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Cardanol-modified alkyd resins: novel route to make greener alkyd coatings

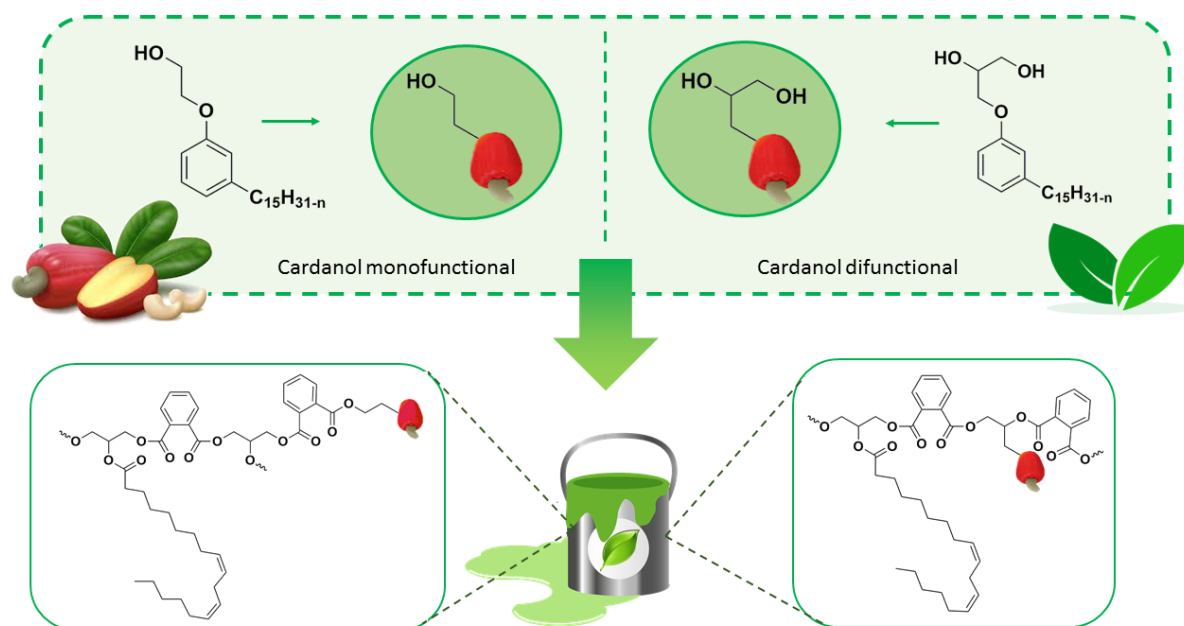
Maxinne Denis^{a,b}, Cédric Totee^a, Damien Le Borgne^b, Sylvain Caillol^a, Claire Negrell^{a*}

a ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

b Lixol, groupe Berkem, 20 Rue Jean Duvert, 33290 Blanquefort, France

*Corresponding author: Claire Negrell, email: Claire.negrell@enscm.fr

Graphical abstract



Abstract

Novel alkyd resins have been synthesized with mono- and di-functional cardanol monomers. This study has demonstrated that those monomers could replace some of the monomers used in alkyd resins, which were petrosourced. Indeed, the renewable carbon content has been increased by up to 12 %. The film properties (gloss, adhesion, drying time) have been investigated and the results showed that the introduction of cardanol monomers did not impact the coatings properties except for the color. Furthermore, thermogravimetric analysis has demonstrated that cardanol highly increased the thermal stability of alkyd resins.

Keywords

Alkyd resins, cardanol, biobased polymers, coatings

1. Introduction

Cardanol is a commercially available bio-based phenol that comes from cashew nut shell liquid (CNSL).^{1,2} CNSL is extracted from the fruit of cashew nut, which is a waste from the food industry. Moreover, it is considered as a very promising bio-based resource due to its unique structural characteristics, abundant availability, low cost and inedibility.³ Thanks to a thermal treatment of CNSL, the main constituent (anacardic acid) is decarboxylated into cardanol, a yellow pale liquid.⁴ Nowadays, the world production of cardanol almost reaches one million ton per years.⁵ Cardanol is composed of a phenol group with an unsaturated 15-carbon side chain which can exhibit until three

double bonds in various percentages (5-8 % for saturated chains, 48-49 % for mono-olefinic chains, 16-17 % of diolefinic chains, 29-30 % of triolefinic chains).^{1,6-9}

Thereby, the structure of the alkyl chain of cardanol could provide interesting coating properties such as flexibility, hydrophobicity, chemical resistance, flame retardant and anti-corrosion properties.^{5,10-17} Numerous of those studies focused on the introduction of acrylate-cardanol-based monomers in order to obtain ultra-violet (UV)-curable coatings. Li *et al.* studied the formation of latex-based coatings with higher adhesion performance thanks to the incorporation of phosphonated acrylated cardanol monomers.⁵ The influence on the coatings flexibility brought by cardanol methacrylate in latexes was highlighted by Li *et al.* thanks to differential scanning calorimetry (DSC) analyses which exhibited lower glass transition temperatures.⁶ Phalak *et al.* synthesized a diphenyl phosphate cardanol acrylate for UV-curable coating application.¹⁶ The results demonstrated better thermal stability and flame retardant properties. Liu *et al.* investigated the coating properties of cardanol-based acrylate oligomers prepared via a four-step procedure using cardanyl glycidyl ether polyacids and biobased polyols as raw materials.¹³ The resulting coatings provided excellent adhesion to aluminum substrates and good mechanical properties.

Further researches described the synthesis of cardanol-based monomer for the synthesis of epoxy coatings. Aggarwal *et al.* modified epoxy resins with cardanol glycidyl ether in order to formulate a paint with anticorrosive properties and better chemical resistance than unmodified epoxy resin-based paints.¹⁴ Another study made by Lv *et al.* demonstrated better performance in water absorption, peel strength test and anti-corrosion properties for coatings obtained with cardanol-based epoxy.¹⁵ Indeed, the study showed the improvement of the coatings properties when bisphenol A diglycidyl ether (DGEBA) was mixed with 20 wt% of cardanol-based epoxy or episulfide than coating with only DGEBA. Cardanol-based reactive polyamides have been developed by Balgude *et al.* in order to obtain curing agents for epoxy coatings.¹⁸ The coatings showed excellent chemical resistance, good thermal stability and anticorrosive performance.

Cardanol-based monomers have also been used in the synthesis of other polymers such as polyurethanes and polybenzoxazines. Huang *et al.* demonstrated the synthesis of cardanol-based polybenzoxazine with SiO₂-NH₂ nanoparticles in order to obtain coatings with superhydrophobic properties and improved corrosion resistance.¹² Mestry *et al.* studied the flame retardant properties of cardanol derived phosphorus and silicone precursors in order to react with diisocyanates and form polyurethane coatings.¹⁷ Recently, Vijayan *et al.* modified cardanol to obtain a diol which was allowed to react with a polyisocyanate in order to obtain a polyurethane resin.¹⁹ The introduction of cardanol improved the anti-corrosive and hydrophobic performance of resulting coatings.

