



## New cardanol/sucrose epoxy blends for biobased coatings



Emilie Darroman<sup>a</sup>, Nelly Durand<sup>b</sup>, Bernard Boutevin<sup>a</sup>, Sylvain Caillol<sup>a,\*</sup>

<sup>a</sup> UMR 5253 CNRS-UM2-ENSCM-UM1, Institut Charles Gerhardt Montpellier, Equipe I.A.M., 8 Rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France

<sup>b</sup> Sogatra Nouvelle, 784 chemin de la Calladette, 30350 Lezan, France

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### ABSTRACT

Commercial epoxidized cardanol, from cashew nutshell liquid (CNSL) is a biobased reactant with interesting aromatic structure. Cured with two different amines, isophorone diamine and Jeffamine T403, the materials exhibit good properties but not enough to replace the bisphenol A diglycidyl ether (BADGE) in epoxy networks. Two kind of sucrose epoxy derivatives, sorbitol and isosorbide, were used as blends to enhance the properties of the epoxy cardanol-derived materials. These epoxy networks with different ratios were characterized by thermogravimetric analysis and differential scanning calorimetry; their hardness and brightness were measured as well as their resistance to chemical solvents. Biobased epoxy blends exhibit interesting properties for coating applications.

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### 1. Introduction

Epoxy resins are an important class of thermoset polymers used for coating applications. Bisphenol A (BPA), a reactant that was initially synthesized as a chemical estrogen [1], is nowadays the most used monomer for the production of epoxy resins. The aromatic ring of BPA is particularly interesting since it confers good thermal resistance to epoxy resins. But this endocrine disruptor can mimic the hormones of the human body and may lead to several negative health effects [2–5]. Thus, a recent review [6] about studies of low-dose effects of BPA found that 94 of the 115 publications reported significant effects. Effects include alterations in brain chemistry, in the immune system, in the enzyme activity, in the male and female reproductive systems in a variety of animals, including snails, fish, frogs and mammals [6]. The negative impact of BPA on human health and on 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 industries for non-harmful reactants allowing the synthesis of epoxy resins without BPA. Moreover, thermoset polymers cannot be recycled due to their cross-linked networks and for that reason they need to be biobased to ensure less environmental impacts. Thus, non-toxic biobased

epoxy reactants are highly needed and studied [7]. Few commercial biobased epoxy reactants are available with the exception of vegetable epoxidized oils which are the most used biobased monomers [8]. Despite their cross-linked networks, epoxidized vegetable oil based resins have low  $T_g$  due to the long aliphatic chain ( $T_g = -38^\circ\text{C}$  with epoxidized-linseed oil cured with amine-functionalized grape seed oil [9]) and low reaction enthalpy. However, coatings need to have excellent thermal and mechanical properties, brought by compounds bearing aromatic rings or a high cross-linked network. Biobased aromatic epoxy reactants would give good properties to coatings as the BPA based resins. Even if literature reports some very interesting works based on natural flavonoids [10] or lignin, these resources exhibit strong drawbacks. Indeed, low purity and high molar masses of these resources limit their development in chemistry. Depolymerization of lignin [11,12] is an alluring route to give an access to biobased aromatic compounds, required by chemical industries, however this route remains deceptive since, like vanillin [13], very interesting product, the availability of this resource is not sufficient. Cardanol [14], extracted from cashew nut shell liquid (CNSL), a non-edible by-product of CNSL industries, is a really promising aromatic renewable resource, available in large quantity and would be suitable for food contact [15]. Cardanol is a yellow pale liquid composed of four meta-alkyl phenols differing by unsaturation degree of aliphatic chain: saturated chains (SC) 8.4%, mono-olefinic (MO) 48.5%, di-olefinic (DO) 16.8% and tri-olefinic (TO) 29.33% chains [16,17]. Cardanol was already extensively studied for material synthesis, through direct polymerization [18], as a

\* Corresponding author. Tel.: +33 467144327; fax: +33 467147220.  
E-mail address: [sylvain.caillol@enscm.fr](mailto:sylvain.caillol@enscm.fr) (S. Caillol).

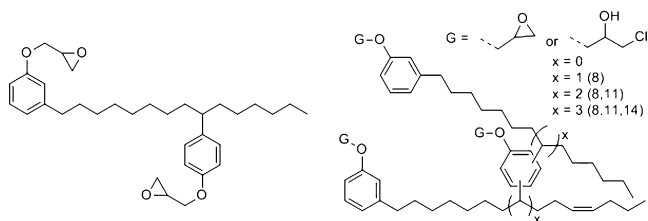


Fig. 1. Idealized structure of epoxidized cardanol by Cardolite and the structure defined by our team [28].

polyol in new polyurethanes [19], in polyester compositions [20], with partial or total substitution of phenol in thermoset resins such as Novolac resins [21–23], vinyl esters [24,25] and also in epoxy resins modification [26,27].

Our team previously worked on epoxidized cardanol [28] provided by Cardolite and depicted the detailed chemical structure compared to the one given by the technical data sheet (Fig. 1). In fact, this commercial epoxidized cardanol is not a dimer but appeared to be a mix of oligomers of cardanol and phenol with various molar masses, with opened epoxy rings and a mean functionality of 2.3 epoxy functions per molecule [28]. Despite a 120 °C curing of epoxidized cardanol formulations, the glass transition temperatures,  $T_g$ , of cardanol resins were too low, and in order to increase them, blends with other epoxy reactants are needed. Some academic products such as isosorbide or prototypes, derivatives from sugar as sorbitol could also be proposed as candidates to substitute bisphenol A in coatings. The objective of this work is to obtain blends of epoxy resins with good thermal and mechanical properties in order to meet required properties for coating applications. In literature, to the best of our knowledge, few works reported the study of blends of biobased epoxy whereas this is crucial since it will be hard to substitute bisphenol A diglycidyl ether (BADGE) by a unique molecule. Our resins were formulated, cured at room temperature and characterized to measure their resistance as coatings in contact with acid or basic solvents. This publication is the first one to compare different biobased commercial epoxy reactants in coating applications.

