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Synthesis of soybean oil-based polymer lattices via emulsion polymerization process

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ABSTRACT

This work presents experimental results on the synthesis of soybean oil-based polymers through emulsion polymerization process. It was shown that polymeric materials can be successfully synthesized with high monomers conversion close to 100% and very high stability, displaying relatively high shelf-life time. Polymeric nanoparticles showing narrow particle size distribution, with average diameter around 80 nm (PdI = 0.213), determined via dynamic light scattering measurements were obtained. It was also observed by calorimetric analysis, that the final polymeric material presents two exothermic transitions and two glass transition temperatures. This complex thermal behavior probably takes place due to the nature of the monomeric mixture (AFFAM—acrylated linolenic, linoleic, and oleic acids in combination with methyl methacrylate), indicating that the final polymer presents a complex macromolecular arrangement. The glass transition temperature of the polymer lattices was reduced because of the AFFAM incorporation into the growing polymer chains, and additionally the thermal stability was improved. Regarding the average molar masses, it was observed that AFFAM comonomer plays an important role, leading to a decreasing in the mass-average molar mass when the AFFAM concentration is increased in the reaction medium. Depending on the AFFAM amount, the mass-average molar masses were found within the range from 70,000 g mol^{-1} to 890,000 g mol^{-1} with molar-mass dispersity lying in the interval from 1.7 to 2.4.

1. Introduction

Polymers derived from vegetable oils are very versatile materials employed in important technological applications. Several polymeric materials of industrial interest are obtained from vegetable oils, such as, polyethers, polyesters, polyurethanes, polyamides, epoxy resins, paints, adhesives, and alkyd resins. Vegetable oils containing unsaturated fatty acids are very important renewable feedstock for the polymer industry, due to the huge potential for changes in their chemical structure and low cost. In this scenario, modified fatty acids derived from soybean oil deserve special attention. In addition, the use of soybean oil contributes to the reduction of the dependence on raw materials derived from non-renewable fossil resources, leading to the development of new classes of polymeric materials.

Although soybean oil is used for the production of biodiesel, undesirable physical and chemical features, such as low oxidation stability, may limit the scope of application of the biodiesel from soybean oil. On the other hand, polymeric materials derived from modified soybean oils (e.g., fatty acids and esters) can exhibit excellent structural properties, which are essential to both the processability and the flexibility of formulation in medical and technological applications, being employed for the synthesis of dyes, coating, pressure-sensitive adhesives resins, thermoplastics, thermosets, and composites, and additionally also finding applications in aerospace, automotive, marine, military, and sportive fields (Gooch, 2001; Wool and Sun, 2005).

It is well known that of different polymeric materials can be obtained from vegetable oils (in natura and/or modified). A quick literature survey reveals that several kind of combinations are possible, resulting in polymers exhibiting distinct final properties (Andjelkovic et al., 2005; Badrinarayanan et al., 2009; Bunker and Wool, 2002; David et al., 2009; de Espinosa et al., 2009; Del Rio et al., 2010a,b; Hoogenboom et al., 2006; Jensen et al., 2014; Li et al., 2001, 2000; Li and Larock, 2000a,b, 2001; Lligadas et al., 2006; Lu et al., 2005; Lu and Larock, 2009; Luo et al., 2011; Oprea, 2010; Öztürk and Küsefoğlu, 2010; Şen and Çaylı, 2010; Sharma et al., 2008; Sionkowska, 2011; Stemmelen et al., 2011; Zuo et al., 2011).

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For example, Andjelkovic et al. (2005) have synthesized innumerous thermoset polymers through cationic reactions of vegetable oils (such as, olive, walnut, peanut, sesame, canola, grapeseed, sunflower, safflower, corn, soybean, and linseed) with divinylbenzene or styrene/divinylbenzene. According to the authors, the synthesis of tailored polymeric materials intended for specific applications is favored by the proper selection of the vegetable oil based on its reactivity.

Bunker and Wool (2002) have showed that adhesives can be successfully obtained from acrylated methyl oleate free-radical reactions carried out in emulsion polymerization process. It has been showed that polymeric materials presenting high average molar masses can be produced in reactions with both the high latex solids content and the elevated conversion. David et al. (2009) have employed acrylated epoxydised triglyceride resin in combination with butyl methacrylate for the synthesis of biodegradable pressure sensitive adhesive. Copolymers obtained via free radical polymerizations presented good shear holding time, peel strength and microbial biodegradability.

Luo et al. (2011) have prepared thermosetting biopolymers based on allyl alcohol ring-opened epoxidized soybean oil and maleic anhydride through free radical polymerization and esterification reactions. It has been demonstrated that thermosetting resins exhibiting high gel content with low swelling ration in toluene can be successfully produced and that the content of maleic anhydride can be properly varied in order to control the glass transition temperature.

