Preliminary Studies on the Surface Layer of Starch

Dariusz Bieliński [1)*], *Leszek Pyskło* [2)], *Jan Dul* [2)], *Ludomir Ślusarski* [1)], *Grażyna Janowska* [1)], *Grażyna Lewandowicz* [3)]

[1)] Institute of Polymers, Technical University of Łódź,
Stefanowskiego 12/16, 90-924 Łódź, Poland
E-mail: dbielin@ck-sg.p.lodz.pl
[2)] Rubber Research Institute „STOMIL",
Harcerska 30, 05-820 Piastów, Poland
[3)] Starch and Potato Products Research Laboratory,
Zwierzyniecka 18, 60-814 Poznań, Poland

Summary: Characterization of the surface layer of starch powder, originated from potato or maize, was carried out applying various experimental techniques: Fourier-transformed infrared internal reflection spectroscopy (FTIR-IRS), inverse gas chromatography (IGC) and scanning electron microscopy (SEM). The main kinds of starch were studied as potential fillers for rubber and results discussed in terms of factors requiring modification to improve starch miscibility and activity towards rubber. Starch of high amylopectine content shows surface enrichment with amylose what makes crystallinity of the surface layer higher than in bulk of the material. Particles of the both kinds of starch have very smooth surface (morphological index, I_m = 0.995), highly resistant to its geometrical development. Dispersive component of the surface energy of starch was found to be similar to that of low energy polymers (γ_s^d = 32.5 mJ/m^2 at 23 °C) and its surface to be of electron-donor character.

Introduction

Starch is an easily accessible and cheap biopolymer from renewable resources. Ways to find out its potential application on a big scale have been looked extensively. In Poland the problem concerns potato starch. The research was devoted to elaboration methods of starch modification, that makes possible its application as a filler of rubber compounds [1]. Polarity of the starch surface, together with its relatively big particles makes however the material difficult to disperse and inactive towards the unpolar rubber matrix (NR, SBR) [2]. Incorporation of starch into rubber compounds, causes significant deterioration of mechanical properties of vulcanizates. Based on above, two approaches to solve the problem can be distinguished and namely: intercalation of the particles and modification of their surface. In order to perform the task properly, characterization of the surface layer of starch has been proposed to start with. Two kinds of starch – originated either from potato or maize were studied. Experimental results are briefly presented below.

 CCC 1022-1360/00/$ 17,50+.50/0

Experimental

Materials

Potato and maize starch powders, obtained from the Starch and Potato Products Research Laboratory in Poznań (Poland), were characterized with the Fritsch scanning photo-sedimentograph "Analysette 20" (Germany) according to area of specific surface and particle size distribution, Table 1.

Table 1. Particle size analysis of the starch.

Starch	Specific surface [m^2/g]	Size of particles [μm]		
		min.	max.	average
potato	0.8	7	200	35
maize	2.9	4	55	15

Thermal properties of the starch were determined with the Netzsch 600 TGA/DTA system (Germany), operating with heating rate of 10 deg·min.$^{-1}$ in the temperature range 30-550 °C, Table 2.

Table 2. Thermal properties of the starch.

Starch	Water content [wt %]	Beginning of degradation [°C]	Degree of degradation [wt %/temp.]
potato	23.3	250	64.4/310 °C
maize	23.9	248	74.4/330 °C

Thermal analysis of the samples revealed that apart water adsorbed physically, the surface of starch also contains some, however difficult to quantify, amount of chemically associated water.

Instrumentation

Fourier-Transformed Infrared Internal Reflection Spectroscopy (FTIR-IRS)

FTIR spectra were acquired in the wavelength range 500-400 cm^{-1}, using the Bio-Rad FTS 175 C apparatus (Germany) equipped with the Split-Pea (Harrick Scientific, USA) attachment, operating with Si crystal. Experimental parameters were as follows: 32 scans / resolution of 4 cm^{-1}. IR absorption envelope in the wavelength range of 950-1100 cm^{-1} was deconvoluted according to the literature [3, 4]. Peaks centered at 1047 cm^{-1} and 1022 cm^{-1} were subscribed to the crystalline and the amorphous phase of starch respectively, whereas that one centered at 995 cm^{-1} was assigned to water present on the surface.

