

PREPARATION AND EVALUATION BIOFOIL MATERIALS

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1. INTRODUCTION

Biopolymer films or biofoils are formed from natural polymers, of animal or plant origin, such as polysaccharides, lipids and proteins. The biopolymers are neutral and always renewable. Currently, the market for biodegradable plastic products is growing, there is a growing "cult", and even become a fashionable application. In our experiments we were looking for materials for thin film's production, which are natural and degradable.

2. MATERIALS

The guar gum in recent years, - as a polysaccharide isolated from natural sources, - have attracted increasing attention in biochemistry and pharmacology, due to their sustainability, biodegradability and biosafety. Guar gum is a natural nonionic polysaccharide extracted from the refined endosperm of cluster bean seeds, chemically classified as galactomannan. It is basically composed of a straight chains of D-mannose units, united by $\beta(1-4)$ glycoside linkages, and bearing a single D-galactose unit on approximately every alternate mannose, joined to it by an $\alpha(1-6)$ glycoside linkage (Fig. 1.)

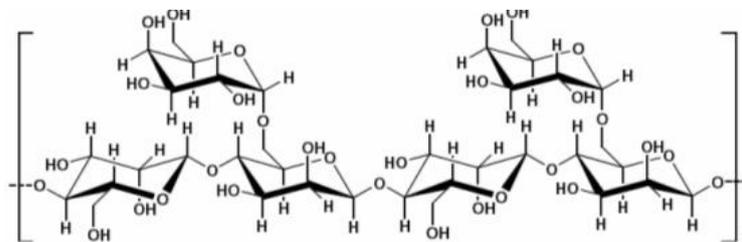


Figure 1. Guar gum

Pectins are cell wall polysaccharides which have a structural role in plants. They are predominantly linear polymers based on a 1,4-linked alpha-D- galacturonate backbone, interrupted randomly by 1,2-linked L-rhamnose. Polygalacturonic acid as the principal constituent is partly esterified with methyl groups, and the free acid groups may be partly or fully neutralized with monovalent ions (Na^+ , K^+ , NH_4^+). The degree of methylation (DM) has an essential influence on the properties of pectin, especially on its solubility and its ration of gelation which are directly derived from the solubility. The DM of 50 percent divides commercial pectins into high methoxyl (HM) pectins and low methoxyl (LM) pectins [1].

M pectins require a minimum amount of soluble solids (SS, e.g. glucose) and a pH within a moderate range around 3.0 in order to form gels. LM pectins require the

presence of a controlled amount of calcium ions for gelation, and need neither sugar nor acid. LM pectin gelation resembles to the behavior of alginate. D-Galacturonic acid blocks in pectins are almost mirror images of the L-guluronic acid blocks of alginates [1].

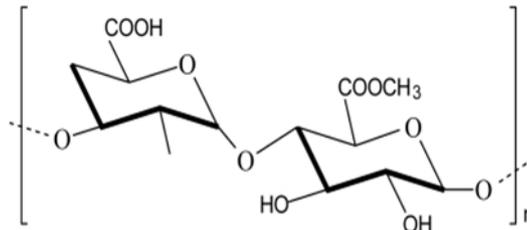


Figure 2. Pectin molecules

Gelatin is an irreversibly hydrolyzed form of collagen. Cattle bones, hides, skins, and fish are the principal commercial sources. The gelatin contains amino acids these values vary, especially the minor constituents, depending on the source of the raw material and processing technique. Gelatin is also used as a gelling agent and as a stabilizer, thickener, and texturiser for a range of products. Gelatin can be used as either a processing aid or an ingredient. In some cases, gelatin will comprise over 5% of a food. It has been commonly used in food, pharmaceutical, photography, and cosmetic manufacturing too.

