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Relation between Mathematically Simulated and Experimental Results of Polyhidroxybutyrate–co-valerate Yarns

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Abstract
The effect of process parameters (extruder temperature, extruder pressure) on the properties of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) yarns was studied and the causes of these effects are discussed. It is observed that with an increase in extruder pressure in the process leads to reductions in mechanical characteristics, while temperature has a larger effect on the stability of extrusion and quality of yarns. The effects of these parameters on the final yarn properties were investigated using linear density and strength tests. Regression equations for the prediction of PHBV yarn properties were also derived. On the basis of the regression equations, optimum process parameters for producing good quality PHBV yarns were obtained, considering that yarns with low instability and high tenacity are desirable.

Key words: *polyhidroxybutyrate–co-valerate, extrusion, mechanical properties.*

Introduction

Natural polyesters, which are produced with a wide variety of bacteria as intracellular reserve materials, are receiving increased attention for possible applications as biodegradable, melt processable polymers which can be produced from renewable resources and still retain the desired physical and chemical properties of conventional synthetic plastics [1, 2]. Polyhydroxyalkanoates (PHAs) are a class of naturally occurring biodegradable and biocompatible polyesters with a wide range of thermoplastic properties which are produced from a wide variety of different microorganisms [3]. Their properties span a wide range, including materials that resemble polypropylene and others that are elastomeric [4].

A combination of the biomedical and biodegradable properties of PHB is a prospective tool in the design of novel medical devices and tissue engineering. Over the past years, PHAs, particularly PHB, have been used to develop devices including sutures, repair devices, repair patches, slings, cardiovascular patches, orthopedic pins, adhesion barriers, stents, guided tissue repair/regeneration devices, articular cartilage repair devices, nerve guides, tendon repair devices, bone marrow scaffolds, and wound dressings [5].

PHA polyesters can be processed by a variety of methods: gel-spun technology, solution casting, electrostatic extrusion, solution press moulding etc [6].

Poly-3-hydroxybutirate (PHB) and its copolymers with 3-hydroxyvalerate (3HV), poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), are the best – known representatives of the PHA family. Poly (3HB) is isotactic and similar to isotactic polypropylene, as both have pendant methyl groups attached to the main chain in a single conformation [7]. But PHB is rather difficult to process because of its relatively low decomposition temperature (T_d = 270 ºC) near the melting points (in the range of T_m = 170 – 180 ºC), a glass transition temperature in the range of T_g = 0 – 5 ºC and brittleness. The low rate of PHB nucleation leads to the formation of large spherulites inside of polymers which can deteriorate the physico – mechanical properties of the products. Various methods such as the use of plasticisers and modification of the polymer structure, as well as the preparation of blends and composites of different compounds are used to improve this situation [8 – 10].

Apart from adding nucleating agents, the presence of hydroxyvalerate in PHB reduces the crystallinity and material crystallisation time, contributing to a slower and more successful orientation of the polymer during processing [11]. As a result these longer alkyl chain polyesters ($[COCH_2CH(CH_3)O]_m$ $[COCH_2CH(C_2H_5)O]_n$) are useful as thermoplastic elastomers, which can have excellent strength and toughness, and yet are also inherently biodegradable.

Various efforts have been made to process PHB and PHB copolymer into fibres, films and other products. PHA polyesters are successfully used for the production of oriented materials and products in the form of films and fibres. It was shown that PHA can be used for the production of monofilaments which are resistant to long-time exposure in biological media [9]. A lot of attention is given to the problem of optimisation of the fibre production process using PHA polyesters. Optimising any given yarn property almost always affects other yarn characteristics, and therefore this must be remembered when selecting suitable process parameters and supply yarns for specific end uses.

The present work proposes the production and investigation of multifilament yarns made out of hydroxyvalerate (PHBV) copolymer. The aim was to study and forecast mechanical indicators of yarns produced through the creation of a mathematical model that defines the relation between the yarn indicator and technological parameters of production.

