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## PREPARATION OF CHITOSAN BASED FILMS FOR FOOD PACKAGING APPLICATIONS

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In the present study, the effect both of the botanical source and proportion of starch produced from agricultural surplus on the microstructure properties of starch/chitosan/glycerin films was tested. Effective gas transport properties gas diffusion transfer was performed. Starch/chitosan/glycerol biodegradable films were obtained by casting method from giant squid (*Dosidicus gigas*) pen chitosan mixed with glycerin and starch. Four starch samples were prepared using exceeding or low quality biomass including broken rice grains, hard yellow corn surplus, banana surplus form exportation activity and low quality cassava in three different weight proportion (chitosan/starch) corresponding to 1/1, 2/1 and 5/1. Extraction of starch from the raw material was carried out by mixing it with a water solution of sodium disulfite (5 wt.%). Afterwards, the obtained suspension was filtered and then decanted at 5°C for 24 h. The obtained starch was washed repeatedly with distilled water and ethanol (96 vol.%). Finally, the starch samples were dried at 55°C for 48 h, crushed and sieved. It was found that the gas diffusion transport properties significantly depend on the starch source used. Differences in diffusion transport rates through the films prepared with different starches are related to the size and distribution of granules of starch in the films and/or the amylose content.

**Introduction**

In the modern society, plastics based on crude oil has become a serious concern from environmental point of view. Due to their low biodegradability, these materials can remain in the environment for long time and could cause the environmental problems such as saturation of landfills and greenhouse gases production<sup>1</sup>. In the most cases these materials can even reach the terrestrial and aquatic ecosystems and, thus effect living organisms.

Starch and chitosan are two of the most used biopolymers to produce biodegradable packages. Although both materials offer advantages when they are used individually, these materials also reveal some drawbacks. Starch possesses such properties as homogeneity, odorless, colorless and very low oxygen permeability<sup>2</sup>. However, its main drawback is high hydrophobicity, high water solubility, brittleness<sup>3</sup>, poor mechanical and barrier properties<sup>4</sup>. On the other hand, chitosan is the material which could form film of a high quality and which reveals only e.g. a lack of water resistance and poor mechanical properties.

Although chitosan compared to starch can be produced from low valuable wastes (chitin), the production process itself (deacetylation) is still expensive and environmentally unfriendly. On the contrary, raw materials and production process of starch are low cost and less polluting compared to chitosan production.

Addition of plasticizers into films offers some advantages for the final materials. Versino et al.<sup>5</sup> found that plasticized starch films reveal lower water vapor permeability compared to unplasticized ones. Additionally, the presence of plasticizer induces structural modifications of starch network leading to a less ordered but a compact structure. It is very important to maintain moisture content in some edible products and keep their quality. Besides Zhong and Xia<sup>6</sup> concluded that the presence of glycerin increases the flexibility of the final films thanks to reduction of the intermolecular bonds between polymer chains.

Within presented study, the effect of the botanical source and proportion of the starch produced from agricultural surplus over the properties of the starch/chitosan/glycerin films is tested statistically. A comprehensive characterization that includes chemical, optical, morphological, biodegradable and gas diffusion properties was also performed.

**Experiment**

Chitosan (molecular weight of 1000 KDa, deacetylation degree of 85.5 %) prepared via chemical method from giant squid (*Dosidicus gigas*) pen (residual biomass of fishing industry) was used for the experiments. Various starch samples were prepared using exceeding or low quality raw materials such as: broken rice grains (RS) ("ñelen"), hard yellow corn surplus (CS), banana surplus form exportation activity (variety Cavendish) (BS) and low quality cassava (CaS). Extraction of the starch was carried out by mixing dried and grounded raw materials with a solution of sodium metabisulfite (5%). The mixture was filtered and then decanted at 5 °C during 24 h.

After that, the obtained starch was washed repeatedly with distilled water and ethanol (96 vol.%). Finally, the starch samples were dried at 55°C for 48 h, subsequently crushed and sieved.

