EFFECT OF CHITOSAN FILM SURFACE STRUCTURE ON THE CONTACT ANGLE

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Abstract

The aim of this study was to evaluate the influence of the surface microstructure of chitosan films on the contact angle. Films without plasticising additives made of chitosan or regenerated chitosan were selected for the tests. A sessile drop method based on the European Pharmacopoeia was used to determine the contact angle. Due to the method of film production, the contact angle measurements were made on both the top and bottom surfaces of the film. For chitosan or regenerated chitosan films, the method of preparation slightly affected the difference in wettability between the top and bottom of the films, as confirmed by scanning electron microscopy. On the other hand, the wettability of the top and bottom of cellulose films varied greatly depending on the side of the film. Both chitosan and cellulose films had a homogeneous structure. There were differences in the microstructure between the top and the bottom of the sample in the cellulose film, a factor that affected the contact angle and thus the wettability of the surface.

Keywords: *films, contact angle, microstructure, chitosan, cellulose*

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1. Introduction

Currently, one way to reduce packaging material waste is to use packaging made from natural polymers. Films made from starch not only provide protection for the food, but can be consumed with the packaged product [1]. The use of biopolymers such as chitosan or cellulose to produce biodegradable packaging materials, especially films, makes it possible to reduce the use of synthetic plastics. The physicochemical properties of packaging films vary depending on the type and source of natural polymers used in their manufacture. Films made from natural polymers on the one hand have good oxygen barrier properties, but on the other hand they have poor mechanical properties and a low water vapour barrier compared with synthetic films.

The above-mentioned features significantly limit their applicability, which is why new ways of improving the properties of packaging are constantly being sought or existing ones are modified by using physical, chemical and biotechnological methods [2, 3]. At the same time, efforts are being made to produce packaging that would not only constitute a physical barrier protecting the product against negative environmental factors, but would also fulfil many additional functions, namely comes from renewable raw materials, is biodegradable and thus does not harm the environment after fulfilling its functions [4]. Films made of natural polymers can be active carriers of antimicrobial substances, fragrances, colours, vitamins or antioxidants, thus improving sensory properties and even complementing the nutritional value of the packaged product [5-7]. To increase hydrophilibility, accelerate decomposition and at the same time reduce the cost of producing packaging from synthetic biodegradable polymers, they are combined with natural polymers such as starch, chitosan or casein. Chitosan is a widely distributed polysaccharide in nature, found in the external skeletons of numerous invertebrates including marine crustaceans and insects, and the cell wall of fungi, yeasts or moulds. The alkaline deacetylation of chitin yields chitosan, a natural polymer composed of *N*-acetyl-D-glucosamine and D-glucosamine residues linked by β-1,4-glycosidic bonds [8].

There are many chitosan preparations available on the market, differing in basic physicochemical parameters such as the deacetylation degree and average molecular weight, which affect the biological and functional properties of this polymer. Due to its non-toxicity, biocompatibility, biodegradability, appropriate biological activity and ability to form polycations in acidic environments, chitosan has found many applications, including pharmaceuticals, medicine, environmental protection and the food and packaging industry [9-12].

One of the most important properties of chitosan is its ability to control the release of active substances that are completely absorbed by the body [13]. The release of medication adsorbed or encapsulated by polymers occurs slowly by controlled diffusion of the medication from the polymeric material [14-16]. Moreover, chitosan films are transparent, colourless or slightly yellowish depending on the source of the chitosan and the thickness of the material [17-19]. In acidic aqueous media, they swell and even dissolve, while in pH around 6 their solubility decreases and depends on the deacetylation degree of the polymer [20]. The mechanical properties of the film are affected by the molecular weight of the chitosan [21] and the type and concentration of acid used to dissolve it [18].

The properties of natural polymer films are determined by their hydrophilic/hydrophobic nature, which directly affects the printing, bonding or laminating processes of films used for packaging and other polymeric materials [22, 23]. As a result of various modifications or the method of production of the film, there may be a change in surface wetting: the film may become more hydrophobic or hydrophilic. Surface wetting usually

increases with an increase in roughness for hydrophilic surfaces, while it deteriorates for hydrophobic surfaces.

