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CATIONIC UV-CURING OF EPOXIDIZED CARDANOL DERIVATIVES

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Abstract: This paper demonstrates the high reactivity and potentiality of bio-renewably obtained cardanol-based epoxy monomers as well as the possibility of tuning the final thermo-mechanical properties, by changing either the epoxy content or the chemical structure of the starting photocurable resin. The reactivity of the cardanol monomers towards the cationic UV-curing process was investigated by FT-IR analysis and it was shown that a high epoxy group conversion was achieved. Furthermore, thermomechanical properties were investigated on crosslinked films by means of DSC and DMTA analysis.

Keywords: cardanol epoxy monomer, cationic UV-Curing, photopolymerization, bio-renewable monomers.

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1. Introduction

Epoxy polymers are one of the most versatile and important classes of thermosetting materials and they have important applications in different fields such as; adhesive, coatings, carbon-fiber and glass-fiber composites, among many others [1-4]. However, most of them are derived from petrochemical feedstock, a source with restricted availability and environmentally controversial. Currently, epoxy building-blocks production is dominated by the DiGlycidyl Ether of Bisphenol-A (DGEBA). This molecule is directly obtained by glycidylation of the Bisphenol A, a reprotoxic substance considered to be of high concern (SVHC). For this reason, bio-based resins are attracting attention in research circles as they combine the advantages of Bisphenol A alternatives and are a renewable resource. [5].

The advantages of bio-resins reside in their availability and diversity, enabling them to reach a wide range of thermo-mechanical properties without complications regarding sustainability. Vegetable oils constitute one of the largest families among bio-renewable monomers capable of competing with petro-based products. Epoxidation of vegetable oils [6] is performed by oxidizing the naturally-occurring unsaturations along the fatty acid chains with, in most cases, a peracid. Epoxy thermoset materials derived from Epoxidized Vegetable Oils (EVOs) usually highlight low thermo-mechanical properties and are thus used in plasticizers, adhesives, packaging and coatings.

In order to enhance performance, aliphatic structures must be limited and cycloaliphatic or aromatic structures must be considered. The cycloaliphatic and aromatic structures generate a great deal of interest since they can be extracted from lignin [7], the most abundant aromatic feedstock. Several aromatic compounds such as cinnamic acid [8], eugenol [9] or vanillin [10] can be epoxidized and used as thermosetting materials [11]. In a previous paper published by this group, it was reported the synthesis of epoxy functionalized bio-renewable monomers achieved from vanillyl alcohol and phloroglucinol that can be applied in cationic photopolymerization. The cationic UV-curing process efficiently gave rise to crosslinked coatings with a wide range of thermo-mechanical properties [12].

A further alternative that sits at a halfway point between pure aliphatic and aromatic structures could be cardanol, which makes up a large percentage of cashew nut shell liquid (CNSL). This molecule is a really promising renewable material since it is a red liquid obtained, as a by-product, from the cashew industry. Cheap and abundant cardanol is made up of a phenol moiety meta-substituted by up to 4 different C_{15} alkyl chains differing in their degree of unsaturation. In fact, it is composed by 8.4% of saturated chains, 48.5% mono-olefinic, 16.8% diolefinic and 29.33% triolefinic [13].

These unique characteristics make cardanol an interesting starting material for the synthesis of highly valuable products. Hence, much research in recent years has focused on cardanol and its derivatives [14]. For example, polyols can be derived from cardanol via epoxidation of the double bonds followed by a ring opening reaction. It is also possible to modify cardanol by grafting polyols or glycidyl groups onto the phenolic moiety. The interest of cardanol as bio-renewable monomer is witnessed by various cardanol derivatives currently commercialized by Cardolite® corporation which proposes a wide range of products for adhesive, composite or coating applications [15-17].

In order (i) to obtain crosslinked materials and (ii) to be able to tune the crosslinking density and thus the material mechanical properties, it was decided to chemically modify the double bonds on the lateral alkyl chains into epoxide rings. We selected 3 epoxy cardanol-based products from Cardolite® catalog, namely (i) Cardolite NC-513 and LITE 2513HP which are monofunctional reactive glycidyl ether diluents and (ii) NC-547, which is a polyglycidylether Novolac resin derived from cardanol.