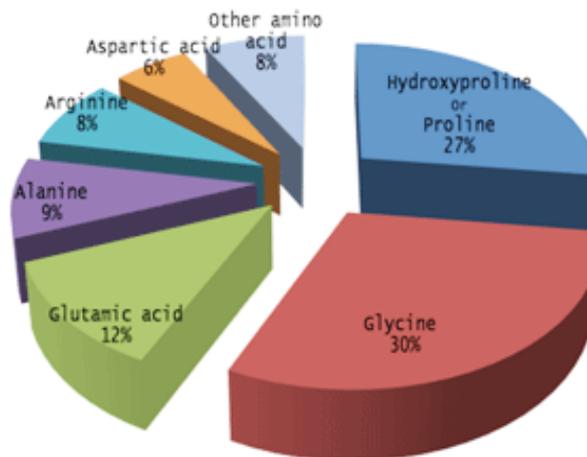


Figure 3. The approximate amino acid composition of gelatin

Gelatin is a mixture of peptides and proteins produced by partial hydrolysis of collagen extracted from the skin, bones, and connective tissues of animals. Gelatin is typical material used in the medical or pharmaceutical fields [2].

2. PREPARATION OF MATERIALS

For using casting techniques the following describes the method for each material. The films were produced of guar gum (DuPont Nutriflex - Danisco Guar gum), gelatin (PB gelatin, Gelatin UF220) and pectin (Kaldeneker(R) household citrus pectin).

Films were made from guar gum and gelatin, using 2 m/m % concentration aqueous solution in case of pectin we had to use 3 % extra glycerine to made useable film for

the measurement. The solutions were stirred using a magnetic stirrer at room temperature until total solving. The solutions were poured as thin layers in Petri dishes and dried at 35°C and 65% relative humidity for 24 hours. After drying the foils thickness varied around 0.20mm. The foils were immersed in distilled water for 1 to 15 seconds.

The foils were kept in desiccators applying CaCl₂ salt. Disks of 26 mm diameter were cut from the dried films and gold electrodes of 18 mm diameter were deposited by cathode sputtering in argon atmosphere. Applied vacuum was 0.05hPa.

3. MEASUREMENT TECHNIQUE

Depolarization measurements were carried out using a Setaram TSC II instrument by short-circuit method [3]. A new type specimen holder was constructed fixing the rim of the specimen. Polarizing field was 500V/mm at 120°C for 10 minutes. Cooling and heating rate was 5°Cmin⁻¹. Start temperature was -120°C, the end temperature was +100°C. The heat transfer medium was helium at about atmospheric pressure.

The evaluation procedure and the resolving method are described in [3] and [4]. Depolarization current was recorded and digitalized for evaluation. All spectra were normalized to 30 cm² electrode area and 1kV/mm polarizing field. Activation energies of transitions were determined by from the half width of the current peak as follows:

$$A = 2.406R \frac{1}{\frac{1}{T_l} - \frac{1}{T_u}} \quad (1)$$

In case of overlapped transitions the lower half of the transition was used,

$$A = 1.443R \frac{1}{\frac{1}{T_l} - \frac{1}{T_m}} \quad (2)$$

or in case of transitions from the upper half

$$A = 0.962R \frac{1}{\frac{1}{T_m} - \frac{1}{T_u}} \quad (3)$$

where T_m , T_l and T_u are the temperatures of maximum, the lower and upper half respectively, R is the gas constant (8.314 J mol⁻¹ K⁻¹).

$$I_{(s)} = C \exp \left\{ -s - B \left[e^{-s} (s^{-2} - 2s^{-3} + 6s^{-4} \dots) \right]_{s_0}^s \right\} \quad (4)$$

where A is the energy of activation, $s \equiv A/RT$, $C = AP_0/\tau_0$, and $B = A/Rb\tau_0$, A is the electrode area, b is the heating rate, P_0 the initial polarization, τ_0 was determined by eq. 5.

$$\tau_0 = \frac{RT_m^2}{bAe^{\frac{A}{RT_m}}} \quad (5)$$

where T_m is the temperature of peak maximum.

In the polarized state the individual molecular segments could began to moving on their specialized temperature. It is possible to measure the polymers in quasi static state, between $10^{-3} - 10^{-4}$ Hz frequency, which means very low deformation state. These means that the TSD is the most sensitive technique the evaluate polymers microstructure and molecular transformations. The depolarization spectra demonstrated in this paper are the output our evaluation software.

