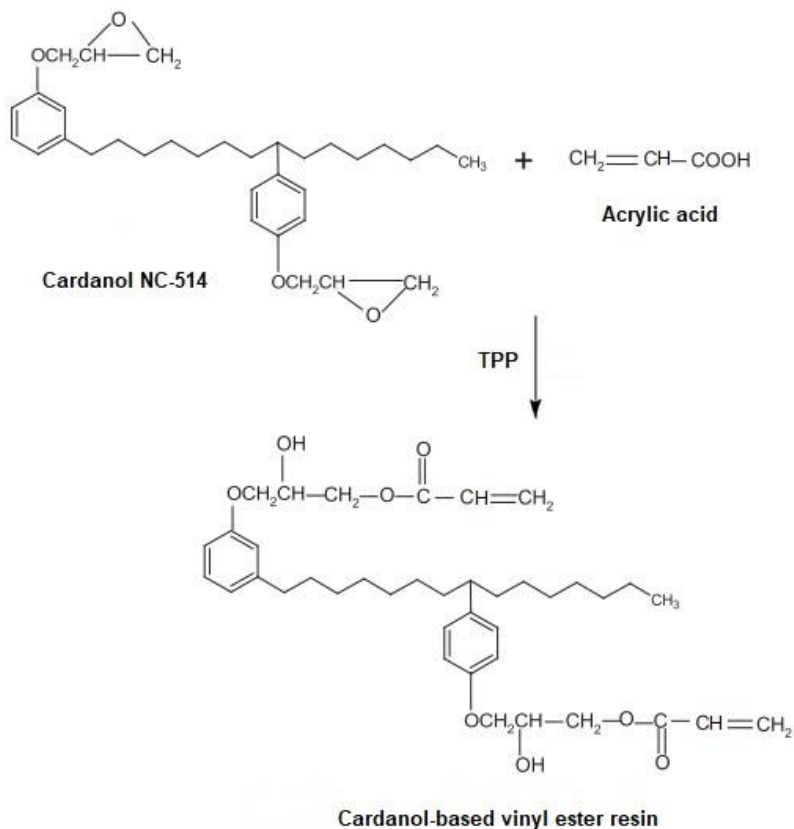


Figure 15 – Reaction scheme for cardanol-based VE resin (Adapted from [50]).



Figure 16 – Experimental set-up for the cardanol-based VE resin.

### 3.2.2 Synthesis of polycardanol

Polycardanol was prepared by a similar method as the one presented in [56], being the reaction scheme for the synthesis represented in Figure 17. The experimental set-ups for the polymerization and with the Soxhlet extractor are presented in Figure 18. Approximately, 0.3 g of cardanol NX-9001 were dissolved in an aqueous solution of NaOH (2 g NaOH / 100 mL H<sub>2</sub>O) and the temperature was raised to 50 °C. Then, at this temperature, potassium ferricyanide (oxidation agent) (0.658 g) was added and the mixture was mechanically stirred for 6 h at 175 rpm. The polymer formed was salted with NaCl, following by washing with water and filtration with the objective of removing any residual NaCl. To remove the unreacted monomer, the polymer was washed with hexane in a Soxhlet extractor for around 24 h [56].

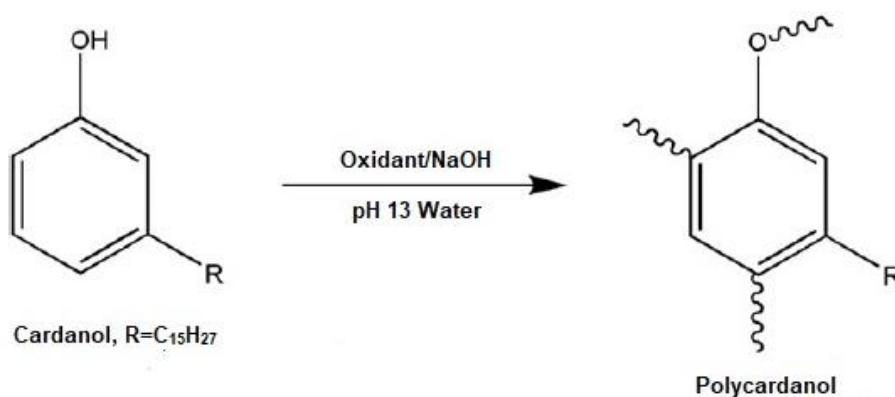


Figure 17 – Reaction scheme for polycardanol synthesis (Adapted from [56]).

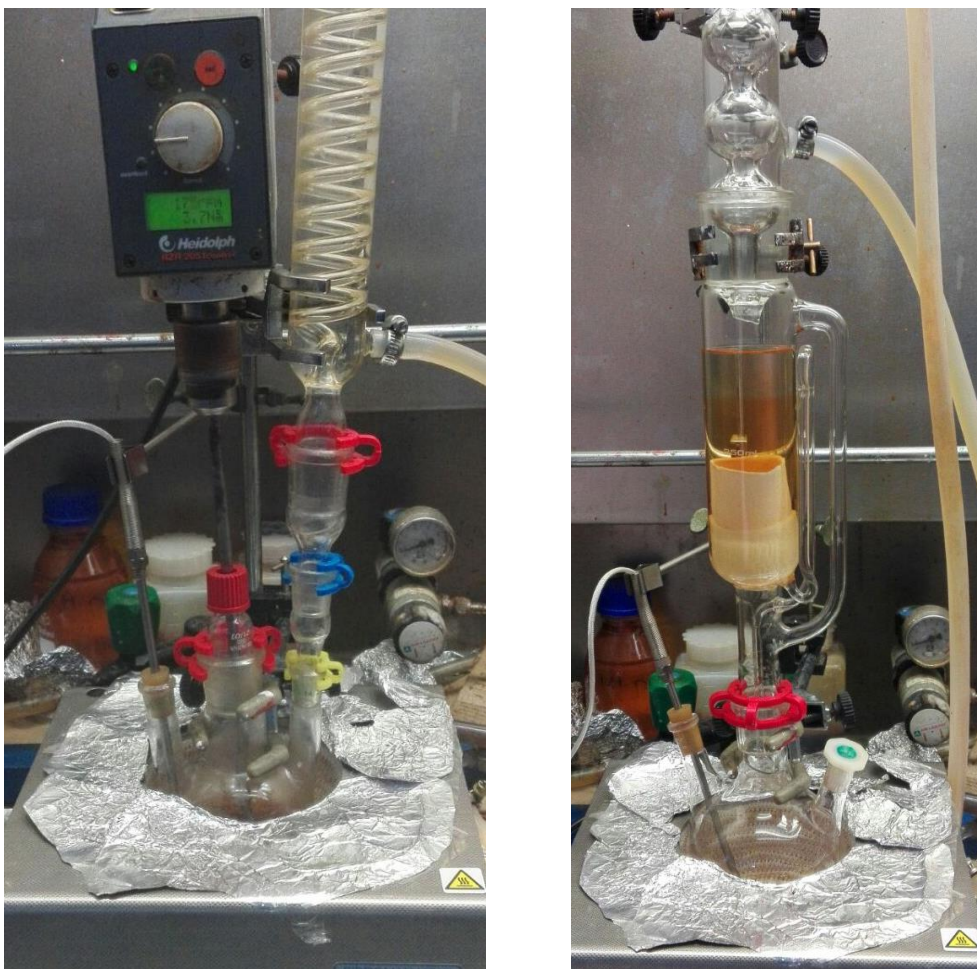


Figure 18 – Experimental set-ups for polycardanol's reaction and with the Soxhlet extractor.

### 3.3 Characterization methods

#### 3.3.1 Attenuated Total Reflectance - Fourier-Transformed Infrared (ATR-FTIR) Spectroscopy

Fourier Transformed Infrared (FTIR) Spectroscopy is based on the vibrations of the atoms of a molecule. It allows to obtain information about the various functional groups present in a sample [57]. In a simple way, the spectrometer's operation consists in passing a beam of IR radiation through a sample and comparing it with the one transmitted with no sample (reference). The spectrum obtained by FTIR spectroscopy is composed by the absorption peaks of a compound. These peaks correspond to the frequencies of vibration that exists between the bonds of the atoms that compose the sample. Since each compound has its unique combination of functional groups, the spectrum obtained represents somewhat a fingerprint of the material, meaning that two compounds will not produce an exact same infrared spectrum. In this way, FTIR is very useful in the identification of different materials [58]. In this work, since the samples obtained are in the bulk form, FTIR spectroscopy by attenuated total reflectance (ATR) was the employed technique. In ATR, the IR radiation impinges on the surface region of the sample to analyze and the reflected radiation is collected by the ATR accessory, resulting in the characteristic ATR-FTIR spectrum of such sample.

The ATR-FTIR spectra were obtained using a PerkinElmer, Spectrum Two, FTIR spectrometer equipped with a Pike Technologies Miracle® Attenuated Total Reflectance (ATR) accessory, between 4000 and 600  $\text{cm}^{-1}$ , with 8  $\text{cm}^{-1}$  of resolution and 8 scans.

### 3.3.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear Magnetic Resonance (NMR) Spectroscopy is a technique that has been revealed as a powerful aid in the structural characterization of all types of chemical compounds. Usually, either carbon or hydrogen spectra are the most useful. However, it is also possible to obtain information, in some cases, through fluorine, phosphorus, silicon or nitrogen spectra [59].

The nucleus of a compound is forced to behave as a bar magnet, due to the magnetic moment. In the absence of an external magnetic field, each magnet is randomly oriented, but when a compound is placed under the action of a magnetic field, this field forces its nucleus to align in favor (low energy) or against (high energy) the same. When an electromagnetic radiation is applied, with a specific frequency, the atomic nucleus of the compound absorbs energy through a process called magnetic resonance, which may lead to a change in its orientation. By detecting the absorption signals, it is possible to obtain the respective NMR spectrum [60][61][62].

