



Short communication

Sustainable synthesis of epoxidized waste cooking oil and its application as a plasticizer for polyvinyl chloride films

Andreia H. Suzuki^a, Bruno G. Botelho^b, Leandro S. Oliveira^c, Adriana S. Franca^{c,*}^a PPGCA, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, 31270-901 Belo Horizonte, MG, Brazil^b DQ, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, 31270-901 Belo Horizonte, MG, Brazil^c DEMEC, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, 31270-901 Belo Horizonte, MG, Brazil

ARTICLE INFO

Keywords:

Epoxidation
PVC
Citric acid
Environmentally friendly
Waste cooking oil

ABSTRACT

For the past decade, environmentally friendly features have been one of the most desired characteristics of most of the arising technologies. The search for materials from renewable sources and the development of novel non-hazardous processes for their production is currently of the utmost relevance. However, significant improvements on the current technologies towards greener less energy-demanding processes are as important as the search for new ones, and sometimes improvements are more easily achievable and more readily applicable. In this work, the feasibility of using waste cooking oil as a feedstock for the production of epoxidized vegetable oil resins in a process devoid of catalyst has been demonstrated. The epoxidation process was carried out using citric acid as the only acidic component, generating no solid residues and a liquid residue less toxic than the one from the conventional processes. The produced epoxidized waste vegetable oil was successfully applied as a primary plasticizer in poly(vinyl chloride) (PVC) films. The produced films showed mechanical and thermal properties matching those of commercial stretch PVC films.

1. Introduction

Poly (vinyl chloride) (PVC) is amongst the most widely produced and consumed thermoplastics worldwide [1] since it is versatile, durable, contamination resistant and of low cost [2]. However, due to its inherent rigidity, brittleness and low thermal stability, PVC is usually compounded with plasticizers and heat stabilizers to adequate its mechanical, workability and thermal stability properties for use in soft products such as blood bags, films, flexible children's toys, medical devices and food packaging [1,3].

Phthalate-based additives are still the most commonly used plasticizers for PVC due to their low cost and excellent overall properties [3]. However, the use of these types of plasticizers is being seriously challenged for food, medical and toys applications because low-molecular mass phthalate-based plasticizers can easily migrate from the polymer matrix to the surrounding media, potentially causing toxic effects on human health and environmental hazards (phthalates are rather difficult to degrade in natural environments) [2,4]. Thus, non-hazardous, non-toxic plasticizers with minimum migration ability are currently being researched worldwide, with the most common being those derived from vegetable oils, e.g., epoxidized triglycerides from soybean, linseed, sunflower and rubber seeds [2], and epoxidized cardanol [5].

Epoxidized edible vegetable oils are one of the most currently studied PVC plasticizer candidates for they are derived from renewable sources, thus being readily available and biodegradable, and furthermore because, as an additive to PVC, they act as both plasticizer and heat stabilizer [1]. However, the commonly unreacted double bonds in epoxidized vegetable oils reduce compatibility between PVC and the plasticizer, causing its migration from the PVC matrix to the surrounding medium, and thus epoxidized oils are commonly applied either as a secondary plasticizer or combined with other additives [4]. Hence, high conversion of the double bonds into oxirane rings (i.e., epoxy groups) is a desirable trait in the production of high quality epoxidized oil-based plasticizers.

Another major drawback associated to the use of bio-plasticizers derived from edible oils, concurrently with their use as raw material for biofuel production, is the contribution to the withdrawal of resources from the food and feed chain, which can negatively affect the price of edible oils in the international market [5,7]. About 80% of the vegetable oils produced worldwide are destined to human consumption [6]. Alternative sources of triglycerides that are currently being considered for use as precursor material for the production of plasticizers and biofuels are the waste cooking oils (WCO), which are generated in significant amounts worldwide and present the potential to meet the

* Corresponding author.

E-mail address: adriana@demec.ufmg.br (A.S. Franca).

needs for low-cost renewable materials and also do not contribute to the subtraction of edible oils from the food chain [7]. Furthermore, the profitable exploitation of WCO also addresses the problem associated to the inadequate disposal of these wastes that currently represent hazards to the environment and constitute a major problem to the waste treatment facilities. In addition, waste cooking oil collection can constitute an additional source of income for the population with lower professional qualifications in developing countries [8].