Their chemical structures as well as their specifications are reported in Table 1. The reactivity of the selected functionalized cardanol was investigated in cationic UV-Curing.

In the field of polymeric coatings, the UV-curing technique shows many interesting advantages over the thermal method, such as reduced energy consumption, high cure speed even at room temperature and absence of VOC emission. [18-20] Furthermore, the cationic UV-Curing reaction shows important advantages with respect to the radical process; in fact, it is not inhibited by the presence of oxygen and after been initiated, is able to continue after the light source has been removed [18]. Nevertheless, very few examples of photo-crosslinked cardanols can be found in literature. Multiarmed cardanol-based acrylate oligomers synthetized with cardanyl ether and biobased polyols has been proposed as UV-curable coating with good mechanical properties [21].

To the best of our knowledge, only two articles have been published concerning the utilization of epoxidized cardanol (ECD) in cationic UV-curable system. In the first study, only LITE 2513 HP products from Cardolite® Corporation were used, which correspond to cardanol glycidylether (Table 1). In this literature report ECD was used both as humidity-blocker and as reactive diluent in formulations based on a mixture of cycloaliphatic epoxy-based materials and different amounts of oxetane and polycaprolactone [22]. In the second study, the epoxidized cardanol resin NC-514S was cured with 5%wt of a cationic photoinitiator and its combination with microfibrillated cellulose was studied in order to obtain a biobased composite [23].

However, no much attention was given to the possible mechanical properties that could be obtained by coatings prepared out of cardanol-based building blocks and no studies have been conducted on the influence of the epoxy groups contents on these properties.

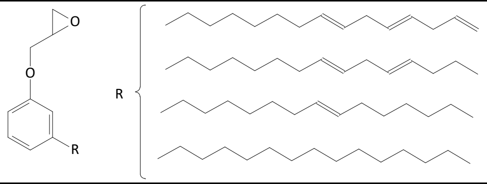
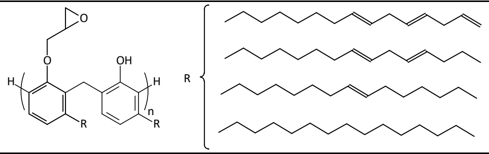
In order to fill this gap, the synthesis of epoxidized cardanol-based resins and their reactivity towards cationic photopolymerization has been discussed in this paper. The thermo-mechanical properties of the obtained crosslinked films were evaluated in detail and the results discussed in relationship with the resins chemical structures.

2. Experimental

2.1 Materials

Cardolite NC-513, LITE 2513HP and NC-547 were kindly provided by Cardolite® Corporation. Their structure and main characteristics are given in Table 1. Epoxidized Cardolite NC-513 (SP-ECO-84), epoxidized Cardolite LITE 2513HP (SP-ECO-85) and epoxidized Cardolite NC-547 (SP-ECO-86) were synthesized as following reported and provided by SPECIFIC POLYMERS. Their chemical structures are reported in Table 2. The cationic photoinitiator triarylsulfonium hexafluoroantimonate salts, mixed 50 wt. % in propylene carbonate were purchased from Sigma Aldrich (Milan, Italy). Amberlite® IR-120 hydrogen form, anhydrous sodium sulfate Na_2SO_4 (99%) and all solvents (> 95%) used were purchased from Sigma Aldrich. Hydrogen peroxide aqueous solution (35%, w/w) was purchased from Alfa Aesar. Acetic acid (99%) was purchased from abcr GmbH. All reagents, reactants and solvents were used as received.

Table 1: Chemical structures of Cardolite® NC 513, LITE 2513HP and NC-547 and their respective specifications

Product	Type	Structure	Glycidyl index[a] (m_{eq}/g)	Double bonds index[b] (m_{eq}/g)
NC-513	Reactive diluent		1.74 – 2.35	5.83
LITE 2513HP	Reactive diluent		2.22 – 2.6	5.68
NC-547	Epoxy novolac resin		1.18 – 1.82	5.0

a. value obtained from the technical data sheet (TDS) provided by the supplier; b. value obtained by ^{1}H NMR titration; n in the NC-547 was not determined.