For a molecule, the magnetic field felt by the nuclei does not correspond to the one applied, since there is not only a shielding effect by the electrons, but also the influence of the neighboring atoms is felt. Therefore, there will be a change in the absorption frequency of radiation by the nuclei [62]. The value at which the different nuclei absorb is given on a relative scale, in order to standardize the NMR spectra. This value is called chemical shift and its value is given in units of ppm. Through the peaks that constitute the NMR spectrum it is thus possible to infer about the chemical environment of the analyzed species (C, H, etc.) and, therefore, about the chemical structure of the compound that is being studied [63].

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Advanced spectrometer, operating at 500 MHz, with deuterated chloroform as solvent.

### 3.3.3 Thermogravimetric Analysis (TGA)

Thermogravimetry, TGA, is an analysis technique used to assess the thermal stability of the materials, where the change in the mass of a substance is monitored as a function of the temperature (or time) at which it is subject, under a controlled atmosphere (nitrogen, or air). The obtained thermogram gives information about the weight loss (in percentage) at different temperatures and over time. It is applicable to most industries, being mainly used in environmental, food, pharmaceutical and petrochemical industries [64][65].

The major limitations of TGA are the difficulty to measure some liquids, the fact that the samples used are very small, so generally non-homogeneous materials cannot be accurately tested, and also the fact that it is only possible to obtain significant data when a change in the mass sample occurs [66].

TGA thermograms were obtained using a Hitachi STA7200 equipment, in nitrogen atmosphere and at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ .

### **3.3.4 Differential Thermal Analysis (DTA)**

Differential Thermal Analysis (DTA) is a technique that measures the difference in temperature between a sample and an inert reference. This differential temperature occurs due to the different heat capacities of both sample and reference, and it is measured as a function of time or temperature, as both cells are subjected to similar conditions, where the temperature increases or decreases at a controlled rate. DTA is used to study thermal properties and phase changes, because it is possible to detect the sample's transition temperature and the reaction temperature from the differential temperature signal obtained. In the graphs obtained, when the DTA signal has a negative direction means that the sample had an endothermic change, and if the direction of the signal is positive, the change was exothermic [67][68].

DTA thermograms were obtained using a Hitachi STA7200 equipment, in nitrogen atmosphere and at a heating rate of 10 °C/min.

### **3.3.5 Differential Scanning Calorimetry (DSC)**

Differential Scanning Calorimetry (DSC) is a thermal analysis technique used to understand how the heat capacity of a material changes when it is exposed to a regulated increase or decrease in temperature [69]. This analytical technique can be considered an evolution of DTA. The DSC technique allows the detection of transitions, which includes melts, glass transitions, phase changes and curing. Since most materials exhibit some transitions, DSC is used in a wide range of industries, such as polymers, pharmaceuticals, food, paper, printing, manufacturing, agriculture, semiconductors and electronics [70]. The chamber of the DSC equipment is composed by a sample cell, containing the material under study, and a reference cell. During a DSC analysis, the temperature in both cells is raised identically over time. The difference between the energy required for the sample cell, when compared with the reference cell, represents the amount of heat in excess that is being released (exothermic reaction) or absorbed (endothermic reaction) by the material in the sample [69]. The major advantage of this technique is that it is an easy and fast method to observe transitions in materials [70]. As for limitations, DSC is very sensitive to any change in the sample or pan, requires a very good thermal contact with the bottom of the sample pan and it is also very sensitive to the heating rate [66].

DSC thermograms were performed using a TA DSC Q20 equipment, with a heating rate of 5 °C/min, in an air atmosphere, and using hermetic pans.



## 4. Results and Discussion

### 4.1 Characterization of the prepolymer cardanol-based VE resin

#### 4.1.1 Characterization by ATR-FTIR

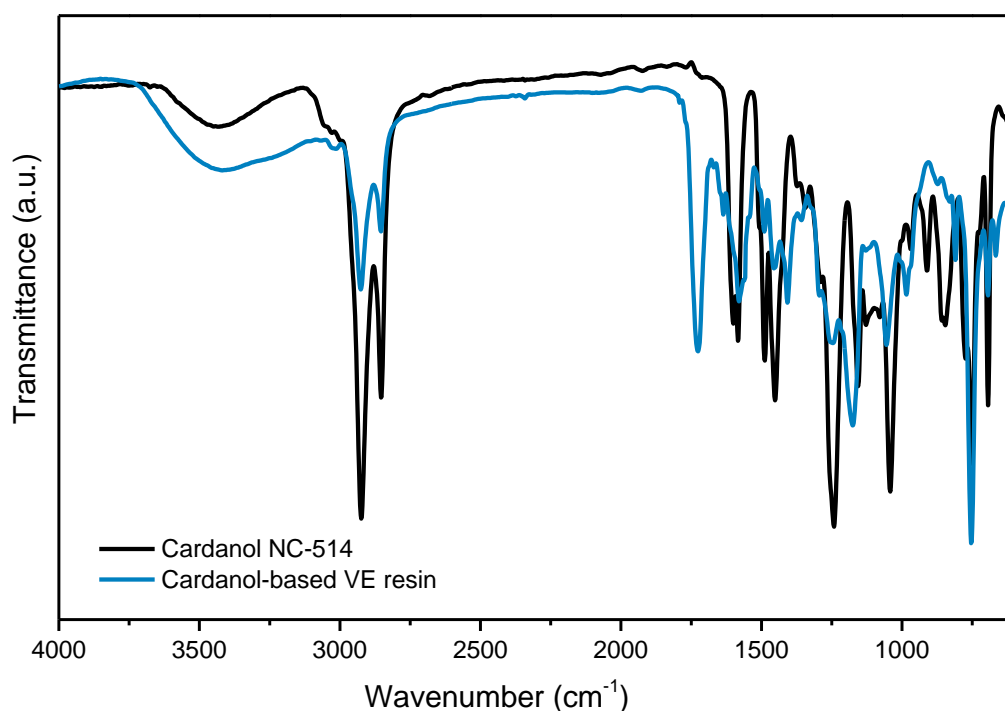


Figure 19 – ATR-FTIR analysis of cardanol NC-514 and the cardanol-based VE resin.

The ATR-FTIR spectra of cardanol NC-514 and of the cardanol-based VE resin are shown in Figure 19. In both, the large band peaked around 3400 cm<sup>-1</sup> denoted the existence of hydroxyl groups (OH), which indicates the presence of water. Besides this, around 1639 cm<sup>-1</sup>, in the VE resin spectrum, appears a small peak also related to the existence of OH groups from water. In the VE resin spectrum, these peaks have higher intensity, which could come, for instance, from the OH groups formed by the oxirane ring opening, and from the presence of water used for the decantation step (which was not totally removed at the rotary evaporator operation). The peaks at 2925 and 2853 cm<sup>-1</sup> are attributed to the presence of CH, CH<sub>2</sub> and CH<sub>3</sub> groups, and, in the VE resin spectrum these peaks have lower intensity. Around 1730 cm<sup>-1</sup> a peak appears and might be due to the presence of an ester group (C=O), in this case an acrylate, which can mean that the ring opening reaction of the epoxy groups occurred, as intended. The same finding was reported in reference [71]. The absence of the peaks at 909, 859 and 846 cm<sup>-1</sup>, in the VE resin spectrum, which are characteristic peaks of C-O-C linkage in the epoxy ring, also confirms the opening of the oxirane groups, meaning that the reaction was well succeeded. The presence of aromatic C=C bonds can be confirmed by the band at 1560 – 1636 cm<sup>-1</sup>, which leads to the conclusion that the reaction (acrylation) only occurred through the opening of the epoxy groups, as intended, and not through the C=C bonds of the aromatic ring. The presence of a peak at 810 cm<sup>-1</sup> might be related to para substitution in the aromatic ring.

