

Preparation and Characterization of Potentially Antimicrobial Polymer Films Containing Starch Nano- and Microparticles

Paulius Pavelas DANILOVAS*, Vesta NAVIKAITĖ, Ramunė RUTKAITĖ

Laboratory of Biopolymer Research, Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu pl. 19, LT-50254 Kaunas, Lithuania

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The forming conditions of biodegradable polymer films containing iodine-modified starch particles as well as the properties of the obtained films were investigated. Cationic cross-linked starch microparticles and cationic starch nanoparticles were dispersed in cellulose acetate and hydroxyethyl cellulose solution, respectively, and composite films were spin-casted. The obtained films were characterized and their mechanical properties were assessed. The cellulose acetate solution has been found to be an appropriate matrix for the dispersion of dry modified starch microparticles, but not in the case of nanoparticles. Starch nanoparticles were obtained in an aqueous medium, and the mechanical properties of the formed cellulose acetate films are significantly reduced by water present in the casting solution. It has been estimated that a fairly high amount of nanoparticles (18 wt%) can be immobilized into films of water-soluble hydroxyethyl cellulose without markedly affecting the mechanical properties of the films.

Keywords: biopolymers; cationic starch; iodophores; nanocomposites.

1. INTRODUCTION

Contamination by microorganisms is of great concern in a variety of areas, such as medical devices, healthcare products, water purification systems, hospitals, dental office equipment, food packaging, food storage, household sanitation, etc [1, 2]. Various kinds of plastics are usually sterilized by means of either dry/wet heat or ionizing radiation [3]. However, these polymers can be contaminated or infected by microorganisms such as bacteria, if they are exposed to the atmosphere. Therefore, there is a definite need for new materials with antimicrobial properties. Antibacterial polymers can provide a very convenient way for achieving this goal.

The use of antimicrobial polymers is promising for enhancing the efficacy of some existing antimicrobial agents and minimizing the environmental problems accompanying conventional antimicrobial agents by reducing the residual toxicity of the agents, increasing their efficiency and selectivity, and prolonging their lifetime. Also, an advantage of polymeric antimicrobial agents is that they are non-volatile, chemically stable and do not permeate through skin. Therefore, they can reduce losses associated with volatilization, photolytic decomposition, and transportation.

Iodine is an antiseptic that has been used in wound care for more than 150 years. It has a broad spectrum of antimicrobial activity, rapidly inhibiting bacteria, yeasts, moulds, protozoa and viruses [4]. However, iodine stains the skin and may lead to sensitization of the skin and mucous membranes. Iodophores (iodine carriers) were developed in the 1950s in order to overcome these disadvantages [5]. Iodophors are complexes between iodine and a carrier or a solubilising agent to sustain the release of iodine and increase its solubility.

Positively charged quaternary ammonium compounds can bind negatively charged triiodide anions (I_3^-) through electrostatic interaction, hence iodophors can be formed in such a way [6]. It has been reported previously that a strong base anion-exchange resin used to ionically bind the triiodide ion was effective as a broad-spectrum bactericide and virucide in water [7]. One method of achieving antimicrobial polymers is to add an inorganic or organic biocide (e.g., particles of iodophores) to the polymers during the processing of the material. Another method is to endow a biocidal function to the polymer after processing [8].

The addition of antimicrobial agents or fillers into the polymer matrix can significantly change the microstructure and mechanical characteristics of polymeric films [9]. The mechanical properties of such composite films strongly depend on the particle size, particle-matrix interface adhesion and particle loading [10]. Obviously, the size of filler particles also affect appearance, i.e. the smoothness, uniformity, optical properties, etc [11].

