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Oxidative Polymerisation of Aniline Hydrochloride in High Viscosity Carbohydrate Gels

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ABSTRACT

The new route to novel class of natural/synthetic polymer system is described. The material based on common and natural carbohydrates i.e. starch and carrageenan as well as synthetic, conducting polymer, polyaniline dissolved in dimethylsulfoxide is shown as a system with interesting viscoelastic properties. The presented research covered synthetic aspects of a new material as well as some rheological properties by means of mechanical and relaxation spectra.

KEYWORDS

starch, carrageenan, polyaniline, mechanical spectra.

INTRODUCTION

As a one of the most common biopolymer starch focuses a lot of research [1]. Most of them concerned on water/carbohydrate system or water/dimethylsulfoxide (DMSO)/starch system [2]. There is only a few papers dealing with non-aqueous starch solution and gels [3]. From the other hand the water free systems may carry interesting physicochemical properties and find hundreds of new nonfood applications.

Nowadays there is a growing interest in introduction of biodegradable materials even there where synthetic materials was up today the only one solution. One of the most interesting, renewable and biodegradable materials are carbohydrates. In this group starch and cellulose of different botanical origin focuses a lot of research and find many non-agricultural application. The further modification of raw carbohydrates could easily guide to the broad group of materials with different properties according to the method of modification.

From the other hand, in the group of synthetic macromolecules conducting polymers could be characterised by the growing interest in as well scientific and industrial application. Such phenomenon seems to be caused by its very interesting physicochemical properties but processing of conducting polymers suffers from insolubility in most common solvents what dramatically limits their application [4]. 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 [5]. The problem of insolubility of PANI is partially solved by protonation of a polymer chain by carboxylic acids with long aliphatic "tails". Such dopants however reduce the conductivity of the polymer [6].

As a continuation of our earlier research on the field of chemical modification of starch and other polysaccharides [7] we now report the synthesis of three component carbohydrate/polyaniline gels. The described material is a carrier of many interesting mechanical properties what was proofed by rheological analysis.

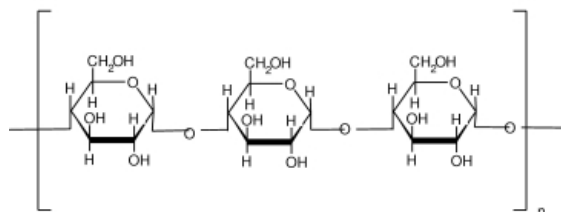


Figure 1: Simplified structure of linear fraction of starch - Amylose

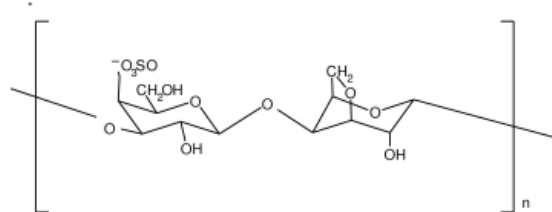


Figure 2: Simplified structure of carrageenan subunit

EXPERIMENTAL

1. Synthesis of the gel

Polymerisation of aniline hydrochloride was carried out in carbohydrate gel obtained by dissolving starch and carrageenan in pure DMSO.

Because of the good solubility the highamylose starch was used for all experiment (*Hylon VII*). Addition of carrageenan allowed to obtain a gel with better stability and elasticity.

a) Carbohydrate gel:

The appropriate gel was obtained by dissolving of starch (Figure 1) and carrageenan (Figure 2) in hot DMSO (70°C) in approximately 3 hours. Carbohydrate matrix was prepared according to keep the concentration of starch at the level of 10%. The concentration of carrageenan varied from 20% to 40% when compared to starch. In typical experiment 4g of starch was used and 0.8g of carrageenan what guide to 20% carrageenan versus starch concentration. Dissolving process was aided by mechanical stirring of the system (200rpm).

b) Polimerisation of aniline hydrochloride (ANI-HCl)

