Characteristics of Selected Rheological Properties of Water Suspensions of Maize TPS Biocomposites

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Summary. The research covered the aqueous solutions of maize thermoplastic starch (TPS). The thermoplastic starch granules were produced from mixtures of maize starch, glycerol and an additive of fillers in the form of natural fibres. In the study, a modified single-screw extrusion-cooker TS 45 was used with L/D=16 and L/D=18 with an extra cooling of the end part of the barrel. The research focused on the effect of the extruder screw speed, the plasticizing system and the type of filler used for apparent viscosity of pulverized granules of maize starch. During the measurements, the top values of apparent viscosity were reported for the maize TPS containing an addition of cellulose fibre extruded with the plasticizing system L/D=16.

Key words: viscosity, thermoplastic starch, extrusion, biocomposites.

INTRODUCTION

The recent decades have seen a growing application of plastics in all the areas of human activity. Today, it is difficult to imagine life without plastics in packaging, toys, cars, medical products, etc. However, besides the unquestionable benefits, there are also some negative consequences of their ubiquity. The method of processing and disposal of different types of plastic after their life cycle has a tremendous impact on the natural environment, including human health [9, 12, 13, 18]. It has been asserted that some chemical compounds used in plastics processing for the production of food packaging (biosphenol A – BPA) can affect the human endocrine system and are ranked among cancer-causing substances. The U.S. companies representing the plastics industry decided to withdraw BPA from the process of manufacturing packaging for food storage, and the U.S. government declared amendments to the relevant law on food safety that are expected to eliminate any products containing BPA that are likely to be detrimental to consumers until tests prove the non-carcinogenic effect of BPA on humans [5, 8]. There are many more examples of similar concerns. Therefore, the general public puts more and more attention to the growing problem of plastics and their recycling.

In order to protect the environment, and above all, protect human health, developed countries undertake research into the manufacture of environmentally friendly polymers. The primary focus is on natural materials, including those made of different types of starch. Biopolymers are obtained after mixing starch with a plasticizer (often glycerol) so as to allow the liquefaction of the material at a temperature lower than the decomposition temperature of the starch. Such starch is referred to as thermoplastic starch (TPS) and is regarded as a biodegradable biopolymer [1, 2, 5, 7]. Biodegradable polymers, like petroleum polymers, must meet certain requirements in terms of physical properties. Biopolymer production is done on the machines and equipment used for the production of synthetic polymers. These materials can be an option in the plastics market offering [3, 10, 17, 19].

The aim of the study was to determine the viscosity of thermoplastic maize starch water solutions with an addition of natural fibre of different origin, depending on the production parameters.

MATERIALS AND METHODS

The basic raw material used in the study was maize starch of the type MERIZET 100 produced by Segezha, Ireland. Also, flax fibre was used from a Polish producer, cellulose fibre Vivapur type 102 JRS from a German producer and ground pine bark. The basic characteristics of the ground bark, cellulose fibre and flax fibre are given in Table 1.

Table 1. Basic characteristics of cellulose fibre, flax fibre and bark.

	Cellulose fibre	Flax fibre	Ground pine bark
Feature	Determination results		
Particle size [m]	$50 \cdot 10^{-6} – 160 \cdot 10^{-6}$	$3 \cdot 10^{-3} – 5 \cdot 10^{-3}$	$50 \cdot 10^{-6} – 180 \cdot 10^{-6}$
Bulk density [kg/m^3]	280–330	1500	120–250
Humidity [%]	3–5	5–7	5–8

From among a considerable group of auxiliary substances used as plasticizers and additives improving the quality of obtained material, the study used technical glycerol of 99% purity in the amount of 20% of dry mass of starch [16].

PREPARATION OF TPS MIXTURES

Starch with 16% of moisture content, cellulose fibres, flax fibres, ground bark and glycerol were used to prepare material mixtures. The glycerol accounted TPS for 20% of the mixture weight, and the proportion of fibres was 10, 20 and 30%. Samples were mixed using a laboratory mixer ribbon. Through repeated trials, the effective mixing time was established at 20 minutes. After mixing, the samples were left in sealed plastic bags for 24 hours to homogenize. Immediately before extrusion, the samples were mixed again for 10 minutes to obtain a loose and powdered structure of the mixture.