Film strength strongly depends on the stress transfer between the particles and the matrix. For well-bonded particles, the applied stress can be effectively transferred to the particles from the matrix; this clearly improves the strength. However, for poorly bonded microparticles, strength reductions occur by adding particles. The ultimate strength of a composite film depends on the weakest fracture path throughout the material [10]. The polymer-filler interaction is not only affected by the filler, important are also the characteristics of polymers such as chemical composition, chain microstructure including molecular weight and molecular weight distribution, configuration, stereoregularity, monomer unit distribution and sequence, and their functionality. All of them have a substantial influence on the physical and/or chemical interactions with filler surface, as well as on the interaction between polymer molecules themselves, which would impact not

*Corresponding author. Tel.: +370-37-456081; fax.: +370-37-456081.
E-mail address: paulius.danilovas@ktu.lt (P. P. Danilovas)

only the filler network formation but also the viscoelastic response of the polymer matrix [12]. Mechanical characteristics are also very important for the quality of products, and for this reason it is necessary to determine the influence of embedded functional particles on the mechanical properties of a polymeric matrix.

The aim of this work was to prepare potentially antibacterial and biodegradable polymer films containing cationic starch triiodide nano- and microparticles and to assess their mechanical properties.

2. EXPERIMENTAL

Materials. 2-Hydroxyethyl cellulose (HEC) (average $M_v \sim 90000$, 2.5 moles of substituent per mol of a cellulose) was purchased from Sigma-Aldrich. Cellulose acetate (CA) (type NCO, acetyl content ca. 54.91 wt%) was purchased from ACETATI S.P.A. (Italy). The native potato starch (Antanavas Starch Plant, Lithuania) was dried at 104 °C before use. Hydroxyethyl starch (HES), Kollotex 1250 ($[\eta] = 0.136 \times 103 \text{ ml/g}$), was supplied by Avebe (the Netherlands). 2,3-epoxypropyltrimethyl ammonium chloride (EPTMAC) (70 %, Fluka), epichlorohydrin (99 %, Aldrich) were used as received. All other chemicals were of analytical grade and prepared or purified by standard procedures.

Preparation of cationic cross-linked starch iodide and triiodide. The cationic cross-linked starch chloride (CCS^+Cl^-) was obtained (see Fig. 1, a) by cross-linking the starch with epichlorohydrin in the presence of sodium hydroxide and cationization with EPTMAC in the presence of sodium hydroxide as a catalyst (the molar ratio anhydroglucoside unit (AGU):EPTMAC:catalyst: H_2O :epichlorohydrin was 1:0.4:0.05:24:0.002) at 45 °C for 24 h. The molecular mass of the AGU was assumed as a mole of starch. After the reaction, CCS^+Cl^- microgranules were washed 5 times with water, 2 times with water-isopropanol mixture, and dried. The number of cationic groups in CCS^+Cl^- was expressed as the degree of substitution (DS = 0.2), which was calculated from the nitrogen content estimated by the Kjeldahl method after purification by Soxhlet extraction with methanol for 16 h.

Further, cationic cross-linked starch iodide (CCS^+I^-) was prepared by reacting CCS^+Cl^- with an excess amount of iodide (according to cationic groups of CCS^+Cl^-) in an aqueous potassium iodide (KI) solution (see Fig. 1, a). The dry CCS^+Cl^- was poured over KI aqueous solution and mixed with a magnetic stirrer for 2 h. After the reaction, the suspension was filtered through a glass filter, washed with distilled water and dried.

Cationic cross-linked starch triiodide (CCS^+I_2^-) was prepared by reacting CCS^+Cl^- with an excess amount of iodine (according to cationic groups of CCS^+Cl^-) in aqueous iodine-potassium iodide (I_2 -KI) solution (molar ratio of I_2 to KI was 1 to 3). The dry CCS^+Cl^- was poured over the I_2 -KI aqueous solution and mixed with a magnetic stirrer for 2 h. After the reaction, the suspension was filtered through a glass filter, washed with distilled water until no traces of iodine in filtrate were detected, and dried.

