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BIODEGRADABLE POLYMERS: POLYLACTIDE – PROCESSING, MECHANICAL PROPERTIES

POLIMERY BIODEGRADOWALNE: POLILAKTYD – PRZETWÓRSTWO, WŁAŚCIWOŚCI MECHANICZNE

***Summary**: In the paper, a short review of literature concerning obtaining of polylactide (PLA, Polylactic Acid) and its properties was presented. The process of degradation was discussed. In the experimental part, the process of injection was carried out and the evaluation of mechanical properties based on the static stretching and impact strength tests was performed. The obtained results confirm that PLA may be processed in standard machines, without the necessity of their modifying. Values of stretching resistance, elongation at break (after fracture) and impact strength do not deviate from the typical parameters of plastics intended, for example, for packaging.*

***Keywords**: polylactide, processing, mechanical properties*

***Streszczenie**: W artykule przedstawiono krótki przegląd literatury dotyczący otrzymywania profilaktyku (PLA) i jego właściwości. Omówiono proces degradacji. W części doświadczalnej przeprowadzono proces wtrysku oraz dokonano oceny właściwości mechanicznych na podstawie próby statycznego rozciągania i udarności. Uzyskane wyniki potwierdzają, że PLA może być przetwarzany na standardowych maszynach, bez konieczności ich modyfikacji. Wartości wytrzymałości na rozciąganie, wydłużenia przy zerwaniu oraz udarności nie odbiegają od parametrów typowych tworzyw przeznaczonych na przykład na opakowania.*

***Słowa kluczowe**: polilaktyd, przetwórstwo, właściwości mechaniczne*

Introduction

Together with the development of plastics industry over the world, the enormous manufacture of plastic products has been commenced [1, 2]. The mentioned industry has become a synonym of technical and economic progress. Plastics processing is simple and generates low costs in the case of mass and high-volume production as compared to other groups of materials. Plastics (polymers) are macromolecular compounds which may be obtained from synthetic or natural polymers. Materials produced from chemical compounds have a main defect – they are not subjected to biological degradation and become rubbish to natural environment [3].

The application of plastics in the world production is very wide. Practically, in each sector of economy, there are produced smaller or greater elements made from polymer materials. The increase of the waste increases the degree of natural environment burden what affects negatively the living conditions of plants, animals and humans. To mitigate the negative effects of this impact, the studies on the methods of obtaining and producing the polymers derived from the so-called "green chemistry", i.e. from renewable resources and the biodegradable ones, have been carried out [4–7]. In spite of a small percentage participation of biodegradable plastics in production, we may note its increasing level year by year. Additionally, the awareness of the consumers in respect of the correct waste selection is important. The care of the natural environment becomes not only a duty but also a trend in the contemporary world [8–11].

The biodegradation itself is the process where the decomposition of polymer material as affected by environmental factors has place [12]. The process is facilitated by the appropriate humidity and temperature of the environment and living organisms such as yeasts, bacteria and fungi which are present in the vicinity of the material. Polymer material may be subjected to the total degradation with the release e.g. of carbon dioxide, ammonia, methane or water, or only to a partial degradation e.g. of one component of the discussed material [11, 13]. The biodegradability of synthetic polymers is determined by their chemical structure [14, 15]. On the other hand, the rate of the biodegradability is affected, apart from humidity and heat, by the shape of the object, its geometry and thickness, etc. [16, 17]. Small crystallinity, a low molecular weight, chemical groups sensitive to effect of certain enzymes are favourable for biodegradation of polymers. The aliphatic polyesters meet the mentioned above requirements [8, 11].

The main branch of the application of biodegradable bioplastics includes packaging; the time of "life" (use) of a simple shopping bag is short and due to this, it is quickly discarded. PLA is more and more frequently used in packaging. It is a thermoplastic polymer material which becomes completely degraded during the period of half-a-year up to two years [8, 18]. Its good processing properties allow moulding by the basic methods such as injection, extrusion, extrusion with blowing and thermomoulding [19].

The aim of the present work is to make a general review concerning production, properties and processing of polylactide and presentation of the results of tests of the mechanical properties obtained in the samples performed during the process of bioplastics injection.

