



Functionalized cork-polymer composites (CPC) by reactive extrusion using suberin and lignin from cork as coupling agents



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ABSTRACT

High density polyethylene (HDPE) and cork powder were compounded in a co-rotating twin-screw extruder to obtain cork-polymer composites (CPC) with improved properties. Benzoyl peroxide (BPO) was used as initiator agent, and suberin or lignin isolated from cork enhanced filler-matrix bonding and promoted mechanical reinforcement with environmental benefits. The novel composites were characterised in terms of dimensional stability, evolution of morphology, thermal and mechanical properties and their performance was compared with that of composites containing polyethylene-grafted maleic anhydride (PE-g-MA) as coupling agent. As expected, composites with coupling agent present higher mechanical properties, lower water uptake and thickness swelling variation. Suberin acts as plasticizer with antioxidant benefits, while lignin works as a coupling agent, improving tensile modulus and maximum strength. Increasing lignin content does not improve the mechanical properties but improves thermal stability.

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1. Introduction

The use of synthetic polymers combined with lignocellulosic materials has become a reliable alternative to develop new sustainable materials with good performance and reduced cost [1–3]. Cork is the outer bark of the Oak tree *Quercus suber* L. [4], where the harvesting of cork is a natural, renewable process that reduces subsequent carbon footprints. During industrial cork processing, up to 30% results in sub-products such as cork powder, which is used in small amounts low value added applications. Cork-polymer composites (CPC) are usually prepared through melt based technologies. Increasing the percentage of cork in the composite without compromising the overall properties is seen as a desirable route towards sustainability. However, commodity thermoplastic matrices, such as polyethylene and polypropylene, are chemically incompatible with lignocellulosic materials, requiring the incorporation of coupling agents to improve interfacial adhesion [1,5]. The addition of functionalized polymers containing

maleic anhydride (MA) groups during compounding showed to be an effective method to improve interfacial bonding, even when using different cork qualities [6–8]. The typical chemical composition of cork is about 40% of suberin, up to 22% of lignin, 18% of polysaccharides and up to 15% of other extractives [4,9]. Suberin and lignin are thus the main constituents and in combination with a closed cellular morphology account for cork's unique properties, namely excellent insulation characteristics, low density and permeability, low thermal conductivity, high energy absorption, resilience, near-zero Poisson coefficient and high friction coefficient [9,10]. Suberin is a natural biopolymer typically found in the cell walls of plants [11]. Cork suberin is constituted by a polyester structure of long chain fatty acids, hydroxyl and phenolic acids, linked by ester groups, with ferulic acid acting as a bridge between the aromatic and the aliphatic domains [12–14]. Whether the aromatic domain is part of the suberin molecule is still a matter of debate [15]. The alkaline depolymerisation in an organic solvent results in the release of the aliphatic constituents through cleavage of the ester linkages and transesterification [13,16,17]. Full characterisation of cork lignin is still incomplete because of the complex relation between true lignin and the aromatic fraction of suberin. Nevertheless, Marques et al. [18–20] found that cork is composed of a G type lignin with 94–96% guaiacyl, less than 3–5% syringyl and 2–3% hydroxyphenyl units [21]. A comprehensive review on

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cork structure and chemical composition can be found in Silva et al. [9] and references within. In a previous study, the potential of suberin and chemically modified suberin to promote adhesion between low density polyethylene and cork was demonstrated [22]. Lignin has been proposed to reinforce the mechanical properties of composites [23–25], to promote adhesion in natural fibre composites [26], or, in combination with a coupling agent, to improve mechanical performance [24,27]. In all cases, high amounts of lignin or the addition of a coupling agent were necessary to reinforce the composites.

This work focus on the development of cork-polymer composites (CPC) using suberin and lignin as bio-based coupling agents through a reactive extrusion (REX) process, in order to overcome with environmental benefits the insufficient adhesion between cork and a high density polyethylene (HDPE) matrix. REX has the capability of functionalize, prepare the composite and produce pellets in a single step. No environmental or health hazardous solvents are used, low investment costs and high production yields are obtained [21,28]. Initiators are usually required, the most widely used in grafting reactions being organic peroxides, including benzoyl peroxide (BPO). The work investigates for the first time: (i) the evolution of morphology during the compounding process; (ii) the dimensional stability and thermal properties of the composites; (iii) the effect of suberin, lignin, and initiator agent on the tensile properties. These properties are compared with those of an equivalent system using a coupling agent based on maleic anhydride (PE-g-MA).

2. Materials and methods

2.1. Materials

Cork powder, with an average particle size <500 µm, a specific weight of $157 \pm 2 \text{ kg m}^{-3}$ and a humidity of ~5.4% was supplied by Amorim Revestimentos S.A. (Oleiros, Portugal). The matrix was a high density polyethylene HDPE, (HMA – 025 from ExxonMobil, Germany), with a MFI of $8.2 \text{ g} \cdot 10 \text{ min}^{-1}$ (190 °C, 2.16 kg), and a melting point of 136.6 °C, containing a thermal stabilizer. HDPE grafted with maleic anhydride (PE-g-MA), containing 0.5–1.0 wt.% of maleic anhydride (Exxelor PE 1040), with MFI of $1.4 \text{ g} \cdot 10 \text{ min}^{-1}$ (190 °C, 2.16 kg), and having a melting point of 131.3 °C, was produced by ExxonMobil, Germany. Benzoyl peroxide (BPO, 75%), USP grade, Luperox[®], was obtained from Atofina Chemicals. The compositions prepared are presented in Table 1. The cork-polymer (20–80) wt.% ratio was maintained in all formulations.

