Available online at www.sciencedirect.com

ScienceDirect

Procedia CIRP 65 (2017) 231 – 235

www.elsevier.com/locate/procedia

3rd CIRP Conference on Bio Manufacturing

Fabrication of PCL/PLA composite tube for stent manufacturing

Antonio J. Guerra[a], Joan San[b], Joaquim Ciurana[a]*

[a]Department of Mechanical Engineering and Industrial Construction - University of Girona, Maria Aurèlia Capmany 61, 17003 Girona, Spain
[b]Department of Medical Sciences - Faculty of Medicine - University of Girona, Emili Grahit 77, 17003 Girona, Spain

* Corresponding author. Tel.: +34 972418265; fax: +34 972418098. *E-mail address:* quim.ciurana@udg.edu

Abstract

This work presents the effect of Dip Coating process over the tube's features to obtain a PCL/PLA tube to stent purpose. The effects of withdrawal speed, number of cycles, and solutions concentration were studied. Four different tubes were fabricated and analyzed by Dynamic Mechanical Analysis (DMA), Degradation Rate, Surface Roughness, Thickness, and Uniformity.
Results have shown the strong influence of withdrawal speed and polymer's concentration over the tube's features. DMA and degradation results showed the limitations of PCL and PLA as material for the stent purpose, meanwhile the PCL/PLA composite tube showed a behavior closer to the stents requirements.

Peer-review under responsibility of the scientific committee of the 3rd CIRP Conference on BioManufacturing 2017
Keywords: Dip Coating, Biodegradable Stent, Composite

1. Introduction

Since their introduction in the market in the early 1990s, nobody was able to predict the advantages that will occur in stent technology over the upcoming decades. Nowadays, stents are the main treatment modality for atherosclerosis. The coronary stent global market, primarily balloon-expanded, bare metal (BMS), and drug eluting stents (DES), was approximately $7.5 billion in 2015 and forecast stent sales will grow at double digit rates [1]. Since stenting appearances it became evident that this approach has significant limitations, such as vessel occlusion, restenosis or migration of the prosthesis. These problems have improved with the development of BMS and more recently, the DES both based on metallic structures.

Although metallic stents are effective in preventing acute occlusion and reducing late restenosis after coronary angioplasty, many concerns still remain, such as thrombosis and restenosis. Bioresorbable stents (BRS) were introduced to overcome these limitations with important advantages: complete bioresorption, mechanical flexibility, etc.

In the design of biodegradable stents several types of materials are currently been investigated: poly-L-lactic acid (PLLA) and magnesium have been the most promising materials [2], although there are other polymers suggested such as polycaprolactone (PCL) [3]. Regardless of material choice, the challenges associated with biodegradable materials remain similar; the mechanical properties, manufacturing process, and biocompability.

Due to these needs, there are numerous authors whose have been analyzing the properties of some different polymeric biodegradable materials. Wiggins et al. [4] found that the degradation rate of polyurethane increased with cyclic strain rate, whereas strain magnitude has essentially no effect employing a circular membrane devices in which vacuum was applied to one side of the membrane. This device applied bi-axial strain to the membrane in the middle region, and largely uniaxial strain in the outer region. Meital et al. [5] studied the effect of degradation on tensile mechanical properties and morphology of PLLA, PDS, and PGACL where PLLA emerged as the most promising materials of the study. Ruben et al. [6] demonstrated that the addition of POSS nanocores to the PCU imparts a type of protective, extending its resistance to degradation. Niels Grabow et al. [7] designed and produced a biodegradable slotted tube stent based on PLLA and P4HB polymers, carried out mechanical and degradation experiment.

