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Biodegradable Fibrous Materials Based on Copolymers of Lactic Acid Obtained by Wet Spinning

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Abstract

It was investigated how the chemical structure of polylactide and the molecular characteristics of the polymer affect the deformability and strength properties of wet-spun fibres. Following a two-stage drawing process, a higher strength value of 396 MPa was recorded for fibres made from a copolymer of L-lactide with glycolide (PGLA), compared with poly-L-DL-lactide (PLDLA) fibres, whose value was 142 MPa. For both polymers it was found to be possible to perform an additional (third) stage of drawing, which was associated with an increase in their strength properties. For both polymers used, under previously optimised conditions of coagulation and plasticisation drawing, the extreme possible as spun draw ratio values at the spinning nozzle were established. This value, as well as the orientation of structural elements in the still liquid stream, determine the achievable value of the total draw ratio in the successive deformation processes, and the related strength properties of the fibres.

Key words: copolylactid fibres, fibre formation, strength properties.

Introduction

Poly(lactide) (PLA) is a biodegradable, thermoplastic aliphatic polyester whose base unit is lactic acid. It is obtained in a polymerisation reaction with the opening of the lactide ring. The properties of poly(lactide), such as the melting point, degree of crystallinity and strength properties, are dependent on its molecular mass. In the human body poly(lactide) undergoes gradual hydrolytic degradation of the ester bonds. Degradation begins in the amorphous areas of the implant material and lead to its fragmentation into small parts, which are then subject to a process of phagocytosis by macrophages and granulocytes. Oligomers of poly(lactic acid) degrade to monomers, which enter a Krebs cycle, as a result of which they are converted to water and carbon dioxide [1].

PLA has a wide range of applications, including use in medicine, pharmaceutical applications, environmentally friendly foils and packaging, household products, clothing and composite materials [2, 3]. Poly(lactic acid) (PLA), poly(glycolic

acid) (PGLA) and their copolymers are commonly used as bioresorbable materials in medical applications, beginning with surgical threads, which were approved in 1960 [4]. At the present time they are being used for medical purposes more and more frequently, mainly as scaffolds and as materials for use in tissue engineering. Their selection for use in materials of this type, as well as the development of research and technologies for producing new medical materials based on them, is primarily dictated by the approval of the FDA (Food and Drug Administration) [5]. The principal reason for such use and for the choice of polymers that degrade in the human body as implant materials is the fact that there is no need to perform a second surgical operation to remove them from the body. Repeat breakages or the cracking of bones sometimes occurs following the use of rigid, non-biodegradable metal implants; this happens when the connecting element is removed and the bone is not able to transfer the stresses and loads caused by the movement, due to the insufficient forces applied during the process of coalescence of the damaged tissue [6]. With a product made from biodegradable polymer it is possible to “design” and appropriately modify the material in order to obtain a strictly defined time of disintegration. The kinetics of the process of degradation of polymeric implant materials depend on many factors, such as the molecular mass, the size of the implant and its form, the character and porous structure, the degree of crystallinity, the pH of the implant environment and temperature, and the presence of enzymes.

The possibility of creating varied fibre types and structures, including woven, knitted, plaited and nonwoven fabrics, using fibres made of bioresorbable polymer, enables the obtaining of materials with controlled porosity, varied form and shape, and distinct architecture not achievable with other techniques. The textile structures appropriate for use in tissue engineering are characterised by the presence of a system of connected pores that ensure good supply of nutritious components to the tissue and removal of metabolism products, as well as support the process of cell adhesion and proliferation and the formation of the bone structure [7]. Fibrous structures, particularly nonwoven ones, are also characterised by the anisotropy of their properties, the same as human tissue. The similarity of the structure, properties and behaviour in *in vivo* conditions provide a basis for the desired functioning of such an implant in the human body, at the same time allowing the proper reconstruction of the damaged tissue without acting as an irritant nor causing processes that impair healing and the adhesion of osteoblasts. Moreover such structures provide great flexibility and freedom of manipulation, as well as the possibility of fitting them freely during an operation to particular tissue damage or defects. In the case of traditional metal implants or rigid polymers it is not possible to adjust the implant so freely to the individual needs of the patient.