## 4.1.2 Characterization by NMR

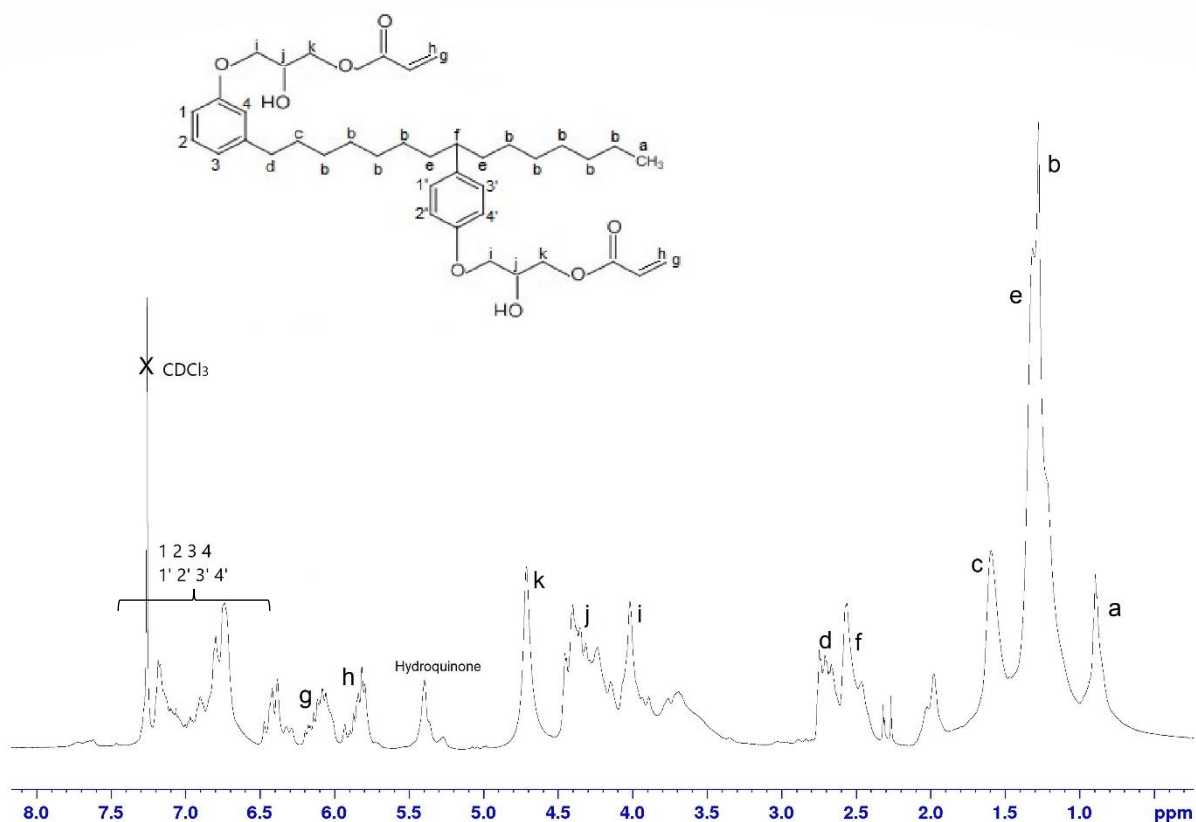


Figure 20 –  $^1\text{H-NMR}$  of the cardanol-based VE resin in deuterated chloroform,  $\text{CDCl}_3$ .

The  $^1\text{H-NMR}$  spectrum of the cardanol-based VE resin is presented in Figure 20. The peaks that compose this spectrum have a lower defined resolution and are broader, when compared to the resolution of a smaller molecule spectrum, such as a monomer. Since the resolution is lower it might indicate that the sample analyzed is constituted by bigger molecules (prepolymer). The multiplet peaks between 4.00 and 4.70 ppm region were attributed to the  $(-\text{OCH}_2-)$  protons and the tertiary  $(-\text{CH}(\text{OH})-)$  proton of the  $(\text{phenyl-OCH}_2\text{-CH}(\text{OH})\text{-CH}_2\text{O}-(\text{C}=\text{O})-)$  moiety. The presence of these peaks also confirms the oxirane ring opening reaction and the resulting acrylation reaction, corroborating the ATR-FTIR results.

The presence of g and h signals, corresponding to the acrylate end group, reveals the acrylation reaction. The average number of acrylate units in the VE resin unit was calculated from the integration of the peaks of ethylene protons of the acrylate end group ( $I_g$ ) and ( $I_h$ ), and the integration of the peak of terminal methyl protons of the aliphatic side chain ( $I_a$ ) of the  $^1\text{H-NMR}$  spectrum (Annex II). Thus, the functionality of the VE resin unit was calculated using the following equation. [55]

$$F = \frac{I_g + I_h}{I_a} \times \frac{\text{number of ethyl protons of the acrylate end group}}{\text{number of terminal methyl protons of the aliphatic side chain}} = \frac{1.26 + 1.02}{3.00} \times \frac{3}{2} = 1.14 \quad 1$$

Considering an epoxy functionality of cardanol NC-514 at 1.32 [55], the acrylate functionality of the obtained VE resin corresponds to about 86 % of conversion of epoxy groups, revealing that the reaction (acrylation) did occur as intended, but it was not fully completed.



In Figure 21 the  $^{13}\text{C}$ -NMR spectrum of the resin is shown. The absence of peaks between 40 and 50 ppm indicates that the epoxy groups of the cardanol NC-514 were found to open, which confirms that the functionalization reaction occurred as intended and was well succeeded. Besides this, the peaks between 110 and 170 ppm represent the carbon atoms of the aromatic ring, being possible to conclude that the polymerization only occurred through the opening of the epoxy groups, as intended, and not through the double bonds of the aromatic ring.

The conclusions drawn from both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the VE resin are consistent with those obtained from the ATR-FTIR spectrum.

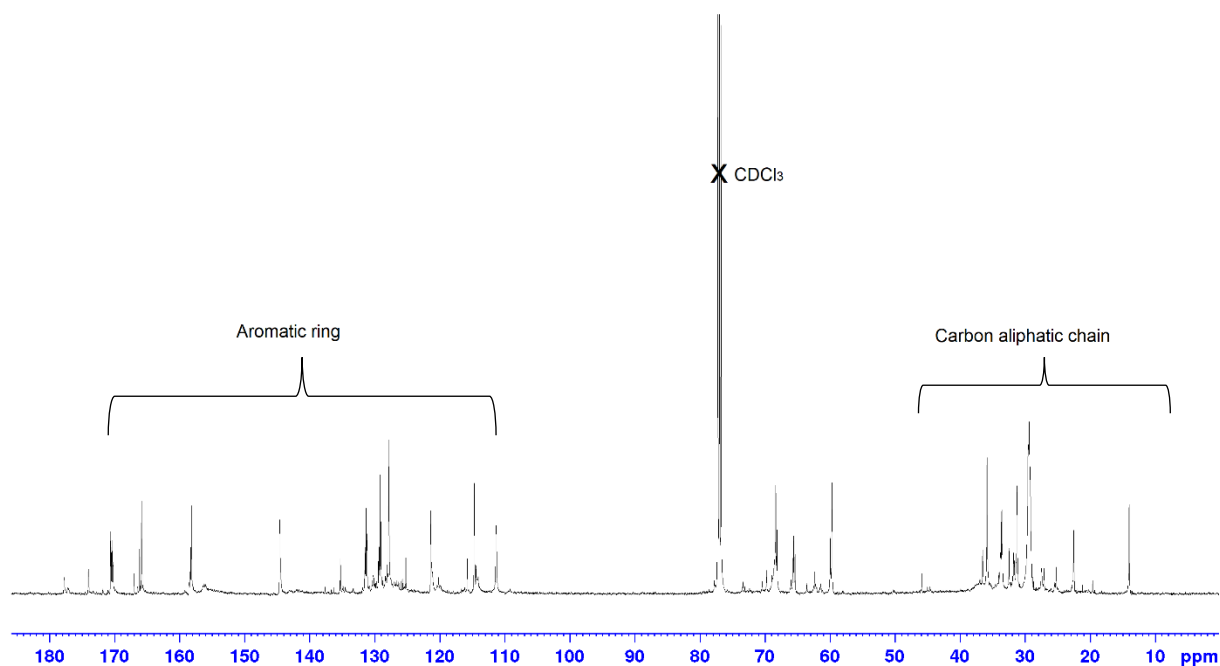


Figure 21 –  $^{13}\text{C}$ -NMR of the cardanol-based VE resin in deuterated chloroform,  $\text{CDCl}_3$ .

### 4.1.3 Characterization by TGA

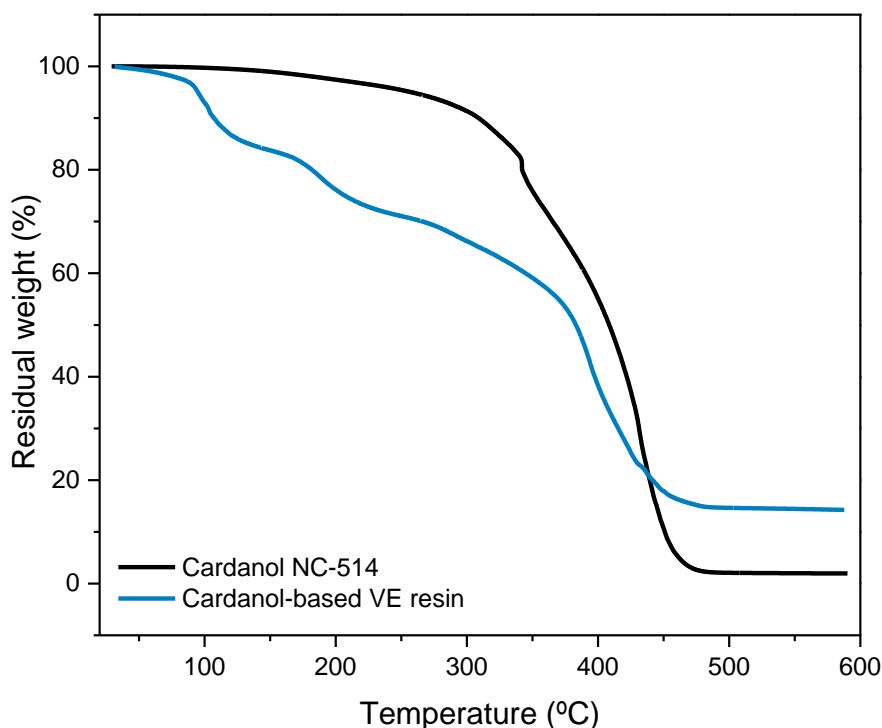


Figure 22 – TG analysis of cardanol NC-514 and of the VE resin, at 10 °C/min in N<sub>2</sub>.

Figure 22 shows both thermograms of cardanol NC-514 and of the VE resin produced. The weight loss around 100 °C observed in the thermogram of the VE resin is related to the presence of unremoved water. This water was added with the intention of removing the unreacted acrylic acid. The char yield obtained, at 550 °C, is 14.2 %, but if the water had been successfully removed, the char yield, at 550 °C, would be ca. 38.4 %, i.e. much higher than for the original cardanol epoxy resin (cardanol NC-514). This means that the acrylation reaction performed on the epoxidized cardanol resin, besides providing vinyl functionality for copolymerization with acrylonitrile, also leads to a higher char yield at high temperatures.

