Materials and Design 82 (2015) 282–289

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Cork–polymer biocomposites: Mechanical, structural and thermal properties

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ARTICLE INFO

Article history:
Received 24 February 2015
Revised 7 May 2015
Accepted 18 May 2015
Available online 21 May 2015

Keywords:
Cork
Sustainable composites
Biocomposites
Eco-friendly
Mechanical properties
Thermal properties

ABSTRACT

This work addresses to the preparation of biocomposites resulting from the combination of different biodegradable aliphatic polyesters with cork (30 wt.%). The lignocellulosic biomass with closed cellular structure was compounded with poly(L-lactic acid) (PLLA), polyhydroxybutyrate-co-hydroxyvalerate (PHBV), poly-ε-caprolactone (PCL) and starch-poly-ε-caprolactone (SPCL) blend using a twin-screw extruder prior to injection moulding into tensile samples. The physico-mechanical and thermal properties of the matrices and the bio-based cork composites were investigated. This study shows that the addition of cork contributes to produce lightweight materials using PLLA and PHBV matrices and promotes an increase on the stiffness of PCL. The fracture morphology observations showed good physical cork–matrix bonding with absence of voids or cavities between cork and the bio-based polyesters. Cork increases the crystallinity degree of the biocomposites. These findings suggest that the cork–polymer biocomposites are a viable alternative to develop more sustainable composite materials, such as automotive interior parts and bio-based caps for wine bottles as it has been shown as proof-of-concept.

1. Introduction

Lignocellulosic biomass represents a renewable, biodegradable, lightweight, abundant and cheap source of raw materials, making them attractive for the development of sustainable products [1–4]. Cork is the outer bark of an oak tree known botanically as *Quercus suber* L.; being the major chemical constituents suberin (33–50%); lignin (13–29%); polysaccharides, (6–25%); and extractives (8.5–24%) [5,6]. Cork reveals an anisotropic closed cellular structure as shown in Fig. 1.

It is composed of an aggregate of cells, about 42 million per cubic centimetre [7]. Cork is a lightweight material, viscoelastic and impermeable to liquids or gases, good thermal, acoustic and electrical insulator, sound and vibration insulator and exhibits a near-zero Poisson coefficient, which found applications from the stoppers, agglomerates to aeronautics [5,8–12]. Furthermore, cork composites are one of the most promising fields of cork technology [8]. The combination of cork with polymers trough melt based technologies brought added-value to cork based materials that can promote the development of a wide range of innovative applications. Studies can be found on the combination of cork and cork by-products with polyolefins such as polyethylene (PE) and polypropylene (PP) and the effect of adding coupling agent in the mechanical properties [13–15], chemical surface modification to improve cork–polymer compatibility [16,17]; cork in sandwich composite structures [18–20] and hybrid cork composite reinforced with natural fibres [21,22]. Recently, the combination of the unique properties of cork with biodegradable matrices [23,24] was also studied aiming the production of more sustainable materials. A sustainable product is a product which will gives as little impact on the environment as possible during its life cycle [25]. Nevertheless, one of the main drawbacks pointed to composites is the low sustainability due to the separation problems of the mixed materials [25]. One interesting approach is to consider the re-manufacturing of old products or the use of biodegradable polymers, as matrices, combined usually with biofibres as the reinforcing element, to produce fully biodegradable materials, the so called biocomposites or green composites [1,26].

Biodegradable polymers and bio-based plastic products from renewal resources can form sustainable and eco-friendly products than can compete in the current market [2,27,28]. According to the market data compiled by European Bioplastics, the global production capacity of bio-based plastics is predicted to quadruple from

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http://dx.doi.org/10.1016/j.matdes.2015.05.040
0261-3069/

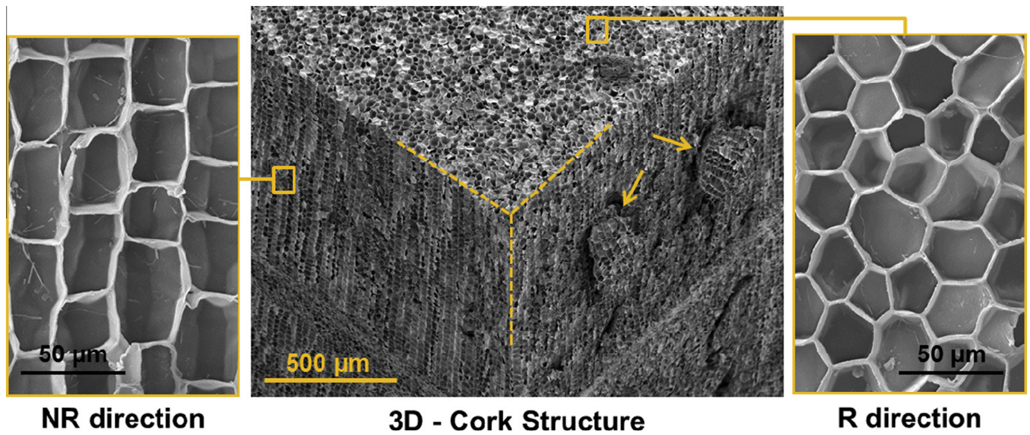

Fig. 1. SEM micrographs of the 3D cork morphology showing in detail the non-radial direction (NR) and radial direction (R).

