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A chemical platform approach on cardanol oil: from the synthesis of building blocks to polymer synthesis

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Abstract – This review proposes a platform approach for the synthesis of various building blocks from cardanol oil in one or two-steps synthesis. Cardanol is a natural phenol issued from Cashew nutshell liquid (CNSL). CNSL is a non-edible renewable resource, co-produced from cashew industry in large commercial volumes. Cardanol is non-toxic and particularly suitable as an aromatic renewable resource for polymers and materials. Various routes were used for the synthesis of di- and poly-functional building blocks used thereafter in polymer syntheses. Phenolation was used to dimerize/oligomerize cardanol to propose increase functionality of cardanol. Thio-ene was used to synthesize new reactive amines. Epoxidation and (meth)acrylation were also used to insert oxirane or (meth)acrylate groups in order to synthesize polymers and materials.

Keywords: Cardanol / epoxide / acrylate / carbonate / amine / vinyl ester

Résumé – Une approche plateforme de l'huile de cardanol : de la synthèse d'intermédiaires réactionnels à la synthèse de polymères. Cet article présente une approche plateforme de synthèse d'intermédiaires réactionnels variés pour l'élaboration de polymères à partir de cardanol. Le cardanol est un phénol naturel issu de l'huile de coque de noix de cajou – *Cashew nutshell liquid* (CNSL), une ressource renouvelable non-alimentaire coproduit de l'industrie de la noix de cajou. Le cardanol est non-toxique est particulièrement adapté pour l'intégration de noyaux aromatiques dans des polymères et des matériaux biosourcés. Différentes voies ont été envisages pour la synthèse d'intermédiaires réactionnels di- et poly-fonctionnels pour la synthèse de polymères. La phénolation a été utilisée pour dimériser/oligomériser le cardanol pour augmenter sa fonctionnalité. Le couplage thio-ene a été utilize pour élaborer de nouvelles amines réactives. L'époxidation et la (méth)acrylation ont permis la fonctionnalisation groupes oxirane ou (méth)acrylate afin d'élaborer des matériaux.

Mots clés : Cardanol / epoxy / acrylate / carbonate / amine

1 Introduction

A large part of key commercial chemicals are aromatic substances and are derived from petrochemical resources (Tuck *et al*., 2012). In the recent years, the demand for renewable resource-derived polymers have increased dramatically owing to increasing environmental concern and restricted availability of fossil resources (Gandini, 2011). Most recently, much focus was put on biobased thermosetting resins such as epoxy resins, phenol resins, unsaturated polyesters and biocomposites. This is particularly due to their difficulty to be recycled owing to their infusibility and insolubilty (Koike, 2012). Literature reports very interesting pieces of works dedicated to the use of natural flavonoids (Benyahya *et al*., 2014)

or lignin-derivatives such as vanillin (Fache *et al*., 2014). However, these resources exhibit strong drawbacks such as a low purity and high molar masses that reduces their industrial development. Moreover, the depolymerization of lignin remains challenging (Brazinha *et al*., 2011; Carrier *et al*., 2011). Thus, cardanol is gaining an increasing interest as natural source of phenol (Balachandran *et al*., 2011). Cardanol is produced from cashew nut shell liquid (CNSL), directly extracted from the shell of the cashew nut, fruit from cashew tree, *anacardium occidentale,* mostly grown in India, East Africa and Brazil (Ionescu *et al*., 2012). The global production of CNSL approaches one million tons annually (Campaner *et al*., 2009) and CNSL became of the few major and economic sources of naturally occurring phenols. This really promising aromatic renewable source represents a good natural alternative to petrochemicals derived phenols (Pillail *et al*., 1990).
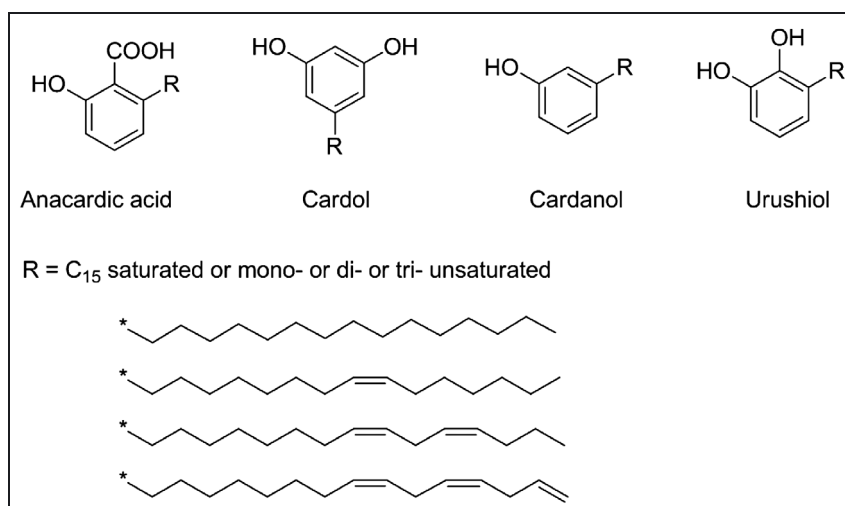
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Fig. 1. Different molecules of CNSL, mono-olefinic (8), di-olefinic (8,11), and tri-olefinic (8,11,14).

