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Cardanol: a small giant of the future of biobased aromatic polymers and additives

Sylvain Caillol^{a*}

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

* Corresponding author. E-mail sylvain.caillol@enscm.fr

ABSTRACT

Among the renewable resource materials, cashew nut shell liquid (CNSL) is considered as an important starting material due to its unique structural features, abundant availability and low cost. A large number of chemicals and products have been developed starting from CNSL by taking advantage of the three reactive sites, namely, phenolic hydroxyl, aromatic ring and unsaturation(s) in the alkenyl side chain. Increasing attention is paid to promising cardanol-based products that could have potential interest in industry, such as epoxy and acrylic monomers, plasticizers and surfactants.

KEYWORDS

Cardanol; cashew nut shell liquid; biobased polymers; surfactant; plasticizer

INTRODUCTION

The use of renewable resources for chemistry and the manufacture of materials represents a very important subject, and has been attracting the growing attention of academic and industrial communities for several years¹. This development is due to the volatility of petrochemical prices associated with growing environmental concerns. Renewable raw materials are already widely used such as natural rubber, cellulose but also vegetable oils and proteins as well as chitin or other polysaccharides. One of the challenges of chemistry derived from renewable resources consists in particular in identifying aromatic resources to replace phenol and provide mechanical and thermal resistance properties to biosourced polymers. The use and choice of renewable resources is closely linked to their availability and the impacts generated for their development. This is notably why access to aromatic resources is an issue². Indeed many research studies have focused on the use of lignin or its derivatives such as vanillin, or eugenol or tannins, but in general the technological access routes are not mature, the processes are pollutants or availability is limited. There is an aromatic resource which has a certain future, it is cardanol and its derivatives. Cardanol comes from Cashew Nutshell Liquid CNSL, co-produced during of cashew nuts industry. CNSL being a non-edible oil, its use as a chemical raw material does

not potentially put undue pressure on the food supply chain unlike other renewable chemical feed-stocks such as edible oils. Moreover, as a co-product, its environmental assessment is very favorable.

CNSL appears as a liquid greenish yellow viscous substance present in the thickness of the cashew nut shell. Cashew is a product of the cashew tree, *Anacardium occidentale*^{3,4}, native to Brazil and abundantly available in many parts of the world, such as Brazil, India, Bangladesh, Benin, Tanzania, Kenya, Mozambique, tropical regions of Africa, Southeast Asia and the Far East. In some of these countries, cashew nuts are a popular agricultural product, while some others import cashew nuts for processing. CNSL belongs to the family of long-chain hydrocarbon phenols which are phenolic lipids found in plants of these families such as Anacardiaceae⁵. The plant can reach 12 m in height. Cashew nuts are the cash crop produced by the tree, but it also produces cashew apples (edible), a gum similar to gum arabic, and the wood is used for building boats or making charcoal. The cashew apple is used in drinks, jams and jellies. Cashew apple juice has anti-tumor and antimicrobial properties⁶. The cashew nut is greenish gray and is attached to the cashew apple, which when ripe turns bright yellow or red. The pericarp of the nut consists of a leathery epicarp, a spongy mesocarp and an endocarp. The core is inside the shell and is covered by a brown skin called the testa. The nut is kidney-shaped and its size varies from 2.5 to 4 cm. CNSL constitutes 18–27% of the total weight of raw nuts.

Traditionally, a number of methods have been used to extract CNSL from cashew nuts. Two processes are mainly used in the extraction of CNSL: the hot oil process and the roasting process in which the CNSL oozes out of the shell^{7,8}. Oil extraction uses solvents such as benzene, toluene, petroleum hydrocarbons or alcohols⁹. Other techniques are also considered, such as the use of a mixture of supercritical CO₂ and isopropyl alcohol¹⁰.

