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

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Summary. The research covered the aqueous solutions of thermoplastic wheat starch (TPS) granules. The thermoplastic starch granules were produced from mixtures of wheat 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 cylinder. The research focused on the effect of the extruder screw rotation speed, the volume and the type of plasticizing system used and on the apparent viscosity of pulverized granules of wheat TPS. During measurements it was observed that higher apparent viscosity values were recorded in those solutions of TPS that were produced with the extended version of the plasticizing system of TS-45 extruder.

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

INTRODUCTION

The production of biodegradable and environmentally friendly materials has recently come into focus of researchers worldwide. Such a material is expected to replace petroleum-based polymers which are very durable, yet represent a major environmental issue [10, 13, 28].

One of the main natural compounds extensively researched for the use as a biodegradable material is starch. The first attempts to obtain materials based on this component focused on the use of starch granules as a filler for synthetic polymers such as polyethylene and polypropylene [3].

In order to be further processed as a biodegradable material, natural starch must be transformed into thermoplastic starch (TPS). In this case, the granular structure of starch is completely degraded by the use of plasticizers in a high temperature during extrusion [1, 6, 14]. Unfortunately, pure thermoplastic starch has several disadvantages. They include low mechanical strength (fragility) and high sensitivity to environmental factors, e.g. moisture [1, 9, 18]. In order to offset these disadvantages, TPS is mixed with other polymers, thus yielding, in a simple, fast and inexpensive manner, mixtures with such properties that are generally not achievable when using individual polymeric materials [11, 27]. In order to improve the processing and mechanical properties of TPS, it is combined with, e.g. polyethylene (PE) [20, 22], polypropylene (PP) [21], and polyamide (PA) [24, 25]. In addition, in an attempt to obtain completely biodegradable materials, numerous TPS mixtures have been developed with various polymers which undergo complete degradation in the natural environment [26]. Among the biodegradable polymers, butylene polysuccinate (PBS) deserves special attention, not only because of its excellent biodegradability quality but also sufficient mechanical strength. Therefore some research has been carried out on the combination of PBS and TPS [5, 31].

Generally speaking, thermoplastic starch is considered a promising material for the production of packaging materials due to its reasonable cost, availability, renewability and biodegradability. Recently, its use has spread to many sectors, e.g. oil refining (grease), metallurgy (extraction of impurities from iron), textile (rubber) and paper (enhancement of paper strength) [15].

The properties of TPS are very much dependent on the natural origin of the starch, more specifically, on the ratio of its main two components: linear amylose and branched amylopectin. The share of amylose chains in starch is determined genetically and generally the same within a particular plant species. In standard starch, the amylose content accounts for 15-30% of the total starch weight; in special, high-amylose species it reaches 35-70% [8]. There are numerous studies on the effect of amylose and amylopectin content on the final properties of starch-based materials [8, 10, 12, 31]. TPS obtained from high-amylose starch has been proven to have better thermal and mechanical properties, still their processing (extrusion, in particular) is much more demanding [16, 17, 29, 30]. In order to enhance the mechanical and physical properties of TPS, various types of fillers can be used such as natural fibre or wood waste [24, 25].

The effect of the type of starch and used additives (fillers, plasticizers) on the properties of TPS is crucial when selecting raw materials for the production of biodegradable plastics. It also allows the optimization of properties of TPS-based mixtures for the industrial application of TPS products [1, 2, 23].

The aim of the study was to examine the apparent viscosity of suspensions of pulverized granules of thermoplastic wheat starch granules with different natural fillers.

MATERIALS AND METHODS

Wheat starch used in the study was Merizet 100 from Segezha, Ireland; flax fibre from a Polish producer; cellulose fibre Vivapur type 102 JRS from a German producer and ground pine bark. Technical glycerol of 99% purity was used as a plasticizer.

Wheat starch, glycerol and fillers in the form of flax fibres and ground bark were mixed for 20 minutes in a laboratory ribbon mixer. The glycerol accounted for 20% of the mixture weight, and the proportion of fillers in the prepared mixtures was 10, 20 and 30%. After mixing, the samples were left in sealed plastic bags for 24 hours in order for the mixture to homogenize [19].