2.2 Synthesis of the epoxidized cardanol derivatives

2.2.1 Synthesis of epoxidized monomers: epoxidized Cardolite NC-513 (SP-ECO-84) LITE 2513HP (SP-ECO-85) and NC-547 (SP-ECO-86)

Quantities were adjusted regarding the unsaturation content (evaluated by ^{1}H NMR titration) of each Cardolite products, presented in Table 2.

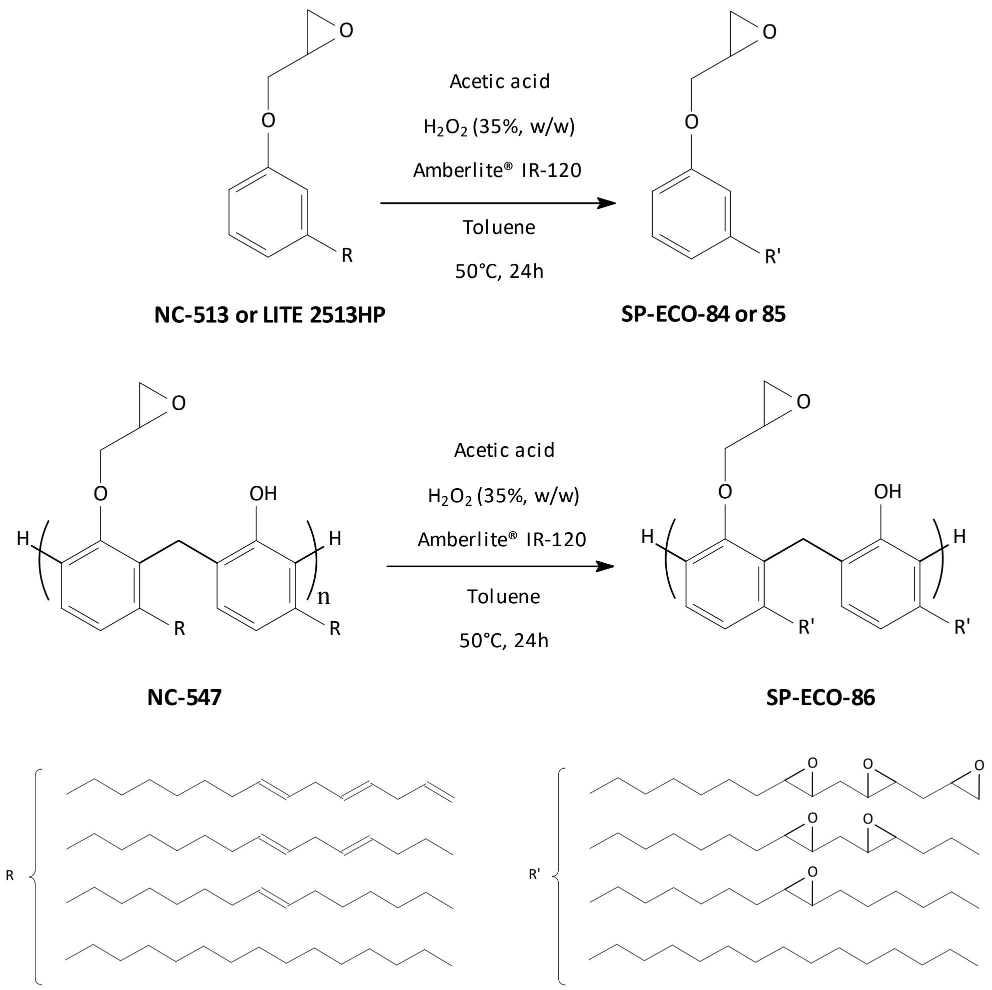
Typically, the epoxidation is carried out under the following molar ratio conditions C=C/Acetic Acid/H_2O_2 (35% w/w); 1/0.5/1.5eq with amberlite® IR-120. Epoxidized derivatives were synthesized in one step as shown in Scheme 1.