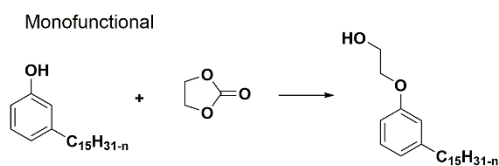
In the coating industry, alkyd resins (AR) are usually applied as binders in paints or varnishes formulations.²⁰ AR are synthesized through the polycondensation of polyols and diacids such as anhydrides. Moreover, AR are defined as polyesters modified by the introduction of fatty acids generally provided by vegetable oils.²¹⁻²⁴ Cardanol, due to its hydrophobic alkyl side chain, which makes it compatible with alkyd resins, and its large commercial availability, is a very attractive biobased raw material.

According to a critical review of the literature, it appears that there is no study neither on the synthesis of alkyd resins through the polycondensation of cardanol with polyols and diacids, nor on its influence on the coating properties. Indeed, several studies focused on the introduction of cardanol-based reactive diluent in alkyd resins but none of them dealt with the use of cardanol-based monomer during the polycondensation reaction.²⁵⁻²⁸

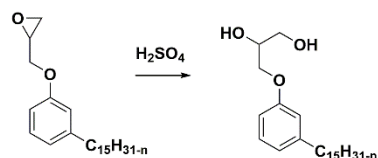
Hence, the first part of this study focused on the synthesis of alkyd resins with monofunctional reactive cardanol, which due to its structure, could replace benzoic acid and partially fatty acids (Figure 1). Then, in a second part, a difunctional reactive cardanol has been synthesized and copolymerized for the synthesis of alkyd resins (Figure 1). The characteristics of all alkyd resins were analyzed through viscosity and size exclusion chromatography (SEC). Furthermore, the impact of the

introduction of cardanol on coating properties such as gloss, flexibility, drying time, adhesion has been investigated.

Monomers synthesis



Difunctional



Alkyd resins synthesis

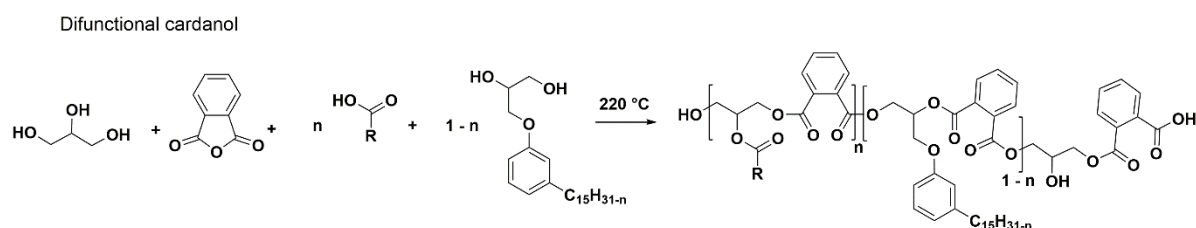
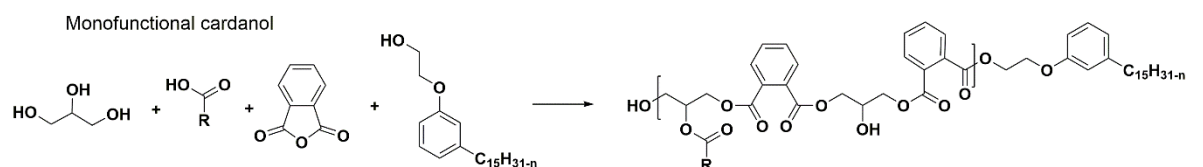


Figure 1: general scheme of cardanol-modified alkyd resins

2. Experimental

1) Materials

Tall oil fatty acid (TOFA), glycerol, phthalic anhydride, benzoic acid and mix of driers (a solution containing cobalt octoate, calcium octoate and zirconium octoate) were kindly supplied by Lixol (Groupe Berkem, Blanquefort, France). Fascat 4350 (tin catalyst) was supplied by PMC Organometallix, Inc. Cardanol NX-2026 and cardanol NC-513 were kindly provided by Cardolite. Xylene, p-toluenesulfonic acid (pTSA), sulfuric acid (H_2SO_4), sodium bicarbonate ($NaHCO_3$), ethylene carbonate and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were purchased from Sigma Aldrich. Tetrahydrofuran (THF), ethyl acetate were purchased from VWR International S.A.S (Fontenay-sous-Bois, France). The NMR solvent used was $CDCl_3$ from Eurisotop. All reagents were used as received.

2) Characterizations

Nuclear Magnetic Resonance

NMR samples were prepared with $CDCl_3$ as solvent and the analyses were performed using a Bruker Avance 400 MHz spectrometer at 25 °C. The structure of monomers was determined by hydrogen nuclear magnetic resonance (1H NMR), and phosphorus nuclear magnetic resonance (^{31}P NMR). The 1H NMR spectra were recorded at 8 kHz for spectral width, 3 kHz for transmitter frequency offset, 4 seconds for acquisition time and 8 scans were performed. Quantitative conditions were obtained

with a 30° pulse (3 μs) and a relaxation delay at 1 second. The ³¹P NMR spectra were recorded at 64 kHz for spectral width, 8000 Hz for transmitter frequency offset, 1 second for acquisition time and 4 scans were performed. Quantitative conditions were obtained with a 30° pulse (2.7 μs) and a relaxation delay at 20 seconds. External references were trimethylsilane (TMS) for ¹H and phosphoric acid (H₃PO₄) for ³¹P NMR. Shifts were given in ppm. Furthermore, to confirm the crosslinking of cardanol modified alkyd resins, high resolution magic angle spinning (HRMAS) NMR experiments have been investigated. HRMAS NMR experiments were carried out on a Varian VNMRS 600 MHz spectrometer equipped with a wide bore magnet (B₀ = 14.1 T). Prior to ¹H HRMAS NMR experiments, cured alkyd resins were grinded thanks to a cryogenic grinder and the powders were injected in a 4 mm quartz zirconia HRMAS rotor. Then, THF-d₈ was injected as solvent and experiments were performed at 20 °C, 9.6 kHz for spectral width, 1200 Hz for transmitter frequency offset, 1.7 seconds for acquisition time and 8 scans. Quantitative conditions were obtained with a 30° pulse (3.9 μs) and a relaxation delay at 1 second.