The baro-thermal treatment was carried out on a modified single-screw extrusion-cooker, TS-45, equipped with two kinds of plasticizing systems with the screw length/diameter ratio of L/D=16/1 and L/D=18/1. A steel die was used with a hole of 3 mm in diameter. Granules were produced at the three extruder screw speeds: 60, 80 and 100 rpm. Temperature values were in the range of 60-110ºC. The temperature was controlled by a purpose-made cooling system. The extruder was equipped with a material feeder, a plasticizing system made up of the screw linked to the drive and housing, and a preheating device. To measure the temperature of the thermal and pressure treatment, thermocouples were used installed in the extruder cylinder; the results were displayed on the machine control panel. The screw speed during extrusion was monitored using a wireless electronic tachometer, DM-223AR [18, 19, 32].

The viscosity of aqueous solutions of thermoplastic starch was measured on the test machine Zwick BDO-FBO0,5TH, equipped with a back extrusion chamber. The granules were ground using a laboratory mill to obtain particles with a diameter of less than 0.8 mm. 10% thermoplastic starch suspensions were prepared with distilled water at 20°C. The viscosity measurements were made after 10 minutes of mixing. During the test, the following parameters were set: total test length 60 mm and the 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 [4, 7]. There were five replications, the final result being the arithmetic mean of the measurements.

RESULTS

Fig. 1 shows the dependence of the viscosity of aqueous solutions of thermoplastic wheat 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 significantly ($p<0.05$) along with the increasing extruder screw speed and a higher addition of cellulose fibre. A similar trend was observed for maize starch.

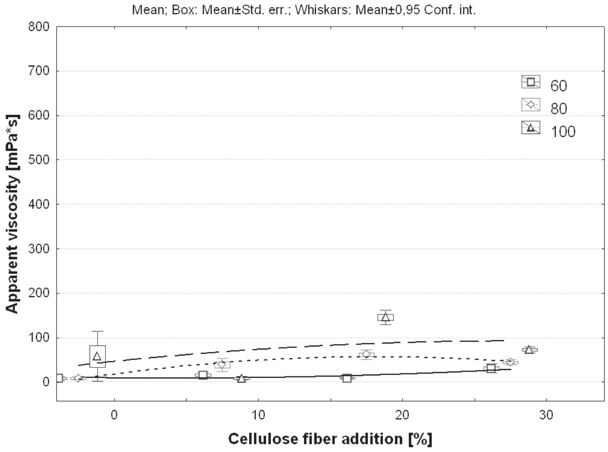

Fig. 1. The influence of cellulose fibres and the extruder screw speed on the apparent viscosity of wheat starch solutions (extruder plasticizing system of L/D=16).

The use of the L/D=18 plasticizing system (Fig. 2) resulted in an increase of apparent viscosity. The highest apparent viscosity values were reported for solutions with a 10% addition of cellulose fibre. It was also reported that with the increasing fibre content in the mixture, the viscosity of the solution decreased. This may be an indication that the addition of cellulose fibres had an adverse impact on their bond with the biopolymer matrix, which, in turn, had a negative bearing on the viscosity of the solution.

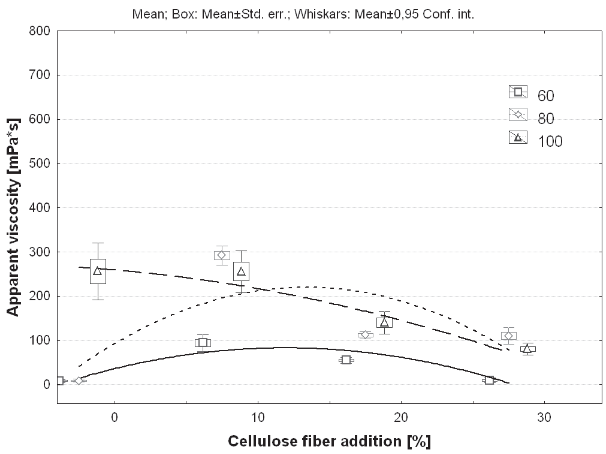

Fig. 2. The influence of cellulose fibres and the extruder screw speed on the apparent viscosity of wheat starch solutions (extruder plasticizing system of L/D=18).

Fig. 3 shows the effect of the addition of flax fibre on the value of apparent viscosity of the solutions of wheat thermoplastic starch. It was observed that with increasing extruder screw rotation speed, the viscosity of solutions rose, regardless of the plasticizing system used.