Synthesis of cationic hydroxyethyl starch. Cationic hydroxyethyl starch (CHES) (see Fig. 1, b) was prepared by the reaction of hydroxyethyl starch with EPTMAC in

the presence of sodium hydroxide at 45 °C for 48 h. The molar ratio of the hydroxyethyl starch: epoxy compound: NaOH was 1:0.35:0.04. The reaction mixture was prepared as follows: a concentrated solution of EPTMAC, an aqueous solution of 2M NaOH and H_2O were thoroughly mixed, then starch was added, the reaction mixture was homogenized and left for two days at 45 °C. After the reaction, the CHES was purified by Soxhlet extraction with methanol for 16 h. The nitrogen content in the CHES was estimated by the Kjeldahl method. The degree of substitution (DS = 0.33) of modified polymers was calculated from the nitrogen content.

Preparation of starch-iodine nanoparticles in HEC solution. Cationic hydroxyethyl starch triiodide nanoparticles ($\text{CHES}^+\text{I}_2^-$) (see Fig. 1, b) were obtained in an aqueous HEC solution by the following procedure. The necessary amount of CHES water solution was added into a viscous, concentrated aqueous solution of HEC by intensive stirring, and then I_2 -KI solution was added dropwise to the mixture. With the formation of CHES-iodine nanoparticles, a viscous brown dispersion was obtained.

Preparation of cellulose acetate casting solutions and composite mixtures. A 14 wt% stock solution of CA in acetone was prepared by adding CA to acetone and stirring at room temperature until the pellets were fully dissolved (~8 h). CA casting solutions containing 5, 10, 15, and 20 wt% of water were prepared by mixing a 14 wt% CA solution in acetone with different amounts of water. Meanwhile, modified starch microgranules were dispersed in the CA-acetone solution to obtain $\text{CCS}^+\text{I}^-/\text{CA}$ and $\text{CCS}^+\text{I}_2^-/\text{CA}$ composite films containing 4, 6, 8, 10, 30, 60 and 70 wt% of microparticles.

Film preparation and characterization. The film samples were prepared by spin-coating as follows. The casting solution or a composite mixture was poured onto a polypropylene plate, spread evenly and spin-casted by using a Spin-150-v3-NPP spin-coating machine (SPS-Europe BV) at different spinning rates (300–3000 rpm). Dried films were obtained after the solvent had been evaporated at ambient temperature. Finally, the films were carefully peeled off from the substrate. $\text{CCS}^+\text{I}^-/\text{CA}$ composite films containing CCS^+I^- microgranules were further exposed to iodine vapor or immersed in I_2 -KI aqueous solution to obtain the CCS^+I_2^- form (see Fig. 1, a). The film thickness was measured using a micrometer (Model 43409) with a 1- μm accuracy. The thickness measurements were taken at 10 different points along the gauge length of each specimen, and the mean values were calculated. The films had been conditioned in the desiccator before they were approached to testing.

Optical images of the films were taken with an Olympus cx31 optical microscope equipped with an Olympus photcamera. For scanning electronic microscopy (SEM) analysis, the samples were mounted on metal stubs, using an adhesive tape, gold-coated under vacuum and examined on a FEI Quanta 200 FEG.

Mechanical testing. The tensile strength, Young's modulus, and elongation at break were estimated on a Zwick Materials testing machine (BDO-FBO.5TH).

The samples were prepared by cutting 15 mm wide strips from the films. No less than 10 samples were used to