around 1.6 million tonnes in 2013 to approximately 6.7 million tonnes by 2018 [29]. The different biodegradable polymers can be divided into 4 classes [30]: The agro-polymers (e.g. polysaccharides) obtained from biomass by fractionation such as starch and lignocellulosic products. The second and third are polyesters, obtained, respectively by fermentation from biomass or from genetically modified plants (e.g. polyhydroxyalkanoates (PHAs), including polyhydroxybutyrate (PHB)) and by synthesis from monomers obtained from biomass (e.g. polylactic acid (PLA)). The fourth family are polyesters, totally synthesized by the petrochemical process (e.g. polycaprolactone (PCL)) [1,4,30]. The interest on these biodegradable polymers has grown, since they present similar mechanical and thermal properties as compared with synthetic thermoplastic such as polyethylene (PE) and polypropylene (PP) [31]. The PLA and PHB reveal higher mechanical properties, with a modulus around 2.8–3.4 GPa and 1.0–2.1 GPa, respectively [2,3,32]. The aliphatic polyesters present proper mechanical and degradation properties that make them good candidates to replace traditional polymers on several applications [26].

Vilela et al. [24], showed that cork residues or chemically modified can be valorised when combined with PLA and PCL and processed by melt mixer followed by injection moulding. The developed biocomposites revealed benefits in terms of weight reduction. The aim of this study was to produce and characterize several biocomposites prepared by combining different matrices from renewable resource including, poly(L-lactic acid), (PLLA); poly hydroxybutyrate-co-hydroxyvalerate, (PHBV); PCL and starch-poly-ε-caprolactone (SPCL), with granulated cork. The biocomposites were compounded through twin-screw extrusion and further processed by injection moulding. We demonstrate that by combining proper melt based technologies this study can provide information for basic properties of several cork biocomposites with potential application in new products from leisure products, to automotive and building sectors.

2. Materials and methods

2.1. Cork and polymer materials

Cork granules, with an average particle size 0.5–1 mm, specific weight of 166 ± 21 kg m^{-3} and moisture of ~7.5% was supplied by Amorim Revestimentos S.A. (S. Paio Oleiros, Portugal). The polymers used in the preparation of the cork based composites includes: (i) PLLA with a L-lactide content of 99.6% and a M_w of 69,000 g mol^{-1}, was obtained from Cargill Dow LLC, USA; (ii) PHBV polymer with 12% HV content and molecular weight (M_w) of ~425,692 g mol^{-1} was provided by PHB Industrial, Serrana, Brazil; (iii) PCL resin (commercially available as TONE® 787), with M_w of 125,000 g mol^{-1}, was obtained from Union Carbide Chemicals and Plastics Division, New Jersey, USA and (iv) A blend of corn starch with PCL (SPCL) containing about 63 wt.% of PCL, 27 wt.% of corn starch and 10 wt.% of natural plasticizers was supplied by Novamont, Italy. The M_w of PCL present in this blend is about 118,000 g mol^{-1}.

2.2. Twin-screw extrusion compounding

Prior to compounding, all natural raw materials were pre-dried at 40 (i.e. PCL and SPCL) to 70 °C (i.e. PLLA; PHBV and cork) during 24 h for moisture content stabilization. All the polymers were thereafter reduced to a grain size less than 0.5 mm in an Ultra centrifugal mill from Retsch. The prepared compositions and processing conditions are summarized in Table 1.

The raw materials were pre-mixed and further compounded in a Rondol SCF modular co-rotating twin-screw extruder (TSE) with the screws diameter of 16 mm, a length to diameter ratio (L/D) = 25 and a single strand die of 3 mm. The mixture was placed in the hopper and automatically feeded at a constant rate with a volumetric dosing unit from SHINI Plastics Technologies (Germany). The temperature profile along the barrel to the die was set according to the information present in Table 1 with the rotation screws at 50 rpm. Part of the extrudate was cooled in water bath and subsequently ground by a lab pelletizer SCHEER (Stuttgart) to produce composite pellets with length ⩽5 mm suitable for injection moulding. Prior to this step, the produced pellets were dried in a vacuum oven at 50 °C until stabilize.

Table 1
Compositions and processing conditions of the polymer matrices and the bio-based composites with 30 wt.% of cork.

	CPC[a] composition (wt.%)		Extrusion	Injection moulding
Sample code	Polymer	Cork	Temperature profile (°C)	Temperature max. (°C)
PLLA	100	0	110; 160; 175; 175; 170	170
PLLA/Cork	70	30		175
PHBV	100	0	110; 150; 175; 175; 180	175
PHBV/Cork	70	30		180
PCL	100	0	40; 60; 70; 75; 80	90
PCL/Cork	70	30		
SPCL	100	0	30; 60; 70; 75; 80	90
SPCL/Cork	70	30		

[a] CPC: cork–polymer composite.