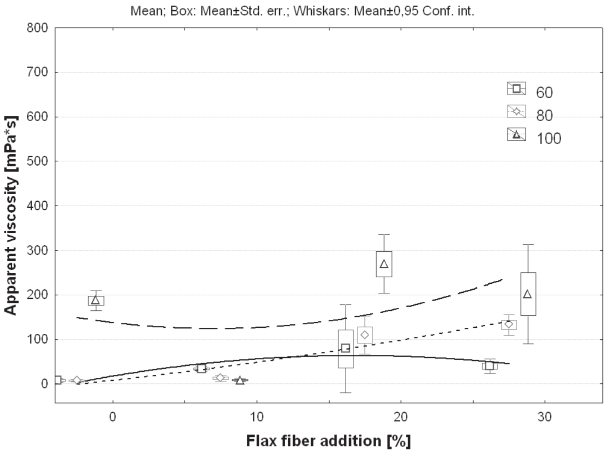

Fig. 3. The influence of flex fibres and the extruder screw speed on the apparent viscosity of wheat starch solutions (extruder plasticizing system of L/D=16).

Higher viscosity values were reported for the solutions of thermoplastic wheat starch with the addition of flax fibre at 100 rpm^{-1} of the extruder screw.

During tests, the TPS solutions delaminated, which testifies to a weak bond between flax fibre and wheat starch. In some cases, there was more resistance between the plunger and and the walls of the machine, which could have led to the high spread of apparent viscosity values (Fig. 4).

The apparent viscosity of solutions of wheat starch granules produced on the shorter version of the plasticizing system slightly increased along with the higher bark content in the granulated matter (Fig. 5). The top viscosity value was reported at a 10% content of ground bark and for the screw speed of 100 rpm^{-1}.

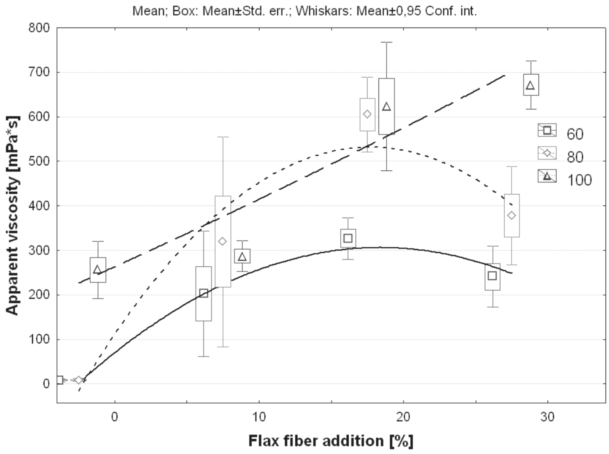

Fig. 4. The influence of flex fibres and the extruder screw speed on the apparent viscosity of wheat starch solutions (extruder plasticizing system of L/D=18).

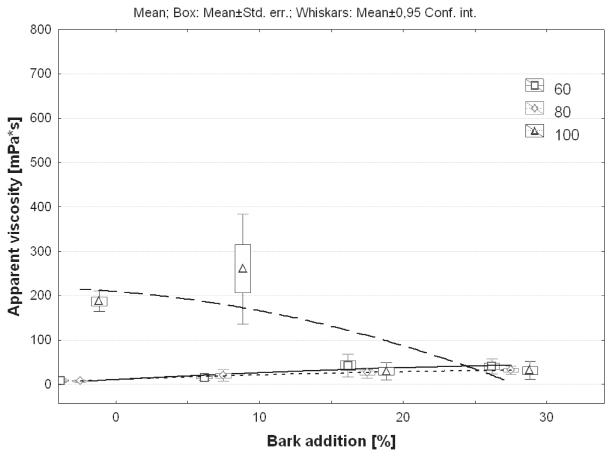

Fig. 5. The influence of ground bark addition and the extruder screw speed on the apparent viscosity of wheat starch solutions (extruder plasticizing system of L/D=16).

