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Carboxymethylcellulose/polyaniline blends. Synthesis and properties

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Summary

Polyaniline (PANI) as one of the conducting polymers focuses intensive research on both scientific and practical field. There are quite a lot of known hybrid materials of PANI and other polymer systems with various synthetic polymers, which results in blends with various properties. The presented research covers the blends of polyaniline with semisynthetic (carboxymethyl) cellulose (CMC). The system could lead to a new antielectrostatic material with interesting properties and seems to be applicable as an additive for packaging in both food and non-food industry. The final material was obtained using both protonated (HCl) and deprotonated form of polyaniline in its semi-oxidized form of leucoemeraldine. Blending consisted in obtaining of thin layer by slow evaporation of the solvent from a mixture of PANI and CMC. For the main investigation atomic force microscopy (AFM) in non-contact mode was used, which gave the topological information about the surface and also some structural information about the material.

The described process seems to be very interesting as a route for obtaining a new hybrid natural/synthetic material with very interesting properties and a potential for application.

Introduction

Among plenty of available synthetic materials, conducting polymers could be characterised by growing interest in their industrial and scientific applications [1]. The phenomenon could be explained by their interesting physiochemical properties. On the other hand, most conducting polymers are completely insoluble in common solvents, which dramatically limits their application [2]. One of the most known and investigated conducting polymer is polyaniline (PANI), a compound existing in several oxidation states, the conductivity of which strongly depends on protonation

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with organic or inorganic acids [3]. The problem of insolubility of PANI is partially solved by protonation of a polymer chain by carboxylic, phosphonic or sulfonic acids [4]. Such dopants, however, reduce the polymer conductivity.

On the other hand, there is a growing interest in introduction of biodegradable materials even in the fields where synthetic materials have been so far the only solution [5]. One of the undepleted and renewable biodegradable materials is carbohydrates in particular starch and cellulose of different origin. Further modification of raw carbohydrates could lead to a large group of materials with different properties depending on the method of modification [6].

Compatibilisation of the two groups of polymers, i.e. carbohydrates and conducting compounds, seems to be the natural evolution of modern polymer technology requiring very specific properties associated with biodegradability of the material.

Experimental

Synthesis of PANI

Polymerization of aniline (vacuum-distilled) was carried out using classical oxidative polymerization conducted in the presence of ammonium peroxydisulfate as the oxidant [7]. The reaction was conducted below 4 ^{o}C in aqueous HCl with the molar ratio aniline: oxidant 1:1.25. Aniline (10 mmol) was dissolved in 50 mL of 1.5 mol/L HCl and cooled to 0°C. To the mixture a solution of oxidant in HCl (1.5 mol/L) was added dropwise below 4°C. After the oxidant was added the mixture was stirred for 2 h to complete the reaction. The precipitated polymer in its emeraldine form was washed with water and methanol. Polymer was deprotonated using 25 % ammonia (24 h), dried and extracted with methanol to remove oligomers.

Blend preparation

(Carboxymethyl) cellulose (CMC) was dissolved in water to 1.5 %wt. solution. PANI was dissolved in tetrahydrofuran during 24 h. THF does not influence the CMC solubility in the mixture. Then the PANI solution was centrifuged to remove some insoluble part. The amount of dissolved PANI was calculated to be ca. 0.15 %wt. in the solution and 0.5 %wt. in the final layer. The molecular weight of the PANI fraction which is soluble in THF is ca. $2\cdot10^3$ g/mol [8]. The THF solution of PANI was mixed with a water solution of CMC and vigorously stirred for 30 min. The obtained mixture was left standing to evaporate the solvents for ca. 72 h. The obtained films were used for further study or protonated in concentrated solution with gaseous HCl at room temperature for 24 h.

AFM

Atomic force microscopy (AFM) provides analysis of surface and internal structure of numerous objects [9]. AFM could be used to characterize the surface of soft organic materials, thin films of biopolymers and blends of polymers [10].

AFM scans were performed using a Quesant “Nomad” model. Scanning was done in the non-contact mode. The parameters of scanning head were as follows: scanning area: 5 μm ×5 μm and 40 μm ×40 μm, scanning frequency range: 5-10 Hz, resolution 1024 (samples/line).