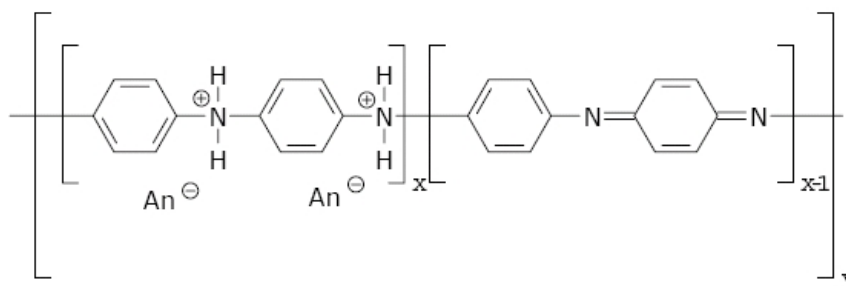


Figure 3: Simplified structure of polyaniline

50mL of obtained carbohydrate gel was cooled down and transferred to the reaction vessel that was equipped with the cooling mantel jointed together with thermostate operating with ethylene glycol as a cooling agent. Temperature was set at 0°C. To the precooled gel ANI-HCl (16mmol) was added and the system was vigorously stirred in order to dissolve the monomer in the medium. Freshly prepared oxidant solution (19mmol ammonium persulphate dissolved in DMSO) was dropwise added when stirring. After the addition of oxidant was finished the system was stirred for another 2 hours and afterwards kept under nitrogen.

2. Rheological measurements [8]

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 [9] was fitted to the experimental data. Calculations were carried out using Tikhonov regularization method [10].

RESULTS AND DISCUSSION

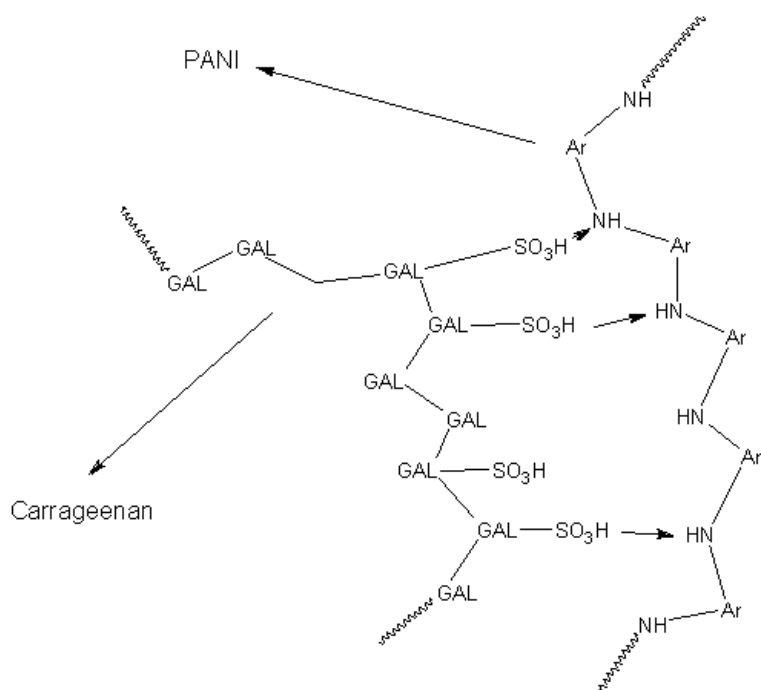


Figure 4: Polyaniline carrageenan compatibilisation mechanism.

biodegradability of the material.

