

The influence of the environment on the degradation of polylactides and their composites

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Materials

ABSTRACT

Purpose: The aim of this paper was to determine the influence of environment on degradation process of polylactide-based materials assigned for the implementation in medical implants and short-life products. The hydrolytic degradation, the biodegradation and the degradation under in vivo conditions were determined for the polylactide (PLA), the lactide and glycolide copolymer (PGLA) and the composites modified by hydroxyapatite particles, carbon fibres and natural fibres (hemp, jute).

Design/methodology/approach: The degradation was analyzed on the basis of the changes occurring in the environment (such as those in pH fluids), the changes of the mass and resistance of the examined materials, as well as the structural infrared analyses.

Findings: It was stated that the degradation time depends on the type of the environment with which the material is in contact. In the water environment, the degradation is faster than in the presence of a compost, and in the Ringer fluid, its speed is higher than in the artificial serum SBF. The in vitro observations focus mainly on the chemical interaction between the examined materials and the artificial environment. The degradation speed is dependent, among others, on the viscosity of the applied fluids and thus, their ability of penetration in the polymer's structure and on the interfacial boundaries. In a living organism, the fundamental role is played by such processes as the protein adsorption, the cellular and tissue reactions, the body fluid flows and the charge exchanges, and thus, the degradation process is significantly faster than that under in vitro conditions.

Practical implications: Result of this study can be used to elaborate the manufacturing method of implants with controlled resorption time and degradable short life time products like packages.

Originality/value: In this paper effect of hydrolytic degradation, biodegradation and in vivo degradation on polymers' and composites' behaviour was shown. Result of this study can be used to prognosis of durability of degradable materials.

Keywords: Polylactide; Composites; Degradation; Fibers; FTIR

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1. Introduction

Many scientific centres searching for inexpensive, environment-friendly materials have been focusing their interest on the degradable polymers and their composites with natural additions. Both in the production phase and the processing and waste management phases, they present an interesting alternative for the stable polymers and the composites strengthened by artificial fibres.

The mass thermoplastic material more and more commonly applied in the production of saleable goods has been, in the recent years, the polylactide (PLA) [1-3]. Initially, due to the small production scale and the high costs of obtaining the material, the polylactide and its copolymers were only used on a limited scale, mainly in medicine [4-5].

In the medical applications (regenerative medicine) the polylactide and its composites are extremely useful. The application of implants produced of such materials makes it possible to avoid a repetition of the surgical procedure in order to remove them. The properly selected chemical content of the implant allows to synchronize the time of its resorption with the time of the tissue's regeneration. The current tendencies in the material development are focused on the search for new possibilities of modification of the resorbable polymers, in order to improve their mechanical and biological properties and thus to increase the functionality of such composites. Among the materials assigned for medical implants, the biomimetic approach is dominant – its idea is to apply the composite materials in which the polymer matrix is modified by a fibre phase imitating the collagen fibres in the organic matrix, as well as by bioactive ceramic grains imitating the mineral phase of the bone [6-9].

Biomaterials based on the resorbable polymers have their application mainly in tissue engineering and bone surgery, including orthopaedics, as medicine carriers [4, 5, 10, 11, 12].

Both in the medical and the technical applications, the course and time of the polymer's degradation is a very significant issue. Depending on the conditions and the environment of the material, it proceeds in different ways. That is why, in order to examine the degradation under laboratory conditions, different media are applied. The most universal one is distilled water. Incubation in water makes it possible to observe the material's behaviour both in a living organism and in a high humidity environment (eg. soil). For implant materials, an even better reflection of the conditions characteristic for a living organism will be provided by incubation in physiological fluids, such as the Ringer fluid, the artificial serum SBF, the artificial saliva etc., as well as by *in vivo* examinations in a living organism.

In the case of environment-friendly consumer products, the degradation can be examined by keeping the former in the soil or by composting. This allows for a determination of the approximate time of the material's decomposition during the pre-planned degradation (composting) or during a non-purposeful one (littering).

The degradation of the resorbable polymers depends also on many macro- and microstructural factors, such as the initial particle mass, the polydispersion level, porosity, the monomer and oligomer concentration, crystallinity, as well as the type, amount and distribution of the introduced additions [10-12].

The time of resorption of pure polylactide, because of its hydrophobic character due to the presence of methyl groups, is much longer than in the case of polyglycolide. That is why by changing the fraction of the lactide and glycolide mers in the copolymers, it is

possible to control their resorption speed, depending on the needs determined by the material's assignment [13].

The paper presents an assessment of the degradation of the composite materials based on the lactide and glycolide copolymer assigned for medical implants and those only based on the polylactide assigned for short-life consumer products. We determined the hydrolytic degradation, as well as the biodegradation and that under *in vivo* conditions.

2. Materials and methods

In the part concerning the studies of composite materials for medicine, as the matrix the poly(lactide-co-glycolide) (PGLA) was used: 84% of lactide and 16% of glycolide ($M_n=85000$ Da, $M_w/M_n=2.1$) produced at the Polymer and Carbon Materials Centre of the Polish Academy of Sciences in Zabrze [14]. As the modifying phase we used 15 wt % carbon fibres (CF): FT 300B Torayka, $d=1.76$ g/cm³, $\sigma_r = 3.2$ GPa, $E=235$ GPa and 15 wt % hydroxyapatite particles of natural origin (an ox's bone) (HAP): $d=3.16$ g/cm³, specific surface $S_w = 79.7$ m²/g [15]. The comparative studies were performed for samples of pure PGLA. The cylinder-shaped implants were obtained with the method of injection at 180°C.

