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Modification of a Polylactide Fibre Surface

Abstract

The properties of polylactide (PLA) fibres were modified by incorporating carboxyl groups into the fibre surface by grafting acrylic acid (AA) or by the entrapment of poly(acrylic acid) (PAA) to the fibre surface. The presence of a PAA layer was confirmed by IR spectrometry. The number of carboxyl groups incorporated into the top layer of the modified fibres was determined by potentiometric titration. The fibres containing carboxyl groups in their top layer were further treated by the Layer-by-Layer method to deposit basic polyelectrolytes such as poly(allylamine hydrochloride) (PAH) or poly(dimethylaminoethyl methacrylate) (PDAMA) alternately with the layers of acidic polyelectrolyte, i.e. PAA. The presence of successive deposited layers was confirmed by electric charge measurements. The modification performed resulted in changes in the properties of PLA fibres, such as dyeability, water sorption and thermal resistance.

Key words: polylactide fibres, grafting, entrapment, layer by layer deposition.

Introduction

Biodegradable polymers are arousing greater and greater interest for many reasons. One of them is that products made from such polymers can be easily utilised. Their decomposition in the environment is faster, and the decomposition of products made from them are harmless to the natural environment. An example of such a polymer is polylactide. Its first commercial application for the production of surgical threads was first implemented by Du Pont in 1975. The *in vivo* degradation of PLA is described in [1]. Numerous studies carried out by Pennings in the eighties [2 - 4] concerned PLA fibres designed for implants in neurosurgery. Further progress in this field consisted in the preparation of fibres with improved properties. The relationship between the properties of PLA fibre and its structure is reported in [5, 6]. In order to improve the properties (mainly hydrophilicity) of products from biodegradable polymer, including PLA, their surfaces have been functionalised by grafting vinyl monomers, entrapping polymers and layer by layer deposition [7 - 14]. However, these studies do not concern the surface modification of textiles made from PLA fibres. There are various known grafting methods used in the surface modification of textiles from other polymers [15 - 18]. In our previous studies on the surface modification of polypropylene nonwovens, we successfully used a method that consists

in pre-activating fibres with ammonium persulphate to form peroxide groups capable of initiating grafting processes [15]. Another method known from the literature consists in grafting by kinetic chain transfer [16]. An effective method in the case of some polymers is the process described by Bamford [17], in which polyester fibres were successfully modified by grafting initiated with benzoyl peroxide [18]. The fibre surface can be also modified by entrapping a polymer layer [9]. Such a process was used to modify PLA film and foam surfaces with such polymers as poly(ethylene glycol), chitosan and alginates [10-13]. Polymeric material surfaces can also be modified by the method of depositing nanolayers of polycomplexes [14, 15, 19 - 22].

The aim of the present study was to modify the surface of PLA fibres by grafting AA or entrapping PAA layers as substrates for depositing functional polyelectrolytes by the layer-by-layer method.

Experimental

Materials

A commercial polylactide staple fibre (6 den; 64 mm) - PLA Ingeo Type SLN-2660D-SOLID (Manufacturer FET Taiwan) was used in the investigation. Prior to use, the fibre was extracted with n-heptane or diethyl ether to remove the spinning finish. Acrylic acid from Aldrich was dried over CaCl_2 and distilled in a vacuum at a temperature of 79 °C. Benzoyl peroxide was twice precipitated with methanol from a solution in chloroform and dried in a vacuum for 48 h. Ceric (IV) ammonium nitrate (Aldrich) was used without any additional purification. Analar organic solvents (Chempur) were used without additional purification. Poly(allylamine hydrochloride),

$M_n = 50\,000$ g/mol., was supplied by Aldrich. Poly(acrylic acid), $M_w = 258\,000$ g/mol, was prepared by the polymerisation of acrylic acid in isopropanole, as described in [15]. Poly(dimethylaminoethyl methacrylate), $M_w = 63\,000$ g/mol, was prepared according to [19]. All other reagents were supplied by POCH Co.

