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Biocatalytic esterification of industrial lignins: structure and antioxidant activity

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PURPOSE OF THE ABSTRACT

2G Biorefineries are aimed to recover mostly polysaccharides from the lignocellulosic biomass. [1] However, in order to build economically viable and sustainable biorefinery processes, it is critical to valorize their byproducts. Lignins, very complex and heterogeneous aromatic biopolymers representing 15-30% of the dry weight of vascular plants, are the major byproduct of lignocellulosic biorefineries. [2]

Lignins are therefore the most abundant renewable source of aromatic carbons; located within the cell walls of plants, they possess a complex and rich structure exhibiting a large number of hydroxy groups, either aliphatic or phenolic. [3] The presence of phenolic groups confers a valuable antioxidant activity to lignins that may be valorized in industrial applications such as either polymer or cosmetic additives. [4] All the hydroxy groups may also be targeted through esterification leading to the modification of the structure of these biopolymers.

In this work, we want to describe our efforts toward the incorporation of lignins in synthetic polymers (PP and PBS) and the investigation of their antioxidant activity when incorporated in these polymers. The main problem relies however in their poor miscibility in synthetic apolar polymers leading to a very heterogenous distribution of lignins within the polymer matrix. When it has been proven that esterification of lignins with fatty acids improves their miscibility in apolar matrices, [5] their antioxidant properties are usually lost due to a complete nonselective esterification process. In order to alleviate this problem, our hypothesis was therefore that a selective esterification of the aliphatic hydroxy groups by fatty acids will enhance this miscibility when preserving the antioxidant activity related to the free phenolic groups.

In this work, we will present the optimization of a biocatalytic process allowing the selective esterification of the aliphatic hydroxy groups of lignins by different fatty acids, the incorporation of these functionalized lignins in PP and PBS matrices and the study of the behavior of these modified polymer films upon oxidative treatment.

First, trials were performed on a lignin model compound, a commercial ?-O-4 dimer bearing a free phenol, a primary and a secondary alcohol. The feasibility of this selective esterification was confirmed by different analyses such as proton and phosphorus NMR, where no phenol reacted, even with extended reaction durations.

A technical soda lignin from wheat straw, byproduct of pulp production, was also esterified with different fatty acids following the same approach. In this case, the experimental conditions of the biocatalytic process as well as the methodology for the precise quantification of the yield of the reaction have been optimized.

Parameters such as the time of the reaction, enzyme load and nature, as well as the nature of the grafting reagent were investigated to optimize the grafting yield. Model kinetic studies were also carried out in order to fully understand the enzyme activity in our systems. Raw and modified lignins were thereafter incorporated into PP

and PBS films in different amounts and it was shown that the antioxidant activity of lignins was preserved allowing the protection of the films against oxidation.

FIGURES

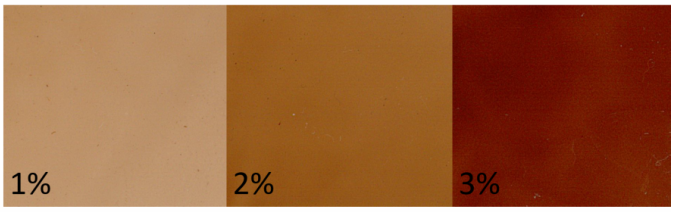

FIGURE 1

FIGURE 2

Pictures of Polypropylene films blended with lignins

Pictures of polypropylene films blended with 1, 2, 3% of modified lignins

KEYWORDS

Lignins | Selective esterification | Antioxidant additive | Polyproylene

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