It should be noted that the RMN results of the developed cardanol-based VE resin have shown that the acrylation reaction was occurring only at 86 % (approximately), which means that some of the weight loss occurring at temperatures below 400 °C could be due to acrylic acid species, or other compounds present in the resulting pre-polymer that were not successfully eliminated during the rotary evaporator. In future experiments, besides adding more acrylic acid and increasing the reaction time (for a higher reaction yield), the rotary evaporation and washing procedure should be improved to get rid of all unwanted species.

Figure 23, is adapted from the literature and shows a thermogram from PAN (typical material of commercial carbon fiber precursors, produced by FISIFE), which shows an abrupt weight loss right above 300 °C and a char yield at 550 °C of ca. 50 %.

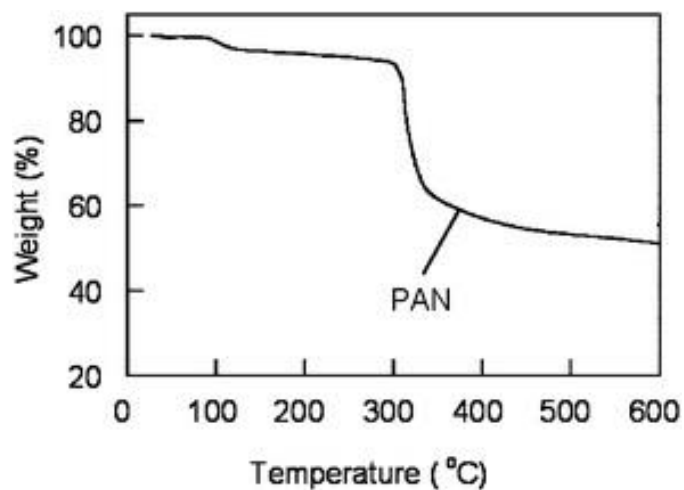


Figure 23 – TG analysis of PAN (Adapted from [72]).

#### 4.1.4 Characterization by DTA

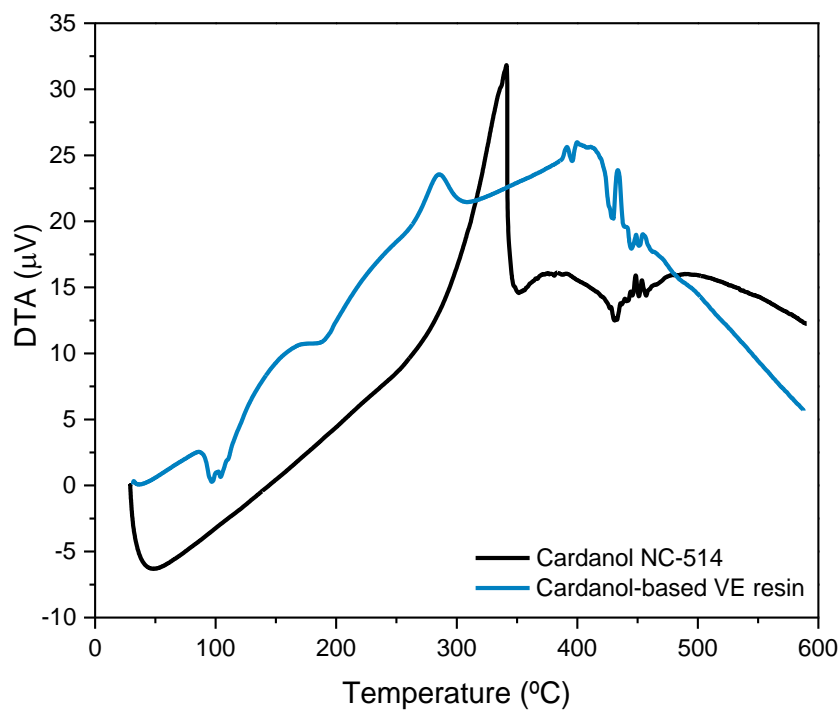
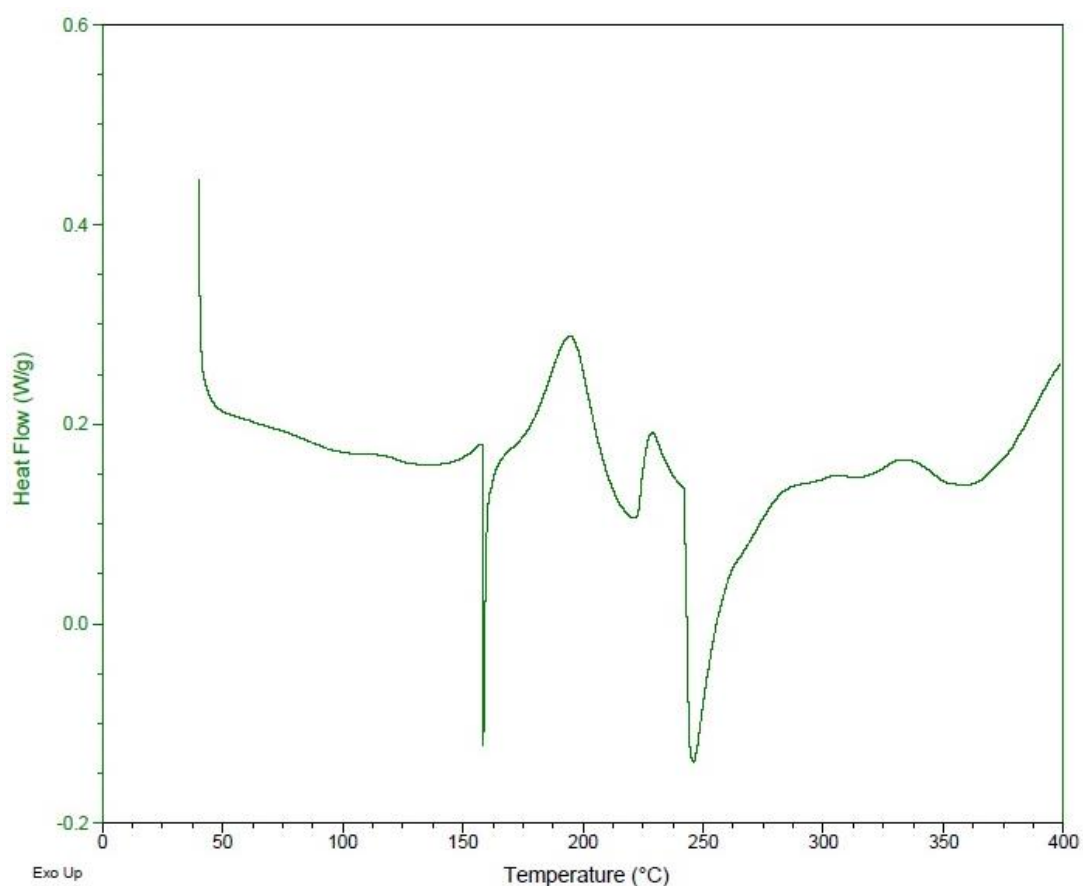


Figure 24 – DTA analysis of cardanol NC-514 and of the VE resin, at 10 °C/min in N<sub>2</sub>.

DTA analysis of cardanol NC-514 and of the VE resin are presented in Figure 24. Cardanol's curve shows an exothermic peak at 341 °C, being attributed to the cleavage of the alkyl side chain of the aromatic ring [73].

As for the VE resin's curve, it is quite complex and shows numerous endo and exothermic peaks. There is a small endothermic peak around 100 °C, which might be related to the evaporation of the water present in the sample, as well as volatile solvent, namely chloroform, in line with what was shown in the TGA thermogram.

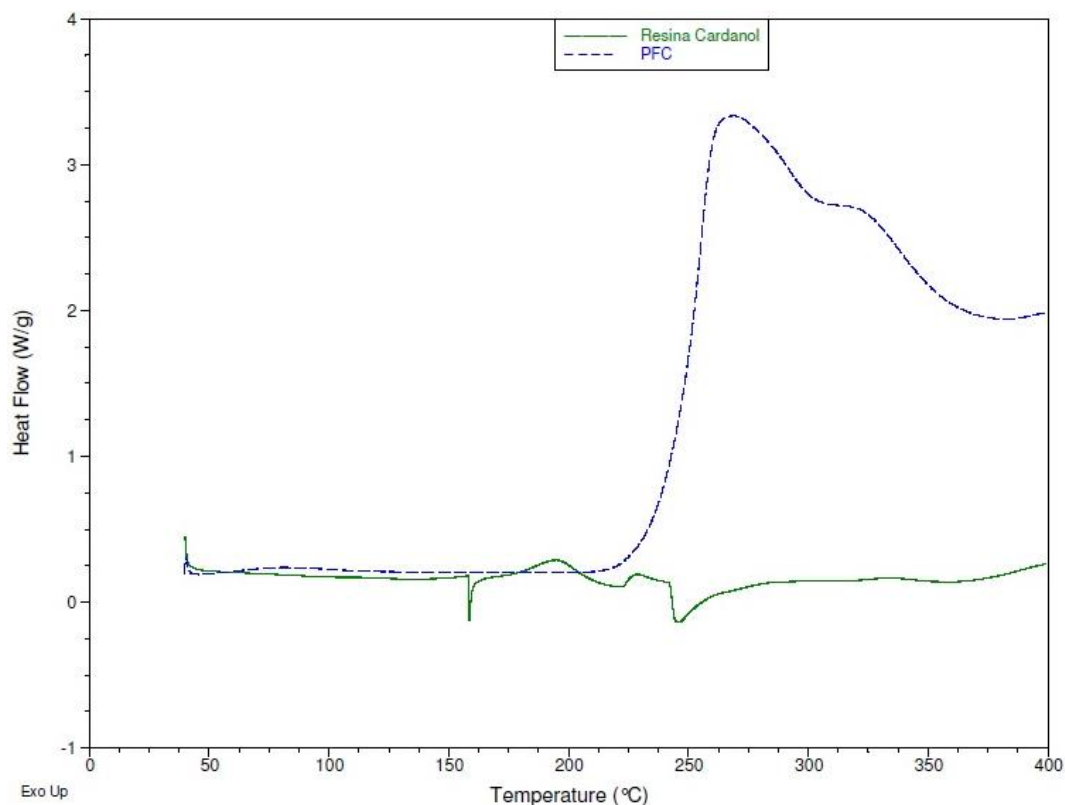
#### 4.1.5 Characterization by DSC



**Figure 25 – DSC curve obtained for the cardanol-based VE resin, at 5 °C/min in air.**

The DSC curve obtained for the VE resin (Figure 25) shows two endothermic processes, at around 160 °C and 250 °C, and an exothermic process, at around 200 °C. The first endotherm, quite well defined, is typical of a melting process, which could be ascribed to some lower molecular weight moieties, or impurities of the VE resin sample, while the second endotherm could be ascribed to more cross-linked moieties.

