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Investigation on the Use of Fibres and Fibrids from Modified Potato Starch in the Manufacture of Paper

Abstract
In the Institute of Chemical Fibres, Łódź, Poland, scientific research is being conducted which is devoted to the manufacture of fibrous forms such as fibres and fibrids from modified potato starch. The applied modification method of the potato starch does not spoil its biodegradability. This paper presents the possible use of starch fibres and fibrids for modifying paper as a replacement for cellulose fibres. A blend of bleached sulphate pulp was used containing 60% spine and 40% beach pulp, a mixture that is commonly used in the manufacture of wood-free papers. The addition of starch fibrids as a binding agent for various fibres in paper was investigated by employing blends of bleached pulps with polyester staple fibres in the proportion of 60:40. The investigations were done on laboratory scale, using the Rapid Koethen apparatus for sheet forming. The starch fibrids are used in the amount of 15% as a substitute for cellulose pulp, which resulted in a triple increase in tenacity of the sheets in wet conditions. The paper properties were best improved with the addition of 7.5% of fibrids as binding agent. An addition of 15% starch fibres to the paper pulp as a substitute for cellulose fibres also results in a fourfold increase in the paper strength at wet condition.

Key words: *potato starch, modified potato starch, starch fibres, starch fibrids, wet spinning, stream-forming, water resistance.*

Introduction

Like cellulose, starch is abundant in the world of natural polymers. It is a homopolysaccharide with the same formula as cellulose, $(C_6H_{10}O_5)_n$, and appears in two varieties:
- amylose - a linear polymer with a molecular weight of 0.5×10^6 Daltons, soluble in aqueous sodium hydroxide, revealing an ability to form films;
- amylopectin - a branched polymer, having a molecular weight of 8.0×10^6 Daltons. It is responsible for the gelatination of starch in water solutions.

Various types of starch usually contain 15-25% of amylose, the rest being amylopectine. The starch of a specific maize grain (*Zea mais cerata*) has 98% of amylose. Availability, low price and attractive properties has for a long time made starch an important raw material for the paper and textile industry. One of the many possible applications of starch in paper manufacturing is its use as a binding agent which can enhance paper's mechanical properties, and also improve paper manufacturing by increasing paper pulp retention on the sieves of the paper machine. The use of native starch in this application does not produce satisfactory effects, as its retention in the paper is low; this causes effluent pollution (an increase in COD). For this reason, cationic starch is mainly being used at present, providing a 90% retention in the paper pulp. However, cationic starch is expensive, and efforts are therefore being made to obtain various starch forms which will be insoluble in water, like fibres and fibrids for the application in paper manufacturing.

According to patents [1-4], starch with a high amylose content is used to produce water-insensitive fibrous forms. In the manufacturing procedure of such forms, an alkaline solution of amylose-rich starch is extruded to a coagulation bath. In the technology, a specific feature of starch called retrogradation is exploited, consisting in the ability to undergo orientation, association and aggregation, followed by precipitation of the linear polymer macromolecules. Amylose's proneness to retrogradation causes it to form water-insoluble, flexible films.

Unfortunately, most native starch has low amylose content. The conversion of low-amylose starch to high-amylose content is not feasible on a commercial scale. This is why in many research centres work has begun to obtain fibrous forms from native starch with a high amylopectin content [5]. To confer water-insensibility upon

***Table 1.** Selected properties of spinning solution containing modified potato starch (*spindle 4, 30 r.p.m.).*

Solution symbol	Starch content, wt %	Viscosity at 20°C, s	K_w	K_w*	Brookfield viscosity at 20°C, Pa·s
S-1	9.3	96	615	47.5	5.2*
S-2	8.9	103	637	44.0	5.5*

***Table 2.** Selected properties of fibres and fibrids applied in the investigation (FB - fibres, FIB - fibrids; a - dimensions of wet fibres and fibrids, b - dimensions of dry fibres and fibrids).*

Sample	Linear density, dtex	Breaking force conditioned, cN	Tenacity conditioned, cN/tex	Elongation at break conditioned, %	Average thickness, μm	Average length, μm	WRV
FB	21.6	7.45	3.45	2.66	50 /a 20 /b	$2.5 \cdot 10^3$ /b	434
FIB	-	-	-	-	200-500 /a 50 /b	1000 /a 400 /b	346

