Synthesis and properties of three component carbohydrate/polyaniline blends

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ABSTRACT

The obtaining of novel class of natural/synthetic polymer blends is described. The material based on common natural carbohydrates i.e. starch and carrageenan as well as synthetic, conducting polymer, polyaniline in dimethylsulfoxide is shown as a system with interesting rheological properties. The presented research is focused on topology of the thin layer obtained by slow evaporation of polymers solution and some rheological properties by means of mechanical spectra.

KEYWORDS

starch, carrageenan, polyaniline, mechanical spectra, AFM.

INTRODUCTION

Because of the fight with environmental pollution as well as the problems with exhausting petroleum deposits modern chemistry and technology has already been touring to biodegradable and renewable materials which originated from plants or animals. The main group of such materials are carbohydrates which could be produced in "never-ending amounts". Starch is an perfect example of such a compound because of the price, accessibility and many possible application [1]. From the other hand there is also a lot of different polysaccharides with many interesting physiochemical properties. The introduction and application of such compounds at the field occupied by full synthetic chemistry is still rising [2].

Among plenty of available synthetic macromolecules conducting polymers could be characterised by the growing interest as well in scientific and industrial application. The phenomenon could be explained by its very interesting physiochemical properties. From the other hand most of conducting polymers are completely insoluble in common solvents what dramatically limits its application [3]. 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 [4]. 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 [5].

As a continuation of our earlier research on the field of chemical modification of starch and other polysaccharides [6] we now report the synthesis of three component carbohydrate/polyaniline blends. The described material is a carrier of many interesting mechanical properties what was proofed by rheological and topological analysis.

EXPERIMENTAL

1. *Synthesis of polyaniline*
   The polymerisation of aniline (prior distilled in vacuum) was carried out using classical oxidative polymerisation process conducted in the presence of potassium peroxidisulphate as the oxidant [7]. The reaction was set up below 4^{o}C in the HCl water solution with the molar ratio aniline:oxidant 1:1,25. Aniline was dissolved in the acid solution, cooled down to 0^{o}C. To this mixture the solution of oxidant in HCl was added drop wised according to the temperature which could not exceed 4^{o}C. After the oxidant was added the mixture was stirred for 2 hours to complete the reaction. The precipitated polymer in its emeraldine form was washed with water and methanol. Polymer was deprotonated using 25% ammonia (24 hours), dried and in order to remove some oligomers the extraction with methanol was done.
2. *Blend obtaining*
   15% w/w of high amylose maize starch (Hylon VII) solution in pure DMSO was obtained by dissolution of the carbohydrate at 60^{o}C with intensive stirring. To the obtained solution carrageenan was added (5 - 35% carrageenan/starch ratio) and suspension was stirred for 30min and the previously described polyaniline solution was added. The final dispersion was stirred for another 30 min what allows to obtain a fine gel.
3. *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^{o}C - 60^{o}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^{o}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].
4. *AFM imaging*
   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: 40µm x 40µm, scanning frequency range: 5-10 Hz, resolution 1024 (samples/line).

RESULTS AND DISCUSION

As a result of our investigation we have obtained a series of dark blue gels with interesting mechanical properties. As it was found after the slow evaporation of the solvent i.e. dimethyldulfoxide the thin layers could be produced which has a good tearing resistance and because of electrical properties of polyaniline may also find many application. The set up of the gel obtaining process is very easy and do not need any sophisticated method. From the other hand it is known that polyaniline can not be dissolved in DMSO completely, so the fraction of conducting polymer introduced into the gel matrix might be characterise rather as low molecular fraction. Because authors have already found that some polysaccharides could also be dissolved and form some kind of gel in N-methylpyrrolidone which is the best known polyaniline solvent, the process of building the higher molecular material (by means of PANI) could be improved [11].

Figure 1 shows the result of the mechanical investigation of three component gels by means of rheological data. It is easy to observed that the increase the carrageenan concentration has a big influence on the mechanical behaviour of the system. For low concentrated (by means of carrageenan) systems the liquid-like behaviour could be noticed, however at higher frequencies the crossover of G' and G" takes place and the elastic properties may be observed. At higher concentration the elastic properties are easy to observed at the whole frequency frame. In this cases the G' and G" curves are almost parallel.