Acid values (AV)

Acid values were determined according to ISO 2114 standard. It is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of alkyd resin. Approximately, 1 g of the reaction mixture was withdrawn and solubilized in a neutralizing solution (80/20 xylene/ethanol). The solution was then titrated with a KOH solution at 0.1 mol.mL⁻¹. Thanks to the following equation (1), the acid value was calculated.

$$AV = \frac{V_{KOH} \times M_{KOH} \times C_{KOH}}{m \times N.V.C.} \quad (1)$$

AV: Acid value; V_{KOH}: volume of KOH solution introduced to neutralize the alkyd resin (mL); M_{KOH}: molecular weight of KOH (g.mol⁻¹); C_{KOH}: concentration of KOH (mol.mL⁻¹); m: mass of alkyd resin withdraw (g); N.V.C.: Non Volatile Content.

Renewable carbon content

The renewable carbon content (%rC) has been calculated using the equation 2, where N_{rTOFA} corresponds to the number of renewable carbon in TOFA (around 18). N_{rCARDANOL} corresponds to the number of renewable carbons for each cardanol (21 for the monofunctional cardanol, 24 for the difunctional cardanol). The N_{rGLYCEROL} corresponds to the number of renewable carbon in glycerol (3). The N_{CARDANOL} corresponds to the total carbon number in each molecule (24 for the monofunctional and the difunctional cardanol). The N_{TOFA} and the N_{GLYCEROL} correspond to the total number of carbons in TOFA (18) and glycerol (3), respectively. The N_{PA} correspond and the N_{BA} to the non-renewable carbons of the phthalic anhydride (8) and benzoic acid (7), respectively.

$$\%rC = \frac{n_{TOFA} \times N_{rTOFA} + n_{CARDANOL} \times N_{rCARDANOL} + n_{GLYCEROL} \times N_{rGLYCEROL}}{n_{TOFA} \times N_{TOFA} + n_{CARDANOL} \times N_{CARDANOL} + n_{GLYCEROL} \times N_{GLYCEROL} + n_{PA} \times N_{PA} + n_{BA} \times N_{BA}} \quad (2)$$

Rheological analyses

Rheological analyses were performed on a ThermoScientific Haake Mars 60 rheometer equipped with a 35-mm-cone-plate geometry. The analyses were performed at 20 °C with a shear rate of 10 s⁻¹. All the resins were compared at the non-volatile content of 60 wt%.

Size-exclusion chromatography (SEC)

Molecular weights of alkyd resins were determined by size-exclusion chromatography (SEC). SEC was recorded using a triple-detection GPC from Agilent Technologies with its corresponding Agilent software, dedicated to multidetector GPC calculation. The system used two PL1113-6300 ResiPore 300 × 7.5 mm columns with THF as the eluent with a flow rate of 1 mL min⁻¹. The detector was a 390-LC PL0390-0601 refractive index detector. The entire SEC system was thermostated at 35 °C.

Polymethylmethacrylate (PMMA) standards were used for calibration between 540 and 2 210 000 $\text{g}\cdot\text{mol}^{-1}$. The typical sample concentration was $15 \text{ mg}\cdot\text{mL}^{-1}$.

Fourier Transform Infrared Spectroscopy

The Fourier transform infrared spectroscopy (FTIR) spectra were acquired on a Thermo Scientific Nicolet iS50 FT-IR equipped with an attenuated total reflectance cell (ATR). The data were analyzed using the software OMNIC Series 8.2 from Thermo Scientific.

Gel content

The resins were mixed with 5 wt% of mix of driers (cobalt octoate, calcium octoate and zirconium octoate) in order to accelerate the autoxidative process. Then, films were obtained thanks to a film applicator. All the dry films exhibited a thickness of $60 \mu\text{m}$. Three samples from the same alkyd resin films, of around 20 mg each, were separately immersed in THF for 24 h. The three samples were then dried in a ventilated oven at $80 \text{ }^\circ\text{C}$ for 24h. The gel content (GC) was calculated using equation (3), where m_2 is the mass of the dried material and m_1 is the initial mass. Reported gel content are average values of the three samples.

$$GC = \frac{m_2}{m_1} \times 100 \quad (3)$$

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. The calibration was performed using adamantane, biphenyl, indium, tin, bismuth and zinc standards. Nitrogen was used as the purge gas. The thermal properties were analyzed at $20 \text{ }^\circ\text{C}/\text{min}$ between -100 and $100 \text{ }^\circ\text{C}$ to observe the glass transition temperature.

Thermogravimetric analyses

Thermogravimetric analyses (TGA) of the cured alkyd resins were carried out to determine the thermal stability and were performed on a Netzsch TG 209F1 apparatus under $40 \text{ mL}\cdot\text{min}^{-1}$ nitrogen flow. The protective gas used was nitrogen with a $20 \text{ mL}\cdot\text{min}^{-1}$ flow. Approximately 10-12 mg of sample was placed in an alumina crucible and heated from room temperature to $850 \text{ }^\circ\text{C}$ with a $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ heating rate.

Film properties

$100 \mu\text{m}$ wet films were applied with a film applicator and dried at $25 \text{ }^\circ\text{C}$ under relative humidity of 30 %. The thickness of dry films was $60 \mu\text{m}$ in all cases. Adhesion was measured using a cross-cut tester 1 mm BYK according to ISO 2409 standard and the method is explained in supporting information (SI). The hardness (Persoz hardness) was determined according to ISO 1522 standard with a TQC SP0500 pendulum hardness tester (method explained in SI). Gloss was measured based on ISO 2813 standard and the measurements were performed on substrates at 60° and 20° using a TQC Polygloss (method explained in SI). The color of the alkyd resins was determined using the Gardner color scale (explained in SI). The values for the hardness and the gloss measurements were determined at day +15 (D+15) after the application of the film. The drying time of the resins was taken as the time required to obtain a tack-free film. The chemical resistance of the alkyd resins was studied on water (H_2O), hydrochloric acid (HCl), sodium hydroxide (NaOH) and sodium chloride (NaCl)²⁹. Approximately $10 \pm 1 \text{ mg}$ of the cured alkyd resins were immersed inside each solvent during six hours at room temperature and stirred at 200 rpm. Then, they were dried in an oven at $80 \text{ }^\circ\text{C}$ for 12 hours. The residual mass percentage (wt% residue) was determined using equation (4). The analyses were made in triplicate for each sample and the reported residual masses percentage are average values of the three samples.

$$\text{wt}\% \text{ residue} = \frac{m_2}{m_1} \times 100 \quad (4)$$

m_1 : mass of the alkyd resin sample before being immersed in solvent; m_2 : mass of the alkyd resin sample after being immersed in a solvent and dried in oven.

3) Synthesis

Two different cardanol compounds with reactive hydroxyl functions were synthesized: a monofunctional and a difunctional.

