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Oxidative Polymerisation of Aniline Hydrochloride in Highly Viscous Carbohydrate Gels.

Part II: Amylopectin - highly branched polysaccharides matrix

Marcin Lukaszewicz¹, Pawel Ptaszek², Piotr Zurek¹, Anna Ptaszek², Szczepan Bednarz²

¹Department of Carbohydrate Technology; Agricultural University in Krakow; ul. Balicka 122, PL-30-149 Krakow; Poland
 e-mail: rrlukasi@cyf-kr.edu.pl

²Department of Engineering and Machinery for Food Industry; Agricultural University in Krakow; ul. Balicka 122, PL-30-149 Krakow; Poland
 e-mail: pptaszek@ar.krakow.pl

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ABSTRACT

The synthesis of conducting polyaniline in highly viscous carbohydrate gel was presented. Polyaniline (PANI) was synthesized chemically by means of oxidative polymerisation of ammonium persulfate. The process was conducted in waxy maize starch which contain only branched fraction i.e. amylopectin. Obtained materials were investigated according to its properties.

KEYWORDS

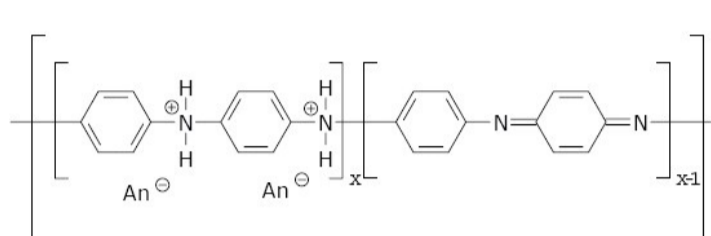
polyaniline, carbohydrate, rheology, conductivity, amylopectin

INTRODUCTION

Starch seems to be one of the most important plant polysaccharides that is produced and stored mostly in grain (cereals) or tubers (potato etc.). It is fully biodegradable, biocompatible and non-toxic polymer. Raw carbohydrate obtained from plants is called a "native starch" and is a kind of blend consisting two different polyglucans: amylose and amylopectin. Amylose is the almost linear fraction build from α -D-glucose jointed together through α -(1-4) linkages and has a molecular weight of approximately 10^5 - 10^6 g/mol. From the other hand amylopectin, with higher molecular weights between 10^6 and 10^7 g/mol, is strongly branched fractions possessing shorter chains linking linear chain via α -(1-6) linkages [1][2][3]. Nowadays, starch is being used in a broad range of applications as a thickener, stabilizer, gelling agent adhesives, detergents, drug carrier etc. and find application in food, cosmetics, ceramics, polishes, explosives, paper coatings, aids in textile industry, in oil recovery operations and many more [5]. Modern trends of chemical industry has been also focuses on other possible application of biopolymers including starch. Such materials follows the new technology trends when synthetic materials are exchange with natural biodegradable and renewable resources [4]. Employing of natural and biodegradable polymers has increased due to a growing awareness of environmental concerns and depleting oil reserves.

From the other hand, in the wide group of synthetic polymers conducting macromolecules are characterised by the growing interest for both industry and science. Up to know there is however a problem with processing of conducting polymers because its very often suffer from insolubility of this compounds in most common solvents what dramatically limits their application [6]. In contrary soluble conducting polymer (e.g. polyaniline protonated by carboxylic acids with long aliphatic "tails" [7]) are much more less "conducting" than we expect and accept for industrial uses.

One of the most known and detailed investigated conducting polymer is polyaniline (PANI), a compound existing in many different oxidation states which conductivity strongly depends on protonation with organic or inorganic acids [8].



Scheme 1: Simplified structure of polyaniline

In presented work, as a continuation of our earlier research on the field of chemical modification of starch and other polysaccharides [9] as well as some research on conducting polymers [10], we would like to report the synthesis of two component carbohydrate/polyaniline gels. The described material based on amylopectin as a matrix is a carrier of many interesting mechanical properties what was proofed by rheological analysis.

