



**IMPROVEMENT ON THE MECHANICAL PROPERTIES OF CORK COMPOSITES USING SUBERIN AS COUPLING AGENT THROUGH A REACTIVE EXTRUSION PROCESS**

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# IMPROVEMENT ON THE MECHANICAL PROPERTIES OF CORK COMPOSITES USING SUBERIN AS COUPLING AGENT THROUGH A REACTIVE EXTRUSION PROCESS

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## Abstract

New functionalized composite structures were prepared using low-density polyethylene (LDPE), cork powder and different suberins extracted from cork and birch outer bark as coupling agents to promote interfacial adhesion. The compounding was performed under reactive extrusion and samples processed by compression moulding. The morphology of the functionalized composites showed good adhesion between cork and the polymeric phase. The mechanical results confirm that the addition of suberin acts as coupling agent improving the strength and leads to cork-polymer composite materials with improved strain and lower modulus. When the suberin was added to the composition a slight increase on the composite density occurred. The new cork-polymer composites demonstrated that this technological approach is industrially appealing.

## Introduction

Composites containing natural materials from renewable resources are gaining international interest due to the environmental benefits, recycling and low cost [1]. Like wood, cork is a lignocelulosic material and it possess a series of properties with close cellular structure, low density, hydrophobic character, excellent sealing ability, good thermal, antivibratic and acoustic insulation [2, 3].

Cork combined with thermoplastic materials presents an environmental alternative with interest for a large field of applications [5, 6]. Cork-polymer composites (CPC) are usually prepared using melt based technologies [6, 7]. The increase of the percentage of natural component promotes specific characteristics such as aesthetic, insulation and cost reduction. Although, for high loads of natural component it is necessary the addition of coupling agents to promote the adhesion between cork with the polymeric phase [7]. To achieve a higher compatibility between the polymeric matrix and cork, it was preferred the use of substances that have chemical similarities with cork. Suberin is present in several plant species, such as cork

and Birch bark. Cork and some hardwood outer barks contain suberin, a natural polyester as a predominant component [3, 8]. Cork is especially rich in suberin, ca 45%. Birch outer bark, which is easily separated from technical Birch bark, contains about 35% of suberin [9]. Suberins may be attractive coupling agents, where the suberin monomers can be used, by grafting, to promote interfacial adhesion in cork-polymer composites.

With the objective of improving the mechanical performance of the cork-based composites a grafting strategy was employed. The more industrially appealing procedure is the reactive extrusion due to the reduction of the steps necessary to prepare the final modified composite pellets.

Reactive extrusion is a technique that can be used for the chemical modification of compounds, usually polymers [10]. The combination of reactive extrusion (no solvents used) and the use of naturally occurring coupling agents (e.g. suberin and modified suberin) transforms this methodology into an environmental friendly process. This process has the advantage of presenting shorter processing times when compared with solvent-based grafting approaches. With the reactive extrusion process it is possible to obtain new modified CPC materials with improved mechanical performance.

The objective of this work was to investigate the potential of suberin and modified suberin (extracted by conventional methods from cork and birch outer bark) as coupling agents in a continuous extrusion process to promote interfacial adhesion and enhanced mechanical performance of cork-polymer composites.

## Materials

The granulated cork was collected at Amorim Revestimentos, S.A. (Portugal) with particle size of 0.5-1mm, density of  $157 \pm 2 \text{ kg m}^{-3}$ .

Low density polyethylene (LDPE) was purchased from ExxonMobil (Germany) and it presented a MFI of  $70 \text{ g } 10 \text{ min}^{-1}$  ( $190 \text{ }^\circ\text{C}$ ,  $2.16 \text{ kg}$ ) and a density of  $911.3 \pm 1.3 \text{ kg cm}^{-3}$ . The LDPE peak melting temperature was  $104.85 \text{ }^\circ\text{C}$  determined by differential scanning calorimetry (DSC).

Benzoyl peroxide (BPO, 75%, Aldrich) was used as initiator of the grafting process.

## Compounding

The granulated cork was pre-dried at 70°C overnight before processing. LDPE and cork were compounded at a 75:25 weight ratio. The use of 1 wt% of initiator and 5 wt% of suberin as coupling agent was maintained constant for all the prepared compositions. The coupling agents were birch “suberin maleic hemi ester” (Suberin BB1), birch “suberin maleic 2-EH ester” (Suberin BB2) and cork suberin extracted by the standard solvent extraction methodologies (Suberin C). The compositions are summarized on table 1.