The presence of sulphides, nitrogenous materials and minerals contained in the crude CNSL directly affects the quality of the oil. CNSL is therefore often subjected to a preliminary treatment with compounds such as hydrocarbon sulphates and sulfuric acid before industrial use. Aqueous solutions of acids such as hydrochloric acid, sulfuric acid, acetic acid, chloroacetic acid or phosphoric acid, or acid sulfates, such as sodium hydrogen sulfate, are used to this effect. This produces two main effects: the precipitation of the mineral salts of ammonium, calcium and potassium as well as the reduction of the content of cutaneous vesicant present in the CNSL such as urushiol. The chemical treatment is accompanied by the release of hydrogen sulphide. It has been found that the reduction in sulphide content roughly corresponds to the elimination of the causative agent of the skin irritation. Treatment with amines or Group IA or II metal hydroxides has been identified to reduce cardol content. Refined CNSL can be easily distilled under reduced pressure or hydrogenated, both processes leading to products with good color stability. Steaming of CNSL treated with

H₂SO₄, followed by distillation, has been found to deodorize the oil to a great extent¹¹. During extraction or refining processes, the anacardic acid present in CNSL is decarboxylated to cardanol¹².

In nature, CNSL contains four main components: anacardic acid, cardanol, cardol and 2-methyl cardol. They are all mono-phenols or di-phenols with an aliphatic chain in the meta position. Figure 1 shows the chemical structures of these compounds. Commercial-grade CNSL contains virtually no anacardic acid due to the decarboxylation reaction occurring during the roasting process, which converts anacardic acid to cardanol¹³. CNSL components are themselves mixtures of four constituents differing in the number of side chain unsaturations. Indeed this chain can be saturated (5–8%), or in the form of monoene (48–49%), diene (16–17%) or triene (29–30%)¹⁴. The composition of natural and technical CNSLs has been studied by several researchers^{15,16,17,18,19,20}. Using primarily chromatographic techniques, Tyman et al.^{21,22} reported the presence of oligomers and polymers in natural and engineered CNSLs. The composition of natural and technical CNSL²³ is given in Figure 1.

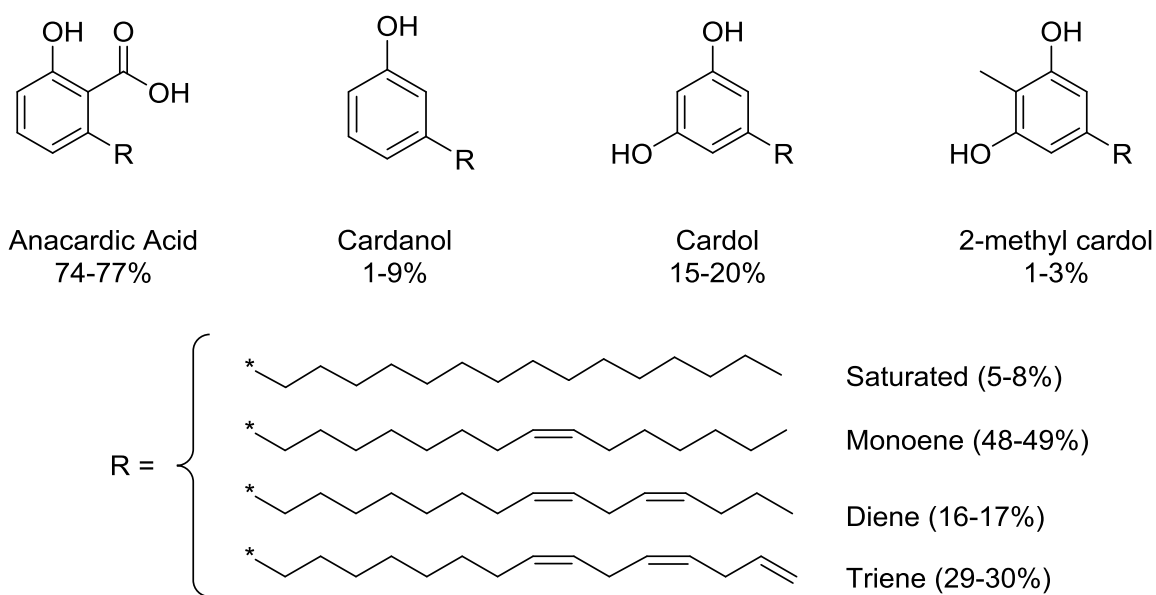


Figure 1: chemical structure of cardanol

Cardanol is very difficult to obtain according to conventional routes of chemical synthesis insofar as the aliphatic side chain is in the *meta* position with respect to the phenol group which generally directs all the substitutions in *ortho* and/or *para* positions. Cardanol lends itself to many functionalizations to lead to specific properties of interest for high additives or value-added polymers. Hence, there is more and more academic work on cardanol including to develop products for industrial applications. Additionally, several review papers^{24,25,26,27,28} have already been reported. However, all these works do not have the same approach or the

same maturity, which is why this perspective article proposes to select the most promising works from cardanol.