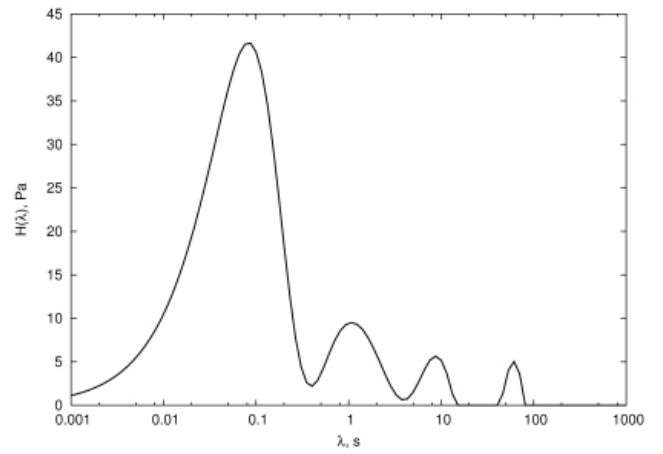
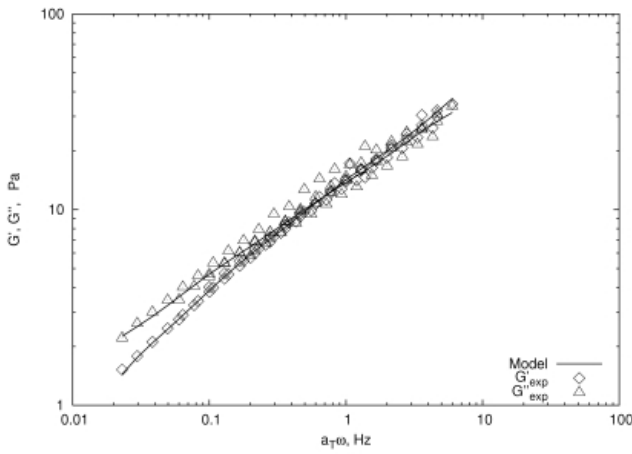
Rheological properties of obtained gels are presented at Figure 5. At is easy to see 20% and 30% systems may be classified as those lying int the flowing zone ($G'' > G'$). Application of superposition of time and temperature does not cause the broadening of the observation horizon. and the a_T parameter lie around 1.00. Relaxation spectra for these two gels are similar and contain two peaks from which, one (at lower frequencies) is multimodal. Such hetroogeneous structure testifies about the complicated mechanism of the relaxation in material. From the other hand 40% gel has completely different properties. $G' > G''$ and the curves shape testifies that system lies near the plateau zone. Superposition rules allowed in this case to broaden the observation window. The relaxation spectra is more homogeneous but the peak is still multimodal. All these phenomena allow to

As a result of our investigation we have obtained a series of dark blue gels with interesting mechanical properties. As far as we know presented synthesis opens the gate to the production specific materials based on biopolymer matrix and conducting polymer in non-aqueous conditions. Although the properties of the final material are interesting, further development of the set up is needed. Especially in order to remove some inorganic ions from the system. Ammonium persulphate is known as a powerful oxidant for polyaniline production but its reduction products may interffer the conductivity in high viscous media and are heavy to remove.

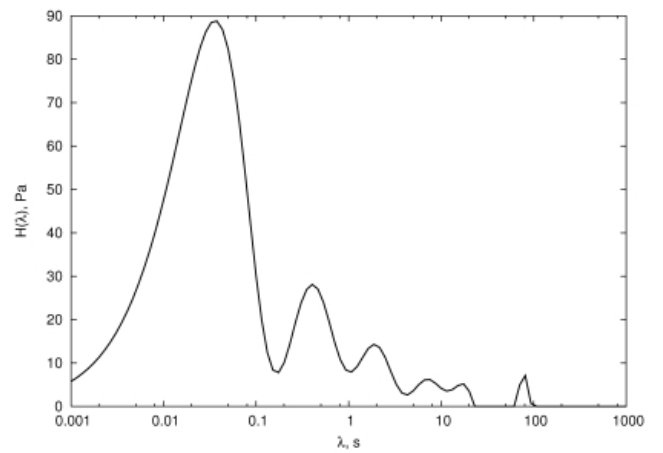
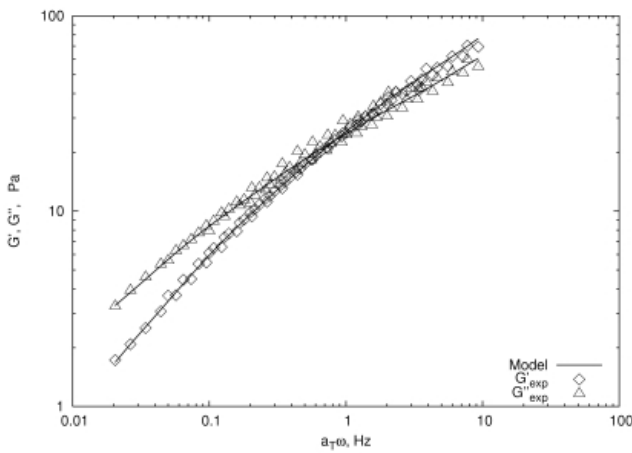
The choice of polysaccharide seems to be crucial for resulting material. First, starch is a common, cheap and worldwide produced carbohydrate that may play the role of true matrix for the system. From teh other hand carrageenan has specific molecular constitution. Galactopyranose subunit are substituted with acidic sulfonic group. Such composition might carry two different levels of compatibilisation. Starch and carrageenan as typical carbohydrate make the matrix homogeneous by means of macro-properties. From the other hand sulfonic group of carrageenan may protonate the amine and imine groups of PANI what causes further compatibilisation of natural and synthetic system (Figure 4) as well as increasing the conductivity. The second effect is weaker due to the presence of HCl from ANI-HCl but can not be passed over. At the presented, preliminary stage of investigation all those mechanism are equally propable.