Table 1. Compositions of the functionalized polymer and composite boards

Board	LDPE:Cork (wt%)	Type of Coupling Agent	Coupling Agent (wt%)
1	100 : 0	---	---
2	75 : 25	---	---
3	75 : 25	Suberin BB1	5 *
4	75 : 25	Suberin BB2	5 *
5	75 : 25	Suberin C	5 *

\* Initiator BPO, 1wt%.

All the mixtures were tumble mixed and processed in a modular co-rotating twin screw mini-extruder with five barrel zones and a L/D = 27mm using a barrel temperature of 110-170°C (see Figure 1), with a screw speed of 50 rpm and a throughput of 100 g/h. The extruded material was cooled, dried and cut in small pellets.

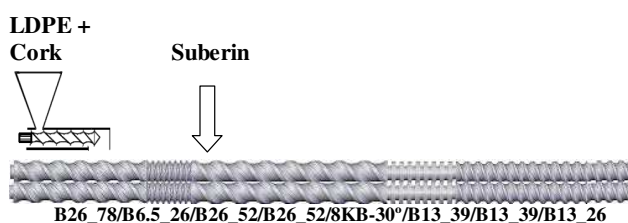


Figure 1. Screw configuration used to produce the cork-polymer composites.

The pelletized materials were compression moulded (P=1.42 MPa and T=140 °C) to produce boards with 3mm thick. Standard specimens were cut in a CNC machine to produce tensile bars according to the standard ISO 527-2.

## Methods

Cork suberin and birch outer bark suberin were obtained following the established methodologies on the literature. In short, the original raw material is refluxed in an alkaline alcoholic medium and subsequently neutralized and extracted with an organic solvent (chloroform for cork suberin and diethyl ether for birch bark suberin [11]).

For the compounding, cork suberin was used as obtained from the extraction procedure. Birch bark suberin was modified with maleic anhydride (herein after designated suberin maleic hemi ester) and the product was further reacted with 2-ethylhexanol (herein after designated suberin maleic 2-EH ester). Following procedures are described elsewhere [9, 12].

FTIR spectra were acquired on a Shimadzu IRPrestige-21 at a resolution of 4cm<sup>-1</sup> using the KBr tablet technique with a spectral range from 4400 to 400cm<sup>-1</sup>.

The density of the LDPE and developed composites was determined according to the standard ASTM D792 and their hardness (Shore A) are presented on table 2.

The morphology of the fractures of the developed cork-polymer composites was evaluated using a Leica-Cambridge S-360 (UK) scanning electron microscope (SEM). All the samples were sputter-coated with gold before being analyzed.

The mechanical performance of the LDPE and the prepared composites were evaluated under uniaxial tensile loading in a Instron 4505 universal testing machine (USA) at a crosshead speed of 5 mm min<sup>-1</sup>, relative humidity of 50% and temperature of 23 °C.

## Results and Discussion

The FTIR spectra of the coupling agents based on suberin are shown in figure 2.

The FTIR spectrum of the cork suberin shows it is composed of long-chain linear carbon molecules with hydroxyl [3500-3000cm<sup>-1</sup>], carboxyl [2500-2750cm<sup>-1</sup>; 1710cm<sup>-1</sup>] and ester moieties [1750cm<sup>-1</sup>].

Some differences are observed in the modified suberin spectra. In the suberin maleic 2-EH ester spectrum it is observed that the absorption bands related to the carboxyl groups are not present while the ones related to the ester bonds are well defined. This band configuration confirms the modification produced with the 2-ethylhexanol which reaction occurs through acylation of the previously maleated hydroxyl groups.

In the spectrum of suberin maleic hemi ester the band configuration shows the presence of both carboxyl and hydroxyl groups jointly with ester bonds. This is expected

as the anhydride will react with the carboxyl groups of the suberin acids resulting in one ester bond and giving rise to one new carboxyl group.

