



# Cork extractives exhibit thermo-oxidative protection properties in polypropylene–cork composites and as direct additives for polypropylene



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## ABSTRACT

The thermo-oxidative stability of polypropylene (PP) in composites containing 15 wt.% of cork and the performance of selected cork extracts as stabilizing additives for PP was evaluated by Oxidation Induction Time (OIT) and by Oxidation Onset Temperature (OOT). The results showed that cork increases the OIT of PP in the composite and it was identified that the cork extractives fraction is responsible for such behavior. Selected cork extracts with high antioxidant capacity (determined by dpph radical scavenging and oxygen reactive absorbance capacity assays) were compounded by extrusion with PP in 0.5 and 1.5 wt.%. It was found that the ethanol extract is the most effective as thermo-oxidative stabilizer for PP. At the loading level of 1.5%, the OIT increases from 3.8 (neat PP) to 29.7 min at 200 °C and from 1.2 (neat PP) to 9.0 min at 220 °C. The OOT also increases from 216 °C (neat PP) to 247 °C. Mechanical tests, performed on PP loaded with the cork extracts, showed that the presence of these extracts has no significant effect on the polymer mechanical performance. The results demonstrate the suitability of cork as a source of thermo-oxidative stabilizing additives for the formulation of polyolefins, and enable the exploitation of new routes of cork valorization.

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## 1. Introduction

Cork is the outer bark of the oak tree *Quercus suber* L., which mainly grows in western Mediterranean regions. The bark is manually harvested every 9–12 years in a process that does not damage the tree, allowing it to continue to develop normally. Europe holds ca 60% of the total area of cork oak forests and harvests more than 80% of the World's cork. Portugal is the major producer, being responsible for the processing of 49% of the total amount of cork harvested in the World [1,2].

The cork chemical composition is variable and is dependent on different factors, such as, geographical origin, climate, age of the trees, etc. Anyway, typical compositions are within the ranges:

25–40% for suberin; followed by 13–29% for lignin; 6–25% for polysaccharides; and 8–24% for extractives [3–5]. Structurally, cork is constituted by an arrangement of cells (that have lost its internal content) with highly suberized walls. When observed on the microscope, this structure resembles a honeycomb pattern. This material presents some remarkable properties, such as: near-zero Poisson coefficient; complete recovery of shape after compression; among many others [6–8]. These properties are devised from its unique chemical composition and morphological structure.

The main industrial application of cork is for the production of stoppers. However, there are large quantities of cork (in different forms), whose lower quality or format limitation, does not allow its processing for the preparation of stoppers. This large amount of unused cork (usually considered as a by-product) has prompted the development of other applications for this unique natural material. In this scope, a series of applications for cork and cork-based materials have been developed; these include the production of: lightweight, sound and vibration insulation materials for housing and aerospace applications; cork–rubber composites for

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automobile engine gaskets; or decorative items. Despite these alternative uses, up to 25% of the processed cork is still transformed into powder that has no direct application [2]. Therefore, the present solution is to use it as fuel for energy recovery. The existence of such an unexploited stream of this natural raw material has prompted the development of new routes for its valorization.

The use of waste materials as fillers for the composite production is receiving increasing attention as an approach to increase the economical value of such streams. In particular, if the fillers are of natural origin and renewable resources, it can result in a material with higher green awareness and environmental benefits. Additionally, some natural fillers can impart new and or improved properties to the composite.

There is an increasing interest (from both the industry and the scientific community) in the development of cork–polymer composites [9–11]. The use of cork has a number of advantages when compared to other lignocellulosic materials. It can be regarded as imminently hydrophobic thus reducing the incompatibility with most polymers (that usually present a very low polarity); while its low density and its high capacity as thermal and acoustic insulator are qualities that are highly desired in diverse fields of application. Recent studies on the development of cork–polymer composites have focused on the increase of the interfacial adhesion by using different chemical (e.g. maleic anhydride [10–12]) and bio-based coupling agents [13,14]. It has been also reported: the improvement of the mechanical properties through the use of natural fibers as reinforcement [15–17]; the surface modifications of the natural component [17–19]; the increment of the damping properties [20,21]; the enhancement of the acoustic insulation [11,21]; and, more recently, the combination of cork with biodegradable and natural origin polymers [22,23]. As a result, solutions where cork is combined with high consumption polymers, such as, typical thermoplastic and thermosets used in the construction, transportation and aeronautical fields, have been developed.