Table 1. The results of the statistical analysis of viscosity of aqueous solutions of thermoplastic wheat 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	$y_{60} = 0.036x^2-0.288x+9.148$	12.839	0.00001
		80	$y_{80} = -0.119x^2+4.287x+17.918$	26.402	0.000000009
		100	$y_{100} = -0.059x^2+3.282x+46.435$	19.459	0.0000002
	18	60	$y_{60} = -0.327x^2+7.808x+36.158$	76.040	0.0000
		80	$y_{80} = -0.710x^2+18.989x+93.064$	319.028	0.00000
		100	$y_{100} = -0.147x^2-2.748x+258.953$	22.267	0.00000006
Flax fibre	16	60	$y_{60} = -0.162x^2+5.454x+17.425$	1.807	0.1658
		80	$y_{80} = 0.044x^2+3.631x+7.813$	36.962	0.0000
		100	$y_{100} = 0.276x^2-3.883x+137.562$	15.189	0.000003
	18	60	$y_{60} = -0.698x^2+25.679x+70.109$	14.351	0.000004
		80	$y_{80} = -1.343x^2+47.508x+111.830$	17.144	0.0000008
		100	$y_{100} = 0.044x^2+14.729x+263.149$	34.734	0.0000
Ground pine bark	16	60	$y_{60} = -0.021x^2+1.747x+10.515$	6.441	0.0015
		80	$y_{80} = -0.016x^2+1.206x+10.685$	5.895	0.0025
		100	$y_{100} = -0.178x^2-2.530x+208.945$	16.957	0.0000009
	18	60	$y_{60} = -0.011x^2+0.866x+12.580$	3.145	0.0385
		80	$y_{80} = 0.300x^2-1.175x+7.140$	13.101	0.000010
		100	$y_{100} = 0.633x^2-15.667x+199.430$	4.097	0.0144

No direct effect was noted of the screw speeds during extrusion on the value of the apparent viscosity of TPC wheat solutions with ground pine bark (Fig. 5).

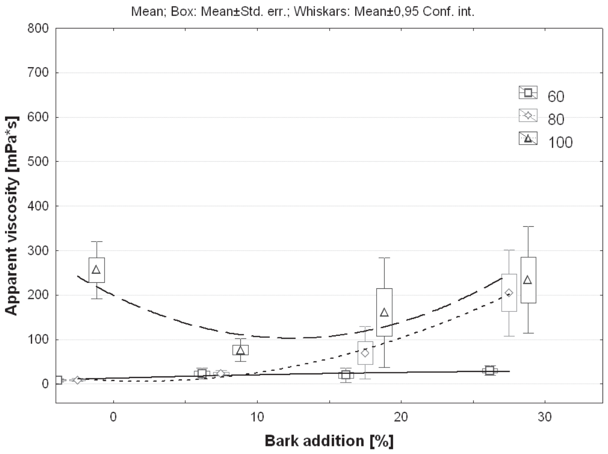

Fig. 6. The influence of ground bark addition and the extruder screw speed on the apparent viscosity of wheat starch solutions (extruder plasticizing system of L/D=18).

The use of the extended version of the plasticizing system of the extruder for the production of wheat TPS granules with the addition of bark had an impact on the increase in the value of apparent viscosity. The highest apparent viscosity values were reported for solutions with a 20 and 30% addition of ground bark. A similar trend was observed in that the rising extruder screw speed resulted in the increased viscosity of tested solutions.

CONCLUSIONS

- The aqueous solutions of thermoplastic wheat starch granules obtained with the extended L/D=18 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.
- The addition of flax fibre enhanced the viscosity of TPS solutions to the greatest extent.
- The rising extruder screw rotational speed resulted in a higher apparent viscosity value in the majority of examined solutions of TPS granules.

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CHARAKTERYSTYKA WYBRANYCH CECH REOLOGICZNYCH WODNYCH ROZTWORÓW PSZENNYCH BIOKOMPOZYTÓW TPS

Streszczenie. Badaniom poddano wodne roztwory granulatów pszennej skrobi termoplastycznej (TPS). Granulaty skrobi termoplastycznej zostały wyprodukowane z mieszanek skrobi pszennej, 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, ilości oraz rodzaju stosowanego wypełniacza na lepkość rozdrobnionych granulatów pszennej skrobi termoplastycznej. Podczas pomiarów zaobserwowano, że wyższymi wartościami lepkości pozornej charakteryzowały się roztwory TPS wytworzonej na dłuższej wersji układu plastyfikującego ekstrudera TS-45.
Słowa kluczowe: ekstruder, włókna, lepkość, skrobia termoplastyczna, ekstruzja, biokompozyty.

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