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Production of polyols and new biphasic mono-component materials from soy hulls by oxypropylation

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ABSTRACT

The present study is aimed at oxypropylating soybean hulls (SH) to obtain two products in a single reaction: a viscous polyol (SHP) and a solid fibrous residue of soybean hulls modified on the surface (SHBM) by a layer of thermoplastic polymer poly (propylene oxide). The oxypropylation reaction was conducted by polymerizing propylene oxide in the presence of the SH in a reaction catalysed by KOH at 150 °C. The chemical composition of the SH was determined. The samples before (SH) and after oxypropylation (SHP and SHBM) were characterized by Fourier Transform Infrared Spectroscopy and thermogravimetric analysis. The SH and SHBM were also characterized by scanning electron microscopy and X-ray diffraction. The SHP was characterized with respect to its hydroxyl index value (IOH), intrinsic viscosity $[\eta]$ and with respect to the amount of poly (propylene oxide) homopolymer (PPO) formed. These characterizations were carried out in order to assess the effectiveness of the process and verify the applicability of both products: (i) for producing polymer derivatives such as polyurethane foams in the case of polyol; and (ii) to prepare biphasic monocomponent composites in the case of the superficially oxypropylated residue.

1. Introduction

The production of energy and new materials from renewable sources is extremely relevant given the growing need to replace materials produced from petrochemical sources, the anticipated shortage of fossil resources and increasing prices. On the other hand, it is also desirable to take industrial fractions of low value, reducing their environmental impact, and thus, contributing to the sustainable development of society (Pinto et al., 2009).

Due to its territorial extent and suitability for forestry, Brazil produces large quantities of plant biomass in crops such as corn, sugar cane, and soybeans, among others, annually. Thus, forest and agricultural residues form an interesting category of biomass that can be explored, especially as a source of renewable energy and raw materials that do not compete with the food sector, have low cost and are available in abundance (Leitão et al., 2010).

Soybeans are the second largest agricultural product of Brazil. Brazilian states leading in soybean production are: Mato Grosso, with 29.0% of domestic production; Paraná with 19.5%, Rio Grande do Sul with 15.4%, and Goiás, with 10.5% (MAPA, 2013).

Due to its composition, soy can be used for various purposes, both as food for humans and animals, and for various industrial products and raw materials for agro-industries. Soybeans can be processed initially, generating oil, bran and flour, the oil being processed into refined oil for food consumption and refined oil for non-food purposes, the meal used in animal feed and the flour used in food for production of breads, pastries, and pasta (CISOJA, 2014).

Soybean hulls are a very thin film that covers the grain, being separated from the embryos by their industrial processing. This film is extracted from the beans before they undergo crushing to obtain the oil. Thus, it is a byproduct of the soybean oil industry with a relatively low cost and is 7–8% of the grain weight. Whereas the production of soybeans in the 2012/2013 harvest was about 81.2 million tons, it was estimated that 5.7 million tons of soybean hulls were generated during this period (CONAB 2013).

Little attention is given to soybean hull applications. Very little of it is directed to animal feed production and therefore, huge amounts of this residue do not have a proper use. Because it is a plant biomass, soybean hulls are a lignocellulosic waste composed of natural polymers, which due to their chemical chain hydroxyl groups are presumably capable of participating in oxypropylation reactions (Gandini and Belgacem, 2008).

Different types of substrates from renewable sources have been studied, namely beet pulp (Pavier and Gandini, 2000), lignin from different pulping processes (Nadji et al., 2005), chitin and chitosan

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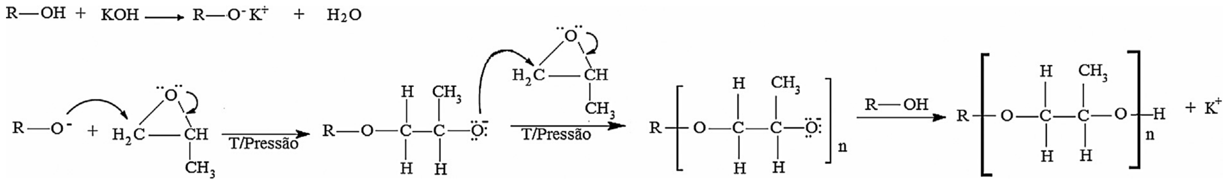

Fig. 1. Schematic view of the oxypropylation chemical reaction.

residues (Fernandes et al., 2005), soybean oil (Monteavaro et al., 2005), cellulose fibres and starch (Da Róz et al., 2009; De Menezes et al., 2009a,b), olive pits (Gandini and Belgacem, 2008), rapeseed cake (Serrano et al., 2010), coffee grounds (Soares et al., 2011), and also obtaining polyol from the liquefaction of lignocellulosic biomass from agricultural and industrial wastes, paper and wood (Hu et al., 2014).