Grafting AA with the use of benzoyl peroxide - the PLA/AA_G1 method

A 0.24 g sample of PLA was immersed in 20 cm³ of 5% wt. toluene solution of benzoyl peroxide for 30 min. at a temperature of 50 °C. Toluene was then removed from the fibre sample by squeezing and drying for 15 min. at a temperature of 80 °C. The sample dried was placed in a glass reactor equipped with a reflux condenser and nitrogen inflow, in which acrylic acid was dissolved in water. The ratio of PLA fibre weight to monomer solution volume was 1:30. Prior to the grafting process, the reaction mixture was thoroughly saturated with nitrogen. The grafting process was carried out for 2 h. The resultant PLA fibre samples grafted were extracted several times with hot water and ethanol to remove the ungrafted portion of PAA and then dried in a dryer to constant weight at a temperature of 60 °C.

Methods

Grafting AA with the use of ammonium persulphate - the PLA/AA_G2, PLA/AA_G3 and PLA/AA_G4 methods

The PLA/AA_G2 method: 2.76 g of PLA fibres extracted with ether was placed in 200 cm³ of 10% aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and heated for 1 h. Next, the fibres were twice rinsed with distilled water, immersed in an aqueous solution of AA and heated. After heating, the fibres were rinsed three times with distilled wa-

Table 1. Effect of selected parameters on the results of grafting acrylic acid on PLA fibres with the use of ammonium persulphate; *room temperature.

Method	Activation			Grafting					Increase in acidic groups ×10 ⁵ , mol/g	Amount of ungrafted polymer
	Ammonium persulphate, %	Temp., °C	Time, h	Acrylic acid, %	Ammonium persulphate, %	Ceric (IV) ammonium nitrate, %	Temp., °C	Time, h		
PLA/AA_G2	10	80	0,5	10	-	-	80	1	0	low
PLA/AA_G3a	-	-	-	3	20	-	50	1 + 24*	7.01	low
PLA/AA_G3b	-	-	-	1.5	10	-	50	1	1.83	low
PLA/AA_G4a	10	100	1	15	-	0.1	100	1	3.94	high
PLA/AA_G4b	10	100	1	5	-	0.1	100	1	0.84	low

Table 2. Results of grafting acrylic acid on PLA fibres by means of redox systems.

Method	System redox	Mass of fibre, g	Total volume, cm ³	AA, % v/v	Temp., °C	Time, h	Increase in acidic groups × 10 ⁵ , mol/g	Amount of ungrafted polymer
PLA/AA_G5_1	(NH ₄) ₂ S ₂ O ₈ /FeCl ₂ ×2H ₂ O 0.09g/0.08g	1.0	100	1	25	24	1.91	low
PLA/AA_G5_2	(NH ₄) ₂ S ₂ O ₈ /FeCl ₂ ×2H ₂ O 0.31g/0.31g	1.5	100	3	60	0.5	<0.2	low
PLA/AA_G5_3	(NH ₄) ₂ S ₂ O ₈ /FeCl ₂ ×2H ₂ O 0.31g/0.31g	1.5	100	2	50	4	<0.2	low
PLA/AA_G5_4	NH ₄) ₂ S ₂ O ₈ /Na ₂ S ₂ O ₃ 0.228g/0.190g	2.0	100	2	50	4	<0.2	low
PLA/AA_G5_5a	(NH ₄) ₂ S ₂ O ₈ /NaH ₂ PO ₂ 0.228g/0.098g	2.0	200	0.5	70	1	1.7	high
PLA/AA_G5_5b	(NH ₄) ₂ S ₂ O ₈ /NaH ₂ PO ₂ 0.8g/0.4g	5.0	400	2.5	25	72	1.54	low

ter and dried at room temperature. Quantitative data are given in **Table 1**.