Wettability is a crucial physical property that characterises the surface of materials. Wettability studies are also fundamental for biomedical applications. A measure of the wettability of a solid surface of a low-molecular-weight liquid is the angle – commonly referred to as the *wetting angle* or *contact angle* – between the tangent to the droplet at the point of contact with the surface under test and that surface [24]. The measuring liquid should be of low volatility (the aim is that its evaporation should not affect the measurement result), should not react chemically or swell the surface layer and should 'form' a relatively large wetting angle with the surface of the material tested (the aim is to make it easy and precise to read). There are different methods for measuring the wetting angle, and the results obtained after applying the different methods vary [25]. It is also known that the wetting angle is affected by many factors, including: physical and chemical homogeneity of the surface, roughness, surface contamination, type of measuring liquid, droplet size, humidity and ambient temperature [22].

Due to its simplicity, relatively low cost of making the determination and high sensitivity, the sitting droplet method was chosen for the study of wetting angle measurement [26]. The volume of the placed droplet should be small enough to eliminate the influence of gravitational forces but large enough so that the micro-roughness of the surface does not obscure the 'energetic' result of the measurement [27]. The droplet volume of the measuring liquid is practically identical in each case, a factor that underlines the very high repeatability of the results. The influence of external environmental conditions (temperature and humidity) is greater the smaller the droplets of the measuring liquid. In addition to the volume of the droplet, which should be reproducible for the entire series of determinations, the speed at which it strikes the tested surface at the moment of contact is also crucial for the measurement result. The effect is certainly dependent on the type of liquid used for the test.

The aim of the study was to show the influence of the surface microstructure of chitosan films on the contact angle. Films without plasticising additives made of chitosan or regenerated chitosan were selected for the tests. In the contact angle test, a sappy drop method was used based on the European Pharmacopoeia.

2. Materials and methods

2.1. Materials

Chitosan films, regenerated chitosan films and cellulose films were produced for the study. The film thickness ranged from 0.03 to 0.04 mm. No plasticising additives were introduced into the polymer solutions. The tested films were produced in the Natural Polymer Fibres Unit of the Łukasiewicz Research Network – Institute of Biopolymers and Chemical Fibres. The films were produced using a laboratory method. To provide a uniform thickness of the prepared films, the cast solution was spread by means of a prototype casting slot knife. The slot height was set to 0.6 mm [27].

The following films were produced for testing:

- chitosan film obtained from a 5% solution of chitosan in 2% acetic acid and dried;
- regenerated chitosan film from a 5% solution of chitosan in 2% acetic acid and dried, then treated with 0.5% NaOH solution and washed and dried.

The following reagents were used:

- commercially available chitosan from Vanson Halo Source (USA) with the following physicochemical parameters – deacetylation degree (DD) 85.0%, average molecular weight 320 kDa and ash content 0.18 wt%;

– cellulose film: obtained from a solution of 7.8% NaOH with a cellulose concentration of 5%. The alkaline cellulose solution was spread on a smooth and even surface and then introduced into a coagulation bath of 10% H_2SO_4. The regeneration resulted in a cellulose film that was washed in demineralised water and dried under laboratory conditions.
– commercially available cellulose was subjected to hydrothermal treatment [28, 29] with a polymerisation degree (DP) of 285 was used to produce the alkaline solution. The average PD of the pulp was estimated viscometrically in ethylene diamine cuprate (CED) according to ISO 5351/1:1981,
– measuring fluid used: glycerine 99% (Fluka Chemie GmbH, Switzerland).

2.2. Methods

2.2.1. Wetting Angle

The wetting angle was determined according to the sitting droplet method based on the European Pharmacopoeia [25]. To determine the wetting angle, an STFI goniometer (AB Lorentzen-Wettre, Sweden) with an attached Optical Smart 5MP PRO microscope camera (Delta Optical, Poland) was used. The wetting angle measurement was determined by analysing the droplet image with the DLT-Cam Viewer software designed for Delta Optical DLT-Cam cameras (Delta Optical).