Synthesis of hydroxyethylation of cardanol (monofunctional cardanol)

The ethoxy cardanol was synthesized following the procedure reported by Li *et al.*⁶ 100 g of cardanol (0.333 mol, 1 eq.) and 29.31 g of ethylene carbonate (0.333 mol, 1 eq.) were mixed under high agitation in a two-neck round-bottom flask equipped with a condenser. The reaction mixture was heated to 150 °C. Then, when the ethylene carbonate had completely dissolved, 0.5 g of DBN (0.003 mol, 1 mol%) was injected into the reaction mixture. The reaction proceeded at 150 °C for 30 min, after which the temperature was increased to 180 °C. The mixture was stirred for additional 4 hours. Then, the dark-brown viscous oil was cooled down and diluted with ethyl acetate. The mixture was filtered over silica gel in order to purify the mixture and distilled under reduce in order to obtain a yellow viscous oil with a 94 % yield. The structure of ethoxy cardanol was presented in Figure 2. The ¹H NMR spectrum was presented in Figure 1 of supporting information (SI).

¹H NMR (400 MHz, CDCl₃, ppm): δ : 7.21 (t, 1H, aromatic proton 2), 6.72–6.83 (m, 3H, aromatic protons 1, 3, and 4), 5.80–5.90 (m, 1H, C₁₅ chain, proton i), 5.34–5.50 (m, C₁₅ chain, internal double bond protons h), 4.98–5.11 (m, 2H, C₁₅ chain, protons of the terminal double bond g), 4.10 (t, 2H, protons 6), 3.98 (t, 2H, protons 5), 2.82 (m, 2H, C₁₅ chain, protons f), 2.61 (t, 2H, C₁₅ chain, protons e), 2.00–2.15 (m, 2H, C₁₅ chain, protons d), 1.64 (m, 2H, C₁₅ chain, protons c), 1.20–1.50 (m, C₁₅ chain, protons b, b'), 0.92 (m, 3H, C₁₅ chain, terminal –CH₃, protons a, a').

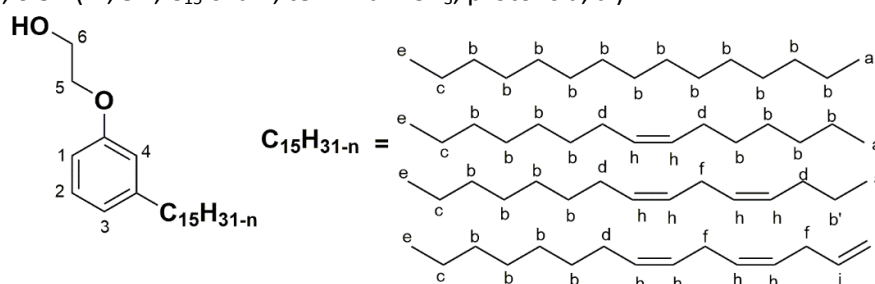


Figure 2: Structure of ethoxy cardanol

Synthesis of cardanol diol (difunctional cardanol)

100 g of epoxidized cardanol NC-513, 5.51 g H₂SO₄ (20 mol%), 300 mL of water and 300 mL of THF were added in round-bottom flask equipped with a condenser. The reaction mixture was heated to 60 °C overnight. Then, the solution was cooled down and neutralized to pH 7 with NaHCO₃. The solvents were removed under reduce pressure and the rest of water was eliminated thanks to a freeze dryer. The mixture was washed with ethyl acetate and filtrated in order to remove the salts. Ethyl acetate was removed under reduce pressure in order to obtain a yellow viscous oil with a 95 % yield. The structure of cardanol diol was presented in Figure 3. The ¹H NMR spectrum was presented in SI Figure 2.

¹H NMR (400 MHz, CDCl₃, ppm): δ : 7.18 (t, 1H, aromatic proton 2), 6.69–6.84 (m, 3H, aromatic protons 1, 3, and 4), 5.77–5.88 (m, 1H, C₁₅ chain, proton i), 5.27–5.47 (m, C₁₅ chain, internal double bond protons h), 4.96–5.10 (m, 2H, C₁₅ chain, protons of the terminal double bond g), 4.05–4.24 (m, 2H, protons 7), 4.01 (m, 1H, protons 6), 3.67–3.85 (m, 2H, protons 5), 2.81 (m, 2H, C₁₅ chain, protons f), 2.56 (t, 2H, C₁₅ chain, protons e), 2.05 (m, 2H, C₁₅ chain, protons d), 1.60 (m, 2H, C₁₅ chain, protons c), 1.31 (m, C₁₅ chain, protons b, b'), 0.90 (m, 3H, C₁₅ chain, terminal –CH₃, protons a, a').

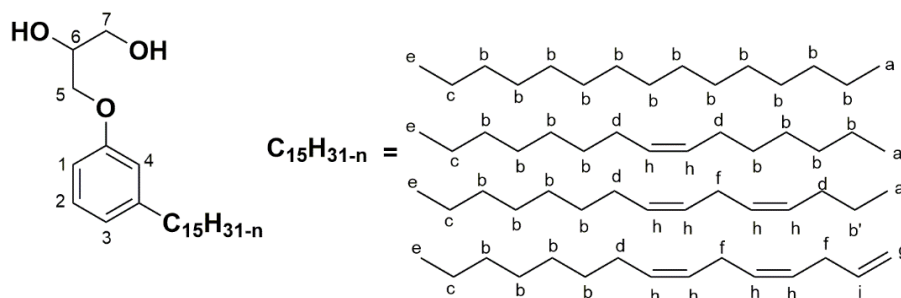


Figure 3: Structure of cardanol diol

Synthesis of tall oil fatty acid (TOFA) alkyd resin with ethoxy cardanol

A short oil TOFA alkyd resin was prepared by solvent process using TOFA, glycerol, phthalic anhydride, benzoic acid or/and ethoxy cardanol (EC). The amount of glycerol and the ratios of TOFA and ethoxy cardanol, presented in Table 1, were firstly added in a five necked reactor flask equipped with a mechanical stirrer, a dean stark, a thermometer and a nitrogen inlet. Then, when the reaction reached 200 °C, phthalic anhydride was introduced. Benzoic acid was also incorporated but only in the reference alkyd resin. The composition of alkyd resins are summarized in Table 1. Reaction mixture was heated to 220 °C using xylene as azeotropic solvent to remove water. The reaction was continued until an acid value of 14 mg of KOH/g of resin was obtained. Xylene was added in order to obtain a solid content of 60 wt%. The resins have been designed to reach the same oil length in their composition. It is defined as the mass percentage of fatty chains on the total mass of the alkyd resin. The resins had 38 wt% of fatty acids in their composition that is why they can be classified as short oil length. The stoichiometry of f_{OH}/f_{COOH} for all the alkyd resins was keep between 1.2 and 1.3.