For the simulation of the biological environment we used the Ringer fluid produced by Baxter Terpol Sp. z o.o. with the following composition [g/cm³]: NaCl⁻ - 8.60, KCl⁻ - 0.30, CaCl⁻ - 0.48. Simultaneously, the material was incubated in the SBF fluid (artificial serum) of the following ion content [mmol/l]: Na⁺ - 142.0, K⁺ - 5.0, Ca²⁺ - 2.5, Mg²⁺ - 1.5, Cl⁻ - 148.8, HCO₃⁻ - 4.2, HPO₄²⁻ - 1.0, SO₄²⁻ - 0.5. The samples were incubated at 37°C for the period of 16 weeks. Each week, before the change of fluids, the measurements of the sample mass and the pH solution were performed with the use of the pH-meter CP-315 ELEMETRON.

The experimental studies were conducted on New Zealand rabbits. All the procedures were performed at the Central Animal Unit of the Śląsk Medical Academy, on permission of the Bioethical Board. The implants were introduced into surgically prepared 3.2 mm diameter placenta in the submaxilla bone. The control periods were set to the 6th and the 12th week counting from the material's implantation.

In the part concerning the studies of environment-friendly materials of a short lifetime, samples in the form of paddles (according to the PN-EN ISO 527 standard) were obtained by the injection method at 165°C. For the matrix we used the Ingeo 3051D polylactide by Nature Works, the USA (PLA), and as the reinforcement – 5 wt % natural plant fibres – hemp and jute – of the 1-2mm length [16].

The composite degradation was examined in distilled water at 37°C and during 15-week composting (eco-composter TERMO-410). As the activator stimulating the bio-degradation process and accelerating the decomposition of organic waste the Radivit formulation by Neudorff was applied.

For both groups of materials, for the degradation assessment, we performed structural analyses by the method of infrared spectroscopy (FTIR) with the use of Fourier Spectrometer BIO-RAD FTS-60V. The experiments were conducted with the 400 – 4000 cm⁻¹ technique. In order to calculate the width at half height C=O band with 1760 cm⁻¹, we performed a correction of the spectra to the base line in the region of 1800-1000 cm⁻¹, with the use of the Win-Pro program Ver. 2.9 BioRad. On a universal testing machine (Zwick 1435), we also determined the tensile strength for the initial samples and those in the process of degradation.

3. Results and discussion

3.1. Materials for medicine

The multi-functionality of the composite biomaterials based on the resorbable polymers assumes a high initial strength and a low Young's modulus of the implant, which allow for the acquisition of biomechanical functions by the healed tissue in the initial period after the implantation, a gradual resorption of the matrix adjusted to the regeneration speed of the healed tissue and its gradual loading, stimulation of the bone's growth and assuring the proper osteointegration, for which the bioactive ceramic additions are responsible, and finally, the creation of a scaffold for the bone's growth after the resorption of the polymer matrix, enabled by the applied fibrous modifiers. Such a complex system makes it necessary for the examination of biomaterials to involve numerous investigative methods, starting from the structural and microstructural analysis, and the physicochemical and mechanical examinations. As for the determination of the degradation speed of this type of resorbable implants in a dependence, it is one of the key parameters which are necessary to be determined already in the preliminary tests.

The performed examinations showed that to such multifunctional materials belong the composites with the poly(lactide-co-glycolide) matrix with such fibrous additions as carbon, alginate, and polylactide fibres, as well as nanometric hydroxyapatite particles, TCP, and even those with nano-tubes and the bactericidal nano-silver [17-19].

In the assessment of the degradation speed of the resorbable polymers, highly useful is the infrared spectroscopy method. The changing character of the bands, the change of their intensity and width at half height are connected with the process of hydrolysis of the polymer and the breaking of the bonds in the chain.

The infrared analysis of the spectra for PGLA+CF and PGLA+HAP showed that the modifying additions accelerate the degradation of the polymer matrix. (Figs. 1, 2, 3) [20]. The polymer's degradation is testified by such changes in the spectra's character as the fading of the spectra connected with the C-H bond vibrations in the CH, CH₃ and CH₂ group, in the range of 2800-3000 cm⁻¹ (stretching vibrations) and 1340-1480 cm⁻¹ (bending vibrations) in relation to the spectrum connected with the vibrations of the C=O groups. These changes are related to the breaking of the polyester chains. Together with the degradation of the polymer, also a decrease of the width at half height of the spectra occurs, which is connected with the increase of the polymer's crystallinity. The increase of the crystallinity level is connected with the degradation mechanism of PGLA. The first to undergo the hydrolysis are the amorphous domains, due to the higher water absorption, and next, the degradation starts to include also the crystalline areas [21]. The remaining polymer chains in the segments not involved in the degradation, as a result of an increase of the free space, become reorganized towards increasing the crystallinity level. These changes are more clearly visible on the composites' spectra, which points to their faster degradation. The interfacial modifier-matrix boundaries are paths for a fast diffusion for the incubation fluids, which influences the composites' degradation, as opposed to the sole polymer.