Mechanical properties

Mechanical properties were measured of a specimen with dimensions of 20 mm·×100 mm on Instron 4301.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was performed on a Netzsch DSC-200, operating in dynamic mode, under the following conditions: sample weight ~4 mg, heating/cooling rate 10 K/min, argon (30 $cm^3 \cdot min^{-1}$), sealed aluminum pan. The calorimeter was calibrated with an indium reference. Analyses were made in single run and in two segment modes including heating/cooling and reheating/cooling.

Results and discussion

As a final result we have obtained thin films of blend of two polymers with different thickness which depends on concentration of the main polymer ,i.e., CMC and the form of PANI. Comparing the thickness of materials based on 1 %wt. CMC (Figure 1) we observed an increase in the thickness especially for the layer including protonated polyaniline.

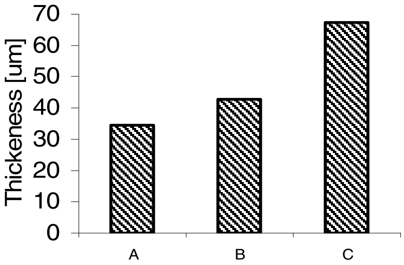

Figure 1: Thickness of blend films obtained from: A – film obtained from 1 %wt. CMC; B - 1%wt. CMC and 0.15 %wt. of deprotonated PANI; C- 1 %wt. CMC and 0,15%wt. of PANI after protonation.

This seems to be the result of the method of protonation with gaseous acid. Water evaporating from the concentrated solution of HCl could loosen the structure of the blend resulting in the thickening. This could be proved also by mechanical measurements.

Table 1. Basic mechanical properties of CMC and its blends.

Sample	Maximum Strain [%]	Stress at Brake [MPa]
1% wt. CMC	9.3	27.9
1 %wt. CMC + PANI	3.38	21.2
1 %wt. CMC + protonated PANI	5.56	2.97

Stress at brake for the protonated material drops dramatically when compared with CMC and CMC/PANI blends. On the other hand, mechanical properties of neat CMC films are in every case better than those of its blend with PANI. However, the lowest value of maximum strain is observed for the blend with deprotonated PANI.

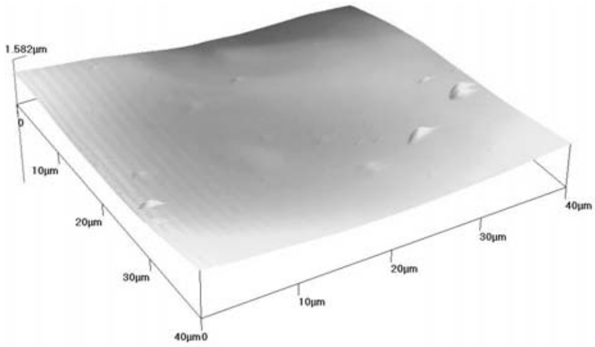

Figure 2: AFM scan (40 µm × 40 µm) of the CMC film surface.

The main goal of the investigation was a topological study at the AFM scale. The film of neat CMC (1 %wt.) shows (Figure 2) complete homogeneity, as it could be predicted. The surface of the film is almost smooth excluding several points which could indicate incomplete dissolution of CMC.

Different morphology is observed for a neat PANI based film obtained by evaporation from THF (Figure 3a and 3b). The surface in this case is much more undifferentiated: however, it is still smooth and homogeneous. Enlargement of the scale (Figure 3b) definitely shows a "granular" structure of the surface but no discontinuity is present. The clusters on AFM scans have the diameter ca. 1 µm, which can be estimated from cross-section analysis through different parts of image. The cross-sections show maxima having separations on the micrometer scale.

The globular morphology observed at all levels of magnitude is consistent with the presence of aggregates which are the result of chain interaction or self-association with hydrogen bonds. This could also suggest that film growth results from the nucleation of particles on the surface where the lateral growth rate is high compared with their growth in height.

Different surface composition is observed for blends of PANI and CMC. On the scan of CMC/PANI base (Figure 4), the surface has a slightly looser composition and the

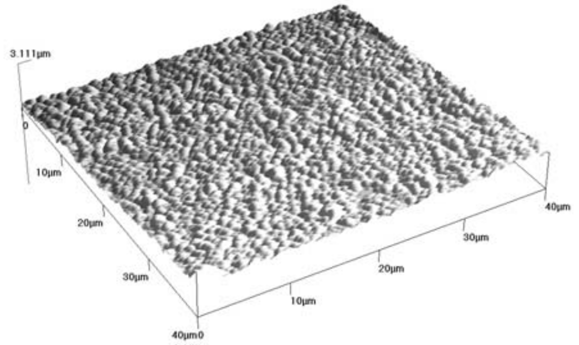

Figure 3a: AFM scan (40 µm x 40 µm) of the PANI film surface.