The principal method for obtaining fibres from PLA and its copolymers is melt spinning. A significant problem with this method is the degradation of the polymer

which occurs during melting, as well as the problem of the instability of the melting process [8]. Significant changes in the polymer's molecular mass have been observed during the spinning process and in the operations that follow it [8 - 10]. Another drawback of this method is the high temperature, which makes it impossible to use temperature-sensitive drugs such as proteins, which would be destroyed during the spinning process [7].

There are also now many works in the literature concerning the obtaining of fibrous structures made of copolymers of lactic acid using the electrospinning method [11 - 16], which makes it possible to obtain nanostructures that may be applied in many fields of medicine, as is evidenced by the numerous patents for new types of materials [17 - 22]. Work is being carried out on uses of such structures as components of systems for the controlled release of drugs in various types of scaffolds used in tissue engineering and regenerative medicine, as well as for other applications.

An alternative to the aforementioned methods for obtaining PLA and PGLA fibres is wet spinning, which was presented as a method for the formation of PLA fibres by Kulkarni in 1966 [5, 23, 24]. However, the method is not commonly used due to the low strength properties of the fibres compared with those formed by melt spinning, and therefore not so much work has been done on this method as with melt spinning, thus the development of the technology has not taken place.

At the same time the development of material technologies is making it possible to modify the fibrous structures obtained by various methods, by introducing various chemical compounds, nanoadditives,

Table 1. Characteristics of PLDLA and PGLA copolymers and rheological parameters of spinning solutions of these copolymers.

Polymer	Intrinsic viscosity, dl/g	Number average molecular mass M_n	Weight average molecular mass M_w	Degree of polydispersity M_w/M_n	Concentration of spinning solution, %	Rheological parameter	
						n	k
PLDLA	2.32	214,120	422,311	2.0	18.5	0.956	31.96
PGLA	1.94	128,116	334,283	2.6	18.5	0.939	30.41

active substances, drugs, proteins or even cells so as to increase the range of possible applications of these materials.

The aim of the present work was to determine how the type and characteristics of a polylactide influence the strength properties of fibres formed by wet spinning using methylene chloride as solvent. It was attempted to achieve as great as possible deformations at the fibre forming stage, and consequently high strength properties of the fibres. The value of this indicator is a condition determining the types of medical application of the fibres, either alone or in nonwoven composites of the 2D and 3D type. On this basis the choice was made to study two polymers with different chemical structures and higher molecular mass, which favours the obtaining of good fibre strength properties. Also of key importance for the forming process and the strength properties of the final fibres is the polymolecularity of the polymer, where a narrow molecular mass distribution curve is preferred.

Materials and methods

Description of the polymer and spinning solution

The polymer used in the experiments were as follows:

- Resomer® LR 704S, a copolymer of L-lactide and D,L-lactide with a ratio of L-lactide to

D,L-lactide units of 67 : 33 to 73 : 27, a commercial product from Boehringer Ingelheim (Germany). It had an intrinsic viscosity of 2.32 dl/g, determined using an Ubbelohde viscosimeter.

- Resomer® LG 824S, a copolymer of L-lactide and glycolide with a ratio of L-lactide to glycolide units of 79 : 21 to 85 : 15, a commercial product from Boehringer Ingelheim (Germany). It had an intrinsic viscosity of 1.94 dl/g, determined using an Ubbelohde viscosimeter.

The solvent used to prepare the spinning solutions was methylene chloride, a commercial product from POCH (Poland).

The rheological characteristics of the spinning solutions are shown in **Table 1**.

Formation of fibres by wet spinning

Fibres were made using a large laboratory spinning machine. The process of obtaining fibres of micrometric dimensions was carried out in accordance with the patent application (**Figure 1**) [25].

De-aerated spinning solutions of PLDLA and PGLA with a concentration of 18.5% by weight of polymer in methylene chloride were forced through the holes in a 240-hole spinning nozzle, with a hole diameter 0.08 mm, into a coagulation bath.