The effect of the modifying additions on the degradation of PGLA and that of the type of environment in which it occurs are verified by the tests of the pH changes of the Ringer fluid and SBF, performed in the function of the incubation time of the analyzed materials and the mass changes of the incubated samples (Figs. 4, 5) [22].

The drop of pH connected with the polymer's hydrolysis and thus the acidification of the environment was the soonest for the composite PGLA+CF. In the case of the composite PGLA+HAP, the pH changes of the Ringer fluid are delayed in time, which is most probably connected with the simultaneous process of the polymer's degradation and the precipitation and dissolution of HAP. All the described changes occurred visibly earlier in the case of the samples incubated in the Ringer fluid than in that of SBF. The higher activity of the Ringer fluid compared to SBF can be the result of the lower viscosity of the Ringer fluid and the facilitated penetration into the polymer's structure and on the phase boundaries.

The measurement of the mass of the samples in the function of the incubation time allows for a direct assessment of the degradation speed of the copolymer connected with the loss of mass, but also enables the assessment of the fluid's absorption level. The absorption of the surrounding fluid determines the speed of the degradation [23]. In all the incubated samples, at the initial stage, an increase of the sample mass was observed, which is a result of the absorption of the physiological fluid (Fig. 7) [22]. This phenomenon is typical at the initial stage of the degradation of the aliphatic polyesters [21]. The highest mass increase reflecting the most visible swelling of the samples is noticeable in the case of the composite PGLA+HAP and it is connected with the absorption of the fluid both by the matrix phase and the modifier's particle. A significant loss of mass in the case of both composites incubated in the Ringer fluid takes place after the 11th incubation week, and for the pure PGLA – after the 14th week. This verifies the conclusion that modifiers accelerate the degradation of the copolymer.

The proceeding degradation of PGLA and its composites is accompanied by a loss of the mechanical properties (Fig. 6). For the composite PGLA+HAP, we observe a significant loss of strength already after 48 hours of incubation, and for PGLA+CF, the biggest loss of strength occurred after 4 weeks of incubation (28 days). After 10 weeks (70 days) in the physiological fluid, the examined materials cease to perform the mechanic function.

Compared to the *in vitro* tests, the natural biological environment significantly accelerates the degradation of PGLA and its composites. It is indicated by the much faster changes in the character of the bands on the FTIR spectra, connected with the degradation of the polymer (Figs. 7,8,9). The *in vitro* observations focused mainly on the chemical interaction between the examined materials and the artificial environment simulating the natural physiological fluid. The living organism is a more complex system and in the interaction with artificial implant materials the basic role is played by such processes as the protein absorption, the cellular and tissue reactions, the body fluid flows and the charge exchanges. Thus the degradation process runs in a different course than that under *in vitro* conditions, especially as far as its kinetics is concerned.

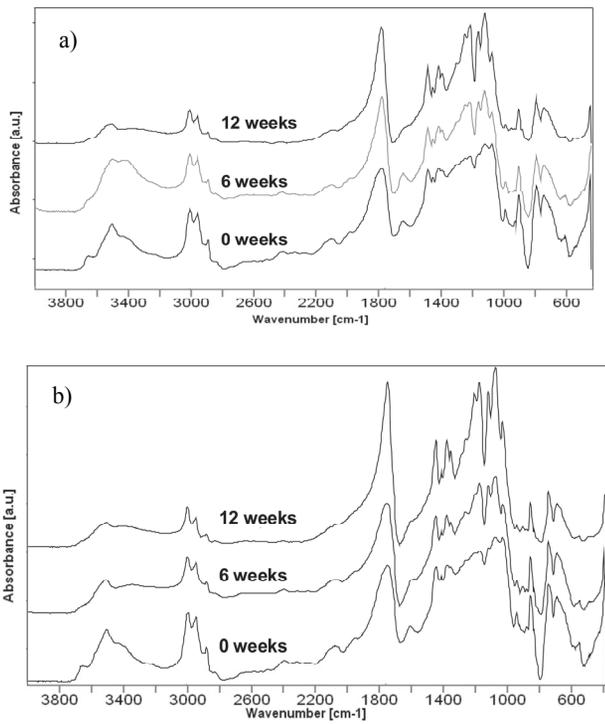


Fig. 1. FTIR spectra for PGLA samples incubated in a) the Ringer fluid b) SBF

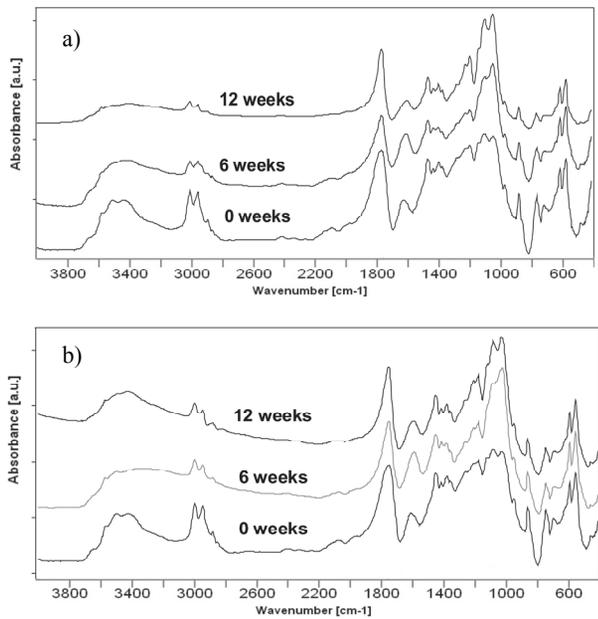


Fig. 2. FTIR spectra for PGLA+HAP samples incubated in a) the Ringer fluid b) SBF

