

3rd International Conference on Tissue Engineering, ICTE2013

## Thermal stability of PCL/PLA blends produced by physical blending process

Tatiana Patrício, Paulo Bártolo\*

*Centre for Rapid and Sustainable Product Development, Polytechnic Institute of Leiria, Centro Empresarial da Marinha Grande, Rua de Portugal - Zona Industrial, 2430 - 028 Marinha Grande - PORTUGAL*

---

### Abstract

The poly  $\epsilon$ -caprolactone (PCL) and poly lactid acid (PLA) were used for prepared blends with different percentage. PCL/PLA blends (70/30 wt% and 50/50 wt%) were prepared by physical blending process, called solvent casting. These blends were analysed by morphological, thermal and rheological tests in order to evaluate the miscibility and thermal stability of the polymers and their blends, important characteristics to apply in scaffold fabrication. The Simultaneous Thermal Analyser (STA) demonstrated two separated melting peaks in the blends, which show the immiscible polymers. The blends surface were analysed through Scanning Electron Microscope (SEM) and the results shows the presence of droplets in the blends surface, characteristic of an immiscible polymer. The results of rheological measurements present a good thermal stability of the polymers and their blends.

© 2013 The Authors. Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Selection and peer-review under responsibility of the Centre for Rapid and Sustainable Product Development, Polytechnic Institute of Leiria, Centro Empresarial da Marinha Grande.

*Keywords:* Biodegradable polymers; blends; physical blending process; extrusion process; miscibility; thermal stability.

---

---

\* Corresponding author. Tel.: +351 244 569 441; fax: +351 244 569 444.  
*E-mail address:* paulo.bartolo@ipleiria.pt

## 1. Introduction

Biodegradable polymers have interesting properties for use in various areas, such as tissue engineering, drug delivery, powder coating and others. Some researchers have been focused on aliphatic polyester including PCL and PLA [1]. PCL is a semi-crystalline biodegradable linear aliphatic polyester susceptible to undergo autocatalyzed bulk hydrolysis and slow degradation [2]. PCL has a low melting point ( $\approx 60^\circ\text{C}$ ) and glass transition temperature ( $\approx 60^\circ\text{C}$ ) [3]. PLA, is an aliphatic polyester, has higher melting temperature ( $\approx 160^\circ\text{C}$ ) and glass transition temperature ( $\approx 60^\circ\text{C}$ ) [4]. At room and body temperatures PCL presents low tensile modulus and high elongation at break while PLA shows high modulus and low elongation at break due to it is higher glass transition temperature [5].

PCL/PLA blends have impact strength properties suitable for temporary implants. However its blends have poor mechanical properties due to the macrophase separation of the two immiscible components and to the poor adhesion between the phases [6, 7].

In terms of biomaterials applications for tissue engineering, there are many additive manufacturing technologies that are able for fabricated 3D structures. One of the interesting technologies is extrusion, where the polymers are exposed to a heating process, which is relevant to investigate thermodynamic and viscoelastic properties of the biomaterials.

The main aim of this research work is to investigate the morphological, thermal and rheological properties of PCL/PLA blends (70/30 wt% and 50/50 wt%), in order to observe the miscibility and evaluate the viscoelastic properties. These tests were also performed to evaluate if the time and temperature to which the materials are exposed in the extrusion process influence the thermal stability of the materials. PCL and PCL/PLA blends were also used for produced scaffolds, through an extrusion process, Biocell Printing system, home-made equipment.

## 2. Experimental Procedure

### 2.1. Materials

The PCL used in this research work was Capa 6500 (Perstorp, UK), and the PLA was PLA 2002D (Cargill Down, USA). Chloroform, from Sharlau, Spain, was used to prepare PCL/PLA blends.

#### 2.1.1. Physical blending process

The PCL/PLA blends (70/30 and 50/50 wt%) were prepared using the solvent casting method. PCL and PLA were solubilized in chloroform (in different glass containers) kept under stirring (300rpm) during 8 hours and once completely dissolved, both solutions were mixed, in order to produce the PCL/PLA blends. In both cases, the films were cut in small pieces, and placed into desiccators to avoid material degradation.

### 2.2. Morphological characterisation

The surface morphology of PCL/PLA blends (70/30 and 50/50 wt%) and PCL/PLA scaffolds (70/30 and 50/50 wt%) were studied through the SEM analysis, using the FEI QUANTA 600F system (FEI Company, USA).