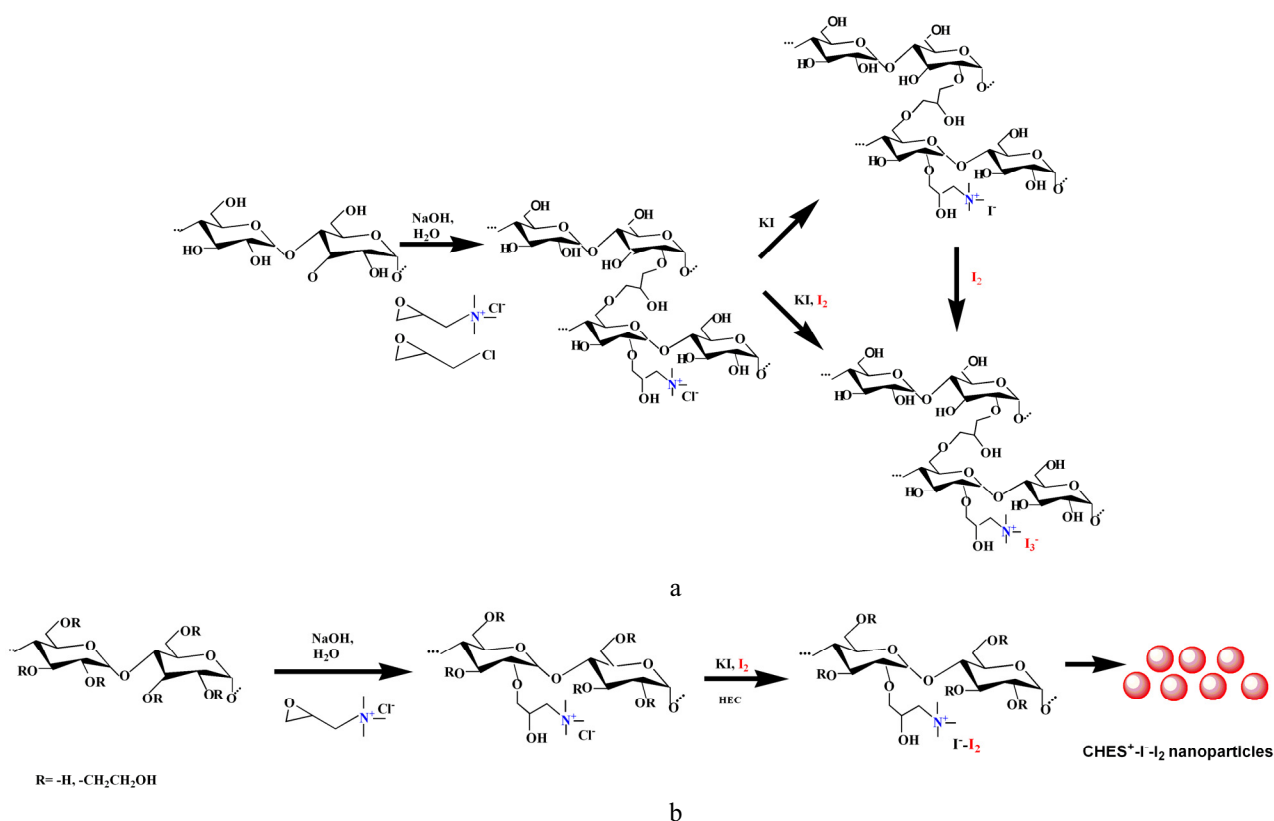


Fig. 1. Synthesis scheme for the preparation of: a – cationic cross-linked starch iodide (CCS⁺I⁻) and cationic cross-linked starch triiodide (CCS⁺I⁻₃); b – cationic hydroxyethyl starch (CHES) and CHES-triiodide nanoparticles (CHES⁺I⁻₃)

characterize each material, and the results were averaged to obtain a mean value. The tests were carried out by the ASTM D882 method, with an initial grip separation of 60 mm and a crosshead speed of 10 mm/min.

DSC analysis. Differential scanning calorimetry (DSC) curves were obtained at a temperature that varied from ambient to 160°C on a Q-100 system (TA Instruments) using a perforated aluminium pan under a nitrogen atmosphere and a heating rate of 5 °C/min.

UV-vis spectroscopy measurements. Spectrophotometric measurements were made using a Unicam UV/Vis spectrophotometer. Absorbance data were taken at 2 nm intervals from 200 nm to 700 nm to obtain spectra. The spectrum of each sample was measured at least twice.