Materials and methods

The experimental materials used in this study were PHBV yarns produced from PHBV copolymer granules with 8% of valerate (Nature Plast Company, France). This copolymer is suitable for extrusion applications. The properties of this type of PHBV copolymer are as follows: density ρ – 1.25 g/cm^2, tensile strength at yield σ_y – 31 MPa, tensile strength at break σ_B – 33 MPa, tensile elongation at break ε_B – 4 %, young's modulus E – 2800 – 3500 MPa, flexural modulus FM – 3520 – 4170 MPa.

The melt spinning of PHBV was carried out using COLLIN® CMF 100 (Dr. Collin GmbH, Germany) laboratory single screw extruder equipment (***Figure 1***). The single screw extruder (L/D = 25:1)

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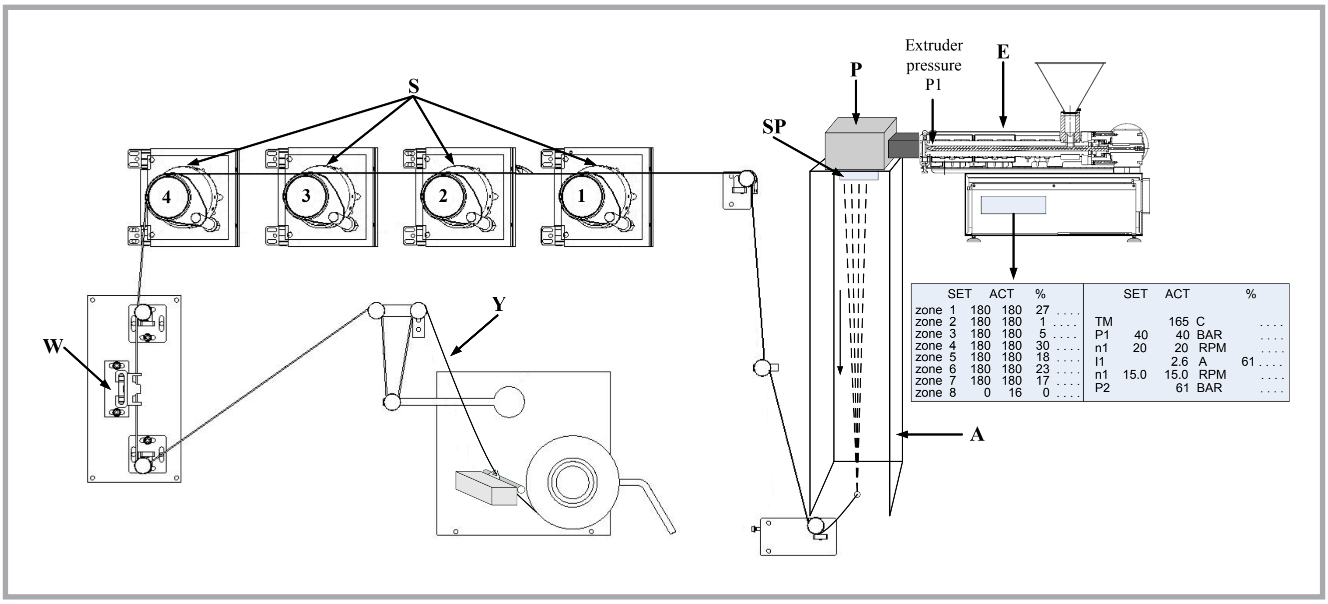

Figure 1. *Principal scheme of the spinning setup – "COLLIN CMF 100": E – extruder, P - melting pump, SP – spinneret, A – air quench cabinet, S – stretching godets (godet No 1, No 2, No 3, No 4), W – whirling unit, Y - yarn.*

includes seven heating zones in which the temperatures are independently and gradually fixed from 10 up to 300 ºC. The extruder pressure was independently set by a pressure controller connected with the electromotor driving the extruder screw. The average speed of the extruder was set at 20 r.p.m. Four godets are driven separately for a speed range of 50 ÷ 800 m/min.