### 2.3. Thermal characterisation

Thermal properties were determined using the Simultaneous Thermal Analyzer, STA 6000 system (PerkinElmer, USA), such as melting temperature ( $T_m$ ), glass transition temperature ( $T_g$ ), enthalpies of fusion ( $\Delta H_m$ ) and degradation temperature ( $T_d$ ). Samples of approximately 10mg were placed into ceramic pans and the tests were performed in a dry nitrogen atmosphere (flow rate of  $20\text{mLmin}^{-1}$ ). Samples were submitted a thermal cycle – 1 minute in  $30^\circ\text{C}$  and heat from  $30^\circ\text{C}$  to  $600^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ .

Melting temperatures ( $T_m$ ) were obtained at the peak of the melting endotherms, while the glass transition temperatures ( $T_g$ ) were taken at the inflection point of the specific heat capacity. The enthalpies of fusion ( $\Delta H_m$ ) were obtained from the areas under the peaks. Indium and silver samples were used as calibration standards. The crystallinity degree ( $X_c$  (%)) was determined according to the following equation [5]:

$$X_c (\%) = \left( \frac{\Delta H_m - \Delta H_c}{w \Delta H_m^0} \right) \times 100 \quad (1)$$

where,  $\Delta H_m$  is the experimental melting enthalpy,  $\Delta H_c$  is the cold crystallization enthalpy,  $w$  is the weight fraction of material. Additionally, it was assumed for  $\Delta H_m^0$ , the enthalpy of melting of 100% crystalline PLA, the value of 106 J/g and  $\Delta H_m^0$  enthalpy of melting of 100% crystalline PCL the value of 139 J/g [2, 8].

#### 2.4. Rheological measurements

The rheological properties of the pure polymers and their blends were determined in the Paar Physica MCR300 Rheometer using circular discs (diameter=25mm and thickness=1mm). The following types of tests were performed on the samples: the thermal stability of the pure polymers and blends were confirmed by dynamic time sweep tests, at 80°C (PCL) and 180° (PLA and PCL/PLA blends), which were the same temperature used in the extrusion process.

#### 2.5. Scaffolds Fabrication

PCL and PCL/PLA scaffolds were produced using the *BioCell Printing* system (Fig. 1), being developed by the Centre for Rapid and Sustainable Product Development of the Polytechnic Institute of Leiria (Portugal). This is a novel additive biomanufacturing system that enables the integration and synchronization of the different stages of production and culture of 3D matrices with reduced manual intervention [9]. Depending on the chosen strategies (acellular or cellular scaffolds), a precision robotic arm transfers the 3D scaffolds between the scaffold fabrication zone to sterilization zone, after the scaffolds are homogenously seeded with cells using a robotic dispenser (cell deposition zone), and finally the scaffolds are cultured *in vitro* under dynamic conditions in the bioreactor. The integration of the different stages into a single device significantly reduces the risk of contamination and increases productivity and the possibility of direct clinical application [10].

All scaffolds were produced using a lay down pattern of 0/90, pore size of 350  $\mu\text{m}$  and slice thickness of 280  $\mu\text{m}$ . PCL was processed at 80°C while PCL/PLA was processed at 180°C. In both cases the deposition velocity was 20 mm/s.

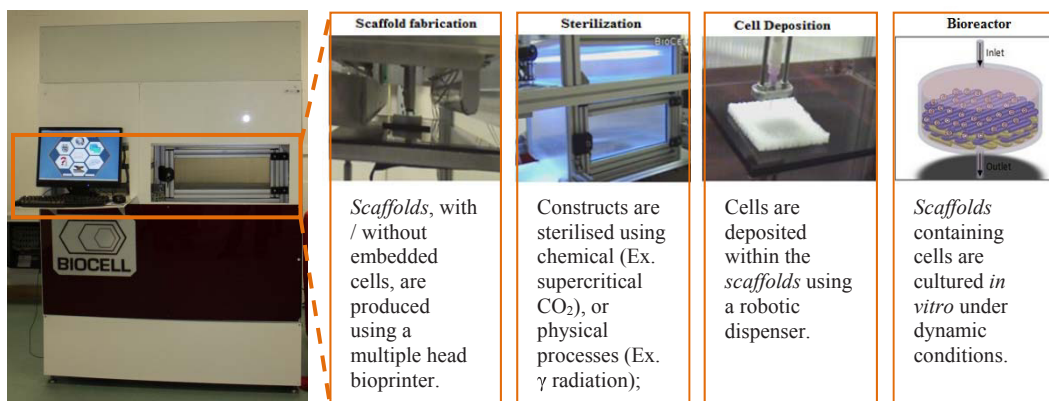


Fig. 1. Biocell Printing system [11].