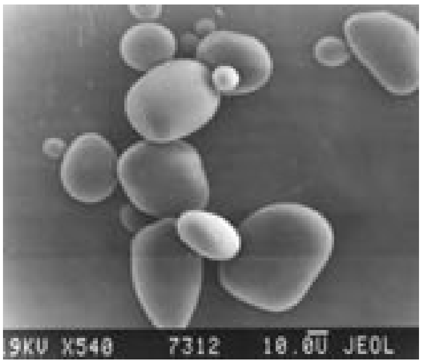

Figure 1. *SEM of native starch granules.*

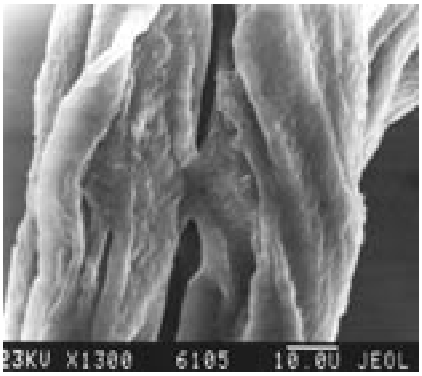

Figure 2. *SEM of dry fibrids.*

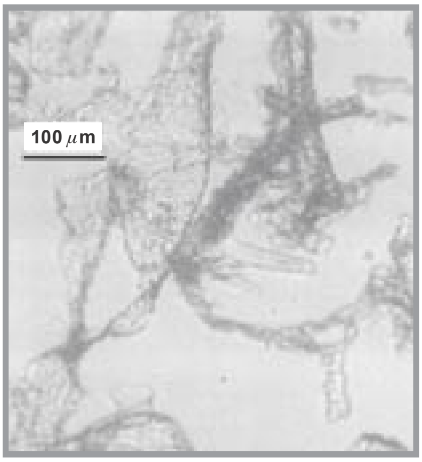

Figure 3. *Photo of wet starch fibrids.*

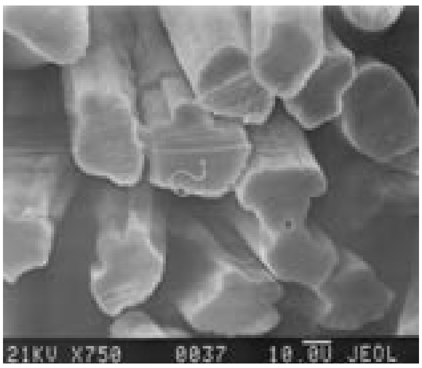

Figure 4. *SEM of starch fibre cross-section.*

such products, crosslinking agents are introduced to the spinning solution such as paraformaldehyde urea-formaldehyde resins, glycosal and formaldehyde-urea-melamine resins. Alternatively, these substances may be applied on the ready-made products (fibres, fibrids). Fibres obtained by this method are not continuous and are used as an additive to paper pulp. Polish native potato starches are of the low-amylose type. The method to modify potato starch which the authors propose allows water-insensitive fibres and fibrids to be produced [6]. The fibrous forms obtained according to the method are biodegradable, contain no harmful ingredients and are human- and environment-friendly. A wide field of applications is open to such ecological fibres and fibrids. In this work, the possibility of using starch fibres and fibrides as substitutes for cellulose fibres in paper manufacturing was investigated. Two aspects were taken into consideration:

- Environmental protection. The most distinct and attractive feature of starch is its biodegradability, largely surpassing that of cellulose [7-8]. Moreover, starch provides the possibility of eliminating harmful agents based on paraformaldehyde from paper pulp, which is traditionally used to improve the wet strength of paper.
- Economy. The fibrous forms made according to the proposed method are cheaper than cellulose pulp. Starch is in rich supply on the domestic market.

