22nd International Conference
ENGINEERING MECHANICS 2016
Svratka, Czech Republic, 9 – 12 May 2016

EFFECT OF WATER ABSORPTION ON THE MECHANICAL PROPERTIES OF BIODEGRADABLE MATERIALS FOR MEDICAL APPLICATIONS

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Abstract: *This article presents results of conducted studies of mechanical properties offered by biodegradable polymers in the production of biodegradable implants. The adopted research methodology comprising specimen geometry and simulating the implant functioning environment allowed the determination of the impact of water absorption during hydrolytic degradation on changes of mechanical properties of polylactide injection moulded pieces. The obtained test results were then analysed statistically, and on this basis a value correlation was defined for the obtained results in change of specimen mass in relation to change in mechanical strength of the given material.*

Keywords: Hydrolytic degradation, Biodegradable implants, Mechanical properties, Water absorption, Medical applications

1. Introduction

Poly(lactide acid), also called polylactide, is a biopolymer, the basic synthesis method of which is polymerisation with Ring-Opening-Polimerization, ROP. As an effect of ROP polymerisation a biopolymer is obtained having a molecular weight (M) within the range of $103 \le M \le 106$ and with specified terminal groups and macro particle structure. Depending on the type of used lactide acid enantiomer, which is the input product in the polylactide polymerisation process, polylactide with defined terminal groups is obtained. Both lactide and lactic acid are characterised by the occurrence of two chilarity centres (asymmetric carbon atom), and consequently the type of lactide acid enantiomer used in the synthesis affects the form of obtained lactide. There is L(-)-lactide, D(+)-lactide or DL- lactide, which following polymerisation allows obtaining poly(L-lactide), poly(D-lactide) or poly(D,L-lactide). Polymerisation executed by the ROP method was described in an article of Żenkiewicz M., Richert J. (2009), and Foltynowicz Z., Jakubiak P. (2002).

Polylactide is a semi-crystalline aliphatic thermoplastic polymer, which is used in medical applications for the production of biodegradable implants. Those implants are made of pure polymer, conformation of pure polymer or copolymers. Polylactide has become widely used as material for the production of stents and vascular grafts, surgical suturing materials, facial fracture fixation plates or plates for osteosynthesis. Taking into account the capability of hydrolytic degradation, polylactide decays in the patient's organism to dioxide and water within a period of circa 12 – 18 months or in an appropriately shorter time, depending on the copolymer type it is comprised by (Das D., et all (2012))

The hydrolytic degradation of polymer occurs in a process involving a chemical factor - water. The human organism is to a large extent built of water, and so placing an implant made of hygroscopic polylactide in the organism of a patient leads to the absorption of water by material. By permeating into the material, the absorbed water changes the water concentration gradient between its surface and the internal part. The impact of water and polymer particles contributes to material erosion in the surface or

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throughout the material, as a result of which the mechanical strength of biodegradable material changes (Vieira A.C at all (2010)). There are different ways to analyze the mechanical properties of biomaterials. One of them is testing through gradually increasing load method (Wirwicki M. at all (2014)).

The aim of this study was to investigate the impact of absorbed degrading medium on changes of mechanical strength of polylactide, subjected to tests of monotonic stretching in the function of time of controlled hydrolytic degradation.

2. Materials and Methods

2.1. Material

In the study use was made of sample of biopolymer characterised by average viscosity - poly(lactide acid), PLA (Ingeo™ Biopolymer 3100HP), manufactured by NatureWorks LLC.

2.2. Material processing

The adopted specimen geometry is appropriate for standard polymer moulded parts had a cross-section of the working specimen amounting on average to 43mm (PN-EN ISO527-2). Polymer moulded parts were prepared in the process of injection moulding. The initially prepared granulate was dried for 3 hours in a vacuum drier at a temperature of 100°C, and then injected at injection parameters allowing obtaining amorphous material.