A 500 mL two-necked round bottom flask, equipped with mechanical stirrer and addition funnel, was charged with Cardolite NC-513 (50 g, 0.292 mol of double bonds, 1eq) with 50 g of toluene. Acetic acid (8.752 g, 0.146 mol, 0.5eq) was added to the reaction mixture. Then, after few minutes, amberlite® IR-120 hydrogen form (5.125 g) acting as strong cation exchange resin was added and the mixture was stirred at 510 rpm at 50 °C. Once the temperature was reached, hydrogen peroxide aqueous solution (35%, w/w) (42.501 g, 0.44 mol, 1.5eq) was added dropwise for 30 min with continuous stirring. The reaction was thus carried out at 50 °C for 24h. Once the reaction was completed, the mixture was filtrated to remove amberlite®IR-120 and 400 ml of diethyl ether was added. The organic layer was washed three times with water, dried on anhydrous Na_2SO_4 and then filtered. Solvents were removed under reduced pressure at 60 °C using a rotary evaporator. A red viscous liquid epoxidized NC-513 was obtained (50 g) with a yield of 93% and the product was characterized by ^{1}H NMR (Fig. 1a). The epoxy value was determined by ^{1}H NMR titration.

The method consists in solubilizing a known mass of the product (NC-XXX or SP-ECO-XXX) and of an internal standard (Benzoic acid (5 equivalent H) in acetone-d6 whose signal is dissociated from the others). The number of moles of epoxide functions per gram of product was measured by comparing the integration of the standard with the integration of a signal accounting for all the oxirane rings (or double bonds) alongside the alkyl chain (H10 on the NMR spectra in Figure 1).

In order to compare theoretical values of glycidyl content (from the TDS) and experimental ones (Table 1).The epoxy index was evaluated at 3.88 m_{eq}/g.

Epoxidized LITE 2513HP and NC-547 were achieved thanks to the same general procedure described above. Their epoxy indexes were respectively evaluated by ^{1}H NMR titration at 3.89 m_{eq}/g and 2.82 m_{eq}/g. The products were characterized by ^{1}H NMR (Fig. 1b and 1c).



Scheme 1. Synthetic route of epoxidized Cardolite products SP-ECO-84, 85 and 86

2.3 Photocuring of epoxidized cardanol oils

Typically, 1g of previously synthetized ECD resins were mixed with 40 mg of the cationic photoinitiator: triarylsulfonium hexafluoroantimonate salts (2 wt% of actual photoinitiator content). The liquid formulations were crosslinked with a Fusion System lamp in air at a conveyor speed of 6 m/min and a light intensity of 235 mW/cm^2. Taking into consideration the lamp window dimension of 15.2 x 15.2 cm and the speed of 6 m/min, the irradiation time was estimated to be 1.52s. Film thickness was about 100µm.

2.4 Characterization

^{1}H NMR spectrum synthesized monomers were obtained using Bruker Advance 300 (300 MHz) spectrometer equipped with a QNP probe at room temperature. Deuterated solvents used are given for each molecule. The Epoxide Index (EI, number of moles of epoxide groups per gram, eq. g^{-1}) was determined according to ^1H NMR titration method.

The FTIR spectra were recorded with a Nicolet iS 50 Spectrometer in transmission mode in air. The measurements were performed on the photocurable formulations coated on a silicon wafer (film thickness of 25 μm) before and after irradiation under the Fusion lamp.

All the measurements were obtained with a scanning rate of 1 scan per 1.2 s in the wavelength range of 500–4000 cm^{-1}, with a spectral resolution of 4.0 cm^{-1}. The Thermo Scientific™ OMNIC™ Specta Software was used to record and process the data.

Differential scanning calorimetric (DSC) analysis were carried out on a Mettler Toledo DSC instrument at a heating rate of 10°C/min. Samples (10–12 mg) were sealed in a 100 μl aluminium pans with pierced lids. Nitrogen was used as a purge gas.

Dynamic thermal-mechanical analysis (DMTA) were performed with a Triton Technology. Uniaxial stretching of samples was performed with a heating rate of 1°C/min, frequency of 1Hz and strain of 0.02%. The approximate sample dimensions used in this test were 12x7x0.2 mm. The storage modulus (E’) and the loss factor (Tanδ) were recorded as a function of temperature. The storage modulus in the rubbery plateau (E'_R) was calculated at generally 50°C above the glass transition temperature. These values were used to estimate the apparent cross-linking density (ν_c), also known as strand density, according to Eq 1. This equation derived from the statistical theory of rubber elasticity, which is not fully correct and therefore was used only to qualitatively compare the level of crosslinking among the obtained networks [24,25].

$$\nu_c = \frac{G'_R}{3RT} \qquad (1)$$

where ν_c is the number of moles of network chains per unit volume of the cured network, R is the gas constant, T is the absolute temperature (i.e. at T_g+50°C).

