Natural origin precursors for carbon fiber production

Inês Moreirinha Lino

ines.m.lino@tecnico.ulisboa.pt

Instituto Superior Técnico

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Abstract

In the present work, to reduce environmental problems, precursor cost and, consequently, the cost and sustainability of carbon fibers, a natural source material, cardanol (obtained from cashew nut shell liquid waste), was used in the production of two different compounds, a polymer (polycardanol) and a prepolymer (cardanol-based vinyl ester (VE) resin), which were investigated as precursors to produce more economically sustainable and more eco-friendly carbon fibers.

Both polycardanol and cardanol-based vinyl ester 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.

1. Introduction

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 [1]. 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 [2][3][4]. 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 [5]. 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 [3][5].
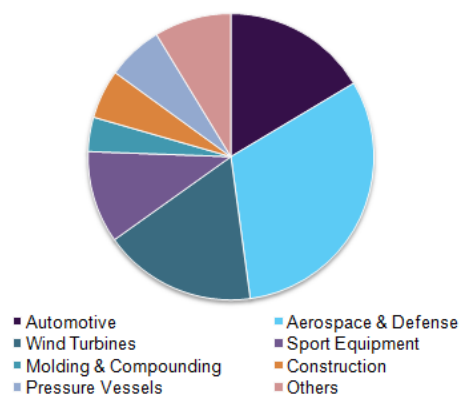
Figure 1 – Global carbon fiber market volume share by application, in percentage, in 2016 [4].

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 [6]. 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 [4][7].

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.

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.
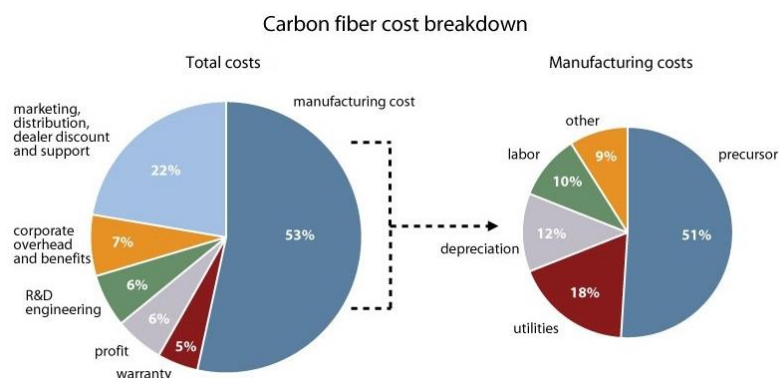

Figure 2 – Carbon fiber cost breakdown (Adapted from [8]).

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.

2. Materials and experimental methods

2.1 Materials

Cardanol NX-9001 and epoxidized cardanol resin NC-514 (EEW=490 g/eq [9]) 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 (≥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.

2.2 Experimental methods

2.2.1 Synthesis of prepolymer cardanol-based vinyl ester resin

The preparation method of the vinyl ester prepolymer resin was adapted from reference [10] (Figure 3). 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 ºC 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 ºC. The AA in the salt form was extracted with water (decantation) and the chloroform was evaporated under vacuum in a rotary evaporator at RT.

2.2.2 Synthesis of polycardanol

Polycardanol was prepared by a similar method as the one presented in [11] (Figure 3). Approximately, 0.3 g of cardanol NX-9001 were dissolved in an aqueous solution of NaOH (2 g NaOH / 100 mL H_2O) and the temperature was raised to 50 ºC. 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 [11].

Figure 3 – Experimental set-ups for both synthesis and with the Soxhlet extractor.

3. Results

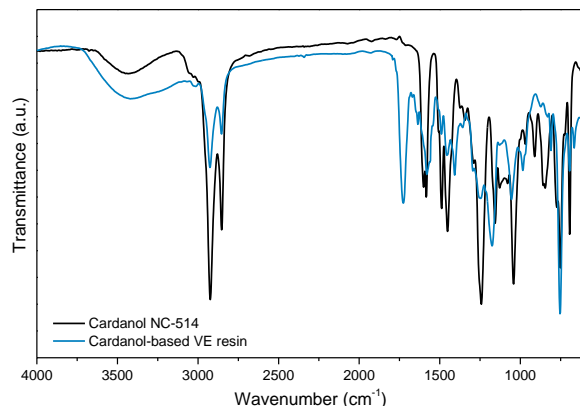### 3.1 Characterization of the prepolymer cardanol-based vinyl ester resin

Figure 4 – ATR-FTIR analysis of cardanol NC-514 and of the VE resin.