The wetting angle was determined by the computer program as the angle between the tangent to the droplet at the point of contact with the surface of the film under test (Figures 1 and 2).

The wetting angle measurements were made according to the following conditions:

– the surface to be tested should be flat, smooth and free from any impurities;
– the timing of the analysis was chosen to minimise the effects of gravitational forces and evaporation,
– the time used to test the dynamics of the contact angle was 1, 60, 120, 180, 240, 300 and 360 s;
– measuring liquid: glycerine, with a droplet volume of 5 µl;
– the tests were carried out at a constant temperature with a well-defined humidity, in this case at a temperature of 23 ± 1 °C and a relative humidity of 50% ± 2%.

Due to the method of film production, wetting angle measurements were performed on both the top and bottom surfaces of the film.

The stability of the droplet spreading process over the surface of the samples was calculated by the rate of change of the contact angle, according to the formula [25]:

$$R = (\alpha - \alpha^{I})/s,$$

where R is the rate of change of wetting angle, α is the wetting angle after 1 s (in degrees), α^{I} is the wetting angle after 60 s (in degrees) and s is the time during which the wetting angle changed.

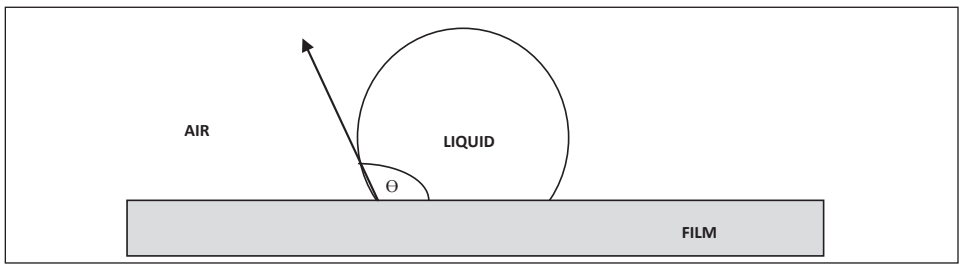


Figure 1. Diagram of the contact angle measurement using the sitting droplet method

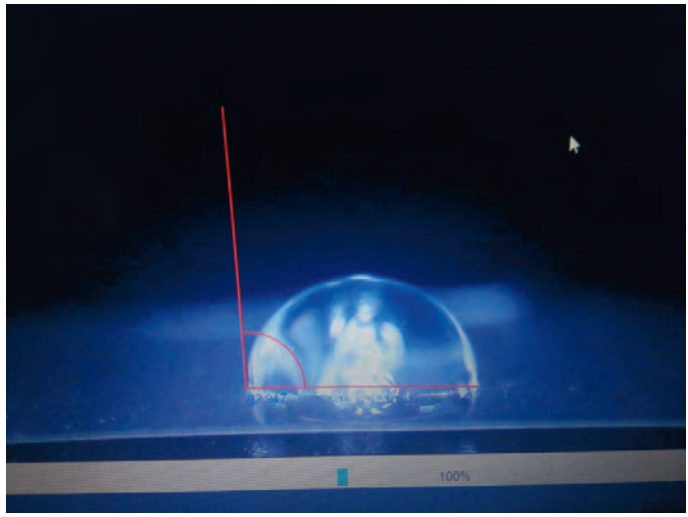


Figure 2. An image of a droplet obtained with Smart Analysis Pro software

2.2.2. Microscopic Surface Analysis

The surface microstructure and cross-section of the films were analysed using a Quanta 200 (W) scanning electron microscope (SEM) (FEI, USA). For surface examination, film samples were stuck on carbon disks placed on a table and then sputtered with a 20-nm layer of gold in a Q 150R S vacuum sputtering machine. After sputtering, the samples were placed in the microscope chamber. For cross-section examination, the sample was fixed in the jaw table, cut with a scalpel and then sputtered with a 20-nm layer of gold.