2.3. Characterization

2.3.1. Hydrolytic degradation

Controlled hydrolytic degradation was carried out in accordance with the adopted technology, which comprises the type of degrading medium and its temperature, as well as time intervals between successive degradation periods.

The samples were weighed (analytical scales RADWAG, d=0.1mg) to determine the initial weight of samples prior to their degradation, and then placed in heated up degrading media. In the tests use was made of three degrading media, and namely distilled water, phosphate buffered saline solution (PBS) and 0.9% sodium chloride solution, which were heated up to a temperature conforming to the temperature of the warm-blooded human organism ($T=37 \pm 1°C$).

The samples were removed from the degrading medium after 1, 2, 6, 12, 26 weeks, dried with paper towels and then weighed and characterised using the following methods.

2.3.2. Mass change

To determine changes in specimen weight as a result of absorption of the degrading medium, the samples were weighed before and after degrading. The specimen mass change percentage was determined from the following dependence: *% change of sample mass = [(final mass – initial mass)/initial mass]* 100*

3.3.3. Mechanical strength

Degradable and non-degradable specimen were subjected to the single-axial tensile test on the Instron 8874 tensile tester. The adopted test conditions were in conformity to the standard PN-EN ISO527-2: distance between grips being 115mm, stretching speed of 1mm/min. The deformation of the tested material was determined with the use of a static clip-on extensometer.

2.4. Statistical analysis

Results of the characteristic description of the material were developed with the use of the STATISTICA 12.5 software. The conformity of decomposition of the tested parameters in relation to normal decomposition was determined by the Shapiro-Wilk test. In the further part of the analysis use was made of parametric and nonparametric tests. The statistical significance of differences in the obtained results was set out using the ANOVA one-way test and by multiple comparisons made using the Tukey algorithm. A review of the correlations was made using the Pearson test. The level of $p<0.05$ was adopted as one of statistical significance.

3. Results and Discussion

It is assumed that an important factor that characterises biodegradable polymers is an assessment of a change in specimen mass over the degradation time. The determination of the actual specimen mass loss is possible by subjecting it to the process of vacuum drying, however, specimen subjected to this process cannot be used in mechanical durability tests. For this reason in this project the adopted method for assessing changes in specimen mass is the determination of water absorption percentage in relation of specimen not subjected to degradation. The specimen mass loss during degradation was calculated for H_2O: T1 = 0.0085%, T6 = 0.0093%, T12 = 0.0103%, T26 = 0.0150%, for PBS: T1 = 0.0088%, T6 = 0.0095%, T12 = 0.0102%, T26 = 0.0106% and for NaCl: T1 = 0.0085%, T6 = 0.0093%, T12 = 0.0099%, T26 = 0.0133%. Results of a specimen mass loss percentage during degradation were presented on fig. 1. tensile strength at break (σ_B).

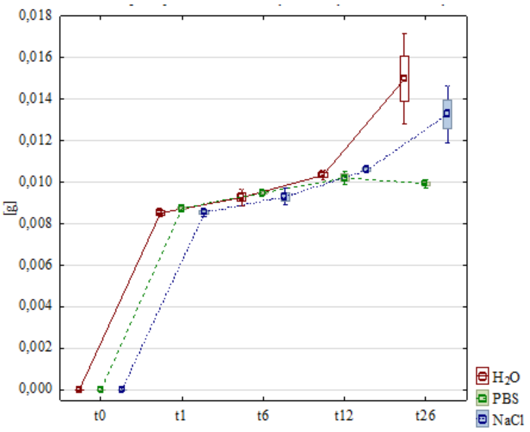

Fig. 1. Percentage mass loss

The initial tensile strength (σ_M), was 57,56 MPa. The average value of mechanical strength in time-points of degradation was measure for H_2O: T1 = 49.78 MPa, T6 = 49.78 MPa, T12 = 55.30 MPa, T26 = 32.95 MPa; for PBS: T1 = 50.12 MPa, T6 = 50.14 MPa, T12 = 55.48 MPa, T26 = 39.45 MPa and for NaCl: T1 = 50.37 MPa, T6 = 50.33 MPa, T12 = 55.46 MPa, T26 = 37.45 MPa. Results of a specimen mechanical strength were presented on fig. 2