Table 1: Composition of ethoxy cardanol-modified alkyd resins

Samples		Reference	25 % EC	50 % EC	75 % EC
Ratio cardanol:TOFA		0:1	1:3	1:1	3:1
Ethoxy cardanol (EC)	mol	0	0.06	0.11	0.15
	f_{OH} (mol)	0	0.06	0.11	0.15
TOFA	mol	0.21	0.18	0.11	0.05
	f_{COOH} (mol)	0.21	0.18	0.11	0.05
Glycerol	mol	0.48	0.43	0.32	0.22
	f_{OH} (mol)	1.44	1.29	0.96	0.66
Phthalic anhydride	mol	0.47	0.46	0.37	0.30
	f_{COOH} (mol)	0.94	0.92	0.74	0.60
Benzoic acid	mol	0.02	0	0	0
	f_{COOH} (mol)	0.02	0	0	0
f_{OH} (mol)		1.44	1.35	1.07	0.81
f_{COOH} (mol)		1.17	1.1	0.85	0.65
Ratio f_{OH}/f_{COOH}		1.23	1.23	1.25	1.25

Synthesis of short oil alkyd resin with cardanol diol

A short oil alkyd resin was prepared by solvent process using TOFA, glycerol, phthalic anhydride, and cardanol diol (CD). Glycerol, TOFA and/or cardanol diol, presented in Table 2, were firstly added in a five necked reactor flask equipped with a mechanical stirrer, a dean stark, a thermometer and a nitrogen inlet. Then, when the reaction reached 200 °C, phthalic anhydride and 5 mol% of tin catalyst were introduced. The composition of alkyd resins are summarized in Table 2. Reaction temperatures, the acid value, the solid content and the stoichiometry of f_{OH}/f_{COOH} were the same as the previous alkyd resins with ethoxy cardanol.

Table 2: Composition of cardanol diol modified alkyd resins

Samples		Reference	50 % CD	100 % CD
Ratio cardanol:TOFA		0:1	1:1	1:0
Cardanol diol (CD)	<i>mol</i>	0	0.10	0.14
	f_{OH} (mol)	0	0.20	0.28
TOFA	<i>mol</i>	0.21	0.10	0
	f_{COOH} (mol)	0.21	0.10	0
Glycerol	<i>mol</i>	0.48	0.28	0.07
	f_{OH} (mol)	1.44	0.84	0.21
Phthalic anhydride	<i>mol</i>	0.47	0.37	0.20
	f_{COOH} (mol)	0.94	0.74	0.40
Benzoic acid	<i>mol</i>	0.02	0	0
	f_{COOH} (mol)	0.02	0	0
f_{OH} (mol)		1.44	1.04	0.49
f_{COOH} (mol)		1.17	0.84	0.40
Ratio f_{OH}/f_{COOH}		1.23	1.24	1.23

3. Results and discussion

1) Synthesis of cardanol-modified alkyd resins

Two different cardanol-based monomers were synthesized: a monofunctional and a difunctional alcohol in order to react with anhydrides during the synthesis of alkyd resins. The mono-functional cardanol monomer was obtained through the hydroxyethylation reaction. Indeed, to increase the reactivity of the function –OH of phenol, the hydroxyl group was moved further away from the aromatic ring of cardanol.⁶ Due to its functionality of one and its aromatic ring, the ethoxy cardanol (EC) was used in the synthesis of alkyd resins to replace the conventional chain stopper which are petrosourced such as benzoic acid. Moreover, as the cardanol contains fatty chains, it may replace the conventional vegetable oils or fatty acids used for the synthesis of alkyd resins. Nevertheless, as the EC acted as a chain stopper, it could not fully replace vegetable oils/fatty acids because it would lead to the formation of shorter polymer chains. Thereby, a di-functional cardanol monomer has been synthesized in order to replace up to 100 % of vegetable oils/fatty acids. Moreover, the introduction of difunctional cardanol allowed to obtain high renewable carbon content (rC%) for the alkyd resins as presented in Table 3. Indeed, the reference alkyd resin exhibited a value of 57 % of renewable carbon content whereas the alkyd resin with 100 % of CD showed a value of 69 rC%.

All alkyd resins have been synthesized through a fatty acid process with the presence of xylene as an azeotropic solvent. The synthesis of EC alkyd resin and CD alkyd resin are presented in Figure 1. The

resins have been designed to reach the same oil length so as not to affect film properties.²¹ Moreover, the amount of phthalic anhydride and glycerol (Table 1 and Table 2) were adjusted in order to maintain a stoichiometry of f_{OH}/f_{COOH} for all alkyd resins, between 1.2 and 1.3. Indeed, an excess of hydroxyl functions was needed in order not to reach the gelation of the network. The final acid value (AV) was also kept in the same range, between 12 and 15 for all the alkyd resins. It is defined as the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of alkyd resin. It is represented the free acids groups in the resins. An AV lower than 10 for short oil alkyd resins could lead to the gelation of the network.³⁰ However, an AV higher than 15 could entail chemical degradation such as hydrolysis.

The molar mass of the six alkyd resins were determined by size exclusion chromatography (SEC) in order to propose a structure of the polymer chains and explain the impact of cardanol on the alkyd resins properties. For the reference alkyd resin, the values of weight (Mw) and number (Mn) average molar mass were respectively $150\,000\text{ g}\cdot\text{mol}^{-1}$ and $5\,000\text{ g}\cdot\text{mol}^{-1}$ with a high dispersity, as presented in Figure 4, which is characteristic of classical alkyd resins. The substitution of up to 50 % of TOFA by ethoxy cardanol allowed to maintain similar Mw value compared to the reference alkyd resin (Table 3). Nevertheless, the substitution of 75 % of TOFA by EC, reduced the Mw down to $40\,000\text{ g}\cdot\text{mol}^{-1}$. This could be explained by a too high amount of mono-functional hydroxyl monomer, which acted as a chain stopper and led to shorter polymer chains. Thus, in the rest of this article, the substitution of 75 % of TOFA by EC will no longer be discussed. In order to increase cardanol content in the alkyd resins and to maintain Mw value close to the one of reference resin, a di-functional hydroxyl cardanol was introduced into the synthesis. The SEC analysis exhibited Mw values of $145\,000\text{ g}\cdot\text{mol}^{-1}$ for the alkyd resins synthesized with CD. Those Mw values were comparable to the one of the reference alkyd resin. Those results allowed to conclude that CD could entirely replace fatty acids in the synthesis of alkyd resins. Nevertheless, for all the ethoxy cardanol-modified alkyd resins the Mn showed values around $3\,000\text{ g}\cdot\text{mol}^{-1}$, which represented a decreased by 40 % compared to the Mn of the reference alkyd resin. Those results were consistent with the increase of dispersity (\mathcal{D}) and the chromatograms in Figure 4. Indeed, there was an intense peak around $1\,500\text{ g}\cdot\text{mol}^{-1}$ for all the cardanol-modified alkyd resins. This difference can be explained by the decrease in the amount of glycerol, a three-functional polyol. Indeed, glycerol was mostly replaced by cardanol monomers which exhibited a lower functionality and could lead to more alkyd chains with lower molar mass, thus decreasing the Mn value.

