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Unconventional plasticization threshold for a biobased bisphenol-A epoxy substitution candidate displaying improved adhesion and water-resistance

Pierre Verge*, Valérie Toniazzo, David Ruch, João A.S. Bomfim

Centre de Recherche Public Henri Tudor, Advanced Materials & Structures, 5 Rue Bommel, Z.A.E. Robert Steichen, Kaërjeng-Hautcharage L-4940, Luxembourg

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ABSTRACT

Toxicity concerns over bisphenol A (BPA) based materials like polycarbonates or diglycidyl ether of bisphenol A (BADGE) lead to their progressive substitution in food packaging and can coating applications, even if the eventual release of BPA in food remains debatable. In this paper, we study the adhesive, water resistance and thermo-mechanical properties of a bio-based BADGE substitution candidate issued from Cardanol (CardDE). Different formulations with increasing ratio of BADGE substitution were evaluated, highlighting a real prospect for BPA-based epoxy substitution. During these studies, an unconventional relationship between water uptake by the biobased adhesive and property loss due to plasticization was evidenced. The water resistance of CardDE adhesives was investigated in detail revealing a plasticization threshold at elevated water content, attributed to their hydrophobic structure. While the adhesive properties of conventional BADGE networks are prematurely affected, the deterioration of CardDE adhesives is delayed.

1. Introduction

Bisphenol A [2,2-bis(4-hydroxyphenyl)propane or BPA] is an important industrial chemical that is primarily used as an intermediate in the production of polycarbonate (PC) plastics and epoxy resins (Staples et al., 1998). Products of BPA range from PC bottles to the inner coating of cans and from dental sealants to cell phone casings. Controversy surrounding BPA mainly involves its potential human health risk due to its estrogenic activities (Maffini et al., 2006; Tsai, 2006). As the release of BPA from coatings has been evidenced (Nam et al., 2010), a strong urgency appears to its substitution in sensitive applications by more eco and human friendly compounds. Renewable resources can provide an interesting sustainable platform to substitute, partially or totally, petroleum-based polymers through the design of bio-based polymers that can compete or even surpass the existing petroleum-based materials on a cost-performance basis with high eco-friendliness values (Raquez et al., 2010).

Literature review reveals several attempts to obtain bio-based epoxy resins from isosorbide (Chrysanthos et al., 2011; Łukaszczyk et al., 2011) or from vegetable oils. Many vegetable oils display high levels of unsaturated fatty acids that can be converted into epoxy fatty acids by conventional double-bond oxidation reactions. Nowadays, epoxydized vegetable oils are receiving a great deal of attention as they are obtained from sustainable and renewable natural resources and are environmentally friendly. Nevertheless, as these oils are obtained from food resources, or as their production would need farmlands otherwise dedicated to growing food resources and despite a potentially positive environmental balance, biosourced materials which can compete with food resources are deemed unethical raw materials (Pimentel et al., 2009). Clearly, truly sustainable, societally acceptable bio-sourced materials should rely on non-alimentary resources, focusing as much as possible on waste materials or by-products.

In this paper, we explore the potential of a derivative of cashew nutshell liquid (CNSL) as an alternative to BPA-derived epoxy. CNSL, which main constituent is Cardanol – an unsaturated *meta*-alkylphenol, is a by-product from the processing of cashew nutshells and thus does not compete with the production of food resources (Mele et al., 2010). Few works treat of the use of Cardanol-based products for the conception of thermosets, in spite of the non-allergenic, non-estrogenic and non-toxic properties of Cardanol and even it is considered for the development of anti-cancer drugs (Hemshekhar et al., 2012). In (Aggarwal et al., 2007), the anti-corrosive properties of a mono-epoxidized Cardanol chemical is

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* Corresponding author. Tel.: +352 42 5991 4943.
E-mail address: pierre.verge@tudor.lu (P. Verge).

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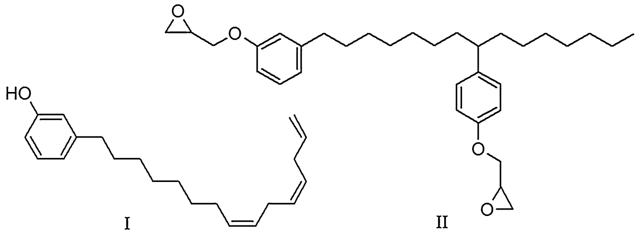

Scheme 1. Molecular structures of the tri-unsaturated component of cardanol (I) and of CardDE (II).

evaluated. The mono-functionality of the molecules limits its use as a grafted plasticizer. In (Huang et al., 2012), the authors report the synthesis of a Cardanol-based amine – as called phenalkamine – with good properties. Nevertheless, the use of phenalkamine is just an option to replace amines, but not diglycidyl ether of BPA. Finally, in (Maffezzoli et al., 2004), the authors report on the use of a Cardanol derivative-Stabilcardo – as a base compound for thermosets matrix. Nevertheless, the epoxidization relies on the treatment of the unsaturations of the alkyl chain, hindering the interest of such chemical structure (Raquez et al., 2010). Formaldehyde-cardanol resins are not discussed here due to the well-known toxicity of formaldehyde (Feron et al., 1991).