The DSC parameters employed in this analysis, namely the low scanning rate, are not optimized for the study of the glass transition temperature ( $T_g$ ). However, there is a weak transition at around 80 °C, which is quite in line with the literature [55].



**Figure 26 – DSC thermograms of cardanol-based VE resin and PFC, at 5 °C/min in air.**

The DSC thermogram of the cardanol-based VE resin obtained in this work was compared with those of a typical commercial carbon fiber precursor, named throughout the text “PFC” (based on PAN), supplied by FISIFE, and also with those, found at the literature, for pitch and rayon based precursors.

PFC’s thermogram (Figure 26) exhibits a clear and intense exothermic peak at around 280°C, characteristic of the cyclization process of PAN, while for the cardanol-based VE resin all transitions are just slightly intense, or even residual, when compared to that of PAN. There is an exothermic process starting at ca. 400 °C, which could not be followed, since this is the upper limit temperature for the DSC analysis in this equipment, when the refrigeration system is employed. That, hypothetically, could give rise to a strong exotherm, but at higher temperature than for PAN, which could be acceptable if the polymer would not degrade up to such temperature. Such difference in terms of exothermic transition (cyclization process) is, therefore, not indicative that the pre-polymer developed in this work will not be feasible as carbon fiber precursor.

In fact, when comparing the cardanol-based VE resin’s DSC thermogram with that of coal tar pitch, present in the literature and presented in Figure 27, it is possible to verify that the latter, at around 400 °C, also exhibits a starting exothermic process. This can indicate that the VE resin obtained in this work might have a behavior similar to pitch, a well-established carbon fiber precursor.

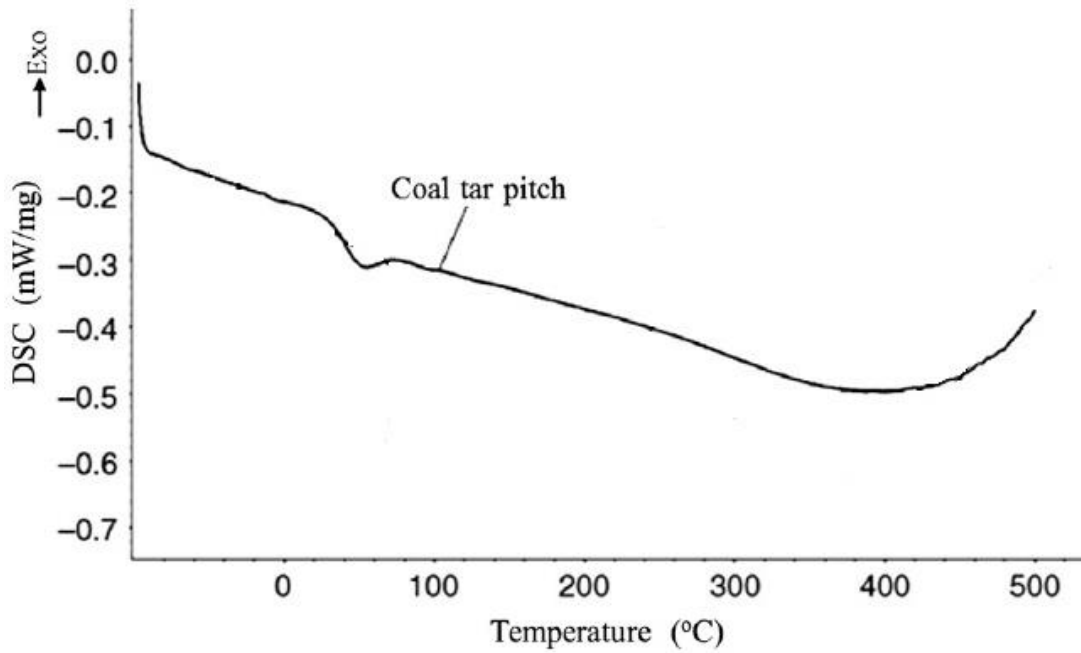


Figure 27 – DSC thermogram of coal tar pitch (Adapted from [74]).

The same finding was observed for rayon-based carbon fiber precursor. Figure 28 shows its thermogram, which also does not exhibit any exothermic process below 400 °C, in line with what happens for the cardanol-based VE resin, but also does not show any melting related peak below 300 °C, in opposition to what is observed for the VE resin.

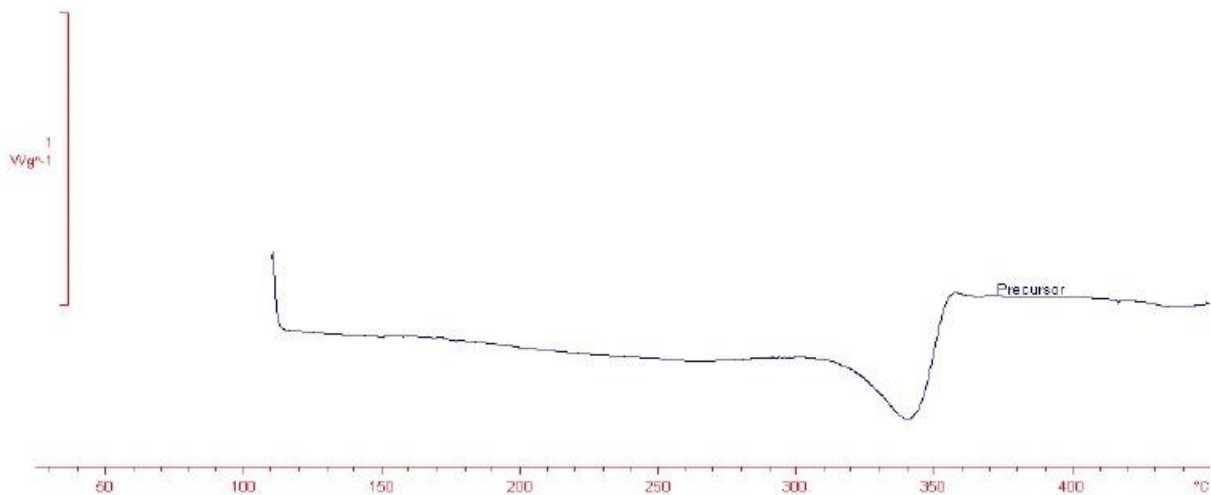


Figure 28 – DSC thermogram of rayon-based carbon fiber precursor (Adapted from [75]).

## 4.2 Characterization of the polycardanol

### 4.2.1 Characterization by ATR-FTIR

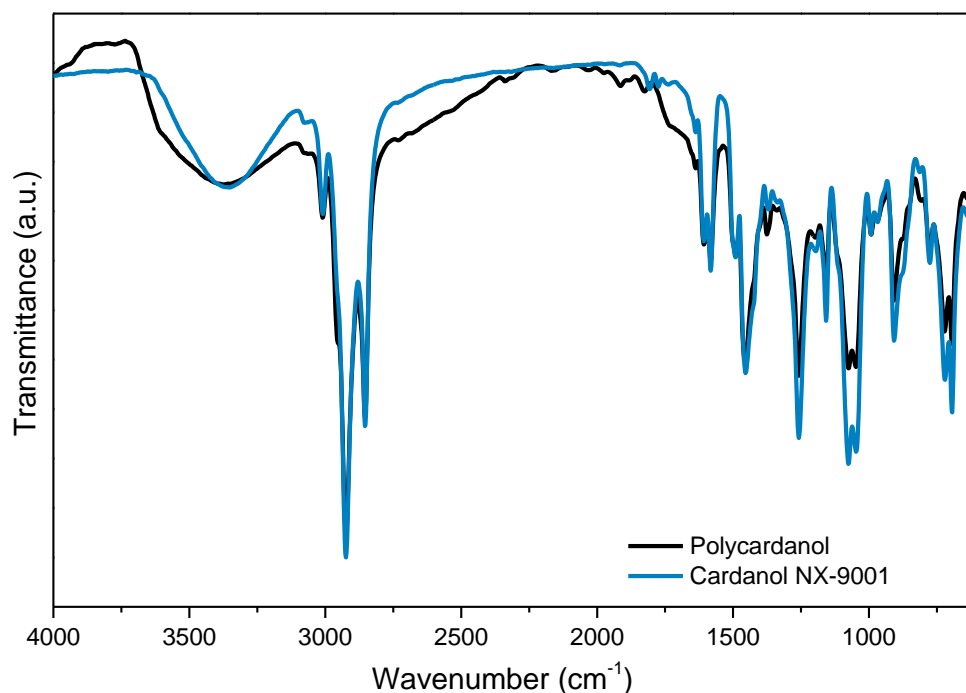


Figure 29 – ATR-FTIR analysis of cardanol NX-9001 and polycardanol.