CNSL constitutes approximately 25% of the total weight of the cashew nut and is composed of anacardic acid (3-n-pentadecylsalicylic acid) and smaller amounts of cardanol (3-n-pentadecylphenol), cardol (5-n-pentadecylresorcinol), and methylcardol (2-methyl-5-n-pentadecylresorcinol) – the long aliphatic side-chain being saturated, mono-olefinic (8), di-olefinic (8, 11), and tri-olefinic (8, 11, 14) with an average value of two double bonds per molecule (Fig. 1). The thermal treatment of CNSL followed by a distillation lead to the decarboxylation of anacardic acid that yields an industrial grade of cardanol (about 90%), with a small quantity of cardol and methylcardol (Phani *et al*., 2002; Carioca *et al*., 2005). Cardanol is a yellow pale liquid composed of four meta-alkyl phenols differing by unsaturation degree of aliphatic chain: saturated chains (SC) 8.4%, monoolefinic (MO) 48.5%, diolefinic (DO) 16.8% and triolefinic (TO) 29.33% chains (Sultania *et al*., 2011; Tyman *et al*., 1975).

Cardanol was already extensively studied for the synthesis of monomers and polymers particularly by Wadgaonkar *et al.* (More *et al*., 2001; Sudhakar *et al*., 2009). Hence, it was used in direct polymerization (Kim *et al*., 2005), as a polyol for the synthesis of new polyurethanes (Suresh *et al*., 2005), in polyester formulations (Lespinasse *et al*., 2011), in thermosets (such as Novolac) (Yadav *et al*., 2009; Huong *et al*., 1996), in vinyl ester networks (Sultania *et al*., 2010) and also in epoxy networks modification (Unnikrishnan *et al*., 2008).
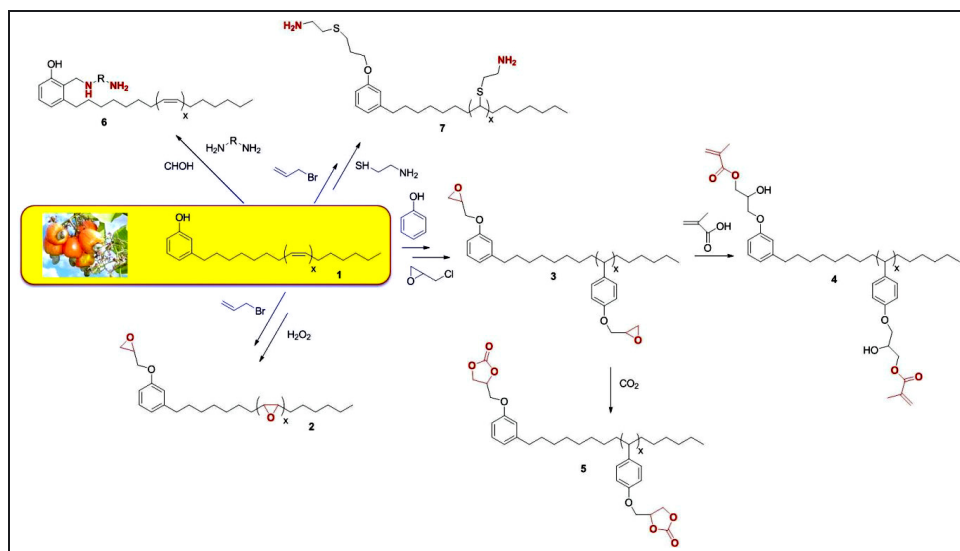
2 Building blocks synthesis

