CORK-POLYLACTIDE COMPOSITES REINFORCED WITH POLYHYDROXYALKANOATES FOR ADDITIVE MANUFACTURING

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Keywords: Cork; Biodegradable matrices; Cork-Polymer Composites; Mechanical properties

Abstract

Cork-polymer composites (CPC) consisting of 85% wt of polymeric matrix and 15% wt. of cork powder residues were developed. The polymeric matrix was composed by PLA, PHA and different blends of PLA/PHA. Three different blend weight ratios of PLA/PHA were studied, namely 75:25, 50:50 and 25:75. CPC were prepared by melt compounding using a Brabender type mixer.
Mechanical analyses, including tensile and impact tests, as well as morphological analyses through scanning electron microscopy, were performed. When compared to composite only prepared with PLA (CPC 1), the addition of PHA to PLA promotes more ductile composites. Through impact tests, it was also observed the toughening effect of PHA when added to PLA. The CPC prepared with the blend PLA:PHA=75:25 revealed to have better mechanical performance among the ones prepared with the other blend ratios. From morphological analyses, it was perceived the miscibility of both polymeric matrices.

1. Introduction

The use of biodegradable polymers and natural fillers for the development of biocomposites have arose great interest in the composite science. Theirs biodegradation ability allows complete degradation in ambient conditions, without toxic compounds emissions. Polylactic acid (PLA) is one of the most promising biopolymers, since it is produced from annually renewable available resources and the industrial technology needed for its processing is relatively low cost, when compared to petrol-based plastics [1,2]. Similar to PLA, the use of polyhydroxyalkanoates (PHA) is an attractive alternative to petroleum-based polymers. PHA are biodegradable polyesters produced from bacterial fermentation of sugars or lipids. PHA can be used as PLA modifier to improve its ductility and flexibility. In addition, PHA has a similar chemical structure as PLA and the preparation of these PLA/PHA blends can result in performance improvements without compromising biodegradability and the need of using compatibilizers [3].

Cork is a natural, versatile and sustainable material, being an emblematic material in Portugal. It is the outer bark of the oak tree Quercus suber L. and its main chemical composition is based on suberin (33-50%), lignin (20-25%), polysaccharides (12-20%) and extractives (14-18%). It presents tiny hollow cells of hexagonal shape in closed-cell foam [4].
Cork-polymer composites (CPC) formulation is a viable solution for the utilization of cork powder industrial residues on the development of new materials based on biodegradable thermoplastic matrices. From cork stoppers industrial processing is generated about 30 % wt. of low granulometric cork powder residues [5]. The development of CPC filaments for Fused Filament Fabrication (FFF) can potentiate new design freedom solutions and products through the combination of cork unique

properties and aesthetics. FFF is an additive manufacturing (AM) technique based on an extrusion process, in which a thermoplastic filament is melted and selectively extruded via nozzle, deposited layer by layer [6].

2. Materials and methods

2.1. Materials

Cork powder from a Portuguese cork producer was used. The material was fractionated through sieving (Retsch, Germany) and it was kept the fraction retained in the sieve of 20 µm. The polymeric matrices used were an Ingeo™ Biopolymer PLA 4032D purchased from NatureWorks with a stereoisomer composition of 1.2-1.6 % D-isomer lactide and PHA from Goodfellow (PH326302).
All materials were dried in vacuum oven at 70 °C for 24 h before using to stabilize the moisture content.

2.2. Blends and CPC preparation

CPC formulation was made in a Brabender type internal mixer. Initially, PLA pellets were charged and melted at 190 °C, during 2 min at 40 rotations per minute (rpm), and then cork powder was added for additional 8 min. In the case of formulations prepared with PLA and PHA, both polymers were added together at the beginning. After compounding, the mixture was granulated in a Dynisco granulator into small granules. CPC formulations containing 85 %wt. of polymeric matrix and 15 %wt. of cork powder were developed, corresponding in terms of volume percentage of 45 and 55. The chemical compositions of the different blends of PLA/PHA are described in Table 1.

Table 1. Chemical composition of the developed CPC.