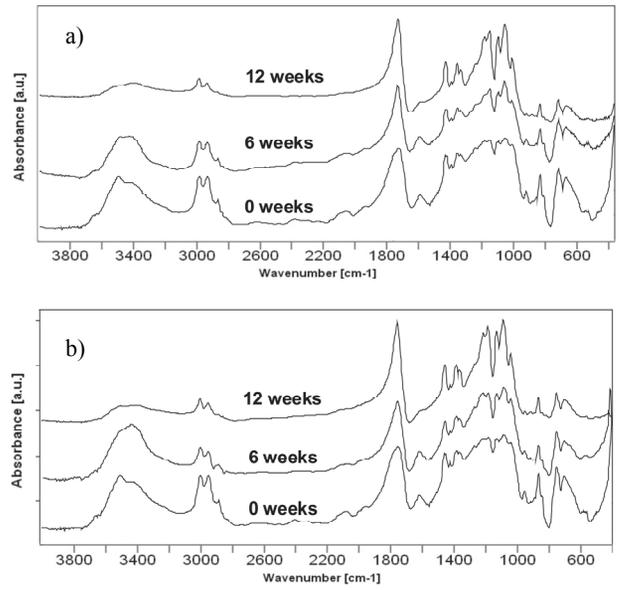


Fig. 3. FTIR spectra for PGLA+CF samples incubated in a) the Ringer fluid b) SBF

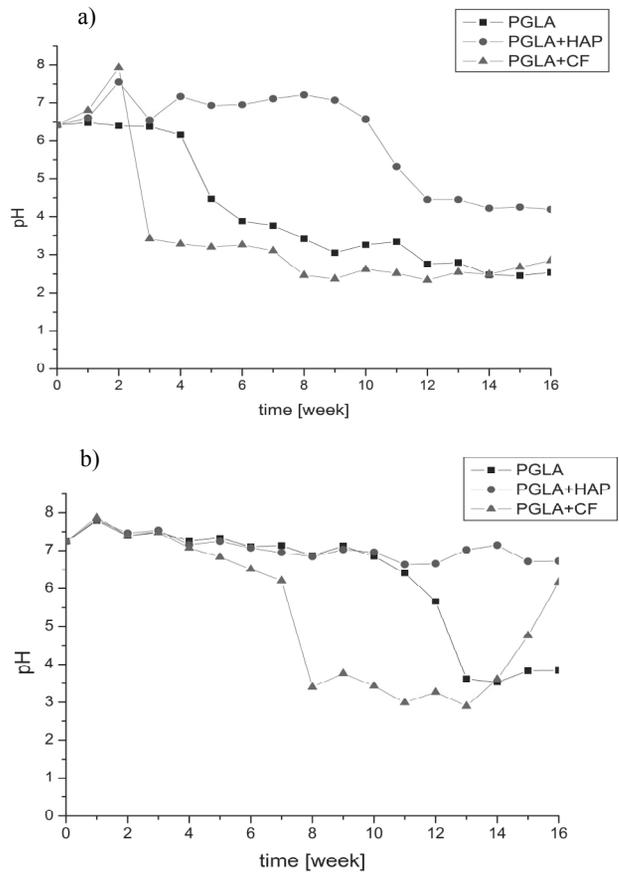


Fig. 4. pH changes of a) the Ringer fluid, b) SBF, in the function of incubation time of samples PGLA, PGLA+HAP and GLA+CF

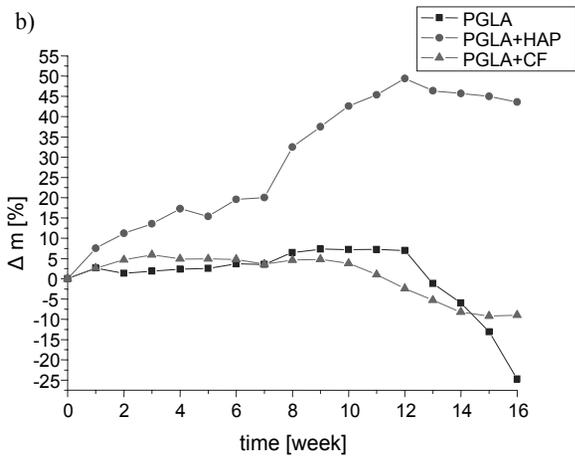
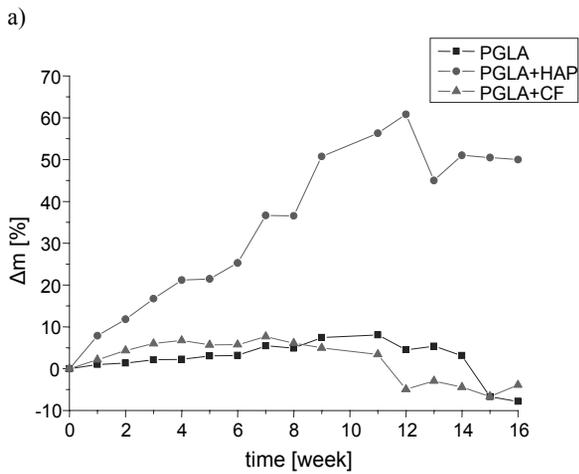


