



# Mechanical behavior of polylactic acid/polycaprolactone porous layered functional composites



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## ABSTRACT

Biopolymeric porous devices exhibiting graded properties can play a crucial role in several fields, such as tissue engineering or controlled drugs release. In this context, the gradient of a specific property can be achieved by developing porous laminates composed by different types of materials. This work presents for the first time a multi-phasic porous laminate based on polycaprolactone (PCL) and polylactic acid (PLA) prepared by combining melt mixing, compression molding and particle leaching. All the materials were characterized from a morphological and a mechanical point of view.

The results put into evidence the possibility to tune and to predict the mechanical properties by controlling the process parameters together with geometrical features.

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## 1. Introduction

Over the past decades there has been a growing interest toward polymeric materials obtained by renewable sources and with potential biodegradability or compostability to reduce the overall environmental impact [1–10].

In particular, porous biopolymeric devices with engineered chemical, physical and mechanical properties can play a crucial role in biomedical fields, such as tissue engineering or controlled drugs release [11–14].

The development of porous laminates composed by different kinds of biopolymer allow controlling these parameters by tuning the properties of each single layer and by eventually assembling them into a single device [15–17]. This feature is of main concern for interface tissue engineering (ITE), a rapidly developing field that aims to the production of structures designed either to repair or to regenerate diseased or damaged zones at the interface of different types of tissue. Interface tissues are more complex than the homogeneous ones because of the presence of multi-phasic and/or anisotropic structures that gradually change from one tissue to another [11,16,17]. The desire to mimic these natural structures has

driven biomechanical engineers to develop custom-made bio-inspired materials with mechanical properties similar to natural tissues [15,18,19]. Usually, porous multiphasic laminates are developed by 3D printing, suturing, glue or press fitting two/three layers, even if the best challenge is achieving a well joint monolith presenting functionally graded properties [17,20–28].

In this context, synthetic biodegradable polymers used in tissue engineering or in other biomedical applications include polylactic acid (PLA) and polycaprolactone (PCL).

PCL is a semicrystalline thermoplastic polymer with low melt temperature, thus enabling the possibility to be easily melt processed [29]. Hydrolytically labile ester linkages are responsible for its degradation although slow (2–3 years) [30]. In addition, it is a ductile polymer at room temperature, with a relative low elastic modulus [31,32].

PLA melting point is higher if compared with that of PCL, although it presents a fragile behavior with high elastic modulus and low elongation at break. For this reason, this latter is preferred for bone repair, whereas the former is usually chosen for the cartilage regeneration [33,34].

In this work, we developed for the first time a chemically graded laminate porous device composed by a PLA-based core and a PCL-based shell in form of monolith.

The novelty of this work can be principally ascribed to the preparation route of the multiphasic porous laminates, conducted

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by melt. In fact, the devices were fabricated by combining melt mixing, compression molding and particulate leaching. The principal advantages of this method lay in the absence of organic solvents during the preparation and in the possibility to easily control and predict both porosity (void-to-total volume ratio) and pore size, by tuning the amount and the dimension of porogen particles, respectively.

The relative volume ratio was controlled by the thickness of each layer in order to investigate the correlation between the preparation, the morphology and mechanical properties of three-layered laminate based on PCL and PLA. In particular, the study of mechanical properties of porous bio-laminates were investigated as a function of the relative contribution of the layers to the whole laminated device.

## 2. Materials and methods

The PLA used in the frame of this work was a sample purchased by Natureworks (PLA 2002D, density 1.24 g/cm<sup>3</sup>) while poly(ethylene glycol) (PEG), Mw = 2000 Da, and PCL, Mw = 80,000 Da, were purchased by Sigma Aldrich, as well as NaCl (purity > 99%, d = 2.17 g/cm<sup>3</sup>). Little amounts (less than 1%) of green PLA filament (Matter Hackers, USA) was used as a masterbatch in order to stain and distinguish the PLA phase from PCL.

In order to avoid hydrolytic scission during processing, all the materials were vacuum dried overnight [35]. More in detail, for each polymer the drying temperature was kept below its own glass transition temperature: i.e. 90 °C for PLA, 25 °C for PEG and 40 °C for PCL. NaCl was dried at 105 °C to ensure the highest drying degree.

The NaCl was sieved in the range of 90–110 μm to obtain homogeneous pore size distribution.

