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Biopolyester from ricinoleic acid: Synthesis, characterization and its use as biopolymeric matrix for magnetic nanocomposites

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ABSTRACT

This work presents a study on the production of ricinoleic acid-based biopolyester derived from castor (*Ricinus communis*) oil with and without in situ insertion of magnetic Fe_3O_4 nanoparticles with their surface modified by ricinoleic acid. Self-catalyzed reactions, due to H^+ from ricinoleic acid, which behaves as a Brønsted–Lowry acid, were performed in a batch bulk polymerization process and some kinetic studies were carried out. It was also observed that the magnetic Fe_3O_4 nanoparticles act as Lewis acid catalysts during the polymerization. The ester formations were followed by acid value and FTIR spectra and it was observed that the reactions without magnetic nanoparticles (only Bronsted self-catalyzed reaction) reached a steady-state after 14 h of reaction. For the reactions with surface-modified magnetic Fe_3O_4 nanoparticles the steady-state rate was reached in 6 h of reaction. In the absence of the magnetic nanoparticles, it was observed at 190 °C that the consumption of the ricinoleic acid follows a second-order behavior and increasing 20 °C the reaction rate was 15% faster. The polymeric materials have been characterized in order to provide information on their structural and thermal features. It was verified that the thermal stability of the product is significantly increased with the reaction conversion. Magnetic measurements were and have shown that the material exhibited a superparamagnetic behavior when using magnetic Fe_3O_4 nanoparticles.

1. Introduction

The synthesis of polymeric materials derived from renewable resource has been intensely studied (Yeganeh and Mehdizadeh, 2004; Krasko et al., 2003; Kundu and Sharma, 2006; Suarez et al., 2007; Meier et al., 2007; Suppes et al., 2008; Larock and Yongshang, 2009). Depending on the nature of the monomeric specie derived from renewable resources it is possible to achieve polymeric materials with physical chemical properties similar to those usually observed in polymer materials obtained from petrochemicals. In addition, some biopolymeric material can also present biodegradability feature and can be tailored in order to be used for controlled drug delivery applications (Okada, 2002; Kundu and Sharma, 2008; Domb and Slivniak, 2005a).

Castor seed oil (CSO), rich in triacylglicerides of ricinoleic acid (RA) (approximately 90% in the fatty acid composition), has been extensively used as renewable resource in the production of polyurethane and polyesters (Ogunniyi, 2006; Yeganeh and Talemi, 2007; Domb and Papkov, 2008). It is also described in the literature the use of CSO as additive in blends and composites in order to improve the final properties of polymers (Patel et al., 2006; Kumar et al., 2007). Due to their renewability and remarkable physical–chemical properties these materials have been pointed out as potential candidates for several applications, like biomedical implants, tissue engineering, controlled drug delivery and coatings, and adhesives applications (Trumbo and Trevino, 2002; Somani et al., 2003).

Pure RA has been also utilized as raw material to produce aliphatic polyesters and lactones. This fatty acid presents specific characteristics, intrinsically related with its chemical structure that involves two reactive functional groups (hydroxyl, carboxyl) and a double bond, which allows through step-growth polymerization mechanism the formation of several polymeric materials (Domb and Slivniak, 2005b). Due to the presence of an alcohol and a carboxylic acid group pure RA molecules react to produce esters and/or polyesters, which can be self-catalyzed because of its

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Bronsted acidity. The main advantage of this renewable resource as monomeric specie is related to the fact that the reaction occur in the absence of volatile organic compounds (VOC) (Dutta et al., 2007).

The use of dispersions of magnetic iron oxide nanoparticles with their surface modified by organic molecules or polymers in polymer matrixes (nanocomposites) have recently emerged in several fields, such as for environmental recovering (Queiros et al., 2006), biomedical applications like magnetic drug targeting, hyperthermia during cancer treatment, enzyme immobilization and magnetic resonance imaging (Pankhurst et al., 2003), as well as for a bottom-up approach to build nanodevices as in high density storage systems. Recently, some research showing the potential use of polyurethane based in castor oil as matrix in magnetic nanocomposites have appeared, special for application in environmental area. For instance, magnetic nanocomposites were prepared curing with toluene-diisocyanate a polyester resin obtained from castor oil and Maleic anhydride in the presence non-modified maghemite nanoparticles (Junior et al., 2010). This magnetic nanocomposite has been used to cleaning of oil spills in water (Junior et al., 2010), which was possible due to the affinity between the oil and the polymer, leading to the formation of low density mixture, with magnetic properties, easily removed from the environment. However, this materials still uses the highly toxic diisocyanate petroleum based monomers, which is controversial from an environmental point of view or if for medical use purposes.

As far as our knowledge, no attempt was done in order to produce magnetic nanocomposites using only bio-based raw materials. Here we report, a work focused on the synthesis of RA-based biopolyester obtained through step-growth polymerization carried out in batch reactions and developing new routes to prepare in situ nanocomposites from castor seed oil and magnetic iron oxide nanoparticles. Thus, the polymeric matrix is formed only by the polyesterification of castor oil fatty acids, which has a carboxylic and a hydroxyl group in its molecule. The magnetic nanoparticles surface has been previously modified also with castor oil fatty acids in order to have hydroxyl groups able to be chemically bonded into the polyester matrix.