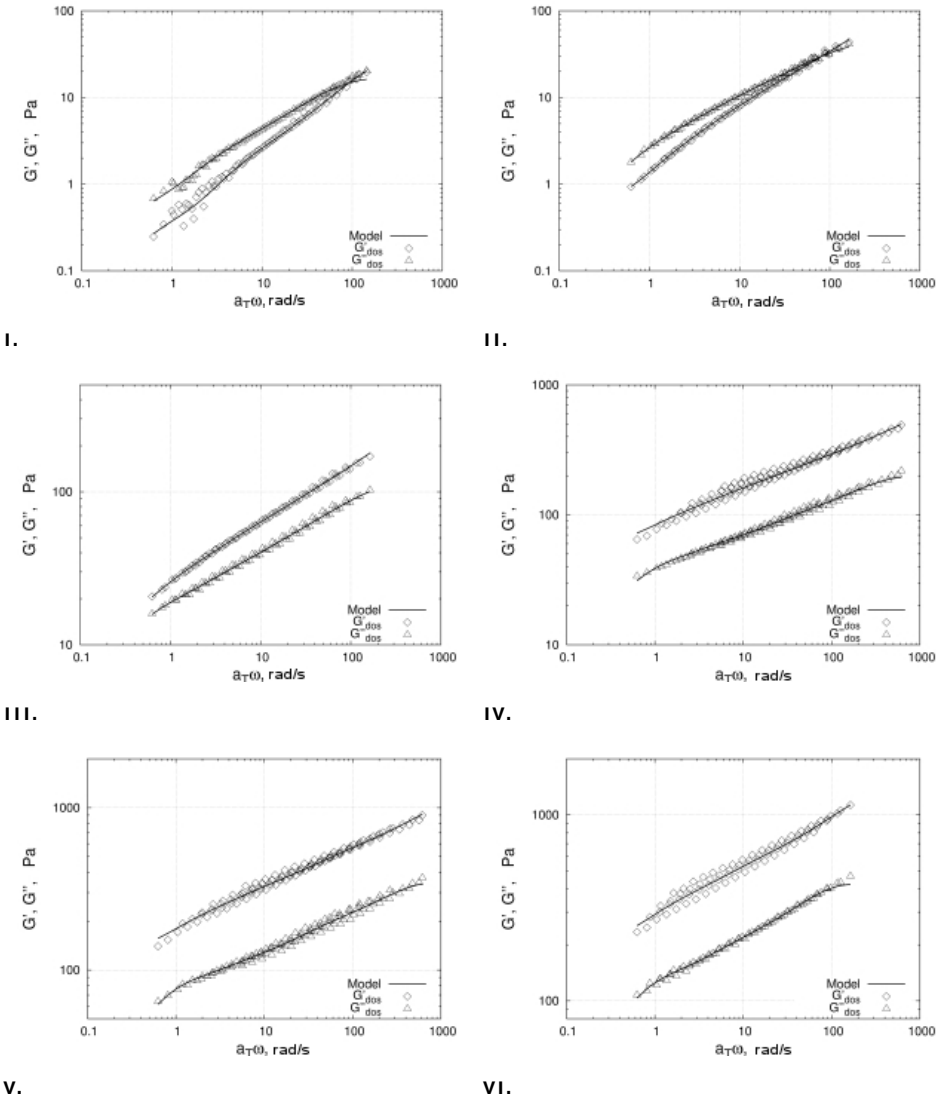


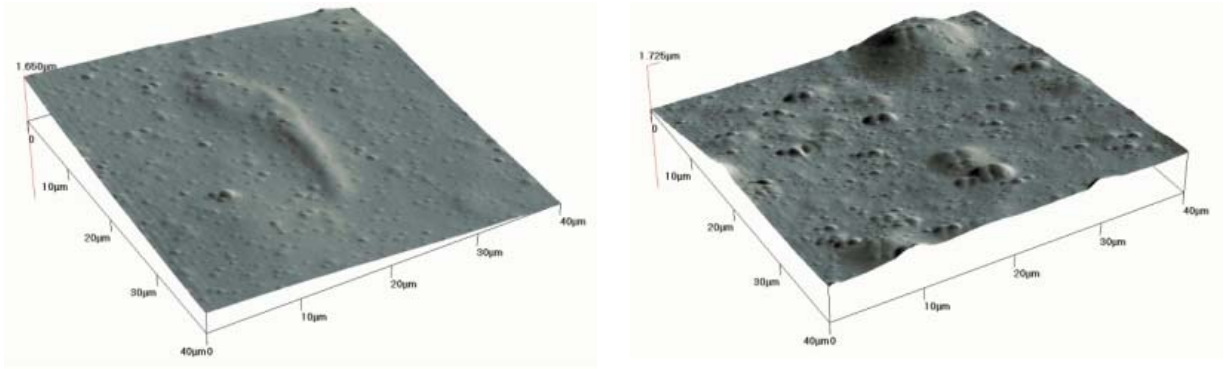
Figure 1: Mechanical spectra of starch/carrageenan/polyaniline gels. I - starch/carregeenan ratio 5%, II - starch/carregeenan ratio 10%, III - starch/carregeenan ratio 15%, IV - starch/carregeenan ratio 20%, V - starch/carregeenan ratio 25%, VI - starch/carregeenan ratio 35%. G'_{dos} and G''_{dos} - experimental data.

The elastic properties of the systems could be also be proofed by the calculation of G_e parameter (Table 1). At is known that if the parameter could be calculated (is not equal to 0) it testifies about the solid state behaviour. The increase of described parameter in the higher concentrated carrageenan systems may be found in Table 1.

Table 1: Equlibria modulus for obtained gels.

ID	carragenan concentration [%]	G_e [Pa]
1	0	-
2	5	-
3	10	10,32±2,00
4	15	17,71±1,07
5	20	56,79±2,28
6	25	126,38±3,53
7	35	195,03±7,67

The AFM spectra presented at Figure 2 shows the heterogeneity of the gel what might be the consequence of the some insoluble parts of the carrageenan but this deduction failed with the rheological investigation. The phenomenon needs further investigation.



I. **II.**

Figure 2: AFM images of starch/carragenan/polyaniline gels. I - starch/carregenan ratio 5%, II - starch/carregenan ratio 10%.

As a conclusion we can say that obtained material seems to be very promising by means of different fields of application. Its rheological properties as well as simply set up might be the key for introduction of polyaniline/polysaccharide gels in both laboratory and industrial scale. From the other hand further investigation i.e. conformational research, mechanical behaviour in protonated state and so long needs to be done and are in progress.

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

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