Initially before the actual yarn preparation, yarns were extruded individually to understand their behaviour under actual running conditions and to select a range of process parameters that is appropriate for the yarns on the machine. The range of process parameters found to be suitable were:

- extruder temperatures: $T = 180, 184, 188$ ºC;
- extruder pressures: $P = 3.2, 3.6, 4.0$ MPa.

Samples were extruded using circular spinnerets with 24 holes of 0.45 mm diameter. Cooling of the resultant filaments was achieved with cross – flow air quenching at a temperature of 12 ºC. The as-spun filaments were drawn in four stages with an overall draw ratio of 2.525, in a continuous spin drawing process. All other processing parameters were kept constant (***Table 1***).

Table 1. *Constant processing parameters.*

	Parameter		Unit
Extrusion	Hole diameter, mm		0.45
	Hole length, mm		1.3
	Melt pump speed, rpm		13
Spinning	Stretching godets temperature, ºC / speed, r.p.m.	No. 1	69 /99
		No. 2	75 / 198
		No. 3	78 / 228
		No. 4	85 / 250
	Drawing ratio		2.525

Tensile tests were made under standard conditions i.e. at a relative humidity of $\varphi = 65 \pm 5\%$ and temperature of $T = 20 \pm 2$ ºC (ISO 139). The yarn linear density was determined using a Zweigle L232 reeling machine. To determine the linear density of the yarn, 5 specimens of PHBV yarn of 200 m length were prepared and the average value was determined according to ISO 2060:1994.

Mechanical properties of the yarns were tested according to ISO 2060:1993 using a universal tensile testing machine Zwick / Z005 and *testXpert*® software. The test conditions were as follows: a specimen gauge length of 250 mm, a crossbar speed of 500 mm/s for all yarns tested and a pretension of 0.5 cN/tex. Yarn stretching was conducted until break.

Yarn properties and usability are affected by various controlled and uncontrolled factors. It is very difficult to evaluate the influence of all parameters. Therefore when consider the appropriate design of yarns, a mathematical experiment planning method is used. Experiment planning theory makes sense of the experimental linking of different factors. During the design proceedings, a mathematical model is obtained which represents the relationship between the factors and optimisation parameters [12].

In view of the research object, other researchers' experience, the many factors influencing the yarn structure, its mechanical and other characteristics, this study investigated the following two parameters [13 – 15]: extruder heating zone temperature (X_1), extruder pressure (X_2).

The D – optimal design for a second order model 2^k (k – number of variables) was chosen to describe this investigation. This optimal design was highly suitable for the study because it reduces the costs of experimentation by allowing statistical models to be estimated with fewer experimental runs. Also the plan enables to explore the maximum latitude of factors, enough to accurately assess the impact of selected factors and mathematically express the relationship between them.

Characteristics of the model are the following: number of levels and variables $k = 2$; 2^2 factorial with one central point, the number of factor level combinations (plan lines) $N = 9$ ($N = 2^k + 2 \cdot 2^{k-1} + 1$). At an established range three different values for each parameter selected at equal intervals were taken as high, medium and low (coded as +1, 0, -1) values, as shown in ***Table 2***, which were used in different combinations according to the D – optimal design for a second – order model to prepare the yarn samples for the study.

Table 2. Actual and coded values of process parameters.

Parameter	Low coded (-1)	Medium coded (0)	High coded (+1)
Extruder zones temperature *T*, ºC	180	184	188
Extruder pressure *P*, MPa	3.2	3.6	4.0

Table 3. D – optimal design parameters.

Variant number		B1	B2	B3	B4	B5	B6	B7	B8	B9
Coded independent variables	X_1	+1	+1	+1	0	0	0	-1	-1	-1
	X_2	+1	0	-1	+1	0	-1	+1	0	-1
Real independent variables	**Extruder zones temperature *T*, ºC**	188	188	188	184	184	184	180	180	180
	Extruder pressure *P*, MPa	4.0	3.6	3.2	4.0	3.6	3.2	4.0	3.6	3.2

The central point (zero level) for the extruder zone temperature was 184 ºC with a step of 4 ºC degrees; extruder pressure at the central point (zero level) was 3.6 MPa with a step of 0.4 MPa. Coded values of factors and their variation limits are given in ***Table 3***.

A second – order model with *k* variables is represented by equation [12]:

$$\hat{y} = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ij} x_i x_j + \sum_{i=1}^{k} b_{ii} x_{ii}^2; \tag{1}$$

Where: y – optimisation criterion (size controlled process), k – number of variables, b_0 – free member, b_i – linear coefficients, b_{ii}, b_{ij} – coefficient dual (pair) interaction, x_i, x_j – changing parameters (controllable factor) of coded values during the experiment.

According to equation (1), the regression equation of the second–order model for $k = 2$ factors is represented as a square regression equation [15]:

$$\hat{y} = b_0 + b_1 x_1 + b_2 x_2 + b_{12} x_1 x_2 + ; \\ + b_{11} x_1^2 + b_{22} x_2^2 \tag{2}$$

where x_1, x_2 – changing parameters (controllable factor) of coded values during the experiment.

Regression coefficients of the mathematical model are calculated with the help of the matrix method using the software program *EKSPLA,* created at the Department of Textile Technology, Kaunas University of Technology. The mathematical regression models were used to assess the homogeneity of variances according to informativeness criteria (F_i). For the new yarn design, regression models were used where inequalities in the system were met [12]: $C_j < C_t$, where C_j, C_t – calculated and tabular Cochrain's criteria. Insignificant regression coefficients are determined by calculating a confidence interval (Δb) for all regression coefficients [12]:

$$\Delta b = t_{0.95}(f_E)\sqrt{S^2(b_i)}; \tag{3}$$

where $t_{0.95}(f_y)$ – Student's criteria; $S^2(b_i)$ – variance of regression coefficients.

Regression equation coefficients are considered significant if b_0, b_i, b_{ii} and $b_{ji} \geq \Delta b$. The mathematical model is considered informative if [12] $F_i > F_{it}$, where F_i, F_{it} – calculated and tabular (at a specified probability level $\alpha = 0.95$) Fisher's criteria. Otherwise, the model is not informative.

A prediction is made by the creation and interpretation of the dependence of the two yarn production parameters. For this purpose, second–order three–dimensional surfaces are created describing these dependencies. The dependence is presented graphically with fair X_1, X_2 factor values.

Results and analysis

The yarn structure of all nine samples was observed to be more similar to monofilament than to a multifilament structure. After extrusion, filaments fall on hot stretching rollers, the temperature of which is presented in ***Table 1***. Stretching over the rollers, the filaments stick together, the reason for which may be that the 12 ºC degrees of cross – flow air in the quench cabin has not cooled down the filaments enough.

When the yarns characteristics are examined, it is seen that some characteristics have a little difference among parameter values. The tensile characteristics of PHBV extruded yarns: breaking force (*RB*, cN/tex), elongation at break (*εB*, %), work at break (*WH*, J), tensile modulus (*E*, cN/tex) and linear density (*T*, tex) are provided in ***Table 4***.

Using a higher polymer extrusion temperature can be achieved with a smaller diameter of yarn. It was found that increasing the extrusion temperature of polymer from 180 ºC to 188 ºC degrees, the linear density values of PHBV yarns decrease significantly. The difference between samples No B1 and B7 is 46.29%, between samples No B2 and B8 – 53.84% and between samples No B3 – B9 - 53.48%. Deviation from the temperatures indicated by several degrees leads to substantial changes in the melt viscosity. For instance, if the temperature is increased by 3 – 5 ºC, the melt viscosity becomes so low that the flow of polymer cannot bear its own weight. A decrease in the extruder temperature (below 180 ºC) leads to larger viscosity and a substantial increase in extruder pressure.

The effect of extruder pressure on the deformation behaviour of PHBV yarns is also seen from ***Table 4*** data. With increasing the extruder pressure from 3.2 to 4.0 MPa, all characteristics decrease linearly, except the linear density. With increasing the extruder pressure, the dif-

Table 4. Mechanical characteristics of PHBV yarns.

Characteristics	Calculated value ± coefficient of variation %								
	B1	B2	B3	B4	B5	B6	B7	B8	B9
Breaking force, cN/tex	4.0 ± 3.8	4.2 ± 4.4	5.8 ± 6.5	4.3 ± 4.9	4.6 ± 4.8	4.7 ± 3.9	4.5 ± 4.2	4.7 ± 4.9	6.6 ± 5.0
Elongation at break, %	1.6 ± 3.7	2.0 ± 2.3	13.4 ± 5.8	1.5 ± 4.8	1.6 ± 6.7	1.7 ± 6.9	2.0 ± 6.2	2.2 ± 5.9	19.7 ± 5.7
Work of break, J	0.003 ± 3.1	0.002 ± 2.7	0.01 ± 8.3	0.005 ± 6.6	0.006 ± 7.1	0.005 ± 6.8	0.007 ± 6.8	0.005 ± 5.3	0.08 ± 6.7
Tensile modulus, cN/tex	120.31 ± 4.5	177.86 ± 6.9	226.37 ± 5.5	75.49 ± 4.7	80.47 ± 3.6	122.25 ± 4.4	63.53 ± 5.7	77.48 ± 5.5	78.99 ± 4.3
Linear density, tex	29 ± 3.6	24 ± 2.8	20 ± 3.8	45 ± 5.1	43 ± 6.8	32 ± 4.3	54 ± 5.9	52 ± 4.5	43 ± 3.6

Table 5. *Values of regression components of PHBV yarns; * insignificant regression coefficients in parentheses.*

Coefficients	b_0	b_1	b_2	b_{12}	b_{11}	b_{22}
RB, cN/tex	4.52	(0.26)	(-0.17)	(-0.32)	(-0.08)	0.74
εB, %	(3.64)	(2.99)	(-4.11)	(-4.31)	(-2.09)	5.34
WH, J	(0.01)	(0.01)	(-0.02)	(-0.02)	(-0.01)	0.03
T, tex	39.80	(-12.66)	4.20	(-0.5)	(-0.2)	(-3.9)
E, cN/tex	180.14	9.70	(-14.61)	(-8.20)	(-101.55)	(6.667)

ference between samples No B1 – B3 is 31%, between samples No B4 – B6 - 28.8% and between samples No B7 – B9 it is 20.3%. Results in ***Table 4*** indicate that for the elongation at break dependencies it is difficult to unambiguously describe the variability of these values because the *εB* of yarn variation is quite different. For example, while maintaining a constant temperature (X_1 = 188 ºC) but lowering the pressure (X_2 = 4.0 ÷ 3.2 MPa), the elongation at break of No B3 sample increased by up to 8.3 times. The same trend was seen for sample B9, whose value increased by up to 9.7 times (X_1 = 180 ºC, X_2 = 3.2 ÷ 4.0 MPa). At the same time the strain at break did not significantly vary at the extruder temperature X_1 = 184 ºC and pressure X_2 = 3.2 ÷ 4.0 MPa, with the differences between samples No. B4 and B6 being 11.7%. The maximum relative elongation at break was shown by yarns produced at the lower extruder pressure (X_2 = 3.2 MPa): B3, B6 and B9.

The breaking force is an important indicator in terms of yarns for many reasons. The breaking force of yarns should be higher, to make it possible to use thinner yarns with the same strength characteristics. As can be seen from the results, the breaking force values are not high. The highest specific breaking force value was shown by sample No B9, but difference between the lower (sample No B1) and higher (sample No B9) values is insignificant – 39.3%. Changes in temperature affect viscosity and shear due to relaxation of the molecular link. It can be assumed that the breaking force results are connected with crystallisation degrees in the newly formed fibre.

Table 6. *Comparison of mechanical properties of yarns of informativeness criterion F_i with criterion F_{it}.*

Characteristics	F_i	F_{it}
Force at break *RB*, cN/tex	6.23	4.15
Strain at break *εB*, %	2.11	3.73
Work of break *WH*, J	2.43	3.73
Linear density *T*, tex	105.24	4.15
Tensile modulus *E*, cN/tex	480.23	4.15

The work of break did not significantly vary with increasing the extruder temperature and pressure. If the temperature is high and the pressure low, the work at break will be high.

In general, fibres have the highest tensile module. PHBV yarn's tensile modulus varies within a wide range from 63.53 cN/tex (B7) to 226.37 cN/tex (B3). It was found that this index is the largest of yarns produced at the polymer temperature X_1 = 188 ºC and minimum extruder pressure X_2 = 3.2 MPa. If the sample has a low tensile modulus, it means it is easily deformed, and conversely if the sample has a high tensile modulus, it means it resists deformation. Yarn samples No B4, B5, B7, B8 and B9 are strong and tough. The range of tensile modulus varied from 2.3% to 5.7%.

The regression coefficients of equations describing the yarns' mechanical characteristic dependence on yarn production parameters are given in the ***Table 5***.

From the data presented (***Table 5***), it can be noticed that yarn production technology parameters (X_1 – extrusion temperature, X_2 – extruder pressure) affect the mechanical characteristics of the yarns tested. The regression coefficients of the statistical approach are significant, except the strain at break and work at break parameters, where five coefficients of expressing the strain at break and work at break dependence are insignificant. The initial modulus, breaking force, linear density and technological parameter dependence on the describing equation of two regression coefficients is significant.

Solving the matrices results in equations which describe the tensile characteristic's dependence on factors X_1, X_2:

$$\text{RB: } \hat{y} = 4.52 + 0.74x_2^2; \qquad (4)$$

$$\text{TEX: } \hat{y} = 39.80 + 4.20x_2; \qquad (5)$$

$$\text{E: } \hat{y} = 180.14 + 9.70x_2. \qquad (6)$$

For better visualisation and practical use, the equations are transformed by introducing actual values. Transition from the coded to actual values is carried out using the relation:

$$X_i = \frac{C_i + C_{oi}}{E_r} \qquad (7)$$

where C_i – actual factor value, C_{oi} – factor value at zero level, E_r – variation range. In this case:

$$X_1 = \frac{T + 184}{4};\ X_2 = \frac{P + 3.6}{0.4}.$$

Receiving this type of equation:

$$\text{RB: } \hat{y} = 64.46 + 3.33\text{P} - 4.625P^2; \qquad (8)$$

$$\text{TEX: } \hat{y} = 2 + 10.5P; \qquad (9)$$

$$\text{E: } \hat{y} = 2.43\text{T} - 266.06. \qquad (10)$$

Another important phase of the study is to set the informativeness of PHBV yarns' mechanical characteristics. A comparison of PHBV yarns' mechanical characteristics of the mathematical model's informativeness criterion F_i with criterion F_{it} is presented in ***Table 6***.

As can be seen from the data presented in ***Table 6,*** mathematical models of the three mechanical characteristics: breaking force, tensile modulus and linear density are informative.

The model describing the strain at break, work at break and X_1, X_2 factor's dependence was non-informative. Particularly high informativeness of the mathematical models was between the X_1, X_2 factors and characteristics of the tensile modulus (F_i = 480.23) and the linear density (F_i = 150.24).

Graphic dependences of PHBV yarns' technological production parameter values are presented below in ***Figures 2***. The study showed that the use of lower extruder pressure in yarn production makes it possible to shrink PHBV yarns' elongation at break.

The dependence of the breaking force on the die temperature and extruder pressure indicates that the yarn's breaking force decreases with an increase in the die temperature, and from 184 °C the die temperature starts to rise.

At the maximum value of the yarn breaking force (***Figure 2.a***), in whose production the maximum (188 ºC) and minimum (180 ºC) die temperature was used, the extruder pressure had no significant influence. At a maximum pressure of

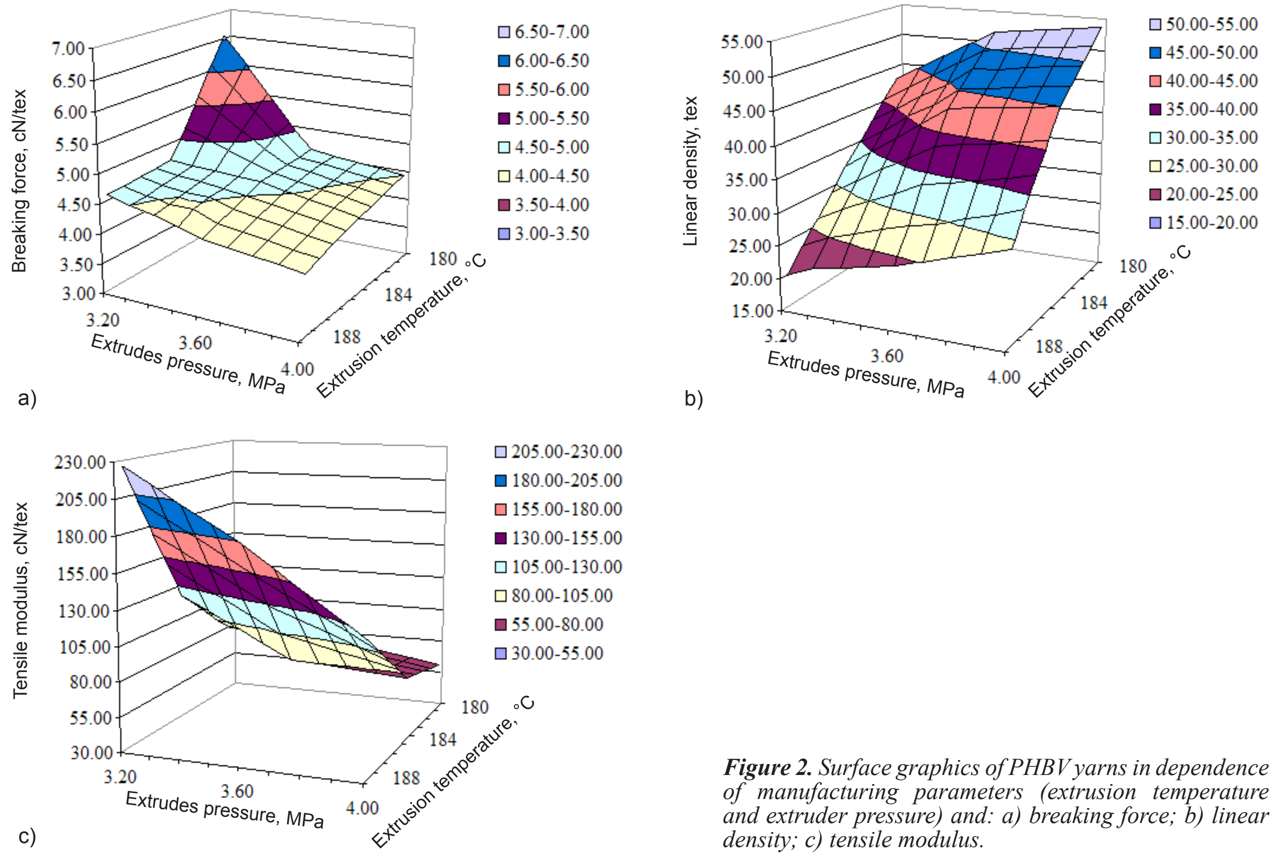

Figure 2. *Surface graphics of PHBV yarns in dependence of manufacturing parameters (extrusion temperature and extruder pressure) and: a) breaking force; b) linear density; c) tensile modulus.*

4.0 MPa, the breaking force increased by only 31%.

As can be seen from the linear density dependency (***Figure 2.b***), the yarn linear density increases when changing the extruder temperature throughout the range. Increasing the temperature from 180 °C to 188 °C degrees, the yarn linear density decreases 2.5 times (62.96%).

The yarn tensile modulus varies consistently, i.e. by decreasing the temperature, the elastic modulus decreases to a certain minimum value in the field X_1 = 184 ºC, and once reached it starts to increase (***Figure 2.c***).

Conclusions

The aim of the study, using a mathematical experimental design (D – optimal design for second – order model), was to derive regression equations that allow to predict and explore the dependencies of factors of PHBV yarn manufacturing parameters (extrusion temperature – X_1, extruder pressure – X_2), and their geometrical and structural indices.

The structure and characteristics results of PHBV yarns examined allow to make the following conclusions: the extrusion stability and quality of the yarns were affected by the technological parameters examined (extruder temperature and pressure). PHBV copolymer was melted – spun to produce yarns with such mechanical characteristics as follows: breaking force – 4.0 – 6.6 cN/tex, elongation at break 1.5 – 19.7%, work at break – 0.007 – 0.08 J, tensile modulus – 63.53 – 226.37 cN/tex and linear density 20 – 54 tex. The pressure affects the mixing of the