4. RESULTS AND DISCUSSION

In case of the guar gum three different reactions could be observed. The first is about -76 °C with 12.7 kJ/mol activation energy, might be the transformation of the two different conformation of the molecules.

The two other peaks at 22.8 °C with 46 kJ/mol, and at 55.5 °C with 45 kJ/mol activation energy belongs the two constitution molecules: the mannose and galactose.

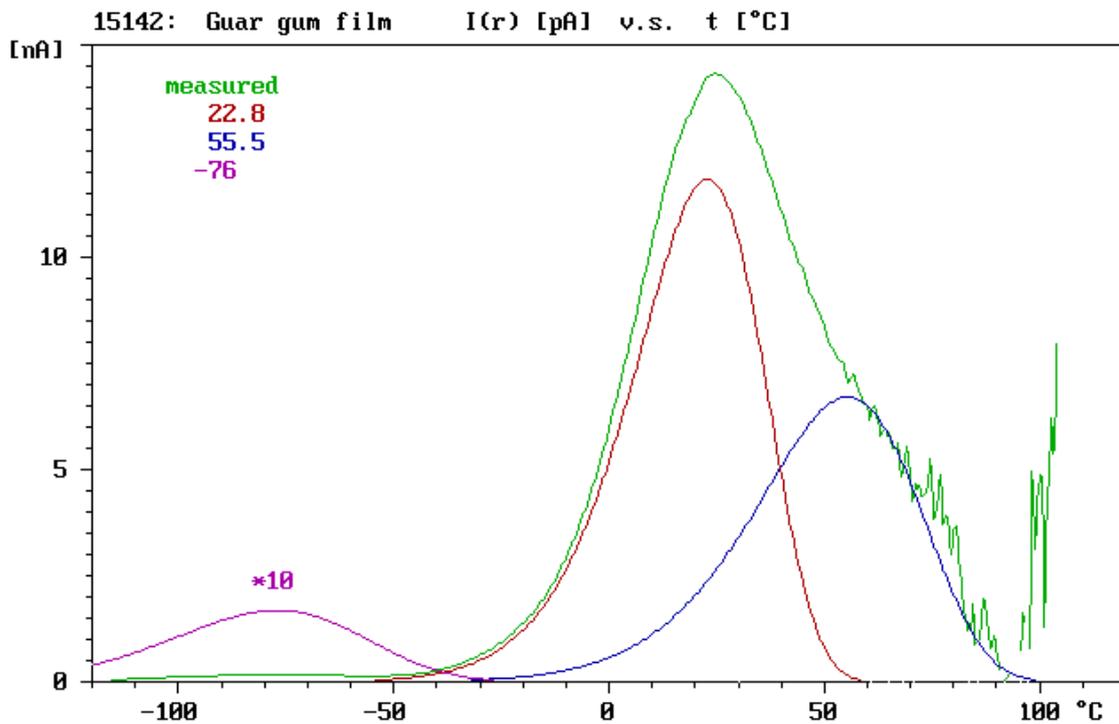


Figure 4. Resolved depolarization spectrum of guar gum

In case of the pectin and gelatine the two or three higher temperature peaks such as high activation energy that we have to highlight the low temperature peaks in another graph.

In case of pectin the first transformation peak is also could be found about -79.5 °C with 16.5 kJ/mol activation energy.

We could be observed four other peaks at -39.7 °C with 30 kJ/mol, at -8.2 °C with 55 kJ/mol, at 34.75 °C with 150 kJ/mol and 49 °C with 72 kJ/mol activation energy. The two lower might belong to the side chains and the two higher for the two constitution molecules. L and M pectins.