Figure 4 shows cardanol NC-514 and VE resin's ATR-FTIR spectra. In both, the large band peaked around 3400 cm^{-1} denoted the existence of hydroxyl groups (OH), which indicates the presence of water. Besides this, around 1639 cm^{-1}, 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^{-1} are attributed to the presence of CH, CH_2 and CH_3 groups, and, in the VE resin spectrum these peaks have lower intensity. Around 1730 cm^{-1} 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 [12]. The absence of the peaks at 909, 859 and 846 cm^{-1}, 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^{-1}, 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^{-1} might be related to para substitution in the aromatic ring.

The ^{1}H-NMR spectrum of the VE resin is presented in Figure 5. 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 (pre-polymer). The multiplet peaks between 4.00 and 4.70 ppm region were attributed to the ($-OCH_2-$) protons and the tertiary ($-CH(OH)-$) proton of the (phenyl-OCH_2-CH(OH)-CH_2O-(C=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}H-NMR spectrum. Thus, the functionality of the VE resin unit was calculated using the following equation. [10]

$$F = \frac{I_g + I_h}{I_a}$$
$$\times \frac{\textbf{Ethyl protons of the acrylate end group}}{\textbf{Terminal methyl protons of the aliphatic side chain}}$$

$$F = \frac{1.26 + 1.02}{3.00} \times \frac{3}{2} = 1.14$$

Considering an epoxy functionality of cardanol NC-514 at 1.32 [10], 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 6 the ^{13}C-NMR spectrum of the VE 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}H and ^{13}C NMR spectra of the VE resin are consistent with those obtained from the ATR-FTIR spectrum.