The ATR-FTIR spectra of cardanol NX-9001 and of polycardanol are shown in Figure 29. In both spectra, the peak around 3400 cm<sup>-1</sup> is due to the stretching vibrations of the hydroxyl (OH) groups, e.g. from phenolic group. Since the peak in the polycardanol spectrum is wider than the one in cardanol NX-9001 spectrum, it means that, besides the existence of OH linkage from the phenolic groups, water could also be present, probably from the NaOH aqueous solution used as the polymerization medium. The existence of this peak in the polycardanol spectrum indicates that, possibly, there is not a C-O-C coupling, meaning that the polymerization (by condensation reactions between OH groups of the phenol units) did not occur as desired. The characteristic peaks around 3009, 2923 and 2853 cm<sup>-1</sup>, existent in both spectra, are attributed to the alkyl side chain present either in cardanol NX-9001 and in polycardanol, being the CH stretching vibration of alkene responsible for the peak at 3009 cm<sup>-1</sup>. The peaks between around 1608 and 1450 cm<sup>-1</sup> correspond to the C=C bonds of the aromatic ring. Both spectra exhibit some characteristic peaks at 1240 and 1190 cm<sup>-1</sup>, which correspond to the vibration of C(Ar)-O-C(Ar) bonds, and at 1155 cm<sup>-1</sup> attributed to C(Ar)-OH linkage. All the peaks referred before, have similar intensity in both spectra, which might mean that the polymerization did not significantly occur, and that the “polycardanol” obtained is mainly constituted by the monomer, cardanol NX-9001, or some oligomeric units.

## 4.2.2 Characterization by NMR

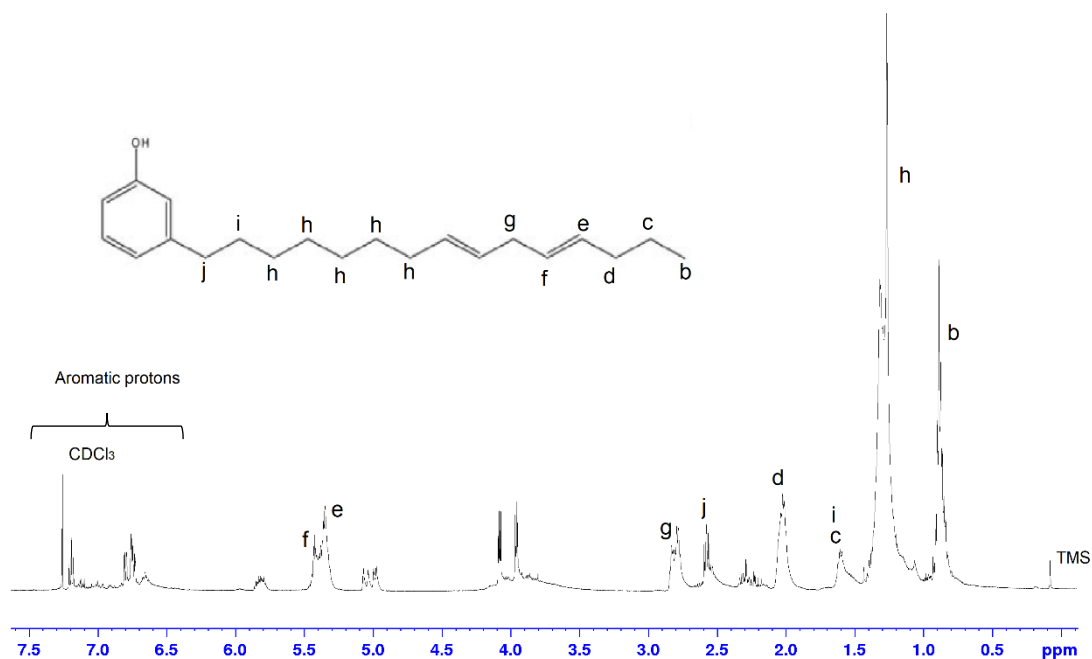


Figure 30 –  $^1\text{H-NMR}$  of polycardanol in deuterated chloroform,  $\text{CDCl}_3$ .

The  $^1\text{H-NMR}$  spectrum of polycardanol is shown in Figure 30. When comparing the peaks in this spectrum with a typical spectrum of a resin, such that of Figure 20, it is possible to verify that the latter is broader and has lower resolution. This shows the almost nonexistent polymerization in the synthesis of polycardanol. In addition to this, the presence of two sharp peaks around 4.0 ppm may indicate that the sample analyzed might be mainly constituted by the monomer, cardanol NX-9001, however the broad, but weak signal in the background of these two peaks might reveal the presence of some oligomeric species, as well. This means that the polymerization did not occur in the intended extension.

Figure 31 shows both  $^{13}\text{C-NMR}$  and DEPT C-NMR of polycardanol. In a DEPT (Distortionless Enhancement of Polarization Transfer) spectrum, CH and  $\text{CH}_3$  peaks appear as normal, but  $\text{CH}_2$  peaks appear inverted, allowing, this technique, to determine the number of hydrogen atoms linked to each carbon. In the  $^{13}\text{C-NMR}$  spectrum, the peaks that appear between 12 and 30 ppm represent the saturated carbon bonds and the ones between 110 and 160 ppm represent the unsaturated carbon bonds [76]. The peak at 145 ppm represents the carbon of the aromatic ring which is linked to the hydroxyl group. The existence of this peak may reveal that the polymerization extension was not as planned. Besides this fact, in DEPT C-NMR it is possible to observe the presence of two inverted peaks, meaning the presence of  $\text{CH}_2$ . The peaks between 60 and 70 ppm are attributed to C-O-C linkages, which could mean that some polymerization had occurred, since this polymerization implies C(Ar)-O-C(Ar). The presence of the two inverted peaks in DEPT C-NMR between 60 and 70 ppm shows, as mentioned, that those carbon atoms are not from an aromatic ring, but from a  $\text{CH}_2$  group, demonstrating that a total polymerization may have not occurred.



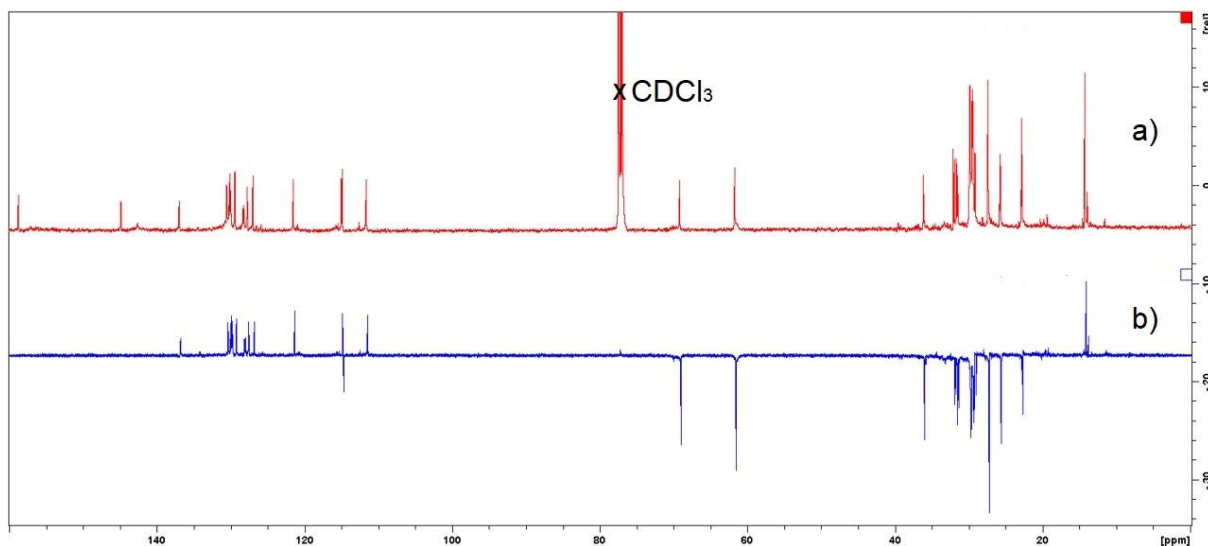


Figure 31 – a)  $^{13}\text{C}$ -NMR and b) DEPT C-NMR of polycardanol in deuterated chloroform,  $\text{CDCl}_3$ .