CARDANOL FOR CHEMISTRY

Cardanol has intrinsic antioxidant and antimicrobial properties. It is thus used for these properties but also as an additive in many formulations (surfactants, etc.). Currently, cardanol is mainly used in friction particles²⁹. However, the structure of cardanol is unique for many reasons which are linked to the properties provided or to the possible polymers obtained thereof. Hence, cardanol-derived polymers have exceptional properties that are unique for many applications (Figure 2). Polymers derived from^{30,31} exhibit flexibility due to "internal plasticization" resulting from the presence of a long side chain which also exhibits hydrophobicity towards materials. Polymer derived from cardanol have also high thermal, chemical even fire resistance due to the presence of the aromatic ring. The phenol groups entails fast curing reaction and adhesion properties. The presence of polar phenol group and long alkyl chain leads to a "surfactant" effect that could also be interestingly used as compatibilizer in formulations^{32,33}. Cardanol is also compatible when mixed with a wide variety of polymers such as alkyds, melamines, polyesters... allowing homogeneous formulations to be obtained.

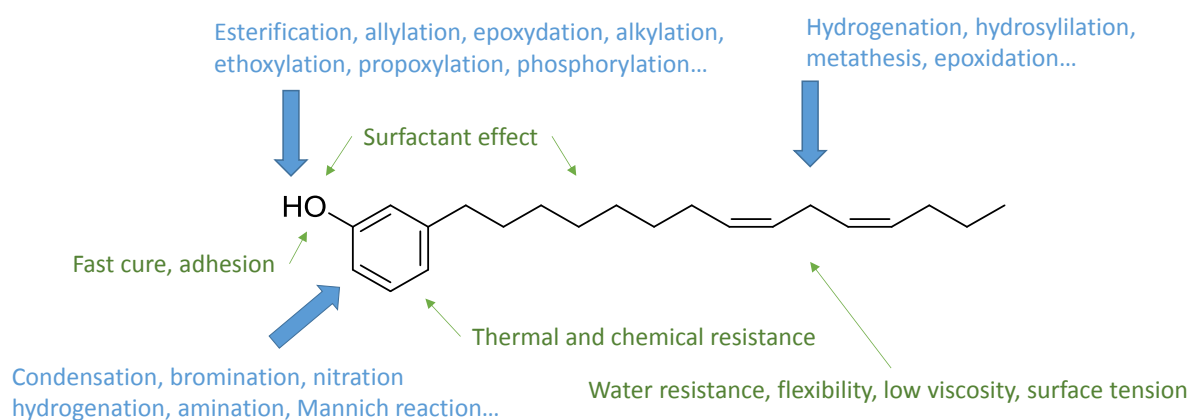


Figure 2: Reactive site and properties of cardanol

Structural modifications can be made at the hydroxyl group, on the aromatic ring and on the side chain (Figure 2). During extraction or refining processes, anacardic acid decarboxylates to cardanol by simple heating (Figure 3, d)³⁴. Hydrogenation (Figure 4, e) is usually carried out using hydrogen and catalysts such as copper, nickel, palladium or platinum³⁵. Hydrogenated cardanol can be separated by distillation, as for crude CNSL. Perdriau et al.³⁶ performed an interesting conversion of CNSL polyenes to monenes by RuCl₃-catalyzed transfer hydrogenation. CNSL derivatives can also be sulfonated to give alkylarylsulphonic acids or their metal salts (Figure 3, f)³⁷. Direct nitration of hydrogenated cardanol leads to nitrate derivatives, which are very useful products (Figure 3, g)³⁸. CNSL

halogenation can be accomplished very easily. For example, chlorine gas can be passed through a solution of CNSL in kerosene to achieve 15% (mass) chlorination³⁹. The reaction of cardanol with acid chlorides in the presence of a base can lead to the corresponding cardanyl esters (Figure 3, h)⁴⁰. The epoxidation of cardanol (Figure 3, i) can be carried out using epichlorohydrin in the presence of caustic soda as a catalyst⁴¹. Finally etherification has also been reported with various alkyl halides (Figure 3, j)⁴². Various techniques can also be used to polymerize CNSL to obtain various resins. The presence of the aliphatic side chain gives these resins a pronounced hydrophobic character, which is a valuable property for many applications such as resistance to polar solvents.

