

IN VITRO OXIDATIVE DEGRADATION OF DIBLOCK COPOLYMERS P(LA-b-TMC)

AGNIESZKA ADAMUS-WŁODARCZYK^{1*}, MARTA SOCKA²,
RADOSŁAW WACH¹, PIOTR ULAŃSKI¹

¹ INSTITUTE OF APPLIED RADIATION CHEMISTRY,
FACULTY OF CHEMISTRY, LODZ UNIVERSITY OF TECHNOLOGY,
WROBLEWSKIEGO 15, 93-590 LODZ, POLAND

² DEPARTMENT OF POLYMER CHEMISTRY,
CENTRE OF MOLECULAR AND MACROMOLECULAR STUDIES,
POLISH ACADEMY OF SCIENCES,
SIENKIEWICZA 112, 90-363 LODZ, POLAND

*E-MAIL: AGNIESZKA.ADAMUS@P.LODZ.PL

[ENGINEERING OF BIOMATERIALS 148 (2018) 87]

Introduction

Biodegradable polymers, especially aliphatic polyesters such as polylactide (PLA), poly(ϵ -caprolactone) (PCL), polyglycolide (PGA), or poly(trimethylene carbonate) (PTMC), as well as their copolymers have attracted great attention because of their acceptable biocompatibility^[1], and have been widely used in various medical applications.^[2] PLA is an intrinsically semicrystalline polymer with the glass transition temperature (T_g) about 65°C and relatively high melting temperature (T_m), typically over 170°C. With good tensile strength, low extension, and a high tensile modulus (ca. 3 GPa), PLA has been considered as an ideal biomaterial in the field of load-bearing applications, e.g. as orthopedic implants. Nevertheless, the high crystallinity of PLA results in poor elasticity and long resorption time of 2-3 years.^[3] Generally, amorphous poly(1,3-trimethylene carbonate) (PTMC) with T_g at ca. -20°C has excellent flexibility.^[4] Copolymerization is usual and efficient method of tailoring polymeric biomaterials properties because the specific architecture and composition of the copolymer can be obtained relatively easily. Therefore, combined properties of a rigid chain from high T_g polyester with a soft segments from rubbery polycarbonate can be achieved by introducing PTMC as a soft block into brittle PLA segments.^[5] Such modification is also crucial in terms of biodegradation mechanism and kinetics of discussed copolymers. In this work, we have focused on oxidative degradation of P(LA-b-TMC) copolymers with lactide (LA) contents 70% and 50%, since the data on that are unavailable in the literature.

Materials and Methods

Samples of P(LA-b-TMC) block copolymers with compositions LA/TMC 50/50 and 70/30 were subjected to oxidative degradation. As controls, homopolymers of PLA and PTMC were used. Rectangular specimens of approximately 50 × 5 × 0.3 mm were incubated in 3% hydrogen peroxide solutions with 60 mM Co²⁺ at 37°C, refreshed once a week. Samples were periodically removed from the incubation solution, washed with deionized water and vacuum dried at room temperature to constant weight. Samples were subsequently investigated by physicochemical methods. Tensile properties were examined and these results were complemented by evaluation of mass loss, water uptake, contact angle, morphology (SEM), molecular weight of polymer (GPC) and its thermal properties (DSC). Data are discussed in comparison with ¹H NMR results which allow to follow changes of the composition and average sequence distribution of LA/TMC components.

Results and Discussion

During the first 5 weeks, all samples exhibit negligible weight loss of less than 0.5% and very similar degradation rate based on the GPC results. Thereafter, the degradation rate becomes different for samples with various LA contents. For PLA and samples of LA/TMC molar ratio 70/30 a small weight loss below 1.0% is detected at 15 weeks. In the case of P(LA-b-TMC) 50/50 and PTMC, apparent weight loss is detected from 10 weeks and steadily increases to 2.0% and 5.0% at 15 weeks, respectively. In contrast to the weight loss, the molecular weight of PTMC sample and P(LA-b-TMC) 50/50 sample remained constant for 10 weeks, further a slight decrease was observed. In the case of PLA and P(LA-b-TMC) 70/30 samples a substantial drop in molecular weight was observed from 5 weeks, which was reflected in mechanical properties of the studied materials. The compositions of investigated polymers remain almost unchanged during the first 5 weeks, as evaluated with NMR, that is in agreement with the fact that no significant mass loss was detected. Beyond that time, LA content decreases from 70% to 66% for P(LA-b-TMC) 70/30, and from 50% to 40% for P(LA-b-TMC) 50/50. These findings indicate that LA units are preferentially degraded in copolymers with higher contents of TMC. The compositional changes indicated that TMC units are degradable in P(LA-b-TMC) 50/50 copolymers although PTMC homopolymer is not degradable.

PLA and P(LA-b-TMC) 70/30 samples were becoming brittle and fell apart into pieces during degradation. PTMC and P(LA-b-TMC) 50/50 samples deformed – attained globular shape, became soft, and adhered to vessel wall. The original samples exhibited a smooth surface, however in the course of degradation their surfaces became rough and a highly hollow structure was detected after 5 weeks, the size and depth of the hollows increased with the incubation time.

Conclusions

In this study, we have demonstrated that homopolymers and their copolymers respond differently to oxidative degradation, depending on the morphological and chemical composition of the material. PTMC is more prone to oxidative degradation as compared to P(TMC-b-LA) 50/50. Given this knowledge on degradation characteristics of different materials, we are able to tailor degradation characteristics by combining PLA backbones with additional PTMC. The toolbox of techniques that has been used to study the degradation of biomaterials can be applied and employed to screen, limit and select biomaterials that are going to be used for pre-clinical in vivo studies with regard to a variety of clinical applications.

Acknowledgments

This study was funded by National Science Center, Poland, grant No. 2012/05/N/ST5/01869.

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