Our team published a comprehensive review on the functionalization of cardanol for the synthesis of monomers, polymers and additives (Voirin *et al*., 2014). Moreover, we synthesized new building blocks from cardanol 1 in one or two step synthesis by various reactions (Jaillet *et al*., 2015), such as thiol-ene coupling, allylation, epoxidation, carbonation or acrylation (Scheme 1). These reactions lead to di- and polyepoxide monomers 2, 3 (Jaillet *et al*., 2013), mono- or di-(meth)acrylic monomers 4 (Jaillet *et al*., 2014, 2016) and carbonate 5 by carbonation reaction (Besse *et al*., 2013), primary
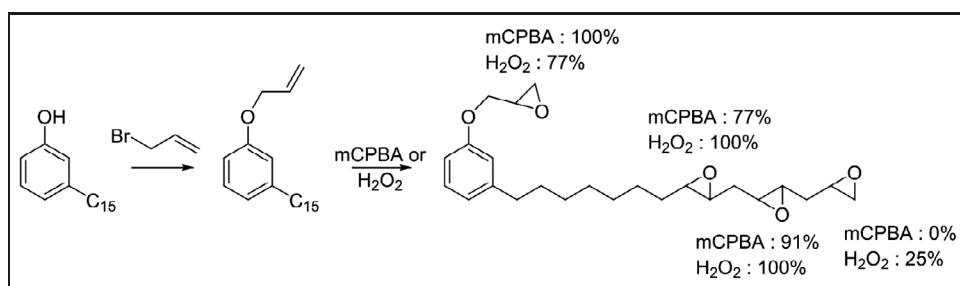
amines 6, 7 (Darroman *et al*., 2014). All these building blocks were used for the synthesis of various polymers such as polyurethanes (PUs), non-isocyanate polyurethanes (NIPUs), vinyl esters and epoxy networks (Darroman *et al*., 2015, 2016).

2.1 From epoxidation of cardanol to polyepoxide networks

Few works reported the direct epoxidation of cardanol for the synthesis of new epoxy networks phenol of cardanol was epoxidized with epichlorohydrin (Verneker *et al*., 1980; Baker *et al*., 1955) in basic conditions, with $ZnCl_2$, at 95 °C. This product is commercialized by Cardolite Coporation. A patent claims also the use of commercial epoxidized cardanol (Agarwal *et al*., 2003). Furthermore, the epoxidation of double bonds of cardanol was also carried out with perbenzoic acid by Patel *et al*. (Patel *et al*., 1989) and by Greco *et al*. (Greco *et al*., 2010). Suresh (Suresh, 2013) performed this reaction with performic acid. Moreover, the epoxidation of these double bonds could also be performed with enzymes such as *Candida Antarctica* lipase (yield 95%) (Kim *et al*., 2007). Additionally, polyepoxy cardanol was synthesized by direct polymerization of double bonds of epoxidized cardanol followed by reaction with various amines (Kanehashi *et al*., 2013). All these studies that report the epoxidation of cardanol neither really described the composition of products of epoxidation reaction nor investigated the properties of synthesized epoxy materials. Indeed, epoxy networks are a major class of thermoset polymers, with a global production around 2Mt/y (Shen *et al*., 2009). Epoxy polymers are extensively used as coatings, adhesives and in structural applications owing to their outstanding mechanical and electrical properties, chemical resistance and adhesion (May, 1988). Diglycidyl ether of bisphenol A (DGEBA) is nowadays the most used monomer for the synthesis of epoxy polymers and materials. DGEBA is synthesized by epoxidation of bisphenol A (BPA). Indeed, the aromatic ring of BPA is particularly interesting since it confers good thermal, chemical and mechanical resistance to epoxy polymers. But this endocrine disruptor mimic the body's own

Schema 1. Synthesis of various building blocks from cardanol.