PLA/AA_G3 method: 1.5 g of fibres extracted with ether was immersed in an 10% aqueous solution of (NH₄)₂S₂O₈, to which 3 cm³ of AA was added, heated for 1 h at a temperature of 50 °C and then left overnight at room temperature. The fibre sample was carefully rinsed several times with distilled water, followed by squeezing of the solution and drying at room temperature. Quantitative data are listed in **Table 1**.

PLA/AA_G4 method: 3 g of fibres was heated in an aqueous solution of (NH₄)₂S₂O₈ for activation purposes. Next, the fibres were rinsed with distilled water and grafted in 200 cm³ of solution containing AA and ceric (IV) ammonium nitrate (V). The fibres grafted were

washed several times with hot water to remove the considerable amount of ungrafted PAA and then dried at room temperature. Quantitative data are listed in **Table 1**.

Grafting AA with the use of the redox system - the PLA/AA_G5 method

The grafting process was carried out as follows: solutions of redox system components with specified concentrations were prepared separately in water saturated with nitrogen, to one of which was added acrylic acid. The fibre sample was then placed in a reactor, to which the solutions of reaction components were added. The content of the reactor was heated during the passage of nitrogen. After a specified reaction time, the fibre sample was removed, rinsed several times with excess distilled water and dried at room

temperature. Quantitative data for each variant of the method are listed in **Table 2**.

Entrapment of PAA: the PLA/PAA_E method

A sample of fibres with a weight of about 0.5 g was immersed in 50 cm³ of a swelling medium containing PAA with a specified concentration for a specified time. Next, the sample was drained on a polyethylene mesh and immersed in 200 cm³ of a stabilizing medium (water) for about 10 min. In some cases, the rinsing operation was repeated. Finally, the sample was drained and dried at room temperature. Quantitative data for each variant of the method are listed in **Table 3**.

Layer-by-Layer deposition

Solutions of polyelectrolytes such as poly(acrylic acid) (PAA), poly(allylamine hydrochloride) (PAH) and poly(dimethylaminoethyl methacrylate) (PDAMA) with a concentration of 10⁻² mol_p/dm³ were prepared. A sample of fibres grafted with PAA was immersed in a solution of PAH or PDAMA. After 10 min. the fibre sample was rinsed with water and transferred to the solution of PAA. This procedure was repeated several times. Finally, the fibres treated were dried at room temperature.

Determination of carboxyl groups in the top layer of fibres

Measurements were carried out with the use of a laboratory pH/conductom-

Table 3. Conditions of entrapped poly(acrylic acid) on PLA fibres.

Method	Medium swelling	Concentration PAA, %	Temp., °C	Time, h	Rinsing water	Increase in acidic groups × 10 ⁵ , mol/g
PLA/PAA_E1	Ethanol/acetone 67/33	0.25	25	24	3x	0.43
	Ethanol/acetone 60/40	0.25	25	48	3x	1.36
	Ethanol/acetone 50/50	0.25	25	24	3x	0.87
PLA/PAA_E2	Ethanol/chloroform 98/2	1.00	25	1	1x	3.27
	Ethanol/chloroform 96/4	1.00	25	1	1x	3.50
	Ethanol/chloroform 94/6	1.00	25	1	1x	4.21
	Ethanol/chloroform 90/10	1.00	25	1	-	6.95
	Ethanol/chloroform 87/13	1.00	25	24	3x	6.67
	Ethanol/chloroform 80/20	1.00	25	1	sample deformation	

eter/salinometer CPC-502 from ELMETRON, operating in the pH measurement mode, equipped with a combined glass electrode. A weighed portion of fibres (from 0.1 to 0.35 g) was submerged in 5 cm³ of 0.01M NaOH solution, to which 75 cm³ of distilled water was added. The whole was titrated by means of 0.01 M HCl solution. A diagram of the dependence of pH on the volume of HCl added was prepared, and the equivalent acid volume, i.e. that at pH 7, was determined. From the difference in titration results between the unmodified (zero) and modified samples was calculated the number of carboxyl groups resulting from the modification, which was recalculated per 1 g of fiber.