Materials Used in the Investigation

Native potato starch from Trzemieszno Poland, characterised by average granulation - 20 μm (Figure 1), number-average molecular weight $\overline{M}_n$=235.1 kD, weight-average molecular weight $\overline{M}_w$=1226.4 kD, polydispersity ($\overline{M}_w$/ $\overline{M}_n$) Pd=5.2, amylose content - 22.0 wt%, humidity - 18.5 wt%.

Modified potato starch - chemically modified characterised by number-average molecular weight $\overline{M}_n$=226.4 kD, weight-average molecular weight $\overline{M}_w$=983.4 kD polydispersity ($\overline{M}_w$/ $\overline{M}_n$) Pd=4.4. The modified starch was used for the manufacture of the fibrous forms.

Fibres and fibrids from modified potato starch

Table 1 presents some starch-containing spinning solutions applied in the manufacture of starch fibres (solution S-1) and

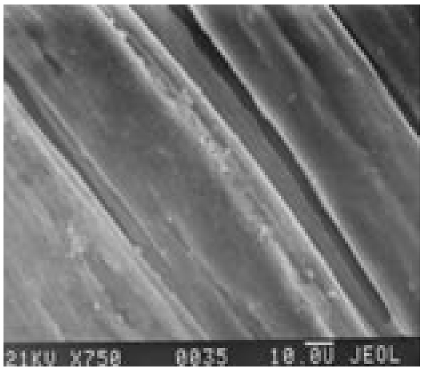

Figure 5. *Side view of dry starch fibres (SEM).*

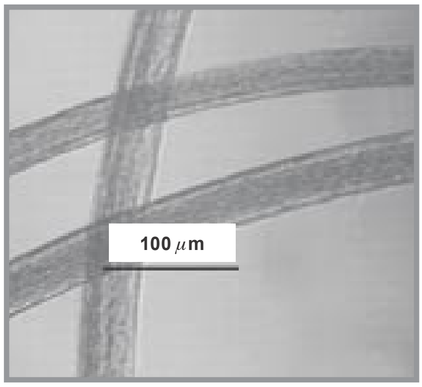

Figure 6. *Photo of wet starch fibres.*

fibrids (solution S-2). The manufacture of both fibres (FB) and fibrids (FIB) was accomplished according to the solution spinning method, using a concentrated solution (about 44%) of ammonium sulphate as a coagulation bath. For the spinning a laboratory machine was used, equipped with a rhodio-platinum spinneret with 600 holes, the hole diameter being 60 μm. The starch fibrids were made according to the jet method [9]. The fibres and fibrids were washed in running water. Both the wet and dry fibrous products were inspected under a microscope (Figures 2-6). Table 2 lists the properties of the fibres and fibrids used for the modification of paper.

Cellulose pulp

A blend of bleached pulps was used which is commonly applied in the manufacture of commodity papers. It was made by International Paper, Kwidzyn, Poland and contained sulphate pine and beach cellulose in the proportion of 60: 40. In the investigation of fibrids as binding agents, a blend of bleached sulphate pulp and polyester staple fibres was used. The polyester staple fibre of 1.3 dtex and 3 mm staple length was made by Elana S.A, Toruń, Poland.

Analytical Methods

The dynamic viscosity was measured using a Brookfield LVT viscometer according to procedure SPR/BB/6 and GLP No G-016.

Gel Permeation Chromatography (GPC) was applied in the estimation of molecular weight distribution for both the native and modified starch. In the analysis, an HPIO50 pump, an HP 1047 refractometric detector and three PI gel Mixed A columns from Polymer Laboratories were used. DMAC with 0.5% LiCl served as solvent. The results were analysed with the use of PL Caliber GPC/Sec Software (Polymer Lab. Ltd.). A method was adapted for the analysis which is known from technical literature [10].

The water retention value WRV was estimated according to a gravimetric method [11].

For the starch spinning solutions, the clogging values K_w ***and*** K_w*, were estimated [12]; the latter is a viscosity-corrected value.

The SEM was used to analyse ***the cross-section and the side view of fibres, and size and shape of dry fibrids***. The Japanese JEOL 35C scanning electron microscope was used in the analysis. The appearance of fibres and fibrids was estimated using the Biolar polarisation microscope (Z.P.O. Warsaw, PL) equipped with the IMAL computer image analyser.