EXTRUSION

TPS biocomposite granules were made by a single-screw extrusion-cooker equipped with two kinds of plasticizer systems with the screw length/diameter ratio of L/D=16/1 and L/D=18/1 (Photo 1). A steel die was used with a hole of 3 mm in diameter. Granules were produced at the extruder screw speed of 60, 80 and 100 rpm. The extrusion parameters were set in the temperature range 60-110°C and maintained by appropriately adjusting the flow intensity of the cooling liquid. The extruder was equipped with a material feeder, a plasticizing system made up of the screw linked to the drive and housing, a preheating device and a cooling system [8, 11, 14, 15].

MEASUREMENT OF APPARENT VISCOSITY

A Zwick testing machine was used in the study equipped with a back extrusion chamber. The obtained extrudate was ground in a laboratory mill to the grain size below 0.8 mm. From the ground extrudateand distilled water at 20°C, 10% suspensions were prepared by continuous mixing. The viscosity measurement of the suspensions was carried out after 10 minutes of mixing. The measurements were made in the back extrusion chamber, 60 mm in height and 50 mm of inner diameter, using a plunger with a diameter of 46

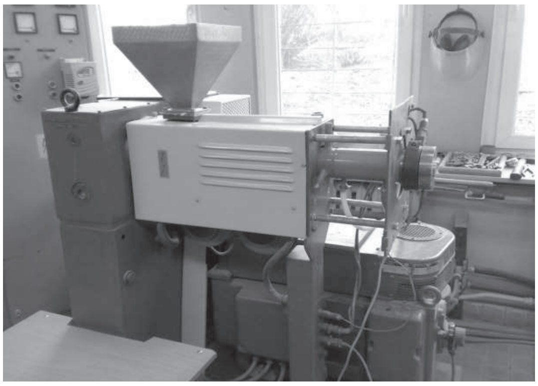

Photo 1. Single-screw extruder TS-45 made by Z. M. Ch. Metalchem in Gliwice, Poland.

mm and a height of 20 mm with a conical bottom surface. The following settings were used in the study: 0.5 kN head force, 2 mm measuring gap, the total test length 60 mm, head speed 50 mm/min^{-1}. During the study, the resistance force of the suspension was recorded during the movement of the plunger in one bottom-up measurement cycle, which was next converted into the apparent viscosity coefficient. The measurements were made using the testXpert 10v11 program. There were five replications, the final result being the arithmetic mean of the measurements [4, 6].

RESULTS

The use of the back extrusion chamber allowed the examination of the apparent viscosity of fine thermoplastic starch granules and of the degree of bonding of the fillers: cellulose fibre, flax fibre and ground bark. These parameters are crucial in determining the processing properties of thermoplastic starch. The addition of natural fillers in the form of granules is intended to stabilize the shape and improve the performance of rigid forms of packaging.

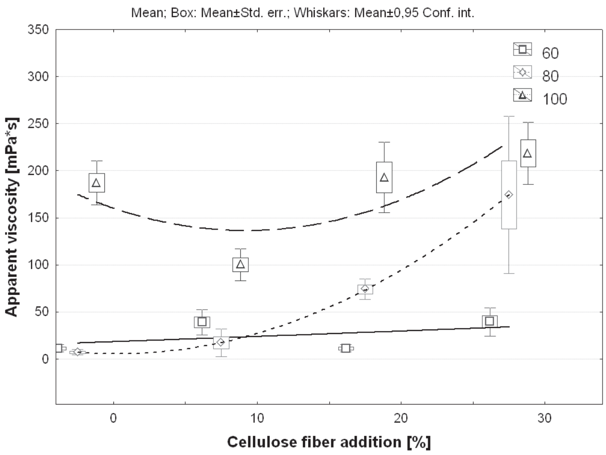

Fig. 1. The influence of cellulose fibres and the extruder screw speed on the apparent viscosity of maize starch solutions (extruder plasticizing system of L/D=16).

