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**Development of polymeric biodegradable materials with  
optimised mechanical properties for the freeforming plastic  
deposition of ureteral stents**

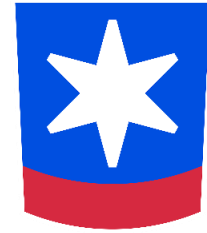
**Leonardo Galli Engler**

**Caxias do Sul**

**Outubro 2024**



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**Development of polymeric biodegradable materials with  
optimised mechanical properties for the freeforming plastic  
deposition of ureteral stents**

A thesis submitted for consideration for the Doctor of Philosophy

By

**Leonardo Galli Engler**

Based on research carried out under the supervision of

Dr Declan M. Devine

Co-Supervisors: Dr Janaina S. Crespo, Dr Noel M. Gately, Dr Ian Major

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Technological University of the Shannon

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**Development of polymeric biodegradable materials with optimised mechanical properties for the freeforming plastic deposition of ureteral stents**

Leonardo Galli Engler

A thesis submitted for the degree of Doctor of Philosophy in a collaboration between the Department of Polymer Engineering of the Technological University of the Shannon: Midlands & Midwest (TUS), Ireland and the Materials Science and Engineering Postgraduate Program of Universidade de Caxias do Sul (UCS), Brazil.

21<sup>st</sup> of October 2024

**Examiners:**

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Dr. Eoin O’Cearbhaill  
University College Dublin (UCD), Ireland

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Dr. Luke Geever  
Technological University of the Shannon: Midlands & Midwest (TUS), Ireland

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Dr. Rosane Michele Duarte Soares  
Universidade Federal do Rio Grande do Sul (UFRGS), Brazil

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Dr. Mariana Roesch-Ely  
Universidade de Caxias do Sul (UCS), Brazil

# Declaration

I hereby declare that this thesis submitted to the Technological University of the Shannon (TUS) and the Universidade de Caxias do Sul (UCS) for the degree of Doctor of Philosophy, is a result of my own work. This work has not been submitted either in the same or altered form, part or in whole, to these institutes or any other institute in support for any degree other than for which I am now a candidate.

21<sup>st</sup> of October 2024

Date

Leonardo Galli Engler

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# Abstract

Over 1.5 million ureteral stents are implanted globally each year, yet more than 80% are reported to fail due to complications such as ureterovesical reflux, tissue irritation, and infectious crystalline biofilm formation. These failures result in significant patient pain and discomfort, frequently necessitating surgical re-intervention, which further lessens patients' quality of life and escalates healthcare costs. While most commercial stents are fabricated from non-biodegradable polymers (e.g., silicone or polyurethane), prolonged indwelling periods (over four weeks) exacerbate risks of biofilm-mediated encrustation, influenced by factors such as stent material, patient comorbidities, and urine composition. There is a critical need for the development of biodegradable materials that maintain functional performance during treatment while biodegrading safely afterward, thereby avoiding secondary removal procedures and reducing biofilm-associated complications. To address these limitations, this research aimed to design, construct, and characterise a novel biodegradable ureteral stent using blends of polylactic acid (PLA), polyhydroxybutyrate (PHB), and polycaprolactone (PCL), modified with functional additives to enhance performance.

Investigated additives included halloysite nanotubes for mechanical reinforcement, ZnO/Ag and SiO<sub>2</sub>/Ag nanoparticles for their antimicrobial properties, and polyethylene glycol (PEG) and epoxidised soybean oil (ESO) for their compatibilising effect. These were incorporated to improve blend miscibility, antimicrobial efficacy, and cytocompatibility. Hot melt extrusion (HME) was employed to process the blends, with mechanical testing prioritising material flexibility, a critical property for ureteral stent functionality. While many blends exhibited insufficient mechanical performance or cytotoxicity, optimised formulations achieving higher flexibility were selected for further development. These were processed via Arburg Plastic Freeforming (APF), a high-precision 3D printing technology requiring methodical parameter optimisation (screw and nozzle temperature, layer height, drop aspect ratio, deposition angle, discharge rate, etc.) to ensure dimensional accuracy and structural integrity in printed parts.

Using APF, a novel stent design was prototyped, departing from the conventional double J stent design introduced in 1978 by Finney, which remains prone to patient discomfort due to rigidity and poor anatomical fit. In vitro degradation studies demonstrated that the novel stent biodegrades within six to eight weeks in artificial urine, aligning with clinically relevant



indwelling periods. Over the eight-week period, the biodegradable stents demonstrated controlled degradation, with significantly reduced encrustation compared to commercial stents, which exhibited complete encrustation by week four. Analytical characterisation using scanning electron microscopy (SEM) and inductively coupled plasma optical emission spectroscopy (ICP-OES) confirmed that encrustation deposits on commercial stents presented calcium phosphate, oxalate, and struvite. In contrast, the biodegradable stents maintained high cell viability and biocompatibility, directly addressing key limitations of existing models. Comparative testing against commercial polyurethane stents showed significantly reduced biofilm formation and encrustation, validating its potential to mitigate complications inherent to current models.

This research study advances the development of biodegradable ureteral stents by integrating advanced biodegradable materials, additive manufacturing for fast prototyping, and patient-centric design. By addressing the limitations of current double J stents, such as patient discomfort and recurrent complications, this research lays the groundwork for advancements in the field of ureteral stents development, with the ultimate purpose of enhancing patient's quality of life.