The coagulation bath was a mixture of methylene chloride (polymer solvent)

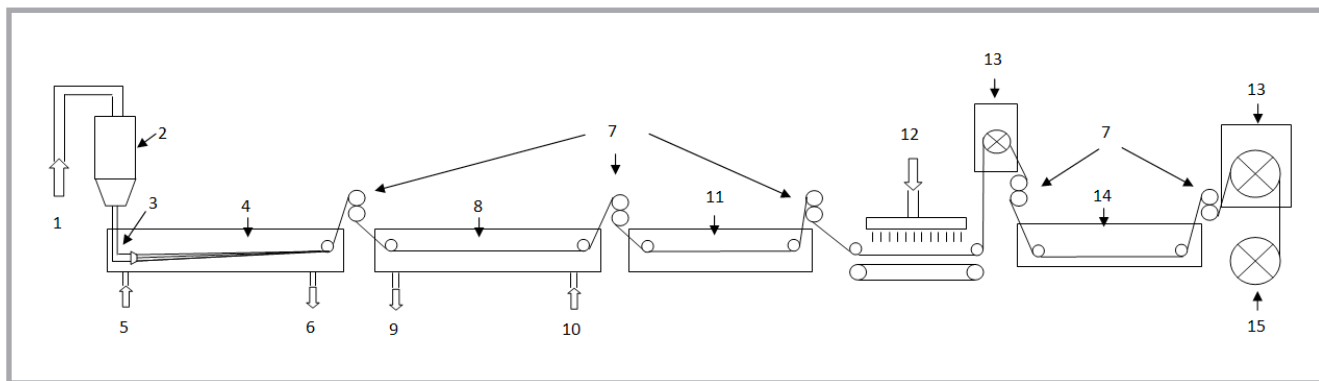


Figure 1. Scheme of wet spinning; 1 - compressed air, 2 - polymer solution tank, 3 - spinning set, 4 - coagulation bath, 5 - bath inflow, 6 - bath outflow, 7 - godets, 8 - plasticization bath, 9 - bath outflow, 10 - bath inflow, 11 - plasticization bath, 12 - rinsing, 13 - drying, 14 - plasticization bath, 15 - winder.

Table 2. Strength properties of fibres made of PLDLA and PGLA copolymers.

Number of drawing stages	Polymer	Sample symbol	As spun draw ratio, %	Total draw ratio, %	Breaking stress, MPa	Tenacity, cN/tex	Elongation at break, %	Young's modulus, GPa
II	PLDLA	PL 1	178	395	137 ± 14	14.0 ± 0.7	17.5 ± 1.1	4.4
		PL 2	64	467	124 ± 8	11.0 ± 0.2	16.1 ± 2.7	4.2
		PL 3	-25	536	142 ± 15	13.9 ± 0.5	20.0 ± 1.4	4.4
III	PLDLA	PLR 2	64	999	248 ± 25	23.4 ± 1.4	16.0 ± 0.9	3.7
		PLR 3	-25	1349	403 ± 44	28.5 ± 2.6	21.4 ± 0.9	5.0
II	PGLA	PG 1	150	301	218 ± 20	17.1 ± 0.7	12.8 ± 1.0	4.9
		PG 2	50	329	298 ± 24	22.7 ± 0.8	20.7 ± 1.0	5.2
		PG 3	9	448	285 ± 35	28.8 ± 4.9	22.4 ± 2.7	4.2
		PG 4	-20	298	396 ± 29	29.0 ± 1.0	22.4 ± 1.5	5.5
III	PGLA	PGR 3	9	645	425 ± 32	38.8 ± 4.6	23.4 ± 1.9	4.0
		PGR 4	-20	751	449 ± 26	37.2 ± 1.8	19.2 ± 0.9	4.3

and ethanol (polymer non solvent) in the following ratio 10 : 90. The coagulation process was made at a temperature of 12 ± 1 °C. The fibres formed were then subjected to the drawing process, where the first and second stages of drawing took place in a plasticisation bath with the same composition as the coagulation bath, but with a temperature of 20 ± 1 °C (for stage I of the drawing process) and 50 ± 1 °C (for stage II). Following stage II of drawing, the fibres were rinsed in water and dried in isometric conditions at a temperature not greater than that of stage II. Stage III of the drawing process was carried out in water at 80 ± 1 °C. After completion of the drawing process the fibres were dried at a temperature not greater than 60 ± 1 °C, in isometric conditions.

