



# Reinforcing anticorrosive properties of biobased organic coatings through chemical functionalization with amino and aromatic groups

João Henrique Lingner Moura\*, Melissa Heinen, Rita Cristina da Silva, Emilse M.A. Martini, Cesar L. Petzhold

Institute of Chemistry, UFRGS, Av. Bento Gonçalves, 9500, Porto Alegre 91501-970, P.O.Box 15003, Brazil

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## ABSTRACT

Novel biobased epoxy and polyurethane (PU) resins were formulated with epoxidized soybean oil (ESO) modified with benzylamine and applied as organic coatings on AISI 1020 steel carbon specimens. For comparison, biobased resins without the modified ESO were also prepared. The functionalization of the resins yielded more hydrophobic materials, with greater crosslinking and bearing amino and aromatic groups which can assist the adsorption of the resins to the metal. In the electrochemical impedance spectroscopy (EIS) analysis, the increase in resistance and decrease in capacitance of coatings with functionalized ESO demonstrate the enhanced barrier effect provided by this component.

## 1. Introduction

Corrosion has a significant impact on materials' durability, maintenance cost, and mechanical resistance in sectors such as industry and construction. In the last years, the global cost of corrosion was assessed to be around \$2.5 trillion (USD). It was estimated that use of appropriate corrosion prevention methods would decrease this value by 15%–35%, representing a saving of \$375–875 billion [1].

Polymer coatings are the most used method of corrosion control on metallic substrates [2]. Besides their high anticorrosive performance, these materials have lower toxicities and higher chemical stabilities than other coatings, such as metallic coatings (e.g., zinc- or chromium-based coatings) [3]. Epoxy and polyurethane (PU) coatings are two of the most representative types of organic coatings with a wide range of applications.

Epoxy resins stand out for their high resistance to weathering, chemical agents, and corrosion, in addition to general toughness and good adhesion [4]. The most common synthetic epoxy resin is based on the reaction between bisphenol-A (BPA) and epichlorohydrin (EPCH), both reagents derived from petrochemicals. The product of this reaction, known as diglycidyl ether of bisphenol A (DGEBA), represents around 90% of the worldwide production of epoxy resins [5]. However, recently BPA has been put under several restrictions due to its potential risks to human health [6]. Additionally, adoption of *green chemistry* practices and the search for more economical products has promoted the development of new formulations. To achieve a more sustainable

production process, some alternative synthetic routes utilize vegetable epoxidized oils for synthesis of polymers. These natural materials, obtained with low environmental impact, have great potential for replacing conventional reagents. Vernonia oil is an example of a naturally epoxidized oil used for preparation of resins, although its low availability is still a limiting factor for its wide spread use [5]. One commonly used alternative is insertion of epoxy rings between the double bonds of vegetable oils. Epoxidized soybean oil (ESO) and epoxidized linseed oil (ELO) are already produced at a large scale [6,7], due to the abundance and affordability of their precursor oils.

PU coatings are primarily employed for protective and decorative applications in which high quality is demanded, such as for aircraft and automotive painting [8]. These coatings are recognized for their esthetic characteristics, such as gloss, in addition to their effective anticorrosive properties. In general, PUs are prepared using isocyanates and polyhydroxyl compounds, known as polyols. Polyols are typically derived from petrochemicals. As for the epoxy resins, the increasing demand for materials from renewable sources has led to replacement of feedstocks derived from fossil fuels. Polyols based on vegetable oils have therefore received increasing attention for preparing of PUs [9,10]. A common method to obtain biobased polyols for the oleochemical industry is epoxidation of a vegetal oil followed by oxirane ring opening. The last step may be achieved using nucleophiles such as amines, alcohols, thiols, water, and others.

Beside environmental and economic issues, considerations about coating performance have motivated modification of these polymers'

\* Corresponding author.

E-mail addresses: [jhlingner@hotmail.com](mailto:jhlingner@hotmail.com), [joao.lingner@ufrgs.br](mailto:joao.lingner@ufrgs.br) (J.H. Lingner Moura).

formulations. One strategy is functionalization of the polymeric backbone with organic compounds to improve the anticorrosive resistance by increasing adhesion, the barrier effect and hydrophobicity of the coating [11]. Molecules containing nitrogen and phosphorous are typical examples of suitable corrosion inhibitors and can be useful for a coating's composition [12,13]. These compounds can bind to metal surface by chemisorption, enhancing interactions between the coating and substrate. Other modifications can be adjusted for specific applications. For example, for submerged material coatings in marine environment, inclusion of hydrophobic groups [14], such as aromatics, may be useful to prohibit attack by aggressive ions in solution.

We propose utilization of ESO modified with benzylamine as a biobased alternative to petrochemicals reagents for resin formulation. The product contains epoxy rings and hydroxyl groups, which allows preparation of epoxy and PUs, respectively. Additionally, the anticorrosive properties of resins with amino and aromatic groups derived from benzylamine are investigated. For comparison, resins were also prepared without the modified oil.

## 2. Experimental

### 2.1. Materials

Biobased Epoxy/Polyol (BEP) was prepared from epoxidized soybean oil (Agnique Eso 81-B) ( $M = 944 \text{ g/mol}$ ) from Trill Química Ltda., benzylamine was purchased from Synth Ltda. and zinc chloride ( $\text{ZnCl}_2$ ) P.A from Vetec Química Fina Ltda. For the purification process was used dichloromethane P.A. (Vetec), magnesium sulfate anhydrous P.A. (Nuclear), sodium chloride from Dinâmica Química Contemporânea Ltda. and deionized water. For the  $^1\text{H-NMR}$  analysis deuterated chloroform ( $\text{CDCl}_3$ , 99.8%, Aldrich) were utilized.