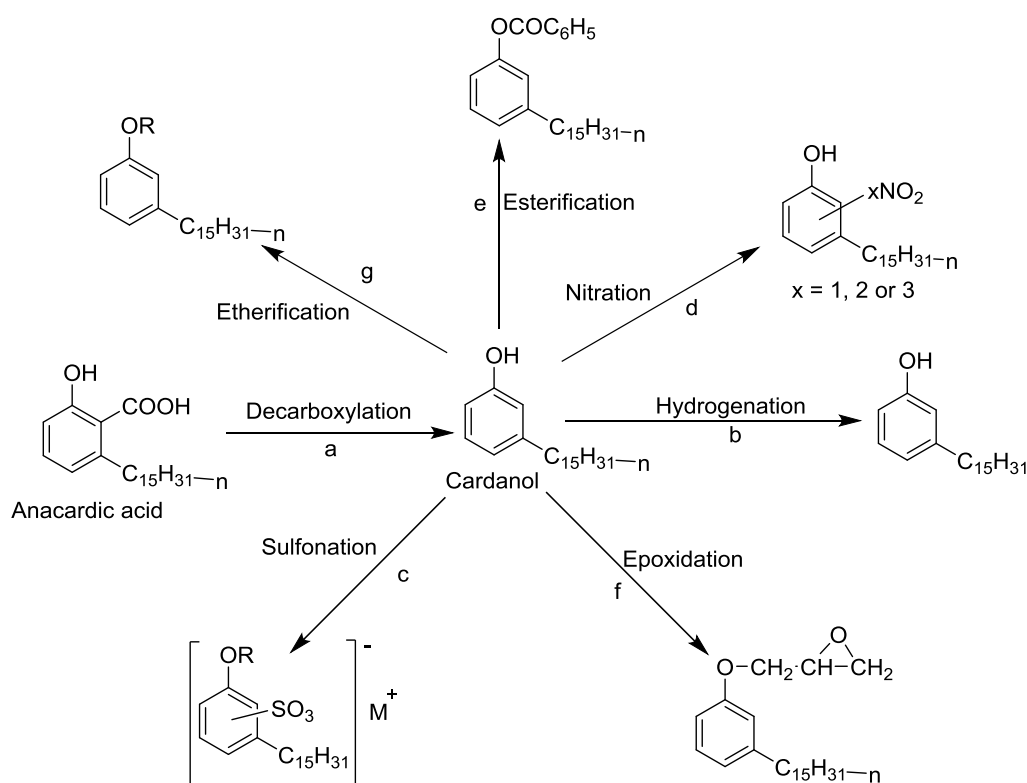


Figure 3: functionalization routes of cardanol

CARDANOL IN ADDITIVES

Cardanol is widely used for the synthesis of many additives, such as antioxidants^{43,44}, doping agents^{45,46} or rubber additives^{47,48}. The most dynamic fields remain that of plasticizers and surfactants.

Plasticizing agents

Poly (vinyl chloride) (PVC) is one of the most widely used polymers in the world due to its great versatility, adaptation to many additives, good mechanical properties and low cost production. Annual PVC production reached around 60 million tons in