Determination of fibre charge

The charge of fibres was determined with the use of a Mütek™ Particle Charge Detector (BTG Germany). A sample of fibres was mechanically disintegrated into single filaments with a length of up to 1 mm. A 0.25 g weighed portion of disintegrated filaments was submerged in 10 cm³ of distilled water, vigorously stirred and then placed in the Charge Detector's container. Depending on the charge sign, the filament suspension was titrated with PAA solution or PAH solution. The concentration of the titration solutions was 1×10⁻³ mol/dm³.

Determination of moisture absorption

The sorption of water moisture in PLA fibres was determined at 100% relative air humidity (RH) in accordance with Polish Standard PN-80/P-04653.

Determination of the grafting degree

The grafting degree of fibres was determined by the gravimetric method.

Dyeing test

Dyeing tests were carried out with methylene blue in solution with a concentration of 10⁻³ mol/dm³. Dry fibre samples were immersed in the dye solution for 10 min., then intensively rinsed twice with distilled water, drained and dried. The fibre samples dyed were pressed using a hydraulic press to form circular discs with a diameter of 16 mm. The discs were placed in a Spectraflash 300 apparatus (Datacolor International) to measure light reemission within the range of 400 to 700 nm. The maximum value of reemission was recalculated into a K/S ratio according to Kubelka-Munk's algorithm.

The results were considered as comparative values only.

Thermogravimetric analysis

Thermogravimetric analysis was performed with the use of a TGA 7 (Perkin Elmer) with Pyris software. Measurements were carried out for a mixture of 80% nitrogen and 20% oxygen (LINDE-Poland), at a heating rate of 15 °C/min. The gas flow rate was 20 cm³/min. Each TG result given constitutes an average value of 5 – 10 single measurements.

FTIR spectra

Using a spectrometer - FTIR Perkin-Elmer, model System 2000 - with Spectrum v3.02 software and an attachment of total attenuated internal reflection (ATR) in the form of multiple internal reflection (MIR) equipped with a KRS5 crystal providing an incidence angle of 45°, FTIR spectra were recorded with a definition of 4 cm⁻¹, making at least 16 runs for the background and 16 runs for the sample tested.

Table 4. Effect of selected parameters of acrylic acid grafting on PLA fibres with the use of benzoyl peroxide (PLA/AA_G1 method) on the grafting degree and moisture sorption.

[AA], mol/dm ³	Temp., °C	Grafting degree, %	Increase in acidic groups x10 ⁵ , mol/g	Moisture sorption at 100% RH, %
		0.00		0.34
0.182	80	1.43	0.33	2.41
0.365	80	2.01	-	2.75
0.365	65	0.49	-	1.15
0.547	80	7.41	11.6	2.85
0.911	80	6.45	-	5.89
1.459	80	8.69	26.5	13.50
1.823	80	9.88	37.2	11.19
3.647	80	16.73	48.4	24.82

Results and discussion

Grafting AA

A series of grafting AA on PLA fibres was performed using benzoyl peroxide in the stage of activation (the PLA/AA_G1 method). Values of the grafting degree, moisture absorption and carboxyl group content depending on the process conditions are listed in **Table 4**. From the results given in **Table 4**, it follows that the degree of grafting AA on PLA fibres increases with an increase in acid concentration in the reaction mixture and decreases with a decrease in the reaction temperature. The results of moisture absorption by PLA fibres grafted with AA clearly indicate that these fibres absorb somewhat more moisture with an increasing grafting degree. However, it was observed that when the concentration of AA in the reaction mixture was about 0.911 mol/dm³, the grafted fibres became brittle. **Figure 1** shows FTIR spectra of unmodified and grafted fibres recorded by the method of total internal