3. RESULTS AND DISCUSSION

Preparation of polymer composite films containing starch-iodine microgranules and nanoparticles. Iodine-containing cationic crosslinked starch microparticles and cationic starch nanoparticles were dispersed in cellulose acetate and hydroxyethyl cellulose solution, respectively, and composite films were spin-casted. Various amounts (0 wt% – 70 wt%) of CCS⁺I⁻₂ microgranules were embedded in CA films. Meanwhile, for the formation of CHES⁺I⁻₂ nanoparticles, the HEC matrix was chosen. In this case, the obtained cationic hydroxyethyl starch triiodide nanoparticles are additionally stabilised by intermolecular interactions between CHES and the polymer matrix. Optical and SEM images revealed an even distribution of starch-iodine microparticles and nanoparticles in the prepared films (see Fig. 2).

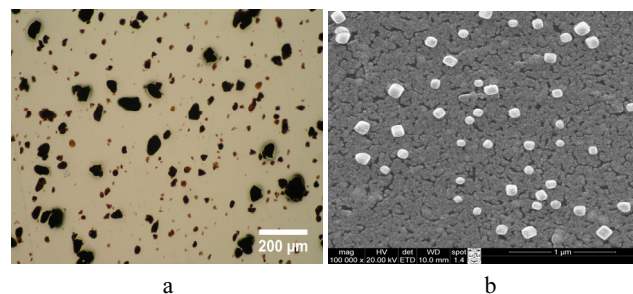


Fig. 2. Optical image of CCS⁺I⁻₂ microgranules in CA matrix (a, magnification ×100) and SEM image of CHES⁺I⁻₂ nanoparticles in HEC matrix (b, magnification ×310000)

Water influence on the mechanical properties of CA films. The particles of polysaccharide derivatives are of hydrophilic nature and could be prepared or modified in an aqueous medium. Therefore, it is important to evaluate the effect of water present in the casting composition on the mechanical properties of the films.

Figure 3 shows the effect of water present in the casting solution on the mechanical properties of CA films. As is evident from the presented data, the mechanical properties of CA films were impaired by the addition of water. At a 5 wt% water content, the reduction in mechanical properties was not very significant: tensile strength decreased by 9 %, Young's modulus by 6 %, and elongation decreased by 11 %, as compared to those obtained for CA films formed from solutions containing no water. However, at 20 wt% water content, a great reduction in the mechanical parameters was observed: tensile strength decreased by 69 %, and Young's modulus and elongation decreased by 66 % and 40 %, respectively.

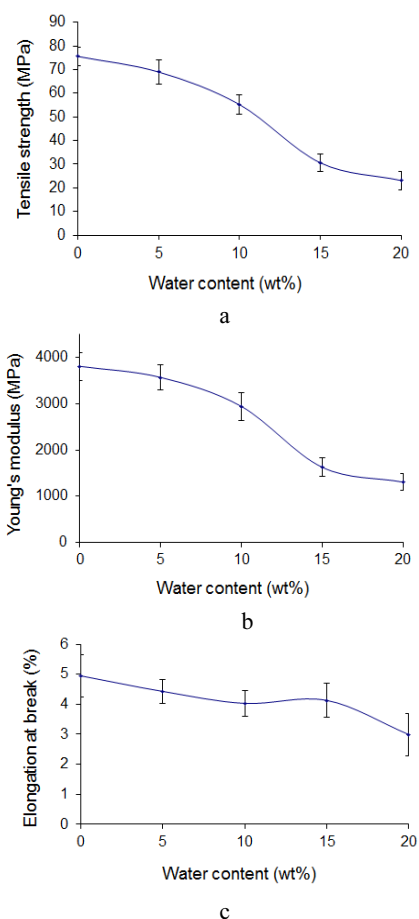


Fig. 3. The effect of water content in casting solutions on tensile strength (a), Young's modulus (b) and elongation at break (c) of CA films. Film thickness was 23 μm . Deviations of the values are indicated