2020. Applications range from very rigid PVC (window profiles, computer cases, outdoor products, containers, blisters) to soft PVC using certain additives, such as plasticizers, with a mass ratio between 30 and 50%. Soft PVC formulations can be used in the medical field, for packaging materials, artificial leather and toys...^{49,50}. Over the past decade, global production of plasticizers has been around 6.4 million tonnes per year. More than 80% of these additives are phthalates with long alkyl chains such as diisononyl phthalate (DINP) or bis(2-ethylhexyl) phthalate (DEHP). Thanks to their low cost and good performance with PVC, these additives are produced in large quantities. However, the reprotoxicity of phthalates on animals and humans is reported and some of them have recently been banned by European regulations 2000/60/EC and European regulations 1907/2006/EC⁵¹. During the last ten years, many studies have been devoted to the synthesis of cardanol-based plasticizers. Indeed, due to its aromatic ring providing thermal stability and its C15 alkyl chain which can confer a plasticizing effect, cardanol is a promising substituent for phthalates. The phenol esterification of cardanol is necessary to obtain good miscibility of cardanol in PVC. Cardanol esterified with short alkyl chains have already shown good results as secondary plasticizers in the presence of DEHP⁵². Epoxidation of the double bonds further improves the plasticizing properties and thermal stability of PVC⁵³. Furthermore, Chen et al. studied cardanol-based epoxidized plasticizers using a mild synthetic route^{54,55}. The same team studied the internal plasticization of PVC after the partial modification of PVC by the Mannich base of cardanol⁵⁶. Recently, cardanol derivatives epoxidized and modified with various fatty acids have demonstrated very relevant PVC plasticization properties, similar to those obtained with DINP (Figure 4).

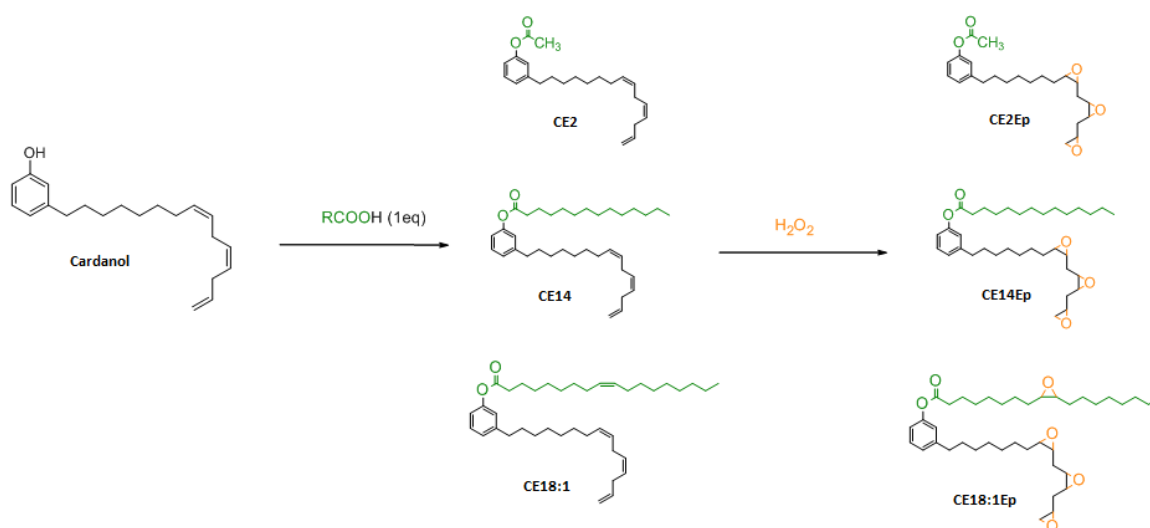


Figure 4: Cardanol-based PVC plasticizers

In addition, these plasticizers derived from cardanol did not demonstrate toxicity⁵⁷. Their biodegradability has not been studied, however, the easily hydrolysable aromatic ester bond makes it easy to return to the starting reagents which are natural compounds entering natural metabolic cycles. In addition, cardanol has made it possible to develop plasticizers for polymers other than PVC. Thus, the properties of natural rubber modified with phosphorylated cardanol were found to be superior to those obtained with DEHP⁵⁸. Additionally, phosphorylated cardanol has demonstrated properties as an effective plasticizing agent for EPDM (ethylene-propylene-diene-monomers) rubber copolymers⁵⁹, polychloroprene and polybutadiene rubber⁶⁰, and LLDPE/EVA copolymer blends. (linear low density polyethylene/ethylene-vinylacetate)⁶¹. The use of CNSL in polyaniline-based conductive composites has also been reported⁶². The CNSL has thus improved the processability of blends of SBS (styrene-butadiene-styrene), polyaniline and dodecylbenzenesulfonic acid copolymers.