3. Results and Discussion

3.1. Synthesis and characterization of ECD

Three different bio-renewable ECD (SP-ECO-84, SP-ECO-85 and SP-ECO-86) were synthesized, as reported in the experimental part. The obtained products were characterized by ^1H NMR spectroscopy in order to evaluate the efficiency of the epoxidation reaction and to determine accurately the epoxy content of final ECD. ^1H NMR characterization are shown in Figure 1.

The epoxidation of the double bonds of the cardanol-based products enabled to approximately double the total epoxy functions content compared to Cardolite® products precursors. However, as observed on each ^1H NMR spectra, epoxidation of cardanol-based products was not complete since double bonds signals were still observed in ^1H NMR (Fig. 1 (a,b,c)). Residual double bonds were evaluated at 1.04m_{eq}/g, 1.4m_{eq}/g and 1.03m_{eq}/g for SP-ECO-84, 85 and 86 respectively. This result was already observed and explained by the lack of reactivity of the terminal double bonds against oxidizing agents like hydrogen peroxide or mCPBA [16]. Finally, the main chemical characteristics of prepared ECD are gathered in Table 2.

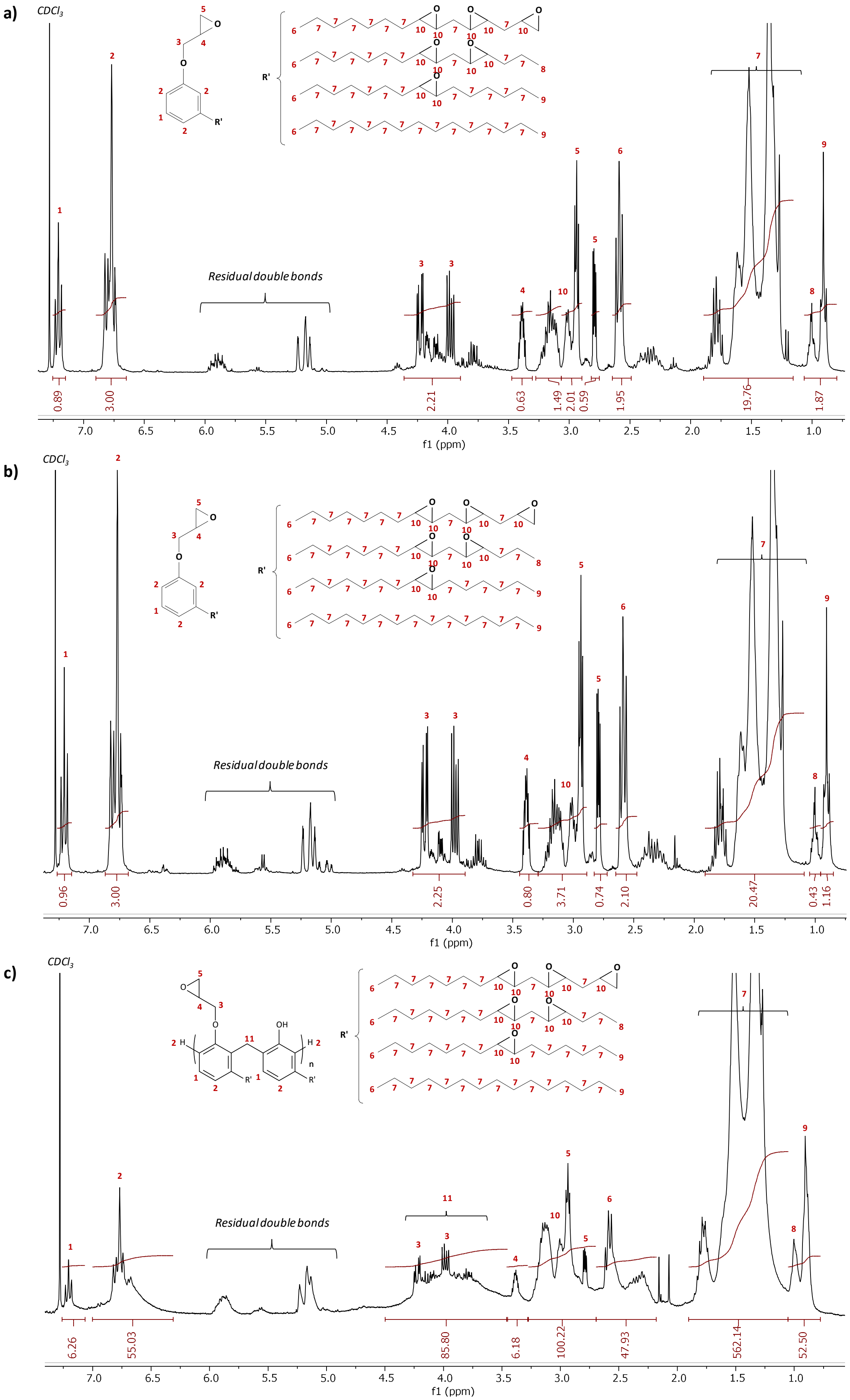


Fig. 1. ^{1}H NMR spectra of SP-ECO-84 (a), SP-ECO-85 (b), SP-ECO-86 (c) in $CDCl_3$.

Table 2. properties of the cardanol epoxidized resins

Polymer network	Starting ECD	Epoxy content in the starting ECD		Epoxy group conversion^c (%)	Tg (°C) (DSC)	Tg (°C) (DMA)
		Glycidyl index^a (m_{eq}/g)	Epoxy index^b (m_{eq}/g)			
ECO-84	SP-ECO-84	1.74 – 2.35	3.88	72	25	38
Eco 85	SP-ECO-85	2.22 – 2.6	3.89	64	36	53
ECO-86	SP-ECO-86	1.18 – 1.82	2.82	66	53	65

a. value obtained from the technical data sheet (TDS) provided by the supplier;
b. value obtained by ^{1}H NMR titration
c. estimated by FTIR

3.2.ECD based UV-cured coatings

