DEVELOPMENT OF A BIOCOMPATIBLE AND BIORESORBABLE YARN FOR TEXTILE SCAFFOLD: EVOLUTION OF MECHANICAL PROPERTIES OF PLA/PCL FIBERS DURING IN VITRO DEGRADATION

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ABSTRACT

In this work, bioabsorbable immiscible polymer blends of poly(D,L-lactide) (PLA) and polycaprolactone (PCL) were studied in a large range of compositions, from $PLA_{90}PCL_{10}$ to $PLA_{50}PCL_{50}$ per 10% slice in order to evaluate the spinnability of these blends. The first step was a twin screw extrusion followed by a melt spinning step in order to obtain the multifilament. The morphologies of the multifilaments were investigated by extracting PCL with acetic acid. Then multifilaments were immersed in a DMEM media at 50°C during 35 days and their mechanical properties were tested in order to understand the relation between the morphology and the degradation process.

Key Words: DEGRADATION, MELT SPINNING, POLYMER BLEND, POLYLACTIDE, POLYCAPROLACTONE

1. INTRODUCTION

Nowadays, there is a growing interest in degradable and bioresorbable polymers, especially for their applications in the medical field, for example with the development of absorbable stents [1, 2]. Even if some studies are performed *in vivo* [3, 4, 5], the large majority of this polymer studies are done *in vitro.* One of the biggest challenges with these materials is to control degradation kinetics in accordance with the intended application.

Most of the used polymer for these kinds of applications are aliphatic polyester such as polycaprolactone (PCL) [3, 4], polybutylene succinate (PBS) [5], polylactide (PLA) [1], polyglycolide (PGA) [5] and poly-3-hydroxybutyrate (PHB, P3HB) [6]. Some other contains ether function like polydioxanone (PDS, PDO) or polyethylene glycol (PEG). All these polymers have a good biocompatibility and are known to be fully absorbable in the body.

PLA/PCL blend has been studied a lot because their individual degradation kinetics are different and this allows to tailor mechanical properties along time depending on the application. The specificity or our work is to study these degradation kinetic behaviors on an original structure: multifilament.

The first purpose of this work was to study the polymer blends ageing by a control of mechanical properties and molar weight. It allowed us to highlight the role of morphology of the blend. The spinning step allowed us to study the spinnability of a wide range of PLA/PCL blends, then the consequence of spinning process on yarns morphologies. Every blend was extruded then went through a spinning process. The media chosen was Dulbecco's Modified Eagle Medium (DMEM) in order to imitate the body fluid and to have a good transferability of these results in our project.

2. EXPERIMENTAL

2.1 Materials

The PCL CAPA 6400 supplied by Perstorp used in this study has a glass transition temperature of -60°C (Tg). The PLA INGEO 6202D supplied by Natureworks has a glass transition temperature which is between 55°C and 60°.

Gibco DMEM media was supplied in solid form by Fischerscientific, 1.5g/L $NaHCO_3$ must be added in order to reach neutral pH.

2.2 Processing

Different compounds were prepared using a co-rotating intermeshing twin-screw extruder from Thermo-Haake PTW 16/25p (L/D = 25) with a rotation speed of 100 rpm. On optimized temperatures profile was used between 60°C and 180°C in order to bring PCL pellets until mixing zones without melting them too fast. The obtained rod was directly cooled by airstream on a conveyor belt and cut in pellets by a granulator.

A Busschaert engineering Spinboy I device was used for the melt spinning process. The PLA/PCL blend pellets were molten in a single-screw extruder heated with a temperatures profile between 159°C and 175°C. The compound goes through a volumetric pump (52.5 cm^3/min), then goes out through two spinnerets with 40 holes 1.2 mm in diameter each in order to produce a continuous multifilament yarn. The material is then cooled down with an airstream and is finally covered with spin finish oil. The multifilament is then drawned between a supply and a drawing roll (with a speed and temperature V_1, T_1 and V_2, T_2 respectively) where V_1 = 80 m/min, T_1 = 25°C and V_2 = 120 m/min, T_2 = 30°C. Finally, the multifilament is wound on a roll.

Several multifilaments (80 monofilaments) were produced from PLA100 to PLA_{50}/PCL_{50} per 10% slice, it means PLA_{100}, PLA_{90}/PCL_{10}, PLA_{80}/PCL_{20}, PLA_{70}/PCL_{30}, PLA_{60}/PCL_{40} and PLA_{50}/PCL_{50}.