Most polymeric materials are susceptible to degradation initiated by external factors, such as, light, heat, oxygen, humidity or shear forces [24–26]. The chemical modifications generated during this process result on the reduction of the mechanical performance and, therefore, decrease of the service life [27]. In the case of polypropylene (PP), its degradation involves the formation of primary alkyl radicals triggered by factors, such as, high temperatures, oxidative atmosphere and mechanical forces and amplified if in the presence of impurities and transition metals. The alkyl radicals can be converted to peroxy radicals in the presence of oxygen, which could further react to yield hydroperoxides [28–30]. Therefore, the rate of degradation of PP is influenced by the presence of radicals and reactive oxygen species. These thermo-oxidative processes from the degradation of PP can occur already during processing and, thus, strategies to reduce its effects usually involve the addition of stabilizing agents during the processing stages.

In order to minimize degradation, it is common to add different types of stabilizers that can act in the different stages of the polymer's lifetime. The most common type of stabilizers used during the processing stages are phosphorous-based, while hindered phenols can also be used to improve the lifetime of the material. Although these are commonly of synthetic origin, the possibility of using natural antioxidants [31–33] and modified natural phenolic extracts [34] as stabilizing additives has been proposed. In a recent study, it was shown that the thermo-oxidative properties of PP in composite materials containing cork are considerably improved, because of the cork material [12]. Further research work is required to identify which are the cork constituents responsible for this effect and evaluate their potential as bio-based stabilizing agents. In the present work we studied the thermo-oxidative properties of PP in composites containing 15 wt.% of cork in order to identify which

cork constituents are responsible for the above-mentioned thermo-oxidative protection. Moreover, we have evaluated if these can be further valorized as direct stabilizing agents for PP and we have quantified the protective effect by oxidation induction time (OIT) and oxidation onset temperature (OOT) parameters.

## 2. Materials and methods

### 2.1. Materials and reagents

Cork powder was selected and collected at the industrial facilities directly from the processing machines and used as received (Amorim Cork Composites, Portugal). This material is produced by reprocessing of cork scrapes from different origins. The leftovers are collected, further milled and sorted by density and particle size in a high frequency industrial vibrating equipment, to obtain homogeneous fractions, before further industrial use. From the different fractions arising from this process, for this work, the criterion for selecting the cork powder sample was the availability in large quantities and the purity (absence of other contaminants). The selected cork powder was collected at the industrial facility during the normal production process, and was considered to be representative of the daily operations by the industry responsible. The matrix was a PP homopolymer (1374 E2, ExxonMobil, Germany), with an MFI of 20.8 g 10 min<sup>-1</sup> (200 °C, 2.16 kg), and a melting point of 162 °C, that was transformed into powder and supplied by Pallmann Maschinenfabrik GmbH & Co. (Germany). All chemical reagents were analytical grade. Ethanol and chloroform were purchased from Fisher Chemicals, while dichloromethane, methanol sulfuric acid, Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), Folin–Ciocalteu reagent, gallic acid, 2,2-diphenyl-1-picrylhydrazyl, 2,2-azobis(2-methylpropionamide) dihydrochloride, fluorescein sodium salt and 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox) were purchased from Sigma–Aldrich. Sodium hydroxide and sodium carbonate were acquired from Fluka.

### 2.2. Cork powder characterization and preparation of extractive-free cork powder

The cork powder particle size distribution was determined on an analytical sieve shaker (model AS200, Retsch, Germany) equipped with a cascade of different mesh sieves. The chemical composition was determined in terms of extractives, suberin and lignin, following already established protocols reported elsewhere [3,35]. The extractive fraction was quantified as the combined mass of the material solubilized and recovered after successive Soxhlet extractions with dichloromethane, ethanol and water, for periods of 6 h each. The resulting cork powder was defined as extractives-free cork powder and was further used for the preparation of composites (hereafter designated by PP–Cork–EF) and for the suberin content determination. The suberin content was quantified as the chloroform soluble fraction after submitting the extractive-free cork powder to alkaline methanolysis. In short, the cork material was kept under reflux in methanol containing 0.1 M sodium hydroxide (1 g per 50 mL), for 6 h, after which, the liquid fraction was recovered, acidified to pH 6 with hydrochloric acid; after solvent removal, the solid residue was suspended in water and extracted with chloroform. The suberin material was obtained by removal of the chloroform under vacuum in a rotatory evaporator. The lignin fraction was obtained from the desuberrated cork material by processing it with 72% sulfuric acid in a 15 mL per 1 g of cork ratio, at room temperature, under constant stirring. After 2 h, 30 mL of concentrated sulfuric acid per gram of material was added and the mixture refluxed for 4 h. After thorough washing with distilled

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