Schema 2. Synthesis of epoxided cardanol with epoxidation yields.

hormones and may lead to several negative health effects (Gor, 2007; O'Connor and Chapin, 2003; Okada *et al.*, 2008; Vom Saal and Myers, 2008). Thus, a recent review of studies of low-dose effects of BPA found that 94 out of the 115 publications reviewed reported significant effects, including alterations in brain chemistry and structure, behavior, immune system, enzyme activity, male and female reproductive system in a variety of animals, including snails, fish, frogs and mammals (Vom Saal and Hughes, 2005). The negative impact of BPA on human health and environment necessarily implies the elimination of BPA especially since some countries, such as Canada or France, have recently banned the use of BPA in food contact materials. Therefore there is an increasing interest of chemical industry for non-harmful aromatic substituents to BPA, especially for the synthesis of epoxy polymers Thus, cardanol could be an interesting substitute to BPA in some polymers such as epoxy polymers. In this context, our team synthesized new building-blocks from cardanol in order to synthesize biobased epoxy networks.

2.2 Synthesis and characterization of epoxide monomers

The aim of the work reported herein was to synthesize fully biobased aromatic epoxide monomers from cardanol. Even if

epoxidation of cardanol was already studied, we both synthesized a polyfunctional epoxyded cardanol and deeply analyzed composition of commercial NC514 epoxidized cardanol, which was never reported in literature to the best of our knowledge. First, we increased the number of double bonds of cardanol by quantitative allylation of phenol groups with allyl bromide. Thus, we obtained an average number of 3 double bonds per cardanol molecule. Then we epoxidized the double bonds and compared the use of both meta-chloroperbenzoic acid mCPBA and H_2O_2, owing to previously reported routes (Aouf *et al.*, 2013; Sato *et al.*, 1996).

We obtained various results owing to position of double bonds and epoxidation routes (Scheme 2). Indeed, terminal double bonds are not epoxided by mCPBA, whereas epoxidation yield is 25% for terminal double bonds with H_2O_2. Internal 11,12 double bonds are nearly quantitatively epoxided by mCPBA and fully epoxided with H_2O_2. Concerning internal 8,9 double bonds, epoxidation yield is 77% with mCPBA and quantitative with H_2O_2. Concerning allylic double bonds, epoxidation is quantitative with mCPBA, and epoxidation yield is only 77%, with H_2O_2. Anyway, a complete epoxidation of all double bonds of cardanol is not possible, which could be a drawback for further use in polymerization. Therefore the diepoxided cardanol NC-514 proposed by Cardolite is an interesting alternative. It is synthesized in two steps by phenolation of aliphatic chain, prior to reaction of
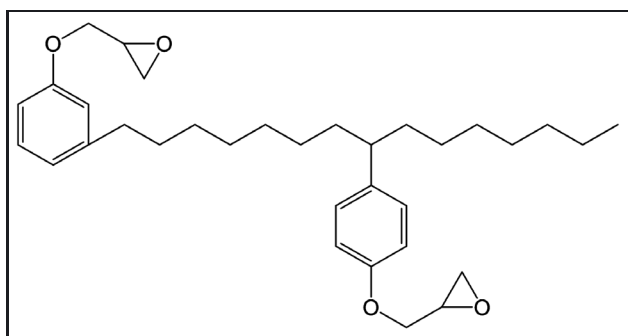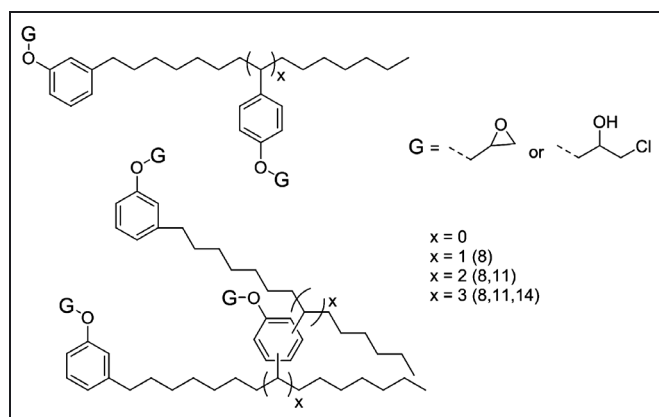
Figure 2. Chemical structure of NC-514.