### 4.2.3 Characterization by TGA

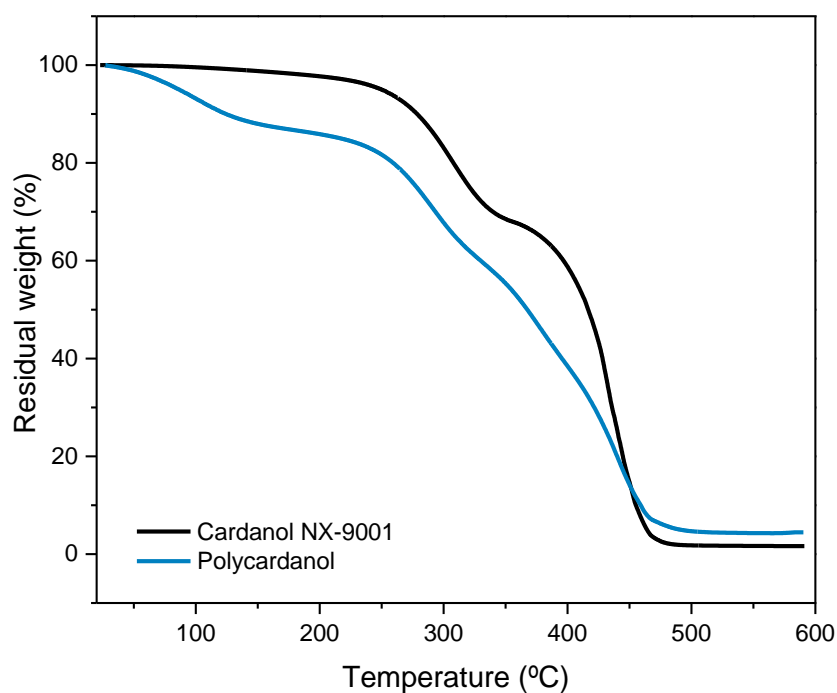


Figure 32 – TG analysis of cardanol NX-9001 and polycardanol, at  $10\text{ }^\circ\text{C}/\text{min}$  in  $\text{N}_2$ .

Figure 32 shows the comparison between TG thermograms of cardanol NX-9001 and polycardanol. It is possible to observe that up to a temperature of  $135\text{ }^\circ\text{C}$ , there was a release of the solvent used in the Soxhlet extraction (hexane), as well as release of water, from the addition of the same for removal of  $\text{NaCl}$ . If this removal had been effective, it is estimated that, at  $550\text{ }^\circ\text{C}$ , the char yield would be  $16.3\%$ . However, the achieved char yield in the present sample is only  $4.4\%$ . It should also be noted that the yield obtained, even when the solvents are effectively removed, is lower than that

shown in the reference [55] (25 %), but higher than that of cardanol NX-9001, which might suggest that some oligomeric, or polymeric (polycardanol) species are present.

Cardanol NX-9001 has two stages of degradation, the first at 249 °C and the second at 387 °C, being the first one attributed to the aliphatic side chain degradation, and the second attributed to the aromatic ring degradation. Polycardanol, on the other hand, exhibits a more gradual weight loss, starting at a lower temperature range, than in cardanol NX-9001. If a total polymerization had occurred, the average molecular weight would be significantly higher than that of the monomer, leading to a higher thermal stability when compared with cardanol NX-9001.

The results obtained through TGA are consistent with those obtained through ATR-FTIR and through NMR, since, for example, the peaks at 1240 and 1150  $\text{cm}^{-1}$  from ATR-FTIR spectrum, corresponding to the C(Ar)-O-C(Ar) bonds, are not much higher than those in cardanol NX-9001, which indicates that the polymerization of cardanol was not complete.

#### 4.2.4 Characterization by DTA

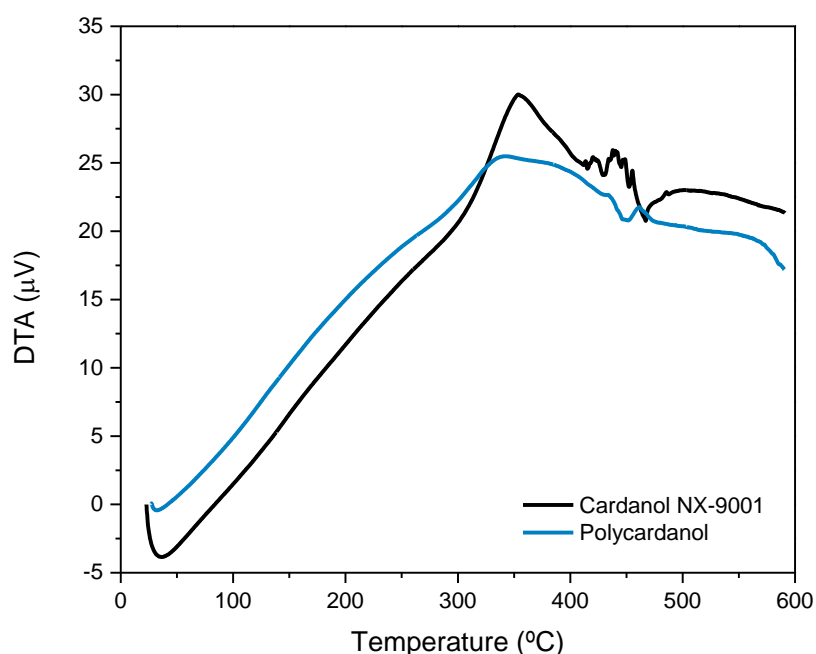
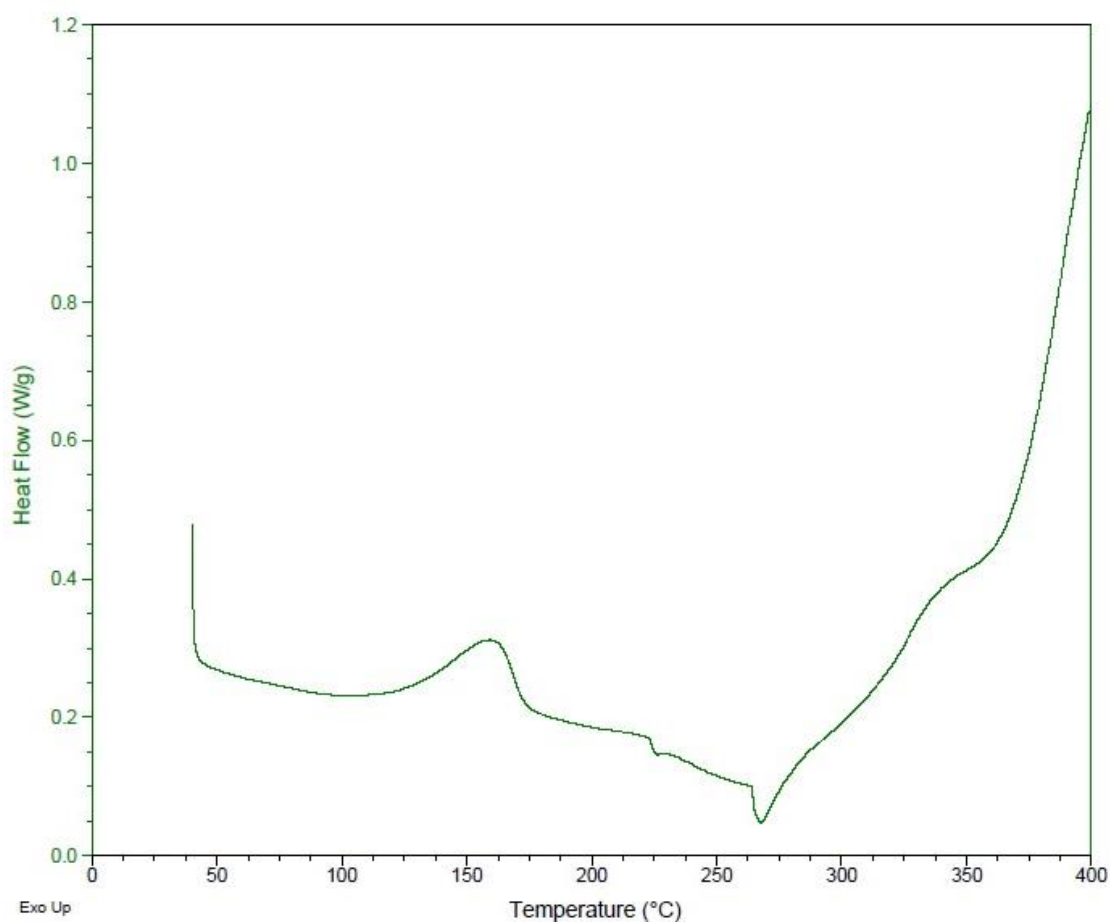


Figure 33 – DTA analysis of cardanol NX-9001 and polycardanol, at 10  $^{\circ}\text{C}/\text{min}$  in  $\text{N}_2$ .

In Figure 33 both DTA curves of cardanol NX-9001 and polycardanol are presented. Cardanol's curve has an exothermic peak around 353  $^{\circ}\text{C}$ , that can be attributed to the cleavage of the alkyl side chain of the aromatic ring [73]. Besides this peak, it has smaller endothermic peaks at 430  $^{\circ}\text{C}$  and 468  $^{\circ}\text{C}$ . Despite not having such a defined exothermic peak around 350  $^{\circ}\text{C}$ , polycardanol's curve is similar to the one of cardanol NX-9001. This fact might indicate, as concluded through the other methods, that polycardanol is mainly composed by monomers of cardanol and some oligomeric compounds.

