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Tailoring the mechanical and biodegradable properties of binary blends of biomedical thermoplastic elastomer

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ABSTRACT

Blending polymers with complementary properties capitalizes on the inherent advantages of both components, making it possible to tailor the behaviour of the resultant material. A polymer blend consisting of an elastomer and thermoplastic can help to improve the mechanical integrity of the system without compromising on its processibility. A series of blends of biodegradable Poly(L-lactide-co-ε-caprolactone) (PLC) and Poly-(l,l-lactide-co-glycolic acid) (PLLGA), and PLC with Poly-(d,l-lactide-*co*-glycolic acid) (PDLLGA) were evaluated as a potential material for a biodegradable vesicourethral connector device. Based on the Tg of the blends, PLC/PLLGA formed an immiscible mixture while PLC/PDLLGA resulted in a compatible blend. The results showed that with the blending of PLC, the failure mode of PLLGA and PDLLGA changed from brittle to ductile fracture, with an significant decreas in tensile modulus and strength. SEM images demonstrated the different blend morphologies of different compositions during degradation. Gel Permeation Chromatography (GPC) and mechanical characterization revealed the degradation behaviour of the blends in this order (fastest to slowest): PDLLGA and PLC/PDLLGA blends > PLLGA and PLC/PLLGA blends > PLC. The PLC/PLLGA (70:30) blend was recommended as a suitable for the vesicourethral connector device application, highlighting the tailoring of blends to achieve a desired mechanical performance.

1. Introduction

Biodegradable polymers such as poly(L-lactide) (PLLA) and poly(L-lactide-co-ε-caprolactone) (PLC) can be co-polymerize and/or made into blends to alter the mechanical and degradation properties according to the intended use. The co-polymerization and blending of these polymers have led to several biomedical applications for examples as sutures, fully biodegradable stents with shape memory, artificial blood vessels, and occluders for septal defects. (Ang et al., 2017; Huang et al., 2014a) PLLA and PDLA are stereoisomeric forms of poly(lactide) (PLA) and are semi-crystalline polyesters. Poly(lactic-co-glycolic acid) (PLGA) is synthesized using random copolymerization of PLA and poly (glycolic acid) (PGA), the addition of PLA introduces methyl group that makes the resultant copolymer more hydrophobic, thereby altering its degradation rate. PLC is polymer obtained the ring-opening polymerization of L-lactide (cyclic dimer of L-lactic acid) and ε-caprolactone as monomers. It is a semi-crystalline polymer with high flexibility with a shorter degradation time compared to PLLA due to lower crystallinity. (Makadia and Siegel, 2011)

Besides co-polymerization and blending, fillers are also employed to enhance and modify the material properties of the polymers. Composite polymeric materials present a novel class of materials with important properties in several engineering and biomedical applications. A polymeric composite comprises of fillers dispersed within a polymer matrix. The concept of a composite material capitalizes on the inherent properties of the base polymer while enhancing the functionality of the composite device by the addition of fillers. (Islam, Masoodi, and Rostami, 2013) The fillers are able to render additional features to the polymer that are usually not available in polymeric materials such as optical, electrical and mechanical properties. (Bunk et al., 2015) Some groups have reported on the effect of blending fillers such as inorganic nanoparticles with polymers and observing an increase in the mechanical properties such as Young's modulus and toughness. (Fujisawa, Saito, Kimura, Iwata, and Isogai, 2014; Wan, Yuan, Tan, Li, and Yang,

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2014) The presence of the filler can reinforce the mechanical strength of the polymer by absorbing energy from the applied stress and disperse it about a larger volume of the material, thereby improving its composite's properties. (Liu, Wang, Chow, Yang, and Mitchell, 2014) In the field of biomaterials, the reinforcement effect of rigid fillers on polymers' mechanical properties is of particular interest.

In localized prostate cancer, radical prostatectomy is known to be the gold standard and it involves the surgical removal of the diseased prostate gland, followed by the urethrovesical anastomosis (UVA) to connect the bladder neck to the urethra. Suturing has been the existing method to achieve UVA and is a tedious process, requiring the surgeon to have good dexterity to ensure a watertight vesicourethral anastomosis. (Ghazi and Joseph, 2013) Complications such as intra- or post-operative haemorrhage, urine leakage and anastomosis stricture may occur if the suturing is not carried out properly. (Tyritzis, Katafigiotis, and Constantinides) Patients would be required to undergo urinary catheterization along with the inconvenience of having an indwelling catheter and other side effects. The issue with suturing is the huge learning curve of anastomosis of a tubular anatomy, so it is difficult to accurately create a connection that is not too loose (thereby causing leakage) and not too tight that may cause poor healing. (Zorn et al., 2011) Hence, there exist a need to have a biomedical device that is able to provide for a constant solution to watertight connection without excessive stress to the healing site.