Polylactide (PLA)

PLA is a thermoplastic polymer which is easily formed. It is rigid, brittle, and has good barrier properties. PLA is bio-compliant; therefore, it is often used in medicine. PLA is characterized by a low degree of combustibility and it does not emit a smoke during the mentioned process. It is resistant to UV radiation, and is transparent [20, 21].

Manufacture

PLA may be obtained in many ways. As obtained by different methods, it has a different molecular weight and different properties in each of them. One of the methods of obtaining polylactide is the process of poly-condensation of lactic acid. It may be also produced by the chemical and biological synthesis. The second mentioned method is more preferred due to obtaining lactic acid from anaerobic fermentation of renewable resources such as glucose, maltose from potato or maize starch, saccharose from sugar cane of sugar beetroots and lactose from whey derived from milk processing [6, 22]. To obtain PLA with a high molecular weight, the reaction of polymerisation of lactide cyclic ring opening (*Ring Opening Polymerization,* ROP) is mainly carried out. During the mentioned reaction, we obtain PLA with a high molecular weight and good mechanical properties. The mentioned reaction runs in two stages [6, 11].

The first stage includes obtaining of lactide in reaction of depolymerisation from oligomers of lactic acid. The mentioned reaction is carried out under a lowered pressure, increased temperature and with the participation of catalysers [11].

During the second stage, the opening of the ring has place at the presence of catalyser. The mechanism of the discussed polymerisation may be cationic, anionic, coordinative or radical [6, 11].

The run of the reaction of poly-condensation and opening of lactide cycling ring is presented in Fig. 1 [11].

The degree of PLA crystallinity may be very high, even up to 60%. The temperature of melting is ca. 170°C–180°C, glass transition temperature is about 65°C. Crystallization occurs most quickly at temperature of 110°C. PLA is a thick plastic (1.2 – 1.3 g/cm^3). The resistance to stretching of PLA is not changed together with the increase of its molecular weight and is equal to ca. 60MPa [6, 10].

PLA has a high flavour (smell and taste) barrier and is resistant to the effect of fats. It reveals a capability of preserving the shape given during the production, for example, of film. Depending on the type of manufacture, molecular weight varies from 100 000 to 300 000.

The defect of PLA includes its water absorption. The lower is the degree of its crystallinity, the higher is the mentioned above capacity. It has a high polarity which makes a good adhesion to polyolefins in the multilayer structure impossible. It is soluble in organic solvents e.g. in petrol [8, 12].

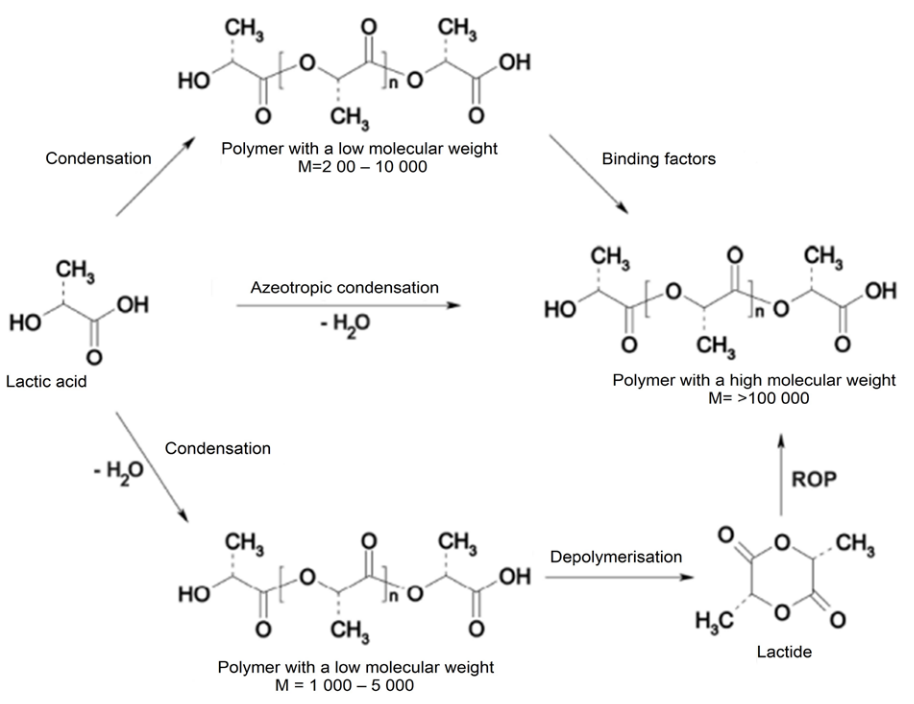

Fig. 1. The run of the process of obtaining PLA [11]

