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Characterization of the Structural and Physical Properties of the Thermoplastic Starch Film with Kaolinite and Beeswax Addition

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ABSTRACT

The aim of the study was to investigate the influence of kaolinite (KA) and beeswax (BW) addition on the structural and physical properties of thermoplastic starch (TPS) films. The casting method was applied and glycerol was used as a plasticizer. Microstructure analyzes were made by a stereoscopic and a scanning electron microscope. Tensile tests were carried out under static load conditions at three different deformation velocities of V = 0.0001, 0.001, and 0.01 m/s. The studies of surfaces characteristic were performed using water contact angle and water vapor isotherm measurements. The most homogeneous structure of the surface with higher mean values of failure stress and elasticity modulus was observed for thermoplastic starch films with kaolinite addition. The significant reduction in dynamics changes of water contact angle (10 %) of BW films in the time 0–20 s as well as tensile strength decrease was noted (compared to pure TPS films). The research results suggest the validity of using BW and KA to improve the barrier and mechanical properties of TPS films. Further research should focus on to improve the starch-beeswax-kaolinite combination and increase the homogeneity of the structure of films in order to upswing their simultaneous impact on barrier and mechanical properties.

Keywords: biocomposites, thermoplastic starch film, kaolinite, beeswax, microstructure, mechanical properties.

INTRODUCTION

Modifications of processing and improvement of functional properties of classical polymer materials are common and widely described in the literature [1]. However, currently a huge amount of traditional polymer materials garbage present a major environmental problem that even their selective collection does not help to reduce their quantity [2]. The interest of scientists is to develop of environmentally friendly, biodegradable biopolymers which are naturally abundant – to response to trouble of ecosystems pollution [3]. According to data provided by the European Commission, more than 80% of all marine litter is plastic [4]. These facts forced legal solutions (throughout the European Union), which entered into force on July 3, 2021 [5]. Article no 5 of this directive prohibits the marketing of ten single-use plastic products. A certain group of products in the gastronomy sector is banned, e.g. popular polystyrene menu boxes, polystyrene cups, cutlery, straws and plastic plates.

These requirements generate new challenges for scientists and producers of disposable packaging and packaging films. New eco-friendly solutions and materials with similar functional and durability properties that can successfully replace

traditional polymers are still being sought [6]. A good solution to reduce the amount of packaging synthetic film materials is the use of biodegradable films that will have similar functional properties and ensure safe and possible long storage of food products.

One of the promising materials used for production of biodegradable packaging films is thermoplastic starch (TPS). It is characterized by such features as: ease of continuous matrix formation, complete biodegradability in soil and water, low cost, easy renewability and worldwide abundance [7, 8].

Pure native starch films are brittle and are characterized by lower mechanical strength [9] – compared to synthetic polymers (such as e.g. polyethylene) as well as have hydrophilic nature. Moisture and water absorption is crucial when polymer composites are applied not only for outdoor structures [10, 11] but also for packaging purposes [12]. As shown in the literature data [13–15], materials with high water absorption swell in all dimensions, and the absorbed water molecules adversely affect the interaction of the polymer matrix with fibres which can stimulate the growth of bacteria. Various functional additives are applied in order to increase the functional properties of films made on a TPS matrix. These include, for example: natural fibers, seeds, protein additives, hydrophobic biodegradable polymers, ceramic additives or waxes [16–19].

Kaolinite or kaolin clay and beeswax are the additions that have recently attracted particular attention of researchers. These additives are only used separately (for TPS films production) to improve mechanical and barrier properties of TPS films [19, 20].

There are no studies showing the synergistic effect of both additives on the microstructure as well as the mechanical properties and wettability of films based on thermoplastic starch. There is also a lack of analysis of the mechanical properties of these type of films in terms of tensile strength at different deformation velocities. This limits the considerations only to a small range of tensile loads. Combined analysis of the mechanical properties and microstructure, will contribute to a more accurate evaluation of the utility properties of the films. The aim of the work was to investigate the influence of both additives (kaolinite and beeswax) on the structural and physical properties of thermoplastic starch films.

MATERIALS AND METHODS

For the preparation of the films, commercial potato starch was purchased from PPZ Trzemeszno, (Trzemeszno, Poland) and kaolinite – KA (Merck KGaA, Darmstadt, Germany) and beeswax – BW (Adam Maciejko, WNI 06093511, Radawczyk Drugi, Poland). Glycerol 99.5% (Stanlab, Lublin, Poland) was used as the plasticizer.

