TEKA. COMMISSION OF MOTORIZATION AND ENERGETICS IN AGRICULTURE – 2014, Vol. 14, No. 4, 125–130

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

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Received December 07.2014; accepted December 18.2014

Summary. The research covered the aqueous solutions of granules of potato thermoplastic starch (TPS). The thermoplastic starch granules were produced from mixtures of potato starch, glycerol and an additive of fillers in the form of natural fibres. In the study, two configurations of the plasticizing system were used (L/D=16 and L/D=18) in a modified single-screw extrusion-cooker TS-45 with an extra cooling of the end part of the cylinder. The research focused on the effect of the extruder screw speed and the volume and types of used fillers on the apparent viscosity of pulverized granules of thermoplastic starch. During the measurements, it was observed that the apparent viscosity of extruded potato starch was influenced by the type of the plasticizing system installed in the extruder used for the production of TPS granules. The highest viscosity was reported for the solutions of potato TPS with the addition of flax fibre.
Key words: extruder, fibre, viscosity, thermoplastic starch, extrusion, biocomposites.

INTRODUCTION

The development of procedures for the mass production of biodegradable materials has recently been an area of extensive research, both academic and commercial. This is attributed to the growing scarcity of crude oil resources and to the fact that petroleum-based materials are non-biodegradable [22, 24]. Polymeric biodegradable materials can be divided into two main groups, depending on the source of raw materials for their production: the polymers produced by the traditional chemical synthesis of natural monomers and the polymers produced by microorganisms or modified bacteria, the so-called biopolymers. A practical alternative replacing the polymers based on petroleum are materials produced with the use of starch and belonging to the latter group. Also, the mixing of this natural component with synthetic polymers is an option. Such mixtures are not biodegradable, still, they reveal a lower carbon emission compared with the corresponding petroleum-based plastic and are less expensive to make [2].

Starch is the most important polysaccharide in plants serving as a reserve and accumulated in the form of grains. Particularly starch-rich are the grains of cereals, potato and manioc tubers, as well as maize cobs. Starch hydrolyses only to α-D-glucose but it is not a chemically uniform compound; in fact, it consists of two fractions: unbranched amylose and branched amylopectin [2]. The main advantages of starch are: biodegradability, broad availability, relatively low cost and ease of chemical modification [1, 6, 19, 21].

Pure and dried starch differs materially from synthetic polymers [6, 23]. It should not be regarded as a thermoplastic material since its glass transition temperature (Tg) is significantly higher than the decomposition temperature.

In recent decades, an extrusion-cooked modified starch has appeared on the market. The addition of plasticizers in the process of extrusion results in the lowering of the glass transition temperature of starch below its decomposition temperature and transforms it into thermoplastic starch (TPS) which lends itself to easy processing [12, 13, 16]. Plasticizers are mostly substances of low molecular weight which can be easily embedded into the polymer matrix in order to destroy the hydrogen inter and intra molecular bonds that occur in starch. This, in the end, leads to the improved strength and heat treatment conditions of starch-based materials [1, 18, 20, 21]. The most commonly used plasticizers are glycerol and water [17].

As auxiliary additives that enhance the mechanical and physical properties of natural polymers, various types of fillers can be used such as natural fibre (hemp, flax, jute, coconut, cellulose, cotton) or wood waste [3, 9, 10, 11].

The aim of the study was to examine the apparent viscosity of water suspensions of pulverized granules of potato thermoplastic starch extruded at several configuration settings of the plasticizing system and to determine the impact of the type and quantity of additives on the viscosity of 10%-solutions.

MATERIALS AND METHODS

The main raw material used in the research was potato starch of the type Superior Standard-F (supplied by „Pepees" S.A., KrochmalniaŁomża). As an auxiliary substance acting as plasticizer, technical glycerol was used of 99% purity in an amount of 20% of starch weight.

As additives of natural origin acting as fillers, cellulose fibre (Vivapur type 102, JRS, Germany), flax fibre and pine bark (Poland) were used after being ground on a laboratory mill LMN-10 TestChemRadlin).