EXPERIMENTAL

Preparation of the gel

Polymerisation of aniline hydrochloride was carried out in carbohydrate gel obtained by dissolving waxy starch i.e. amylopectin in pure dimethylsulfoxide. a) Carbohydrate gel: The appropriate gel was obtained by dissolving of waxy maize starch in hot DMSO (120°C) for approximately 3 hours in order to obtained a gel with concentration 10%, 15%, 20% and 30%(w/w) respectively. Dissolving process was aided by mechanical stirring of the system (200rpm).

b) Polymerisation of aniline hydrochloride (ANI-HCl):

30g of obtained carbohydrate gel was cooled down and transferred to the reaction vessel that was equipped with the cooling mantel jointed together with thermostat operating with ethylene glycol as a cooling agent. Temperature was set at 0°C or 20°C. To the pre cooled gel ANI-HCl (3.2mmol) was added and the system was vigorously stirred in order to dissolve the monomer in the medium. Freshly prepared oxidant solution (3.2mmol ammonium persulfate dissolved in DMSO) was drop-wised added when stirring. After the addition of oxidant was finished the system was stirred for another 2 hours and afterwards kept under nitrogen.

Rheological measurements [11]:

Rheological measurements were performed using a RS-150 rheometer (Haake, Germany), in a cone/plate sensor system in temperature range of 10°C - 60°C. The range of linear viscoelasticity was estimated in a frequency domain by changing the amplitude of deformation at constant frequency and observing changes in the absolute value of complex relaxation modulus. The amplitude was set to 0.01 at 40°C. Changes of complex modulus were registered as the function of frequency 0,628 - 6,283 rad/s and temperature what allowed the master curve to be estimated. Complex continuous Maxwell model [12] was fitted to the experimental data. Calculations were carried out using Tikhonov regularization method [13].

Conductivity measurement:

Analysis of final gel conductivity was performed using RLC bridge: RLC QuadTech 1920. Conductance of the material was measured employing amplitude of 1V. The range of applied frequencies was set up to 20Hz to 1MHz. Before the measurements the cell was calibrated at 20°C using KCl solutions with known conductivity(concentration).

AFM analysis

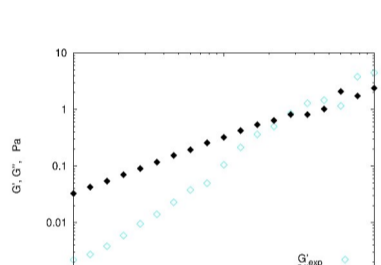
AFM scans were performed using Quesant Nomad model. Scanning was done at non-contact mode. The following parameters of scanning head were applied: scanning area: $401\frac{1}{4}\mu\text{m} \times 401\frac{1}{4}\mu\text{m}$, scanning frequency range: 5-10 Hz, resolution 1024 (samples/line).

Molecular mass of matrix detrimination:

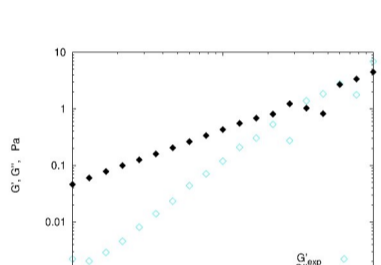
Molecular mass distributions were performed by means of Gel Permeation Chromatography (GPC) The system of two columns connected in a series was used: Ultrahydrogel-2000 and Ultrahydrogel-500 (Waters) and RI detector (Knauer). As an eluent 0.1 mol/L NaNO₃ and 0.02% NaN₃ solution in water was applied. Flow rate was 0.6 μ l/min, sample volume 100ml and sample concentration 5mg/ml. A calibration using pullulan standards was performed.