Figure 3. Likely chemical structure of cardanol NC-514.

phenol hydroxyl groups with epichlorohydrin (Ionescu and Petrovic, 2011). Thus, we thoroughly analyzed the composition of epoxidized cardanol NC-514 supplied by Cardolite. Thesupplier indicates an EEW of 400 g/eq and following chemical structure of diepoxided cardanol (Fig. 2).

The epoxided cardanol NC-514 was extensively studied in a previous paper from our team using ^{1}H- and ^{13}C-NMR, size exclusion chromatography and titration (Jaillet *et al.*, 2013). It was shown that NC-514 contains saturated and mono-olefinic chains with a respective composition of 95% saturated chains and 5% mono-olefinic chains. ^{1}H-NMR calculations allow determining a functionality of 2.3 epoxy groups per molecule. It was also demonstrated that NC-514 has a macromolecular structure: the experimental molar mass of NC-514 is 1029 g/mol (dispersity of 2.16), which is far higher than the idealized molar mass of about 460 g/mol. The most likely chemical structure of NC-514 after extensive characterization is the one proposed in Figure 3. The phenol groups are respectively in position (8), (8, 11) or (8, 11, 14).

2.3 Synthesis and characterization of polymers

Epoxy networks were formulated with various epoxide monomers and amines. We tested cardanol NC-514 (Scheme 1, 3) and diglycidyl ether of bisphenol A (DGEBA) with isophorone diamine (iPDA), cardanol NX-5454 (Scheme 1, 6) and synthesizd cardanol cysteamine (Scheme 1, 7). Epoxy formulations were stirred 3 min at room temperature and put in a mold at 120 °C during 5 h, then at 170 °C dur-

ing 30 min. Five different formulations were carried out with various ratios: DGEBA/iPDA, cardanol NC-514/iPDA, cardanol NC-514/Jeffamine D400, cardanol NC-514/Cardanol NX-5454 and cardanol NC-514/cardanol cysteamine.
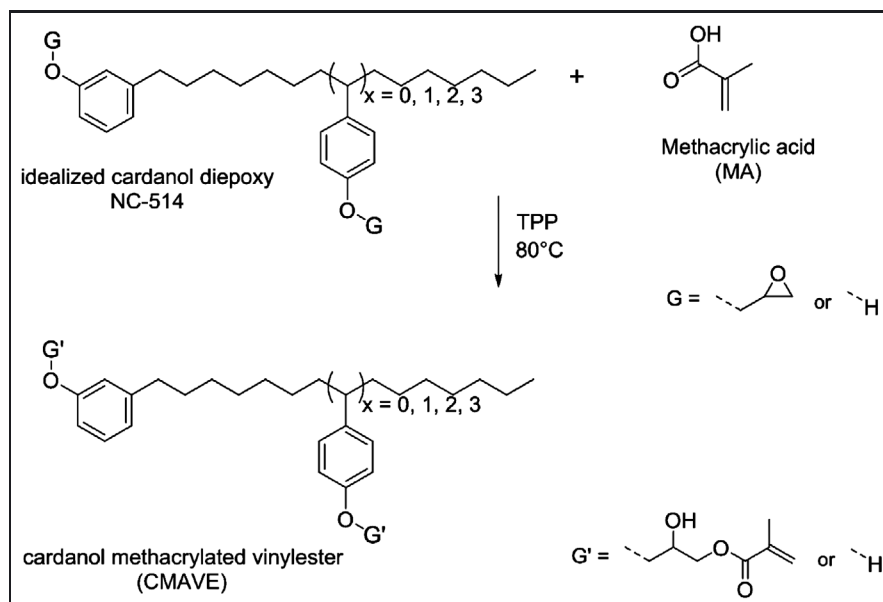
The polymers synthesized with epoxidized cardanol NC-514 exhibit lower T_g values than with DGEBA, due to the long aliphatic chain of cardanol. All epoxy networks exhibit very interesting thermal stabilities. The mechanical properties for NC-514 are lower than for DGEBA however the moduli recorded could be interesting for coating applications (Table 1).