Before spinning step, the Melt Flow Index (MFI) of each compound was determined to characterize its fluidity and, indirectly, the spinnability. Then once the spinning performed, each multifilament was tested with selective phase extraction to get information on morphology of different systems.

2.3 Material degradation method

The In Vitro degradation was carried out at 50°C and 80% relative humidity in a climatic chamber during 35 days. 40 cm of each yarn was cut and immersed in DMEM media. This media was chosen in order to simulate body fluid. After 35 days, each multifilament was taken out to follow degradation by performing mechanical characterizations and molar weight tests.

2.4 Characterization methods

2.4.1 Polymer fluidity

These tests were performed with a Thermo-Haake Melt Flow Tester. A mass and a temperature are set constant, the mass of polymer flowing through a 2 mm hole during a determined time interval is measured. The mass applied is 2.16 kg (ISO 1133) and the temperature is set on 175°C.

2.4.2 Morphological properties

Morphology of all the blends was estimated with selective phase extraction protocol of PCL. Polymer compounds and yarns were immersed in acetic acid during 4 hours. Then, they were filtered and dried at 50°C. The weight is measured and the immersion process is repeated until the mass tends toward a constant value. PCL continuity in the compound or the yarn is linked to PCL mass fraction before and after the protocol, these are linked as follows in the equation:

$$\text{PCL continuity (\%)} = \frac{mi-mf}{wPCL*mi} * 100 \qquad (1)$$

With *mi* the initial mass (g), *mf* the final mass (g) and *wPCL* the polycaprolactone weight ratio.

2.4.3 Linear density

The linear density (dTex) of each monofilament is measured with a vibroscope in order to follow the swelling behavior of the different materials.

2.4.5 Molecular weight

Size-exclusion chromatography (SEC) measurements of materials were performed in chloroform (CHCl3) at 23 °C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic high-performance liquid chromatography (HPLC) pump LC 1120 (flow rate = 1 mL min^{-1}), a Marathon autosampler (loop volume = 200 µL, solution conc. = 1 mg mL^{-1}), a PL-DRI refractive index detector and three columns: a PL gel 10 µm guard column and two PL gel Mixed- B 10 µm columns (linear columns for separation of molecular weights (MW) ranging from 500 to 106 Daltons). Poly(styrene) (PS) standards were used for calibration.

2.4.4 Mechanical properties

Mechanical tests were performed on isolated monofilament extracted from multifilament with a Zwick 1456 test device. According to the ISO 5079 standards, the distance separating the clamps was 20 mm and the crossbar speed was 20 mm/min. The cell force on the bench was 10 Newton. Every test was performed sticking to the atmospheric standard conditions: a temperature of 20 +/- 2°C and a room humidity of 65 +/- 5%.

The main characteristics measured are tenacity (cN/Tex), elongation at break (%) and Young Modulus (MPa).

3. RESULTATS AND DISCUSSION

3.1 Spinnability of PLA/PCL blend

The information on polymer fluidity is crucial to foresee the ability to produce a multifilament with the Busschaert engineering Spinboy I device. Every compound was tested and the values are represented above (figure 1). A rise of polymer fluidity is observed when the PCL ratio is increasing. Usually, the polymers which are the easiest to process present a MFI between 15 and 30 g/10min. PLA_{50}/PCL_{50} and PLA_{60}/PCL_{40} were the hardest polymers

to process and limited the linear density of the yarn around 5200 dTex. As a consequence, every multifilament was produced with the exact same machine setup in order to obtain this linear density.

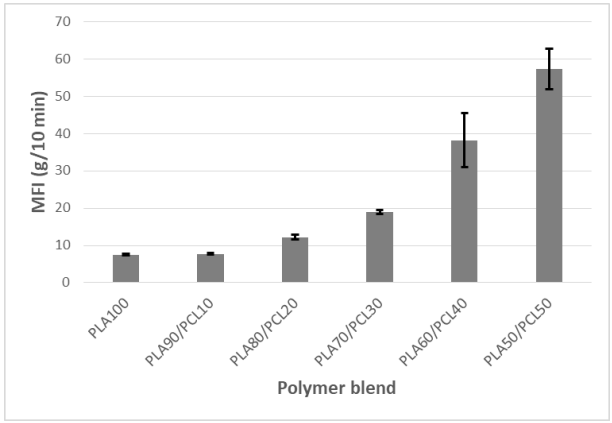

Figure 1. Melt Flow Index of PLA/PCL blends, 175°C under 2.16 kg

3.2 Influence of processes on blend morphology

For the systems PLA90/PCL10 and PLA80/PCL20 a ratio between 0% to 30% of PCL incorporated in the blend can be extracted. This means the accessibility of PCL is limited and the morphology is nodular or fibrillary [7]. Between PLA70/PCL30 and PLA60/PCL40, there is a phase inversion region which is on 100% PCL continuity because in theory, 100% of the PCL mass included was extracted. The last region is over 100% PCL continuity : in this area, PLA fragments can be taken out of the pellets because PLA is not the matrix anymore and 100% of the PCL is reachable by acetic acid.