Potato starch with a moisture content of 16% and glycerol were used to prepare TPS raw material mixtures to which cellulose fibre, flax fibre and ground bark were added in the amount of 10, 20 and 30% of the mixture weight. So prepared raw material was mixed by means of a laboratory ribbon mixer for 20 minutes. After mixing, the material was left in sealed plastic bags for 24 hours to homogenize the whole mass of the sample. Directly before extrusion, the material was mixed again for 10 minutes in order to loosen the mass before extrusion.

PRODUCTION OF GRANULES

Potato starch granules with the addition of natural plant fillers were extruded in the temperature range 60-110ºC and moulded through a die with a single hole of a diameter of 3 mm. In the process, a modified version of the single screw extrusion-cooker TS-45 was used (ZMCh Metalchem, Gliwice, Poland). The modification involved the application of two types of a plasticizing system with the screw/diameter ratio of L/D=16/1 and L/D=18/1, equipped with a temperature control system and the cooling of the end part of the cylinder. Granules were produced at a variable extruder screw rotation, namely 60, 80 and 100 rpm. The obtained granules were ground before tests in the laboratory mill LMN-10 (TestChem, Radlin) to the particle size of 0.8 mm and stored in dry environment until measurements [5, 8, 14, 15].

MEASUREMENT OF APPARENT VISCOSITY

To measure apparent viscosity, 10%-solutions were prepared of ground granules and distilled water of 20°C. Prepared suspensions were mixed for 10 minutes and subjected to a viscosity testing cycle. A back extrusion component was mounted on the testing machine Zwick/Roell BDO-FB0.5TH, equipped with a 0.5 kN force head (Fig. 1). The chamber parameters were as follows: cylinder height – 60 mm, inner diameter – 50 mm, plunger diameter – 46 mm, plunger height – 20 mm, the plunger having a conical bottom surface. During the test, the head speed was set to 50 mm•min^{-1}, the measuring gap was 2 mm, and the total test length was 60 mm.

During the test, the value of the apparent viscosity coefficient was determined based on the recorded resistance force of the suspension during the movement of the plunger in one bottom-up measurement cycle; the force was next converted into apparent viscosity in the testXpert 10v11 program. There were five replications, the final result being the arithmetic mean of the measurements [4, 7].

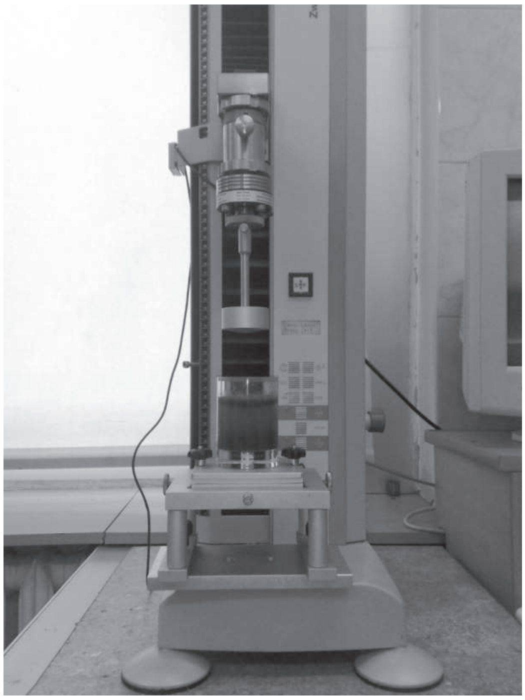

Photo 1. Testing machine Zwick BDO-FB0.5TH with mounted back extrusion component to measure viscosity

RESULTS

The apparent viscosity of aqueous solutions of potato thermoplastic starch with the addition of cellulose fibre extruded in a plasticizing system configuration of L/D=16 increased along with the increasing extruder screw speed (Fig. 1). The increase in the content of cellulose fibre in the mixture of raw materials caused higher viscosities of potato starch solutions and significant ($p<0.05$) differences between the means (Table 1).