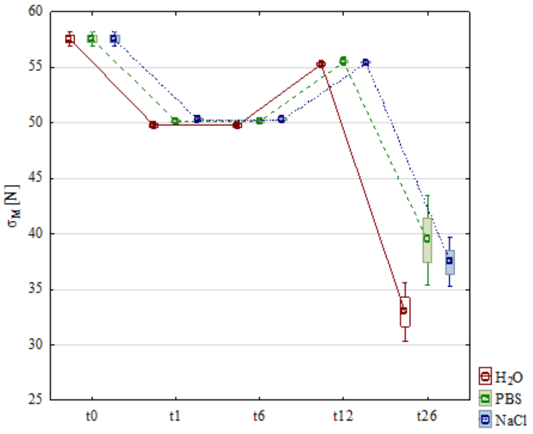

Fig. 2. Tensile strength (σ_M)

The initial tensile strength at break (σ_B), was 56.05 MPa. The average value of mechanical strength in time-points of degradation was measure for H_2O: T1 = 38.24 MPa, T6 = 39.48 MPa, T12 = 48.60 MPa, T26 = 30.53 MPa; for PBS: T1 = 39.03 MPa, T6 = 39.89 MPa, T12 = 47.91 MPa, T26 = 39.45 MPa and for NaCl: T1 = 39.84 MPa, T6 = 40.24 MPa, T12 = 47.32 MPa, T26 = 36.91 MPa. Results of a specimen mechanical strength were presented on fig. 3

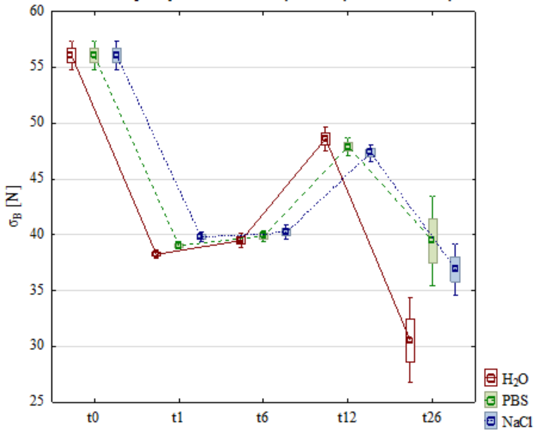

Fig. 3. Tensile strength at break (σ_B).

The implemented correlation analysis pointed to a robust linear dependence between the increase in the mass of tested specimens and their lower strength defined as parameter σ_M and σ_B. The analysed dependencies occurred in a similar way for the H_2O, PBS and NaCl medium (Tab.1). In addition a significant statistical dependency may be indicated between changes between changes in parameters given the degrading medium in which the tested specimens were immersed.

Tab. 1. Correlation table

Parameter		Degradation medium		
		H2O	PBS	NaCl
σ_M	R^2	-0.7461	-0.4936	-0.6905
	p-value	p=0.000	p=0.001	p=0.000
σ_B	R^2	-0.7646	-0.7402	-0.8131
	p-value	p=0.000	p=0.000	p=0.000

4. Conclusions

The changes in tensile strength and tensile strength at break are the effect of absorption degradation medium. The results show that with the time of degradation increase a degradation medium absorption and at the same time are reduced mechanical properties of investigated material. It has been shown that in the early stages of hydrolytic degradation (up to 12 weeks), degradation medium in which were polymer specimens immersed, has influence on polymer plasticization. But a follow up of degradation, shown that specimens, after 26 weeks time of immersion, were brittle. On this basis can conclude that the amount of absorbed fluid by amorphous material and aging time, is changing the arrangement of the polymer linkages within the specimen volume.

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