For the multifilament case, almost 100% of PCL has been removed for each blend. The PCL accessibility increased through spinning process..

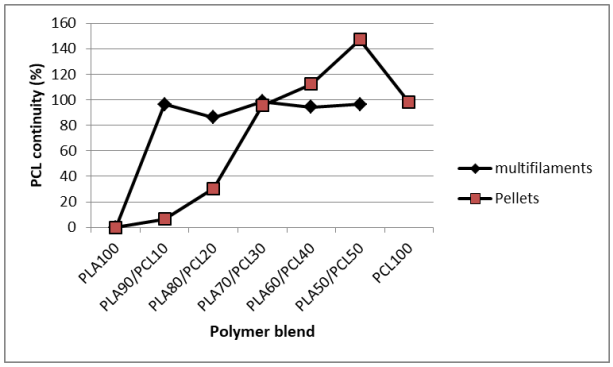

Figure 2. PCL continuity in PLA/PCL multifilaments and pellets

3.3 Evaluation of molar weight and polydispersity index during degradation

During the accelarated ageing study, molar weight and polydispersity index were followed. Every molar weight (Mn in g/mol) have decreased during the in vitro tests, in particular it seems that this decrease is inversely proportionnal to the PCL rate in the blend except for the case of PLA100. An explanation for this specific case is the quick increasing of crystallinity in PLA according to litterature [8] which slows degradation process. It is interesting to note that polydispersity index of PLA100 has increased quite little compared to PLA90/PCL10 and PLA80/PCL20. This shows a degradation behaviour which is different as soon as 10% of PCL is introduced.

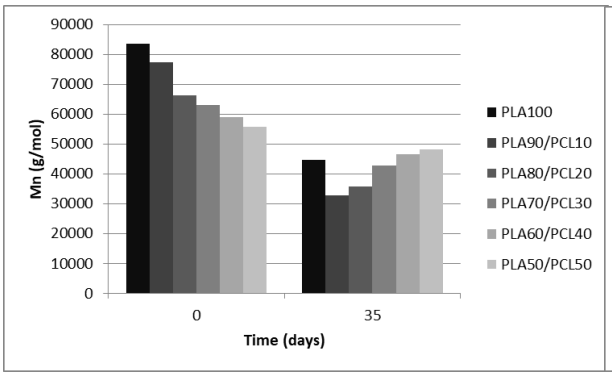

Figure 3. PLA/PCL blends molar weight (Mn)

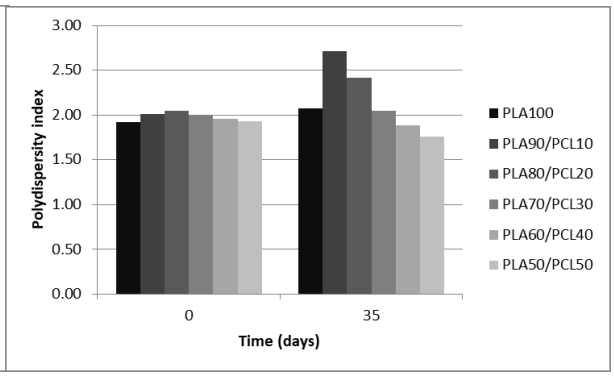

Figure 4. PLA/PCL blends polydispersity index

3.4 Mechanical properties of PLA/PCL blend

Before tensile tests, every monofilament count was measured with a vibroscope and it allowed us to see the swelling of PLA_{100} (figure 8) which explain the homogeneous chain cleavage of neat PLA (figure 4). This confirm that PLA alone undergoes a bulk degradation [9]. The mechanical properties of the neat PLA are those that have fallen the most during degradation, the total loss of elongation at break can be noticed (figure 7), it has fallen from 200% in average to almost 0%. An other material that has specific degradation behaviour is the PLA_{50}/PCL_{50} : indeed, its tenacity and Young modulus have increased slightly (figure 5 and 6). At the same time, elongation at break went from around 10% to more than 150%. The hypothesis to explain that phenomenon is that the PCL matrix is taking the whole effort after PLA loss of properties. Monofilaments between PLA_{90}/PCL_{10} and PLA_{70}/PCL_{30} had their tenacity decreasing slightly but neither Young modulus nor elongation at break decreased significantly. PLA_{60}/PCL_{40} had a slight decrease in every mechanical properties.