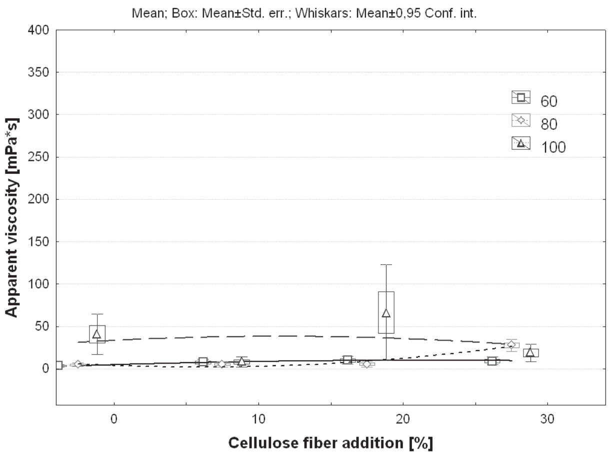

Fig. 1. The influence of the addition of cellulose fibre and the extruder screw speed on the apparent viscosity of potato starch solutions (extruder plasticizing system of L/D=16).

Fig. 2 illustrates the results of measurements of apparent viscosity of 10% aqueous solutions of granules with the addition of cellulose fibre. The use of extended plasticizing system of L/D=18 and a variable extruder screw speed during the production of potato starch granules with the addition of 30% of cellulose fibre in the recipe did not entail any significant changes in the viscosity of thermoplastic starch solutions.

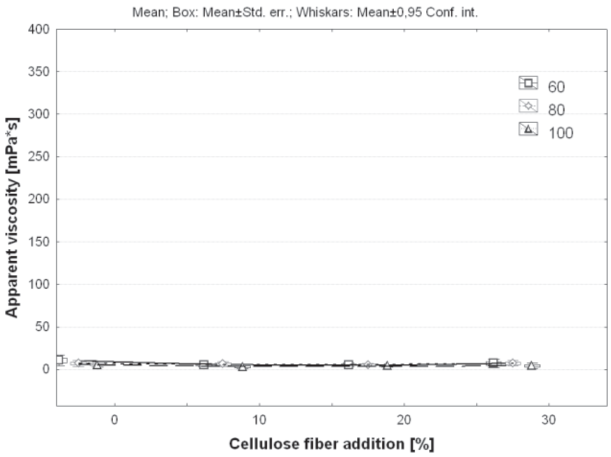

Fig. 2. The influence of the addition of cellulose fibre and the extruder screw speed on the apparent viscosity of potato starch solutions (extruder plasticizing system of L/D=18).

A very low viscosity of the examined solutions may indicate insufficient pressure and thermal treatment in the cooling conditions and with the application of the extended plasticizing system, which prevented the granules with the addition of cellulose fibre to obtain a stable structure.

Fig. 3 and 4 show the effect of the addition of flax fibre and the extruder screw speed on the apparent viscosity of aqueous solutions of TPS extruded in different configurations of the plasticizing system. The aqueous solutions of TPS granules obtained with the extruder plasticizing system at L/D=16/1 displayed higher viscosity values.

Both the increase of the screw speed during the production of granulates and the higher content of natural flax fibre significantly improved the viscosity values (Table 1). The highest apparent viscosity values were reported for TPS solutions containing 30% of flax fibre. However, in this case, the higher screw speed during extrusion resulted in the lower values of the tested parameter (Fig. 3).

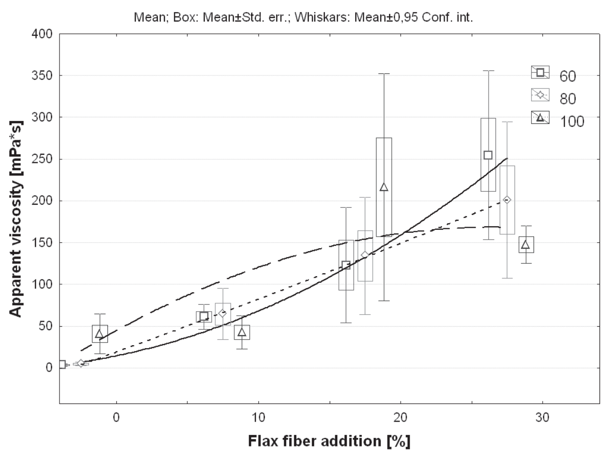

Fig. 3. The influence of flex fibres and the extruder screw speed on the apparent viscosity of potato starch solutions (extruder plasticizing system of L/D=16).