## 2. Materials and methods

### 2.1. Materials

Trifunctional polyetheramine Jeffamine T403 (amine hydrogen equivalent weight (AHEW)=81 g/eq), isophorone diamine Aradur 42BD (AHEW=42.5 g/eq) were purchased from Huntsman (Switzerland). Diglycidyl ether of cardanol NC-514 (epoxy equivalent weight (EEW)=400 g/eq) was obtained from Cardolite (Belgium). Polyglycidyl ether of sorbitol Denacol EX622 (EEW=188 g/eq), and two epoxidized isosorbide Denacol GSR100 (EEW=155 g/eq) and Denacol GSR102 (EEW=158 g/eq) were purchased from Nagase (Japan). Bisphenol A diglycidyl ether (BADGE) (EEW=187 g/eq), ethyl acetate, and sodium hydroxide were purchased from Thai Organic Chemicals Co, Brenntag and Univar, respectively. Glacial acetic acid and deionized water were purchased from Analytic Lab. All reactants were used as received.

### 2.2. Formulations

Several mixtures were obtained from diglycidyl ether of cardanol NC-514 (EEW=400 g/eq) at different mass ratios (100 wt%, 75 wt%, 50 wt% and 25 wt%) with various epoxy reactants: polyglycidyl ether of sorbitol Denacol EX622 (EEW=188 g/eq), and two epoxy reactants of isosorbide Denacol GSR100 (EEW=155 g/eq) and Denacol GSR102 (EEW=158 g/eq). These mixtures were cured

at room temperature with two commercial amines, trifunctional polyetheramine Jeffamine T403 and isophorone diamine Aradur 42BD, and were compared to the formulation obtained with DGEBA.

Theoretically, all the formulations should be prepared in 1:1 M ratio of epoxy group to active H of amine in the view to obtaining the maximal crosslinking density of cured epoxy agent. Therefore, we used the given data (EEW and AHEW) from technical sheet of the different reactants. Each formulation is carried out with 75 g of epoxy resin which EEW is given by the technical sheet for mass content of 100 wt% or calculated as below:

$$\text{mol\% epoxy 1} = \frac{\frac{m_{\text{epoxy 1}}}{\text{EEW}_1}}{(m_{\text{epoxy 1}}/\text{EEW}_1) + (m_{\text{epoxy 2}}/\text{EEW}_2)} \times 100 \quad (1)$$

where mol% epoxy 1,  $m_{\text{epoxy 1}}$ ,  $m_{\text{epoxy 2}}$ ,  $\text{EEW}_1$  and  $\text{EEW}_2$  are respectively the molar percentage of epoxy 1, the mass (g) of epoxys 1 and 2, and the epoxy equivalent weight of epoxys 1 and 2.

$$\text{EEW}_{\text{mixture}} = \text{EEW}_1 \times \text{mol\% epoxy 1} + \text{EEW}_2 \times (1 - \text{mol\% epoxy 1}) \quad (2)$$

where  $\text{EEW}_{\text{mixture}}$ , mol% epoxy 1,  $\text{EEW}_1$  and  $\text{EEW}_2$  are respectively the epoxy equivalent weight of the mixture of epoxys 1 and 2, the molar percentage of epoxy 1, and the epoxy equivalent weight of epoxys 1 and 2.

The mass of curing agent is determined as below:

$$m_{\text{curing agent}} = m_{\text{epoxy}} \times \frac{\text{AHEW}}{\text{EEW}} \quad (3)$$

where  $m_{\text{curing agent}}$ ,  $m_{\text{resin}}$ , AHEW and EEW are respectively the mass of the amine curing agent, the mass of epoxy or mixture of epoxys, the amine hydrogen equivalent weight and the epoxy equivalent weight of epoxy or mixture of epoxys.

Formulations were carried out without solvent. After weighing, reactants were mixed and vigorously manually stirred during 3 min. Then mixtures were poured in a silicon mold and on a sable glass. These preparations were cured at 22 °C during at least 5 days.

### 2.3. Analytical techniques

Viscosity and density of different mixtures were performed at 33 °C with a DV-E Brookfield viscosimeter and an Erichsen pycnometer (100 mL, model 290/1).

Gel times were measured on a mixture of 100 g with a Trombotat purchased from *Matériau Ingénierie*.

The micro-applicator (BYK) allowed us to cast a layer of 500 μm on the glass (length: 165 mm, width: 110 mm and thickness: 4 mm).

The brightness was evaluated by a Picogloss 560MC on different places on the glass.

**Swelling index:** The study of swelling is based on the materials cured in the silicon molds with different solvents and conditions. These materials were immersed into 100 mL (high: 150 mm and diameter: 40 mm) of the simulants as below:

- in 3 wt% of acetic acid solution at 40 °C during 10 days;
- in 3 wt% of sodium hydroxide solution at 22 °C during 10 days;
- in ethyl acetate at 22 °C during 30 min.

The swelling index SI is given by following equation:

$$\text{SI} = \frac{m_1 - m_0}{m_0} \times 100 \quad (4)$$

where SI,  $m_1$  and  $m_0$  are respectively, the swelling index, the mass in grams of the sample after being in the simulant and the initial mass of the sample.

Thermogravimetric analyses (TGA) were performed on a Q50 from TA Instrument. 10 mg of sample in an aluminum pan

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