In the presence of excess water, a polymer may become swollen, exhibiting major changes in its mechanical and chemical properties. Water can plasticize the polymer matrix or form stable bridges through hydrogen bonding, resulting in an anti-plasticizing effect [13]. DSC curve profiles of a CA film formed from solutions in acetone containing no water and a CA film formed from solutions in acetone containing 20 wt% of water showed a broad endothermic event between the ambient temperature (25 $^{\circ}\text{C}$) and 120 $^{\circ}\text{C}$, which is attributed to water desorption from the polysaccharide structure. The enthalpy values of water vaporization for both samples almost coincide ($\Delta H_{\text{vI}} = 109.9 \text{ J/g}$ and $\Delta H_{\text{vII}} = 111.5 \text{ J/g}$). Hence, the energy required for water evaporation is almost the same for both samples. At the same time, the determined water content in a CA film formed from solutions in acetone containing no water was 4.57 %, and in the case of CA film formed from solutions in acetone containing 20 wt% of water it was 4.65 %. Thus, it could be deduced that the dramatic changes in mechanical properties observed are not due to the influence of water remaining in films during testing.

Interestingly, the films formed from CA solution in acetone containing no water were transparent, at 5 wt% water content films were opaque with discontinuous striations of clear and opaque regions, and at larger amounts of water ($\geq 10 \text{ wt}\%$) the films were completely

white and opaque. It is clear that the presence of water in the casting solution causes a reduction in the mechanical parameters of CA films (see Fig. 3), probably due to the decreasing effect of water molecules on the intermolecular interactions such as van der Waals and hydrogen bonds between matrix molecules after the solvent evaporates from the casted film, making the film more bulky and porous [14, 15]. Therefore, water content above 5 wt% in the casting solutions should be avoided in order to maintain the mechanical strength of CA films.

Mechanical properties of $\text{CCS}^+\text{T}^- \text{I}_2/\text{CA}$ composite films. Various amounts of iodine-modified starch microgranules were added to the CA solution, and thus $\text{CCS}^+\text{T}^- \text{I}_2/\text{CA}$ composite films were prepared. The effect of the inclusion of microparticles on the tensile strength, Young's modulus and elongation at break of the composite films was evaluated, and the obtained data are summarized in Table 1.

Table 1. Variations in the values of mechanical parameters of composite films relative to those of blank CA film. Film thickness was 23 μm

| $\text{CCS}^+\text{T}^- \text{I}_2$ concentration in CA films (wt%) | Tensile strength relative to that of CA film (%) | Young's modulus relative to that of CA film (%) | Elongation at break relative to that of CA film (%) |
|---|--|---|---|
| 0 | 100.0 \pm 3.5 | 100.0 \pm 5.0 | 100.0 \pm 9.0 |
| 4 | 92.9 \pm 4.6 | 104.3 \pm 9.4 | 71.3 \pm 15.5 |
| 6 | 92.8 \pm 3.9 | 105.3 \pm 7.3 | 70.1 \pm 15.7 |
| 8 | 85.7 \pm 5.1 | 98.2 \pm 4.0 | 71.6 \pm 11.1 |
| 10 | 86.4 \pm 8.9 | 102.6 \pm 9.7 | 69.5 \pm 15.3 |
| 30 | 83.1 \pm 8.9 | 105.2 \pm 8.5 | 65.4 \pm 11.4 |
| 60 | 54.2 \pm 17.9 | 99.5 \pm 12.5 | 38.8 \pm 16.4 |
| 70 | 50.5 \pm 14.5 | 137.9 \pm 18 | 26.6 \pm 7.7 |

The tensile strength of the films was decreased slightly but significantly by increasing the content of $\text{CCS}^+\text{T}^- \text{I}_2$ in composite films up to 30 wt% and decreased dramatically (by $\sim 46 \%$) at $\geq 60 \text{ wt}\%$ $\text{CCS}^+\text{T}^- \text{I}_2$ addition. Meanwhile, experimental data revealed no significant changes in Young's modulus with increasing the content of microparticles. Using Young's modulus as a marker of the rigidity of these films, it may be concluded that the rigidity of CA films was not significantly influenced by the presence of microgranules. When the content of $\text{CCS}^+\text{T}^- \text{I}_2$ in the films did not exceed 10 wt%, the elongation at break was decreased by $\sim 30 \%$, and it was reduced extremely (by $\sim 61 \%$) when the $\text{CCS}^+\text{T}^- \text{I}_2$ content was 60 wt%. Relatively large $\text{CCS}^+\text{T}^- \text{I}_2$ microparticles decreased the strength of CA composite films because of the lack of structural continuity. Thus, upon increasing the $\text{CCS}^+\text{T}^- \text{I}_2$ content in the composition, microparticles, are probably more agglomerated, and this weakens the stress distribution in the films.