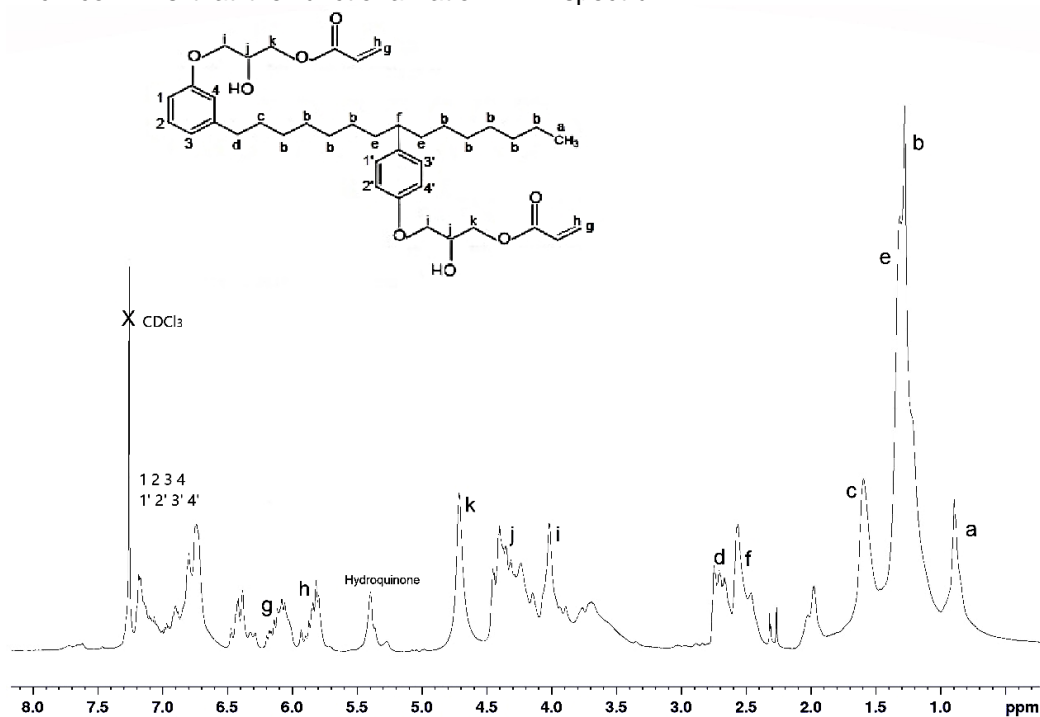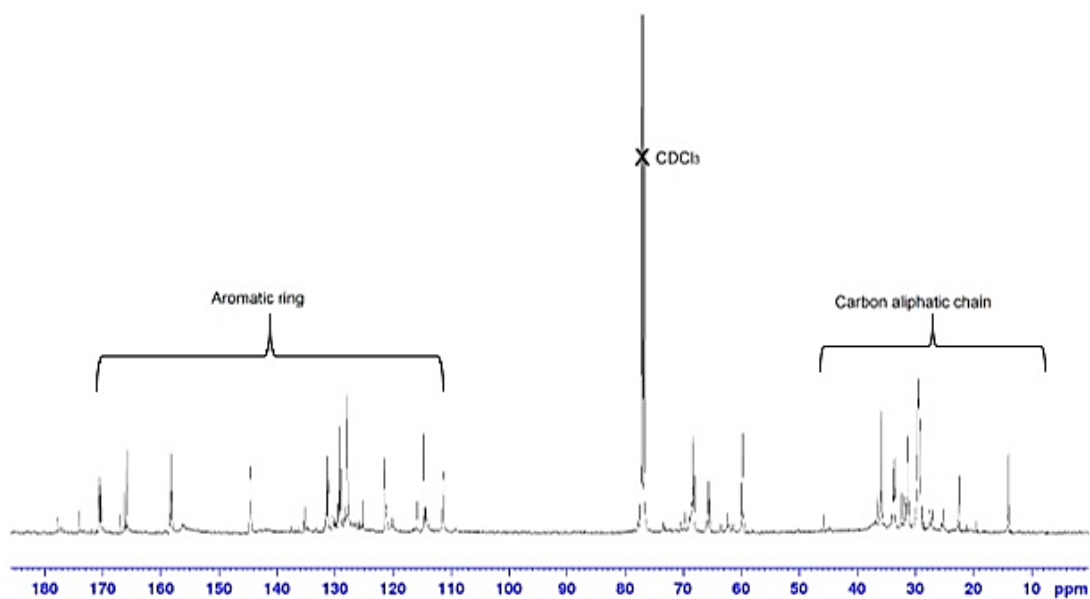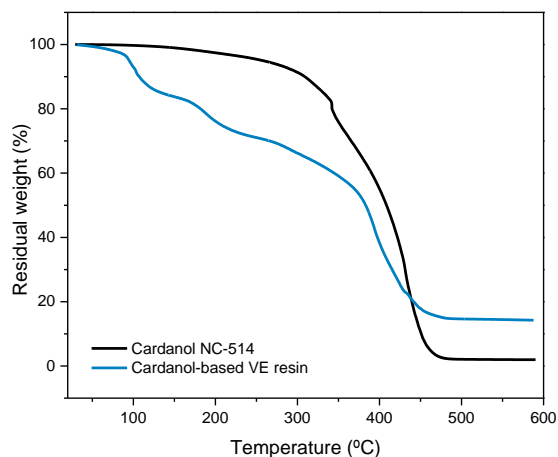**Figure 5 – ^{1}H-NMR of the VE resin in deuterated chloroform, CDCl$_3$.**

Figure 6 – ^{13}C-NMR of the VE resin in deuterated chloroform, CDCl$_3$.

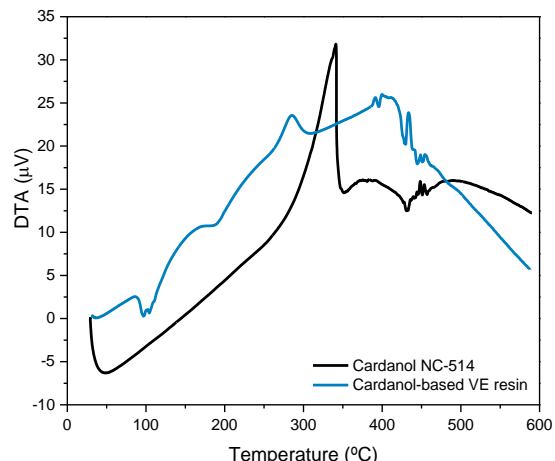**Figure 7 – TG analysis of cardanol NC-514 and of the VE resin, at 10 ºC/min in N₂.**

Figure 8 – DTA analysis of cardanol NC-514 and of the VE resin, at 10 ºC/min in N₂.