Fig. 5. Mass changes in samples PGLA, PGLA+HAP and PGLA+CF in the function of the time of incubation in a) the Ringer fluid b) SBF

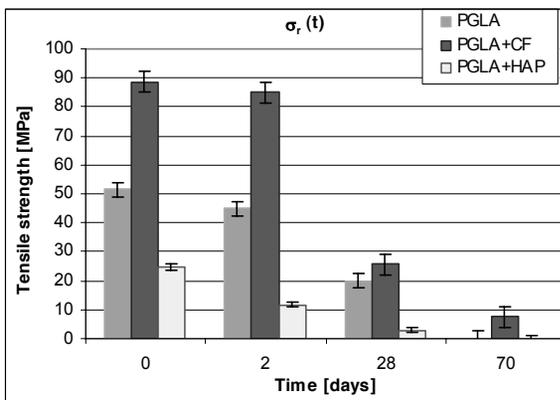


Fig. 6. Mechanical property changes of PGLA+HAP, PGLA+CF in the function of the time of incubation in the Ringer fluid

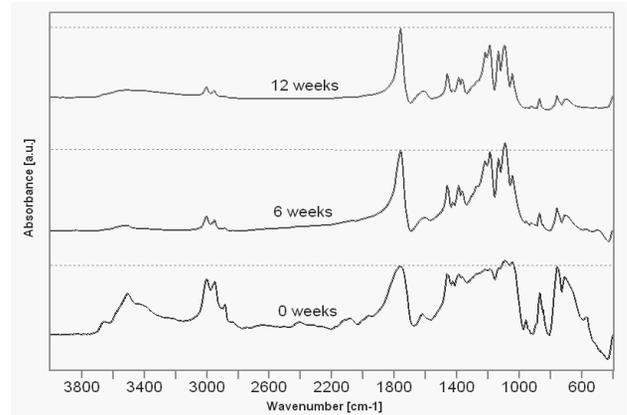


Fig. 7. FTIR spectra for PGLA implants in rabbit submaxilla bone

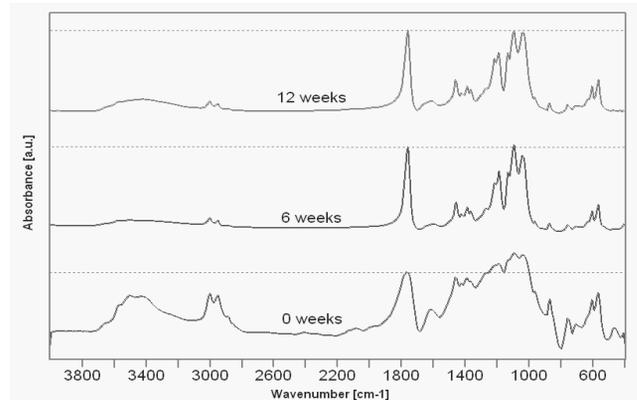


Fig. 8. FTIR spectra for PGLA+HAP implants in rabbit submaxilla bone

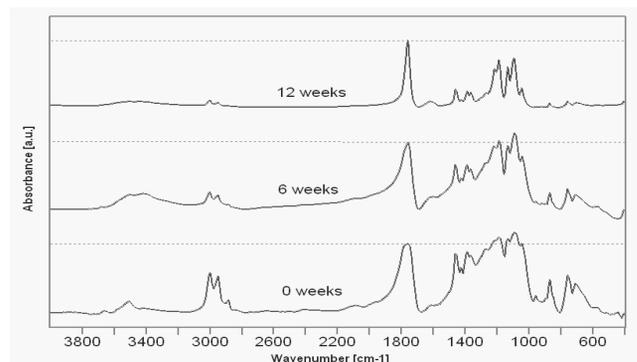


Fig. 9. FTIR spectra for PGLA+CF implants in rabbit submaxilla bone

3.2. Eco-composites

The degradable materials obtained from renewable resources are an important alternative for the materials obtained from the petro-chemical resources. The polymer more and more commonly

used in mass production is the polylactide. Applied, among others, for the production of short-life goods, it is gradually replacing the bio-stable polymers which do not decompose in natural conditions. The microbiological degradation of the polylactide is stimulated by the presence of selected bacterial strains and proceeds relatively slowly, especially at lower temperatures. The speed of the process can be controlled by means of combining the polymer with other biodegradable materials, such as natural fibres. The presence of the fibres modifies the properties of such composite. Above all, it facilitates the population of the soil micro-organisms in those polymers which are harder to biologically decompose. Moreover, it increases the surface roughness and thus facilitates the composite's degradation. Polymers' degradation speed is dependent on the state of the surface and additionally, the polymers with a non-homogenous surface decompose faster than those whose surface characterizes in a lower roughness.