The ***amylose and amylopectin content*** was measured according to a method known from literature [13].

A method [6] prepared by the authors was applied to analyse ***the content of starch in the spinning solution***.

Table 3. *Impact of the starch fibrids substituting the cellulose pulp on paper water fastness (*dry fibrids modified with the solution of Honolu with 1.5 g/l concentration).*

Fibrid content, %	Extension resistance index, N·m/g		Water fastness, %
	dry	wet	
0	64.0	1.54	2.4
Wet fibrids			
15	54.9	4.34	7.9
30	48.1	1.91	4.0
45	41.7	1.36	3.3
Dry fibrids			
30	44.6	3.14	7.0
30*	47.2	3.40	7.2

Table 4. *Impact of additionally drying paper sheets containing fibrids on paper water fastness (temp. 140°C, 10 min).*

Fibrid content, %	Extension resistance index, N·m/g		Water fastness, %
	dry	wet	
0	64.5	1.64	2.54
Wet fibrids			
15	64.0	5.40	8.40
30	48.5	3.00	6.20
45	41.4	2.45	5.90

Mechanical testing of the starch fibres was carried out according to standards PN-ISO 1973:1997 p. 9.1 for linear density, and PN-EN 5079:1999 for breaking force, tenacity and elongation at break (conditioned).

The moisture content in the native starch was estimated at 50°C in a vacuum dryer over 24 hours. The moisture content of fibres and fibrids was measured using a scale-dryer made by Z.M.P. Radwag, Radom, Poland.

Laboratory Test

The investigation concerning the impact of the starch fibres and fibrids additive on the mechanical properties of paper, including its water fastness, was carried out in the Pulp and Paper Institute, Łódź, Poland according to methodology known from literature [14].

For the laboratory testing, small paper sheets with 1006HS were first prepared from selected blends of bleached sulphate pulp defibrated and ground in a laboratory Valley hollander to 27°SR wetness. A 10 dm^3 defibrator, equipped with a metal agitator rotating at 1500 or 3000 r.p.m., was used to prepare the paper pulp suspension. The forming and drying of the sheets with 200 mm diameter was accomplished in the Rapid-Koethen apparatus. The drying temperature was 95°C. For possible additional drying above 100°C, a typical lab dryer was used.

The quality parameters of breaking length, extensibility, burst, tear resistance, stiffness of the tested sheets were measured according to standards in force in the paper-making industry [15].

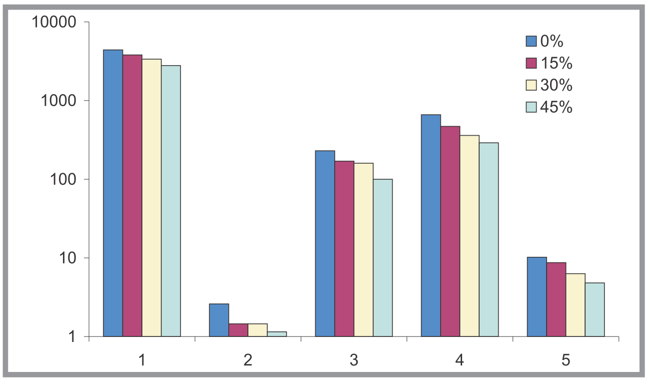

Figure 7. *Mechanical properties of paper sheets modified with varying content of starch fibrids; 1 - breaking length, m; 2 - extensibility, %; 3 - burst, kPa; 4 - tear resistance, mN; 5 - stiffness, mN.*

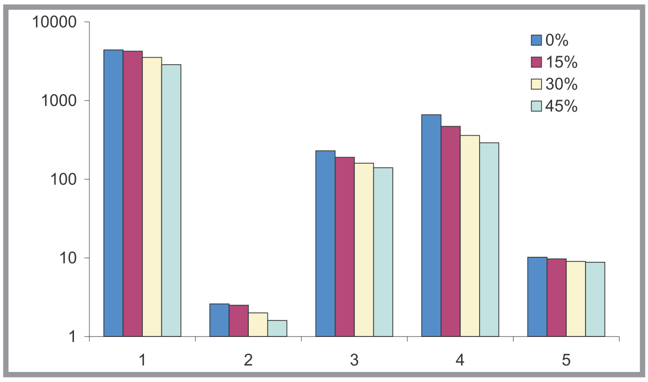

Figure 8. *Impact of additional drying at 140°C on the mechanical properties of paper sheets; 1 - breaking length, m; 2 - extensibility, %; 3 - burst, kPa; 4 - tear resistance, mN; 5 - stiffness, mN.*

Table 5. Impact of the starch fibrids used as binding agent for various fibres in the paper on its water fastness.

