Research paper

All natural cork composites with suberin-based polyester and lignocellulosic residue

Hugo De Oliveira, Bumyong Yoon, Véronique Michaud, Jae-Do Nam, Jonghwan Suhr

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A B S T R A C T

Suberin is an aromatic-aliphatic cross-linked polyester structure which constitutes cell wall structures of cork. It is particularly interesting for its use of monomeric compounds towards renewable bio-based polymers. In this study, the extraction of suberin monomers was successfully done by green method using alkaline hydrolysis combined with mechanical grinding. As the mechanical grinding was applied along with hydrolysis process, the maximum yield of depolymerized suberin monomer (DSM) with relatively low energy and less time was achieved. The polarity and functionality of DSM extracted in this study also showed higher values compared to conventional reflux hydrolysis process. Polyesterification and curing behavior of DSM were examined with molecular weights and mechanical properties of the ensuing polyesters. Tensile properties of suberin-based polyesters are reported for the first time that the maximum strength was found to be 7.3 MPa while Young's modulus was found to be 105 MPa. Furthermore, all natural cork composites were fabricated which comprise suberin-based polyester as matrix and lignocellulosic residue as reinforcement, and also reported their significantly enhanced tensile properties showing the great potential as an alternative green polymer composites for various engineering applications.

1. Introduction

Recently, the concept of developing macromolecular materials from renewable resources as alternatives to the current fossil-based polymers has received wide attention (Gandini and Lacerda, 2015). From an environmental perspective, one of the ways to decrease the amount of carbon dioxide in the atmosphere is to reduce fossil fuel dependency by producing long-life products based on plant biomass, which will undoubtedly include, cork products (Gil, 2015). Cork has been widely used in various applications ranging from wine stopper to construction structures due to its intriguing properties such as super compressibility without fracture, full-recovery, impermeability, heat insulation and so on (Silva et al., 2005; Pereira, 2007). Such unique properties of cork are derived from its main component, called suberin. Although suberin is extractable from the outer bark of higher plants throughout the vegetable realm (Miranda et al., 2013; Ferreira et al., 2016; Pereira, 1988; Karnaouri et al., 2016), it is especially abundant in cork oak (Quercus suber L.), where it represents almost 50% of the total weight of cork.

Chemical structures of suberin have revealed that it is a natural polyester which aromatic and aliphatic monomers are linked through ester bonds with a three-dimensional structure, which plays the role of a protective layer (Pereira, 2007; Bernardes, 2002; Gandini et al., 2006). Interestingly, the polyester structure of suberin can be broken down chemically via hydrolysis or methanolysis so that the depolymerized suberin monomer (DSM) is likely to be re-polymerized by polyesterification of hydrolyzed monomer or methanolyzed monomer. This chemically reassembled polyester derived from natural cork is a promising candidate to produce renewable materials completely from plant biomass.

Moreover, in the processing of cork and its products, significant amount of cork by-products (powder) are produced. Cork stopper industry in Portugal generates cork by-products at around 40,000 tons per year which is about 40 wt% of total annual cork production (Sousa et al., 2011). Currently, cork by-products are mostly used as burning fuel for energy production. Therefore, a durable application of suberin-rich cork by-products fulfills the concept of bio-based polymers from renewable resources as an alternative to current fossil-based polymers, while valorizing an existing source of by-products.

Previous investigations on suberin-based polyesters mainly focused on the extraction of suberin monomers from cork and corresponding