Biodegradation of PLA

Biodegradation of PLA in natural environment is dependent on many factors. From analysis of literature it is followed that the higher is the degree of crystallinity, molecular weight and the higher temperature of PLA melting, its degradation runs slower [23].

Hydrolytic and microbiological degradation

Biodegradation of PLA runs mainly in the environment with a high humidity and is divided into two stages [24]. During the first stage, the hydrolytic degradation occurs; water from the environment penetrates into the depth of the material, into its structure and it leads to hydrolysis of ester bonds in amorphous phase of PLA. As a result of such water activity, the shorter polymer chains are generated. Water-soluble oligomers penetrate the surrounding environment. In the case of a higher rate of the oligomers' release, as compared to the speed of water diffusion inside the material, we speak about surface erosion. When the rate of water penetration dominates over the speed of the release of oligomers, the erosion occurs in the total volume. In the successive stage, water-soluble mers and oligomers are metabolized by microorganisms, present in the environment to carbon dioxide, methane and water [3–12].

Biodegradation of PLA may run according to the existing conditions: slower or quicker. At the high temperature and at a high humidity of the environment, surrounding the material, the discussed process occurs relatively quickly. It is important that the rate of PLA degradation is equalized by the rate of assimilation of the products of its degradation by microorganisms. It was observed that most of the PLA-degrading microorganisms are capable of its degradation into carbon dioxide and water, and this, by turn, prevents accumulation of oligomers in the environment. Microorganisms capable of degrading microbiological and synthetic aliphatic polyesters, including PLA, were isolated from different soil environments [5, 24]. The population of microorganisms capable of degradation of PBH and PCL occurred to be most numerous; the lowest one was that of capable of PLA degradation. The tests, comparing the rate of degradation of the mentioned polyesters in the soil revealed that PLA was least sensitive to microbiological attack. To commence the process of PLA degradation, a long period is necessary; later, it runs also very slowly [24].

Under the composting conditions where the temperature is found at the level of 50-60°C and humidity is equal almost to 100%, the degradation of PLA into monomers and oligomers runs for 45-60 days. On the grounds of literature studies, it was stated that the greatest decrease of the molecular weight and a distinct PLA degradation occurred in the conditions of industrial composting. The industrial compost means creation of a special environment, the content of which includes a specified composition of biological material e.g.: 40% of leaves, 30% of wood chips and ca. 30% grasses. The process of PLA products' composting is carried out at the depth of one meter. In the case of degradation of the same samples in a normal soil is very slow [1–24].

PLA application

Due to its thermal flexibility and the possibilities of processing in typical equipment and good mechanical properties, biodegradability, non-toxicity of the material itself as well as the products of its decomposition, PLA finds a very wide application in medicine. It is employed as biodegradable plastic in production of bioresorbable surgical threads, clips, staples, surgical nets as well as screws for osteosynthesis of fractured bones and the capsules, releasing the assumed dose of medicine at the assumed time. The products, made from PLA include also membranes, which accelerate healing of the extensive wounds, sanitary agents, surgical masks and medical protective clothes [25–36].

Another application includes packaging such as bands, labels, bags for wastes, bottles for drinks and food packaging. It is perceived as the main direction of the future PLA application [11, 17].

In agriculture, the discussed material is used as protective films in plant cultivation, and for the tunnels that protect flowers, vegetables and also young trees against the effects of pests and negative temperatures. After termination of the utilization period, the mentioned products remain in the soil and are subjected to biodegradation, additionally enriching it [11].