Iodine sorption experiments. As mentioned previously, the antibacterial $\text{CCS}^+\text{T}^- \text{I}_2$ form of microgranules can be obtained by exposing CA films containing CCS^+T^- microgranules to iodine vapour or by immersing them into $\text{I}_2\text{-KI}$ aqueous solution. CCS^+T^- interacts electrostatically

with I_2 molecules, and a CCS^+I_2 complex is formed. A colour change of microgranules from white to dark brown was observed as the CCS^+I_2 complex was formed (Fig. 4).

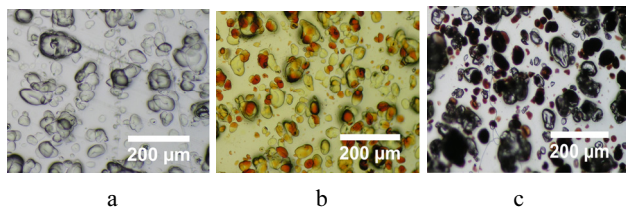


Fig. 4. Optical image of CCS^+I_2 microgranules in CA matrix: a – prior to exposure, b – after 62 h of exposure to iodine vapour, c – after 120 min of sorption in I_2 -KI aqueous solution. Particle concentration in the film 30 wt%, magnification $\times 100$

Figure 5 shows the UV-vis spectra of the system evolution after CCS^+I_2/CA films have been exposed to the iodine-containing medium. One can see significant changes in the absorption spectra in the region varying from 260 nm to 600 nm, where absorption peaks at $\lambda_{max} = 288 \text{ nm} - 292 \text{ nm}$ and $\lambda_{max} = 350 \text{ nm} - 365 \text{ nm}$ can be attributed to the CCS^+I_2 complex formation.

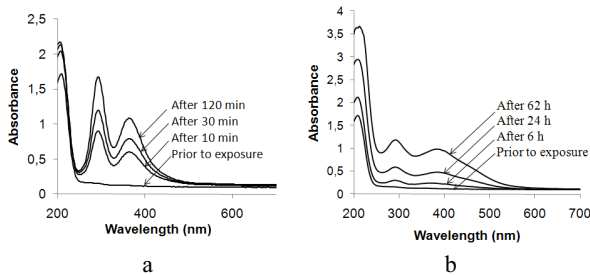


Fig. 5. Absorbance spectra of CCS^+I_2/CA films containing 4 wt% CCS^+I_2 after different periods of exposure to: a – I_2 -KI aqueous solution (0.05 mmol/l) and b – iodine vapour

Both peaks increased in intensity with increasing exposure time and it could be deduced that more iodine molecules were bound to the modified starch. Similarly, Fig. 6 shows the same dependence of absorption peak intensity on exposure time for cellulose acetate films with a different CCS^+I_2 content.

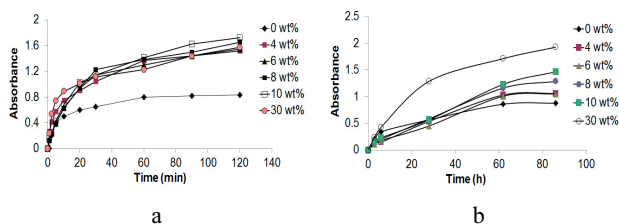


Fig. 6. Absorption peak intensity at $\lambda_{max} = 288 \text{ nm} - 292 \text{ nm}$ dependence on exposure time of CA films with different CCS^+I_2 content to: a – I_2 -KI aqueous solution (0.05 mmol/l) and b – iodine vapour

It is obvious that the iodine-binding capacity of the films increases with increasing CCS^+I_2 content. The latter tendency was more pronounced in experiments performed in iodine vapour. Moreover, the results have shown that iodine sorption appears to be more than 60 times faster in the I_2 -KI aqueous solution, as it takes ~ 60 min for the

samples to be completely saturated with iodine in this solution and more than 60 hours in the case of sorption from the vapor phase.