Fibrid content, %	Extension resistance index, N·m/g		Water fastness, %
	dry	wet	
0	27.6	4.48	16.2
Wet fibrids			
2.5	27.9	2.78	10.0
5.0	27.3	2.70	9.90
7.5	30.3	4.10	16.1
15.0	28.0	4.35	15.5

Table 6. Impact of starch fibres as substitute for fibrous pulp on paper water fastness.

Fibre content, %	Extension resistance index, N·m/g		Water fastness, %
	dry	wet	
0	64.0	1.54	2.41
15	55.4	5.30	9.60
30	46.4	3.50	7.60

Investigation Concerning the Usefulness of Starch Fibres and Fibrids for the Pulp Modification of Papers

The starch fibrids were evaluated as:
- a substitute for cellulose fibres in paper,
- an agent able to bind different fibres in the paper.

The percentage of used starch fibres and fibrids was calculated on the dry mass of the paper sheets. The usefulness of starch fibres was investigated with regard to their possible use in paper fibre composition as a substitute for cellulose fibres.

Investigations and Discussion of Results

Starch fibrids as substitute for cellulose pulp in the fibrous paper pulp

Aqueous solutions of fibrids with 15-16% concentration were introduced to paper pulp to attain 15%, 30% and 40% contents of the fibrids in the blended paper pulp. The formed sheets were normally dried at 95°C, and in the second version, additionally at 140°C for 10 minutes. The results of the investigation are shown in Tables 3 and 4 and Figures 7 and 8.

Air-dry starch fibrids with a moisture content of 12.4% were also used in the amount of 30%, as were specially prepared starch fibrids. The latter were subjected to a surface treatment with a bath containing 1.5g/l of a preparate called Honol made by Takemoto Co., Japan. After application of the preparate, the fibrids were air-dried to 13% moisture content and used in the amount of 30% for preparing the paper sheets. The results of the investigation are presented in Table 3. From the results in Table 3 and Figure 7, it can be concluded that the presence of fibrids deteriorates the mechanical properties of the paper sheets. The desired increase in the wet resistance of the paper, particularly for the blend with the lowest amount (15%) of fibrids, which manifests a wet tenacity three times higher than for papers from pure cellulose, is noteworthy.

In the version with the additional drying at 140°C, some improvement in the static tenacity can be seen. It is most pronounced for the lowest fibrid content (15%) in the paper blend. The breaking load, breaking length and extensibility of such paper sheets are close to or equal the level of sheets made from cellulose alone (Figure 8). For all fibrid-containing papers, the wet resistance increases, meaning better water fastness (Table 4). The use of dry fibrids at the amount of 30% in both versions enhances the paper's wet resistance, thus improving the wet fastness, a very important paper feature.

Starch fibrids as binding agent for various fibres in the paper

In this part of the research, we explored the usability of a new preparate in fibrid form for binding fibres in paper technology. We investigated blends of bleached cellulose pulps with staple polyester fibres (Elana) with the addition of fibrids at the amounts of 2.5, 5.0, 7.5 and 15%. The results of the investigations are shown in Table 5 and Figure 9. It can be seen that the best results in water fastness arise for the 7.5% addition of starch fibrids. The water fastness for this paper composition is above 16%, i.e. a value comparable to that of the control paper sheet.