For manufacturing samples the casting method was used. The procedure of casting TPS films – the pure (TPS/P) and with the functional additives (kaolinite – TPS/KA, beeswax TPS/BW and KA + BW films –TPS/KABW) was similar. Distilled water was used and potato starch, KA and BW were added to distilled water in the amounts given in Table 1. The solution was heated to 80 °C under constant stirring (300 rpm) using a magnetic stirrer – Steinberg SBS-MR-1600/1T (Steinberg Systems, Zielona Góra, Poland) for 30 minutes. Afterward, the solution was cooled to 40 °C and 1.3% (w/w) of glycerol was added. The complete solution was mixed using an ultrasonic homogenizer TF-650N (Tefic Biotech CO., Beijing, China) for 50 minutes. The suspensions were poured into 200×200 mm acrylic glass molds and dried in a KBC-65 thermal research chamber (WAMED, Warszawa, Poland) at 35 °C for 20 hours. After removing from the molds, the all films were conditioned (for 24 hours) at the temperature of 22 °C and 40% relative humidity (RH).

Table 1. The films compositions and thickness.

Specification	TPS/P	TPS/KA	TPS/BW	TPS/KABW
Distilled water (g)	754			
Starch (g)	34			
Glycerol (g)	10.6			
Kaolinite (g)	-	16.9	-	16.9
Beeswax (g)	-		8	
Thickness (mm)	0.09 ± 0.01	0.12 ± 0.01	0.17 ± 0.02	0.21 ± 0.03

The thickness of each film was measured (Table 1) with a digital micrometer (accuracy of ± 1 μm) after it was removed from the acrylic glass mold. Thickness measurements of five locations were taken (one in the center and four around the perimeter of the each film). The ten repetitions of measurements were made and the mean value was used for the calculations.

The microstructure of the samples were analyzed with a Nikon SMZ18 stereoscopic microscope equipped with a DS-Fi3 digital camera and a scanning electron microscope (SEM) Phenom ProX (Thermo Fisher Scientific INC., US). For SEM observations, films were mounted without pre-treatment onto aluminum specimen stubs, using high purity conductive double-sided adhesive carbon tabs.

For tensile test the TA.HD plus texture analyzer (Stable Micro System, Godalming, UK), equipped with Exponent 6.1.16.0 software was used. The measurements were carried out at three measuring head speeds of 0.0001 m/s, 0.001 m/s, and 0.01 m/s. Load cell capacity was 30 kg. The specimens were mounted on the testing machine using A/HDT jaws and had the shape of cuboids of constant length and width, 200 mm and 40 mm, respectively. The measuring length of the samples was 130 mm. The tests were performed at a sampling frequency of 100Hz. The accuracy class of the measuring head was 0.1%. For each deformation velocity, ten repetitions were made. Tests were performed at 24 °C and 45% RH.

Characterization of the surface of samples was performed base on the water contact angle (WCA) analysis and water sorption isotherms determination. The goniometer (Drop Shape Analysis System DSA100, Krüss, Germany) was used, and sessile drop method (distilled water in a volume of 2 μl) was applied according to the procedure described in previous study [2]. The changes in the contact angle was investigated after 0, 5 and 20 s. The analysis also included the change in the drop volume (V) and the ratio of the drop height to base length (H/L). Each measurement was carried out in three replications under steady temperature (20 °C) and 45% RH. To determine water sorption isotherms the gravimetric method was used. The values of water activity were obtained by using sulphuric acid with gradually decreasing (adsorption isotherm) and increasing (desorption isotherm) concentrations. The samples were equilibrated at each point for two days. The amount of adsorbed water at a given water activity was calculated from the difference in weight between the sample with adsorbed water and the dried sample. From the experimental data, the specific surface area (SSA) was calculated using the linear form of the standard BET equation [21].

RESULTS AND DISCUSSIONS

Microstructure observations

Figures 1 and 2 shows representative images of the microstructure of the tested films (TPS/P, TPS/KA,TPS/BW,TPS/KABW) observed using a stereoscopic microscope (Fig. 1) as well as SEM (Fig. 2). The TPS/KA films (Fig. 1b and Fig. 2b) were characterized by the most homogeneous structure compared to TPS/P films (Fig. 1a and Fig. 2a) and TPS/BW films and the films of KA and BW combination (TPS/KABW). SEM observation (Fig. 2a) showed that the microstructure of TPS/P films had heterogeneous morphologies with many "small round granules" which can be attributed to incompletely gelatinized starch.