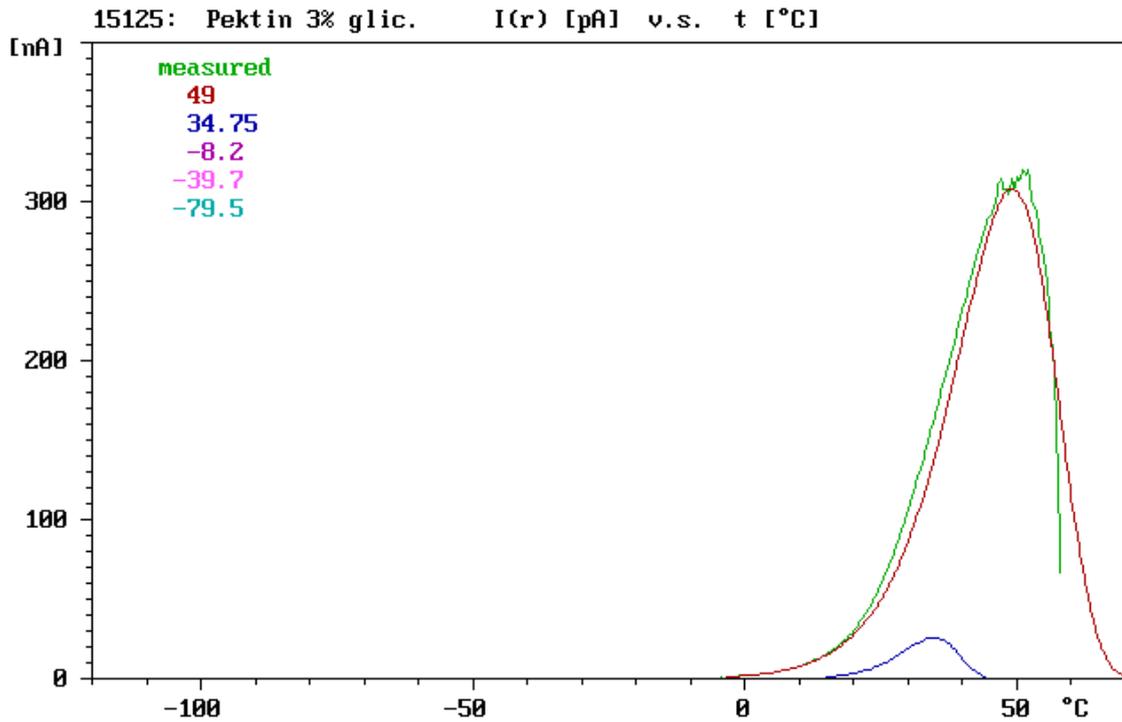


Figure 5. Resolved depolarization spectrum of pectin, higher temperature part

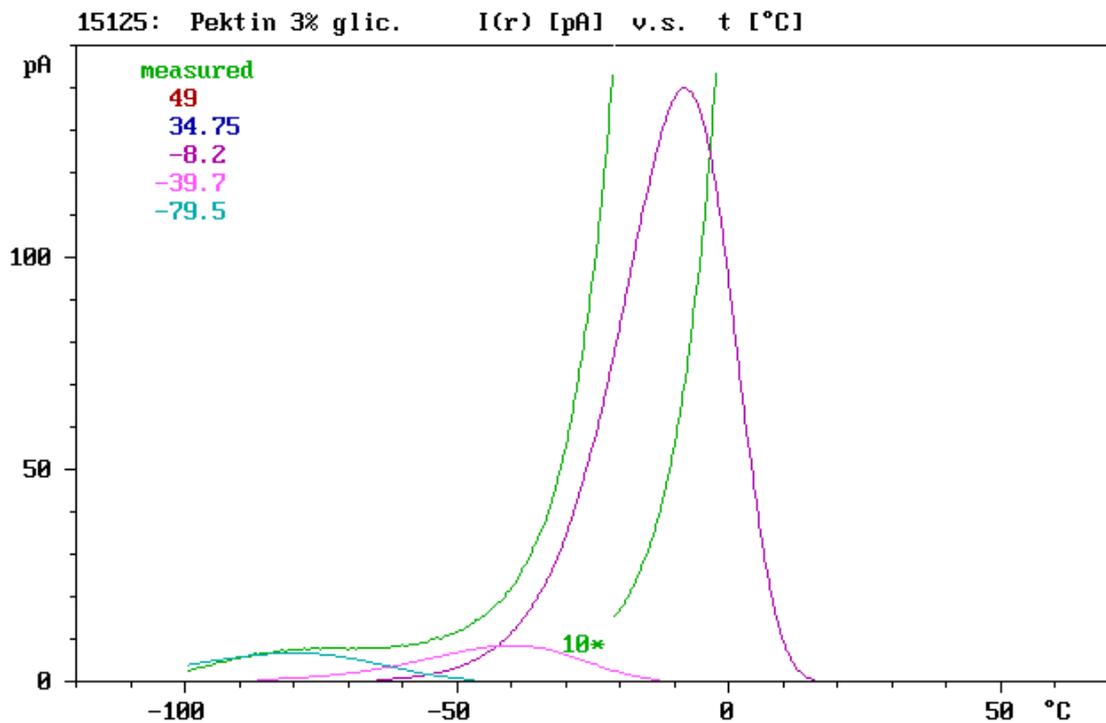


Figure 6. Resolved depolarization spectrum of pectin, lower temperature part

In case of gelatin the first transformation peak is also could be found about -81°C with 23 kJ/mol activation energy.

We could be observed four other peaks at -58°C with 51 kJ/mol , at 41°C with 42 kJ/mol , at 84.4°C with 76 kJ/mol and 113°C with 78 kJ/mol activation energy.

The first might belong to the side chains (-COOH) and the three higher for the different constitution structures.