Regardless of the oil sources, there are a few synthetic routes that can be used to epoxidize vegetable oils and all the known procedures require the employment of a catalyst, usually a strong acid (sulfuric, phosphoric, etc.) or an ion exchange resin to form a peracid *in situ*, which in turn is responsible for the generation of oxirane rings (epoxidation) from the double bonds present in oils triacylglycerols [9]. The most commonly employed organic acids for the formation of the peracid to be used in epoxidation reactions are either acetic or formic acid. The mechanism for the formation of the peracid consists on the hydrogen proton from a dissociated acid catalyst acting as an activator of the carbonyl carbon in the organic acid (acetic or formic acid) with the subsequent addition of the hydrogen peroxide and concomitant loss of a water molecule [10]. In the subsequent epoxidation reaction, the peroxy group (–COOOH) acts as an oxygen carrier for the formation of the oxirane ring in the unsaturated fatty acid esterified to the glycerol backbone. Even in the absence of an acidic catalyst the formation of the peracid can still occur since the organic acid can dissociate a hydrogen ion, which can further promote the reaction [11]. With that in mind, citric acid, a tricarboxylic acid, with three distinct dissociation constants was herein considered as a potential candidate for the formation of the peracid without the use of an acidic catalyst, since it can act as both a hydrogen proton generator, by independent dissociation of one of its carboxylic groups, and an oxygen carrier, by the formation of a peracid preferentially in its central carboxylic group [12]. Hence, in this work, we developed a new environmentally friendly synthetic route for the production of epoxidized waste cooking oil using citric acid as both oxygen carrier and catalyst and we have demonstrated the potential of the prepared epoxidized oil as a primary plasticizer for PVC films with no need for further additives.

2. Materials and methods

2.1. Materials

The reagents employed in this study were: waste cooking soybean oil, donated by the cafeteria located in the Engineering College at Universidade Federal de Minas Gerais, Brazil, and used with no further treatment; anhydrous citric acid PA/ACS, hydrogen peroxide 50%, Wijs solution, chloroform, soluble starch, pentahydrate sodium thiosulfate, potassium iodide, potassium iodate, hydrochloric acid 35%, glacial acetic acid, tetrahydrofuran (THF) P.A./ACS and methyl violet, all acquired from Synth, Brazil; hydrobromic acid 48% and diethyl ether acquired from Vetec, Brazil; and PVC resin SP 1300, with K value of 71 ± 1 , provided by Braskem, Brazil.

2.2. Epoxidation procedure

The epoxidation procedure was carried out in a jacketed glass reactor, coupled to a thermostatic water bath (Nova Ética, Brazil), and a three-bladed mechanical stirrer (Fisatom, Brazil). Fifty grams of WCO were placed in the reactor and stirred until the desired temperature was reached. Subsequently, a solution of citric acid and hydrogen peroxide was added. The mixture was kept at a controlled temperature until the established reaction time was reached, point at which distilled water at room temperature was mixed with the epoxidized soybean oil (ESO), in order to decrease the temperature and stop the ongoing reactions. The remaining polar compounds were extracted from the ESO with lukewarm distilled water, in a separation funnel, until the extraction residue

Table 1
Selected independent parameters for the epoxidation optimization procedure.

Temperature (°C)	Time (h)	Citric acid/unsaturation ratio ^a
80	3.0	1.0
80	4.0	0.5
80	4.0	1.5
80	5.0	1.0
75	3.0	0.5
75	3.0	1.5
75	4.0	1.0
75	4.0	1.0
75	4.0	1.0
75	5.0	0.5
75	5.0	1.5
70	3.0	1.0
70	4.0	0.5
70	4.0	1.5
70	5.0	1.0

^a Molar ratio of citric acid and WCO unsaturation.

reached a neutral pH. Diethyl ether was used to eliminate water traces, and was later removed from the ESO by a rotary evaporator. The ESO was left for 12 h, at 50 °C in an incubator, for the complete elimination of remaining solvent.

2.3. Optimization of the epoxidation route

Optimization of the epoxidation process was carried out in two steps. The first step was performed according to a Box-Behnken statistical procedure employing the Minitab 17 software [13]. The influence of the following parameters was tested: reaction temperature (70–80 °C), reaction time (3–5 h), and molar ratio of citric acid to WCO unsaturation (0.5–1.5). The amount of hydrogen peroxide used was the minimum necessary to dissolve the acid.

The three-level factor Box-Behnken design was used in this work, with a second-order response surface and repetitions of the center point, totaling N = 15 experiments [13]. The combination of the selected independent parameters is presented in Table 1.

The second step of the optimization procedure was performed using a central composite design, since only reaction time and reagents molar ratio were used.

The maximum theoretical percentage of oxirane oxygen (OO_{max}) obtained from the WCO was calculated by

$$OO_{max} = \left(\frac{\frac{I_i}{2A_i}}{100 + \frac{I_i}{2A_i}} \right) \times A_o \times 100 \quad (1)$$

where I_i is the iodine value of the WCO, A_i is the iodine atomic number and A_o is the oxygen atomic number. The relative percentage conversion of oxirane oxygen (RC) was calculated by

$$RC = 100 \times \left(\frac{OO}{OO_{max}} \right) \quad (2)$$

where OO is the experimentally determined oxirane oxygen content of the epoxidized sample. The following equation was used to calculate the double bond conversion (DBC) into oxirane ring:

$$DBC = 100 \times \left(\frac{I_{ios} - I_i}{I_{ios}} \right) \quad (3)$$

where I_{ios} is the initial iodine value of the WCO, and I_i is the iodine value of the epoxidized sample. The selectivity calculation used for each experimental procedure was described in a previous work [14] and is given by

$$Sel = 100 \times \left(\frac{RC}{DBC} \right) \quad (4)$$

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