The reactivity of the epoxidized cardanol monomers was investigated, towards the cationic photopolymerization, by FT-IR analysis. The epoxy group conversion was measured by following the decrease of the peak in the range from 892 to 818 cm^{-1}. The epoxy-ring opening was also confirmed by the increase of the peaks at 1118 and 1050 cm^{-1} that can be attributed to the C-O-C stretching vibrations of ether groups. The FT-IR before and after UV-irradiation are reported in Figure 2. All the data are summarized and collected in Table 2. A high epoxy group conversion is always achieved (between 64% and 72 %) and fully tack-free films were always obtained.

The thermal and viscoelastic properties of the crosslinked networks were evaluated by means of DSC and DMTA analysis (data reported in Table 2). While DSC analysis gives information about the thermal behaviour, DMTA allows the evaluation of the elastic and viscous component of the modulus of the material in a very large temperature interval. In the Tg region the tanδ curve (tanδ = E''/E': ratio loss modulus/storage modulus) shows a maximum which is assumed as the Tg of the cured films [26]. Therefore, by combining these techniques, a good characterization of the thermal and viscoelastic properties of the materials is obtained.

The Tg measured by DMTA are higher than the one determined by DSC The Tg measured by DMTA and DSC are always different, and this can be attributed to the fact that each technique measures a different physical property, where DMA measures mechanical changes, the DSC measures calorimetric changes; these changes could begin measurable at different temperatures.[27].When Tg is measured in term of mechanical changes (DMTA) a molecular relaxation occurs that involves cooperative segmental motion whose rate will depend on temperature. Therefore, as the frequency of the test increases, the molecular relaxations can only occur at higher temperatures and, as a consequence, the Tg will increase with increasing frequency. [28].

The DMTA tanδ and storage modulus curves of the crosslinked cardanol based coatings are reported in Figure 3.