Investigations were conducted in high vacuum at an electron beam accelerating voltage of 10 KV, at magnifications of 1000× (cross-sections) and 5000× (surface area). Thickness measurements were performed with the analySIS Docu Soft Imaging Solutions software in a Quanta-adapted system (Olympus, Germany). This program takes interactive measurements of quantities with automatic recording of results in a spreadsheet.

2.2.3. Mechanical Properties of the Film

The mechanical properties of the films were determined using the following standards:

- film thickness – PN-EN ISO 4593:1999 Plastics – Film and sheeting – Determination of thickness by mechanical scanning;
- mechanical properties – PN-EN ISO 527-3:2019-01 Plastics – Determination of tensile properties – Part 3: Test conditions for films and sheets and PN-EN ISO 527-1:2012, p.10.3 Plastics – Determination of tensile properties – Part 1: General principles.

The test was carried out with a film width of 15 mm, the distance between the clamps was 50 mm and the speed of movement of the clamps on the testing machine was 10 mm/min. To determine Young's modulus, a clamp travel speed of 1 mm/min was used.

3. Results and Discussion

The main goal of the research was to examine the influence of the surface microstructure of a film made of natural polymers (chitosan or cellulose) on the contact angle. Films without plasticising additives, made of chitosan, regenerated chitosan or cellulose were selected for the tests.

The wetting angle (Θ) was determined according to the sitting droplet method based on the European Pharmacopoeia. Due to the method of film manufacture (so-called laboratory method of film formation), wetting angle measurements were performed on both the top and bottom layers of the film.

3.1. Wetting Angle Measurement of the Tested Films

Figures 3 and 4 show the contact angle measurements for the top layer of the tested films, and Figures 5 and 6 show the contact angle measurements for the bottom of the tested films. Wetting angle dynamics were determined in 10 replications for seven time points: 1, 60, 120, 180, 240, 300 and 360 s.

The dynamic wetting angle is determined for absorbent materials and when there is a chemical reaction with the substrate causing a change in the surface tension of the liquid or the surface properties of the material. The high surface energy of the material and the low surface tension of the solution reduce the size of the contact angle [30]. The measurement of the dynamics of the wetting angle (droplet spreading rate) requires the recording of a sequence of images where the droplet shape changes, showing the dynamics of the entire process.

In the case of chitosan film or regenerated chitosan film, the film-forming conditions had little effect on the difference in wettability between the top and bottom layers. In the case of cellulose films, however, the wettability varied considerably depending on the side of the film. To investigate the reason for this difference in wetting angle between the top and the bottom of films made from the same type of polymer, the surface was analysed microscopically (Figure 7).

3.2. Analysis of the Surface Topography of the Tested Films

Figure 8 presents micrographs of the cross-sections of the films.

Based on microscopic analysis of the cross-sections, both chitosan and cellulose films are characterised by a homogeneous structure. There is a difference in surface