The compatibilisation of two group of polymers i.e. carbohydrates and conducting compounds seems to be the natural evolution of modern polymer technology requiring the very specific properties linked with

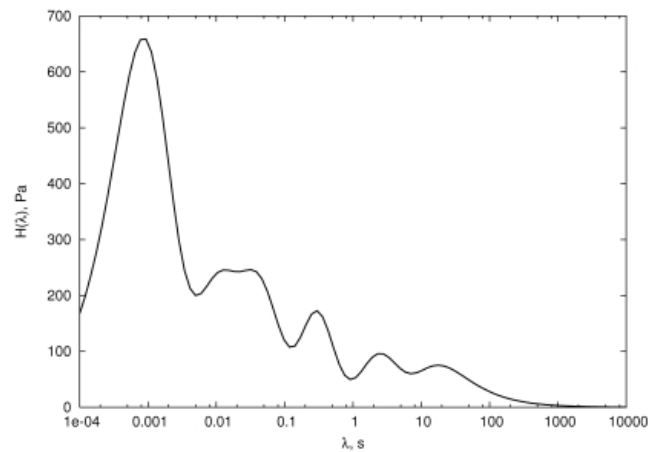
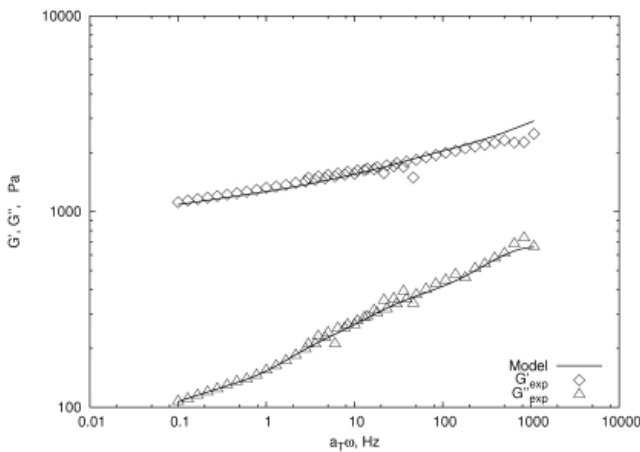
suppose that described material is more elastic than two gels discussed above.



I.



II.



III.

Figure 5. Mechanical (left -A) and relaxation spectra (right -B) of investigated polyaniline gels at different carageenan concentration: I - 20%, II- 30% and III - 40%.

Going into conclusion it is worth to pointed out that, the described investigation shows the possibility of obtaining new hybrid natural/synthetic blend with interesting properties which could be used at different fields of application. From the other hand obtained materials are almost fully biodegradable what is one of the most important factors of modern materials.

There is also worth to pointed out that the applying of the time and temperature superposition for the described system is possible in broad the range of frequency and give a lot of interesting application about system behaviour.

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