Samples	Cork Powder (wt. %)	PLA (wt. %)	PHA (% wt.)
CPC 1	15.0	85.0	-
CPC 2	15.0	63.8	21.2
CPC 3	15.0	42.5	42.5
CPC 4	15.0	21.2	63.8
CPC 5	15.0	-	85.0

2.3. Mechanical analyses

Samples tensile properties were measured on a universal testing machine Autograph AG-IS (Shimadzu) with a 10kN load cell. Tests were performed at a constant crosshead speed of 1 mm/min. All measurements were done at ambient temperature and the reported results are averaged values of at least six samples. Specimens were injected using a Babyplast 610P with the conditions presented in Table 2.

Table 2. Injection moulding conditions.

	Conditions
Temperature profile (°C)	160-170-180
Injection pressure (bar)	150
Second pressure (bar)	130

The mould cavity was designed considering the standard ISO 527-2:1996 for the preparation of specimens type IV.
Charpy impact tests were performed in a Ray Ran system. The impact velocity of testing of machine hammer was 2.9 m/s and the biggest impact energy of the striker was set as 0.5 J. Un-notched specimens with a dimension of 20 mm × 5 mm × 2 mm (L×W×T) were used.

2.4. Morphological analyses

Morphological studies of samples were carried out using a SEM Hitachi S4100. Fracture surface after tensile tests were analysed. Then, they were assembled on aluminium stubs and subsequently fixed in a sputter coater chamber (Polaron E 5000). Samples were sputtered with Au/Pd target for 2 minutes at 12 mA in order to avoid electrostatic charging during SEM analyses.

3. Results and discussion

3.1. Mechanical behaviour
3.1.1 Tensile tests

Figure 1 illustrates the granulated CPC 5 and the composite after injection molding along with the pure PHA biopolymer. The remaining CPC specimens presented a similar aspect.

(a) **(b)**

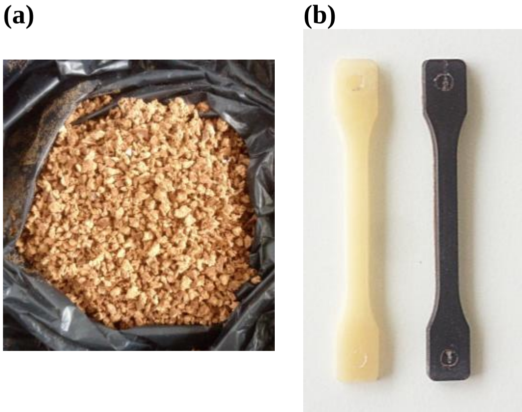


Figure 1. (a) CPC 5 granules; (b) Injected specimens for tensile tests: pure PHA and CPC 5.

The stress-strain curves of pure matrices and the corresponding CPC (CPC 1 and CPC 5) are presented in Figure 2. The tensile properties of these materials and its standard deviations, including tensile strength, maximum strain and Young modulus are given in Table 2. Pure PLA exhibited higher tensile strength when compared to pure PHA, but also showed a brittle behaviour, i.e. a lower maximum strain at break. PHA revealed an elastomeric behaviour given by a lower Young modulus and a higher strain at break.

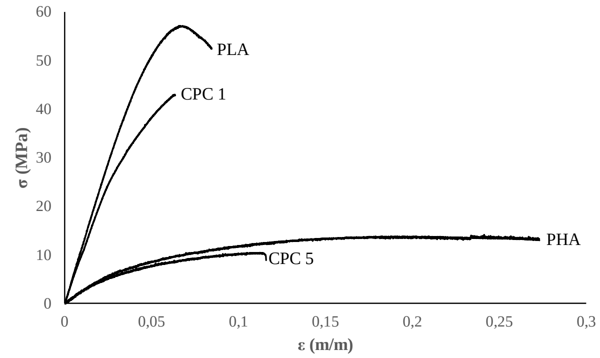


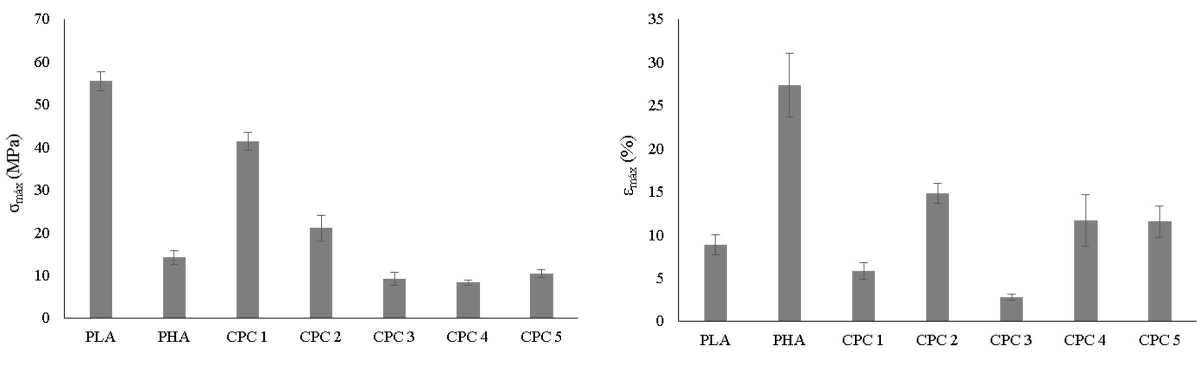
Figure 2. Tensile stress-strain curves of pure PLA, PHA, CPC 1 and CPC 5.