RESULTS AND DISCUSSION

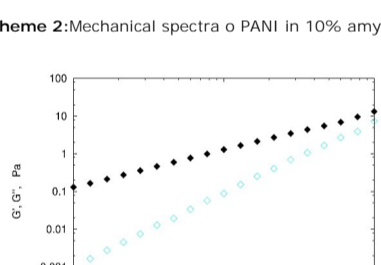
As a result of our investigation we have obtained a new series of dark blue gels with interesting mechanical properties. Although the properties of the final material are fascinating, further development of the set up is needed, especially in order to remove some inorganic ions from the system. Ammonium persulfate is known as a powerful oxidant for PANI production but its reduction products may interfere on the conductivity in high viscous media and are heavy to remove.



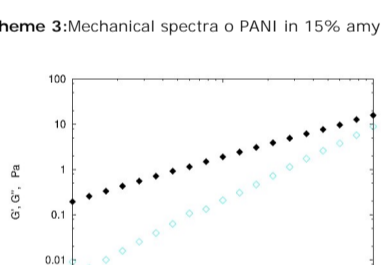
Scheme 2: Mechanical spectra of PANI in 10% amylopectin matrix.



Scheme 3: Mechanical spectra of PANI in 15% amylopectin matrix.



Scheme 4: Mechanical spectra of PANI in 20% amylopectin matrix.



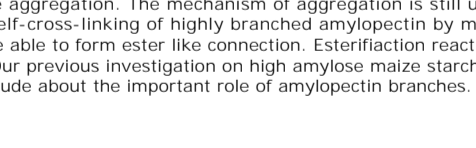
Scheme 5: Mechanical spectra of PANI in 30% amylopectin matrix.

Going into details it is worth to point out that the conductivity of designed material is almost independent on matrix (polysaccharide) concentration (Table 1). Such phenomenon seem to be important from practical point of view because concentration of the matrix influence on viscosity. Depending on viscosity the future application of the material may vary what broaden the spectra of usefulness of material. Detailed rheological investigation clearly shows that all systems may be classified as those lying in the flowing zone ($G'' > G'$). The values of G'' and G' parameters increase according to concentration of matrix. Such occurrence has the origin in the concentration of polymer entanglement junction that shoot up when polymer concentration increase. In this case the rheological and mechanical stability is higher than in less concentrated systems. Another important factors are changes in rheological properties depending on the temperature of PANI polymerisation and also on oxidant:ANI molar ratio (data not presented). In both occurrences there was no significant changes detected. The result testifies that polymerisation process does not influence on matrix stability.

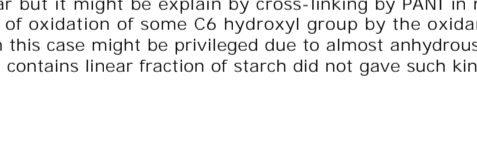
Table 1: Basic properties of obtained materials.

Starch concentration, % (w/w)	Temperature, °C	Mw x 10 ⁻⁵ , g/mol	Conductance at 10kHz, mS	Conductivity, mS/cm
10%	0	5,6	6,85	2,33
	20	15,50	7,19	2,45
15%	0	13,8	5,08	1,73
	20	18,17	5,70	1,94
20%	0	11,10	9,48	3,23
	20	7,30	6,08	2,07
30%	0	12,90	6,13	2,09
	20	9,39	7,17	2,44

The investigation of molecular masses clearly shows that in less concentrated system, the higher temperature of the process influence on some kind of polysaccharide aggregation. The mechanism of aggregation is still unclear but it might be explain by cross-linking by PANI in media with lower viscosity or by self-cross-linking of highly branched amylopectin by means of oxidation of some C6 hydroxyl group by the oxidant. The resulting carboxyl might be able to form ester like connection. Esterification reaction in this case might be privileged due to almost anhydrous but hygroscopic reaction media. Our previous investigation on high amylose maize starch that contains linear fraction of starch did not gave such kind of results what forced us to conclude about the important role of amylopectin branches.