Chitosan/glycerol/starch films were prepared by the casting method. A solution of chitosan 1% (w/v) in 1% (v/v) of acetic acid was prepared. 1, 2 and 5% (w/v) aqueous solutions of the starch samples were prepared via constant and exhaustive agitation at room temperature for 30 min and then at 90°C for 60 min until gelatinization of the solution was finished. The solutions were filtered to remove insoluble particles. The chitosan solution and the solutions with different starch proportions were mixed in order to prepare the samples summarized in Table I. The mixture was stirred for 30 min and a glycerol solution (1.5% w/w) was added in a volumetric ratio corresponding to 2:1 with respect to the starch solution. The mixture was stirred for additional 30 min and then was put into an ultrasonic bath for 20 min. Finally, it was dispersed over acrylic molds. The samples were dried at 60°C for 23 h and afterwards prepared films were stored in a desiccator.

Table I  
Composition of the prepared films

Samples	Chitosan (g)	Glycerol (g)	Starch source	Starch (g)	Starch/Chitosan Ratio
Ch-G	0.4	0.3	–	–	–
Ch-G-RS1	0.4	0.3	Rice	0.4	1
Ch-G-RS2	0.4	0.3	Rice	0.8	2
Ch-G-RS5	0.4	0.3	Rice	2.0	5
Ch-G-CS1	0.4	0.3	Hard yellow corn	0.4	1
Ch-G-CS2	0.4	0.3	Hard yellow corn	0.8	2
Ch-G-CS5	0.4	0.3	Hard yellow corn	2.0	5
Ch-G-BS1	0.4	0.3	Banana	0.4	1
Ch-G-BS2	0.4	0.3	Banana	0.8	2
Ch-G-BS5	0.4	0.3	Banana	2.0	5
Ch-G-CaS1	0.4	0.3	Cassava	0.4	1
Ch-G-CaS2	0.4	0.3	Cassava	0.8	2
Ch-G-CaS5	0.4	0.3	Cassava	2.0	5

Binary counter-current gas diffusion measurements were performed in the Graham's diffusion cell<sup>7</sup>. Samples of a circle shape (20 mm diameters) were prepared from the parent film sheet by using a die cutting tool. All gas transport measurements had to be performed very carefully owing to soft and easily deformable structure of films.

The diffusion cell is divided into two flow-through chambers with equal volumes ( $V = 150 \text{ cm}^3$ ) separated by an impermeable disc with the fixed and sealed (by using a sealing O-ring) samples of films. During the gas diffusion measurements different gases flowed steadily through the upper and the lower cell chambers (gas flow rate of  $150 \text{ mL min}^{-1}$  for the both gas streams) until the steady state was established. Immediately after that, the gas inlet and outlet in one of the cell chambers (typically the lower chamber) were closed by the 4-way valve and the net diffusion volumetric flux was determined by the digital bubble flowmeter (Optiflow HFM 570, Agilent Technologies, USA) connected to the bottom of the cell chamber. The heavier gas was always fed into the upper cell chamber. Two gas pairs and argon (99.99% grade, Linde Gas, Czech Republic), were used for the diffusion tests. All diffusion tests in the Graham's cell were performed under ambient temperature and pressure.

Gas diffusion measurements were carried out using Graham's diffusion cell with two gas pairs Ar/He and He/H<sub>2</sub> in order to measure directly volumetric diffusion flux by a digital bubble flowmeter ( $V^d$ ). After that the net diffusion molar flux density ( $N^d$ ) was calculated from  $V^d$ .

## Discussion and results

Size, shape and distribution of starch granules in the films are showed in Figure 1. All samples revealed two phases, the first is a compact structure that is constituted by chitosan/glycerin and soluble fraction of starch. The second is composed by granules of starch distributed in the first phase. The granules of rice starch reveals irregular shape, elliptical forms and they are distributed in almost whole surface of the film. The granules of corn

starch were round, more regular and homogeneously distributed in the film. The granules of cassava starch were ovals to round with edges and they were distributed rather anisotropic. Lopez and García<sup>8</sup> found that materials based on corn starch present more homogeneity and compactness than films produced from tuberous starches such as cassava starch, coinciding with this study. Finally, the granules of banana starch are faintly recognizable with irregular round shape and irregular distribution.

The size of starch granules decreased in the order to Ch-G-RS>Ch-G-CS>Ch-G-CaS>Ch-G-BS. Additionally, it follows from the SEM micrographs, all starch granules are over the relief of the films (except for banana starch).