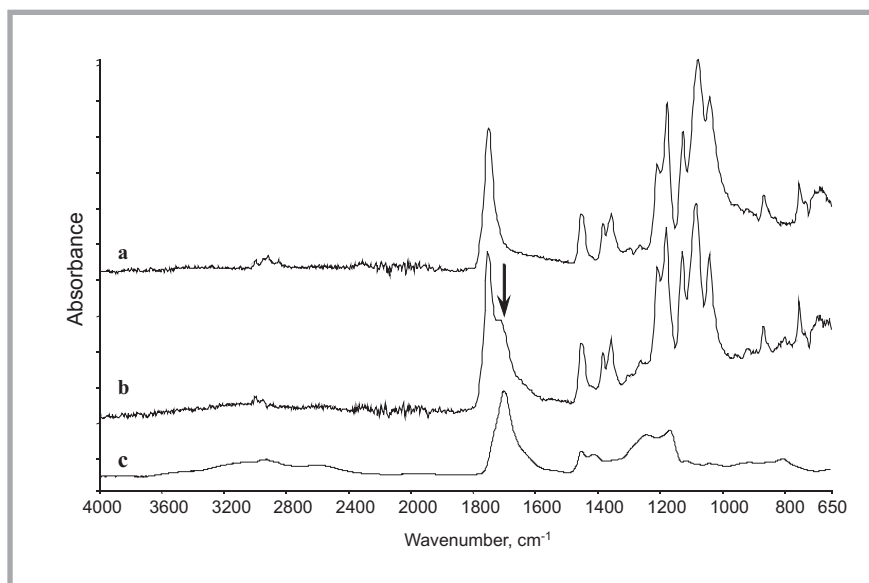


Figure 1. FTIR ATR spectrum: a – initial fibre, b – fibre grafted with acrylic acid (grafting degree = 6.45% by wt.), c – PAA.

reflection. The FTIR spectrum of PLA fibre grafted with AA shows an additional band at 1710 cm⁻¹ derived from the carboxyl group, as well as a broad band of low intensity at 3650-3100 cm⁻¹ that may be ascribed to the -OH group. All the determinations performed confirm the effectiveness of PLA fibre grafting by this method.

The effectiveness of several variants of grafting AA with the use of ammonium persulphate was examined. In the PLA/AA_G2 and PLA/AA_G3 methods, ammonium persulphate was used without other components besides the monomer, either in the activation process only (free radicals formation on the surface of PLA) or in the grafting process (kinetic chain transfer) only, respectively. For variant PLA/AA_G4 performed according to Bamford [17], after activation with ammonium persulphate, a salt of cerium (IV) was used in the grafting process. The number of carboxyl groups in each sample was determined. The grafting conditions and results are listed in **Table 2**. As is known, the grafting process is accompanied by the formation of homopolymer (ungrafted). The formation of ungrafted PAA, partly in the form of a gel, was observed with the PLA/AA_G3a method. In the remaining cases, the grafting medium was limpid. The presence of ungrafted polymer and its quantity were estimated by precipitating it in the form of a complex with PDAMA.

The conditions and results of grafting with the use of redox systems are listed in **Table 3**. As follows from this Table, effective grafting by this method requires a long reaction time, otherwise the grafting is insufficiently effective.

Entrapment of PAA

The deposition of a PAA layer on the surface of PLA fibres was carried out by the method of entrapment with the use of various swelling systems. The conditions and results of this method of modification are listed in **Table 5**. According to our knowledge, PLA fibres have not yet been modified by this method. In the entrapment method the most important role is played by the selection of a swelling medium. During preliminary trials, it was observed that the ethanol/acetone system (PLA/PAA_E1 method) could slightly swell PLA without its dissolution. However, to obtain a positive effect of the entrapment, it is necessary

to use a very long swelling time. On the other hand, the use of low quantities of chloroform in the swelling medium (PLA/PAA_E2 method) allows one to obtain higher amounts of PAA within a considerably shorter time. It was established in preliminary trials that the proportions of swelling and stabilising media constitute a homogeneous system. It should be mentioned that the use of too high contents of chloroform can lead to sample deformation as a result of too strong swelling.