Şen and Çayli (2010) have synthesized bio-based polymeric nanocomposites based on acrylated epoxidized soybean oil, styrene, and organophilic montmorillonite clay through in situ free radical copolymerization reactions. According to the authors, polymeric nanocomposites with different fractions of the modified organoclay can be prepared with improved thermal stabilities and dynamic mechanical properties.

More recently, Jensen et al. (2014) have developed copolymers based on styrene and acrylated methyl oleate by using an emulsion polymerization process. According to the experimental results, reactions exhibiting high monomers conversions close to 100% can be successfully carried out, exhibiting very stable polymeric lattices and high average molar masses. Additionally, it has been illustrated that glass transition temperature of copolymers was significantly affected by the acrylated methyl oleate concentration into the copolymers chains.

Production of polymeric materials from modified soybean oil through emulsion polymerization process presents as main advantage, the fact that it can be carried out free of organic solvent, potentially harmful to the environment (Gooch, 2001). Additionally, due to the inherent features of classical emulsion processes, raw-materials derived from soybean oil can be successfully be polymerized at high ratios in emulsion polymerizations with easy removal of the heat of reaction and temperature control, leading to formation of attractive and economically feasible polymeric materials (Jensen et al., 2014).

There is a growing interest in the use of new polymeric materials from renewable sources to replace petroleum-based polymers. It is highly desired to produce polymeric lattices presenting proper morphological features and storage stability. The combination of modified unsaturated fatty acids (and its derivatives) with several vinylic monomers (such as styrene, vinyl acetate, ethyl acrylate, vinyl pivalate, butyl acrylate, and among others) to synthesize polymer materials in heterogeneous processes, such as emulsion polymerization, is very promising. In addition, the copolymerization reactions can be properly performed with operating conditions similar to those practiced in industrial processes, exhibiting high reaction rate and monomer conversion.

Methyl methacrylate is regarded as a very attractive monomer employed to the synthesis of a very important class of polymeric commodity, poly(methyl methacrylate)—PMMA. In spite of its importance, PMMA homopolymers commonly behave as a brittle material. In the particular case of the experimental studies performed in this work, soybean oil-based modified fatty acids are used as comonomer in order to overcome the undesirable feature of PMMA homopolymer.

The main objective of this work was the development of a new class of polymeric materials obtained from the copolymerization of soybean oil-based modified fatty acids and methyl methacrylate.

2. Materials and methods

2.1. Materials

Vinyl monomer methyl methacrylate with purity of 99% and hydroquinone with purity of 99%, employed to avoid polymerization of acrylic acid during acrylation step, were supplied by Merck (Rio de Janeiro, Brazil). A commercial grade of soybean oil was used as precursor of modified fatty acids (epoxidized and acrylated). Distilled water was used as the reaction medium. The reagents sodium hydroxide with purity of 99%, hydrochloric acid (HCl, 36.5–38.0% w/w), formic acid with 88% purity, hydrogen peroxide 30 wt%, acrylic acid with purity of 99%, anhydrous sodium sulfate with purity of 99%, potassium persulfate with purity of 99%, and dichloromethane with 99.5% purity were supplied by Vetec Química Fina Ltda. (Rio de Janeiro, Brazil). Diethyl ether was provided by Ecibra Analytical Reagents (Curitiba, Brazil) with 99% purity. Sodium dodecyl sulfate was supplied by Reagen (Curitiba, Brazil) with 90% of purity. Sodium bicarbonate was supplied by J.T. Baker (Deventer, The Netherlands) with purity of 99.6%. All chemicals were used as received without further purification.

2.2. Modification of soybean oil

The first stage for the synthesis of soybean oil-based monomers corresponds to the production of a mixture of free fatty acids (rich in unsaturated, such as oleic, linoleic, and linolenic acids) through saponification reaction followed by acidification step (see Fig. 1). The reaction of soybean oil with sodium hydroxide was carried out with 200 g of soybean oil and an aqueous solution containing 160 g sodium hydroxide under vigorous stirring at 70 °C for 7 h. The final material was washed with distilled water, and then acidified with 300 mL of concentrated hydrochloric acid at 70 °C for 4 h. At the end of the process, the free fatty acid rich phase was washed with distilled water, followed by treatment with dichloromethane, which was subsequently removed with the aid of a rotary evaporator.

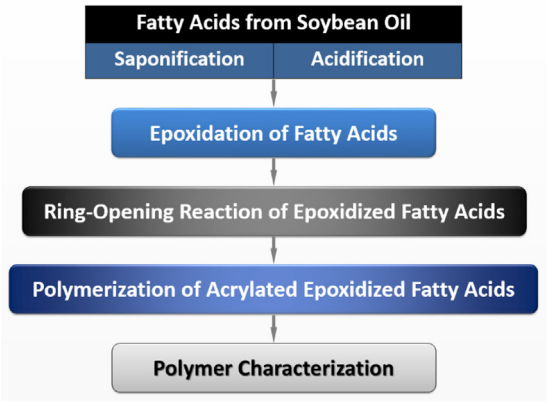

Fig. 1. Experimental methodology for the synthesis of polymers.