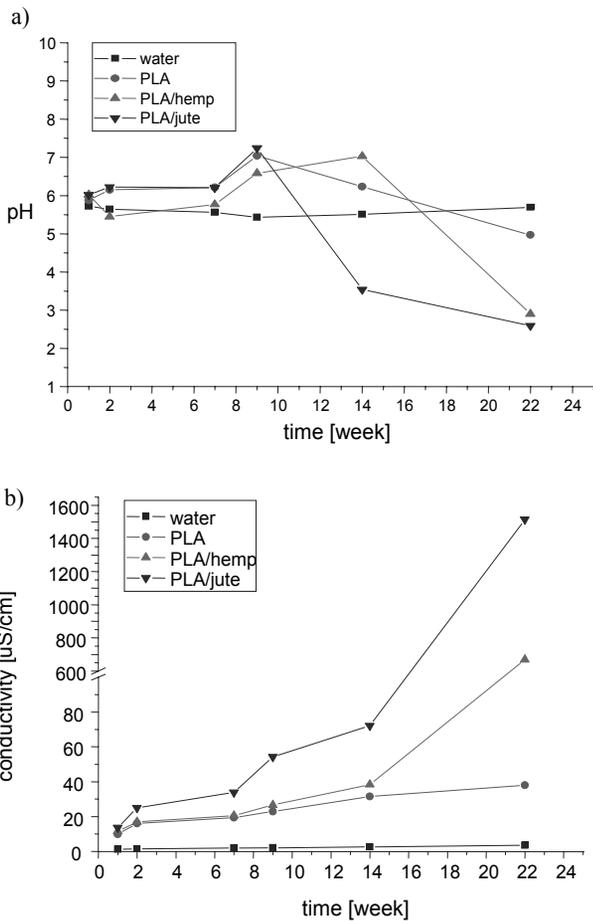


Fig. 10. Changes in the pH and the conductivity during incubation in distilled water of PLA, PLA/hemp, PLA/jute

Analyzing the changes which take place in the materials (such as the structure, the mechanical properties, the mass – Fig. 11) and the changes in the immersion medium during incubation

(pH, conductivity – Fig. 10) it can be stated that the composites with a polylactide matrix with the addition of an even small amount of natural fibres (5 wt %) are more easily degradable than the pure polymer. The changes in the pH and the conductivity of the immersion medium (Fig. 10) in the case of the composites (especially PLA/jute) take place significantly sooner than for the initial polylactide.

In all the incubated samples, at the initial stage, we observe, similarly to PGLA, an increase of the samples' mass, which is a result of water absorption (Fig. 11).

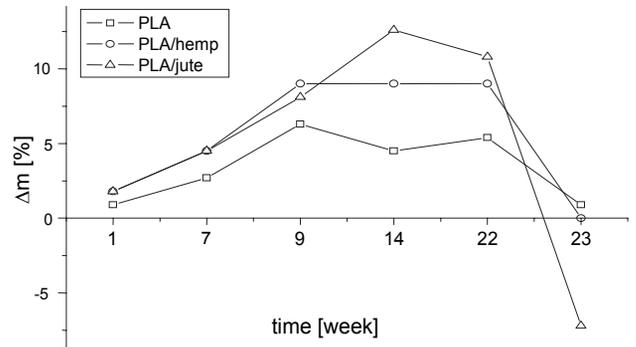


Fig. 11. Mass change of PLA, PLA/hemp and PLA/jute versus time of the incubation in water

Also, the infrared tests visibly point to a faster degradation of the composites (especially with jute fibres). Figure 12 presents the infrared spectra for the initial PLA and that after the incubation in distilled water. The gradual degradation of the polymer is testified by the increase in the intensity of all the bands in relation to the band connected with the vibrations of the groups C=O with 1760 cm^{-1} ; yet, it is the most visible in the case of the bands originating from the groups CH and CH_3 (2800-3000 cm^{-1} , 1452 cm^{-1} , 1367 and 1386 cm^{-1}). Characteristic for the process of degradation is also the decrease of the width at half height of the bands, which is mainly visible for the band with 1760 cm^{-1} originating from the groups C=O.

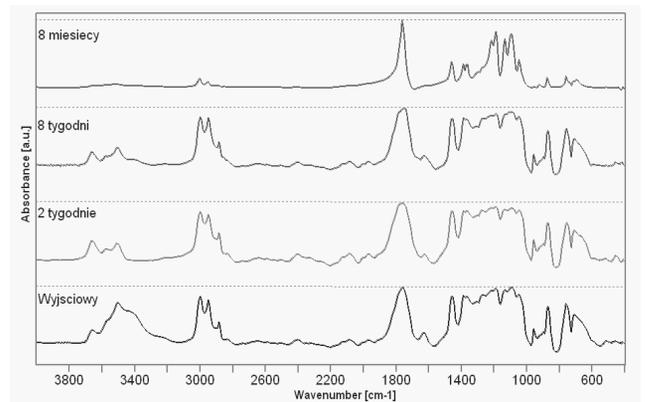


Fig. 12. FTIR spectra for the initial polylactide and after incubation in distilled water

Figure 13 presents the spectra of the polylactide composite with jute before and after incubation in distilled water and after composting. Their analysis makes it possible to compare the speeds of degradation in both environments. Due to the fact that the band with 1760 cm^{-1} possesses the highest intensity, it was selected as the reference point in the analysis of the relations with the remaining bands. Similarly to the case of the sole polylactide, the gradual degradation of the matrix is testified by the decrease of the intensity of the bands connected with the vibrations of the bonds C-H in the range $2800\text{-}3050\text{ cm}^{-1}$ and $1340\text{-}1480\text{ cm}^{-1}$, in relation with the band C=O with 1760 cm^{-1} . These changes are the biggest in the case of the composite after 15 weeks of incubation in distilled water and 25 weeks of composting, which suggests that the water environment significantly accelerates the polymer's degradation, compared to the compost one. The process of the polylactide's degradation is accompanied by an increase of the crystallinity level of the polymer, connected with the loosening of the polymer's structure, as a result of the degradation and thus the facilitated reorganization of the polylactide chains [21]. On the FTIR spectra, it is reflected by the decrease of the width at half height of the bands. Such changes are visible in the case of the composites after 15 weeks of incubation in water and 25 weeks of composting. This verifies the fast degradation of the polylactide in the water environment. Moreover, these changes are more clearly visible than in the case of the pure polymer after composting. This allows to draw a conclusion that the addition of a modifier in the form of jute fibres accelerates the degradation of the polylactide matrix.