Peer-review under responsibility of the scientific committee of the 3rd CIRP Conference on BioManufacturing 2017
doi:10.1016/j.procir.2017.03.339

The results showed that the PLLA/P4HB stent allows rapid balloon-expansion and exhibited adequate mechanical scaffolding properties suitable for a broad range of vascular and nonvascular applications. Yang et al. [8, 9] studied the effect of cyclic loading on the in vitro degradation of PLGA scaffolds for 12 weeks. Their mode of deformation was unconfined compression of <5% strain at 1Hz for 8 h per day for 12 weeks and compared results with static controls. The authors have found that water absorption was higher in dynamic conditions and observed markedly higher reductions in mass, dimensions, and molecular weight when compared with static conditions. Vieira et al. [10] studied the evolution of mechanical properties of PLA-PCL fibers during degradation based on experimental data. The decrease of tensile strength followed the same trend as the decrease of molecular weight. More recently, Chu et al. [11], have analyzed the effect of fluid shear stress in the in vitro degradation rate of PLGA membranes. Their work showed that the fluid shear stress affects over the viscosity of the degradation solution, the ultimate strength and has a great effect on the surface morphology of PLGA membranes.

Despite, the efforts for understand and develop news fully biodegradable materials for medical applications, nowadays is still necessary to continue the study of new material or configuration of them, and the employed manufacturing process. In the stent industry, many steps are require until achieve an implantable stent. The original material should be dissolved to make the tube, by dip coating, for the subsequent laser cutting process, ending by a cleaner and sterilization processes. The effect of the parameter involved in these processes over the material properties are still unclear.

The ideal stent should be uniform, has smooth surface for a better vessel placing, fully corrosion resistant, vascular compatible, fatigue resistant, and visible using standard X-Ray and MRI methodology, and a good relation between hardness and soft. The above properties are interrelated and sometimes contradictory, requiring careful compromise.

The authors aim to analyze the effect of process parameters over the tube's physical features to obtain a PCL/PLA composite tube that accomplish with the stents requirement. The effect of withdrawal speed, the number of cycles, and the solutions concentration was studied. Four different tubes were made, namely, PCL, PLA, PCL/PLA, and PLA/PCL. The tubes were analyzed by Dynamic Mechanical Analysis (DMA), Surface Roughness, Dimensional Uniformity, in order to find the best tube for the stent purpose.

2. Material and Method

2.1. Dip Coating Machine

Dip coating techniques can be described as a process where the substrate to be coated is immersed in a liquid and then withdrawn with a well-defined withdrawal speed under controlled temperature and atmospheric conditions. Taking advantage of a 3D Printer Machine, we developed a Dip Coating Machine. A male stainless steel cores of 4 mm outer diameter are lodged in a superior support grip to the vertical axis. The process is defined by the start-up time, withdrawal speed, evaporation time, and number of cycles **(Fig. 1)**.

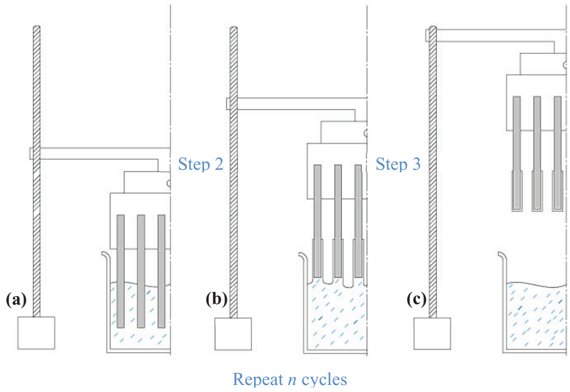

Fig. 1. Dip Coating Method (a) Start-up time (b) Withdrawal speed (c) Evaporation time

2.2. Materials

Polycaprolactone (PCL) Capa 6500® supplied by Perstorp and Polylactide (PLA) 3251D® supplied by NatureWorks were used as material for the experiments. PCL is a biodegradable polyester with a low melting point (60ºC) and a glass transition of about -60ºC. PLLA is a biodegradable thermoplastic aliphatic polyester derived from renewable resources, such as corn starch, or sugarcane. Their melting point is about 173–178 °C with a glass transition of 60–65 °C. Both PCL and PLA degradation is produced by hydrolysis of its ester linkages in physiological conditions and has therefore received a great deal of attention for using it as an implantable biomaterial for long term implantable devices, such stents, because of their properties **(Table 1).** The solvent employed were $CHCl_3$.

Table 1. Material Properties.

Material	Molecular Weight [g/mol]	Young Modulus [MPa]	Strain at Break [%]	Degradation Time [Months]
PCL	50000	470	700	>24
PLA	90000	108	3.5	12-24