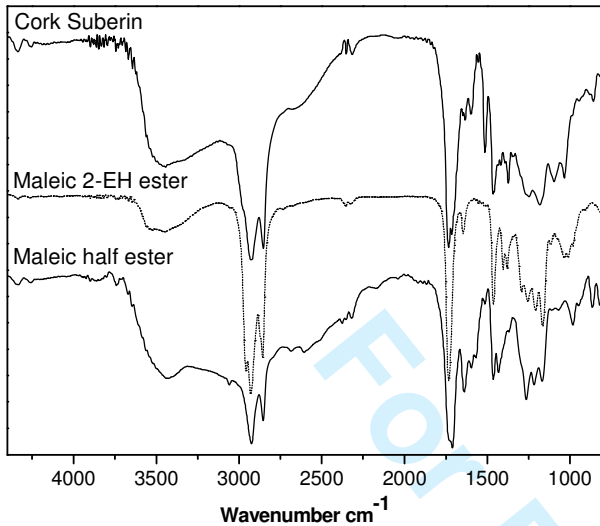


Figure 2. FTIR spectra of the suberin from cork and modified suberins from birch outer bark.

Table 2 presents the physical properties of the developed boards in terms of density and hardness after a two step processing.

Table 2. Physical properties of the cork-polymer composites and the LDPE matrix.

LDPE:Cork (wt%)	Coupling Agent	Density kg cm <sup>-3</sup>	Hardness Shore A
100 : 0	---	911.3 ± 1.3	91.5 ± 1.0
75 : 25	---	918.4 ± 6.0	92.0 ± 0.7
75 : 25	Suberin BB1	935.4 ± 2.7	91.1 ± 0.7
75 : 25	Suberin BB2	933.2 ± 2.4	91.1 ± 0.7
75 : 25	Suberin C	937.4 ± 2.1	91.7 ± 0.7

± Standard deviation.

The density of the matrix presents a small increase with the addition of cork. The increase is more evident when the 5 wt% of coupling agent is added. The grafting reaction induces an increase on the shear rate that compresses the cork granules. Consequently, a densification of the disperse phase occurs. In terms of hardness no significant changes were observed between the LDPE and the developed composites.

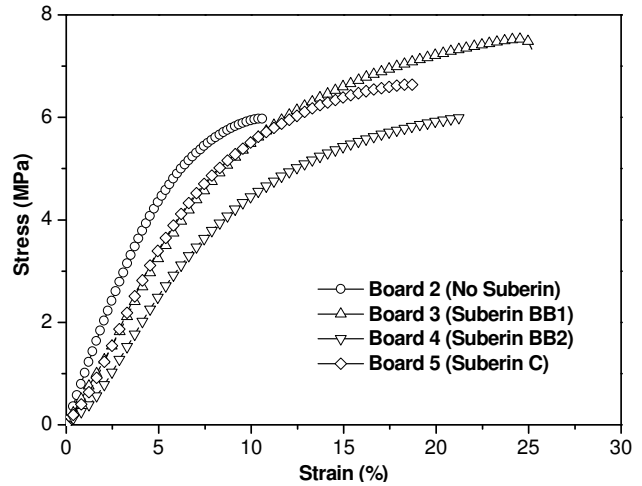


Figure 3. Stress-strain curves of the prepared composites.

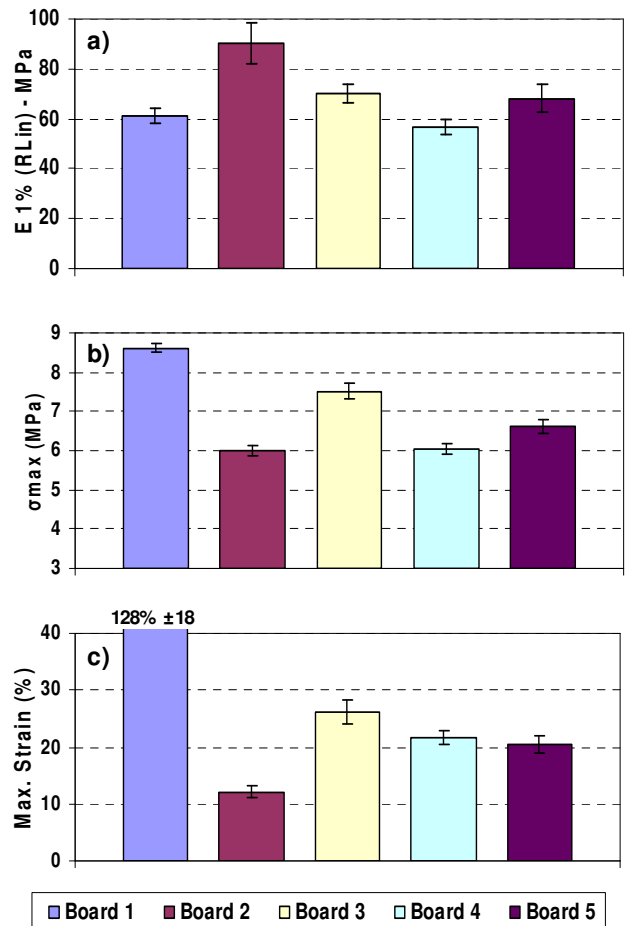


Figure 4. Elastic modulus (a) maximum stress (b) and maximum strain (c) of the LDPE and prepared composites.