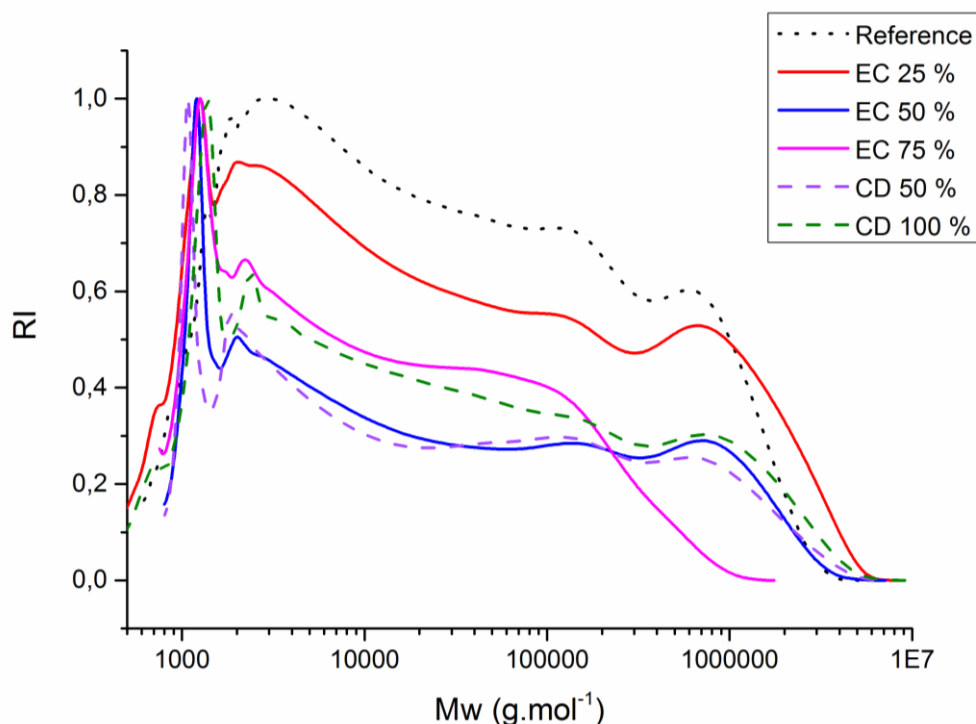


Figure 4: SEC chromatograms of alkyd resins

Moreover, the introduction of cardanol in the synthesis of alkyd resins increased the content of aromatic rings. Indeed, as presented in Table 3, the reference alkyd resin exhibited 23 wt% of aromatic rings and this percentage increased with the amount of cardanol introduced. The total substitution of TOFA by cardanol diol has allowed to reach aromatic rings content of 30.5 wt%. This represented a 33 % increase compared to the reference alkyd resin. Moreover, the aromatic rings are well known to confer rigidity to polymers. Thereby, the increased content of aromatic rings could modify the physical properties of alkyd resin coatings.

Table 3: Acid value, rate of aromatic rings and molar masses of cardanol-modified alkyd resins

Samples	Reference	25 % EC	50 % EC	75 % EC	50 % CD	100 % CD
Acid value (AC)	14	13	13	12	14	14
Aromatic rings (wt%)	23.0	23.5	25.3	27.6	26.0	30.5
%rC (%)	57	60	61	62	63	69
Mn (g.mol ⁻¹)	5 000	3 000	3 000	3 000	4 000	3 500
Mw (g.mol ⁻¹)	140 000	150 000	145 000	40 000	135 000	150 000
Đ	28	51	51	14	31	50

2) Mechanical and thermal properties

Thermal and mechanical properties analyses were investigated in this part in order to highlight the impact of cardanol on the coating properties of alkyd resins.

Viscometry analyses were performed at 20 °C with a shear rate of 10 s⁻¹. All the resins were compared with the same non-volatile content of 60 wt% and the results are presented in Table 4. The viscosity of the reference alkyd resin was higher than the viscosity of cardanol-modified alkyd

resins. Indeed, even if the Mw values were similar for all the resins, the Mn, decreased by almost half of the value for the cardanol-modified alkyd resins. Nevertheless, all the viscosities exhibited close values and the difference is not significant to impact the application. Hence, viscosity results were in agreement with SEC results previously discussed.

Differential scanning calorimetry (DSC) analyses were investigated in order to determine the glass transition temperature (T_g), and the results were reported in Table 4. The reference resin exhibited a T_g value of 18 °C while the increasing amounts of cardanol increased the T_g values. Indeed, the higher T_g was obtained for the alkyd resin synthesized with 100 % CD, with a T_g of 33 °C. As the oil length and the Mw remained the same for all the alkyd resins of this study, the increasing value of T_g may be explained by the difference in aromatic rings content (Table 3). Indeed, aromatic rings confer rigidity to the materials. Thereby, it was consistent to obtain higher T_g for the alkyd resins with higher aromatic ring contents. However, all the T_g were in the same range of values and corresponded to room temperature. Thus, the performance of the cardanol-modified alkyd resins could be maintained as well as the intended application.

Table 4: Viscosity and T_g of cardanol-modified alkyd resins

Samples	Reference	25 % EC	50 % EC	50 % CD	100 % CD
η (Pa.s)	7.1	6.0	5.8	5.7	5.6
T_g (°C)	18	19	24	26	33

The thermal stability of alkyd resins was determined by thermogravimetric analyses (TGA) under nitrogen flow. Figure 5 showed the thermograms of the reference and cardanol-modified alkyd resins. Thermal stability increased with the addition of cardanol. Thermal factors such as the decomposition temperature at 5 % weight loss, temperature at 50 % weight loss, and the residue yield at 750 °C, are summarized in Table 5. Firstly, temperature at 5 % weight loss ($T_{d,5wt\%}$) increased by 35-40 °C for the cardanol-modified alkyd resins. Indeed, the reference alkyd resin showed a $T_{d,5wt\%}$ value of 160 °C, whereas all the cardanol-alkyd resins exhibited $T_{d,5wt\%}$ values between 195 and 200 °C. Nevertheless, the values of $T_{d,5wt\%}$ were very low and those temperatures could be associated to polycondensation reactions.