Scanning Electron Microscopy (SEM)

Pictures were acquired using the Philips 500 scanning electron microscope (Holland) in the magnification range 300-3000 ×. Samples were gold coated to remove charging.

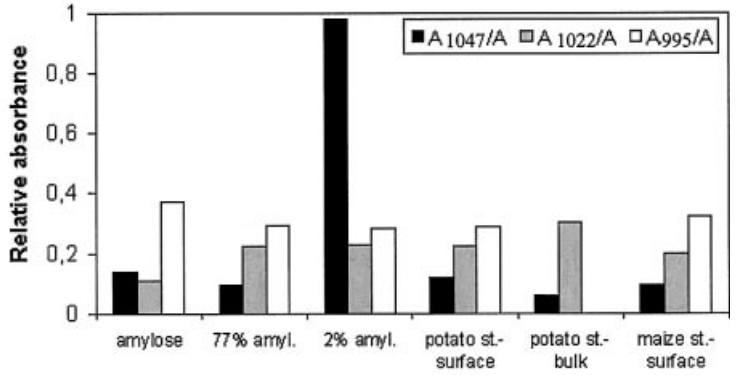
Inverse Gas Chromatography (IGC)

Measurements were carried out with the Perkin-Elmer 900 apparatus (USA) equipped with the flame ionization detector of high sensitivity. Columns of ≈ 500×0.175 mm, packed with one of the starch powder (similar degree of packing was controlled by maintaining pressure drop Δp ≈ 100 mmHg) were conditioned at 150 °C for 24 hrs before all determinations. The carrier gas applied was helium with flow rate of 25 $ml \cdot min.^{-1}$ The temperature of the column was maintained constant in the range 35-55 °C. The amount of probe injected approached the limit of the detector sensitivity and varied from 0.5-1.0 μl. The following groups of probes were used: 1. unpolar: hexane, heptane, octane, nonane, decane, 2. polar: acetone, chloroforme, benzene, ethyl acetate, THF, diethyl ether and 3. branched – for determination of the morphology index [5]: 2,3,4-trimethylo pentane, 2,5-dimethylo hexane, 2,2,4-isooctane. The hold-up volume of the columns was determined by injecting methane. IGC data were analyzed adopting the procedure described elsewhere [6, 7].

Results and Discussion

Fourier-Transformed Infrared Reflection Spectroscopy (FTIR-IRS)

Composition and structure of the surface layer of starch were studied in order to elaborate effective ways of its physical or chemical modification. Experimental results derived from FTIR-IRS spectra are demonstrated in Figure 1, presenting composition and structure of the surface layer of different kinds of starch. Linear amylose adsorbs more water that samples of the starch studied. The surface layer (3-4 μm as calculated according to Harrick [8]) of maize starch showed lower content of regular phase than potato starch (≈20 % lower absorption at A_{1047}). However it exhibits simultaneously lower content of amorphous phase (≈10 % lower absorption at A_{1022}). Taking into consideration that the surface of maize starch absorbs more water than the potato one (≈12 % higher absorption at A_{995}), one can come to conclusion that water particles present in the surface layer of starch influence organization of its macromolecules, in agreement with literature [9].



Absorption description [3, 4] (subscripts are related to wavenumbers in cm^{-1}):
A_{1047} – crystalline phase, A_{1022} – amorphous phase, A_{995} – water, $A = A_{1047} + A_{1022} + A_{995}$

Figure 1. Analysis of the surface layer of potato and maize starch powders by FTIR.