Table 2. Tensile properties of pure PLA, PHA, CPC 1 and CPC 5.

Samples	$\sigma_{máx}$ (MPa)	$\varepsilon_{máx}$ (%)	E (MPa)
PLA	55.4 (2.2)	8.8 (1.2)	1110.9 (40.3)
PHA	14.1 (1.6)	27.3 (3.7)	227.4 (2.9)
CPC 1	41.3 (2.2)	5.8 (1.0)	1024.1 (18.9)
CPC 5	10.4 (0.9)	11.5 (1.8)	210.2 (2.9)

The addition of cork led to the reduction of tensile strength for both matrices. CPC 1 presented a 25% reduction of tensile strength against the 26% shown by CPC 5. This reduction can be explained by the lower mechanical properties of cork as compared with the pure matrices. Other mechanisms can also influence the mechanical behaviour of CPC, namely (1) the type of matrix; (2) the compatibility between polymeric matrix and cork and (3) cork content [7]. A compatible polymeric matrix and filler is crucial to obtain a composite with sufficient interfacial adhesion between both materials. The maximum strain also decreased when cork was added. In this case, the elasticity of cork was not observed in both biocomposites (CPC 1 and CPC 5). It was observed a decrease in Young modulus when cork was present. This can be attributed to the lower stiffness and to the foamed cork structure, which exhibits a lower Young modulus when compared to neat biopolymers.
Three different polymeric blends and correspondent CPC were prepared based on PLA and PHA (CPC2, CPC3 and CPC 4) in order to overcome the brittleness of PLA and CPC 1 and to take advantage of cork elasticity. Tensile tests were also applied to these composites to evaluate dispersion and adhesion of PHA into PLA and the adhesion between cork particles and the polymeric blends (Figure 3).

(a) **(b)**



(c)

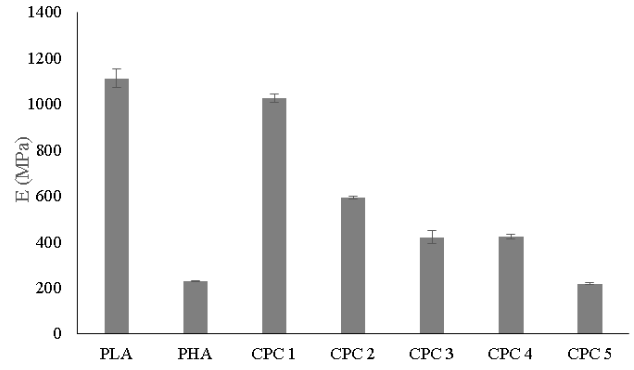


Figure 3. Tensile properties of all samples: (a) tensile strength, (b) maximum strain and (c) Young modulus.

From Figure 3(b), it can be seen that the addition of PHA to PLA resulted in the increase of maximum strain for CPC 2 and CPC 4 when compared to CPC 1. It can be assumed a reduction of the inherent PLA brittleness. At this point, it is important to remember that CPC 2 presents a ratio of PLA to PHA equal to 75%/25%, while CPC 4 has the opposite ratio of 25%/75%. CPC 3 has the half amount of both polymers. However, on the other hand, tensile strength and Young modulus decreased when PHA was added to the matrix. This can be associated with the lower tensile strength and Young modulus of the neat PHA, as displayed in Table 2.

3.1.2 Impact tests

Impact tests were performed and the impact strength results are presented in Figure 4. It is visible that when PHA is present in the matrix, the composites (CPC 2, CPC 3 and CPC 4) possess a higher impact strength when compared to CPC 1.