■ Experimental methods

To obtain the *molecular characteristics of the polymers*, which involved determining the number average molecular mass M_n , the weight average molecular mass M_w , and the degree of polydispersity, the method of gel chromatography (SEC/GPC) was used. The mobile phase was chloroform at a temperature of 35 ± 1 °C, the solvent flow speed 0.7 ml/min, and the spray quantity 100 µl.

The *characteristics of the spinning solutions* were obtained using an Anton Paar rotary rheometer. Measurements were made at a temperature of 20 ± 1 °C. The rheological parameters n and k were determined based on the flow curves.

The *fibre strength properties* were determined using an Instron tensile tester, using a force acting in a lengthwise direction with a constant increment of elongation on the sample, based on the PN-EN ISO 5079:1999 standard.

For tests of the macroscopic structure of wet spun fibres a JSM 5400 JEOL scanning electron microscope (SEM) was used.

For determination of the *degree of crystallinity* a URD 6 diffraction meter from Seifert (Germany) was used, with a copper lamp emitting radiation of wavelength $\lambda = 1.54$ Å at supply parameters $U = 40$ kV and $I = 30$ mA. The radiation was monochromatised using a graphite monochromator. The diffraction curves were recorded using the reflection method and stepwise measurement. The angular recording range was from $2\theta = 3^\circ$ to 60° with a step size of 0.1° . The recording time for a single step was 20 s, and the recording time for the entire diffractogram was approximately 3 hours 30 minutes. Samples were prepared by breaking down using a microtome and then pressing into tablets of diameter 2 cm and thickness 1 mm. WAXS diffraction curve analysis and calculation of the degree of crystallinity were performed using the WAXSFIT computer program [26].

■ Results and discussion

The strength properties of the fibres for a given type of polymer are strongly dependent (assuming constancy of the basic parameters of the coagulation process – temperature and bath composition) on the as spun draw ratio and the related deformation at the drawing stage. For both types of polylactide used in the work, the as spun draw ratio was varied over a range that covered both positive and negative values. For the PLDLA copolymer the range was from approximately +180% to -25%, and for the PGLA copolymer it was from +150% to -20%. The use of a more highly negative as spun draw ratio than -25% (favourable

in terms of the fibre strength properties) caused a large fall in the stress at the solidification stage, and thus had an adverse effect on the stability of the fibre forming process.

Analysis of the effect of the as spun draw ratio shows that for the PLDLA copolymer the highest fibre strength properties are obtained when highly positive (+178%) or extremely negative (-25%) as spun draw ratio values are applied. The breaking stress for these fibres was 137 MPa and 142 MPa, respectively, corresponding to a tenacity of approximately 14 cN/tex. In the case of the PGLA copolymer the highest breaking stress was recorded for fibres formed with a negative as spun draw ratio (-20%) and for those formed with a value of +50% (Table 2). At the same time the breaking stress value obtained for fibres made of PGLA copolymer is significantly higher than that of fibres made of PLDLA copolymer. Comparison of the values for the total draw ratio shows that higher values of 395% and 536% were obtainable for the PLDLA polymer. However, for the PGLA polymer, in spite of their higher strength properties, the values for the total draw ratio of the fibres with the highest strength properties are approximately 298% and 329%. The reasons for the lack of correlation between the total draw ratio and the strength properties can be sought mainly in the differences in the chemical structure between the two polymers. With both polymers having a similar intrinsic viscosity in the range 2.0 – 2.3 dl/g, and with the use of a spinning solution concentration of 18.5%, there are similar values of rheological parameter k , equal to 30 (Table 1). The character of the changes in the breaking stress as a function of the as spun draw ratio is shown in Figure 2.