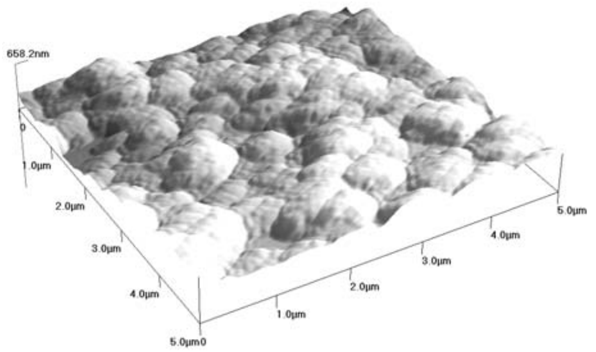

Figure 3b: AMF scan (5 µm x 5 µm) of the PANI film surface.

fragments of identified PANI are separated by CMC. The AFM scans also shows that during evaporation of the solvents no absence of mixing of polymer chains occurs, which was very often one of the obstructions in repeated obtaining of blends.

Increased changes are observed for a protonated blend (Figure 5a and 5b). The structure shows wide bands and the regions occupied by CMC are much easier to identify. It seems there is no bouncing network. Such observation corresponds with worse mechanical properties of the blend discussed above. The scan (Figure 5b) shows some crystal-like structure. The origin of such phenomenon might be the reaction of gaseous HCl with CMC which is the sodium salt. The products of the reaction could be the corresponding acid form of CMC and sodium chloride. On the other hand, the shape of crystals does not fit to those known for NaCl but deformation may be the result of polymer interactions so the problem needs further investigation.

The final stage of research was investigation of thermal properties of blends. Polyaniline is one of thermally stable polymers [11]. Such fact has a great importance depending on application. The matrix which belongs to long-chain polysaccharides is also known as heat-resistant. Differential scanning calorimetry of CMC and its blends with PANI shows that all kinds of the material degrade above 300°C. All samples show a broad endothermic peak at about 80 – 85°C which is probably the result of residual water evaporation from both carbohydrate matrix and polyaniline [12].

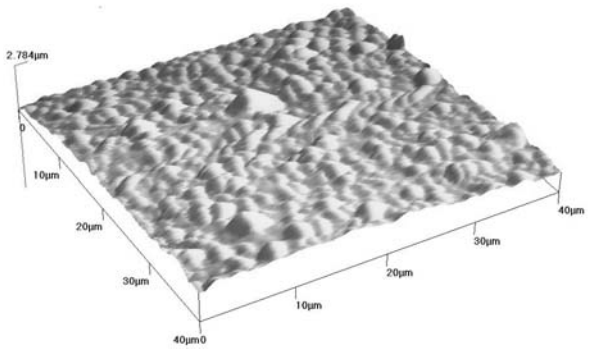

Figure 4: AFM scan (40 µm x 40 µm) of the CMC/(PANI acid form) film surface.

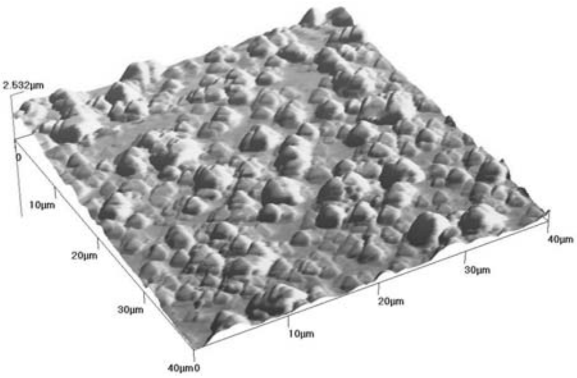

Figure 5a: AFM scan (40 µm x 40 µm) of the CMC/(PANI acid form) film surface.

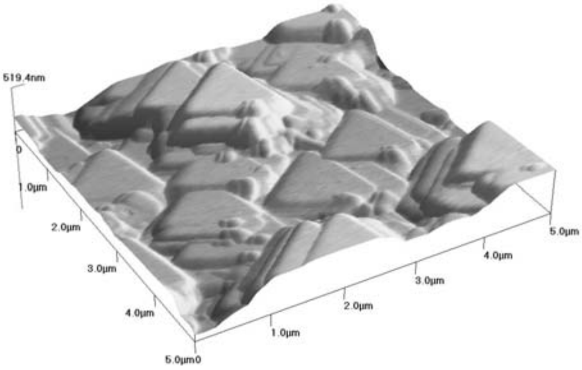

Figure 5b: AMF scan (5 µm x 5 µm) of the CMC/(PANI acid form) film surface.