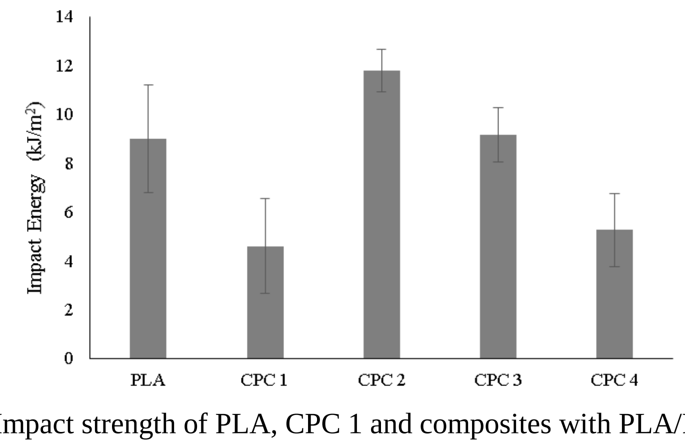


Figure 4. Impact strength of PLA, CPC 1 and composites with PLA/PHA blends.

These results can indicate a toughening effect of PHA to the PLA matrix. It is also visible that, as the amount of PHA present in the matrix increases, the mechanical behaviour became closer to CPC 1. The blend with higher impact resistance is equal to 75%/25% wt.% (PLA/PHA). This blend also exhibited higher tensile strength, maximum strain and Young modulus when compared to CPC 3 and CPC 4.

3.2. Morphological behaviour

PLA/PHA blends morphology and cork powder distribution in those blends were analysed by SEM. In Figure 5 it is represented the morphology of the blend with 50% of PLA and PHA along with the correspondent composite (CPC 3).

(a) (b)

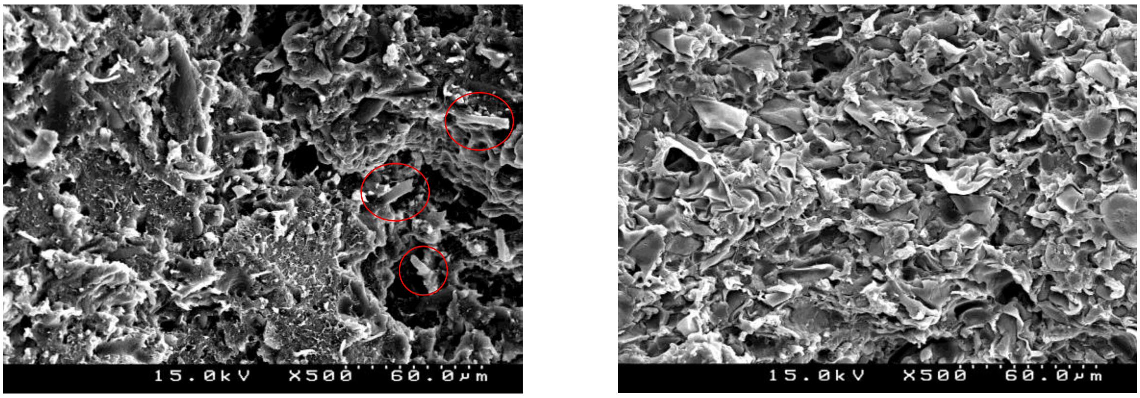


Figure 5. SEM images of: (a) PLA/PHA (50%) blend and CPC 3.

From Figure 5(a), it is visible a good dispersion of both polymers and the elastic behaviour of PHA. As seen in the areas surrounded by the red circles, the PHA particles presented plastic deformation (ductile behaviour) as a result of the tensile trial. In Figure 5(b) it can be seen that the polymeric matrix recovered totally the cork powder particles.

4. Conclusions

This work showed that a more elastic behaviour was obtained when PHA was added to PLA. The composites prepared with PLA/PHA blends exhibit a more ductile behaviour when compared to CPC 1. In addition, the impact strength was also improved when PHA was added to the matrix, revealing the toughening effect of PHA. Morphological analyses revealed a good dispersion of PHA into PLA and a good dispersion of cork powder particles into the polymeric matrices.
The combination of cork powder residues into polymeric matrices can led to the development of sustainable composites. The use of such composites on the development of filaments for FFF technology can bring new design solutions and products.

Acknowledgments

This work was supported by COMPETE 2020 – Programa Operacional Competitividade e Internacionalização within TT@ESAN project (NORTE-01-0246-FEDER-000001).

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