Oxypropylation of natural polymers is a very different approach for exploiting biomass. Cellulose and starch have been modified industrially for years to obtain their corresponding hydroxypropylated derivatives. This technology and the materials associated with them are well established, and the reaction consists in the activation of functional hydroxyl residues by a strong Brønsted base generating the corresponding oxyanions, which work as beginner's sites of reaction of spreading oxyanions. Both ethylene oxide (EO) and propylene oxide (PO) respond effectively to this type of polymerization, which occurs under vacuum, high temperature and high pressure (Gandini and Belgacem, 2008).

The oxypropylation reaction is very simple and does not require a solvent or a separation process, so everything that enters the reactor is removed as the desired final product (Evtouguina et al., 2002). It is, therefore, a good example of a green chemistry process. The important variable is the proportion of PO added to the substrate, which governs the polyol's properties such as viscosity and hydroxyl index (IOH), as well as the proportion of PO homopolymer that always accompanies the oxypropylated substrate (De Menezes et al., 2009a). This type of reaction is based on the idea of producing a liquid polyol moiety through conversion of the initial morphology of the corresponding substrates, which are intractable solids.

The probable mechanism for the reaction of PO addition to lignocellulosic molecules may be outlined. The first stage of the oxypropylation process consists in the activation of functional hydroxyl residues by a strong Brønsted base, which are protonated and the molecule are displaced to form water, a good leaving group, compared to the hydroxyl, thereby generating the corresponding oxyanions, which work as beginner's sites of reaction of spreading oxyanions. Propylene oxide (PO) respond effectively to this type of polymerization, which occurs under vacuum, high temperature and high pressure. The second stage is an addition of a PO molecule to oxygen atom deprotonated units of residues. Oxypropylation takes place directly after the nucleophilic attack on the CH_2 group of PO by one of the adjacent hydroxyl group.

Upon complexation in such a manner, the oxygen atom of PO exhibits electron donating properties, while hydroxyl group shows an electron accepting ability and attack the less hindered carbon of the epoxide hysterical (propylene oxide), opening the chain and forming a hydroxyl oxiranion, now more accessible to other reactions. Next molecules of PO can be added in a similar way to other hydroxylic oxygen atom, with much less probability, to the OH group of the formed oxypropyl fragment, leading to the final product according to the scheme in Fig. 1.

The polyols obtained from the oxypropylation of natural polymers are compounds containing more than two reactive hydroxyl groups per molecule. These are used at the industrial level, i.e. isocyanates in the synthesis of polyurethanes (a polymer family with several applications including flexible and rigid foams, fibres, elastomers, adhesives and coatings) (Gandini and Belgacem, 2008). The structure, average molecular weight and other functional groups have an important influence on the final properties of the polyurethanes. Polyols that give rise to flexible foams and elastomers have average molecular weights between 1000 and 6000 Da. Short chain polyols (250–1000 Da) with a high polydispersity index (3–12) produce rigid polymers with high levels of branching and are used to produce rigid foams and as an ingredient in high performance paints (Soares et al., 2011).

Some studies reported in the literature show the possibility of using oxypropylation reactions in a controlled manner to produce polyols chemically bonded to the substrate surface (cellulose and starch), forming a layer of thermoplastic poly propylene oxide. This layer would act as a thermoplastic matrix and the substrate as reinforcement in the preparation of self-reinforced composites, just by simple thermopressing (Gandini et al., 2005; De Menezes et al., 2009a,b; Rosa et al., 2014). The resulting modified substrates are composed of both matrix and reinforcing agent linked by covalent bonds and, as a consequence, can be called a biphasic mono-component.

This paper intends to apply the process of oxypropylation to soy hulls (SH), which is a lignocellulosic waste, in order to obtain both polyol and superficially oxypropylated soy hulls. The resulting materials were characterized by different techniques before and after the oxypropylation reaction in order to assess the effectiveness of the process and verify the applicability of both products: (i) for producing polymer derivatives such as polyurethane foams in the case of the polyol; and (ii) to prepare biphasic monocomponent composites in the case of the superficially oxypropylated residue.

2. Experimental

2.1. Sample preparation

The soy hulls (SH) were supplied by Algar Agro S. A. (Uberlandia, Minas Gerais, Brazil). The sample was ground in a Wiley mill and subsequently sieved with sieves of 35–80 mesh. The fraction retained between these screens, with sizes from 0.180 to 0.425 mm, was used for the oxypropylation reaction.

2.2. Characterization of SH

The SH lignocellulosic residue was characterized as to moisture content (TAPPI Standard T264 om-88), ash (TAPPI Standard T211 om-93), soluble extractive content in a cyclohexane/ethanol mixture and in water (TAPPI Standard T204 cm-97), α-cellulose and hemicelluloses content (acid chlorite method described by (Browning, 1967) and total Klason lignin content (TAPPI standard T13 m-54).

2.3. Oxypropylation of SH

The procedure for oxypropylation of SH consisted of impregnating 5 g of the sample in 50 mL of an alcoholic solution of KOH 1% (w/v), and then, drying in an oven for 12 h at 105 °C to dry the sample and evaporate the solvent (ethanol). After evaporation of