3 From acrylation of cardanol to vinyl esters synthesis

Vinyl ester (VE) networks are one of the most important classes of thermoset polymers, with a global production of 1 Mt/y, combining chemical, mechanical and thermal properties of epoxy networks with rapid cure of unsaturated polyesters (UP). Therefore VE are used for various industrial applications such as surface coatings, adhesives, radiation curable inks, printed circuit board coatings, spherical lens materials and composites (Agrawal *et al.*, 2003; Gaur *et al.*, 1993). VE prepolymers are synthesized by reaction between epoxy monomers and (meth)acrylic acid. The most commonly used epoxy monomer for the synthesis of VE prepolymers is DGEBA. DGEBA is methacrylated by reaction with methacrylic acid to yield methacrylated diglycidyl ether of bisphenol A (MDGEBA). By means of the two terminal reactive double bonds, MDGEBA can easily yield cross-linked network structures by a free-radical polymerization mechanism. Due to the high viscosity of VE prepolymers, it is necessary to add some vinyl monomers as reactive diluents (such as styrene, acrylates or methacrylates) (Agrawal *et al.*, 2003; Gaur *et al.*, 1993) that copolymerize with VE prepolymers. Styrene is highly polymerizable with acrylate or methacrylate functions. MDGEBA is the most commonly used prepolymer since it allows to obtain vinyl ester materials with styrene as reactive diluent, exhibiting good thermal resistance and mechanical properties. The main issues of vinyl esters concern the use of MDGEBA as prepolymer, since it is derived from bisphenol A. Indeed, bisphenol A is classified as carcinogenic, mutagenic, reprotoxic (CMR). Literature reports interesting studies on the replacement of MDGEBA prepolymer for VE networks. Thus, the use of isosorbide diglycidyl ether (Lukaszczyk *et al.*, 2012; Sadler *et al.*, 2013; Chrysanthos *et al.*, 2011) or furfuryl derivatives (Jeong *et al.*, 2013) was reported, but the properties of obtained materials do not meet the needed thermal properties for targeted applications. The synthesis of VE networks from vegetable oils is also reported in literature. Thus, La Scala *et al.* proposed the functionalization of vegetable oils with methacrylic functions in order to obtain materials with T_g values around 70 °C (La Scala *et al.*, 2004). Furthermore, Adekunle et al. reported the functionalization of epoxidized soybean oil with methacrylic acid or methacrylic anhydride to obtain biobased composites (Adekunle *et al.*, 2010). Recently, Webster *et al.* reported the methacrylation of epoxidized sucrose soyate to yield thermoset materials with high properties (Yan *et al.*, 2014).

Table 1. Thermal and mechanical properties of epoxy polymers from cardanol.

Formulations	T_g (°C)	T_α (°C)	E' (MPa) at 20 °C	Under air	
				$T_{d30\%}$ (°C)	Char at 600 °C (%)
DGEBA/IPDA	150	158	1480	375	0.9
NC-514/IPDA	50	59	1218	363	1.8
NC-514/Jeff400	9	15	7	361	0.4
NC-514/NX-5454	30	38	350	374	1.2
NC-514/Cardanol cysteamine	19	21	1.4	400	1.4

Schema 3. Synthesis of cardanol (idealized structure) methacrylated VE prepolymer.

3.1 Cardanol prepolymer and VE networks synthesis

The esterification reaction of epoxided cardanol NC-514 was carried out with methacrylic acid using TPP as catalyst and hydroquinone as inhibitor at 80 °C, as shown in Scheme 3 to yield cardanol methacrylated VE prepolymer (CMAVE).

The cardanol-based VE prepolymer (CMAVE) and the DGEBA-based VE prepolymer (BMAVE) were prepared as described earlier (Jaillet *et al.*, 2014). Then, they were diluted in styrene (ST) or isobornyl methacrylate (IBOMA) reactive diluents (ratio prepolymer/reactive diluent 60/40) and cured 12 h at 120 °C and 2 h at 150 °C using 3% of tert-butyl peroxybenzoate (Trigonox C) as initiator to yield the VE networks: cardanol-based methacrylated VE networks CMAVE/ST, and CMAVE/IBOMA and the DGEBA-based methacrylated VE networks BMAVE/ST and BMAVE/IBOMA. There is no difference of crosslinking rate between VE with styrene and IBOMA. Each VE had a gel time around 30 min.