Fig. 1 shows the dependence of the viscosity of aqueous solutions of thermoplastic maize starch upon the applied screw speed of the L/D=16 version extruder and upon the content of cellulose fibre in the mixture. It was observed that the viscosity of the solution increased along with the increasing extruder screw speed and a higher addition of cellulose fibre. This dependency is corroborated through the positive values of the slope coefficients of polynomial trend lines for all the applied screw speeds (Table 2). Also, the most significant differences were indicated between the means ($p < 0.05$).

The highest viscosity values were obtained for granulated material produced at the extruder screw speed of 100 rpm^{-1}. This testifies to a good bond between the fibres and biopolymer matrix.

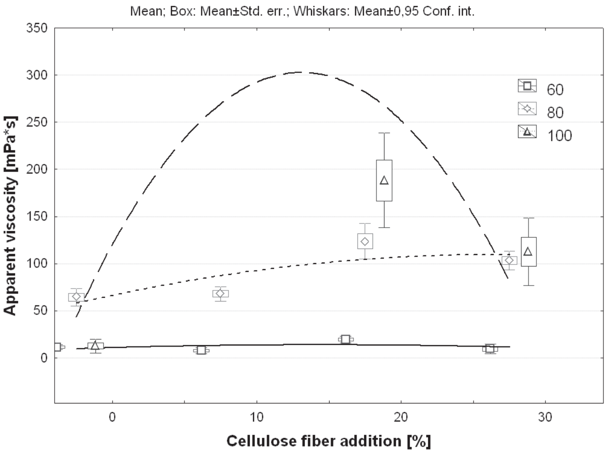

Fig. 2. The influence of cellulose fibres and the extruder screw speed on the apparent viscosity of maize starch solutions (extruder plasticizing system of L/D=18).

The solution of the granulated material obtained using the plasticizing system of the extruder with L/D=18 demonstrated lower apparent viscosity values compared with the results obtained for the shorter version. A similar trend was observed: viscosity increased along with the increasing extruder screw speed and a higher addition of the filler. Also in this case, significant differences were reported between the means (Table 2).

An additive of flax fibre caused a slight increase in the viscosity of solutions (Fig. 3). The highest viscosity values were obtained for granulated maize starch produced at the extruder screw speed of 100 rpm^{-1}. Along with the rising content of flax fibre in all the tested materials, viscosity increased only slightly. The addition of 30% of flax fibres caused a decrease in the viscosity of solutions, which demonstrates a weak bond between the flax fibres and the biopolymer matrix.

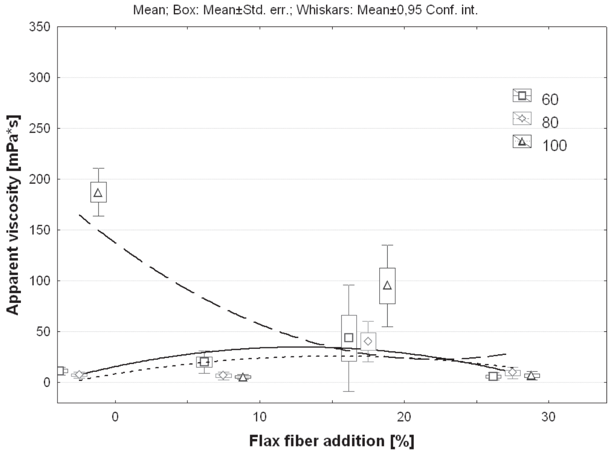

Fig. 3. The influence of flex fibres and the extruder screw speed on the apparent viscosity of maize starch solutions (extruder plasticizing system of L/D=16).

During the examination of the solution of extrudates produced on the longer version of the plasticizing system,

Table 2. The results of the statistical analysis of viscosity of aqueous solutions of thermoplastic starch depending on the additives used.