A similar trend was observed for the extended plasticizing system, namely along with the increasing content of flax fibre, the apparent viscosity of aqueous solutions of granules rose; yet, the measured viscosity values were slightly lower.

Such considerable differences in viscosity measurements were caused by problems occurring during the measurement. During the measurement, the solution began to delaminate, which significantly affected its viscosity. This, in turn, demonstrates an uneven internal structure of potato starch

Table 1. The results of the statistical analysis of viscosity of aqueous solutions of thermoplastic potato 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} = -0.011x²+0.494x+4.612	3.094	0.0407
		80	y_{80} = 0.053x²-0.641x+3.712	35.581	0.0000
		100	y_{100} = -0.037x²+0.837x+33.352	3.606	0.0238
	18	60	y_{60} = 0.018x²-0.539x+8.695	1.837	0.1603
		80	y_{80} = 0.007x²-0.173x+6.647	0.507	0.6804
		100	y_{100} = 0.008x²-0.237x+4.903	1.103	0.3623
Flax fibre	16	60	y_{60} = 0.186x²+3.523x+14.372	16.214	0.000001
		80	y_{80} = 0.018x²+6.151x+19.198	10.551	0.00006
		100	y_{100} = -0.177x²+9.365x+44.631	7.815	0.0005
	18	60	y_{60} = 0.421x²-5.174x+6.922	3.889	0.0178
		80	y_{80} = -0.057x²+2.909x+9.933	2.277	0.0985
		100	y_{100} = 8.0556E-5x²+2.559x+7.989	3.089	0.0409
Ground pine bark	16	60	y_{60} = -0.287x²+8.724x+19.972	13.053	0.000010
		80	y_{80} = -0.638x²+16.426x+61.465	52.863	0.0000
		100	y_{100} = -0.233x²+7.359x+59.625	9.576	0.0001
	18	60	y_{60} = -0.005x²+0.243x+8.908	4.906	0.0065
		80	y_{80} = 0.006x²+0.090x+7.207	1.835	0.1607
		100	y_{100} = 0.003x²+0.118x+6.449	2.991	0.0454

biocomposites and a weak bond between flax fibres and the starch matrix in the conditions of intense cooling and with the application of the extended plasticizing system.

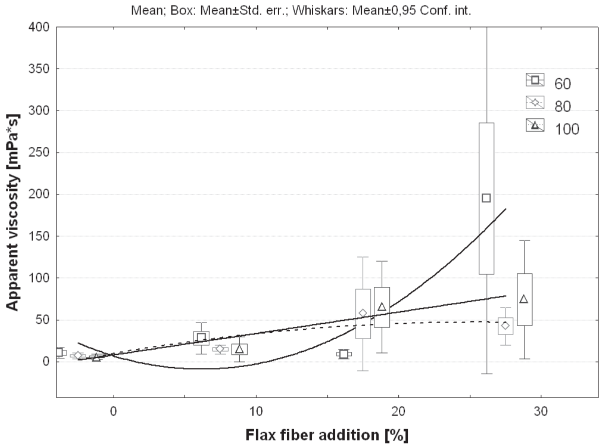

Fig. 4. The influence of flex fibres and the extruder screw speed on the apparent viscosity of potato starch solutions (extruder plasticizing system of L/D=18).

The addition of ground bark to the potato TPS potato starch resulted in higher apparent viscosity of its aqueous solutions than in the case of granules without this added content. The lowest viscosity was reported in TPS solutions that contained no filler (Fig. 5). The highest value of the apparent viscosity was obtained while testing granules with a 10% addition of ground bark. Raising the bark content to 30% in the whole range of applied extruder screw speeds had a significant influence ($p<0.05$) one the decline in the apparent viscosity of TPS solutions, as shown by the negative values of the slope coefficients of the lines of the trend expressed by a square polynomial (Table 1).