3.2 VE networks characterizations

All networks were stable up to 300 °C and started losing weight above this temperature. Rapid decomposition was then observed in the temperature range of 400 °C and almost total volatilization of the sample was occurred around 500 °C. These results showed the similar thermal stability of cardanol-based (Fig. 4) and DGEBA-based VE networks under nitro-gen atmosphere. Dynamic scanning calorimetry (DSC) studies were performed to study the glass transition temperature of the cured VE networks. The T values are reported in Table 2. Complete crosslinking of the DGEBA-based and cardanol-based VE resins by the cure procedure was ensured since no exothermal cross-linking peak was observed during the first heating ramp. Indeed, the aliphatic chain of cardanol confers higher mobility to the chains, which leads to lower T_g. However, higher T_g was obtained with IBOMA reactive diluent compared to styrene because the isobornyl bis-cyclic group is much more bulky and rigid than benzene ring. Thermomechanical properties of the cured VE networks were determined using dynamic mechanical analysis (DMA).

Similarly, $T\alpha$ of cardanol-derived VE are lower than the ones of MDGEBA-derived VE. However, T_α obtained with IBOMA are very interesting for composite applications. The mechanical properties for cardanol-derived VE are a bit lower than for DGEBA. However the moduli recorded could be interesting for composite applications.
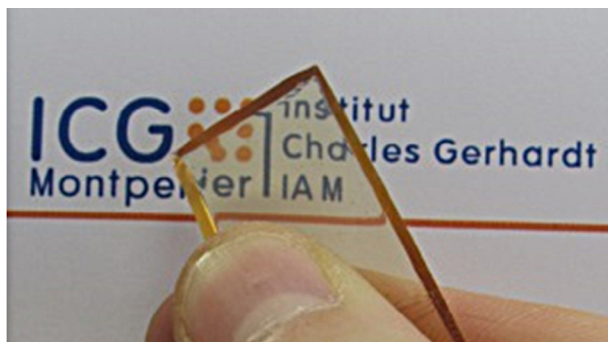
4 Conclusion

We developed a chemical toolbox based on phenolation, epoxidation, oxidation, acrylation, carbonation and amination to synthesize a library of biobased building blocks with various functions from cardanol derived from cashew nutshell liquid. The synthesized building blocks reported in this contribution

Table 2. Thermal and mechanical properties of VE from cardanol.

Materials	T_α (°C)[a]	T_g (°C)[b]	E' (MPa) at 20 °C	$T_{30\%}$ (°C)[c]
BMAVE/ST	158	138	1270	402
BMAVE/IBOMA	175	154	1960	327
CMAVE/ST	86	69	1060	406
CMAVE/IBOMA	116	92	1050	313

[a] T_α determined by DMA at the peak of tan δ. [b] T_g determined by DSC, 2nd $T°$ scan 20 °C/min. [c] Temperature of 30% weight loss as given by TGA under N_2 atmosphere.

Figure 4. Cardanol-derived VE network.

are polyfunctional phenols, epoxides, amines and cyclocarbonates. They could lead to polymers such as polyurethanes, polyhydroxyurethanes, epoxy resins and vinyl esters. Thus, we synthesized partial and fully cardanol-derived epoxy materials from epoxidized cardanol and cardanol amines. These epoxy polymers are very interesting since they bear aromatic rings for interesting formulation. We obtained different mechanical and thermal properties owing to the various formulations. We demonstrated that cardanol-derived epoxy polymers could find promising properties for coatings applications. Indeed, cardanol is a promising non-edible biobased aromatic resource for polymer applications.

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Cite this article as: Fanny Jaillet, Emilie Darroman, Bernard Boutevin, Sylvain Caillol. A chemical platform approach on cardanol oil: from the synthesis of building blocks to polymer synthesis. OCL 2016, 23(5) D511.