In the epoxy resins preparation were used maleic anhydride and triethylamine,  $\geq 99.5\%$  provided by Sigma Aldrich and ESO (Agnique Eso 81-B), and for preparation of PUs toluene diisocyanate provided by Betannin Industrial S/A, crude castor oil Resinol 160/10 from Azevedo Óleos, dibutyltin dilaurate (DBTDL) provided by Killing S.A. and tetrahydrofuran (THF) from Synth.

### 2.2. Synthesis of the Biobased Epoxy/Polyol (BEP)

A molar ratio of 2:1 (amino groups:epoxy ring) was employed for synthesis of biobased epoxy/polyol (BEP). 40 g of epoxidized soybean oil (containing 3.64 epoxy rings per molecule), 17 g of benzylamine, and 2.7 g of  $\text{ZnCl}_2$  were added to a round-bottom flask. The system was previously purged with argon and the reaction was conducted at  $100^\circ\text{C}$  with magnetic stirring at 400 rpm for 10 h. After that, the reaction mixture was cooled to room temperature and dissolved in 150 mL of chloroform. The mixture was purified with deionized water and saturated NaCl solution. The product was dried with  $\text{MgSO}_4$  anhydrous and filtered. Finally, the solvent was removed using a rotatory evaporator.

### 2.3. Preparation of epoxy resins

Epoxy resins were prepared using a 1:1 M ratio of epoxy:anhydride. For the epoxy resin prepared with biobased epoxy/polyol, Ep-BEP, 0.17 g of maleic anhydride (M.A.) was used per gram of BEP, and 0.37 g of M.A. was used per gram of ESO for Ep-ESO preparation. Triethylamine (TEA) was used as a catalyst at a molar proportion of around 4%. After dissolution at  $60^\circ\text{C}$ , curing was completed in an oven at  $150^\circ\text{C}$  for 14 h.

### 2.4. Preparation of the polyurethanes

PUs were prepared by reaction of toluene diisocyanate, TDI, with the polyols, using an equimolar proportion of hydroxyl and isocyanate groups. The sets were prepared with different polyol components: one

**Table 1**  
AISI 1020 steel composition (balance in iron).

	C	Mn	P	S	Si	Cu	Ni	Cr
%	0.0830	0.2130	0.0160	0.0130	0.0120	0.0120	0.0050	0.0180
	Mo	Sn	Al	N	Nb	V	Ti	B
%	0.0030	0.0050	0.0410	0.0038	0.0030	0.0010	0.0110	0.0035

group with the biobased epoxy/polyol (PU-BEP) and another with castor oil (PU-CO). The polyol component was first dissolved in THF in a Falcon tube with magnetic stirring at room temperature. After dissolution 0.05 g of dibutyltin laurate was added. Finally the system was mixed with the calculated amount of TDI. To set the stoichiometric proportions in the reactions, hydroxyl content of BEP (210.95 mg KOH/g) and of castor oil (162 mg KOH/g) were accounted for. Both determined were by titulometric measurements according to the AOCS Official Method Tx 1<sup>a</sup>-66 and the AOCS Official Method Cd 3<sup>a</sup>-63. Thus, 0.32 g of TDI was added for each gram of polyol in the PU-BEP and 0.25 g of TDI/g of polyol in the PU-CO. Specimens were cured for 24 h in a desiccator.

### 2.5. Preparing of the specimens

Resins were used to cover AISI 1020 metal plates with a length of 3.75 cm, a width of 1.27 cm, and a thickness of 0.147 cm. Specimens had 0.5 cm diameter holes where cooper wires were attached for electric contact. The metal/iron interface was isolated with commercial epoxy resin (Durepóxi) to prevent interference in tests. The plates were sanded, polished, and kept in a desiccator before use. Table 1 summarizes the composition of AISI 1020 plates.

### 2.6. Characterization

The epoxy content of ESO and BEP was determined by  $^1\text{H-NMR}$  analysis, performed with a Varian INOVA - 300 MHz. Samples were dissolved in deuterated chloroform ( $\text{CDCl}_3$ ).

FTIR analysis was performed with a Bruker Alpha-E spectrometer with a diamond accessory in the ATR module (attenuated total reflectance), over a spectral range of  $4000$  to  $600 \text{ cm}^{-1}$ , with a total number of 32 scans and a resolution of  $4 \text{ cm}^{-1}$ .

The hydroxyl number is the weight, in milligrams, of KOH needed to neutralize all the hydroxyls presents in 1 g of sample. This test was done according to the AOCS Official Method Tx 1<sup>a</sup>-66. The acidity index was determined by an acid-base titration, based on the AOCS Official Method Cd 3<sup>a</sup>-63. The acidity index is defined as the weight, in milligrams, of KOH used to neutralize the free fatty acids in 1 g of sample. Both tests were conducted in triplicate.

Water contact angle was measured to evaluate the superficial wettability of the resins. The sessile drop method was used. It consists in the application, with a microsyringe, of 1 mL of deionized water over the sample surface. At the same time a cam coupled to the Kruss DAS 30 collects an image that is digitalized by the Drop Shape Analysis System software. Water contact angle is measured by SurfTens 4.5 software. Tests were conducted in triplicate. The angle obtained is an average of the right and left angles of the image formed by the drop placed on the sample.

The dynamic mechanical properties of the resins were analyzed using DMA equipment, TA Instruments Q800. The PU and epoxy specimens were cured under the same conditions used for coatings, using rectangular silicon molds with approximate dimensions of  $17 \times 14 \times 3.5 \text{ mm}$ . The tests were carried out at a fixed frequency of 1 Hz and the temperature was ramped from  $-50$  to  $150^\circ\text{C}$  for the epoxies and  $-100$  to  $90^\circ\text{C}$  for the PUs.

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