Surfactants

A recent review reports the uses of cardanol for surfactants synthesis⁶³. Hence, cardanol has been widely studied for the elaboration of various surfactants, such as cationic surfactants^{64,65}, nonionic^{66,67} and anionic surfactants^{68,69}. There are two main structures of cardanol-based anionic surfactants, one with sulfonate directly on the aromatic ring, and one with aromatic grafted on phenol. Similarly, two main structures of cationic cardanol-based surfactants have been reported, either with alcoholate or carboxylate in the molecule, or with a halogenated counterion (Figure 5). Peungjitton et al.⁷⁰ synthesized sodium cardanol sulfonate and found similar properties than dodecylbenzene sulfonate. Thus, cardanol sodium sulfonate can be used as a raw material for the commercial production of detergents. All these works reported that cardanol is easily sulfonated with excess sulfuric acid in halogenated solvents at room temperature^{71,72,73}. It has been demonstrated that cardanol easily reacts with ethylene sulphate, to yield sulphonated derivatives which have excellent surfactant properties⁷⁴. The use of ethylene sulfate with the phenoxide interestingly avoids both the reaction with sulfuric acid and initial hydroxyethylation step. Moreover, several cardanol-based amphiphilic molecules have successfully studied for many industrial applications^{75,76,77,78}.

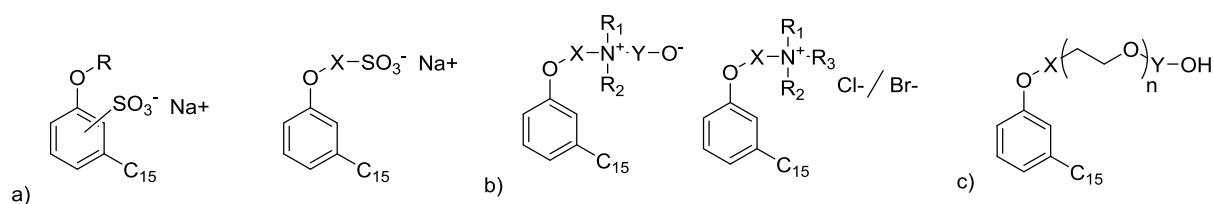


Figure 5: Generic structures of main CNSL-based surfactant a) anionic, b) cationic, c) non-ionic

Cardanol-derived amphiphilic azobenzenes generated stable emulsions^{79,80,81}. Cardanol-based sodium-5-n-pentadecylphenol 2,4-disulfonate, allowed micellization, and the authors reported that the presence of multiple CH₂ groups was important for micelle formation^{82,83}. The presence of the phenoxy group in addition to the long alkyl hydrocarbon chain significantly influences the hydrophobic character of these new amphiphilic molecules. Tyman et al.^{84,85} reported the synthesis of cardanol and cardol polyethoxylates. Cardanol polyethoxylate and its saturated analogue demonstrated similar surfactant properties. Carboxylate derivatives of cardanol and anacardic acid have also been prepared and tested as anionic surfactants⁸⁶. They lower the surface tension, have a critical micellar concentration and produce microemulsions when mixed with dodecyl sulphate. Cationic surfactants containing imidazolium and pyridinium units have been synthesized from cardanol^{87,88,89,90,91}. In 2017, Faye et al proposed a platform approach to allow the synthesis of cardanol-based anionic, cationic and zwitterionic surfactants³².

CARDANOL IN POLYMERS

Cardanol has intrinsic antioxidant and antimicrobial properties. It is thus used for these properties but also as an additive in many formulations. Polymers derived from CNSL have some exceptional properties that make them unique for many applications^{92,93}. Hence these cardanol derived polymers exhibit flexibility due to “internal plasticization” resulting from the presence of a long alkyl chain which also imparts hydrophobicity to the materials. Cardanol is also compatible in mixtures with a wide variety of structures such as vegetable oils, natural phenols or polymers such as alkyds, polyesters, etc., allowing homogeneous formulations to be obtained^{63,94}.