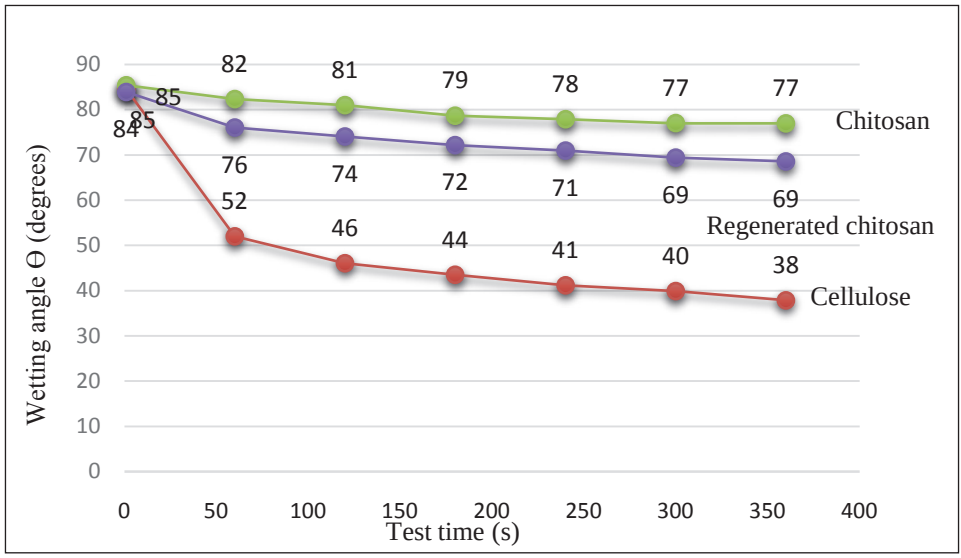


Figure 3. Dynamics of the wetting angle of film samples in time (sample top)

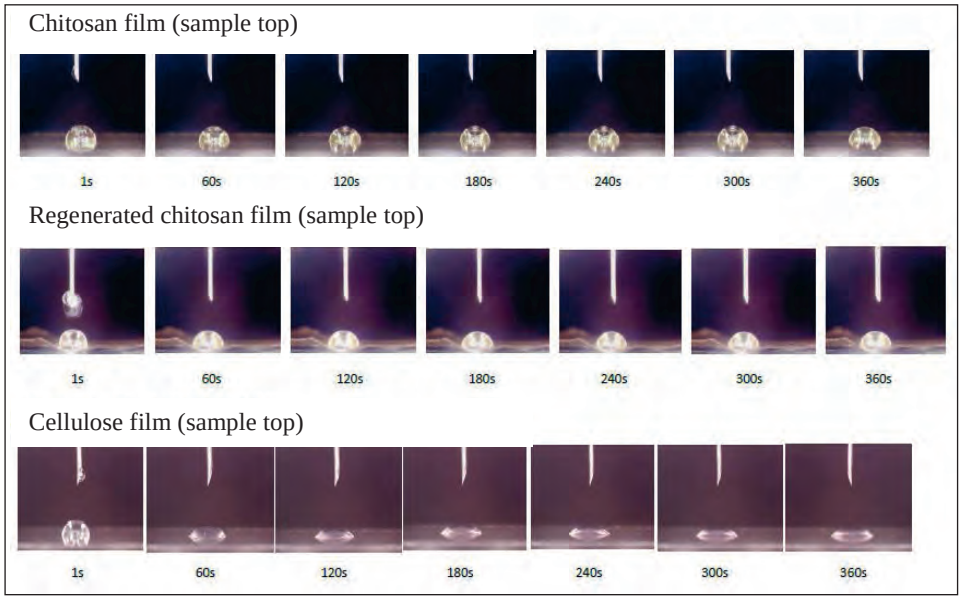


Figure 4. Change in droplet shape over time (sample top)

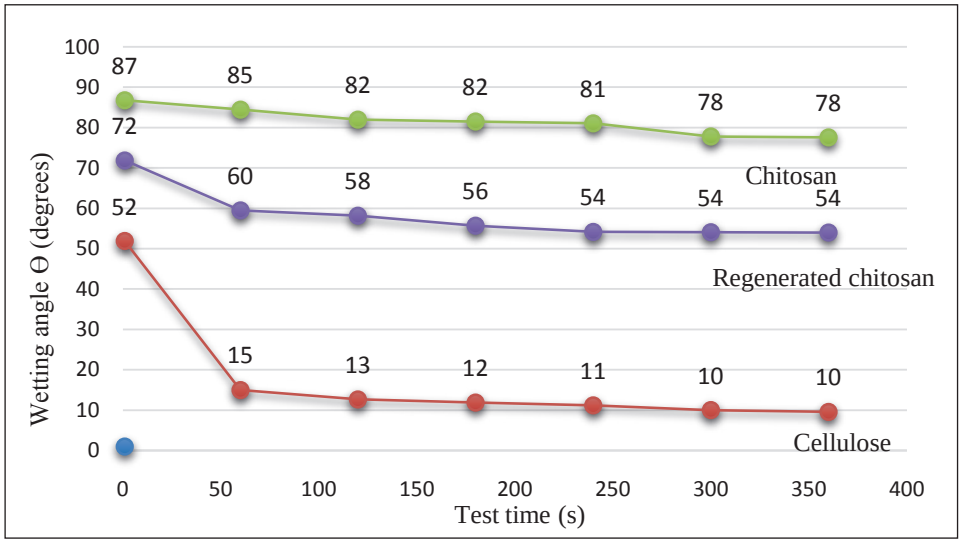


Figure 5. Dynamics of the wetting angle of film samples in time (sample bottom)

microstructure between the top layer and the bottom of the sample. This translates into the value for the wetting angle and thus the wettability of the surface.