Scheme 6: AFM image of PANI in 10% amylopectin matrix.



Scheme 7: AFM image of PANI in 30% amylopectin matrix.

From the other hand the topography of gels shows that PANI do not form any form of agglomeration what may testify on homogenic distribution of PANI chains in the carbohydrate matrix. It may influence on conductivity of the gel but must be treated as a big advantage by means of processing of the material.

As a conclusion it might be said that obtained new group of materials seems to be very interesting from scientific point of view. The behaviour of carbohydrate matrix is rather independent on polymerisation of PANI parameters. From the other hand the final product possess, by means on macro and microscopic point of view, homogenic structure what is important for further processing. The very next stage of investigation i.e. discovering the molecular structure and mechanism of incorporating of conducting material into biopolymer/PANI will give further information that allow to connect mechanical, electrical and mechanical properties and understand the system: carbohydrate/PANI as a whole.

LITERATURE

[1] A.C. Eliasson; *Starch in Food: Structure, Function and Applications*; Woodhead Publishing; 2004
 [2] R. L. Whistler, J. N. Bemiller; *Starch: Chemistry and Technology*; Academic Press 1994.
 [3] H. F. Zobel; *Starch-Stärke*; 1988, 40, 2, 44.
 [4] a) G. Crini; *Progress in Polymer Science*; 2005, 30, 38; b) H. Sashiwa, S Aiba; *Progress in Polymer Science*; 2004, 29, 887.
 [5] K. J. Yarema (Ed.); *Handbook of Carbohydrate Engineering*; CRC Press; 2005.
 [6] a) C. Weidlich, K. Mangold, K. Juttner; *Synthetic Metals*, 2001, 119, b) T. Nguyen, N. Barisci et al, *Synthetic Metal*, 2003, 137. c) M. Trioljanowicz, *M. Chemica Acta*, 2003, 143. d) J. Duval, P. Retho, et al; *Synthetic Metal*, 2003, 135 e) A.G. MacDiarmid, *Science and Application of Conducting polymers*, IOP Publication 1991
 [7] J. Laska, J. Widlarz; *Synthetic Metals*, 2003, 135, 261.
 [8] a) J. Anand, S. Palaniappan, D.N. Sathyanarayana; *Progress in Polymer Science*, 1998, 23, 996. b) N. Gospodinova, L. Terlemezyan; *Progress in Polymer Science*, 1998, 23, 1443 c) A.A. Syed, M.K. Dinesan; *Talanta*, 1991, 38, 815.
 [9] a) M. Lukaszewicz, S. Bednarz; *XIV International Starch Convention*; Krakow, 2006. c) P.Ptaszek, M. Lukaszewicz, A.Ptaszek; *Functional and Biological Gels and Networks: Theory & Experiment*; Sheffield, 2006.
 [10] a) M. Lukaszewicz, B. Achremowicz, P.Pitala; *9th Electronic Conference in Synthetic Organic Chemistry, ECSOC*, 2005. b) M. Lukaszewicz, A. Ptaszek, L. Koziel, B. Achremowicz, M. Grzesik; *Polymer Bulletin*, 2006, 58, 1, 281 c) M. Lukaszewicz, P.Ptaszek, B. Achremowicz; *XIV International Starch Convention*; Krakow, 2006.
 [11] P. Ptaszek, M. Lukaszewicz, B. Achremowicz, M. Grzesik; *Polymer Bulletin*, 2006, 58, 1, 1, 295.
 [12] N.W. Tschoegl; *The Phenomenological Theory of Linear Viscoelastic Behaviour*, Springer, Berlin 1989
 [13] A.N. Tikhonov, A.V. Goncharsky, W. Stepanov, A.G. Yagola; *Numerical Methods for the Solution of Ill-Posed Problems*. Kluwer, Dordrecht 1995