Figure 7 shows both thermograms of cardanol NC-514 and the VE resin produced. The weight loss around 100 ºC 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 ºC, is 14.2 %, but if the water had been successfully removed, the char yield, at 550 ºC, 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 vinyl ester 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 ºC could be due to acrylic acid species, or other compounds present in the resulting prepolymer that were not successfully eliminated during decantation or the rotary evaporation process.

DTA analysis of cardanol NC-514 and of the VE resin are presented in Figure 8. Cardanol's curve shows an exothermic peak at 341 ºC, being attributed to the cleavage of the alkyl side chain of the aromatic ring [13].

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 ºC, 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.

The DSC curve obtained for the VE resin (Figure 9) shows two endothermic processes, at around 160 ºC and 250 ºC, and an exothermic process, at around 200 ºC. 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.
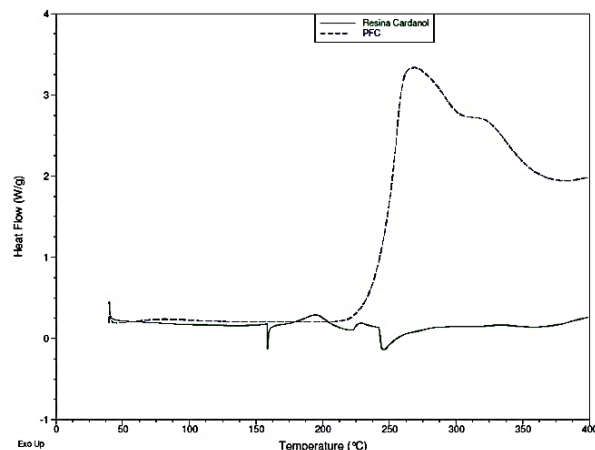
Figure 9 – DSC thermograms of the VE resin and PAN (commercial carbon fiber precursor, PFC), at 5 ºC/min in air.

PFC's thermogram (Figure 9) exhibits a clear and intense exothermic peak at around 280 ºC, 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 ºC, 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 prepolymer 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 [14], it is possible to verify that the latter, at around 400 ºC, 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.

The same finding was observed for rayon-based carbon fiber precursor, according to reference [15], where its thermogram is shown, and which also does not exhibit any exothermic process below 400 ºC, in line with what happens for the cardanol-based VE resin, but also does not show any melting related peak below 300 ºC, in opposition to what is observed for the VE resin.

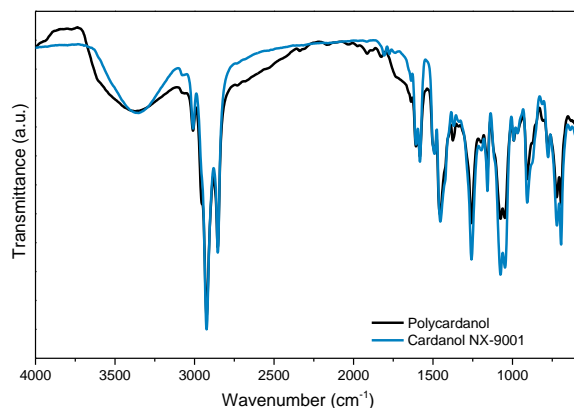## 3.2 Characterization of the polycardanol

Figure 10 – ATR-FTIR analysis of Cardanol NX-9001 and polycardanol.

The ATR-FTIR spectra of cardanol NX-9001 and of polycardanol are shown in Figure 10. In both spectra, the peak around 3400 cm^{-1} 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^{-1}, 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^{-1}. The peaks between around 1608 and 1450 cm^{-1} correspond to the C=C bonds of the aromatic ring. Both spectra exhibit some characteristic peaks at 1240 and 1190 cm^{-1}, which correspond to the vibration of C(Ar)-O-C(Ar) bonds, and at 1155 cm^{-1} 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.