Polymers obtained by step polymerization (polyaddition and polycondensation) constitute one of the most important classes of thermoplastic materials used in industry. Most of these polymers are obtained from difunctional monomers derived from fossil fuels. Cardanol was used as a starting reagent for the synthesis of polycondensation monomers. Various difunctional monomers such as diamines, diacids, diols, dialdehydes, diacylhydrazide, etc. were synthesized from

cardanol^{95,96,97,98}. These difunctional monomers have been used for the synthesis of a wide variety of high performance polymers such as aromatic polyimides, polyamides, poly(azomethine), poly(amideimides), poly(esterimides), polyesters, polyhydrazides, polyoxadiazoles, etc.. The presence of the C15 alkyl chain along the polymer backbone disrupted the organization of the polymer chains, and provided additional sites for interaction with solvents, thus improving the solubility of these polymers compared to reference polymers. The cardanol-derived polymers also exhibited lower Tgs than the reference polymers, attributed to the presence of pentadecyl chains which decrease intermolecular interactions and increase the segmental movement of the polymer chains through an "internal plasticization" effect.

Moreover, cardanol was used in the synthesis of various monomers for the synthesis of various polymers. Indeed, cardanol allowed to synthesize aromatic monomers such as benzoxazines^{99,100} or Mannich-based polyols¹⁰¹ for highly crosslinked polyurethanes. Cardanol was also used for the synthesis of BPA substituents in vinyl esters^{102,103}, cyanate esters^{104,105}. Additionally, recent papers reported its use in hybrid and flame retardant alkyd resins^{106,107}. Recently, interesting biobased latex have been synthesized by homo- or co-polymerization of cardanol-based acrylates with petro- or bio-based comonomers in direct or mini-emulsions^{108,109,110}. The phenolic and the epoxy networks constitute the most dynamic domain of cardanol-based use in polymers, including for industrial products.

Phenolics

The phenol group in cardanol allows it to react with formaldehyde under various conditions to form resole or novolac-like resins^{111,112,113}. Compared to conventional phenolic (phenol-formaldehyde) resins, cardanol-formaldehyde resins have greater flexibility (due to the "internal plasticizing" effect of the C15 side chain). The side chain allows a higher processability and gives also a more hydrophobic character to the network, more resistant to erosion. These polymers have also demonstrated a very low loss of efficiency during friction, which makes them very interesting polymers as additives for the formulation of organic materials for brakes¹¹⁴. In order to reinforce the cardanol-formaldehyde resins, natural fibers have been added such as ramie, flax, hemp or jute fibers¹¹⁵. Several teams have studied cardanol phenolic resins, and particularly with the addition of various polymers. Hence, Chuayjuljit et al.¹¹⁶ reported the synthesis of cardanol-formaldehyde resins for the reinforcement of natural rubber (NR). The aliphatic side chain of cardanol reduced the polarity of phenolic resins and, therefore, increased their compatibility with NR. Shibata et al.¹¹⁷ synthesized thermosetting resins composed of cardanol-novolac and bismaleimide. Shukla et al.¹¹⁸

synthesized a phenolic resin using cardanol and maleic anhydride and studied its reaction kinetics. Nanocomposite foams of cardanol phenolic resin and organo-modified montmorillonite were prepared and the results showed that cardanol could reduce the crosslinking density of the phenolic foams while improving its mechanical properties¹¹⁹. Cardanol-based phenolic resins are particularly studied since cardanol could advantageously replace phenol that is a toxic substance classified carcinogenic, mutagenic, reprotoxic, hence subject to ban due to Reach regulations.

Epoxy resins

Some cardanol-based epoxy monomers are already commercialized by Companies such as Cardolite NC-514 supplied by Cardolite® Corporation which led to epoxy resins with interesting properties (Figure 6). Jaillet et al., studied networks obtained by reaction between NC-514 and various diamines¹²⁰. The structural characterization led to the conclusion that NC-514 was an oligomer mainly composed of diepoxy monomers, with a small percentage of unsaturated compounds. The presence of C15 alkyl chain, endowed plastifying properties that led to a low glass transition temperatures of the epoxy network. However, the reactivity of NC-514 was comparable to the one of Bisphenol A diglycidyl ether (BADGE). GX-2551 was also described¹²¹. This is a molecular cardanol-based epoxy synthesized by epoxidation of both phenol (with epichlorohydrin) and double bonds of alkyl chain (with hydrogen peroxide). The reactivity of internal double bonds is poor with amines, but the curing with anhydrids or acids led to high Tg, since the dangling chain is part of the crosslinked network (Figure 6).