Additive	L/D version	Screw rotation [rpm^{-1}]	Polynomial regression equation	F test values (3,23)	P value
Cellulose fibre	16	60	$y_{60} = 0.001x^2 + 0.545x + 18.360$	12.599	0.00001
		80	$y_{80} = 0.226x^2 - 0.070x + 5.488$	17.099	0.0000008
		100	$y_{100} = 0.282x^2 - 5.185x + 160.265$	17.048	0.0000009
	18	60	$y_{60} = -0.014x^2 + 0.420x + 10.906$	9.807	0.00010
		80	$y_{80} = -0.06x^2 + 3.220x + 66.557$	28.842	0.000000003
		100	$y_{100} = -1.065x^2 + 27.89x + 120.263$	61.304	0.0000
Flax fibre	16	60	$y_{60} = -0.116x^2 + 2.973x + 15.788$	2.029	0.1295
		80	$y_{80} = -0.075x^2 + 2.301x + 8.523$	12.355	0.00002
		100	$y_{100} = 0.233x^2 - 10.350x + 137.523$	72.707	0.0000
	18	60	$y_{60} = -0.261x^2 + 7.562x + 45.621$	0.932	0.4363
		80	$y_{80} = -0.007x^2 + 0.538x + 77.042$	0.395	0.7567
		100	$y_{100} = -0.029x^2 + 3.914x + 17.891$	1.941	0.1428
Ground pine bark	16	60	$y_{60} = -0.043x^2 + 1.290x + 11.446$	10.963	0.00004
		80	$y_{80} = 0.056x^2 + 0.973x + 12.322$	29.406	0.000000003
		100	$y_{100} = 0.509x^2 - 15.957x + 139.557$	39.170	0.0000
	18	60	$y_{60} = -0.092x^2 + 2.648x + 12.712$	14.284	0.000004
		80	$y_{80} = -0.162x^2 + 3.482x + 57.042$	24.721	0.00000002
		100	$y_{100} = -0.392x^2 + 10.101x + 34.344$	40.680	0.0000

some problems emerged with maintaining the homogeneity of solutions which began to delaminate. Friction rose in the places of fibre settlement, hence the considerable differences in the the viscosity of solutions, which is visible in Fig. 4, showing the results of measurements of the viscosity of solutions of biopolymers obtained by using the extruder plasticizing system of L/D=18. There were no significant differences reported between the means for these granules (p>0.05) (Table 2).

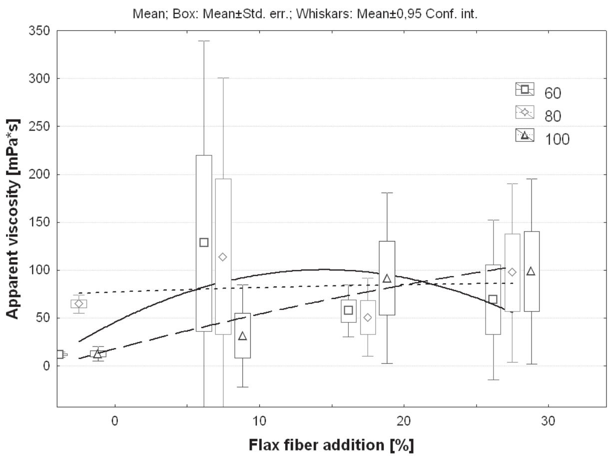

Fig. 4. The influence of flex fibres and the extruder screw speed on the apparent viscosity of maize starch solutions (extruder plasticizing system of L/D=18).

Another type of thermoplastic starch biocomposites subjected to analysis were maize starch granules with the addition of ground bark. Fig. 5 and 6 show the measurement results of the apparent viscosity depending on the version of the plasticizing system used. The viscosity values of the thermoplastic starch solutions with the addition of ground bark were lower than the viscosity of TPS solutions with the cellulose fibre content. During the study, as in the case of flax fibre solutions, the suspensions were delaminated.