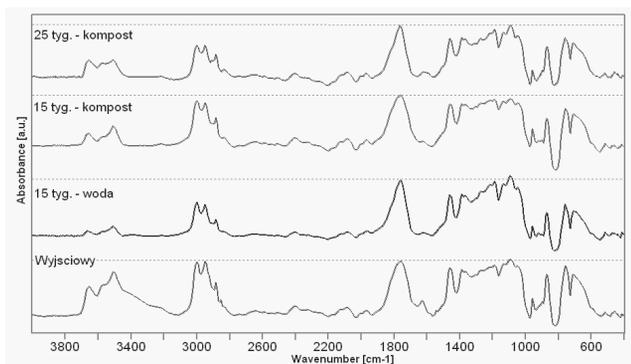


Fig. 13. FTIR spectra of the initial PLA+jute composite, after incubation in distilled water and after composting

The proceeding degradation of the materials after composting can also be verified by the changes in the mechanical properties (Fig. 14). The initial composites possess the strength comparable to that of the matrix's material. During the over 3 months of composting, there are no records of any strength decrease of the pure polylactide, while in the water environment, an over 20% decrease in the strength can be observed. In the case of the composites with hemp fibres, after the above mentioned time, we can observe a dropping tendency both during the composting and the incubation in water. For the composites with jute fibres, already after 3 weeks of composting, the strength decreases by 60%, and after 15 weeks, it drops to only 1/3 of the initial value.

The deterioration of the mechanical properties in the water environment is clearly visible also for the PLA/jute composites. In the second week of incubation, the strength drops already by approximately 15%, but in the following weeks, the further decrease is less intense than in the case of the biodegradation.

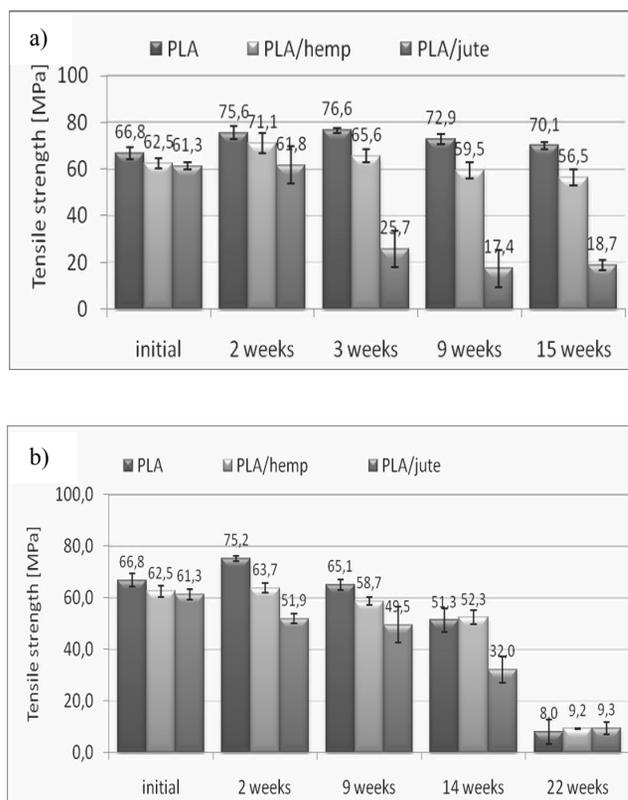


Fig. 14. Tensile strength changes of PLA, PLA/hemp, PLA/jute a) during incubation and b) during composting

4. Conclusions

The modifying additions, both fibrous and particle (natural and synthetic fibres, particles), introduced in the polylactide have a significant influence on the mechanical, structural and utilitarian properties of the produced composites. The modifying additions accelerate the degradation of the polylactide and its copolymer with the glycolide.

The degradation speed depends on the type of the environment with which the material is in contact. The speed is different in the water environment, in artificial physiological fluids and in the presence of micro-organisms or in the environment of a living organism. Independently of the application areas of the resorbable polymers, the determination of the speed of their degradation in relation to such factors as the polymer structure, the applied modifiers and the external environment, is the basic parameter necessary to be determined already in the preliminary tests.

The polymer's degradation is visibly faster in the Ringer fluid than in SBF, which testifies to its higher activity and can be a result of the lower viscosity of the Ringer fluid and thus the facilitated penetration into the polymer's structure and on the phase boundaries. Yet, the degradation speed determined under *in vitro* conditions is not directly reflected in the speed of this process in a living organism. The latter is a more complex system and in the interaction with artificial implant materials, the basic role is played by such processes as the protein adsorption, the cellular and tissue reactions, the body fluid flows and the charge exchanges. That is why the degradation process in the natural biological environment is much faster than under simulated conditions.