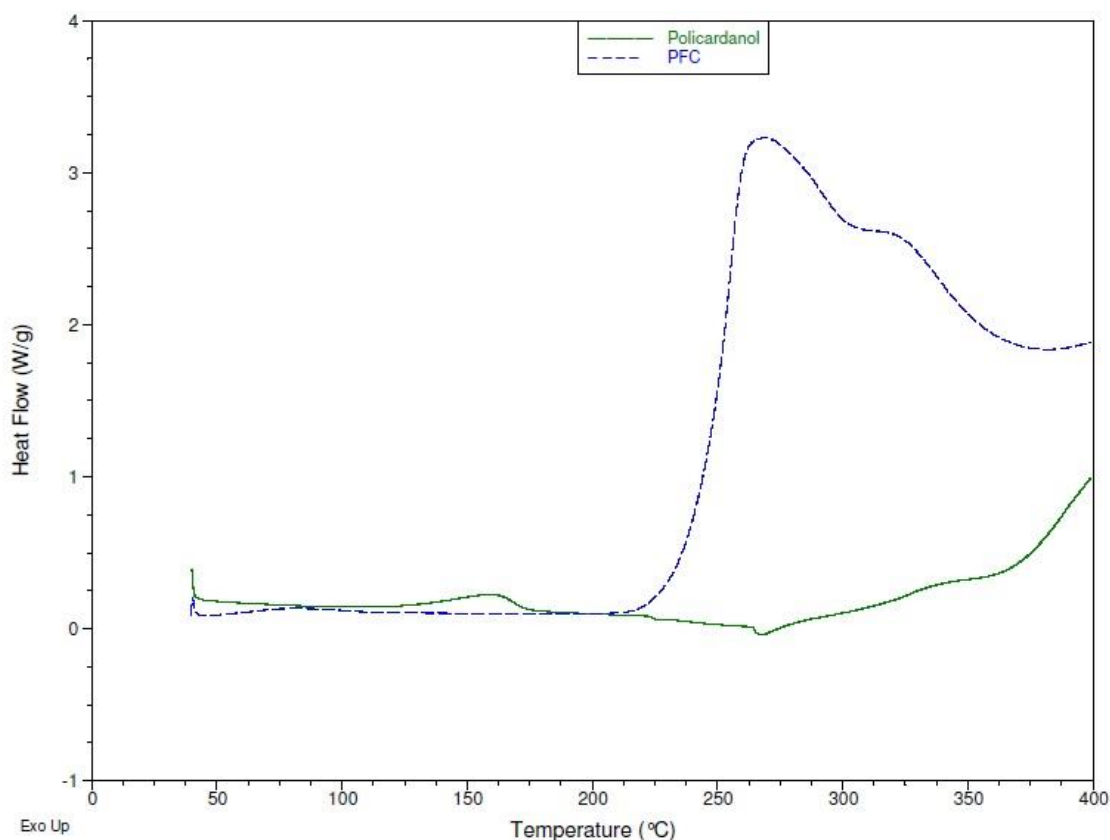
## 4.2.5 Characterization by DSC



**Figure 34 – DSC curve obtained for polycardanol, at 5 °C/min in air.**

The DSC curve obtained for polycardanol (Figure 34) shows a small exothermic process, at around 160 °C, and a small endothermic process, at around 265 °C. The former one (exo) could be related to some crystallization occurring (it has been reported that the conversion of the monomers to polycardanol has not occurred at a full extent), while the latter one (endo) could be related to a melting process.

The DSC thermogram of polycardanol sample obtained in this work was compared with those of a typical commercial carbon fiber precursor, PFC (based on PAN) (Figure 35), supplied by FISIFE, and also with those, found at the literature, for pitch and rayon based precursors.



**Figure 35 – DSC thermogram of polycardanol and PAN, at 5 °C/min in air.**

As explained before, PFC sample exhibits a thermogram with a clear and intense exotherm peaked at around 280 °C, characteristic of the cyclization process of PAN, while for polycardanol all transitions are weak, or even residual, when compared to that of PAN.

As for the DSC thermogram of polycardanol, it is interesting to note an exothermic process starting at ca. 400 °C, which could not be followed, since this is the upper limit temperature for the DSC analysis in the equipment used, when the refrigeration system is employed. That, hypothetically, could give rise to a strong exotherm, but as higher temperature than for PAN, which could be acceptable if the polymer does not degrade at such high temperature. This is, therefore, not indicative that polycardanol might not be feasible as carbon fiber precursor.

Comparing both DSC thermograms of polycardanol and of coal tar pitch (Figure 27) it is possible to verify, in both of them, the presence of a starting exothermic process around 400 °C, which may indicate that polycardanol might have a similar behavior to pitch, i.e. might be acceptable as a carbon fiber precursor.

The same finding was observed for rayon-based carbon fiber precursor. Figure 28 shows its thermogram, which also does not exhibit any exothermic process below 400 °C, in line with what happens for polycardanol, and shows an endothermic peak at 350 °C, contrary to what is observed for polycardanol.

## 5. Conclusions

In this thesis, a feasibility study was carried out. In particular, two different materials were developed to be studied as sustainable carbon fiber bio-derived precursors. Both compounds were characterized through various methods, ATR-FTIR, NMR, TGA, DTA and DSC.

The selected bio-source employed in this work was cardanol, derived from cashew nutshell liquid waste, namely polyol cardanol NX-9001 and epoxidized cardanol resin NC-514.

Through all the characterization methods applied it is possible to conclude that, the synthesis of a polymer resultant from condensation of cardanol (polycardanol) was not so efficient, but the acrylation reaction (functionalization) of cardanol-based epoxy resin was effectively achieved in this work (86 % of epoxy groups conversion), giving rise to a cardanol-based VE prepolymer.

The obtained prepolymer might be co-polymerized with acrylonitrile, in a near future, and might result in acceptable quality carbon fibers.



## 6. Future Work

In order to obtain more information regarding the composition of the synthesized polycardanol sample, namely the presence of oligomeric, or polymeric species, NMR diffusion experiments (Dosy) could be performed.

Regarding cardanol-based VE resin, in order to improve the cardanol polymerization reaction, more quantity of acrylic acid and longer reaction time, will be employed, and other forms of ester group sources will be tested.

In a next step, cardanol-based VE resin, will be copolymerized, initially in batch, with acrylonitrile, to produce carbon fibers. The properties of these new fibers will be studied and compared with the commercial PAN-based carbon fibers, in order to verify if the copolymer resin/AN would be an acceptable substitute for PAN.





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## 8. Annex

### 8.1 Annex I

Table 1 – Risk phrases of the chemical compounds used.

Chemical compound	Molecular formula	R-phrases
Acrylic acid	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	R10; R20/21/22; R35; R50. [77]
Cardanol NX-9001	-	-
Cardanol NC-514	-	-
Chloroform	CHCl <sub>3</sub>	R20/22; R38; R40. [78]
Hexane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	R11; R38; R48/20; R51/53; R62; R65; R67. [79]
Hydroquinone	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	R22; R40; R41; R43; R50; R68. [80]
Potassium Carbonate	K <sub>2</sub> CO <sub>3</sub>	R22; R37/38; R41. [81]
Potassium Ferricyanide	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	R32. [82]
Sodium Chloride	NaCl	N/A [83]
Sodium Hydroxide	NaOH	R35. [84]
TPP	C <sub>18</sub> H <sub>15</sub> P	R20/22; R36/37/38. [85]

#### R-phrases:

R10: Flammable;

R11: Highly flammable;

R20: Harmful by inhalation;

R21: Harmful in contact with skin;

R22: Harmful if swallowed;

R32: Contact with acids liberates very toxic gas;

R34: Causes burns;

R35: Causes severe burns;

R36: Irritating to eyes;

R37: Irritating to respiratory system;

R38: Irritating to skin;

R40: Limited evidence of a carcinogenic effect;

R41: Risk of serious damage to eyes;

R43: May cause sensitization by skin contact;

R48: Danger of serious damage to health by prolonged exposure;

R50: Very toxic to aquatic organism;

R51: Toxic to aquatic organisms;

R53: May cause long-term adverse effects in the aquatic environment;

R62: Possible risk of impaired fertility;

R65: Harmful: may cause lung damage if swallowed;

R67: Vapors may cause drowsiness and dizziness;

R68: Possible risk of irreversible effects;

## 8.2 Annex II

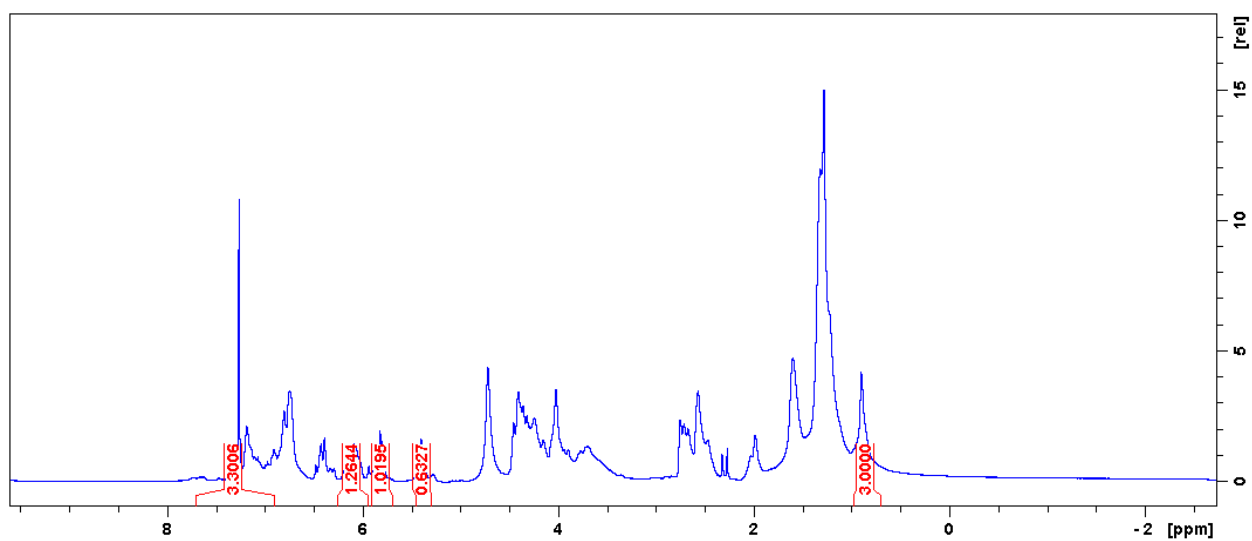


Figure 36 – <sup>1</sup>H-NMR spectrum of the cardanol-based VE resin with the integration values.