In this work we are testing a Cashew Nutshell Liquid based di-epoxy resin (CardDE, Scheme 1), a commercially available di-functional glycidyl ether which chemical structure is reported in Scheme 1, as a BADGE substituent. Its chemical structure affords a higher flexibility (due to C8 alkyl chain separating the aromatic groups) and water resistance (due to the C7 pending alkyl chain) than traditional BPA thermosets epoxy. Moreover, its hydrophobic character is a potential advantage for moisture- or water-exposed applications (such as packaging or outdoor uses) since anti-corrosive properties are strongly expected from this kind of coating (Aggarwal et al., 2007), preventing degradation of metallic outer layers or leaching of metallic ions.

First, we evaluated the thermochemical, adhesive and water resistance and properties of neat CardDE and BADGE/CardDE co-networks with different rate of BADGE substitution by CardDE, leading to the conclusion that CardDE has a strong potential when mixed with a small part of BADGE, and even alone for some specific applications. More particularly, the water resistance of the adhesive was investigated to shed more light on the water uptake mechanisms occurring in these systems and its consequences onto the properties of the adhesives.

2. Experimental

CardDE (commercial name NC514) was kindly supplied by Cardolite. CardDE is a di-functional glycidyl ether epoxy resin (EEW = 190 g/equiv.) with similar reactivity than traditional bisphenol A type resin. Diglycidyl ether of bisphenol A (BADGE, DER332, EEW = 175 g/equiv.) and 1,2-diaminocyclohexane (mixture of isomers) were purchased from Sigma–Aldrich and used as received.

2.1. Networks and composites preparation

For each composition, the equivalent epoxy weight EEW was calculated to determine the stoichiometric amount of hardener. Each epoxy mixture was heated and magnetically stirred at 80 °C under vacuum for 1 h. The hardener was then added and the solution incorporated into a high temperature silicone mold for curing at 160 °C for 2 h followed by a post-cure treatment at 190 °C for 2 h.

2.2. Pull-off tests

Pull-off tests (PoT) were performed as described in published standards (D4541-95e1) using a force-controlled, self-aligned DeFelsko AT-A adhesion tester at 0.2 MPa s^{-1} (Petersen et al., 2012). Adhesive "dolly-plate" bonded assemblies were prepared using standard 20 mm Al dollies. Aluminum plates were degreased with acetone, before applying the composition to test. Once the surface was dried, a droplet of the adhesive composition was applied and the dolly set down on it. Assemblies were cured at 160 °C for 2 h, and then post-cured at 190 °C for 2 h. Each composition was tested ten times.

2.3. Water resistance tests

The water resistance tests were adapted from "wet cataplasm" published ASTM standards. Al "dolly-plate" assemblies were wrapped in 10 g of dry cotton. 100 ml of deionized water were then added to the cotton layer and the wet assemblies were placed in a polyethylene pack and sealed. A thermal treatment of 24 h at 80 °C was performed before placing the sample at −20 °C during 4 h. The samples were let stand for 24 h before performing Pull-off Tests (PoT).

2.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry thermograms of composites were recorded by means of a Netzsch DSC 204 F1 Phoenix apparatus operating in inert atmosphere (nitrogen), and with a heating rate of 20 °C min^{-1}. The samples were weighted (5–10 mg) and placed into alumina crucibles and were subjected to the following heating step: from 30 to 250 °C.

2.5. Dynamic mechanical analysis (DMA)

DMA tests were performed on a dynamic mechanical analyzer Netzsch DMA 242C. For this study, 20 mm × 8 mm × 1 mm rectangular specimens cut using a precision cutting saw from molded specimens were used. They were subjected to sample cantilever mode of flexural loading with a maximum displacement of 40 μm in the temperature range −50 °C to 250 °C (rate 10 °C min^{-1}) and a frequency of 1 Hz.

2.6. Swelling tests

Samples of 1 cm × 1 cm × 1 mm approximately were cut from composites prepared as described previously. The surfaces were slightly polished to remove any over oxidation that occurs on the surface during the thermal treatment. The water uptakes were measured by weighting the samples at different time. A particular attention was paid to remove any solvent excess (i.e. water or toluene) at the surface of the samples.

3. Results and discussion

The thermo-mechanical properties of the networks were evaluated by means of dynamic mechanical analysis (Fig. 1). The E' values for all 5 samples at temperatures far from the T_g are within a 10% range.

As expected, the incorporation of CardDE in BADGE networks leads inevitably to the decrease of the T_g of the networks, as a result of the higher flexibility of the bio-diepoxy. However, even though the thermal resistance is reduced, the observed transition values for CardDE-containing materials are above room temperature, slightly so for neat CardDE (40 °C) but considerably more for the 70% bio-based formulation (90 °C).