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Novel biobased and food contact epoxy coatings for glass toughening applications

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ABSTRACT

Three series of novel food contact approved and low-toxic coatings for glass toughening applications were successfully prepared based on dicyandiamide and biobased epoxy compounds, e.g. epoxidized cardanol (NC514), diglycidyl ether of vanillin (DGEVA), triglycidyl ether of phloroglucinol (TGEP). Processability of formulations in bulk and in aqueous phase, and optimum materials were carefully investigated. The cure temperature of these epoxide:amine systems ranged from 160 to 250 °C, for which TGEP showed the highest reactivity. The developed materials exhibited excellent thermal stability and a wide range of glass transition temperature (Tg) was achieved, from 29 to 187 °C. The glass adhesion and mechanical properties were characterized by adhesion test and by mechanical ring test, respectively. The results revealed excellent glass adhesion properties without adhesion promotor addition and enhanced glass mechanical properties with all materials. These food contact and lowly-toxic materials are promising alternatives for DGEBA-based materials in widespread applications.

1. Introduction

Recent years have witnessed an increased demand for renewable resource-derived polymers (biobased polymers), owing to increasing environmental concern and restricted availability of petrochemical resources [1,2]. Several biobased polymers, e.g. cellulose [1], starch [1], or triglycerides [3], have been already commercially available and industrially used. However, properties, and thus their applications are limited, due to their aliphatic or cycloaliphatic structure. Moreover, aromatic polymers, such as polyethylene terephthalate (PET), represent key chemicals with approximatively 56 million tons of production each year from petrochemical feedstocks.

Among different types of material, epoxide thermosets are the most popular [4–6], due to their broad spectrum of properties through the selection of epoxy prepolymers and curing agents, and therefore, their use in various applications, e.g. coatings, adhesives, composites, laminates, and electrical castings, among others.

Over 90% of these epoxide materials are based on bis(4-hydroxyphenylene)-2,2-propane, known as bisphenol A (BPA), that the aromatic ring confers good thermal resistance to the polyepoxide network. Commercialized for more than 50 years, BPA is nowadays utilized in many common products, included in food containers and human health applications such as filling materials or sealants in dentistry. However, BPA was initially synthesized as a chemical estrogen [7] and can mimic the body's own hormones, leading to severe negative health effects [8–12]. This endocrine disruptor has been recently classified as CMR R1b, and since the corresponding polymers are sensitive to hydrolysis, leaching of BPA can lead to widespread human exposure. Consequently, new regulations based on European and Canadian directives focused on reduction of waste and pollutants volume, and have forbidden the production and commercialization of BPA since January 2015. This awareness on BPA toxicity combined with the limitation and high cost of fossil resources implies necessary changes in the field of polyepoxide networks. Major issues are to find alternative materials containing both biobased and non-toxic reactants, especially for food or beverage containers applications.

Currently, epoxidized diaromatic cardanol, obtained from cashew nutshell liquid (CNSL), is the only natural non-toxic and food contact approved epoxide compound [13], commercially available in the market. This biobased extract is already a promising building block for thermoset materials and has been studied by our team for many years [14–19]. Its structure containing a long alkyl chain led to lower thermal and mechanical properties than BPA-based materials. Recently, our research group has developed more rigid architectures with series of poly-functional glycidyl ether derivatives based on both biobased and barely toxic extracts, such as vanillin [20–24] and phloroglucinol

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[25–27], which are from lignins and tannins [28,29], and used as food flavoring or active ingredient in medicine. Obtained materials showed excellent thermal and mechanical properties, which can complete with diglycidyl ether of bisphenol A (DGEBA)-based materials.

The present article describes the formulation in bulk and in aqueous solution, of food contact approved materials, based on barely toxic reactants. A particular attention has been focused on European food contact regulation and toxicity data of each compound. For this purpose, we chose epoxidized cardanol (NC514), diglycidyl ether of vanillin alcohol (DGEVA) and triglycidyl ether of phloroglucinol (TGEP), as epoxide monomer. Materials were prepared by curing the former derivatives with dicyandiamide, a non-toxic amine, at suitable cure temperature without any use of catalyst. The reactivity and the functionality of each reactant will be discussed. Thermal properties will be analyzed and compared with DGEBA-based material which was already reported for reinforcement of glass [43]. The application of these materials as glass coating will be examined by an adhesion test and a mechanical ring test. Thus, for the first time, a paper will be focused on the preparation of non-toxic and food contact materials, and their use as coatings.

2. Experimental section

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) (99%), dicyandiamide (DICY) (99%), dimethylsulfoxide (DMSO) and 3-aminopropyltriethoxysilane (99%) were purchased from Aldrich. Epirez 3510W60 was obtained from Hexion, epoxidized cardanol (NC514) from Cardolite and diglycidyl ether of vanillyl alcohol (DGEVA) and triglycidyl ether of phloroglucinol (TGEP) from Specific Polymers. All reactants and reagents were used as received, and their food contact approval and their toxicology were controlled.