Mechanical properties of nanocomposite films.

Since starch nanoparticles are formed in an aqueous medium, it is impossible to incorporate large amounts of nanoparticles into the CA matrix due to the strength loss of the CA film prepared by using a water-containing casting solution. Hence, a water-soluble polymer – hydroxyethyl cellulose – was chosen as the matrix for embedding starch nanoparticles. Figure 7 shows the effect of $CHES^+I_2$ nanoparticles on the mechanical properties of $CHES^+I_2$ -HEC composites. As implied by the obtained data, upon adding 18 wt% of nanoparticles into the HEC film no significant changes in the mechanical properties of the films were observed. Their tensile strength decreased from 21.6 MPa to 20.8 MPa ($\sim 3.9\%$) and Young's modulus increased from 736 MPa to 839 MPa ($\sim 14\%$), whereas the elongation at break decreased from 8.2% to 6.6% ($\sim 19.9\%$).

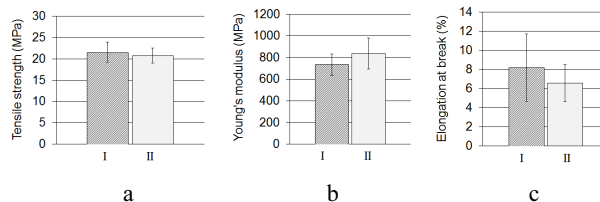


Fig. 7. Tensile strength (a), Young's modulus (b) and elongation at break (c) parameters for: I – HEC films, and II – HEC films containing 18 wt% of $CHES^+I_2$ nanoparticles. Film thickness was 27 μm

The obtained results show that even a relatively high content (18 wt%) of $CHES^+I_2$ nanoparticles in the HEC matrix did not impair the mechanical properties of films as only slightly more rigid and less elastic nanocomposite films were formed.

4. CONCLUSIONS

In this work, different ways to prepare polymer films containing natural polysaccharide nano- and micro-additives were studied. It was found, that the modified starch microparticles can be easily incorporated into the cellulose acetate matrix. Two types of modified starch microgranules have been incorporated: CCS^+I_2 and CCS^+I_2 . In the latter case, casted films were exposed to iodine vapour or immersed in the I_2 -KI aqueous solution to obtain microgranules containing molecular iodine. The results have shown that iodine sorption appears to be more than 60 times faster in the I_2 -KI aqueous solution as it takes ~ 60 min for the samples to be completely saturated with iodine from this solution and more than 60 hours in the case of sorption from the vapor phase. Mechanical tests showed that the strength of CA microcomposite films decreased with increasing the content of microparticles.

In the case of modified starch nanoparticles which are formed in an aqueous medium, CA becomes an unsuitable matrix, since the existence of water in the CA casting solution greatly reduces the mechanical parameters of the obtained films. At 20 wt% water content in the casting solution, tensile strength decreases by 69%, and Young's

modulus and elongation of films decrease by 66 % and 40 %, respectively. Hence, water-soluble polymer hydroxyethyl cellulose was chosen as the matrix for the embedding of starch nanoparticles. The results showed that upon addition of 18 wt% of nanoparticles into the HEC film, no significant changes in mechanical properties of the films were observed.

To sum up, it may be concluded that both nano- and microparticles of modified starches with potential antimicrobial properties can be synthesized and, in a proper formulation, could be incorporated into a polymer matrix, without reducing the strength of the composite films.

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