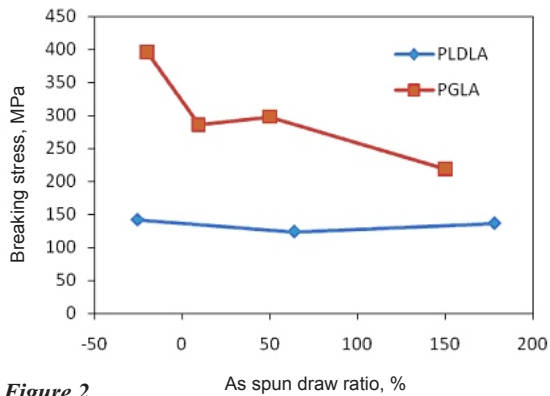


Figure 2.

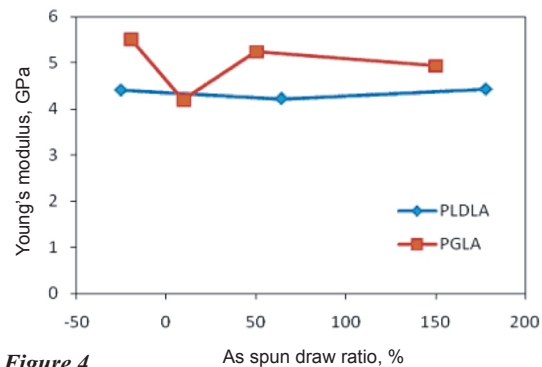


Figure 4.

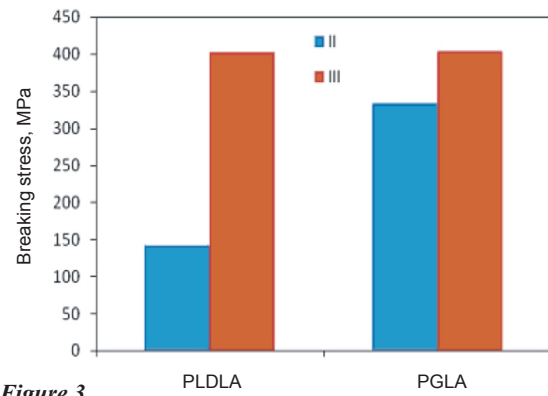


Figure 3.

Figure 2. Breaking stress as a function of the as spun draw ratio.

Figure 3. Changes in the breaking stress of the final fibres with the highest strength properties for each polymer, as a function of the number of stages used in the drawing process (II = two stages of drawing, III = three stages of drawing).

Figure 4. Changes in Young's modulus depending on the as spun draw ratio and type of polymer.

In an effort to obtain the maximum possible strength properties for the fibres formed from both polymer types, an additional stage of the drawing process was applied, carried out in conditions which avoid the hydrolytic and thermal degradation of the material, as confirmed in [27]. There was found to be a significant increase in the breaking stress of both types of fibres. For fibres made from PLDLA and formed with a negative as spun draw ratio of -25%, which had the highest strength value (142 MPa) after the second stage (equivalent to a tenacity of 13.9 cN/tex), the application of a third stage of drawing led to an increase in strength of 261 MPa. However, the highest strength after the third stage of drawing was recorded for PGLA fibres formed with an as spun draw ratio of -20%, for which the increase in strength was around 50 MPa. For the PLDLA fibres this large increase in strength is a result of the high value of the total draw ratio (1349%) obtainable due to the third drawing stage. However, the use of a third drawing stage in the case of PGLA fibres provided significantly smaller values of the total draw ratio, at a level of 751% (sample PGR 4). The result of this differentiated deformability and effectiveness of the third stage of the drawing process was the obtaining of similar strength properties for both

types of final fibres. Figure 3 shows a comparison of the breaking stresses for fibres after two and three drawing stages.

The elongation at break of the fibres following the second stage of drawing is in the range 12.8 – 22.4% for both polymers. Similar values were obtained for fibres after the third stage of drawing. The Young's modulus of the fibres obtained is in the range 4.1 – 4.9 GPa, irrespective of the type of polymer, as spun draw ratio and number of stages in the drawing process.