In terms of mechanical performance, figure 3 shows the behaviour of the cork-polymer composites in terms of elastic modulus, maximum stress and maximum strain.

Figure 4 summarizes the mechanical properties of the composites under tensile loading.

From the mechanical properties presented in figure 4, it is clear that the cork phase promotes an increase in the elastic modulus, inducing higher rigidity to the composite. Similar results were observed in previous works when cork was used in 50wt% with similar thermoplastic matrixes [7]. Additionally, the maximum stress and strain reduces significantly. This is clearer for the maximum strain where a reduction to 10-25% is observed.

In the case of the modification of the composites with different suberin grafting agents (boards 3 to 5) the stiffness of the boards decrease and the maximum strain increases.

Comparing the maximum strain of the board prepared without functionalization (board 2) and using the different suberins as grafting agents (board 3-5) it is clear an increase on its value. These changes clearly indicate an improvement in the adhesion between cork and the polymeric phase, allowing additional strain to be supported by the composites without mechanical failure.

The increase on the cork-polymer adhesion is also observed in figure 4 by the increase of the composite strength mainly for the board 3, using Suberin BB1 and board 5 using Suberin C.

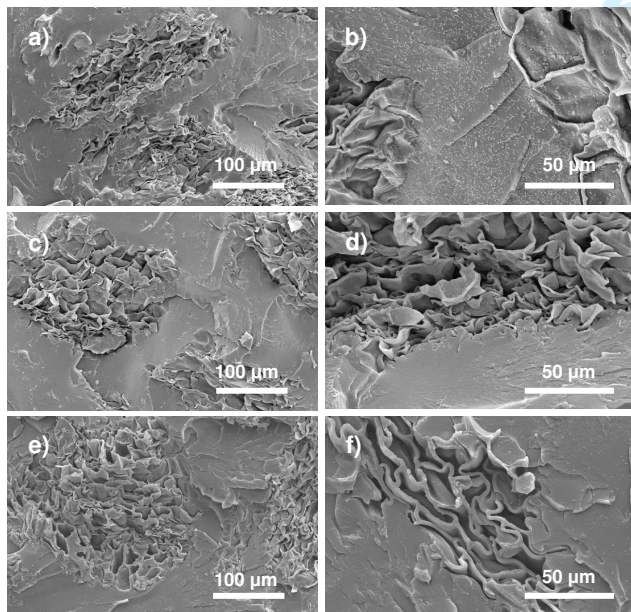


Figure 5. SEM micrographs of the prepared composites: Suberin BB1 (a,b) Suberin BB2 (c,d) and Suberin C (e,f).

The morphology of each of the composites was analysed by SEM. The boards obtained by compression moulding were cut using liquid nitrogen in order to observe the microstructure of the processed composites. Figure 5 presents representative SEM micrographs of fractured surfaces.

Analysing the SEM micrographs it is possible to observe a good adhesion between cork and the polymeric phase (for all the conditions). No relevant changes were observed between the non-grafted cork-based composite as it is presented in figure 5a and 5b. Similar result was obtained for the suberin-grafted composites materials (figure 5c, d, e and f). The combination of cork with LDPE promotes aesthetics properties and a non plastic touch to the final materials. Finally it was possible to observe the improvement of the mechanical properties applying reactive extrusion methodologies and suberin extracted from cork and birch bark as grafting agents.

## Conclusions

The developed cork-polymer composites present good distribution of the cork in the LDPE matrix and good aesthetic properties promoted by the cork granules.

The density of the composites increases when suberin grafting agents are used. In terms of hardness no significant variation was observed.

It is clear that the use of grafting agents based on suberin or modified suberin from cork or birch outer bark induces a significant increment in the mechanical performance of the final composites. It was observed a significant increase on the tensile strength resulting on a enhanced interface between cork and the polymeric phase. The composites with suberin are more flexible presenting a higher elongation at break and lower modulus indicating better dispersion of the cork phase on the matrix.

The novel cork-polymer composites demonstrated that this technological approach can be industrially appealing.

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Key Words: Polymer-matrix composites, Suberin, Grafting agent, Mechanical properties, Cork.