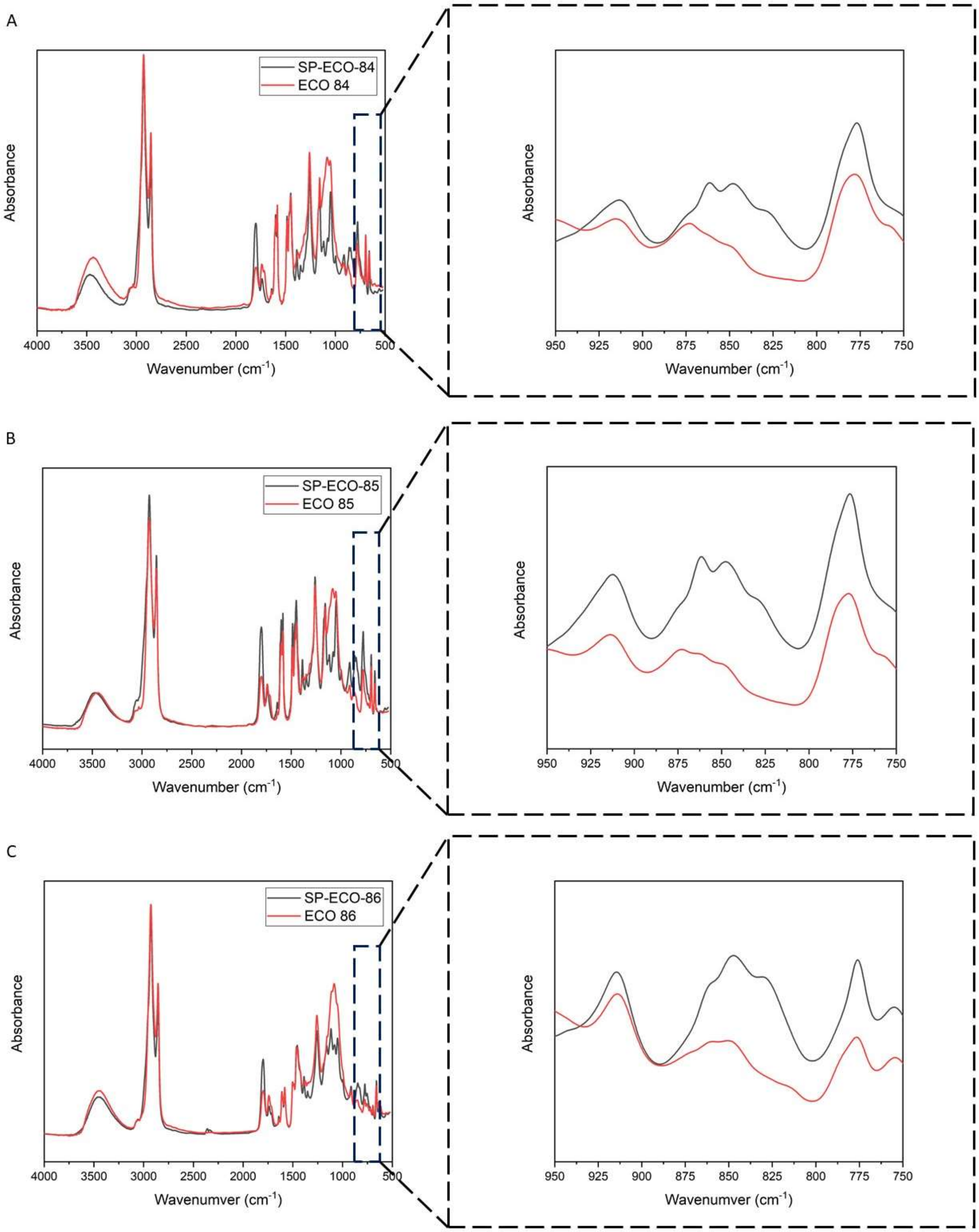


Figure 2. FT-IR spectra of the SP-ECO-84 (2A), SP-ECO-85 (2B), SP-ECO-86 (2C) formulations, before (black spectra) and after (red spectra) UV-irradiation. Fusion lamp, conveyor bel velocity 6 m/min, film thickness 25 μm, cationic photoinitiator content 4 wt%, light intensity 235 mW/cm^2.