The ^{1}H-NMR spectrum of polycardanol is shown in Figure 11. When comparing the peaks in this spectrum with a typical spectrum of a resin, such that of Figure 5, it is possible to verify that the latter is broader and has lower
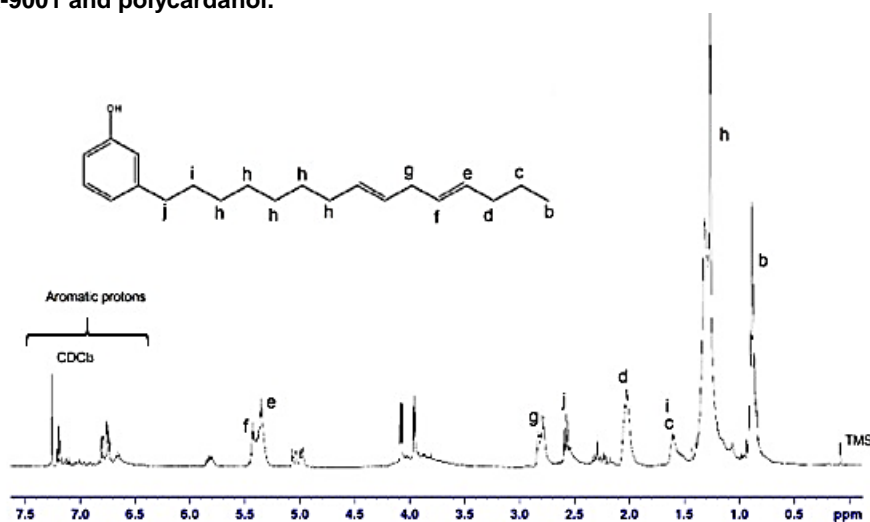

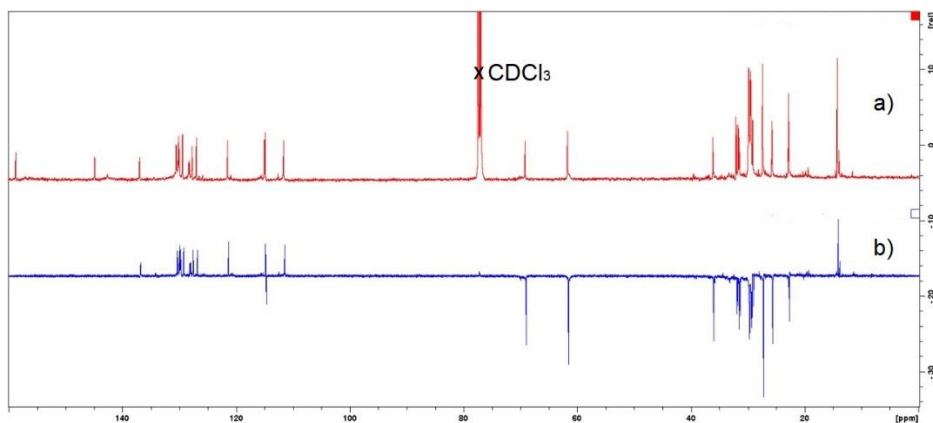Figure 11 – ^{1}H-NMR of polycardanol in deuterated chloroform, CDCl$_3$.

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Figure 12 – a) ^{13}C-NMR and b) DEPT C-NMR of polycardanol in deuterated chloroform, CDCl$_3$.

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 occurred in the intended extension.

Figure 12 shows both ^{13}C-NMR and DEPT C-NMR of polycardanol. In a DEPT (Distortionless Enhancement of Polarization Transfer) spectrum, CH and CH$_3$ peaks appear as normal, but CH$_2$ peaks appear inverted, allowing, this technique, to determine the number of hydrogen atoms linked to each carbon. In the ^{13}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 [16]. 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 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 CH$_2$ group, demonstrating that a total polymerization may have not occurred.