2. Materials and methods

2.1. Materials

Technical CSO with an iodine index of 86 g $I_2 \cdot 100\,g^{-1}$, density of 0.95 g cm^{-3} and saponification index of 182 mg KOH g^{-1} was purchased from Campestre (São Paulo, Brazil); hydrochloric acid (37%), potassium hydroxide (85%), sodium hydroxide (99%), $FeCl_3 \cdot 6H_2O$ (97%) and $FeSO_4 \cdot 7H_2O$ (99%) were purchased from VETEC (Rio de Janeiro, Brazil); chloroform (99.8%) was purchased from Synth (São Paulo, Brazil); nitrogen gas (99.5%) was provided by White Martins (Rio de Janeiro, Brazil). All these materials were used as received, without further purification.

2.2. Synthesis of ricinoleic acid

RA was prepared from castor oil by saponification followed by acidification. A total of 932 g of castor oil and 600 mL of potassium hydroxide aqueous solution (3 M) were heated to 100 °C and kept stirring at this temperature for 5 h. Then, hydrochloric acid solution (2 M) was added and the mixture was kept for 30 min under mechanical stirring at 70 °C, when was obtained a two phases mixture (aqueous phase and organic phase rich in RA and others fat acids in minor amount), which was separated by decantation. The organic phase was washed three times with heated distilled water (50 °C) to remove inorganic impure and glycerol. Finally, the organic phase was purified by dissolving the fatty acids in chloroform, kept standing over magnesium sulfate, filtering in celite and evaporating the solvent in a rotaevaporator.

2.3. Synthesis of magnetic nanoparticles

Magnetite (Fe_3O_4) nanoparticles were prepared by chemical coprecipitation of aqueous Fe^{2+} and Fe^{3+} salts solution and NaOH solution (Tourinho et al., 1989). Initially, 6.1 g of $FeCl_3 \cdot 6H_2O$ and 3.1 g of $FeSO_4 \cdot 7H_2O$ were dissolved in distilled water (125 mL) and hydrochloric acid (5 mL) and kept at 60 °C with bubbling nitrogen gas. Separately, NaOH (37.5 g) was dissolved in distilled water (625 mL). The base solution was added into the iron salts solution and kept under nitrogen atmosphere and vigorous stirring at 60 °C for 30 min. The resulting black magnetic nanoparticles were isolated by magnetic decantation and washed with distilled water until neutral pH.

2.4. Surface modification of nanoparticles

Magnetite nanoparticles (40 g) were mixed with distilled water (1 L) and mechanically stirred. Thus, the suspension was acidified with hydrochloric acid (1 M) until pH 5 was achieved. Thus, the mixture was heated to keep the temperature at 85 °C and the ricinoleic acid, RA, (50 mL) was slowly dropped. Finally, the mechanical stirring was stopped and the modified nanoparticles decanted. The aqueous solution was removed and the nanoparticles were washed three times with distilled water.

2.5. Synthesis of polymer

Batch polymerizations were carried out in a 1-L reactor system consisting in a five-necked round-bottom flask equipped with a mechanical stirred, a Pt100 thermocouple, nitrogen (used to keep the reaction environment free of oxygen) inlet tube and an adjacent Dean-Stark partial/condenser (used to remove water and volatiles). The reaction vessel was heated to the desired temperature with an electrical heating mantle, connected to an automatic temperature controller, in order to control the reaction medium temperature. The monomer RA (or a dispersion of surface-modified magnetic nanoparticles in the RA) was added into the reaction vessel and the mechanical stirring was adjusted to 500 rpm.

2.6. Characterization of materials

IR spectroscopy analyses of the RA monomer and polymer samples were performed on ATR cell on a Shimadzu IR spectrophotometer (IR Prestige-21 System FT-IR). Thermal analyses were performed on a Shimadzu DSC-60 differential scanning calorimeter, calibrated with Zn and In standards, at a different heating rate (1, 5, 10 and 20 °C min^{-1}) under a nitrogen atmosphere (50 mL min^{-1} flowing rate). Thermal stability of the materials was evaluated on a Thermogravimetric Analyzer Shimadzu DTG-60 instrument, under nitrogen atmosphere (50 mL min^{-1} flowing rate), from room temperature to 600 °C, using heating rates of 10 °C min^{-1}.

^1H NMR spectra were recorded on a Varian Mercury Plus M300 MHz spectrometer (Varian Instruments, Palo Alto, California, USA) using TMS as internal standard. Samples were previously dissolved in $CDCl_3$.

Viscosity was analyzed by bubble viscosimeter NYK-Gardner following AOCS (Ka 6-63), ASTM (D1131, D1545 and D 1725) and FTMS 141ª4272 standard methods.

Acid value was determinate by acid–base titration of samples previously dissolved in DMF using ASTM D465-9 standard method.