Investigation on the usability of starch fibres in the manufacture of paper in sheet form

Starch fibres were dried to 10% water content, cut into 2.5 mm staples and added to cellulose pulp in the amount of 15% and 30%. The results of the investigation are presented in Table 6 and Figure 10. It can be seen from the results that a pronounced, fourfold increase in the wet tenacity and the water fastness appears for the lowest (15%) content

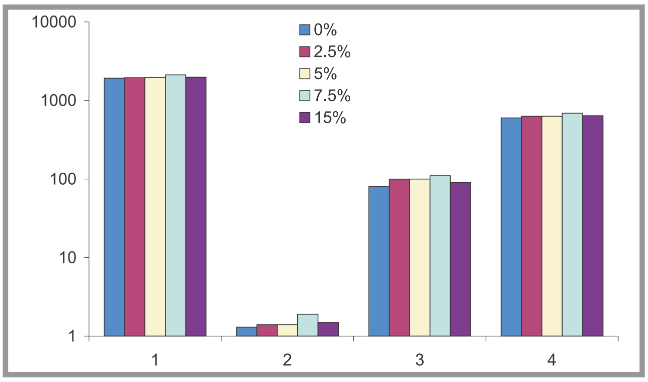

***Figure 9.** Mechanical properties of sheets modified with varying amount of starch fibrids as binding agent; 1 - breaking length, m; 2 - extensibility, %; 3 - burst, kPa; 4 - tear resistance, mN.*

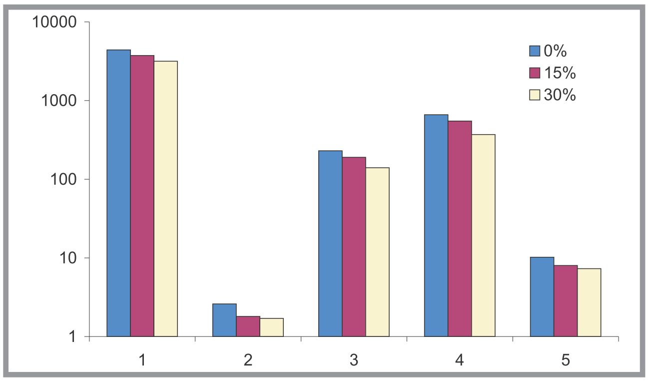

***Figure 10.** Mechanical properties of sheets modified with varying content of starch fibres; 1 - breaking length, m; 2 - extensibility, %; 3 - burst, kPa; 4 - tear resistance, mN; 5 - stiffness, mN.*

of starch fibres in the paper pulp. The increase in the starch fibres to up to 1/3 of the total fibrous material in the paper also increases the wet tenacity of the paper sheet; however, the increase is not as spectacular for the lower fibre content.

Summary and Conclusions

- Fibrids added to paper pulp cause an increase in the paper water-fastness, and the mechanical properties deteriorate with growing fibrid content. The most favourable paper properties, notably a threefold increase of water-fastness, can be attained for the 15% fibrid content.
- Additional drying of the paper sheets up to 140°C over 10 minutes produces an improvement in the static mechanical properties, particularly for the 15% fibrid content, as well as an increase of the water fastness for all fibrid contents, compared to sheets dried at 95°C.
- The use of dry fibrids in the amount of 30% increases the paper's mechanical properties in wet conditions.
- The paper prepared with 7.5% of fibrids used as a binding agent for cellulose and synthetic fibres reveals the best mechanical properties and a maintained water fastness of 16% equal to the control paper sheet.
- The addition of 15% of starch fibres as substitute for cellulose pulp results in a fourfold increase in the paper wet mechanical properties.
- The results of the investigation are encouraging, indicating a possibility of using fibrous materials from potato starch in the manufacture of paper.

The insignificant decrease in the paper's mechanical properties can be explained by the loss of integrity proceeding in the fibrous forms of modified starch, causing a decline in integrity of the pulp components. A similar problem is known from literature [16] for fibres and fibrids made from starch with high amylose content and used in the modification of paper. To prevent this phenomenon, paraformaldehyde is used as a cross-linking agent for the ready-made starch products.

Investigations are continuing to improve the integrity of the pulp components in blends with fibrous starch forms, thus increasing the paper mechanical properties. We intend to apply environment-friendly additives to eliminate the preparations based on the cancerogenic paraformaldehyde, which is presently widely used for improving the mechanical properties and water fastness of papers.

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