Because of the potential use of the fibres for medical purposes, and to identify changes in the supramolecular structure resulting from the drawing process proposed, the degree of crystallinity was also tested using the following procedure. At the first stage a linear background was subtracted from the curves, this being determined on the basis of the level of radiation intensity in the range of small and large scatter angles. Also the diffractograms were normalised to a uniform level of integral radiation intensity over the entire range of measurement. Next the experimental diffraction curves were approximated by a theoretical curve that is the sum of functions representing particular crystalline peaks and an

amorphous component. The curve fitting procedure was carried out using multi-criteria optimisation and a hybrid system combining a genetic algorithm with Powell's classical optimisation method [29]. In this procedure both the crystalline peaks and amorphous maxima were represented by a function that is a linear combination of the Gauss and Lorentz functions. The initial angular positions of the crystalline peaks and corresponding Miller indices were determined based on the parameters of the elementary PLA cell, as determined by Miyata and Masuko [30]. According to these authors the polymer crystallises in a rhombic arrangement, and the lengths of the edges of an elementary cell are $a = 10.78 \text{ \AA}$, $b = 6.04 \text{ \AA}$ and $c = 28.73 \text{ \AA}$. Based on these data, interplanar distances were calculated for particular families of lattice planes (dhkl), and then using Bragg's law, the angular positions (2θ) were found for the peaks corresponding to given families of planes. The amorphous component was approximated using two wide maxima, one at a scatter angle of $2\theta \approx 16.5^\circ$, and the other at $2\theta \approx 31^\circ$. Figure 4 shows an example decomposition of the diffractogram into component elements for sample PL 3. The degree of crystallinity was calculated as the ratio of the integral intensity contained in the

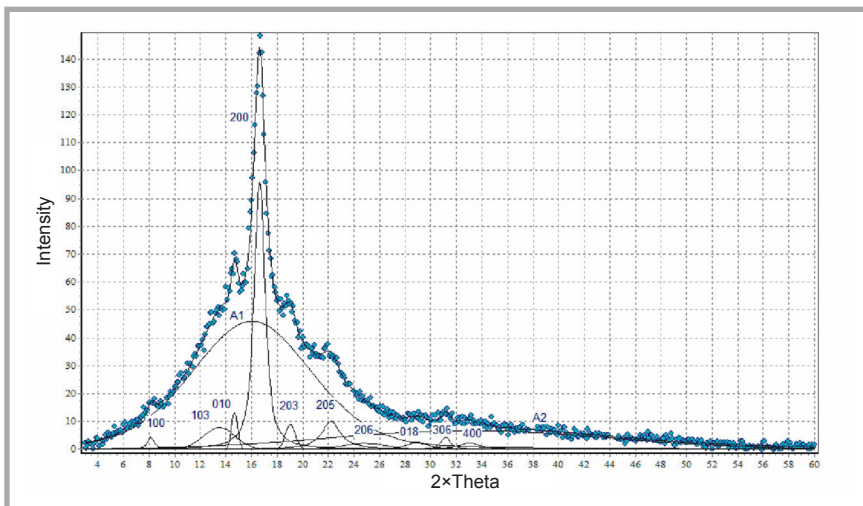


Figure 5. Example decomposition of the diffractogram of sample PL 3 into component elements.

Table 3. Properties of the crystalline structure.

Sample symbol	Degree of crystallinity, %	Crystallite dimensions D_{200} , Å
PL 3	23	88
PLR 3	27	74
PG 3	16	39
PGR 3	22	56