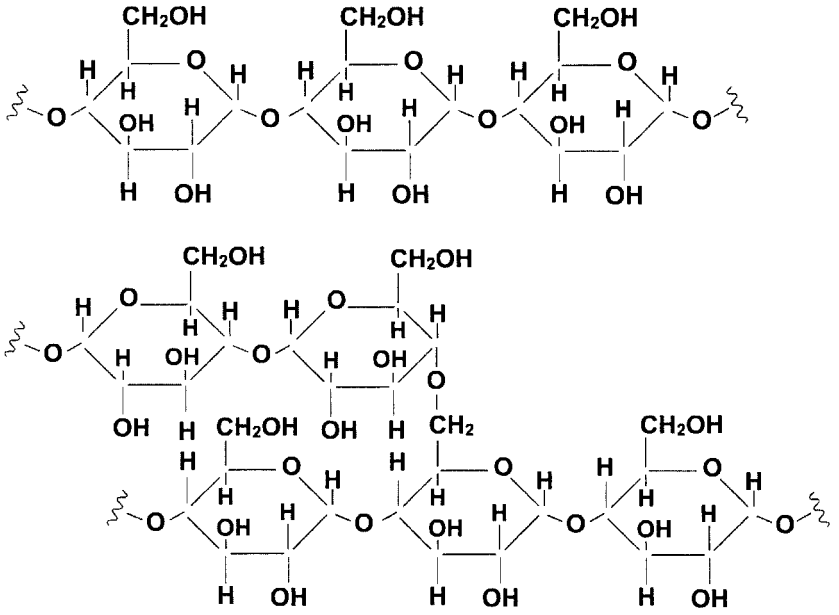


Figure 2. Amylose (top) and amylopectine molecules.

Generally, the surface layer of starch contains more water than in the bulk of material. Apart this it was also found that the higher amylopectine content in starch particles the lower regular phase contribution. For the sample of almost pure amylopectine structure, the rest of amylose segregates completely to the surface. Generally, the surface layer of

starch is likely to be enriched with amylose in comparison to the bulk, what seems reasonable taking into account that amylose has significantly lower molecular weight than amylopectine [10].

Scanning Electron Spectroscopy (SEM)

In order to decrease diameter of starch particles intercalation by means of water and ionic surfactant (oxy-ethylated lauryl alcohol – Rokanol 10, Rokita S.A., Poland) was applied to the starch samples. Results obtained however, were not encouraging - Figure 3, probably because of inadequate structure of the material – too high amylose content.

A) B)

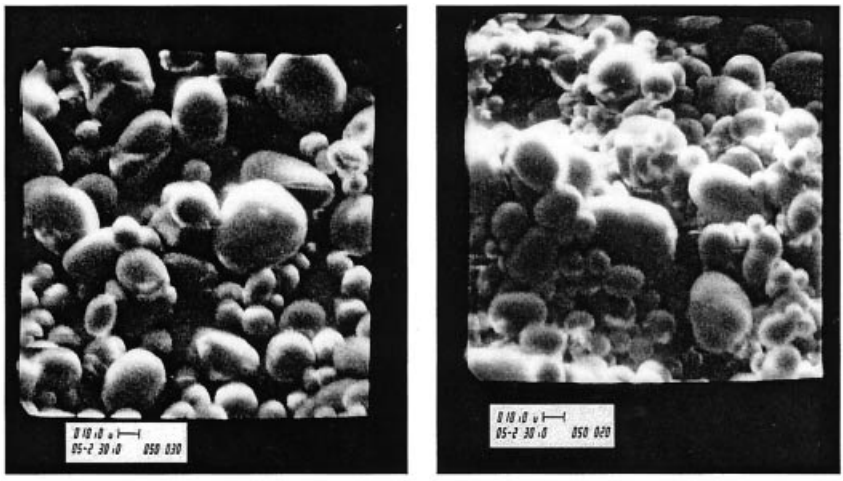


Figure 3. Potato starch: A) native, B) intercalated (water+non-ionic surfactant).

Starch particles of low amylose content should be more susceptible to freezing process, due to limited possibility for accommodation of stress [11], accompanying crystallization of water. In this context studying amylose-free mutant, waxy maize, could be of particular interest.

Inverse Gas Chromatography (IGC)

Physical character of the starch surface was studied in order to estimate its potential interactions with rubber matrix. Dispersive component of the surface energy of material (γ_s^d) was calculated from values of retention time determined at various temperature, according to procedure described elsewhere [6]. The values obtained for the potato starch, extrapolated to 23 °C, showed to be similar to that of low energy polymers - γ_s^d = 32.5 mJ/m^2, Figure 4. Calculations on specific interactions between the potato starch

and polar probes were carried out adopting procedure described in the subject literature [7], Figure 5. Values of KA and KD parameters [12], characterizing the degree of acidity of electron-acceptor or basicity of electron-donor of the potato starch surface respectively, are given in Table 3.