### 3. Results and Discussion

This research work presents a morphological and thermal analysis, in order to observe the miscibility of the blends. The rheological test was performed in polymers and in blends, to evaluate the thermal stability. These tests were important to observe the viscosity behaviour of the polymers and blends during the extrusion process.

Fig. 2 presents the SEM micrographs of PCL/PLA blends with different percentages (a) PCL/PLA (70/30 wt%); (b) PCL/PLA (50/50wt%), in order to evaluate the morphological surfaces of the blends. In most cases, the minor component of the blend forms the dispersed phase, whereas the major component forms the continuous phase. The blend morphologies can be controlled by some parameters such as, the nature of the polymers (interfacial energy and viscosity ratio), the composition of the blend as well as the processing conditions. Fig. 2a) show a smooth surface and small drops into the material and in the Fig. 2b) the blend present a surface with homogeneously dispersed droplets of materials. However, by increasing the addition of PLA into the blends, the structure presents more droplets, caused by the coalescence phenomena. Basically, the coalescence phenomena, is a process in which two or more particles collide and physically merge into one particle. Two classes of coalescence play critical roles in the development of morphology during the processing of immiscible polymer blends [12].

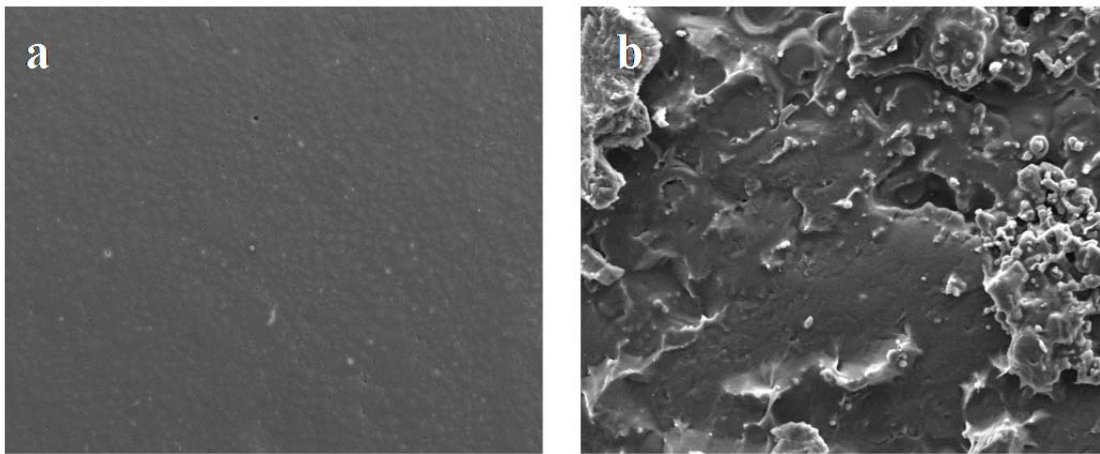


Fig. 2. Morphological surfaces of blends. a) PCL/PLA (70/30wt%) blend; b) PCL/PLA (50/50wt%) blend.

As a conclusion, the results obtained by the morphological analysis show the immiscible blends, but some authors [13, 14] refers that this phenomena can be reduced with various experiments, such as block or graft copolymers.

The thermal analysis was another test allowing to investigate the miscibility of the blends. The values of  $T_g$ ,  $T_m$ , enthalpy, crystallinity level and  $T_d$ , of the materials are illustrated in Table 1. Results show that PCL melting temperature is  $56,9 \pm 0,2$  °C, and the crystallinity is 47,9%. The PLA melting temperature is  $153,3 \pm 0,1$ °C, the  $T_g$  is  $58,5 \pm 0,8$  °C and the crystallinity is 14,7%. Regarding these blends, the Table 1 displays the values for two independent melting peaks, one dominant endothermic peak corresponding to PCL (around 56°C) and a smaller peak corresponding to PLA (around 150°C), which suggests that PCL and PLA are not miscible. It is also possible to observe that these blends do not present the  $T_g$  peak of PLA, because this temperature is masked by the melting region of the PCL (Yeh *et al.*, 2009). Table 1 also indicates the degradation temperature of the polymers and PCL/PLA blends. Results show that the degradation temperature ( $T_d$ ) varies between 300°C and 400°C, showing that no degradation events occur during the scaffold fabrication, since the maximum temperature was 180°C. The degradation profiles of PCL/PLA blends show two degradation stages, corresponding to the PCL degradation ( $\approx 380^\circ\text{C}$ ) and PLA degradation ( $\approx 320^\circ\text{C}$ ).

