OLIVE STONE AS A RENEWABLE SOURCE OF BIOPOLYOLS

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Introduction

The manufacturing process of olive oil yields, additionally to the actual oil (20%), a semi-solid waste (30%) and an aqueous liquor (50%). The crude olive cake, composed of olive pulp and olive stones, is thereafter collected in central seed oil plants, where the residual oil is extracted with hexane after being dried in rotary driers using hot air (60 ºC). A rich olive stone material with low moisture content is obtained as a by-product[1].

Three main processes are currently used to produce olive oil, i.e., discontinuous traditional pressing, and the continuous three-phase and two-phase processes. The discontinuous process is being progressively replaced, firstly by the continuous three-phase system and subsequently by the two-phase system. The two-phase process delivers olive oil and a very wet olive cake (moisture content around 57%). Despite the advantages of this process, it approximately doubles the amount of "solid" residue that further presents a limited storage life and high transportation costs. As a consequence, it is not a profitable feedstock for seed-oil extraction posing a problem of waste disposal[2]. As a solution to overcome this constraint some two-phase olive oil industries have implemented a stage for olive stone recovering.

This olive stone residue is most often used as a fuel in ceramic plants, bakeries, as well as in the olive oil and seed oil mills themselves[3]. Recently, some applications are emerging such as its use as a raw material to produce activated carbon and furfural, and as a biosorbent for heavy metals. Steam explosion was also applied to this material in order to separate the main components, namely cellulose, hemicelluloses and lignin. Concerning the field of materials preparation, the examples are particularly scarce and mainly devoted to its direct use as reinforcing agents or fillers in polymeric composites[4]. Faced with this scenario, research aiming at finding new uses for the olive oil industry by-products is of great relevance, both because environmental concerns and economic reasons.

The Strategy

The development of polyols from abundant and renewable biomass resources constitute attractive choices for polyurethane and other industrial sectors where green chemistry and sustainable processes are in focus. By means of oxypropylation, the solid biomass can be converted into liquid polyols thanks to the introduction of oilgo(propylene oxide) grafts[5]. Chitosan, chitin, different types of lignins, cork and more complex structures like sugar beet pulp are among the documented examples. The promising results obtained with the ensuing polyols and their subsequent incorporation into polyurethane formulations corroborate the interest to exploit these biomass resources[6-9].

The purpose of this work was to establish the feasibility of converting the olive stone residue by means of both total and partial oxypropylation. In the first case, the oxypropylation reaction conditions are chosen in order to promote extensive grafting, thus assuring a complete "liquefaction" of the material and, in the second case, partial oxypropylation would limit the reaction to the outer shell in view of the preparation of all-"olive stone" composites. This approach involves a straightforward transformation of the olive stone particles outer layer, giving rise to a thermoplastic matrix around its unreacted reinforcing inner structure, as already applied to cellulose and starch[5]. To the best of our knowledge, oxypropylation was never applied to olive-stone.

Results and Discussion

Olive stone (OS) was kindly provided by a local industry (Azeites Milénium Lda, Mirandela, Portugal). This granular material has fragments with 2-5 mm average size and low contamination of skin and seeds. This material was ground using a Restch blade mill equipped with a 0.25 mm mesh sieve. Its main composition on a dry basis (%, w/w) was 31.1% of lignin and 63.8% of holocelluose. The ash content was around 0.7%.

The oxypropylation was carried out in a 300 ml stainless steel PARR autoclave equipped with stirring, heating elements and both pressure and temperature sensors. The olive stone samples (both original and ground materials) were preactivated with an ethanol-KOH solution during 1 hour at room temperature under a nitrogen atmosphere. The dried activated substrate was thereafter mixed with propylene oxide (PO) using an OS/PO ratio (w/v, g/ml) of 10/20. The amount of KOH used corresponded to 1% (w/w) of the olive stone substrate (10 g). After closing the reactor, the mixture was heated at different temperatures under stirring depending on the desired transformation, viz. partial or total oxypropylation.

The characterization of these new materials involved FTIR and NMR spectroscopy, DSC, viscosity and OH index measurements, as well as morphological observation through SEM. The results of the initial experiments will be presented and discussed.

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