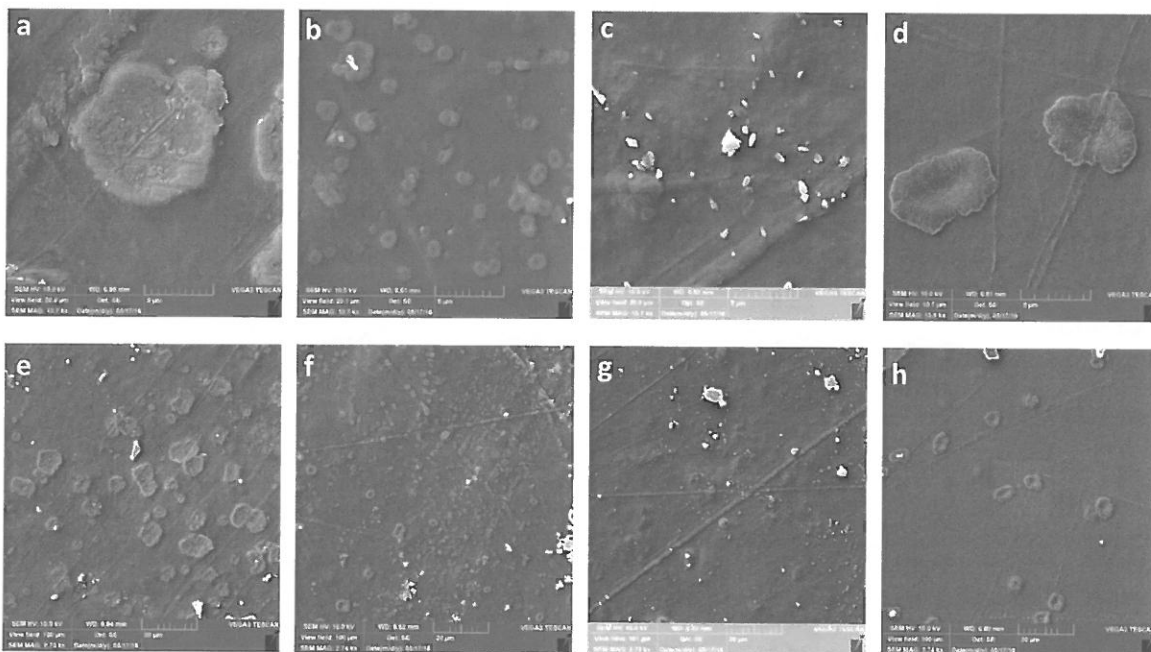


Figure 1. SEM pictures of the prepared films with 2% of starch: Ch-G-RS (a-e), Ch-G-CS (b-f), Ch-G-BS (c-g), Ch-G-CaS (d-h)

Gas diffusion measurements were conducted with inert gas pairs (Ar/He and He/H<sub>2</sub>) based on the fact that these gases neither are able to react with the components of the films nor may be adsorb on the surface. Every experimental point was replicated three times and corresponding mean values both the volumetric diffusion fluxes and the net diffusion molar flux densities are summarized in Table II. Statistically, there was a significant variation in this parameter which depend on starch source. There was not a significant difference of the starch concentration over this parameter. Thus in the case of the gas pair Ar/He, the net diffusion molar flux densities of the Ch-G-RS samples (average  $0.11 \mu\text{mol cm}^{-2} \text{s}^{-1}$ ) and Ch-G-CS ( $0.11 \mu\text{mol cm}^{-2} \text{s}^{-1}$ ) are higher compared to the samples of Ch-G-BS (average  $0.06 \mu\text{mol cm}^{-2} \text{s}^{-1}$ ) and Ch-G-Ca (average  $0.07 \mu\text{mol cm}^{-2} \text{s}^{-1}$ ). While in the case of the gas pair He/H<sub>2</sub>, the net diffusion molar flux densities of the samples Ch-G-CS (average  $0.09 \mu\text{mol cm}^{-2} \text{s}^{-1}$ ) is higher than for the samples Ch-G-RS (average  $0.06 \mu\text{mol cm}^{-2} \text{s}^{-1}$ ), Ch-G-BS (average  $0.05 \mu\text{mol cm}^{-2} \text{s}^{-1}$ ) and Ch-G-Ca (average  $0.05 \mu\text{mol cm}^{-2} \text{s}^{-1}$ ). This behavior could be related to the distribution of starch. As it was aforementioned in the SEM micrographs, the films are composed of a compact structure (chitosan/soluble starch and glycerin) and the area occupied by starch granules. The areas composed of chitosan/soluble starch and glycerin might be less gas permeable than the granules of starches, thus films with homogeneous distribution of starch present higher net diffusion molar flux density. Since the sample Ch-G-CS presented the most homogeneous distribution of starch, this sample has the highest net diffusion molar flux density. The sample Ch-G-RS presented a more and less distribution of starch in the films and the second highest net diffusion molar flux density. The samples Ch-G-BS and Ch-G-Ca with very heterogeneous distribution of starch showed higher gas diffusion resistance.