Based on previous studies, wettability – the susceptibility of a solid to wetting – is affected by the roughness and micro-roughness of the material [21, 31]. Specifically, the greater the micro-roughness, the better the wettability and therefore the smaller the wetting angle. In the case of the tested films, the method of film production, formed from

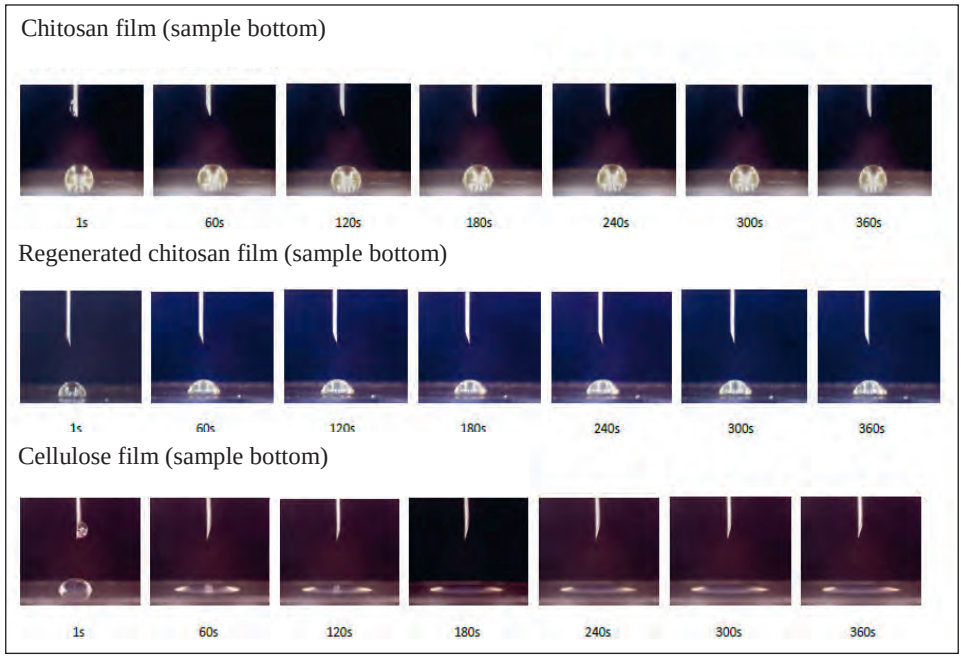


Figure 6. Change in droplet shape over time (sample bottom)

alkaline solutions, had an additional influence on the surface porosity and thus the wetting angle. The cellulose film showed the most susceptibility to the formation of micropores.

3.3. Evaluation of the Rate of Wetting Angle Changes

The wetting angle rate of change was calculated to determine the stability of the droplet dispersion on the surface of the samples (Figure 9). Overall, the rate of droplet dispersion was highest on cellulose films, a finding that corresponds to the easy wettability of hydrophilic materials.

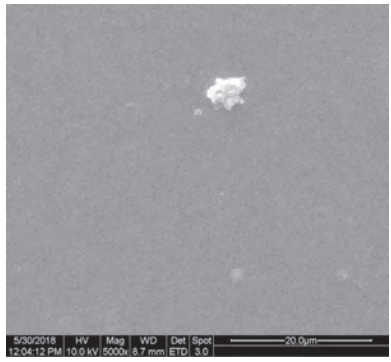
3.4. Evaluation of the Mechanical Properties of the Tested Natural Polymer Films

The mechanical properties of the formed films are presented in Table 1. The maximum load and stress parameters increased for the regenerated chitosan films, whereas the strain decreased. The strain of the regenerated chitosan films was similar to the cellulose film. Moreover, the maximum load and stress values of the cellulose film were significantly higher compared with both the chitosan and regenerated chitosan films with similar thickness.