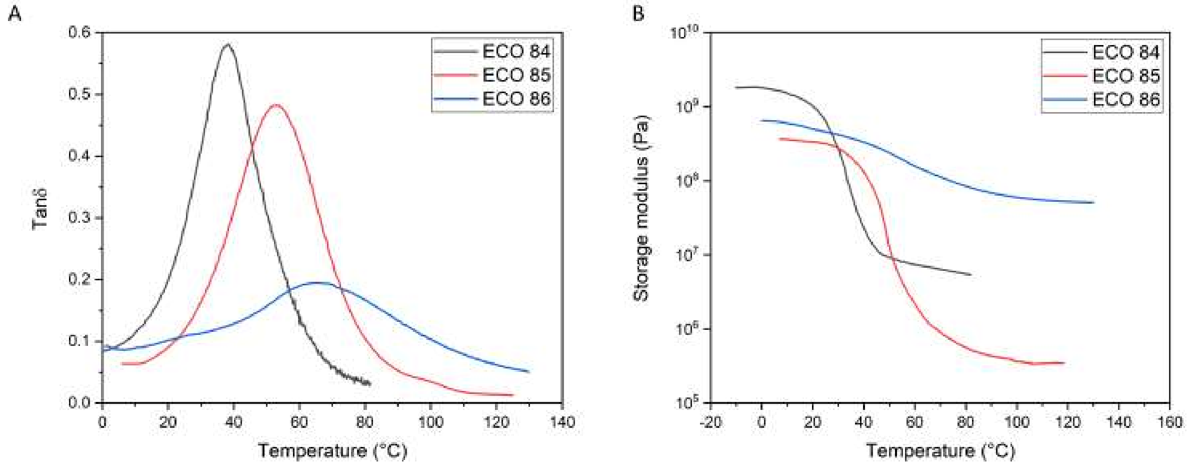


Figure 3. The DMTA-tanδ (A) and Storage modulus (B) curves for the crosslinked cardanol epoxy resins.

It is possible to observe a shift of the maximum of tanδ curves towards higher temperature going from the crosslinked ECO84 with a Tg of about 38 °C, to ECO 85 with a Tg of about 53 °C and finally to a Tg of about 65 °C for the crosslinked ECO 86 resin. These Tg values are comparable with others epoxidized bio-based resins studied in a previous paper from our team [12].

While SP-ECO 84 and SP-ECO 85 have similar epoxy aliphatic content, the resin SP-ECO 85 is characterized by a slightly higher epoxy glycidyl content. This induces the formation of a higher crosslinked epoxy network and therefore to its higher Tg. This is also responsible of an earlier vitrification and therefore to a lower final epoxy group conversion (see data reported in Table 2).

On the other hand, ECO 86 is characterized by both lower epoxy aliphatic and epoxy glycidyl content. Nevertheless, the crosslinked film is characterized by the higher recorded Tg value among the 3 different cardanol investigated systems. The higher rigidity of the crosslinked ECO 86 can be attributed to the polyaromatic structure of the starting resin. Also, the lower damping value (0.2 compared to 0.45 for crosslinked ECO 85 and 0.58 for ECO 84) suggest the formation of a highly rigid polymeric network. The Tanδ peak width broadens as the epoxy content increase due to higher branching modes and results in a wider distribution of structures.

All the ν_c and the E'_R data are listed in the Tab.3. The low crosslinking density obtained in the ECO 85 network is in good agreement with the low conversion obtained in the FT-IR conversion.

Table 3. Storage modulus in the glassy state (E’), storage modulus in the rubbery plateau region (E'_R) and the crosslinking density of the cardanol epoxidized resins.

Reference	**E’ [MPa]**	**E'_R[MPa]**	**ν_c [mol/dm^3]**
ECO-84	1810.63	5.14	0.601
ECO-85	323-37	0.61	0.065
ECO-86	648.59	53.48	5.527

4 Conclusions

In this paper, various epoxy cardanol-based resins were synthesized as a bio-renewable alternative to petroleum-based epoxy resins. Different ranges of cardanol-based products were used and chemically modified in order to convert double bonds from the lateral aliphatic chains into epoxy rings. Although it was not possible to reach 100% conversion, we were able to double the epoxy content of synthesized ECD compared to corresponding precursors. The reactivity of the ECD towards cationic UV-curing process was investigated by FT-IR analysis. It was always possible to achieve a high epoxy group conversion, from 64% to 72%. The thermo-mechanical properties of the crosslinked films were analysed by means of DSC and DMTA analysis. Enhancement of the Tg values was observed by increasing the epoxy content in the photocurable cardanol resin or by exploiting the polyaromatic starting structure. In conclusion, this study demonstrates the high reactivity and potentiality of these epoxy monomers obtained by bio-renewable resources as well as the possibility to tune the final thermo-mechanical properties by changing either the epoxy content or the chemical structure of the starting photocurable resin.

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