

# THE FACTORS GOVERNING HYDROLYTIC DEGRADATION OF POLYESTERS-BASED SCAFFOLDS IN BONE TISSUE ENGINEERING

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[ENGINEERING OF BIOMATERIALS 153 (2019) 86]

## Introduction

Degradation of the tissue-engineered constructs is considered to be one of the main subjects of interest in case of designing and fabricating polymeric scaffolds. Degradation rate of such scaffolds should, in this case, follow a strictly defined pathway, in which tissue formation should be preceded by gradual degradation while ensuring certain mechanical support [1]. There are many factors, which in fact can affect the degradation kinetics of the constructs fabricated via additive manufacturing. One of them are certainly structural properties of the constructs, which for instance, relate to adopted architecture of the scaffold. Many studies demonstrated that degradation rate can be also easily modified by using different materials and their composition [2,3]. As some of internal features controlling the degradation kinetics was above stated, it is worth mentioning that the external factors could also play an important role in accelerating degradation rate, especially in the laboratory conditions. Instead of conducting time-consuming and tedious *in vitro* degradation of long-time degrading constructs, new methods of accelerating their degradation kinetics has been proposed. One of them pertain to the static and dynamic medium systems, in which degradation occurs slower in case of dynamic environment [4]. The degradation can be also accelerated by conducting the experiment in the elevated temperatures[5]. But it is worth considering wheatear the properties of the material will not be affected and the scaffolds degradation will not be falsified in any way.

As such we would like to communicate the topic of scaffold's degradation and by presenting some of the methods of accelerating it provides a special insight in the broad topic of manipulating the degradation kinetics.

## Materials and Methods

The L-lactide-co-glycolide (PLGA), L-lactide-co- $\epsilon$ -caprolactone (PLCL) and their tricalcium-phosphate-loaded (TCP) composites containing 20 and 40 wt% of filler were fabricated using modified fused deposition modeling. We designed scaffolds with filament lay-down pattern of 0°/90° and with or without the modifications of filament distance in n+2 layer, shifted and non-shifted constructs were obtained, respectively. To investigate the effect of the temperature on degradation profile, we conducted two separate degradation experiments, dynamic and static, in which the change of mass, pH, water absorption and initial molecular weight loss ( $M_{w0}$ ) was detected in phosphate buffered saline (PBS) at 37°C for up to 48 weeks and 50°C for up to 3 weeks, respectively. Subsequently, the effect of architecture modifications and its effect on degradation behaviour was explained utilizing fluid flow simulations. The scaffolds morphology was evaluated utilizing scanning electron

microscopy (SEM) and the visualization of the topography was performed utilizing atomic force microscopy (AFM). Surface area to volume ratio (SVR) and porosity were determined using micro-computed tomography ( $\mu$ CT). Thermogravimetric measurements were used to assess the characteristic temperatures for investigated materials.

## Results and Discussion

### Architecture

In the case of dynamic and static degradation, accelerated degradation was observed in the case of shifted constructs. We assume that faster degradation may be attribute to their tortuosity, making them less permeable in which accumulation of acidic products in the tortuous architecture is observed.

### Static and dynamic conditions

The degradation of PLGA- and PLCL-based scaffolds proceeded faster in case of static conditions. We observed a decrease of  $M_{w0}$  in the shorter time comparing to dynamic conditions at 37°C. Our findings agree with other studies, where degradation rate was reduced in case of scaffolds undergoing dynamic degradation, in which continual removal of acidic degradation products was observed.

### Degradation at elevated temperatures

The rapid decrease of initial  $M_n$  and  $M_w$  was observed during 3 weeks of degradation at 50°C. Interestingly, PLGA-based scaffolds as the first started to crumble and disintegrate, contrary to PLCL-based ones. However, a different situation was observed at 37°C, where PLGA-based samples sustained mechanical integrity up to 24 weeks. It is believed that glass transition temperature ( $T_g$ ) of polymer determines the behaviour of polymeric chains during various experimental conditions. Degradation performed below material's  $T_g$  will be dependent on mobility of polymer chains, which in this case is essentially zero. Thus performing degradation at elevated temperatures is not always suitable for certain materials.

## Conclusions

There is a need to develop standard protocols for assessing accelerated polyester-based scaffold degradation. However, the establishment of such protocols is challenging due to complexity of factors accounting hydrolysis. In the present study, we investigated some factors leading to accelerated degradation, pointing that not only architecture, materials' properties but also degradation conditions can change the degradation rate of polyester-based scaffolds.

## Acknowledgments

This work was supported by the National Centre for Research and Development in the frame of project iTE (STRATEGMED3/306888/3/NCBR/2017).

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