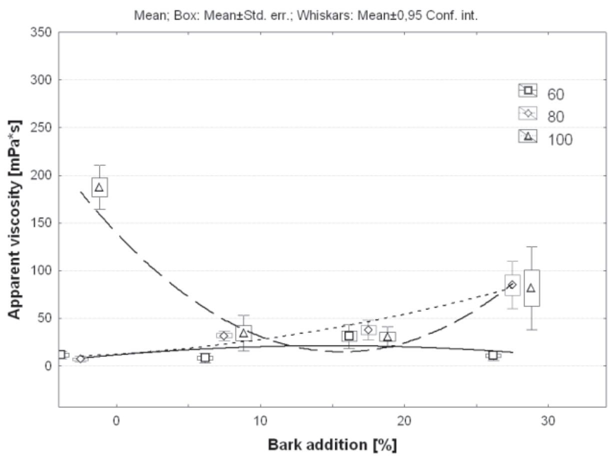

Fig. 5. The influence of ground bark and the extruder screw speed on the apparent viscosity of maize starch solutions (extruder plasticizing system of L/D=16).

The addition of 30% of ground bark to maize starch granules (extruder plasticizing system of L/D=16) contributed to the dispersion of the apparent viscosity values, which was caused by resistance occurring during the study. TPS granule solutions containing ground bark obtained by using the plasticizing system of the extruder with L/D=18 showed higher apparent viscosity values (Fig. 6). The top values were recorded for the addition of 20% of ground bark to the thermoplastic starch extruded at the screw speed of 80 rpm^{-1} (120 mPas).

The lowest viscosity values were demonstrated by the mixtures of maize starch and glycerol containing a 30% addition of ground bark in the whole range of extruder screw speeds.

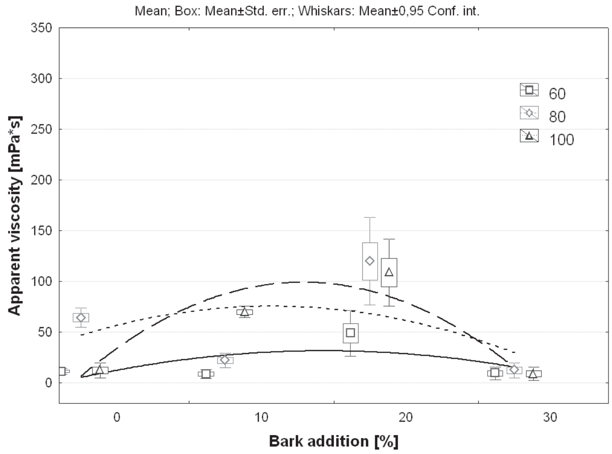

Fig. 6. The influence of ground bark and the extruder screw speed on the apparent viscosity of maize starch solutions (extruder plasticizing system of L/D=18).

CONCLUSIONS

- It was observed that the apparent viscosity of the solutions of thermoplastic maize starch was determined by the rotational speed of the extruder used for the production of the granulated matter.
- The highest apparent viscosity values were reported for solutions of maize TPS with the addition of cellulose fibre.
- The aqueous solutions of granules obtained with the extruder plasticizing system at L/D=16/1 showed higher apparent viscosity values.
- The addition of fillers such as natural fibres increased viscosity in the majority of examined aqueous solutions of extruded maize starch.

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CHARAKTERYSTYKA WYBRANYCH CECH REOLOGICZNYCH WODNYCH ROZTWORÓW KUKURYDZIANYCH BIOKOMPOZYTÓW TPS

Streszczenie. Badaniom poddano wodne roztwory granulatów kukurydzianej skrobi termoplastycznej (TPS). Granulaty skrobi termoplastycznej zostały wyprodukowane z mieszanek skrobi kukurydzianej, gliceryny oraz dodatku wypełniaczy w postaci włókien naturalnych. W badaniach zastosowano zmodyfikowany ekstruder jednoślimakowy TS 45 o L/D=16 i L/D=18 z dodatkowym chłodzeniem końcowej części cylindra urządzenia. Badano wpływ prędkości obrotowej ślimaka ekstrudera, zastosowanego układu plastyfikującego oraz rodzaju stosowanego wypełniacza na lepkość pozorną rozdrobnionych granulatów skrobi kukurydzianej.Podczas pomiarów zaobserwowano, że najwyższe wartości lepkości pozornej występowały w przypadku granulatów skrobi kukurydzianej zawierających dodatek włókien celulozowych ekstrudowanych przy zastosowaniu układu plastyfikującego o L/D=16.
Słowa kluczowe: lepkość, skrobia termoplastyczna, ekstruzja, biokompozyty.

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