Figure 13 shows the comparison between TG thermograms of cardanol NX-9001 and polycardanol. It is possible to observe that up to a temperature of 135 ºC, 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 NaCl. If this removal had been effective, it is estimated that, at 550 ºC, 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 [10] (25 %), but higher than that of cardanol NX-9001, which might suggest that some oligomeric, or polymeric (polycardanol) species are present.
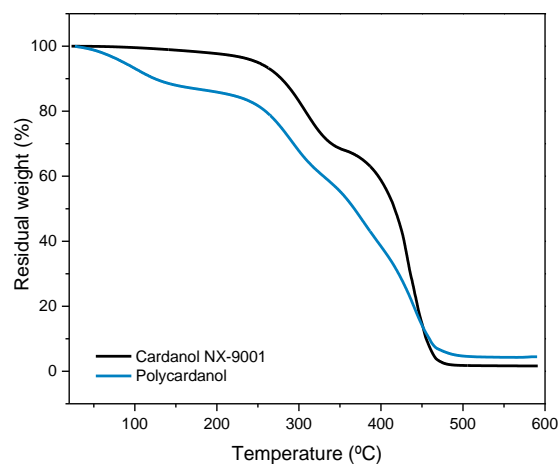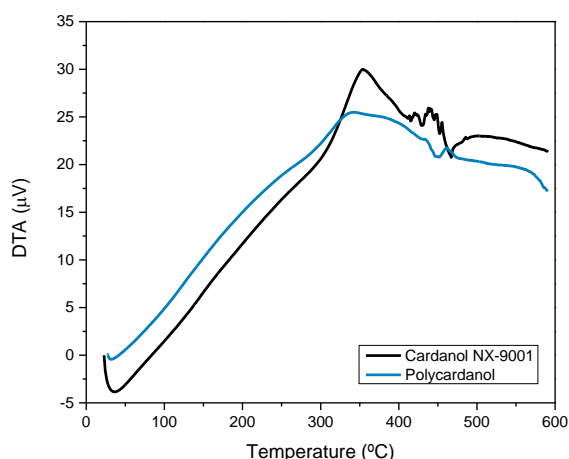

Figure 13 – TG analysis of cardanol NX-9001 and polycardanol, at 10 ºC/min in N$_2$.

Cardanol NX-9001 has two stages of degradation, the first at 249 ºC and the second at 387 ºC, 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.

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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 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.

In Figure 14 both DTA curves of cardanol NX-9001 and polycardanol are presented. Cardanol´s curve has an exothermic peak around 353 ºC, that can be attributed to the cleavage of the alkyl side chain of the aromatic ring [13]. Besides this peak, it has smaller endothermic peaks at 430 ºC and 468 ºC. Despite not having such a defined exothermic peak around 350 ºC, 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.

Figure 14 – DTA analysis of cardanol NX-9001 and polycardanol, at 10 ºC/min in N$_2$.

The DSC curve obtained for polycardanol (Figure 15) shows a small exothermic process, at around 160 ºC, and a small endothermic process, at around 265 ºC. 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 15), supplied by FISIPE, and also with those, found at the literature, for pitch and rayon based precursors.
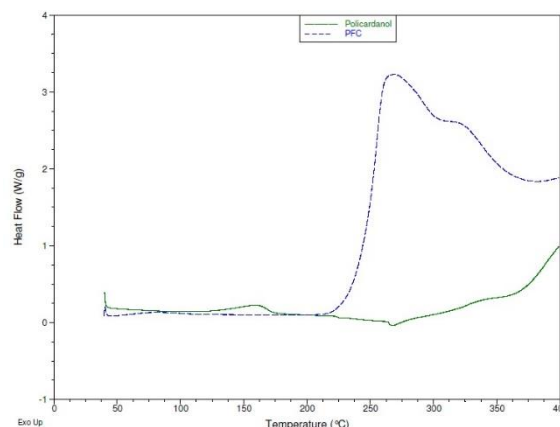
Figure 15 – DSC thermogram of polycardanol and PAN, at 5 ºC/min in air.

As explained before, PFC sample exhibits a thermogram with a clear and intense exotherm peaked at around 280 ºC, 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 ºC, 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 [14], it is possible to verify, in both of them, the presence of a starting exothermic process around 400 ºC, 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 [15], whose thermogram also does not exhibit any exothermic process below 400 ºC, in line with what happens for polycardanol, and shows an endothermic peak at 350 ºC, contrary to what is observed for polycardanol.

4.   Conclusions

In the present work, 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 the 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 vinyl ester prepolymer.

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

5.   References

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