Table 1. Thermal properties of non-processed materials.

Material	T <sub>g</sub> (°C) (PLA)	T <sub>m</sub> (°C) (PCL)	ΔH <sub>m</sub> [J/g] (PCL)	T <sub>m</sub> (°C) (PLA)	ΔH <sub>m</sub> [J/g] (PLA)	(X <sub>c</sub> %) (PCL)	(X <sub>c</sub> %) (PLA)	T <sub>d</sub> (°C)
Non-processed PCL	---	56.9±0.2	66.53±15.3	---	---	47.9	---	375.48
Non-processed PLA	58.5±0.8	---	---	153.3±0.1	13.7±1.6	---	14.7	329.60
Non-processed PCL/PLA (70/30 wt%)	---	70.31±0.73	75.09±3.78	152.13±0.4	7.12±0.18	54.2	6.7	PLA: 334.14 PCL: 376.83
Non-processed PCL/PLA (50/50 wt%)	---	56.7±0.9	32.1±10.3	148.7±0.4	19.4±2.7	23	18.3	PLA: 325.20 PCL: 390.17

Rheological measurements are an illustrative method to investigate the thermal stability of the polymers and the blends. This work is particularly relevant considering that polymers are subjected to high temperatures, during the scaffold fabrication process.

Firstly, Fig. 3 (a and b) shows the thermal stability of PCL at 60°C and PLA at 180°C, both during 3600s. In the case of the PCL, the results shows the elastic modulus ( $G'$ ) is around 2100Pa, during all of experiment. For the PLA, initially the test of the elastic modulus present a decreased from  $\approx 600$ Pa to 100Pa, after the value stabilized in 100Pa, probably due to the intermolecular forces. Comparing both figures, it is possible observed that whenever the temperature increases the material have a decrease in  $G'$ , because of the materials properties and the less intermolecular forces into the structure. Fig. 3c presents the thermal stability of the blends: PCL/PLA 70/30wt% and PCL/PLA 50/50wt%. Comparing the values of PCL and PLA elastic modulus with the values of the blends, it is possible observed that the elastic modulus decrease and the values are similar with the PLA elastic modulus. Comparing the elastic modulus of both blends, it is possible observe that the elastic modulus is around 100Pa. This result show that the increase of PLA percentage into the PCL structures do not influence the elastic modulus. Results also suggest that PCL, PLA and both PCL/PLA blends (70/30 wt% and 50/50 wt%) present a linear viscoelastic behaviour, ie, a good thermal stability.

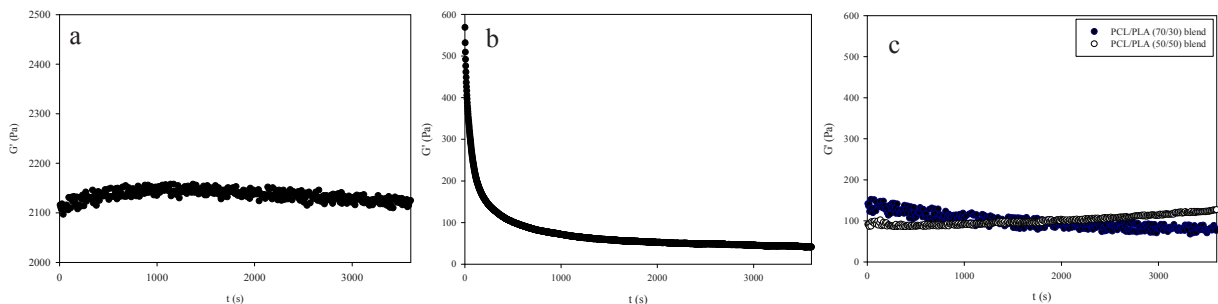


Fig. 3. Thermal stability of PCL at 60°C (a); thermal stability of PLA at 180°C (b); thermal stability of PCL/PLA blends at 180°C (c).

The Biocell Printing system allows to produce PCL and PCL/PLA scaffolds (with blends 70/30 wt% and 50/50 wt%). Fig.4 presents the PCL, PCL/PLA 70/30wt% and PCL/PLA 50/50wt% scaffolds. SEM micrographs represent the different scaffolds and a well-defined internal geometry and pore interconnectivity for all scaffolds.