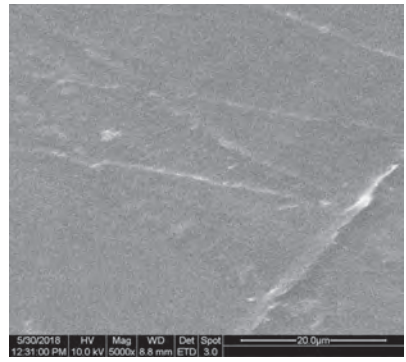
4. Conclusions

The wetting angles for the different materials were statistically different. Samples with a wetting angle $\geq 80°$ are considered hydrophobic. Only regenerated chitosan film exhibited hydrophobic properties. That film had the greatest stability and thus the lowest contact angle rate of change over time. The cellulose film showed the greatest decrease in the wetting angle, which is indicative of its hydrophilic properties. The wetting angle of the cellulose film was 40% lower for the top of the sample and as much as 80% lower for the bottom of the sample compared with the regenerated chitosan film. Hence, the film-forming conditions had the greatest influence on the surface properties of the cellulose

Cellulose film

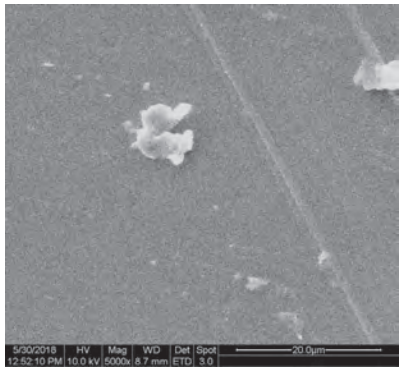


Top of the sample

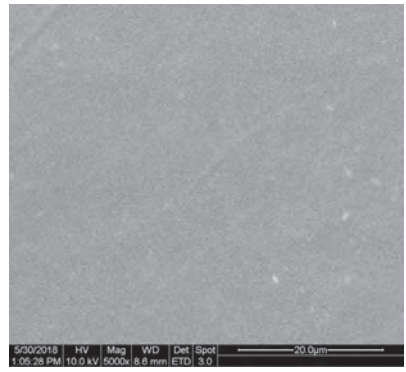


Bottom of the sample

Chitosan film

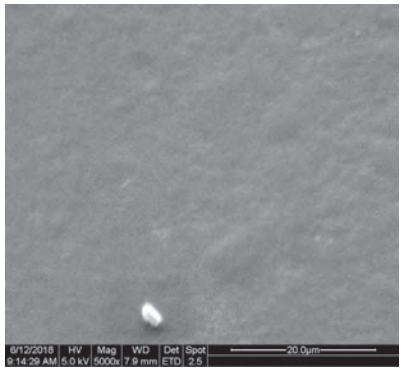


Top of the sample

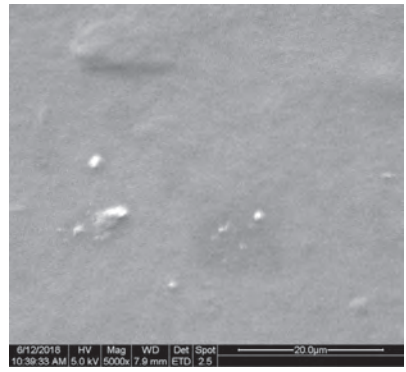


Bottom of the sample

Regenerated chitosan film



Top of the sample



Bottom of the sample

Figure 7. Scanning electron micrographsof the surface of the tested films (5000× magnification).