2.2. Extraction of suberin and lignin

Extractive free cork powder was obtained after three consecutive 6 h soxhlet extractions with dichloromethane, ethanol and

Table 1
Compositions of the cork-polymer composites (CPC) using suberin and lignin and maleic anhydride as coupling agent.

Sample	CPC composition (wt.%)					
	HDPE ^a	Cork	BPO ^b	Suberin	Lignin	PE-g-MA ^c
CPC1	80.0	20.0	–	–	–	–
CPC2	80.0	20.0	–	–	–	2
CPC3	77.6	19.4	1	2	–	–
CPC4	77.6	19.4	1	–	2	–
CPC5	76.0	19.0	1	–	4	–
CPC6	76.0	19.0	1	–	4	–
CPC7	79.2	19.8	1	–	–	–

^a HDPE – high density polyethylene.

^b BPO – benzoyl peroxide.

^c PE-g-MA – coupling agent based on maleic anhydride, with a level content of 0.5–1.0 wt.%.

water. The resulting material was used to obtain the suberin and lignin fractions. Suberin extraction procedure was adapted from Ekman and Eckerman [29] and Pinto et al. [30]. The product (1 g to 13 ml) was refluxed in ethanol:water (25:1) containing 0.5 M sodium hydroxide for a period of 6 h. After cooling, the resulting mixture was filtered and the liquid fraction was acidified to pH 5–6 with hydrochloric acid. After filtration, the solvent was removed in a vacuum evaporator. The resulting solid residue was suspended in water and extracted with 3 times the volume in chloroform. The organic fraction was recovered and the solvent removed in a vacuum evaporator, resulting in a brownish paste-like material.

The methodology for lignin extraction was adapted from Ekman and Eckerman [29] and Browning [31]. The solid residue resulting from the suberin extraction was thoroughly washed with distilled water until neutral pH. 350 ml of a 72% sulphuric acid solution were added to 30 g of this residue and the mixture was maintained under agitation for 2 h at room temperature, followed by the addition of 550 ml of distilled water and refluxing for 4 h. After cooling to room temperature, the solid residue was recovered through filtration and washed with distilled water until neutral pH, a dark powdery material being obtained.

2.3. Twin-screw compounding

Before compounding, the cork powder was pre-dried at 80 °C in a vacuum oven until constant weight. The raw materials, including the pulverized polyethylene, the benzoyl peroxide (BPO) and PE-g-MA, were pre-mixed. Compounding was performed in a prototype modular laboratorial mini intermeshing co-rotating twin-screw extruder (TSE), with a screw diameter of 13 mm, and a length to diameter ratio (L/D) = 27, coupled to a rod die with a diameter of 3 mm. The screw profile is built by sliding along a shaft conveying and kneading elements with a maximum channel depth of 1.5 mm. As seen in Fig. 1, the configuration used in the experiments induces polymer melting in the first restrictive block upstream and dispersive and distributive mixing in the second kneading block, which comprises 8 discs staggered at -30° . The extruder is provided with sampling devices along its length which are capable to collect in circa 1 second small amounts of material from within the screw channel [32]. This allowed to obtain cork-polymer samples at locations A and B identified in Fig. 1, i.e., where most of the dispersive mixing action should take place. The temperature profile along the barrel and die was set to 165/180/185/185/175 °C for all the experiments, the feed rate was kept at 130 g h^{-1} , and the screws rotating at 70 rpm. Fig. 2 shows the compounding methodology adopted. Due to the low density and high volume of cork powder fraction, the pre-mixed polymer and cork were feed upstream (position 1) by a miniaturized volumetric feeder (based on a Moretto DVM 18 L), together with the BPO initiator, or the PE-g-MA. Suberin and/or lignin were added in position 2, by means of an automatic syringe pump (AL-1000, from WPI, USA), or manually, respectively. After air-cooling, part of the extruded composite was pelletized.

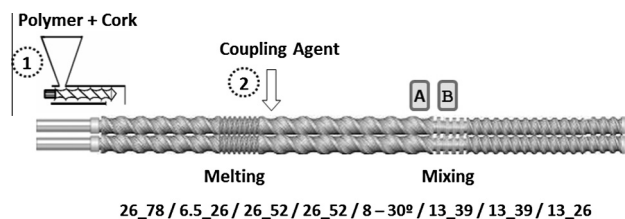


Fig. 1. Twin-screw extruder set up. Screw profile is defined in terms of (pitch_length) of the various elements. A and B denote locations of material sampling.

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