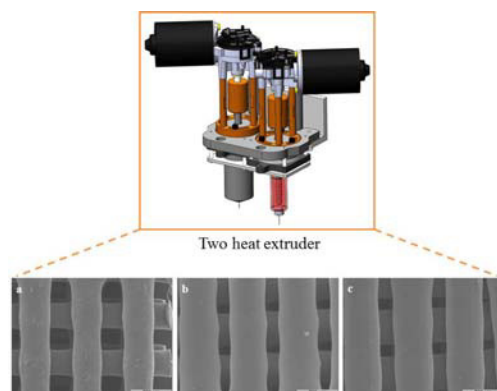


Fig. 4. Scaffolds fabricated by Biocell Printing system. a) PCL scaffold; b) PCL /PLA 70/30wt% scaffolds; c) PCL/PLA 50/50wt% scaffolds.

#### 4. Conclusion

This research work presents two polymers PCL and PLA, which were used to produce blends with different ratios of polymers, through a solvent casting process. It is possible to conclude that PCL and PLA are immiscible polymers, which is demonstrated by the morphological and thermal tests. Rheological tests show that PCL, PLA and blends have a linear viscoelastic behaviour, i.e., good thermal stability, an important property for polymers in the extrusion process.

#### Acknowledgements

This work was supported by the Portuguese Foundation for Science and Technology through the projects PTDC/EME-PME/098037/2008 and Pest-OE/EME/UI4044/2011.

#### References

- [1] Noroozi N, Thomson JA, Noroozi N, Shafer LL and Hatzikiriakos SG. Viscoelastic behaviour and flow instabilities of biodegradable poly( $\epsilon$ -caprolactone) polyester; *Rheol Acta* 2012; 51: 179-192.
- [2] Woodruff MA and Hutmacher DW. The return of a forgotten polymer - Polycaprolactone in the 21st century; *Prog Pol Sci.* 2010; 35: 1217-1256.
- [3] Puppi D, Chiellini F, Piras AM and Chiellini E. Polymeric materials for bone and cartilage repair; *Prog Pol Sci.* 2010; 35: 403-440.
- [4] Garlotta D. A literature review of Poly(Lactic Acid); *J Pol Env.* 2001; 9: 63-83.
- [5] Lopez-Rodriguez N, Lopez-Arraiza A, Meaurio E and Sarasua JR. Crystallization, Morphology and Mechanical Behavior of Poly(lactide)/Poly( $\epsilon$ -caprolactone) blends; *Pol Eng Sci.* 2006; 46: 1299-1307.
- [6] Dell'Erba R, Groeninckx G, Maglio G, Malinconico M and Migliozi A. Immiscible polymer blends of semicrystalline biocompatible components: thermal properties and phase morphology analysis of PLLA/PCL blends; *Polymer.* 2001; 42: 7831-7840.
- [7] Maglio G, Malinconico M, Migliozi A and Groeninckx G. Immiscible Poly(L-lactide)/Poly( $\epsilon$ -caprolactone) Blends: Influence of the Addition of a Poly(L-lactide)-Poly(oxyethylene) Block Copolymer on Thermal Behavior and Morphology; *Macrom Chem Physics.* 2004; 205: 946-950.
- [8] Weir, N. A., Buchanan, F. J., Orr, J. F., Farrar, D. F., Boyd, A. Processing, annealing and sterilisation of poly-L-lactide; *Biomaterials.* 2003; 25(18): 3939-3949.
- [9] Bártole P, Domingos M, Gloria A and Ciurana J. BioCell Printing: Integrated Automated Assembly System for Tissue Engineering Constructs; *CIRP Annals Manuf Tech.* 2011a; 60: 271-274.
- [10] Bártole P, Domingos M, Patrício T, Cometa S and Mironov V in: *Advances on Modeling in Tissue Engineering*, Edited by P. Fernandes and P.J. Bártole, Springer, 2011b.
- [11] Patrício T, Gloria A., Bártole P. PCL and PCL/PLA scaffolds for bone tissue regeneration. *Advanced Material Research*; 2012; 683 (2013): 168-171.
- [12] Lyu S, Bates FS and Macosko CW. Coalescence in polymer blends during shearing; *AIChE J.* 2000; 46: 229-238.
- [13] J.M. Willis and B. D. Favis. Processing-morphology relationships of compatibilized polyolefin/polyamide blends. Part I: The effect of an ionomer compatibilizer on blend morphology; *Polym Eng Sci*; 1988; 28: 1416.
- [14] G. Serpe, J. Jarrin and F. Dawans: *Polym Eng Sci* (1990), Vol.30, p.553.