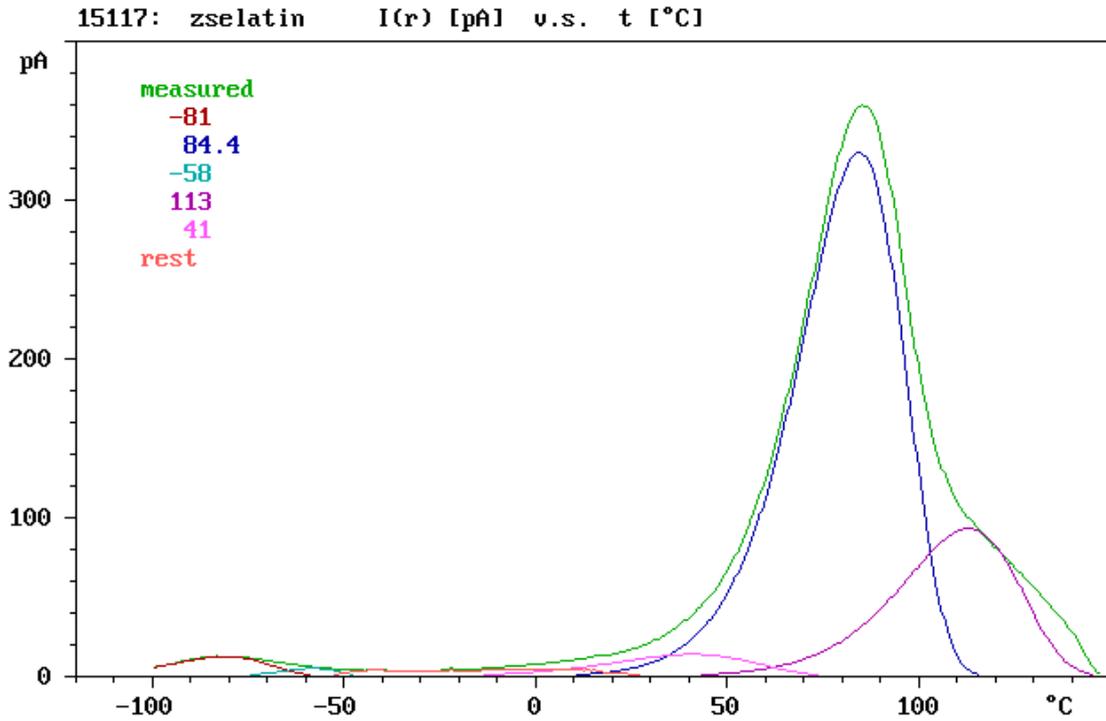


Figure 7. Resolved depolarization spectrum of gelatin

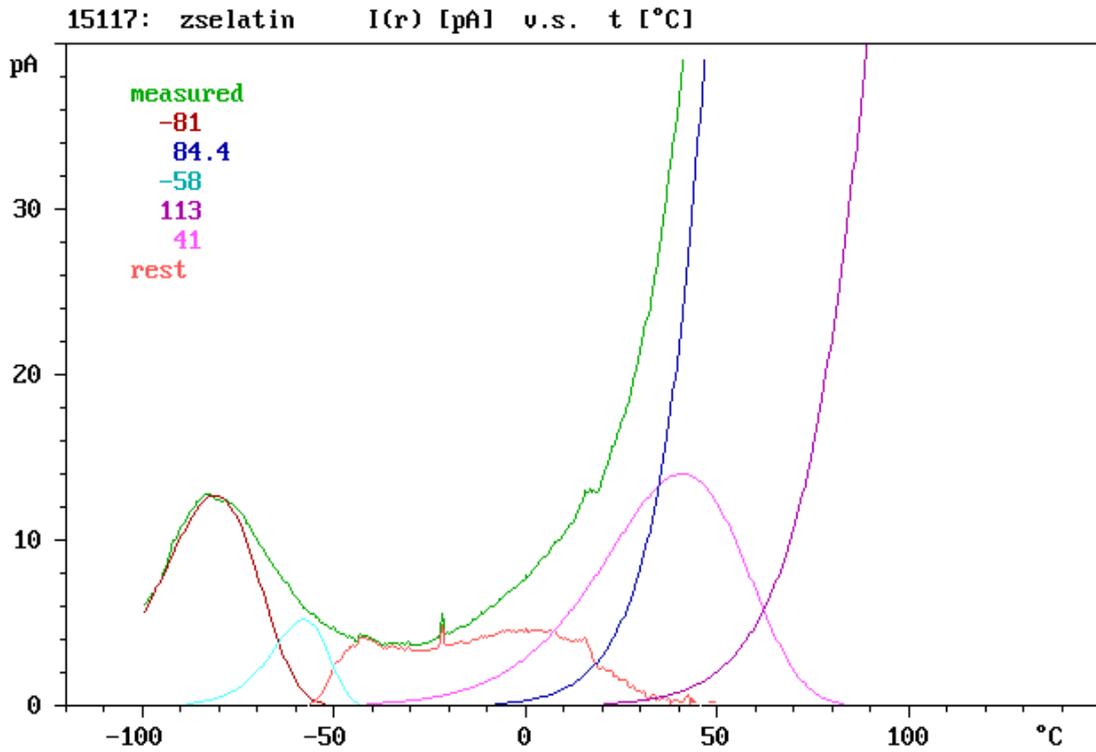


Figure 8. Resolved depolarization spectrum of gelatin, lower temperature part.

5. ACKNOWLEDGMENTS

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6. BIBLIOGRAPHY

- [1] Meenakshi Bhatia and Munish Ahuja, Thiol Modification of Psyllium Husk Mucilage and Evaluation of Its Mucoadhesive Applications, *The ScientificWorld Journal*, Volume 2013, Article ID 284182, pp1-7
- [2] Jian-Hua Li, Jing Miao, Jiu-Lin Wu, Shan-Fei Chen, Qi-Qing Zhang, Preparation and characterization of active gelatin-based films incorporated with natural antioxidants, *Food Chemistry*, Vol.02, 2014, pp. 632-638
- [3] Marossy,K: Assessment of activation energies of transitions by thermally stimulated discharge current (TSD) experiments. *Polymer Bulletin* Vol. 22, pp.213-220, 1989.
- [4] Marossy,K: Thermally stimulated discharge current (TSD) study on PVC-CPE blends. *Polymer Bulletin* Vol. 25, pp.385-390, 1991.