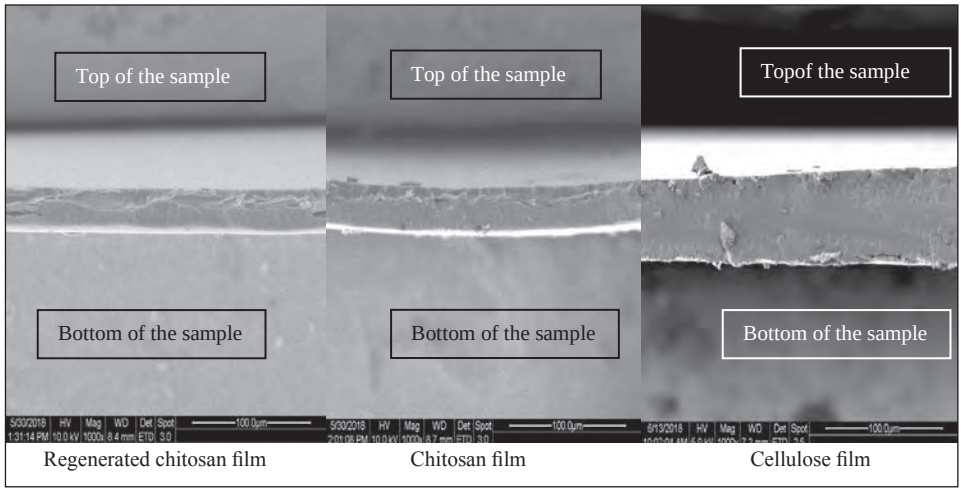


Figure 8. Scanning electron micrographs of film cross-sections (1000× magnification)

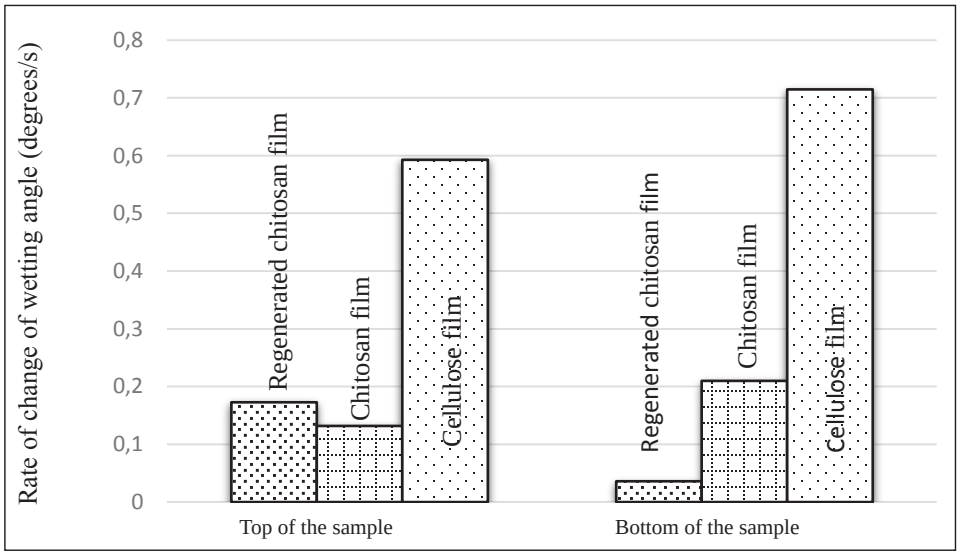


Figure 9. Rate of change of the wetting angle

Table 1. Mechanical properties of the tested films

	Maximum load (N)	**Strain (%)**	**Stress (MPa)**	**Thickness (mm)**
Chitosan film	17.8 ± 3.5	4.57 ± 2.36	33.0 ± 9.8	0.04 ± 0.01
Regenerated chitosan film	23.9 ± 2.7	3.16 ± 0.33	50.7 ± 7.8	0.03 ± 0.00
Cellulose film	49.6 ± 2.6	3.18 ± 0.30	86.9 ± 4.3	0.04 ± 0.00

film. The developed polymer films meet basic functional requirements, and thus they could be potentially used as a packaging material for food. In this form, they would not only constitute a physical barrier protecting the product against negative environmental factors, but also would not burden the environment after fulfilling its functions, because it is biodegradable.

5. References

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