Another factor that could explain this tendency is the amylose content in the starch. The higher amylose content in the starch, the higher amount of free OH- that could form hydrogen bonds with chitosan in solution after gelatinization and retrogradation. Thus, in films containing starch with higher amylose content, the number of hydrogen bonds are higher leading to films of stronger interaction between starch and chitosan and possibly with less porosity for a gas diffusion transport. Therefore, films with higher amylose content based on banana

and cassava starches (Table II) revealed higher gas diffusion resistance compared to the films based on rice and corn starches with lower fraction of amylose.

Table II  
Results of the gas diffusion measurements performed in Graham's diffusion cell

Sample	Gas pair	$t$ [°C]	$p$ [kPa]	$V^d$ [cm <sup>3</sup> min <sup>-1</sup> ]	$N^d$ [μmol cm <sup>-2</sup> s <sup>-1</sup> ]
Ch-G-RS1	Ar/He	25.0	98.6	0.42	0.09
	He/H <sub>2</sub>	25.0	98.6	0.32	0.07
Ch-G-RS2	Ar/He	25.2	97.9	0.60	0.13
	He/H <sub>2</sub>	25.2	97.9	0.33	0.07
Ch-G-RS5	Ar/He	26.0	97.8	0.49	0.10
	He/H <sub>2</sub>	25.8	97.6	0.23	0.05
Ch-G-CS1	Ar/He	23.8	98.4	0.58	0.12
	He/H <sub>2</sub>	23.6	98.4	0.40	0.08
Ch-G-CS2	Ar/He	23.8	98.7	0.49	0.10
	He/H <sub>2</sub>	23.8	98.7	0.46	0.10
Ch-G-RS5	Ar/He	25.6	97.8	0.55	0.11
	He/H <sub>2</sub>	25.2	97.8	0.47	0.10
Ch-G-BS1	Ar/He	24.6	98.6	0.35	0.07
	He/H <sub>2</sub>	24.6	98.6	0.29	0.06
Ch-G-BS2	Ar/He	24.4	98.6	0.18	0.04
	He/H <sub>2</sub>	24.4	98.6	0.16	0.03
Ch-G-BS5	Ar/He	24.4	98.6	0.36	0.08
	He/H <sub>2</sub>	24.6	98.6	0.29	0.06
Ch-G-CaS1	Ar/He	24.6	98.7	0.31	0.07
	He/H <sub>2</sub>	24.6	98.7	0.26	0.05
Ch-G-CaS2	Ar/He	25.2	98.6	0.32	0.07
	He/H <sub>2</sub>	24.8	98.6	0.24	0.05
Ch-G-CaS5	Ar/He	24.2	98.6	0.31	0.07
	He/H <sub>2</sub>	24.0	98.6	0.24	0.05

## Conclusion

Starch/chitosan/glycerol films were prepared to study the significant influence ( $p < 0.05$ ) of starch source and starch proportion over their microstructural properties. All samples revealed two phases, the first is a compact structure that is constituted by chitosan/glycerin and soluble fraction of starch. The second is composed by granules of starch distributed in the first phase. The granules of rice starch reveals irregular shape, elliptical forms and they are distributed in almost whole surface of the film. The granules of corn starch were round, more regular and homogeneously distributed in the film. The granules of cassava starch were ovals to round with edges and they were distributed rather anisotropic. It was found that the effective gas diffusion transport properties significantly depend on the starch source used. Differences in diffusion transport rates through the films prepared with different starches are related to the size and distribution of granules of starch in the films and/or the amylose content.

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