Considering the temperature at 50 % weight loss ($T_{d,50wt\%}$) the thermal stability was higher when the introduced amount of cardanol increased. Indeed, $T_{d,50wt\%}$ varied from 330 °C for the reference resin to 384 °C for the resin with 100 % CD. This augmentation of 54 °C allowed to conclude that cardanol conferred thermal stability to alkyd resin.

Moreover, the residue yield at 750 °C was 3 wt% for the reference resin, while it reached above 7 wt% for the resin with 25 % EC. Therefore, the residue yield increased with the content of cardanol, with a maximum at 12 wt% for alkyd resins with 100 % CD. Thereby, the residue yield was promoted by the amount of cardanol in the polymer. Furthermore, it can be noted that there was no difference on the thermal stability with the introduction of EC or CD. Indeed, alkyd resins with 50 % EC and 50 % CD exhibited similar values for all the parameters studied.

Thus, the increase of both the char content and the degradation temperature could be attractive for paints with improved fire resistance properties.

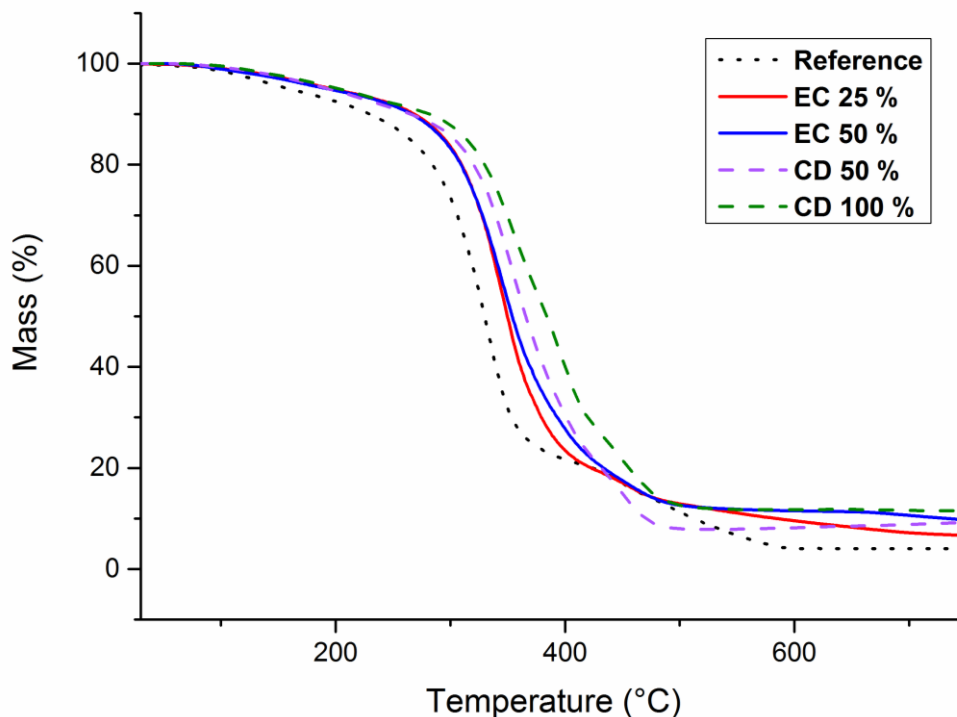


Figure 5: TGA thermograms of the six alkyd resins synthesized

Table 5: Results of TGA analyses of cardanol-modified alkyd resins

Samples	Reference	25 % EC	50 % EC	50 % CD	100 % CD
$T_{d,5wt\%}$ (°C)	160	197	195	194	200
$T_{d,50wt\%}$ (°C)	330	350	358	361	384
Residue at 750°C (%)	3.0	7.4	9.0	10.1	12.1

3) Films properties

Dry films with a thickness of 60 μm were obtained from the different resins with a film applicator. Adhesion, flexibility, gloss, drying time and chemical resistance have been determined and the results are presented in the following section in table 6 and table 7.

Table 6: Adhesion, hardness, gloss and drying time of cardano- modified alkyd resins

Samples	Reference	25 % EC	50 % EC	50 % CD	100 % CD
Gel content (%)	93 \pm 0.8 %	91 \pm 1 %	91 \pm 1 %	91 \pm 0.3 %	92 \pm 0.6 %
Adhesion	0	0	0	0	0
Hardness (s)	70	65	82	86	127
Gloss 20°/60°	85/99	68/95	67/97	82/99	74/99
Drying time (min)	70	70	75	85	95
Color	4.5	7	6.5	12	17

The gel content (GC) was calculated in order to confirm the presence of a covalent network after drying. For all the alkyd resins the GC were higher than 90 %, which confirms crosslinking (Table 5). Moreover, all the resins exhibited very close GC, allowing to conclude that the introduction of monofunctional or difunctional cardanol did not modify the crosslinking. Then, Figure 6 demonstrates the curing of alkyd resins through the C=C of alkyl chains of cardanol.³¹ Indeed, the disappearance of the characteristic peak of olefinic C-H of cardanol at 3003 cm⁻¹ in all the alkyd resin films containing cardanol is shown in Figure 6.

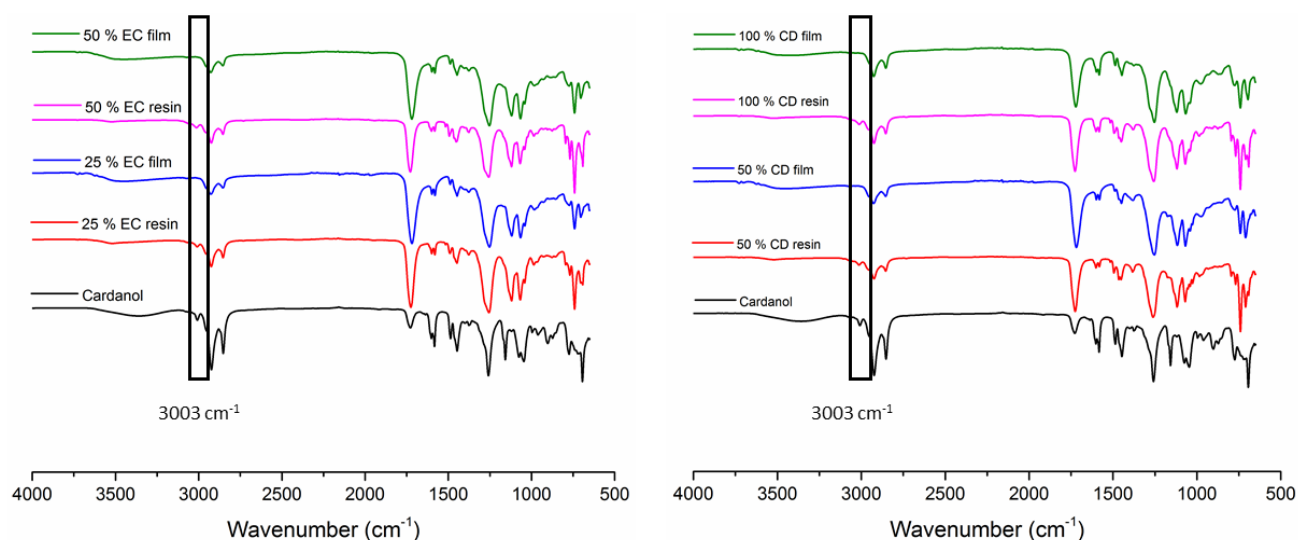


Figure 6: FTIR spectra of cardanol, alkyd resins and alkyd resin films with EC and CD