Modification by the method of layer-by-layer deposition

The selection of conditions for the deposition of polyelectrolyte layers by the L-b-L method was based on the statement made in literature [14] that above a certain critical concentration, macromolecules occur in the form of separated curls with a size of about 10 nm. A concentration of 10⁻² basic mole per liter is assumed as the critical concentration. Solutions with this concentration were used in the present study.

Fibre samples grafted by Bamford's method (PLA/AA_G4b) or the redox method (PLA/AA_G5b) were selected for modification by L-b-L deposition.

In the L-b-L series based on sample PLA/AA_G5b, the layers of PAH and PAA were deposited alternately on the PLA fibre surface. In order to confirm the presence of alternate layers with opposite charges, electric charge determinations were performed. A grafted sample was titrated with a 10⁻³ M solution of PAH. A sample with a deposited PAH layer was titrated with a 10⁻³ M solution of PAA, while a sample with a successive deposited PAA layer was titrated with a 10⁻³ M solution of PAH. The results of titration are shown in **Figure 2**. As is seen, the initially negative charge of the grafted fibre surface increases with the PAH titration to positive values. The sample with a de-

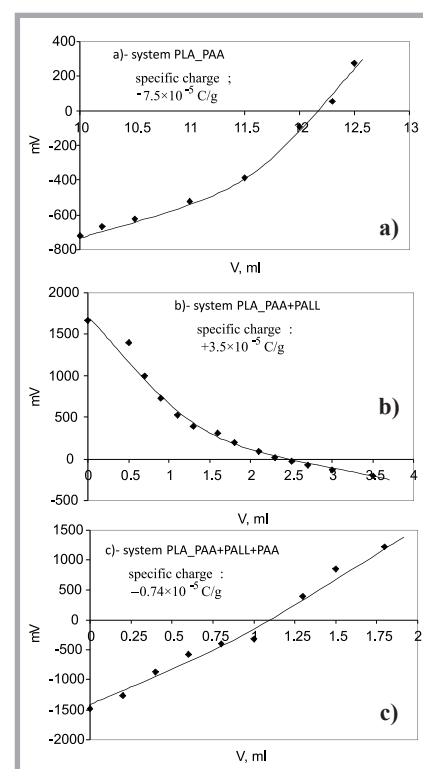


Figure 2. Potential changes during the titration of PLA fibres with repeatedly deposited layers, dependent on the top layer: a) PLA_PAA system titrated with a PAH solution; b) PLA_PAA+PAH system titrated with PAA solution; c) PLA_PAA+PAH+PAA system titrated with PAH solution

posited PAH layer has a positive charge that changes into a negative one as a result of titration with PAA solution. The sample with a successive deposited PAA layer has again a negative charge. The neutralisation point (charge sign change) was determined from the diagrams in **Figure 2**. The quantity of charge in coulombs per gram was calculated according to the following formula:

$$q = (a/m) \times 10^{-6} \text{ in Q/g}$$

where:

- a – volume in cm³ of the solution to reach the neutralisation point of the charge;
- m – sample weight in g.

Table 5. Results of dyeing tests with methylene blue; K/S values in the initial sample depending on the number of layers and the type of final layer.

Type of deposited layers	K/S	
	Initial sample PLA/AA_G4b	Initial sample PLA/AA_G5_5b
PLA	0.04	0.04
PLA_PAA	0.23	0.29
PLA_PAA +PDAMA	0.16	-
PLA_PAA +PDAMA+PAA	0.83	1.33
PLA_PAA +PDAMA+PAA+PDAMA	0.22	-
PLA_PAA +PDAMA+PAA+PDAMA+PAA	4.56	3.49

The values of charge calculated per gram of fibre are given in the applicable diagrams in **Figure 2**.