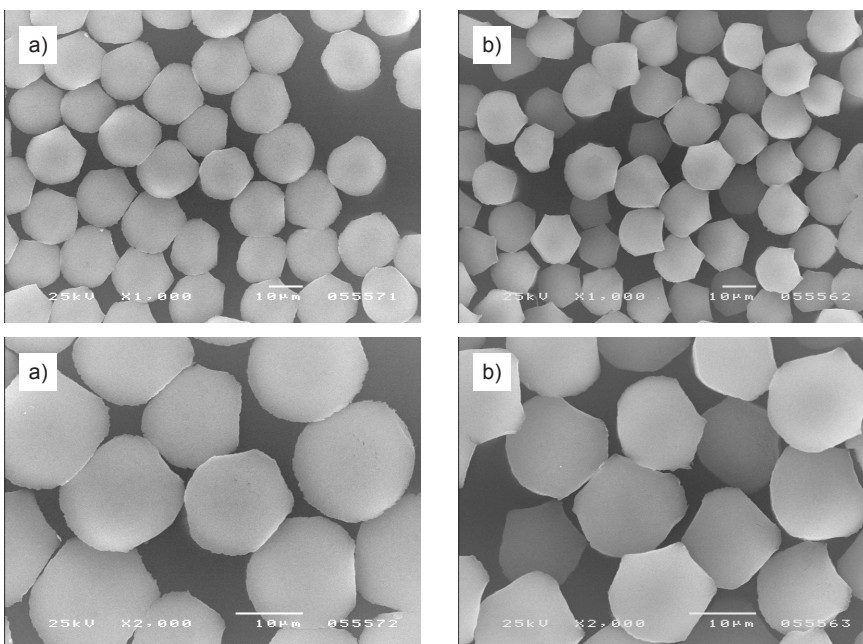


Figure 6. Cross-section of fibres made from PGLA (a) and PLDLA (b) with the highest strength properties.

crystalline peaks to the integral intensity of radiation scattered by the sample over the entire range of measurement (after subtraction of background radiation). Moreover using Scherrer's formula, the crystallite dimensions D_{200} in a direction perpendicular to the family of lattice planes (200) were calculated. These provide the strongest crystalline reflex on the diffractogram, which occurs at a scatter

angle of $2\theta \approx 16.50$. In the case of the fibres labelled PL 3 and PLR 3, we observe a small but clear increase in the degree of crystallinity together with a decrease in the crystallite dimensions (**Figure 5**). The higher degree of crystallinity in the case of fibres made from PLDLA is probably related to the significantly higher values for the total deformation compared with PGLA. Fibres obtained from both types

of polymer have a degree of crystallinity of 16 – 23% and crystallite dimensions in the range 39 – 88 Å, which is shown by way of example in [27]. The effect of the number of stages in the drawing process on changes in these two structural indicators is presented in **Table 3**.

The shape of the cross-section of the fibres from each type of polymer having the highest strength properties is shown in **Figure 6**. The cross-sectional shape is typical for a solidification process using a diffusion mechanism with stream ratio $j_c/j_n < 1$ (where j_c is the stream of solvent and j_n the stream of non-solvent).

A survey of the literature and work carried out on the subject and problems of wet spinning fibres made of polylactide and its copolymers shows a noticeable abandonment of this method, because of the very poor fibre strength properties obtained. In the research reported in [23, 28] into formation of PLA fibres by the wet spinning method, the solvents used were various compounds and mixtures of them, such as chloroform, 1,4-dioxane, a mixture of chloroform and toluene, and a mixture of chloroform and hexane. Also used were various forms of coagulation baths: isopropyl alcohol, alkanes (heptane, hexane, pentane and cyclohexane), and polyethylene glycol. However the strength properties of the resulting fibres were quite poor, and the value of stress that they could withstand was less than 120 MPa. It is purely for this reason that so little work has been done on developing a proper technology for wet spinning – for the type of polymer which is exceptionally sensitive to high temperatures – enabling the production of “high-strength” polylactide fibres characterised by high porosity. However, this method has many advantages over melt spinning, for example it allows the precision control of process parameters in order to obtain the fibre properties desired, making it possible to obtain fibres with a much smaller diameter of around 10 µm. It is also much easier (compared with the melt spinning method) to modify the polymer by introducing biocompatible, bioactive nanoparticles such as HAp, bioglass, TCP and SiO₂, or by introducing proteins or antibiotics to assist the process of bone tissue reconstruction.

Conclusions

As regards obtaining high strength properties of fibres made from both types of

polymers, it is advantageous to carry out the forming process using a negative as spun draw ratio: -20% in the case of PGLA, and -25% in the case of PLDLA. The fibres obtained after the second stage of drawing have breaking stress values of 396 MPa and 142 MPa, respectively.

The use of a third stage of drawing leads to a significant increase in the breaking stress of both PLDLA and PGLA fibres. In both cases the value exceeds 400 MPa.

The obtaining of high strength properties of fibres made of PLDLA copolymer is primarily due to their high deformability at the third stage of the drawing process, and consequently the obtaining of significantly higher values for the total draw ratio than in the case of the PGLA copolymer.



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