2.2. Formulations

Every material was prepared by formulation between epoxy and dicyandiamide, in which several epoxy/amine functionality ratios were investigated to determine the reaction stoichiometry and then the optimum material.

The functionality of the epoxy derivatives is defined by its epoxide number, which is expressed as the equivalent weight, which is the weight in grams of epoxy reactant containing one mole epoxide group (g eq^{-1}). In this work, the Epoxy Equivalent Weight (EEW) was noticed from the product technical data sheet. As for the commercial epoxidized cardanol (NC514), the EEW was calculated by ^{1}H NMR, according to the more accurate structure described by Jaillet *et al.* [17].

In the same way, the functionality of the amine derivatives is expressed as the weight in grams of hardener containing one mole N—H group (g eq^{-1}). The Amine Hydrogen Equivalent Weight (AHEW) was calculated from the molecular weight of the hardener (M_{NH} in g eq^{-1}) and its functionality (f_{NH}), as follow:

$$AHEW = \frac{M_{NH}}{f_{NH}}$$

Various epoxide:amine ratios were investigated, in order to determine the reaction stoichiometry of each system as a function of the highest glass transition temperature. For a 0.8:1 epoxide:amine ratio, the mass of hardener was calculated as follow:

$$m_{Hardener} = \frac{m_{Epoxy} \times (1 \times AHEW)}{0.8 \times EEW}$$

In the general procedure used for preparation of epoxide:amine materials, epoxide and diamine derivatives were both introduced in a cryogenic mill. The reactants emerged in liquid nitrogen, were micronized for two minutes. Then, the thin mixture was placed in a mold and heated at 120 °C for 30 mins and then, in between 160 and 250 °C for 10 min, as a function of the cure temperature of each epoxide:amine couple. The formed material was cooled down at room temperature.

In emulsion, epoxide and dicyandiamide were put together in optimum ratio as previously determined in bulk. Optimum mixture was stirred in deionised water using an Ultra-Turrax T 25 digital. DMSO, as co-solvent, was slowly added up to the aqueous solution and was homogenized up to reach a stable dispersion or dissolution of the overall mixture. Then, the mixture was placed in a mold and heated at 120 °C for 1 h and then, in between 160 and 250 °C for 10 min, as a function of the cure temperature of each epoxy/amine couple.

2.3. Characterization of materials

Commercial products were characterized by NMR (^{1}H and ^{13}C), to confirm their structure and their functionality.

The thermal properties of thermoset materials were examined by thermogravimetric analysis (TGA) and by differential scanning calorimetry (DSC). Thermogravimetric analyses were performed by heating 10 mg of sample at a heating rate of 10 °C min^{-1} up to 800 °C under air or nitrogen, using Q50 from TA Instrument. The decomposition temperature ($T_{5\%}$) was noted at 5% of weight loss.

Differential scanning calorimetry measurements were carried out by heating 10–15 mg of sample sealed in aluminum pan, at a heating rate of 10 °C min^{-1} from −50 to 200 °C under N_2 flow, using Netzsch DSC200 calorimeter. Cell constant calibration was performed using indium, *n*-octadecane and *n*-octane standards. The glass transition temperatures (T_g) were observed from the second heating run.

The adhesion test was performed using a TQC Adhesion Test Kit CC1000. The glass plate was cleaned up using dishwashing liquid, rinsed in deionised water and then in ethanol. 0.5 g of formulation in bulk was deposed at room temperature by drop or spread-deposition on the cleaned glass plate. The formulation on the glass plate was cured as previously. Two series of cuts through the coating angled to each other was drawn to obtain a pattern of 25 similar squares. The detached coating was removed with an adhesive tape and the ruled area was evaluated by using a table chart ISO 2409.

The mechanical test was performed on 70 × 70 mm glass flat plates, which were previously cleaned up using dishwashing liquid, rinsed in deionised water and then in ethanol. The glass plates were heated at 580 °C, and then an indentation damage was carried out using a 4-sided pyramidal Vickers diamond. The formulation at 20% aqueous solution was deposed at room temperature by drop or spread-deposition within 24 h and cured as previously. The glass plates were placed on a mechanical ring bench and a weight was charged up to break, to determine the break strength. For each series of formulation, a series of five non-treated glass plates was used as reference and a series of ten treated glass plates was tested for an average value. The reinforcement was calculated as followed:

$$Reinforcement = \frac{\overline{F_m} - \overline{F_0}}{\overline{F_0}} \times 100$$

where $\overline{F_m}$ is the average force acting on the glass plate treated with an epoxide:DICY material in N, and $\overline{F_0}$ is the average force acting on the glass plate with no treatment in N.

Gel content measurements of the polymer network were carried out using THF as diffusing agent. The gel content was calculated from the differences between weights of initial networks and weights of dried networks after solvent immersion. For each material, 3 samples (written m_0^i and ranging from 20 to 30 mg) were separately dipped into the solvent (THF, 30 mL). After 24 h, the samples were removed from the solution and were dried into a vacuum oven at 40 °C during 2 days. Their resulting weights were written (m_2^i) and the insoluble fraction (IF_i) was calculated according to the equation below: