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Natural Modified Starch and Synthetic Sizes in Function of Characteristics of Sized Yarn

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Abstract
The aim of this study was to investigate the changes in properties of yarn made by sizing with synthetic and natural modified corn starch. Different procedures for obtaining modified natural (corn) starch and various combinations of natural and synthetic sizes were used to explore the differences in the properties of sized yarn. The sizing process was carried out wunderith constant conditions in a newly developed laboratory sizing machine on twisted cotton yarns of 20×2 tex and 30×2 tex. According to the results obtained, yarn sized with synthetic sizes has substantially better properties than those which are naturally sized with modified starch. However, sometimes these differences are not significant or they do not exist at all. Twisted yarn is not always necessary in sizing in order to increased its strength but rather to protect the surface from wear and refine projecting fibers; in this case natural modified starch from corn can meet the requirements. The significance of this research is the application of natural sizes, improvement of the sizing process with natural modified sizes using new achievements in the development of the sizing process, and thus creating a positive environmental and economic impact.

Key words: *yarn, natural modified starch, synthetic sizes: polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), physico-mechanical properties of yarn.*

Introduction

Cotton yarn with frequent weak and thick places needs sizing to increase its physico-mechanical properties such as the strength, abrasion resistance and uniformity, as well as to reduce surface hairiness and prevent greater decrease in the elasticity of the yarn. The aim of the sizing process is to achieve satisfactory use of weaving machines and fabric quality with an optimal cost of the sizing process. Progress in the sizing process enables the achievement of this goal with relatively weak yarn. Unfortunately sizing is still one of the major pollutants of wastewater in the textile industry due to the use of synthetic sizing agents, often because of poor or no facilities for wastewater treatment [1 - 7].

The high cost of installation, maintenance, and sizes, as well as high energy consumption and work all suggest an extremely important stage in preparing the ground for weaving. Much attention was paid to this stage of processing during technical and technological development, which contributed to size machines becoming one of the most complex and automatic machines in the process of making fabric, with the aim of more efficient and higher quality fabric production. With the advent of synthetic sizes, their application quickly came into use and completely excluded natural sizes. Their advantage was not only in getting better performances of yarn, but also easier and faster preparation of the size mass, as well as easy removal from the base in chemical finishing, lower consumption of sizes and the possibility of recycling. The negative impact of synthetic sizes has a bad effect on human health (respiratory tract, allergic effects, harder preparation, etc.), and it damages parts of the size box (bearings, pumps, dipping and squeezing rollers). Nevertheless it was not possible to stop their use in sizing. Modified natural sizes were abandoned because of their bad viscous properties, removal in the process of weaving (formation of dust), heavier and longer removal from the basis, which affected the cost of desizing, and the quality of the final fabric. Despite the fact that they were cheaper, more accessible, environmentally favourable and did not adversely affect human health, they did not do any harm by destroying contact parts in the bed sizing; however, they have failed to be kept in the industry. This paper will explore the negative sides that accompany natural modified sizes compared to the synthetic ones today, with the possibility of improving the properties of natural modified size resources as well as their combination with synthetic sizes for twisted yarns that require less size pick-up [8 - 11].

The sizing effect depends on the quality of sizes, the size of the share, the method of preparation, and thus on the properties of the prepared and sized base. When the frequency of the weak points is higher and yarn less monotonous, it is necessary to size with bigger and better size pick-up in order for the base to meet the requirements of weaving. Greater size pick-up is required when using natural modified sizes to achieve the same efficiency in weaving. Optimising of the size pick-up is one of the most complex tasks in making fabrics, especially if the properties of sizes or yarn are changing [12 - 16].

Despite the many benefits of synthetic sizes, natural modified sizes have certain advantages that are still very important today (***Table 1***), and hence they should not be allowed to become completely abandoned. Nevertheless attempts should be made with further research and use of modern technology to partially return sizing to twisted yarns in combination with synthetic sizes.

Experimental part

This research was possible and reproducible on laboratory sizing machines under customized manufacturing conditions.

For comparison of sizing synthetic and natural modified sizes, the most important properties of yarn were examined, including the breaking force, elongation at break, work to rupture, strength, unevenness, hairiness, resistance to abrasion as well as size pick-up.

Materials and methods

Tests were conducted on cotton ring yarns with a yarn count of 20×2 tex, twist level 480 (t.p.m.), and 30×2 tex, twist

level 322 (t.p.m.). Standardised methods were used for examination of the yarn. Thus the actual yarn count of the yarn was tested in accordance with ISO 2060:2003. The unevenness of the yarn was examined by the capacitive method, in which thin and thick places are recorded in the yarn and nodes (lumps), as well as the coefficient of variation of mass unevenness (CV/%), on a Kiesokki, Evanness Tester 80, type B device, according to Standard ISO 16549:2004. Parameters of the breaking ability - breaking force, elongation at break, work to rupture and breaking strength were tested according to ISO 2062 dynamometer Statimat M tt. Textechno. Hairiness of the yarn before and after sizing was tested on the basis of the registration of fibres protruding from the structure of the yarn, with a length of 25 m. Protruding fibres were measured with the lengths n_1 = 2 mm, n_2 = 4 mm, n_3 = 6 mm and n_4 = 8 mm, according to ASTM D 5674-01 on a Zweigle G 565 device. The twist level of yarn of1 m was tested on a MesdanLab Twist tester device, according to ISO 17202. Abrasion resistance was tested on aZweigle G551 device, wherein each of the 20 threads, under a load of 20 g, was simultaneously subjected to the abrasion process to rupture of the thread. The movement of the cylinder, coated with 600 yarn-count grit sandpaper, from left to right over a length of 7 cm, and spun around its axis, achieves a certain intensity of yarn and sandpaper abrasion. During abrasion, the thread weakens and at the time when the mass of the weight hanging on the thread prevails its strength, a rupture occurs, and the motion of the roller for the broken thread is registered. The size pick-up in relation to the sized yarn was determined according to the equation:

$$S_p = \frac{m_2 - m_1}{m_2} \times 100 \quad (1)$$

S_p – size pick-up in%, m_2 – mass of dry sized yarn in g, m_1 – mass of dry unsized yarn in g.

Preparation of sizes

Overview of the making of sizes with samples:

Sample IA (10%) and **Sample IB** (15%) - preparation procedure of starch according to references [17, 18] with a minor modification.

***Oxidation process**:* Corn starch ("Jabuka", Serbia) mash (35 g/100 ml of water) is prepared with deionised water, heated to and maintained at 35 °C during 30 min with vigorous stirring; the pH of the mash is then adjusted to 9.5 with 2 M NaOH ("Mol", Serbia). Sodium hypochlorite ("Tehnohemija", Serbia) (1 g/100 ml - concentration of active chlorine) is then slowly added to the starch mash within 30 minutes while maintaining the pH at 9.5 optionally with 1 M H_2SO_4 ("Mol", Serbia). After the addition of NaOCl, the pH of the mash was maintained at 9.5 with 1 M NaOH in the course of the next 50 min. The mash is then adjusted to pH 7.0 with 1 M H_2SO_4, filtered by suction through a Buhner funnel, washed with twice the amount of deionised water, and dried in an oven at 60 °C until an absolute dry sample was obtained. The total carbonyl and carboxyl contents [19, 20] of the oxidised starches were 28% and 2.1%, respectively, (total carbonyl and carboxyl contents of the raw starch were 5% and 0.2%, respectively).

Grafting-copolymerization process:
Ten percent of oxidised starch and 5% of acrylamide ("Merck", Germany) are added to an aqueous solution of ammonium persulfate ("Centrohem", Serbia) the initiator, 1%. The temperature is maintained at 50 °C under intensive stirring in a magnetic mixer. The reaction product is precipitated and then washed with pure ethanol ("Reahem", Serbia) at room temperature. Then comes rinsing with a solution of ethanol-water and drying at 60 °C. The graft percentage [21] of the copolymer (sample I) was 72%, while the graft yield was 17%.

Sample IIA (10%) **and Sample IIB** (15%) **-** preparation procedure of the starch according to the references [18, 22] with a minor modification.

***Hydrolysis process**:* Starch hydrolysis is carried out in a hydrochloric acid ("Centrohem", Serbia) solution of 0.1 M at 60 °C with the addition of 17% starch compared to water, and then intensively stirred with a magnetic mixer. Upon expiration of 60 minutes, the reaction product is precipitated with ethanol and neutralised with sodium carbonate ("LG Hemija", Serbia) solution. In the end, washing and drying processes follow at 60 °C. The hydrolysis yield [9] of the hydrolysed starch was 76%.

Grafting-copolymerisation process for samples 1 and 2: Ten percent of hydrolysed starch and 5% of acrylic acid ("Sigma–Aldrich", SAD) are added to an aqueous solution of ammonium persulfate (the initiator, 1%). The temperature is maintained at 50 °C under intensive stirring in a magnetic mixer. The reaction product is precipitated and then washed with pure ethanol at room temperature. Rinsing with a solution of ethanol-water and drying at 60 °C follow. The graft percentage of the copolymer (sample II) was 79%, while the graft yield was 19.5%.

Sample III: ***Oxidation process:*** Starch is poured into a 500 ml container with a stopper, then sodium chloride ("Centrohem", Serbia) solution (1 g/100 g starch) and thiourea ("Centrohem", Serbia) (0.4 g/100 g of starch) are added. Usage of phosphoric acid ("Tehnohemija", Serbia) prior to the start of the oxidation is adjusted to the pH of the medium. Water is added at a starch-water ratio of 1:3. The vessel is closed by a stopper and kept in a water bath at a constant temperature of 50 °C and is periodically shaken during the 60-minute reaction. Upon time expiration, the product is filtered on a glass frit, washed with water, dried at room temperature, and then in a drier at 50 - 55 °C. The total carbonyl and carboxyl contents of the oxidized starches were 30% and 2.7%, respectively.

Table 1. *Advantages and disadvantages of synthetic and natural modified sizes.*

	Advantages	Disadvantages
Synthetic sizes	■ Reduced consumption of sizes ■ Greater utilisation of weaving machines ■ Better quality of raw fabric ■ Possibility of recycling ■ Easily removed from the base	■ Harmful effects on human health (respiratory damage, allergic reactions, unpleasant odour) ■ Damaging parts of the box (beds, rollers for dipping, extrusion rollers, wall box, pumps, cooking pots, pipeline) ■ Expensive ■ Air pollution and wastewater
Natural modified sizes	■ Do not harm human health ■ Do not damage parts of the box ■ Cheaper ■ Fourth less polluting wastewater harmful agents	Shortcomings that were valid at the time of the old technology which can be repaired now: ■ Higher consumption of sizes ■ Lower use of weaving machines ■ Poorer quality of raw fabrics ■ Recycling is not possible ■ Not easily removed.

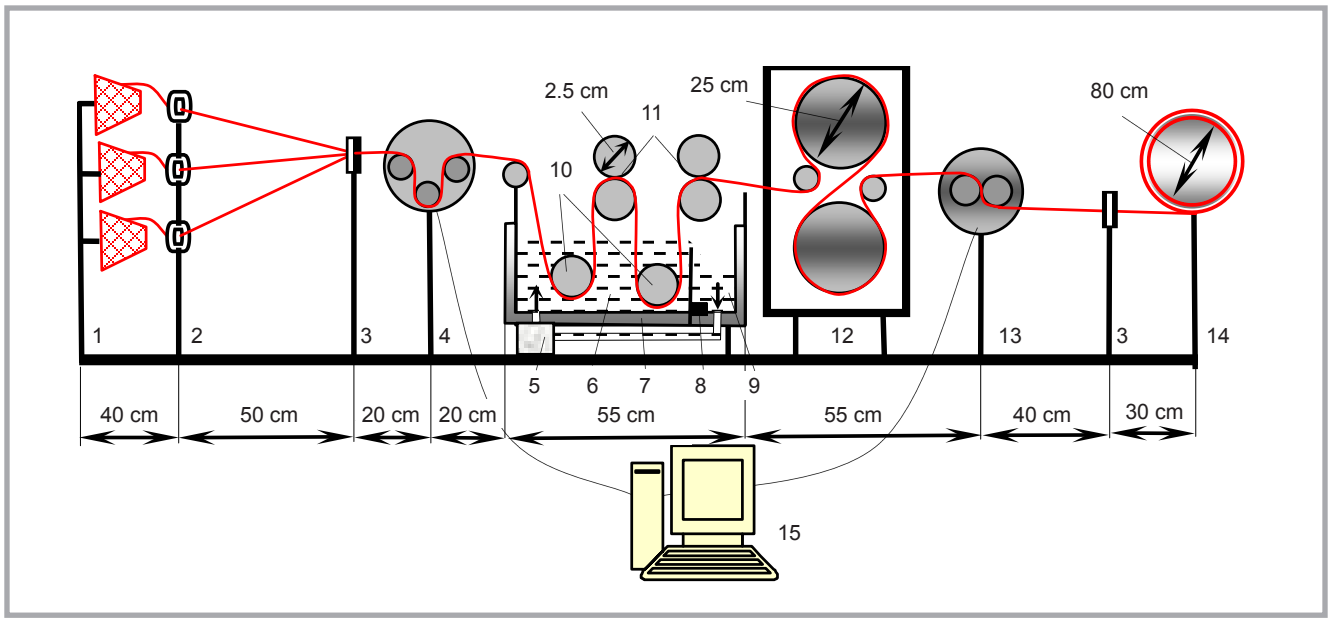

Figure 1. *Laboratory sizing machines, 1 - bobbin creel, 2 - thread guides and brakes, 3 - comb, 4 - tensiometer, 5 - pump, 6 - size box, 7 - double wall of the box with heater, 8 - thermostat, 9 - support box, 10 - dipping rollers, 11 - extrusion size rollers, 12 - contact dryer, 13 - moisture tester, 14 - sized yarn winder, 15 - computer with A/D converter for data storage and processing.*

Grafting-copolymerization process: Ten percent of oxidised starch and 5% of acrylamide are added to the aqueous solution of ammonium persulfate (the initiator, 1%). The temperature is maintained at 50 °C under intensive stirring in a magnetic mixer. The reaction product is precipitated and then washed with pure ethanol at room temperature. Then rinsing with the solution of ethanol-water and drying at 60 °C follow. The graft percentage of the copolymer (sample III) was 70%, while the graft yield was 14%.

Sample IV: ***Oxidation process:*** 100 g of corn starch is added to water (starch to water ratio of 1:5) and stirred using a mechanical mixer at room temperature. Then hydrogen peroxide ("LG Hemija", Serbia) (2.9 ml, 35%) is added with continuous stirring, followed by the addition of 0.01 g of anhydrous iron sulfate ("Centrohem", Serbia) (oxidation catalyst), and the pH solution is adjusted (11) using 1% of aqueous solution of NaOH; the temperature rises to 50 °C and oxidation is continued at this temperature for 2 hours. Thereafter the pH of the solution is adjusted (7), filtered, washed several times with 90% ethanol until it is free of salt, and then dried under ambient conditions. The total carbonyl and carboxyl contents of the oxidised starches were 31% and 2.9%, respectively.

Grafting-copolymerization process: 10% of oxidised starch and 5% of 2-hydroxyethyl methacrylate ("Sigma–Aldrich", SAD) are added to the aqueous solution of ammonium persulfate (initiator, 1%). The temperature is maintained at 50 °C with vigorous stirring in a magnetic mixer. The reaction product is precipitated and then rinsed with pure ethanol at room temperature. Then rinsing with the solution of ethanol-water and drying at 60 °C follow. The graft percentage of the copolymer (sample IV) was 72%, while the graft yield was 15.5%.

Sample V: ***Oxidation process:*** 50 g of starch and 250 ml of distilled water is heated to 80 ºC over 1 hour with gentle mixing. Then the temperature is lowered to 20 ºC and a mixture of 200 ml of distilled water and 24.6 ml of hydrogen peroxide is added, followed by continuation of the reaction for a period of 1 hour. During the oxidation, the mixture is strongly and mechanically stirred in order to ensure an even distribution of hydrogen peroxide to gelatiniaed starch. The reaction temperature is maintained at 25 ºC with the pH solution (7). After 24 hours, the mash is separated by centrifugation and the product is washed five times with 200 ml of distilled water. The product is dried for 24 hours at 50 ºC and then goes through a vacuum at 120 ºC for a period of 2 hours. The total carbonyl and carboxyl contents of the oxidised starches were 33% and 3.2%, respectively.

Grafting-copolymerization process: 10% of oxidized starch and 5% acrylamide is added to an aqueous solution of ammonium persulfate (the initiator, 1%). The temperature is maintained at 50 °C under intensive stirring in a magnetic mixer. The reaction product is precipitated and then washed with pure ethanol at room temperature. Then rinsing with a solution of ethanol-water and drying in a drier at 60ºC follow. The graft percentage of the copolymer (sample V) was 74%, while the graft yield was 16.5%.

Sample VI: 7% sample I + 5% PVA ("Kuraray Europe Gmbh", Germany).

Sample VII: 2% sample I + 2% CMC ("Lovochemie", Czech Republic).

Sample VIII: 12% sample II + 5% PVA.

Sample IX: 2% sample II + 2% CMC.

Sample X: 5% sample I + 2% CMC +2% PVA.

Sample XI: 5% sample II + 2% CMC+2% PVA.
Sample XII/A: 10% TUBOFLEX 80 (PVA) + 0.3% TUBOWAX 24 (greasiness) from Bezema Company.

Sample XII/B: 15% TUBOFLEX 80 (PVA) + 0.3% TUBOWAX 24 (greasiness) from Bezema Company.

Laboratory sizing machines

Sizing was performed with innovative laboratory sizing machines customised for the sizing industry (***Figure 1***).

The temperature of the size mass can be controlled and maintained constant by using the built-in thermostat and heater, which indirectly heat the size mass through the box walls. Drying sized yarn is carried out by contact while passing through the two heated cylinders. Speed sizing can be controlled and maintained constant by using the winch and extra speed regulator.

The temperature of the size mass was 75 - 85 °C. The sizing speed was 3 m/min, while the pressure of the rear pair of excess rollers in the extrusion of size mass was 19.1 N/cm^2. The temperature of contact drying on the cylinders of the contact dryer was 140 °C. Yarn tension was measured by a tensiometer TT, Schmidt model ETM, when entering the box, and was 60 cN. Yarn humidity was measured by using a contact hygrometer (moisture tester) at the exit of the dryer, and was 8%. After drying, the yarn was separated in the comb so that each thread was specially wound onto a common winch with 1 m in diameter. When unwinding the sized yarn from the winch, the first and last 10 m of the sized yarn were thrown away, due to size pick-up deviations, for the establishment of uniform velocity and constant conditions (temperature of the size mass and temperature of the drying cylinders). Sizing conditions were not changed for all the samples. Ten threads of yarn count 20×2 tex and ten threads of yarn count 30×2 tex were sized simultaneously.

The sized yarn was used to weave fabric selvedges on a Picanol Omni 4P weaving machine. ***Figure 2*** shows the input parameters (yarn count, breaking force, elongation at break, yarn harness, yarn abrasion) and output parameter (recording the number of breaks on the weaving machine).

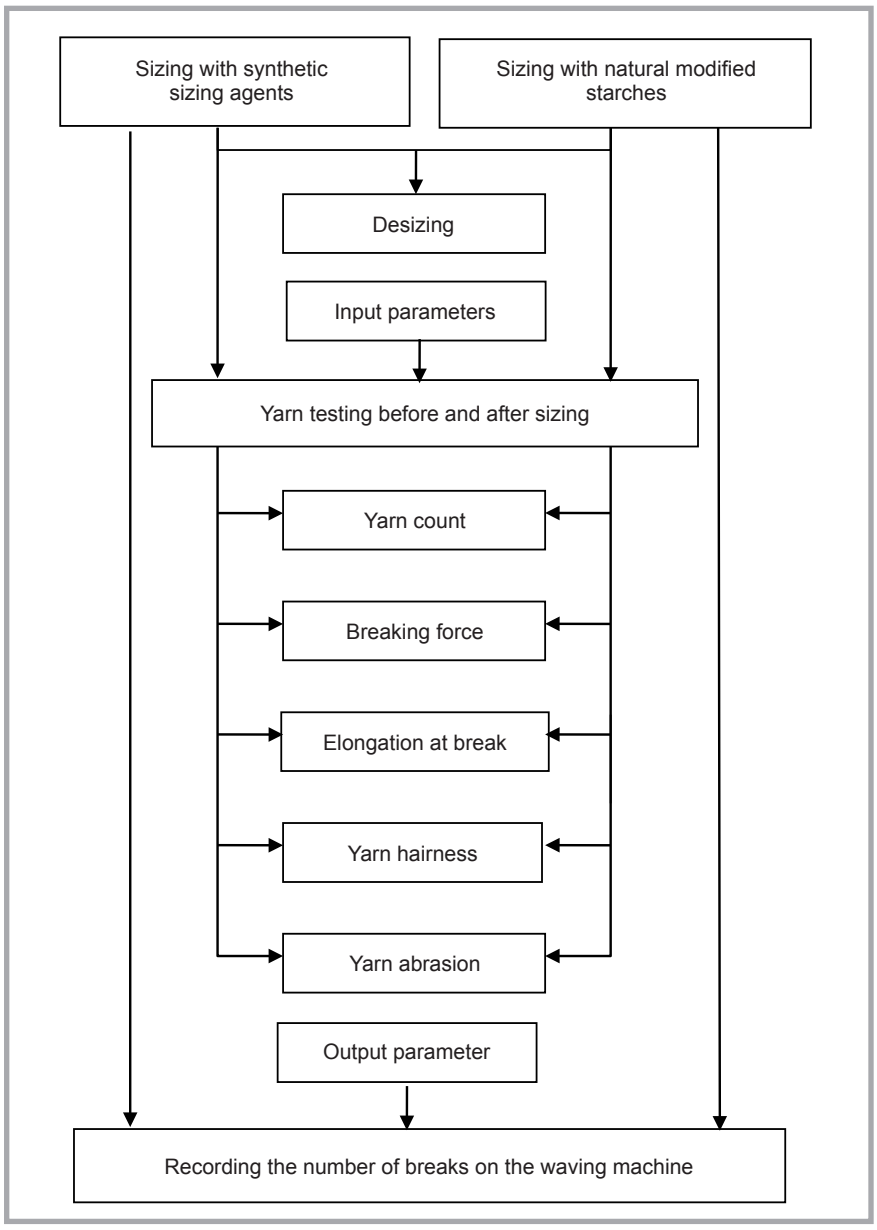

Figure 2. *Scheme with input and output parameter.*

Results and discussion

Results of the yarn examination before and after the implementation of the sizing process, relevant to its analysis, are shown in ***Tables 2*** to ***7*** (see also page 60 & 63) and in ***Figures 3*** to ***6*** (see also page 61 & 62).

Statistical analysis of test results

Multivariate analysis was used to analyse data of the interrelationship among occurences observed in the sizing process and to simultaneously monitor a number of variables in mutual correlations.

Table 2. *Size viscosity at different concentrations.*

Samples	Size designation	Viscosity (η), mPa·s					
		20×2 tex			30×2 tex		
		40 °C	60 °C	85 °C	40 °C	60 °C	85 °C
I/A (10%)	HS-5	38.8	57.1	53.9	11.5	16.3	14.9
I/B (15%)	HS-10	46.2	65.2	61.9	22.6	37.1	35.5
II/A	HS-15	53.6	71.8	70.2	38.8	57.1	53.9
II/B	HS-AA-5	42.9	60.2	58.9	12.9	19.9	16.2
III	HS-AA-10	53.9	66.1	63.5	26.6	39.2	37.7
IV	HS-AA-15	66.5	70.5	68.9	42.9	60.2	58.9
V	HS-AK-5	41.2	59.5	55.5	12.4	18.1	16.5
VI	HS-AK-10	53.2	61.1	60.9	24.5	37.9	36.1
VII	HS-AK-15	63.5	69.3	68.6	41.2	59.5	55.5
VIII	HS-HEMA-5	44.8	62.0	60.0	14.3	21.7	20.1
IX	HS-HEMA-10	56,8	68.9	64.0	29.7	42.3	42.8
X	HS-HEMA-15	69.3	72.9	70.6	44.8	62.0	60.0
XI	HS-MK-5	41.0	58.1	52.3	12.5	17.5	17.0
XII/A (10%)	HS-MK-10	52.9	63.4	60.1	24.4	37.3	36.6
XII/B (15%)	HS-MK-15	63.2	70.1	68.4	41.0	58.1	52.3

Table 3. *Percentage of size in water, size pick-up.*

Samples	Share of size in water		Size pick-up			
			20×2 tex		30×2 tex	
	$\bar{X}$, %	CV, %	$\bar{X}$, %	CV, %	$\bar{X}$, %	CV, %
I/A (10%)	10	15.6	4.1	7.7	4.9	12.4
I/B (15%)	15	14.2	6.1	6.9	7.6	15.9
II/A	10	11.7	4.7	7.5	5.0	12.8
II/B	15	11.4	5.9	9.4	7.1	13.6
III	10	15.7	4.4	11.4	5.5	12.9
IV	10	9.3	4.6	9.4	6.8	14.6
V	10	13.4	5.8	7.4	6.7	13.3
VI	10	12.9	5.2	5.7	6.8	12.1
VII	10	14.3	5.9	9.0	5.8	14.8
VIII	10	13.2	5.6	14.0	6.9	12.5
IX	10	13.7	5.4	11.5	6.5	12.4
X	10	10.4	5.4	13.4	6.2	15.3
XI	10	11.4	5.6	10.4	6.5	12.0
XII/A (10%)	10	13.6	4.0	5.8	5.5	12.1
XII/B (15%)	15	11.4	5.4	5.5	7.0	11.4

Table 4. *Breaking force, elongation at break, work to rupture and breaking strength of the yarn shown by samples.*

Yarn count	Samples	Breaking force		Elongation at break		Work to rupture		Tenacity	
		F, cN	CV, %	ε, %	CV, %	W, cN×cm	CV, %	ε, cN/tex	CV, %
20×2 tex	Unsized	678.10	4.69	6.08	3.97	1050.2	8.47	16.95	4.69
	I/A	708.79	4.72	3.87	7.83	776.18	10.23	17.72	4.72
	I/B	709.58	5.25	3.42	9.86	681.11	11.33	17.74	5.25
	II/A	743.92	4.12	3.51	6.71	737.02	10.76	18.60	4.12
	II/B	698.06	4.27	3.57	5.67	712.42	9.48	17.45	4.27
	III	869.00	6.35	3.58	8.60	864.84	11.37	21.73	6.35
	IV	900.63	4.65	3.92	6.29	682.90	10.54	22.51	4.65
	V	768.03	5.46	3.62	6.51	777.58	12.37	19.20	5.46
	VI	746.23	4.05	3.65	5.72	715.78	8.98	18.65	4.05
	VII	821.49	5.29	3.14	6.52	721.25	10.29	20.54	5.29
	VIII	913.58	4.14	2.53	7.22	642.27	10.4	22.84	4.14
	IX	926.75	4.34	2.44	6.01	610.67	9.99	23.17	4.34
	X	762.68	4.89	2.17	8.62	889.94	10.79	19.07	4.89
	XI	804.70	4.78	3.45	7.07	777.83	10.3	20.12	4.78
	XII/A	946.41	4.42	3.04	9.04	739.82	11.14	23.66	4.42
	XII/B	943.99	4.36	2.77	8.27	807.39	12.08	23.60	4.36
30×2 tex	Unsized	849.23	4.84	5.19	4.27	1163.76	8.81	14.15	4.84
	I/A	874.08	4.33	3.62	7.114	893.96	10.20	14.57	4.33
	I/B	1044.85	5.95	3.82	8.87	1122.62	12.91	17.41	5.95
	II/A	887.40	4.97	3.50	6.30	875.86	9.14	14.79	5.27
	II/B	941.83	4.83	3.45	5.81	917.59	9.42	15.70	4.83
	III	912.34	3.97	3.15	6.94	818.28	9.53	15.21	3.97
	IV	1211.77	8.26	3.39	7.77	822.57	15.62	20.19	8.26
	V	1190.79	5.28	3.29	6.42	1130.62	10.65	19.85	5.28
	VI	955.25	5.06	3.34	6.35	933.42	10.48	15.92	5.06
	VII	1084.28	5.52	2.88	6.79	858.80	9.31	18.07	5.52
	VIII	1112.70	4.31	2.81	8.19	795.76	11.34	18.54	4.31
	IX	1094.31	4.16	2.86	5.59	642.31	9.45	18.24	4.16
	X	871.75	4.55	3.25	8.48	844.58	10.08	14.53	4.55
	XI	936.26	4.82	3.76	7.20	907.81	8.66	15.60	4.82
	XII/A	1326.87	4.16	3.93	6.73	993.55	9.61	22.11	4.16
	XII/B	1318.64	4.53	3.76	8.81	1011.81	12.08	21.98	4.53

An analysis and application of multiple linear regression showing the realtionship between several predictor variables (independent variables) and criterion (dependent) variables and/or the prediciton of the value of the dependent variable based on one or more predictor variables was performed. It is the extension of the simple linear regression, in which there are more independent variables. It is used to analyse the effects of more than one independent variable on the dependent variable *y* [23 - 25].

In this case, the dependent variable (response) is the size pick-up, as a variable of primary interest regarding the results to be described and/or to be predicted. Independent variables (predictors) of the same case, twist level, yarn count, size concentration, yarn hairiness index and viscosity at 40, 60 and 85 °C are used to explain the variability of the dependent variable – size pick-up; in other words, these are the variables describing and/or predicting the results of the variable – size pick-up.

Tables 9 - 10 show basic data of this kind of analysis, starting with the parameters used and their coefficients, then the most basic statistical performance data, and finally to Anova analysis, i.e. analysis of variance.

According to ***Table 9***, the equation of the dependence of the dependent on the independent variables is:

$$\textit{Size pick-up} = 1.15 - 0.003 \times \textit{Twist level} - 0.0115 \times \textit{Yarn count} + 0.072 \times \textit{Size concentration} + 0.012 \times \textit{Yarn hairiness index (8 mm)} + 0.55 \times \textit{Viscosity at 40 °C} - 0.186 \times \textit{Viscosity at 60 °C} - 0.126 \times \textit{Viscosity at 85 °C}$$

As regards the coefficients of the regression equation, the following can be claimed:

- for each unit increase in the number of twists, with other independent variables being constant, the size pick-up is reduced by 0.003%.
- for each tex increase in yarn count, with other independent variables being constant, the size pick-up is reduced by 0.0115%.
- for each increase in size concentration, with other independent variables being constant, the size pick-up is increased by 0.072%.
- for each new protruding fibre within the zone of 8 mm of the yarn hairiness

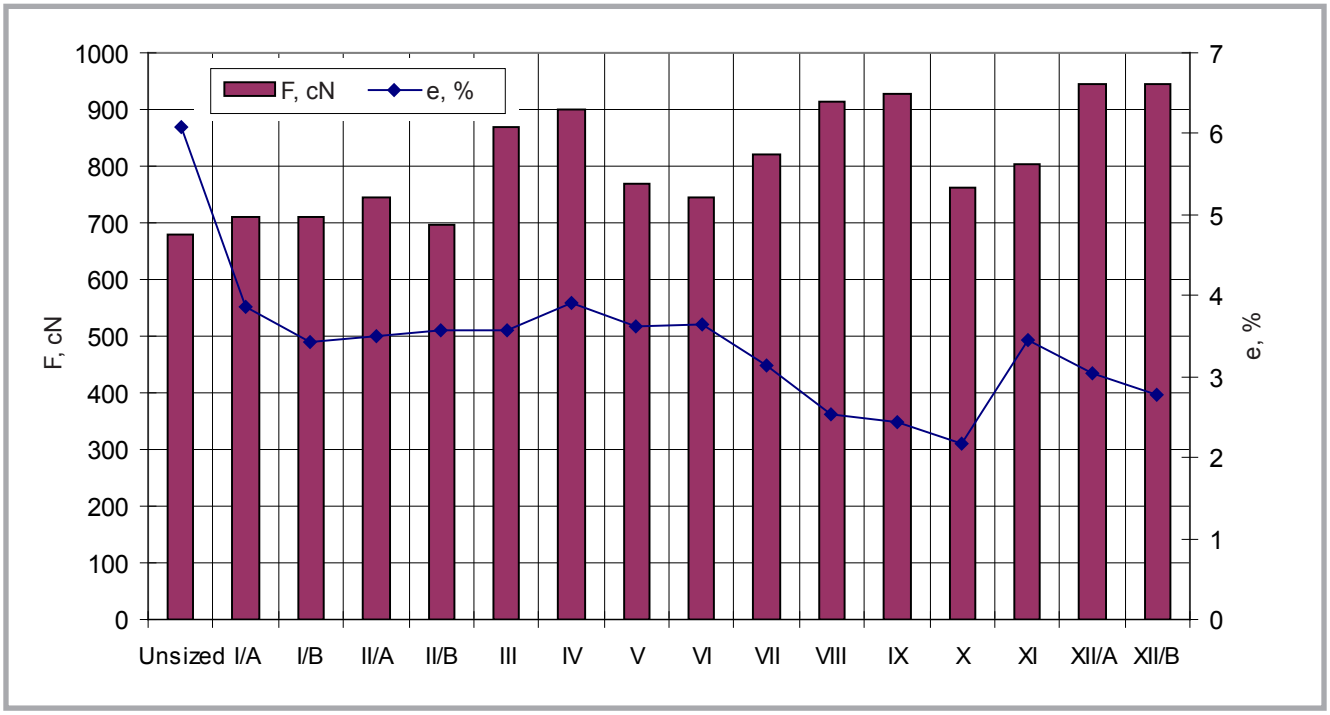

Figure 3. *Breaking force and elongation at break of yarn with a count of 20×2 tex.*

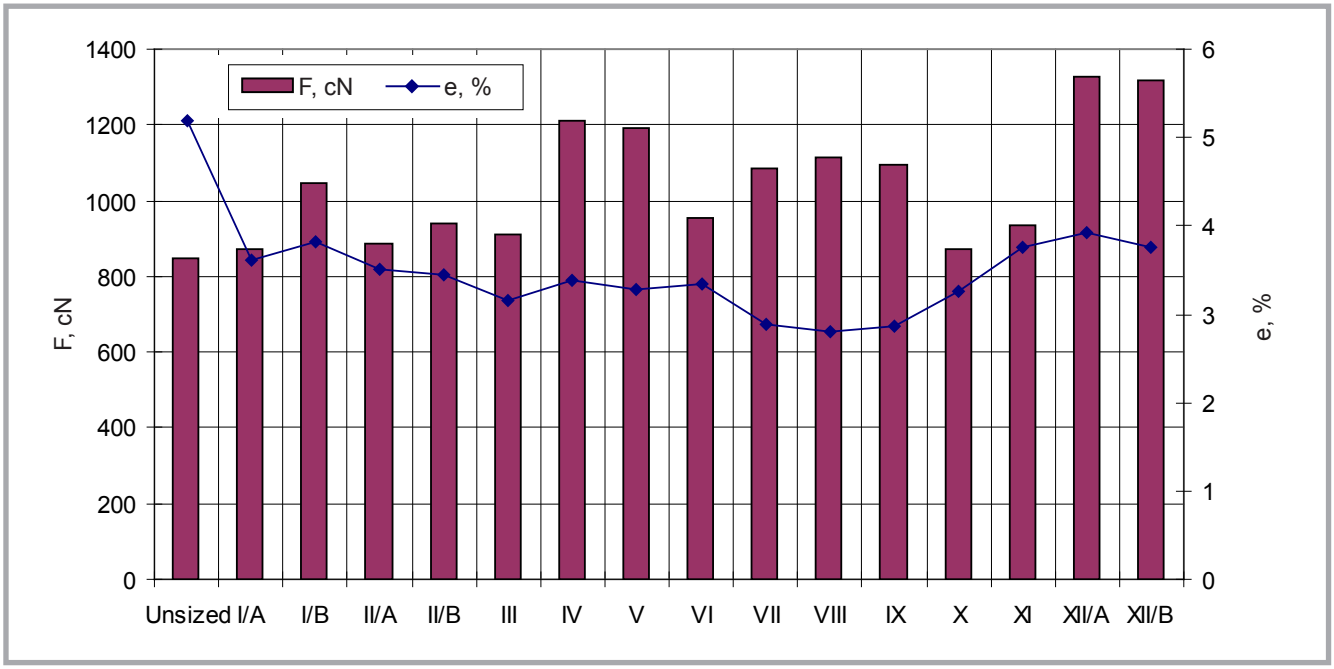

Figure 4. *Breaking force and elongation at break of yarn with a count of 30×2 tex.*

index, with other independent variables being constant, the size pick-up is increased by 0.02%.

- for each degree of increasing viscosity at 40 °C, with other independent variables being constant, the size pick-up is increased by 0.55%.
- for each degree of increasing viscosity at 60 °C, with other independent variables being constant, the size pick-up is reduced by 0.186%.
- for each degree of increasing viscosity at 85 °C, with other independent variables being constant, the size pick-up is reduced by 0.126%.

As shown in ***Table 5*** (see page 63), only the variable *Viscosity at 40 °C* contributes to the model compared to all others, as cofirmed statistically ($Prob > |t| = 0.011 < 0.05$), and therefore it is necessary for good predictions. Thus the variable *Viscosity at 40 °C* mostly contributes to the model, followed by *Viscosity at 60 °C,* then *by Viscosity at 85° C, Size concentration, Yarn hairiness index, Yarn count* and finally *Twist level.*

Table 6 determines the following parameters:

- R value = 0.99 - multiple correlation coefficient - is a high correlation between the criteria and set of predictor variables inserted in the procedure;

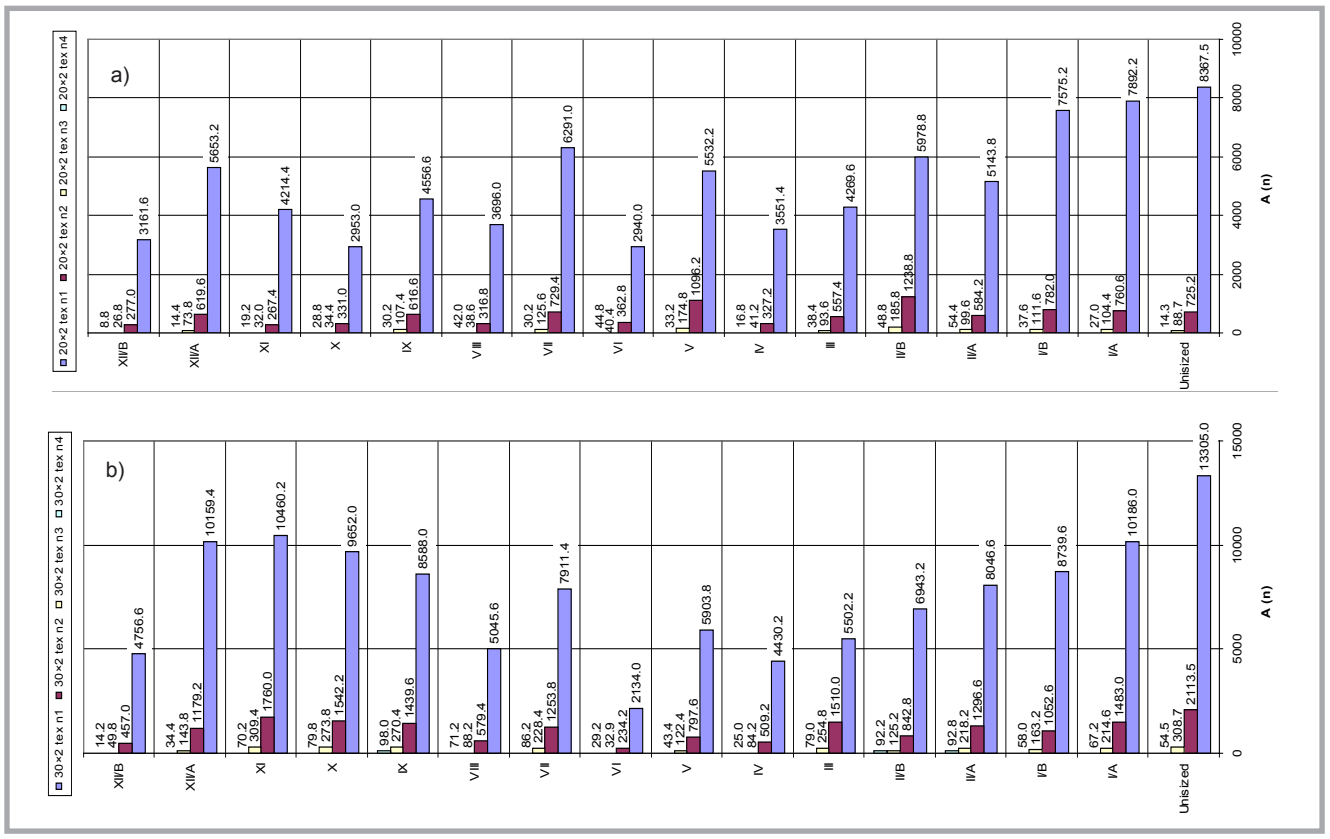

Figure 5. *Hairiness of unsized and sized yarn of samples: a) yarn count 20×2 tex, b) yarn count 30×2 tex; A - number of protruding fibres (n).*

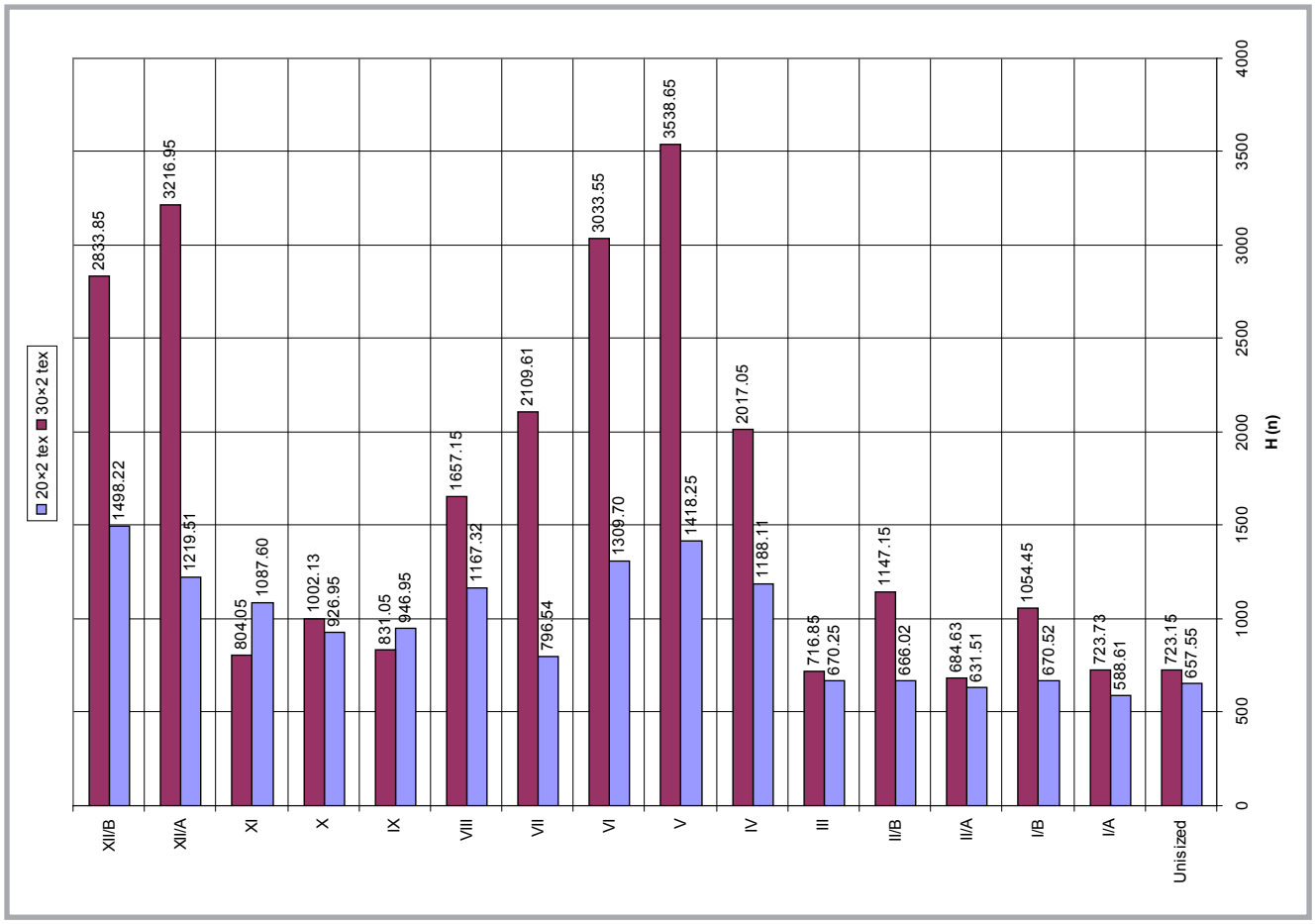

Figure 6. *Resistance of yarn to abrasion by samples: H - average number of roller moves on abrasion board until rupture (n).*

- R-square = 0.98 COD - coefficient of multiple determination - represents the percentage of variance that is common for the criterion and the set of predictor variables used in the procedure; the equation describes the model appropriately;
- Adjusted R square = 0.976 - adjusted coefficient of multiple determination presents an assessment of the percentage of variance that is common for predictors and criteria;
- Standard error of an assessment (Root-MSE (SD)) = 0.805 - is a measure of variability around the regression line. It is similar to the standard deviation, except that it is based on the squared deviations from the regression line (instead of from the middle). A lower value is a good indication of agreement between the regression line and the data;

Analysis of variance for multiple regression, ***Table 7***, shows the results of how well (if more appropriate) the regression model predicts the criterion. This table provides a statistically significant *F*-value *(Prob > F = 0 < 0.05);* the use of this model is better than guessing the mean value, i.e. predictors *Viscosity at 40, 60, 85 °C*, *Size concentration, Yarn hairiness index, Yarn count and Twist level* cause about *99%* of the variable variance *Size pick-up.* Thus there is a statistically significant linear relationship between the key variable and its predictors.

Figures 7 - 8 (see page 64) make predictions of the dependence of y on x, or the dependence for the residuals; it is a diagram of standardised residuals in relation to the modelling of values.

In the following case, the dependent variable is *Yarn breaking force*, while the independent variables are: *Twist level, Yarn count, Size pick-up* and *Yarn hairiness index* (2 mm).

According to ***Table 8***, the equation of the dependence of the dependent on independent variables is:

$$\textit{Yarn breaking force} = 694.31 + \\ - 0.49 \times \textit{Twist level} + 3.86 \times \textit{Yarn count} \\ + 8.93 \times \textit{Size pick-up} + 0.006 \times \textit{Yarn hairiness index (2 mm)}$$

Table 9 determines the parameters showing the effectiveness and validity of the multiple regression model. The correlation coefficient (R value) and coefficient of determination (R-square (COD)) almost have the maximum possible value, indicating a high correlation between the criterion and the predictor variable set. The standard error of the assessment (Root-MSE (SD)) is slightly higher, suggesting a poor agreement between the regression line and data.

There is a statistically significant linear relationship between the key variable - criterion variable and its predictors - input variable (***Table 10***).

Discussion

According to the results obtained in the experimental part (***Tables 2 - 4*** and ***Figures 3 - 6***), the following can be concluded:

Test results related to size viscosity, with variation in the concentration and temperature of the copolymer solution, are given in ***Table 2***. It is noticeable that a reduction in size concentration reduces viscosity, as expected.

There is an evident influence of the temperature on the viscosity of the copolymer solution, which firstly rises at a temperature of 40 °C to 60 °C, and finally declines at a higher temperature of 85 °C. By increasing he temperature, size particles swell and begin to break down, which causes the entire structure of starch macromolecules to weaken, i.e. after irreversible swelling it comes to dissolving, which increases the viscosity at the temperature of gel formation (C°60-70), and with a further increase in the temperature it comes to complete dissolution and a slight decrease in viscosity.

A share of the sizes in water affected the size pick-up (***Table 3***). However, despite the fact that the share of the sizes in most samples is the same (10%), the size pick-up is different, and thus it can be determined that with yarn of a yarn count of 20×2 tex, sample VII, has the highest size pick-up (5.9%), and the smallest is with sample XII/A (4%). Samples with a higher share of sizes (15%) have a slightly

Table 5. *Values of the coefficient of the regression model of the variable size pick-up.*

		Value	Standard Error	t-Value	Prob > |t|	95% LCL	95% UCL
Size pick-up	Intercept	1.150	3.440	0.335	0.740	-5.856	8.159
	Twist level	-0.003	0.003	-0.809	0.424	-0.009	0.004
	Yarn count	-0.0115	0.055	-0.208	0.836	-0.124	0.101
	Size concentration	0.072	0.393	0.184	0.855	-0.729	0.874
	Hairiness index 8 mm	0.012	0.019	0.608	0.547	-0.027	0.050
	Viscosity at 40 °C	0.550	0.205	2.689	0.011	0.134	0.968
	Viscosity at 60 °C	-0.186	0.115	-1.625	0.114	-0.420	0.047
	Viscosity at 85 °C	-0.126	0.093	-1.357	0.184	-0.315	0.063

Table 6. *Parameters of the performance of the regression model of the variable size pick-up.*

	Size pick-up
Number of points	30
Degrees of freedom	26
Residual sum of squares	20.76
R value	0.990
R-square (COD)	0.980
Adj. R-square	0.976
Root-MSE (SD)	0.805

Table 7. *Anova for multiple regression of variable size pick-up.*

	df	SS	MS	F	Significance F
Regression	1	7978.178	7978.178	0.949564	0.347615
Residual	13	109225.2	8401.938	-	-
Total	14	117203.4	-	-	-

Table 8. *Values of the coefficient of the regression model of variable Yarn breaking force.*

		Value	Standard Error	t-Value	Prob > |t|	95% LCL	95% UCL
Yarn breaking force	Intercept	694.31	68.51	10.13	5.96E-12	555.23	833.38
	Twist level	-0.49	0.06	-7.93	2.51E-09	-0.62	-0.37
	Yarn count	3.86	1.03	3.76	6.17E-04	1.78	5.95
	Size pick-up 20×2 tex.	8.93	0.89	9.92	1.03E-11	7.10	10.75
	Hairiness index 2 mm	0.005	0.002	2.44	1.96E-02	9.36E-04	0.01

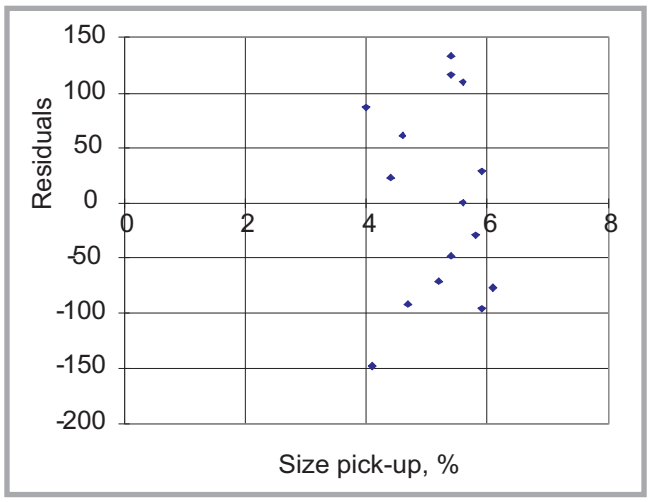

Figure 7. *Analysis of residuals in relation to the value of the dependent variable predicted (size pick-up).*

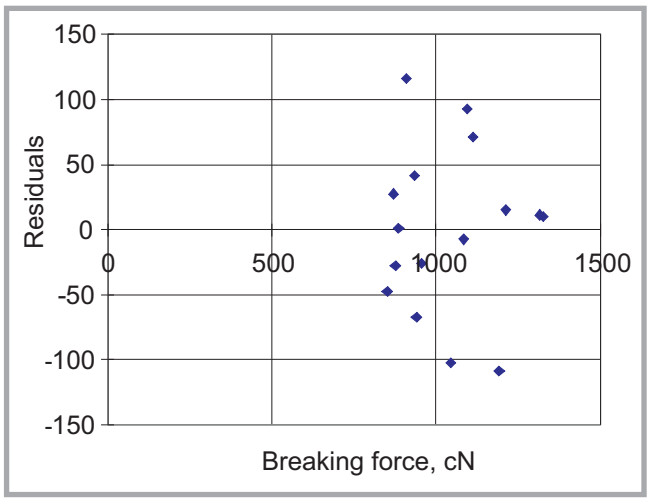

Figure 8. *Analysis of residuals in relation to the value of the dependent variable predicted.*

higher size pick-up, ranging from 5.4% (sample XII/B) to 6.1% (sample I/B). With yarn of a yarn count of 30×2 tex, the size pick-up is higher in all samples compared to those with a yarn count of 20×2 tex, which means that the coarse yarn with a low twist level (20×2 tex = 480 t.p.m., 30×2 tex = 322 t.p.m.) absorbed more size liquor and carried more size with it. With yarn of a yarn count of 30×2 tex and samples of the share of sizes (10%), the highest size pick-up was for sample VIII = 6.9% and the smallest for sample I/A = 4.9%. From the samples with a share of sizes (15%), the lowest size pick-up was for sample XII/B = 7.0%, and the biggest for sample I/B = 7.6%.

Sizing makes the breaking force increase in all samples and in yarn of a yarn count 20×2 tex of 698.06 cN (sample II/B) to 946.41 cN (sample XII/A),and for yarn of a yarn count 30×2 tex the minimum and maximum values are repeated in the same samples as with yarn count 20×2 tex, which are from 871.75 cN (sample X) to 1326.87 cN (Sample XII/A), ***Table 4*** and ***Figures 3*** & ***4***. According to the results, it can be concluded that the last two samples (XII/A and XII/B), with synthetic sizes and yarn of yarn count, have the highest breaking force. However, it is interesting that their breaking force is higher at a smaller share of sizes or smaller size pick-up, which is due to the fact that in sample XII/B, the use of the size pick-up was exaggerated and produced a negative sizing effect (***Figure 1*** on the curve to the right of the optimal size pick-up). A higher size pick-up results in a more intense mutual bonding of threads, and thus the occurrence of a larger force in the dry separation process, which all has an influence on the yarn's non-uniformity, higher stiffness and strength reduction. In addition, in the process of weaving, the consequence of larger size pick-up is reflected by the lower elasticity, greater abrasion and greater ruptures. Elongation of the yarn decreased with sizing in all samples tested, which is a negative phenomenon in the properties of sized yarn. With a careful analysis of the share of individual assets in the recipe of the size mass and optimisation of the size pick-up, it is possible to keep the elasticity of the yarn required and, at the same time, achieve the strength required by carefully adding fat.

Table 9. *Parameters of performance of the regression model of variable yarn breaking force.*

	Yarn breaking force
Number of points	30
Degrees of freedom	25
Residual sum of squares	12991.78
R value	0.994
R-square(COD)	0.988
Adj. R-square	0.987
Root-MSE (SD)	19.27

Table 10. *Anova for multiple regression of variable yarn breaking force.*

	df	SS	MS	F	Significance F
Regression	1	74798.84	74798.84	17.26723	0.000971321
Residual	14	60645.73	4331.838	-	-
Total	15	135444.6	-	-	-

With yarn of yarn count 20×2 tex, its elongation before sizing amounted to 6.08%, and after sizing from 2.17% (sample X) to 3.92% (sample IV) in a 10% share of sizes, shown in ***Table 4*** and ***Figures 3*** & ***4***. In a larger share of sizes (15%), while the elongation of yarn 30×2 tex was 5.19% before sizing, and quite balanced after sizing for samples with 10% of sizes, it ranges from 2.81% (sample VIII) to 3.93% (sample XII/A). In a larger share of sizes (15%), elongation amounts from 3.45% (sample II/B) to 3.76% (sample XII/B). According to the analysis results, it can be seen that the elongation was significantly reduced by the sizing of finer yarn, i.e. yarn count of 20×2 tex, but with no significant differences between the samples. Reducing of yarn elongation by sizing decreased the work until rupture despite an increase in the breaking force, amounting from 610.67 cN×cm (sample IX) to 889.94 cN×cm (sample X) in smaller share of sizes (10%) and for yarn of yarn count 20×2 tex, while with a higher share of sizes (15%), it was from 681.1 cN×cm (sample I/B) to 807.39 cN×cm (XII/B). Yarn of yarn count 30×2 tex has work until rupture in a small share of sizes (10%), which ranges from 642.31 cN×cm (sample IX) to 1130.62 cN×cm (sample V), and with a larger share of sizes (15%), it ranges from 917.59 (sample II/B) to 1122.62 cN×cm (sample I/B). According to the results of work until rupture, it is evident that the last samples with synthetic sizes do not have the highest values.

The strength of the yarn is directly affected by the breaking force and yarn count,

hence its course of values is identical to those of the breaking force; its minimum value with t yarn of 20×2 tex yarn count and smaller share of sizes (10%) amounts from 17.72 cN/tex (Sample I/A) to the maximum of 23.66 cN/tex (sample XII/A); and with a larger share of sizes (15%), it amounts from 17.45 cN/tex (sample II/B) to 23.60 cN/tex (sample XII/B), (***Table 4***). With yarn of a yarn count of 30×2 tex and smaller share of sizes (10%), it amounts from 14.53 cN/tex (sample X) to 22.11 (sample XII/A), and with a larger share of sizes (15%), it ranges from 17.41 cN/tex (sample I/B) up to 21.98 cN/tex (sample XII/B).

The hairiness of unsized and sized yarn is higher with coarser yarn, i.e. the yarn whose yarn count is 30×2 tex. Yarn hairiness reduces on average due to the sizing of yarns of both yarn count characteristics (***Figure 5***). However, looking at the length of the fibres protruding from the body of the yarn (n_1 = 2 mm, n_2 = 4 mm, n_3 = 6 mm and n_4 = 8 mm) with a yarn count of 20×2 tex, there is not a significant difference between unsized yarn (n_1 = 8367.5, n_2 = 725.2, n_3 = 88.7, n_4 = 14.3) and sized yarn with a 10% share of sizes: (n_1 = 2940 (sample VI) up to 7892.2 (sample I/A), n_2 = 267.4 (sample XI) up to 1096.2 (sample V), n_3 = 32 (sample XI) up to 174.8 (sample V), n_4 = 14.4 (sample XII/A) up to 54.4 (sample II/A), and then sized yarn with 15% share of sizes: (n_1 = 3161.6 (sample XII/B) up to 7575.2 (sample I/B), n_2 = 277 (sample XII/B) up to 1238,8 (sample II/B), n_3 = 26.8 (sample XII/B) up to 185.8 (sample II/B), n_4 = 8.8 (sample XII/B) up to 48.8 (sample II/B). With yarn of yarn count 30×2 tex, also visible are significant differences between unsized yarn (n_1 = 13305, n_2 = 2113.5, n_3 = 308,7, n_4 = 54.5) and sized yarn with a 10% share in sizes: (n_1 = 2134 (sample VI) up to 10460.2 (sample XI), n_2 = 234.2 (sample VI) up to 1760 (sample XI), n_3 = 32.9 (sample VI) up to 309.4 (sample XI), n_4 =25 (sample IV) up to 98 (sample IX), also sized yarn with 15% share of sizes: (n_1 = 4756.6 (sample XII/B) up to 8739.6 (sample I/B), n_2 = 457 (sample XII/B) up to 1052.6 (sample I/B), n_3 = 49.8 (sample XII/B) up to 163.2 (sample I/B), and n_4 = 14.2 (sample XII/B) up to 92.2 (sample II/B). According to these results, it can be determined that the sizing reduced short protruding fibres (n_1), but longer protruding ones (n_2, n_3 and n_4) were not reduced by sizing in all the samples, and the longer they are the smaller the number of samples where protruding fibres are shortened by sizing. It is also seen, as with yarn of 20 tex yarn count, that sizing reduces short protruding fibres, and the longer they are, the smaller the number of samples where the protruding number of fibres is shortened by sizing.

Generally speaking, we can determine that samples VI and XII/B have the smallest number of protruding fibres after sizing and give the best results, while samples I/B and XI give the worst. The abrasion resistance of the yarn is one of the most important parameters of yarn intended for weaving (***Figure 6***). One of the tasks of sizing is to increase yarn resistance to abrasion, which is achieved in the forthcoming weaving by going through the guards of basic threads, sheets and hill. From the results it can be determined that the abrasion resistance is higher with yarn of 30×2 yarn count for unsized and sized yarn. Sizing almost all the samples with both types of yarn count increased abrasion resistance. With yarn of 20 tex yarn count, the abrasion resistance was 657.55 before sizing and increased for all samples, as well as for the yarn with a smaller share of sizes (10%) from 588.61 (sample I/A) to 1418.25 (sample V), and for the yarn with higher sizes (15%) from 666.02 (sample II/ B) to 1498.22 (sample XII/B). For yarn of 30×2 tex yarn count, the abrasion resistance was 723.15 before sizing, and sizing mostly increased it, as was with the yarn of a smaller share of sizes (10%) of 684.63 (sample II/A) to 3538.65 (sample V), and for the yarn with higher sizes (15%) from 1054.45 (sample I/B) to 2833.85 (sample XII/B).

From the results, it can be determined that samples I/A, II/A, I/B & II/B had the least abrasion resistance, while samples V and XII/B saw highly increased abrasion resistance properties.

The individual research results in terms of statistical modelling and prediction of events, which is of great importance when planning the sizing (***Tables 5 - 10***, ***Figures 7 & 8***), were analyzed.

Conclusion

Based on the research conducted and results of the discussion analysed, the following can be concluded:

- The investigation determined that the properties of the tested and sized yarn vary and depend on the type of starch and ways of modifying their mutual share in starch and later in water.
- The conclusion was reached that the yarn sized with natural modified starch does not always have weaker properties than those of the yarn sized with synthetic agents, especially in blends with synthetic agents.
- Natural modified corn starch may be used for yarn which does not need to be sized with a higher size pick-up. The function of sizing such yarns is often not only to increase strength, but also to protect the surface from abrasion, smooth-out protruding fibres, strengthen the structure and reduce the static electricity in synthetic fibres.

This gives some hope that weavers would find justification for restoring natural modified sizes to be used as the sole sizing agent or in combination with synthetic size, especially in sizing with smaller size pick-ups, which are used for tighter single yarns, filament and twisted yarns. This would contribute to economic justification, healthier working conditions, longer lifetime of sizing facilities (boxes) and reduction of air pollution and wastewater.

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