



Improved cardanol derived epoxy coatings



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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 diamines, isophorone diamine and Jeffamine T403, the synthesized materials exhibit good properties but they do not meet properties of bisphenol A diglycidyl ether (BADGE) epoxy resins. Therefore epoxidized cardanol cannot replace directly BADGE for the synthesis of epoxy resins. Three epoxy reactants, resorcinol, hBADGE and TMP, were used as reactive additives to enhance the properties of the cardanol derived materials. These epoxy networks with different ratios were characterized by thermogravimetric analysis, differential scanning calorimetry. Their hardness and gloss were measured as well as their resistance to chemical solvents.

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1. Introduction

Epoxy networks are an important class of thermoset polymers used as coatings. Bisphenol A (BPA), a reactant that was initially synthesized as a chemical estrogen [1], is nowadays the most used monomer for the annually production of 2Mt of epoxy polymers. The aromatic ring of BPA is particularly interesting since it confers good thermal resistance to epoxy resins. But this endocrine disruptor can mimic the body's own hormones and may lead to several negative health effects [2–5]. Thus, a recent review of studies [6] of low-dose effects of BPA, found that 94 of the 115 publications reviewed reported significant effects. Effects include alterations in brain chemistry and structure, behavior, the immune system, enzyme activity, the male reproductive system, and the female reproductive system in a variety of animals, including snails, fish, frogs and mammals [6]. The negative impact of BPA on human health and environment necessarily implies the elimination of BPA. Indeed, some countries, such as Canada or France, have recently banned the use of BPA in food contact materials. Thus, there is an increasing interest of chemical industry for non-harmful reactants allowing the synthesis of epoxy resins without BPA. Moreover, thermoset polymers cannot be easily recovered by mechanical recycling due to their crosslinked networks and

consequently they need to be biobased to ensure to reduce environmental impacts. Therefore, non-toxic biobased epoxy reactants are highly needed and studied [7]. Few commercial biobased epoxy reactants are available, except epoxidized vegetable oils which are the most used as biobased monomers [8]. Despite their crosslinked networks, epoxidized vegetable oil based resins exhibit low T_g due to the long aliphatic chain (T_g = –38 °C with epoxidized-linseed oil cured with amine-functionalized grapeseed oil [9]) and low reaction enthalpy. However, epoxy formulations are generally used to confer needed properties, such as high mechanical and chemical resistance, to coatings. These properties are generally brought by aromatic rings, highly stable groups, cycloaliphatic compounds or a highly crosslinked network. Indeed, biobased aromatic epoxy reactants would confer high 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] would be an alluring route to give access to biobased aromatics needed by chemical industry. However, this route remains deceptive since despite extensive research, there are very few reports of efficient ways of recovering such aromatic products. Vanillin [13] is a very interesting building block which is industrially produced from lignin, but its availability is not sufficient for coating industry. Cardanol [14], extracted from cashew nut shell liquid (CNSL), a non-edible by product of CNSL industry, is really a promising aromatic renewable source available in large

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quantity and would be suitable for food contact [15]. Cardanol is a yellow pale liquid composed of four meta-alkyl phenols differing by the unsaturation degree of aliphatic chain: saturated chains (SC) 8.4%, monoolefinic (MO) 48.5%, diolefinic (DO) 16.8% and triolefinic (TO) 29.3% chains [16,17]. Cardanol was already extensively studied for material synthesis, through direct polymerization [18], as a polyol in new polyurethanes [19], in polyester compositions [20], with partial or total substitution of phenol in thermoset networks such as Novolac [21–23], vinyl esters [24,25] and also in epoxy polymers modification [26,27].

Our team previously worked on epoxy cardanol [28] provided by Cardolite. Even if we cured epoxy formulations at 120 °C at least, the glass transition temperatures, T_g , of polyepoxide cardanol networks were too low and in order to increase them, blends with other epoxy monomers are needed. We used also two kinds of sucrose epoxy derivatives, sorbitol and isosorbide, in addition to epoxidized cardanol, to enhance the properties of the epoxy cardanol-derived materials with interesting results [32].

The objective of this work is to use academic products such as hydrogenated BADGE (hBADGE), tris-epoxidized trimethylolpropane or tannin derived resorcinol as epoxy additives to epoxidized cardanol to obtain blends of epoxy polymers with good thermal, chemical and mechanical properties in order to meet required properties for coating applications. In literature, few works to the best of our knowledge studied blends of biobased epoxidized monomers whereas this is not only the real life of formulation in industry, but it is also crucial since it will be hard to substitute Bisphenol A Diglycidyl Ether (BADGE) by a unique molecule. These polymers 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 these epoxidized reactants with epoxidized cardanol in coating application.

2. Material 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) and triglycidyl ether of trimethylolpropane Aradilte DY-T/CH (Epoxy Equivalent Weight (EEW)=125 g/eq) were purchased from Huntsman (Switzerland). Diglycidyl ether of cardanol NC-514 (EEW=400 g/eq) was obtained from Cardolite (Belgium). Diglycidyl ether of resorcinol Denacol EX201 (EEW=116 g/eq), and hydrogenated Bisphenol A diglycidyl ether Denacol EX252 (EEW=214 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 massic ratios (100%w, 75%w, 50%w and 25%w) with various epoxy reactants: diglycidyl ether of resorcinol Denacol EX201 (EEW=116 g/eq), hBADGE Denacol EX252 (EEW=214 g/eq) and triglycidyl ether of trimethylolpropane Aradilte DY-T/CH (EEW=125 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 BADGE. 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 polymer which EEW is given by the technical data sheet for weight ratios of 100%w or calculated as below:

$$\%mol\ epoxy\ 1 = \frac{\frac{m_{epoxy\ 1}}{EEW_1}}{\frac{m_{epoxy\ 1}}{EEW_1} + \frac{m_{epoxy\ 2}}{EEW_2}} \times 100 \quad (1)$$

where %mol epoxy 1, $m_{epoxy\ 1}$, $m_{epoxy\ 2}$, EEW_1 and EEW_2 are respectively the molar pourcentage of epoxy 1, the mass (g) of epoxy 1 and 2, and the epoxy equivalent weight of epoxy 1 and 2.

$$EEW_{mixture} = EEW_1 \times \%mola\ epoxy\ 1 + EEW_2 \times (1 - \%mol\ epoxy\ 1) \quad (2)$$

where $EEW_{mixture}$, %mol epoxy 1, EEW_1 and EEW_2 are respectively the epoxy equivalent weight of the mixture of epoxy 1 and 2, the molar pourcentage of epoxy 1, and the epoxy equivalent weight of epoxy 1 and 2. The mass of curing agent is determined as below:

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

where $m_{curing\ agent}$, m_{resin} , AHEW and EEW are respectively the mass of the amine curing agent, the mass of epoxy or mixture of epoxy, the amine hydrogen equivalent weight and the epoxy equivalent weight of epoxy or mixture of epoxy. 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 characterized 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 gloss was evaluated by a Picogloss 560MC on different places on the glass with 60° measurements.

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%w of acetic acid solution at 40 °C during 10 days;
- in 3%w 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:

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

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.

Thermogravimetry Analyses (TGA) were performed on a Q50 from TA Instrument. 10 mg of sample in an aluminum pan was heated from room temperature to 580 °C under a nitrogen (60 mL/min). The experiments were carried out at a heating rate of 10 °C/min.

Differential Scanning Calorimetry (DSC) analyses were carried out on a NETZSCH DSC200 calorimeter. Cell constant calibration

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