The hydrolytic degradation of the polylactide-based materials begins sooner than the biodegradation and applies both to the initial polymer and its composites. The addition of natural fibres accelerates the biodegradation of the polylactide.

Acknowledgements

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References

- [1] C. Nyambo, A.K. Mohanty, M. Misra, Polylactide-Based Renewable Green Composites from Agricultural Residues and Their Hybrids, *Biomacromolecules* 11 (2010) 1654-1660.
- [2] A.A. Shah, F. Hasan, A. Hameed, S. Ahmed, Biological degradation of plastics: A comprehensive review. *Biotechnology Advances* 26 (2008) 246-265.
- [3] G. Kalea, R. Auras, S.P. Singha, R. Narayan, Biodegradability of polylactide bottles in real and simulated composting conditions. *Polymer Testing*, 26 (2007) 1049-1061.
- [4] J.C. Middleton, A.J. Tipton, Synthetic biodegradable polymers as orthopedic devices, *Biomaterials* 21 (2000) 2335-2346.
- [5] L.S. Nair, C.T. Laurencin, Biodegradable polymers as biomaterials, *Prog Polym Sci* 32 (2007) 762-794.
- [6] M. Wang, Developing bioactive composite materials for tissue replacement, *Biomaterials* 24 (2003) 2133-2151.
- [7] R. Vanderby, P.P. Provenzano, Collagen in connective tissue: from tendon to bone, *Journal of Biomechanics* 36 (2003) 1523-1527.
- [8] A.R. Boccaccini, J.J. Blaker, V. Maquet, R.M. Day, R. Jérôme, Preparation and characterisation of poly(lactide-co-glycolide) (PLGA) and PLGA/BioglassR composite tubular foam scaffolds for tissue engineering applications, *Materials Science and Engineering C25* (2005) 23-31.
- [9] S. Teixeira, M.H. Fernandes, M.P. Ferraz, F. Monteiro, Adhesion and Proliferation of human bone marrow cells on hydroxyapatite and hydroxyapatite/collagen porous scaffolds for bone tissue engineering, *Proceedings of the 8th World Biomaterials Congress*, Amsterdam, 2008, 1138.
- [10] N. Ashammakhi, P. Rokkanen, Absorbable polyglycolide devices in trauma and bone surgery, *Biomaterials* 18 (1997) 3-9.
- [11] S. Gogolewski, Bioresorbable polymers in trauma and bone surgery, *Injury* 31, Supplement 4 (2000) D28-D32.
- [12] M. Vert, Biodegradable aliphatic polyesters with respect to temporary therapeutic applications, in: *Biomaterials, Hard Tissue Repair and Replacement*, Muster D. ed., Elsevier Science Publisher, The Netherlands, 1992, 223-233.
- [13] R.A. Miller, J.M. Brady, D.E. Cutright, Degradation rates of oral resorbable implants (polylactates and polyglycolates): rate modification with changes in PLA/PGA copolymer ratios, *Journal of Biomedical Materials Research* 11 (1977) 711-719.
- [14] P. Dobrzyński, J. Kasperczyk, H. Janeczek, Synthesis of Biodegradable Copolymers with the Use of Low Toxic Zirconium Compounds. 1. Copolymerization of Glycolide with L-Lactide Initiated by Zr(Acac)₄, *Macromolecules* 34 (2001) 5090-5099.
- [15] K. Haberko, M. Bućko, M. Haberko, W. Mozgawa, A. Pyda, J. Zarębski, Natural hydroxyapatite – preparation, properties, *Eng. Biomat.* 30-33 (2003) 32-38.
- [16] B. Szaraniec, T. Goryczka, Degradation of PLA/hemp and PLA/jute composites, *Modern Polymeric Materials for Environmental Applications* 4 (2010) (in press).
- [17] J. Chłopek, A. Morawska-Chochół, C. Paluszkiwicz, J. Jaworska, J. Kasperczyk, P. Dobrzyński, FTIR and NMR study of poly(lactide-co-glycolide) and hydroksyapatite implant degradation under *in vivo* conditions, *Polymer Degradation and Stability* 94 (2009) 1479-1485.
- [18] J. Chłopek, A. Morawska-Chochół, Cz. Paluszkiwicz, FTIR evaluation of PGLA – carbon fibres composite behaviour under ‘*in vivo*’ conditions, *Journal of Molecular Structure* 875 (1-3) (2008) 101-107.
- [19] A. Morawska-Chochół, J. Chłopek, A. Wietecha, Mechanical properties of polylactide modified with fibres and particles for intramedullary nails, *Engineering of Biomaterials* 99-101 (2010) 117-120.
- [20] J. Chłopek, A. Morawska, L. Umańska, C. Paluszkiwicz, The “*in vitro*” study of degradation process in composites made of resorbable polymers, *Engineering of Biomaterials* 38-42 (2004) 132-136.
- [21] I. Grizzi, H. Garreau, S. Li, M. Vert, Hydrolytic degradation of devices based on poly(DL-lactic acid) size-dependence, *Biomaterials* 16 (1995) 305-311.
- [22] S. Li, S. McCarthy, Further investigations on the hydrolytic degradation of poly (DL-lactide), *Biomaterials* 20 (1999) 35-44.