### 2.1. Laminates fabrication

Porous laminates were prepared by melt mixing as described in our previous works [12,13]. In brief, PLA (or PCL), PEG and NaCl, with weight percentage composition of respectively 20/5/75, were fed to a batch mixer (Plasticorder PLE-330 Brabender, Germany). The temperature was set to 190 °C in the case of PLA and to 100 °C for PCL, the rotor speed was 64 rpm, the mixing time was around 10 min, in order to ensure achieving a constant value of torque. Thereafter, the samples were fed out and rapidly cooled in liquid nitrogen. The materials collected were ground and compression-molded in a laboratory press (Carver, USA) at 190 °C for PLA and 100 °C for PCL at 180 bar in appropriate cylindrical molds with a diameter of 10 mm and different thickness as summarized in Table 1. The pre-compressed monolayers were finally assembled by further compression molding at 130 °C at 180 bar, in order to obtain the final laminates.

Finally, the porogen part of the blends (NaCl and PEG) was removed by selective leaching in demineralized water for 5 h. The resulting structure were then allowed to dry for 12 h at room temperature. Laminates are schematically represented in Fig. 1.

**Table 1**

Sample code of the mono-phasic and multi-phasic porous laminates as a function of the thickness of each layer.

Sample code	PCL Layer (mm)	PLA Layer (mm)	PCL Layer (mm)
PCL	3	0	0
LAM_0.5	1.25	0.5	1.25
LAM_1	1	1	1
LAM_2	0.5	2	0.5
PLA	0	3	0

### 2.2. Morphological analysis

The morphology of the laminates was evaluated by scanning electron microscopy (SEM), by using a Phenom Pro x, Phenom-World (The Netherlands). The samples, cryo-fractured in liquid nitrogen, were attached on an aluminum stub using an adhesive carbon tape and then sputter coated with gold (Sputtering Scancoat Six, Edwards, UK) for 90 s under argon atmosphere before imaging to avoid electrostatic discharge under the electron beam.

### 2.3. Laminate pore size

Pore size analysis was carried out using a MATLAB (MathWorks Inc., MA, USA)-based software previously described [36]. The custom-made software is able to accomplish the segmentation of images containing pores of any geometry in a semi-automatic way, and it converts the digital images into binary form, thus calculating the pores area distribution (PAD); the software reports the percentage of the total area occupied by the pores having diameters in a given interval. The red, green and blue colors are assigned to three increasing intervals of the size of the pores.

### 2.4. Porosity, connectivity, water uptake

The parameters related to porous properties of the laminate were obtained by gravimetric measurement. Theoretical porosity, porosity and connectivity were calculated according to the following expressions [37]:

$$\text{Porosity}_{th}(\%) = \frac{V_{porogen}}{V_{total}} \times 100\% \quad (1)$$

$$\text{Porosity}(\%) = \left(1 - \frac{\rho_{laminate}}{\rho_{matrix}}\right) \times 100 \quad (2)$$

$$\text{Connectivity} = \frac{(m_0 - m_{dry})}{m_{NaCl} + m_{PEG}} \times 100\% \quad (3)$$

Where,  $m_{NaCl}$ ,  $m_{PEG}$  are the theoretical weights of NaCl and PEG, respectively, by assuming a homogeneous mixture.  $m_0$  and  $m_{dry}$  are, respectively, the weights of laminate before leaching and after leaching and drying. The density ( $\rho$ ) of NaCl, PEG, PLA and PCL are respectively 2.16 g/cm<sup>3</sup>, 1.12 g/cm<sup>3</sup> and 1.24 g/cm<sup>3</sup> and 1.14 g/cm<sup>3</sup>.  $\rho_{laminate}$  is the apparent density of the laminate.

The theoretical porosity was calculated by assuming the complete solvation of all the porogen agents (PEG plus NaCl). The real porosity was calculated as the reciprocal of the ratio between the apparent densities of the laminate and of the non-porous polymeric material, by using expression (2). It expresses the ratio between the empty volume and the overall volume of the laminate (empty + full). The connectivity is a parameter indicating the continuity of the porogen phases and was assessed by using Eq. (3), i.e. by taking into account the weight variation of the laminate before and after the porogen agent extraction, with respect to the overall weight of porogen compounds.

The bulk water absorption (water uptake) was calculated as the difference between the weight of the devices filled by water ( $m_{wet}$ ) and the weight after drying in fume hood, according to Eq. (4):

$$\text{Water uptake}(\%) = \left(\frac{m_{wet} - m_{dry}}{m_{dry}}\right) \times 100\% \quad (4)$$

The percentage of pores filled by water was evaluated as the

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