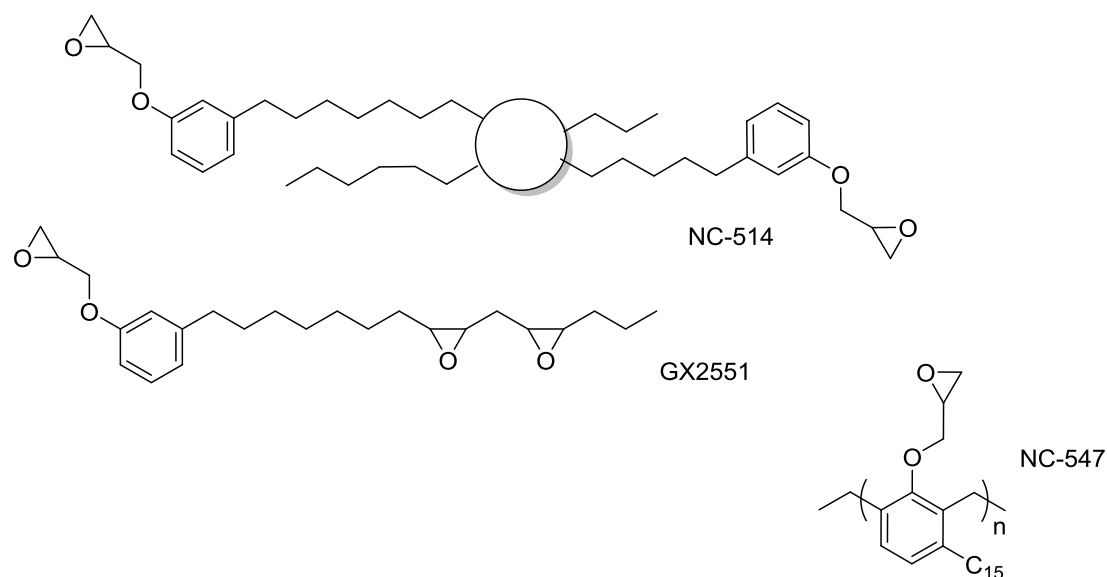


Figure 6: Commercialized cardanol-based epoxy monomers

It is also possible to obtain a cardanol-novolac prepolymer from the condensation reaction of cardanol with formaldehyde¹²². Subsequently, the epoxidation is carried out with ECH in a basic medium. This novolac epoxy resin is also marketed by Cardolite® Corporation as NC-547 (Figure 6). It has a higher viscosity than NC-514 (between 20,000 and 50,000 mPa s) and a slightly lower density. The materials obtained with this epoxy resin are very flexible hydrophobic elastomeric materials, even at low temperatures. The tensile strength is lower and the Tg higher than that obtained with NC-514 due to the higher aromatic density of NC-547¹²³. The reactivity is similar since it also contains glycidyl ether functions, and could possibly be fully cured at room temperature.

CONCLUSION

Cardanol is a major constituent of CNSL which is a by-product of the cashew nut industry whose current production exceeds 900kt per year. Cardanol, is a non-food, cheap and abundantly available versatile industrial raw material of great promise for the replacement of certain products based on fossil resources. The presence of phenolic hydroxyl group and olefinic linkages in the C15 alkyl chain, combined with the aromatic ring makes cardanol an interesting starting material for the synthesis of various value added products by making use of reactivity of each of these functionalities. Hence, dynamic research is developed by several academic teams [98]. In industry Cardolite Corporation (Bristol, PA, USA) is the world's leading developer, manufacturer and marketer of CNSL products^{124,125}. Palmer International is one of CNSL's leading suppliers in North America. In India, several companies are involved in the production of CNSL and derivative products such as: Satya Cashew Chemicals Ltd., Adarsh Industrial Chemicals, Akshar Cashew Industries... Since the beginning of the 2010s, new players have appeared such as Senesel in Poland or Orpia Innovation in Montpellier, France.

Currently, the most promising products from cardanol are epoxy monomers, phenolics, PVC-plasticizers and emulsion surfactants. But very interesting development recently gained attention, such as the work of Lemaire et al. who succeeded in the synthesis of 3-pentadecylcyclohexanone, which has structural similarity with the cyclohexanone, a very important building block of the petro-based chemical industry¹²⁶. Thus, it is only a question of time and the demand for renewables until CNSL-based products would find widespread applications especially for the production of polymers with a unique combination of properties.

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