A biodegradable vesicourethral connector device that functions like a stent can help to aid in the healing process and avoid the complications arising from suturing after the anastomosis of the bladder and urethra. The proposed device consists of three components, an umbrella, spoke and connector as shown in Fig. 1. (Huang, Venkatraman, and Chia, 2015) The device can be used to replace the suturing and act as a connection between the bladder and urethra, held by umbrella component of the device. This allows for the drainage of urine from the bladder, thus serving as a temporary catheter. Furthermore, the device will be fully biodegradable and no addition procedure will be required to remove the device.

The connector should be: (1) flexible for ease of insertion with a catheter, (2) expand well, (3) has good strain recovery, and (4) has good processibility and sufficient mechanical strength to provide the required support. Hence in this study, several co-polymers and their blends are examined to investigate the effects of blending and fillers on the resultant material properties. The polymers were chosen due to their mechanical strength, flexibility and degradation rates. Barium sulphate ($BaSO_4$) has been used extensively as a radiocontrast agent in X-ray imaging and other diagnostic procedures and $BaSO_4$ fillers were used in this study to reinforce the polymeric materials. The suitability of the co-polymers composites as material for the connector will be evaluated based on their mechanical and degradation properties.

Table 1
Compositions of the polymer blends used in this study.

Sample name	wt% PLC	wt% PLLGA	wt% PDLLGA	wt% $BaSO_4$
PLC	100	0	0	0
PLLGA	0	100	0	0
PDLLGA	0	0	100	0
Co-polymers with fillers				
PLC_B	100	0	0	30
PLLGA_B	0	100	0	30
PDLLGA_B	0	0	100	30
Co-polymers blends with fillers				
PLCPLLGA7030_B	70	30	0	30
PLCPLLGA5050_B	50	50	0	30
PLCPLLGA3070_B	30	70	0	30
PLCPDLLGA7030_B	70	0	30	30
PLCPDLLGA5050_B	50	0	50	30
PLCPDLLGA3070_B	30	0	70	30

2. Materials and methods

2.1. Materials

Poly (L-lactide-co-ε-caprolactone) (PLC, Mw = 202,000 g/mol, I.V 1.53 dl/g) with a molar ratio of L-lactide/ε-caprolactone 70/30, Poly-(d,l-lactide-co-glycolic acid) (PDLLGA, IV 1.06) with lactide/glycolide ratio of 53/47 and Poly-(l,l-lactide-co-glycolic acid) (PLLGA, IV 1.7–2.6) with lactide/glycolide ratio of 80/20, were purchased from Corbion (Netherlands). Barium sulphate microfillers ($BaSO_4$, Mw = 233.43 g/mol) were purchased from Sigma-Aldrich (MS, USA). High performance liquid chromatography (HPLC) grade Chloroform, dichloromethane (DCM) from Tedia Company Inc. (OH, USA). and phosphate buffered saline (PBS) were purchased from Sigma Aldrich.

2.2. Preparation of co-polymers blend samples

Composite blends of PLC/PLLGA/BaSO4 and PCL/PDLLGA/BaSO4 of various compositions (Table 1) are prepared by knife casting method. The polymer solutions were first prepared by dissolution in DCM and underwent 30 min of sonication and 12 h of mixing on a magnetic stirrer. The wt% of the polymer blends was based on the total polymer weight while the wt% of the fillers in the composite was calculated based on the total composite weight. After mixing, the film applicator height was fixed at 94 µm and the polymer solution was casted onto glass plates at 50 mm/s, under room temperature and pressure. The casted films were covered and left to dry at room temperature for 2 days and further drying was conducted at 37 °C in vacuum oven for 2 weeks before being tested. Thermogravimetric analysis (TGA, TA instruments Q500) was performed on the films to ensure that the residual solvent amounts were less than 1 wt% before further testing.

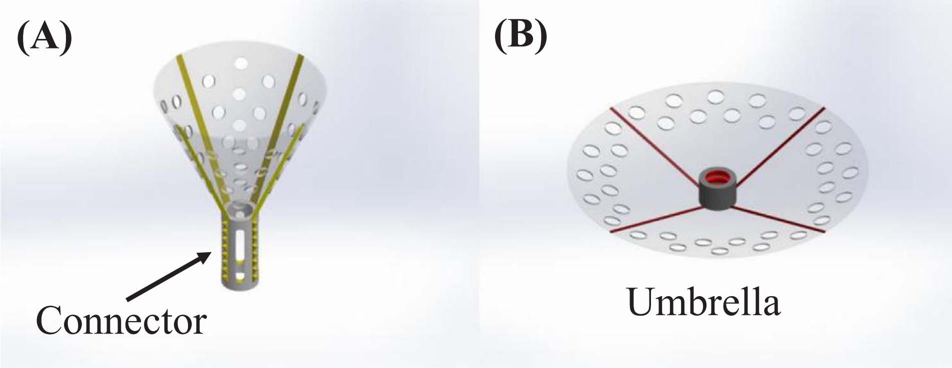

Fig. 1. Proposed biodegradable vesicourethral connector device. (A) The connector is used to connect the bladder and urethral together in order to drain urine out. (B) The umbrella is designed to be slotted and seated at the opening of the bladder. (Y. Huang et al., 2015).