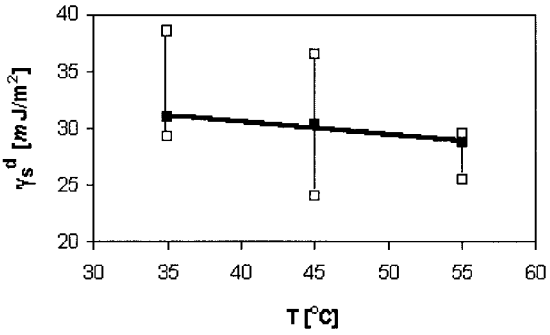


Figure 4. Dispersive component of the surface energy of potato starch.

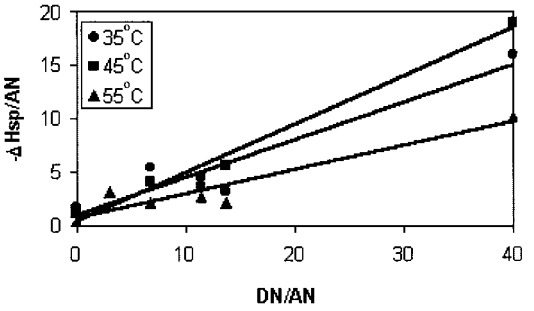


Figure 5. Electron donor-acceptor character of the potato starch surface.

Despite some scatter of the data, a decrease of donor-acceptor interactions of the starch takes place with an increase of temperature, what favours its slightly better dispersion in rubber matrix and justifies mixing at elevated temperature.

Table 3. Donor (KD) and acceptor (KA) parameters of the potato starch.

Temp. [°C]	KA	KD	I_m
35	0.36	0.89	6.85
45	0.45	0.37	15.34
55	0.23	0.64	18.18

Table 3 additionally contains value of the morphological index of the potato starch particles (I_m), corresponding to nanoroughness of their surface [5]. I_m extrapolated to

23 °C is equal to 0.99 what means that the surface of starch is very purely developed not only in the micro- (see data in Table 1) but also nanoscale. An increase of its surface geometry could be another factor facilitating higher interactions with rubber matrix.

Conclusion

Increase of amylopectine content in starch makes the material more crystalline. At highest amylopectine content, linear amylose seems likely to segregate onto the surface of starch particles. Starch particles, taking into consideration their structure, resemble amylopectine phase covered with amylose one. Crystallinity of the surface layer is higher than in the bulk of material. and depends on the amount of water being adsorbed. Water particles make order of starch macromolecules, especially of branched amylopectine. Starch particles have very smooth surface (I_m=0.99), not susceptible to morphological development. Dispersive component of the surface energy of starch is similar to low energy polymers (γ_s^d=32.5 mJ/m^2 at 23 °C) and the surface is of electron-donor character (KD/KA=0.63/0.34). To increase dispersability and activity of starch in rubber compounds it is necessary to modify its particles by chemical or physical way. Possibility of potato starch modification by means of plasticizers, coupling agents and enzymes are being evaluated.

Acknowledgement

The work was carried out under frame of the KBN Project no T08E-017-18. The authors thank the Polish State Committee for Scientific Research for financial support.

[1] Goodyear, US Patent 5,672,639 from 30.09.1997.

[2] G.R. Hamed, *Rubber Chem. Technol.* **2000**, *73*, 524.

[3] A.L.M. Smits, F.C. Ruhnau, J.F.G. Vliegenthart, J.J.G. van Soest, *Starch/Stärke* **1998**, *50*, 478.

[4] J. Szymońska, F. Krok, P. Tomasik, *Int. J. Biol. Macromol.* **2000**, *27*, 307.

[5] E. Brendle, E. Papirer, *J. Colloid Interf. Sci.* **1997**, *194*, 217.

[6] M. Zaborski, M. Lipińska, A. Kosmalska, L. Ślusarski, *Chem. Anal. (Warsaw)* **1999**, *44*, 505.

[7] J-B. Donnet, S-J. Park, *Carbon* **1991**, *29*, 955.

[8] N.J. Harrick, *Phys. Rev. Lett.* **1960**, *4*, 224.

[9] S. Perez, A. Imberty, *Carbohyd. in Europe* **1996**, *15*, 17.

[10] P.A. Perry, A.M. Donald, *Polymer* **2000**, *41*, 6361.

[11] K.R. Morgan, R.H. Furneaux, N.G. Larsen, *Carbohyd. Res.* **1995**, *276*, 387.

[12] V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions,* Plenum Press, New York 1978.