¹H HRMAS experiments (SI Figure 7, 8, 9, 10) were also performed to confirm the crosslinking of alkyd resins through the C=C double bond of cardanol. They are compared to ¹H NMR spectra of the alkyd resins before curing presented in SI Figure 3, 4, 5 and 6. All alkyd resins exhibited ¹H HRMAS NMR spectra with good resolution, except the alkyd resin with 25 % EC. That is why, analysis carried out on this alkyd resin has not been discussed. The peaks centered at 5.14 and 5.95 ppm correspond to the three protons of the terminal double bonds and the peak centered at 5.47 corresponds to the protons of internal double bonds. In all the HRMAS NMR spectra of the cardanol-modified alkyd resins, the peaks of the protons of terminal double bonds (Hi and Hg visible on SI Figures 1 to 6) disappeared. This result was expected because the protons of the terminal double bonds are more reactive than the protons of internal double bonds in the alkyl chains. Moreover from the peaks of double bonds, a decrease of the integrations by 50 % for the reference alkyd resin and cardanol modified alkyd resins was observed and is consistent with the results obtained from the GC. This last result confirmed the crosslinking of alkyd resins through the C=C of cardanol. These results allowed us to consider similar results with 25 % EC alkyd resins.

The adhesion was measured by using the crosscut method. All the alkyd resins exhibited excellent adhesion properties. The edges of the cuts were completely smooth and none of the squares of the grid were torn off, that is why they were evaluated at class 0. The introduction of EC and CD did not have impact the adhesion properties of the resins.

The hardness of the coating was determined thanks to Persoz hardness measurement. The more flexible is the film, the faster the pendulum is damped and therefore the less oscillations are required (One second corresponds to one oscillation of the pendulum). Indeed, the more flexible is the film, the more it is able to absorb the energy of the pendulum. The number of oscillations increased with the increased amount of cardanol. Indeed, the reference alkyd resin exhibited a value of 70 whereas with 50 % EC and 50 % CD, the results showed values of 82 and 86, respectively. The highest value

was reached for the alkyd resin with 100 % CD. This could be explained by the content of aromatic rings (Table 3), which confers rigidity and hardness to the alkyd resins. Thus, the introduction of cardanol improved the hardness of the alkyd resins. Thereby, it could be possible to formulate primers coatings.

The gloss of the coatings were firstly determined with a measurement at 60 ° to determine the gloss level. All the alkyd resins exhibited high gloss level with values between 95 and 99. The measurement was then made at 20 °. The reference resin showed a value of 85 whereas the resins with 25 % EC and 50 % EC exhibited a gloss value of 68 and 67, respectively. The introduction of EC slightly decreased the gloss of the resins. The introduction of CD also slightly decreased the gloss value of the alkyd resins but they were similar to the one of the reference alkyd resin. Moreover, all the alkyd resins were classified with a high gloss level.

All the alkyd resins showed equivalent drying times, as expected. Indeed, all the resins exhibited Mw around 150 000 g.mol⁻¹. To conclude, the introduction of cardanol in the synthesis of alkyd resins did not deteriorate the drying time.

The color of all the alkyd resins was measured thanks to the Gardner color scale. The values are comprised between 1 and 18. The darker is the color, the higher is the value. The introduction of cardanol darkened the resins a lot. It was expected because when cardanol is heated, it becomes darker.

Table 7 presents results of determination of chemical resistance of the resins. The higher is the weight loss, the lower is the residual mass percentage and the less resistant is the resin to the solvent. The synthesis of cardanol-based alkyd resins did not deteriorate the chemical resistance of the resins. Indeed, all the cardanol-containing alkyd resins exhibited similar chemical resistances with the reference alkyd resin. Moreover, alkyd resins were highly resistant to NaCl solution with a residual mass higher than 95 %. Nevertheless, the lower resistance to alkali solution (NaOH 0.1 M) can be due to hydrolysable ester groups in the alkyd resins^{29,32}.

Table 7: Chemical resistances of cardanol-modified alkyd resins

<i>Samples</i>	<i>Reference</i>	<i>25 % EC</i>	<i>50 % EC</i>	<i>50 % CD</i>	<i>100 % CD</i>
<i>Water</i>	90 ± 3 %	96 ± 1 %	97 ± 1 %	95 ± 2 %	96 ± 2 %
<i>HCl (0.1 M)</i>	80 ± 4 %	78 ± 2 %	80 ± 3 %	79 ± 3 %	78 ± 2 %
<i>NaOH (0.1 M)</i>	69 ± 1 %	70 ± 3 %	68 ± 2 %	67 ± 2 %	71 ± 3 %
<i>NaCl (5 %)</i>	95 ± 3 %	97 ± 4 %	96 ± 1 %	96 ± 2 %	95 ± 2 %

4. Conclusion

In this article, two cardanol-derived monomers were synthesized, a mono-functional (EC) and a di-functional (CD) cardanol, in order to design greener alkyd resins. Different contents of cardanol were introduced during the polycondensation reaction. Then, the impact of cardanol on the film properties were studied. The cardanol-based alkyd resins showed improved thermal stability compare to reference alkyd resin. The introduction of cardanol did not impact neither the chemical resistance of the resins, nor the drying time. Nevertheless, the color of alkyd resins got darker and darker with the increasing amounts of cardanol used for the synthesis. The hardness was also increased with increasing content of aromatic rings in modified alkyd resins. In addition, the good adhesion and chemical resistance of cardanol-based alkyd resins as well as the improvement in hardness even if the color darkens make it possible to formulate primers. Indeed, these formulations are the first layer to be applied on a support before proceeding to its finishing and the color does not matter. To conclude, the introduction of cardanol in alkyd resins synthesis allowed to reduce the

amount of petro-based monomer and valorize waste product of food industry. Indeed, the introduction of 100 % CD allowed to increase the renewable carbon content by 12 % compared to the reference alkyd resin synthesized with TOFA and benzoic acid.

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