In the L-b-L series based on samples PLA/AA_G4b and PLA/AA_G5b, the layers of PDAMA and PAA were alternately deposited on fibre samples. The latter were then dyed with methylene blue, and the reemission of light was measured at 600 nm. Results in the form of Kubelka-Munk values (K/S) are given in **Table 5**. The acidic layers show a higher K/S value than that of amine layers. Moreover, the K/S increases with an increase in the number of layers deposited. The series with alternate PAA/PDAMA layers based on the initial sample PLA/AA_G4b was subjected to thermogravimetric analysis. To describe the thermogravimetric curves, we selected the temperature of 50% sample decomposition, $T_{50\%}$, as an objective parameter that quantitatively describes the differences between individual curves well, the results of which are shown in **Figure 3**. As can be seen, $T_{50\%}$ clearly increases with the number of layers deposited. The extreme differences in $T_{50\%}$ amount to more than 30 degrees. In the literature, one can find isolated cases of TG analysis of samples modified by the L-b-L method [23 - 25], but they concern unmodified polyelectrolytes [23] and silicone layers [24]. There have been discovered [25] minimal changes (below 5 degrees) in the course of TG curves (analysis under nitrogen) after depositing 40 polyelectrolyte layers on the surface of "nafion". However, there is a lack of literature data concerning the thermal properties of PLA fibres modified by the L-b-L method, with which one could compare the results obtained in the present study.

Conclusions

Several methods for the surface modification of PLA fibres have been examined with respect to their effective use. Each of the methods investigated shows both positive and negative features. Some of the grafting methods turned out to be ineffective (grafting using pre-activation with ammonium persulphate and some systems of grafting by means of redox systems). However, it was found that the remaining methods can be successfully used to incorporate carboxyl groups into the top layer of polylactide fibres. Using the Layer-by-Layer method, one can effectively change the character of a fibre

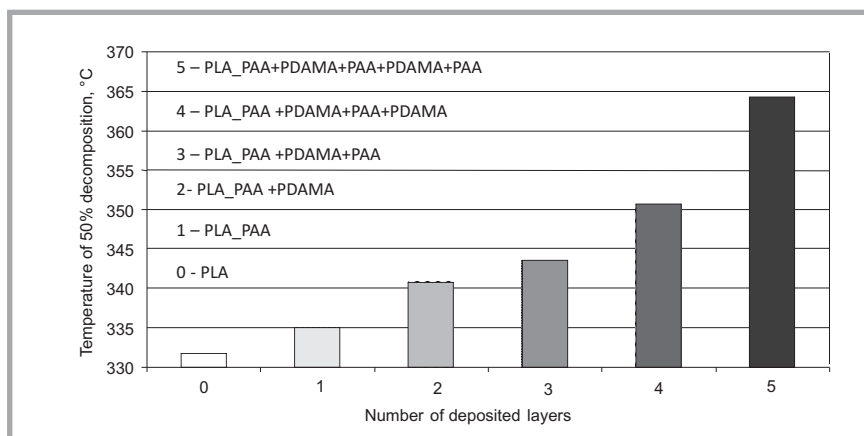


Figure 3. Temperatures of 50% thermal decomposition of PLA fibres and a sample grafted by the PLA/AA_G4b method, with deposited layers, measured in mixture 80% nitrogen and 20% oxygen.

surface from acidic to basic as well as the electric surface charge from negative to positive, which offers an opportunity for further modification, e.g. the deposition of sol particles of metals or metal oxides with a specified charge. All the methods used allow to change the hydrophilicity of a PLA fibre surface.

The results of thermogravimetric analysis after the deposition of polyelectrolyte layers by the L-b-L method observed in this study are surprising and unprecedented in scientific literature. It has been suggested that the differences in the thermal curves of PLA decomposition are brought about, to a large extent, by the fact that the layers deposited form an isolation barrier that protects the polymeric material against oxygen access and, consequently, retards the degradation of PLA.

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