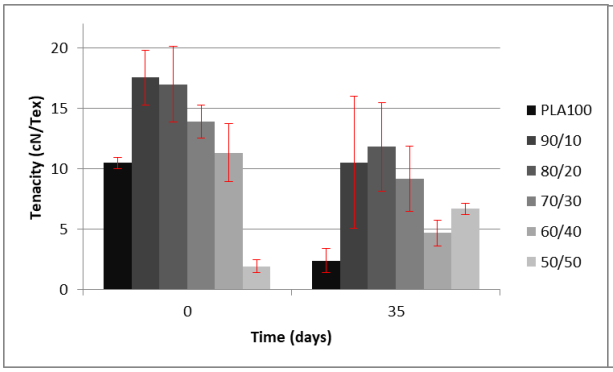

Figure 5. Tenacity (cN/Tex)

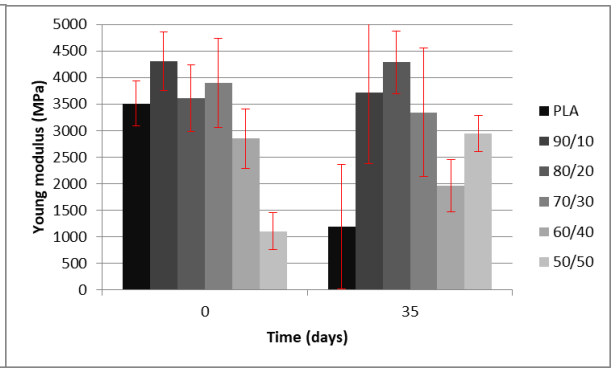

Figure 6. Young modulus (MPa)

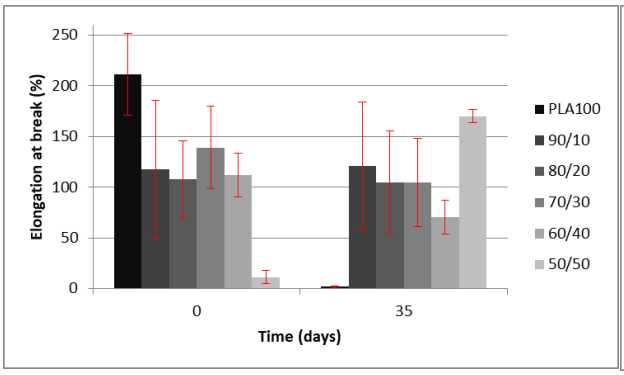

Figure 7. Elongation at break (%)

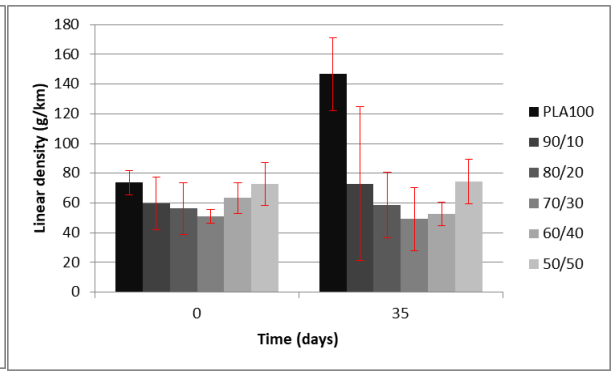

Figure 8. Linear density (dTex)

4. CONCLUSIONS

In this study, the immiscible PLA/PCL blend was prepared by extrusion and spinning in order to study ageing of multifilaments depending on their morphologies. The ability to spin the blend and then the morphology were studied. Results have shown that not every multifilament can be spun easily. Then, the phase inversion can be found around 40% PCL. The incorporation of PCL, even 10%, has a huge impact on degradation kinetics of PLA matrix, especially on elongation at break. Finally the two monofilaments which displayed most interesting mechanical performances along time were PLA_{90}/PCL_{10} and PLA_{80}/PCL_{20}. These results show that morphology plays a critical role on mechanical properties during degradation process.

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