Moreover, PLA is used as a feedstock material in 3D printers in a form of threads with ea specified diameter, being called filaments. It is one of the basic materials, employed in 3D printers, working in the additive manufacture technology FDM (*Fused Deposition Modelling*). It is characterized by a high simplicity of printing and strength properties appropriate for most of prototype elements, especially those decorative ones. PLA is available in a very wide spectrum of colours. The discussed material is not resistant to long-lasting effect of increased temperatures, above 60°C and after a certain time, it becomes irreversibly deformed. PLA is not suitable for printing of elements, working long time under the pressure. It is anticipated that the range of PLA applications will become systematically increasing [33–36].

Material and methods of the studies

In the studies on the evaluation of the possibility of PLA processing, the material of Nature Works company, type Ingeo Biopolymer 3251 D intended for processing in the injection technology, was employed.

In the preparation of the test samples, the screw injection moulding machine by Ponar Żywiec, series UT 90 for thermoplastic materials, was used. It is a horizontal screw injection machine; it has 5-score, double level system of closing a mould and a direct driving system of the screw with high-momentum hydraulic engine. The remaining laboratory equipment included: injection mould, electronic balance DARwag, dryer KC 100/200 and mill for grinding of plastics.

Before commencing the injection process, the initial material in a form of granulate, was dried in order to remove water. After drying, plastic was subjected to process of injecting the samples in order to evaluate mechanical properties. In Table 1, the parameters of the injection process have been given.

Endurance properties in the test of static tensile properties were conducted in accordance with standard PN-EN ISO 527-2:2012 Plastics –Part 2: Determination of tensile properties of plastics – test conditions for moulding and extrusion plastics.

Table 1. Parameters of injecting the polymer material (PLA)

Injection parameters	Values
Injection:	
Speed	20%
Pressure	80 bar
Alloy temperature	200°C
Pressing:	
Time	5s
Pressure of holding	40 bar
Force of closing	
Mean	887 N
Closing of mould:	
Pressure	175 bar
Speed	40 %
Time of mould protection	5 s
Time of cycle	90 s
Counter pressure	5 bar
Opening of mould:	
Counter pressure	10 bar
Time of cooling	15 s
Temperature of mould	20°C

The determination of impact strength was carried out by Charpy method, in pendulum hammer in conformity with standard PN-EN ISO 179-1:2010 Plastics – Charpy impact strength of plastics under defined condition. Part 1: Non-instrumented impact test.

The results and their discussion

Determination of the material strength and deformation were carried out in accordance with standard PN-EN ISO 527-2:2012. The measurement consisted in stretching, with a constant velocity, of standardized samples in a form of paddles, performed by injection technology in conformity with the respective obligatory standards in this respect. In Table 2, the obtained results of the tensile properties, elongation after fracture and impact strength of plastic have been presented.

The impact strength test was carried out by Charpy method in accordance with standard PN-EN ISO 179-1:2010. The mentioned method consists in placing a sample in a form of standardized beam on a special bed in the vicinity of its ends and it is hit with the hammer of a respective energy [1, 2]. In Table 2, the impact strength of the material has been presented.

Table 2. The results of the test of mechanical properties of plastics

Parameter	Result	Standard deviation
Mean tension, MPa	74,7	0.62
Mean deformation, %	11.0	0.08
Mean impact strength, kJ/m²	19.0	0.12

The obtained results of the basic mechanical properties do not deviate from those ones, found in literature. The employed material did not make any serious troubles during determination of the parameters of injection of test beams and paddles. During the tensile strength test, the material was showed a brittle cracking. Its behaviour was similar to that one of low-impact PS (polystyrene) what was also confirmed by the results obtained for impact strength test.

Summing up

Due to a fact of decreasing world oil resources and the need of protecting the natural environment, the search for the materials obtained from renewable resources and subjected to controlled biodegradation processes, becomes our target. Aliphatic polyesters belong to a group of the mentioned materials, where PLA is a subject of the intensive research and implementation work. The progress in technology of PLA manufacture causes that the discussed material becomes cheaper and by this, it drives out the traditional polymer materials from the market.

The subjected trials of processing and the results of the tests of mechanical properties of the discussed material have demonstrated that it may be successfully processed in typical processing machines without the necessity of their special modification.

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