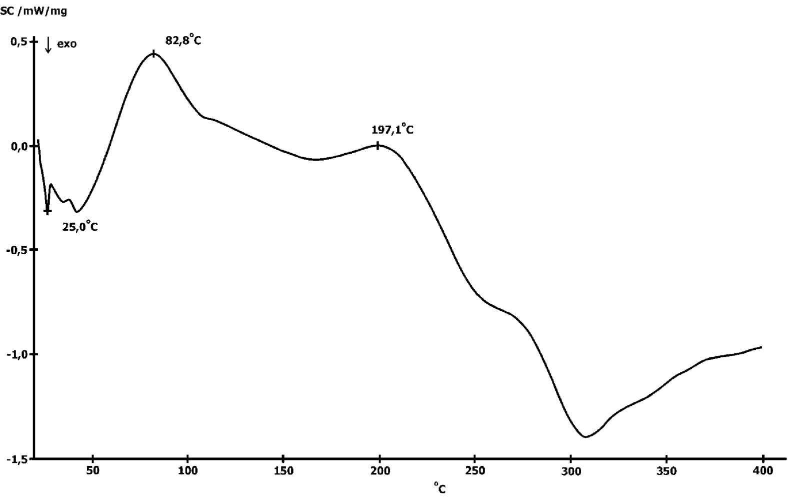

Figure 6: Thermogram of the blend obtained from 1 % wt. CMC and 0.15 %wt. of PANI after protonation.

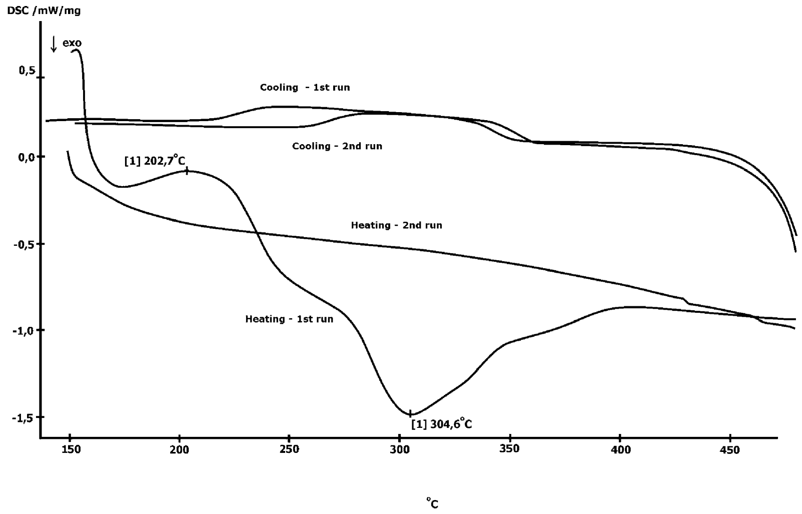

Figure 7: Thermograms of blend obtained from 1%wt. CMC and 0.15 %wt. of PANI after protonation.

For neat CMC and its blend with deprotonated PANI there is only one peak except those corresponding to degradation. In the thermogram of protonated CMC/PANI (Figure 6) an additional, small endothermic peak appears at about 197°C, which might be the result of some changes in the blend structure occurring at protonated nitrogen atom of polyaniline such as the acid dopant (HCl) loss or decarboxylation of CMC [13]. The DSC measurement in the heating-cooling mode (Figure 7) confirms the elucidation because all transformations are irreversible, not detected in the second run.

Conclusion

The described investigation shows the possibility of obtaining new hybrid natural/synthetic blends with interesting properties which could be used in different fields of application. The phase separation observed especially in protonated films could result in worsening of mechanical properties of the blends and probably lower conductivity of PANI but the material should still be able to serve as an antielectrostatic additive, which has a great importance, e.g. packaging. On the other hand, the obtained material is almost fully biodegradable, which is one of the most important factors for modern materials.
We have also prooved that AFM technique is very useful for investigation of changes in morphology of both conducting polymers and synthetic-natural polymer blends.

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