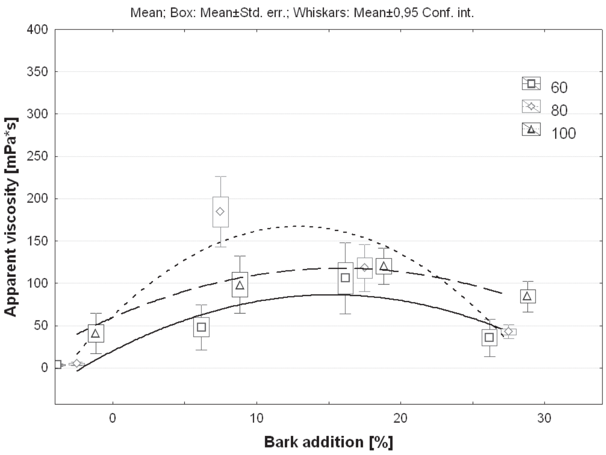

Fig. 5. The influence of ground bark addition and the extruder screw speed on the apparent viscosity of potato starch solutions (extruder plasticizing system of L/D=16).

No explicit effect was observed of the applied screw speeds during extrusion; still, the lowest screw speed resulted in the lowest viscosity of granulate solutions produced in the proposed conditions with the shorter version of the plasticizing system. The viscosity of solutions of potato TPS granules produced with the L/D=18 plasticizing system with the addition of ground bark changed only slightly. The higher filler content and the extruder screw speed did not have a noteworthy effect on the value of apparent viscosity in this case. The results indicate only a loose bond between bark and potato starch in the granulated structure, which translates into the low viscosity of prepared aqueous solutions.

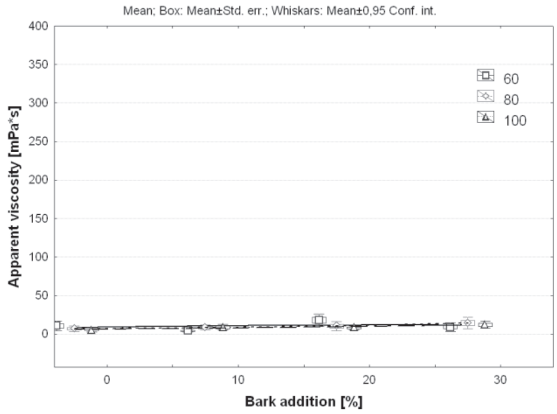

Fig. 6. The influence of ground bark addition and the extruder screw speed on the apparent viscosity of potato starch solutions (extruder plasticizing system of L/D=18).

CONCLUSIONS

– The highest apparent viscosity values were reported for solutions of TPS with the addition of flax fibre.
– The apparent viscosity of the solutions was determined by the rotational speed of the extruder used for the production of the TPS granulated matter.
– The aqueous solutions of TPS granules obtained with the L/D=16 extruder plasticizing system displayed higher apparent viscosity values.
– The addition of fillers such as natural fibres increased viscosity in the majority of examined aqueous solutions of TPS.

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CHARAKTERYSTYKA WYBRANYCH CECH REOLOGICZNYCH WODNYCH ROZTWORÓW ZIEMNIACZANYCH BIOKOMPOZYTÓW TPS

Streszczenie. Badaniom poddano wodne roztwory granulatów ziemniaczanej skrobi termoplastycznej (TPS). Granulaty skrobi termoplastycznej zostały wyprodukowane w z mieszanek skrobi ziemniaczanej, gliceryny oraz dodatku wypełniaczy w postaci włókien naturalnych. W badaniach zastosowano dwie konfiguracje układu plastyfikującego (L/D=16 oraz L/D=18) zmodyfikowanego ekstrudera jednoślimakowego TS-45 z dodatkowym chłodzeniem końcowej części cylindra. Badano wpływ prędkości obrotowej ślimaka ekstrudera, ilości oraz rodzaju stosowanych wypełniaczy na lepkości rozdrobnionych granulatów skrobi termoplastycznej. Podczas pomiarów zaobserwowano, że na lepkość pozorną roztworów ekstrudowanej skrobi ziemniaczanej miał wpływ rodzaj zastosowanego układu plastyfikującego ekstrudera stosowanego do produkcji granulatów TPS. Najwyższą lepkością charakteryzowały się roztwory ziemniaczanej TPS z dodatkiem włókien lnianych.
Słowa kluczowe: ekstruder, włókna, lepkość, skrobia termoplastyczna, ekstruzja, biokompozyty.

This research work has been supported by the funds for science for the years 2010-2012 as a research project NN313275738.