polymer and melt temperature. Insufficient mixing may affect product weakness and excessive temperature may lead to product degradation or cooling / sizing problems. Using higher extruder pressure in the process leads to a decreasing elongation at break, breaking force and tensile modulus. With increasing the extruder pressure, the difference in linear density between samples is 20 – 31%. Maximum values of geometrical and structural indices were achieved when the coded values of the factors studied (X_1 / X_2) were: +1 / -1, 0 / -1 and -1/-1, meaning that in the experiments described, the optimal pressure was 3.2 MPa (coded value -1). Minimum values of the indices investigated were achieved when the actual value of factor X_2 was 4.0 MPa (coded value +1).

It was revealed that temperature has a considerable effect on the quality of yarns. It was shown that a low linear density of PHBV yarns could be obtained at higher polymer melting temperature (188 ºC) combined with low extruder pressure (3.2 MPa). Generally yarns produced at higher temperature are inelastic and have a lower breaking force than those produced at lower temperature. Even at a constant drawing ratio, extruding temperature and pressure affect the mechanical characteristics of the yarn.

Analysis of design methods and forecasting results showed that technological parameters extrusion temperature (X_1) and extruder pressure (X_2) analysed have an impact on the tensile characteristics of the PHBV yarns and can be used as parameters of optimisation of the fibre production process. It was found that of the five mathematical models for generalized yarn characteristics and technological parameters, three of them are informative. Mechanical properties of PHBV yarn allows to select a more appropriate regime for spinning yarns intended to be used for a specific purpose in medicine.

The yarns structure obtained is not perfect; it will be enhanced by improving the production parameters. The investigation showed that in order to get multifilament yarns from PHBV copolymer the filament cooling path must be increased because the filaments fail to cool and on stretching rollers experience repeated heating, where repeated crystallisation occurs. The investigation showed that PHBV copolymer is sensitive to temperature changes. This may be the reason why the samples produced are not strong.

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