This was supported by [22, 23] research for films made using an extrusion process. The authors explained this phenomenon with low temperature during extrusion. Other works indicated fully gelatinized starches in the blown process with higher temperature (the highest processing temperature reaches 170 °C and 155 °C, respectively) [24, 25]. According to previous report [26], the observed small number of micro-cracks (on the TPS/P surface) may be caused, by the electron beam during SEM observation. Moreover, Figure 1c and d demonstrated, nevertheless that a satisfying miscibility between the TPS matrix and beeswax could not be achieved. Larger sizes of residual, spherical beeswax insoluble elements were observed for the TPS/KABW samples (Fig. 1d). The good quality connection between the wax and the starch polymer matrix is preferable because smaller lipid globules and their more homogenous distribution enhance mechanical film properties [27]. The extended homogenization step may improve the structural homogeneity of the films with the beeswax addition. Muskat and co-authors [28] indicated the roughness and wax droplets aggregation on the surface of film samples, with the 5–10% w/w beeswax addition, made without homogenization. On the other hand, Auras et al. [29] effectively used a

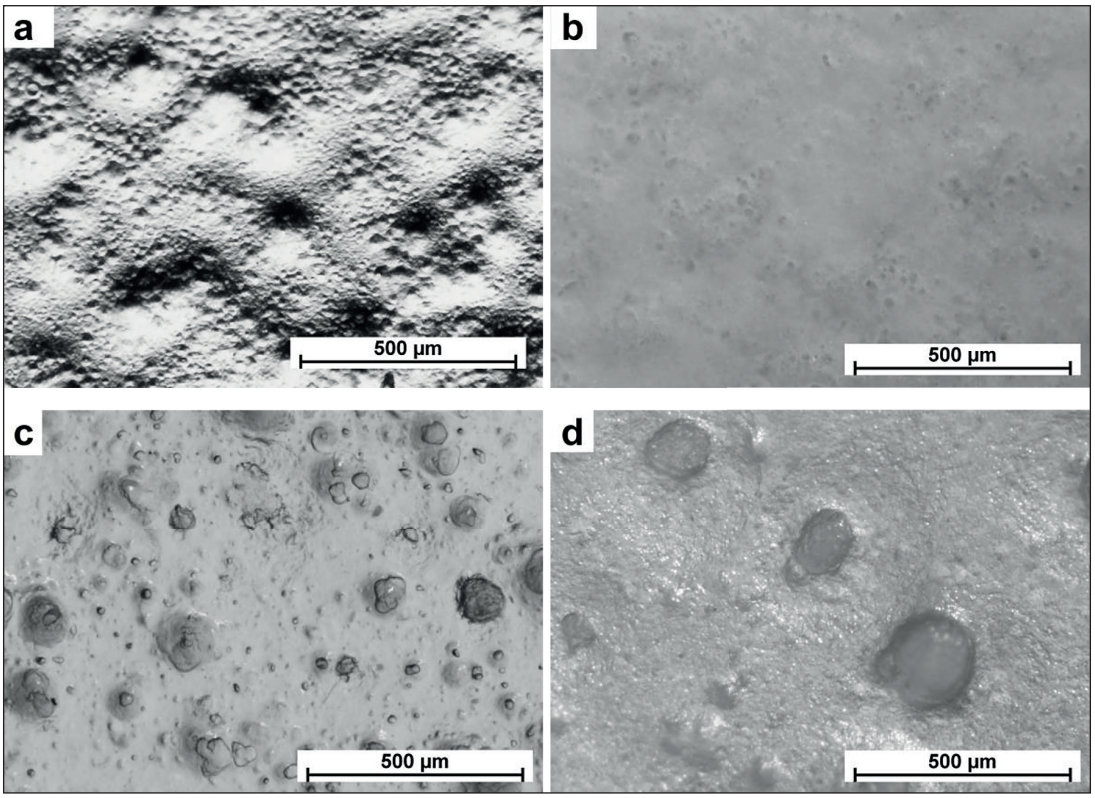

Figure 1. Microstructure images of the films surfaces: a) TPS/P; b) TPS/KA; c) TPS/BW; d) TPS/KABW.

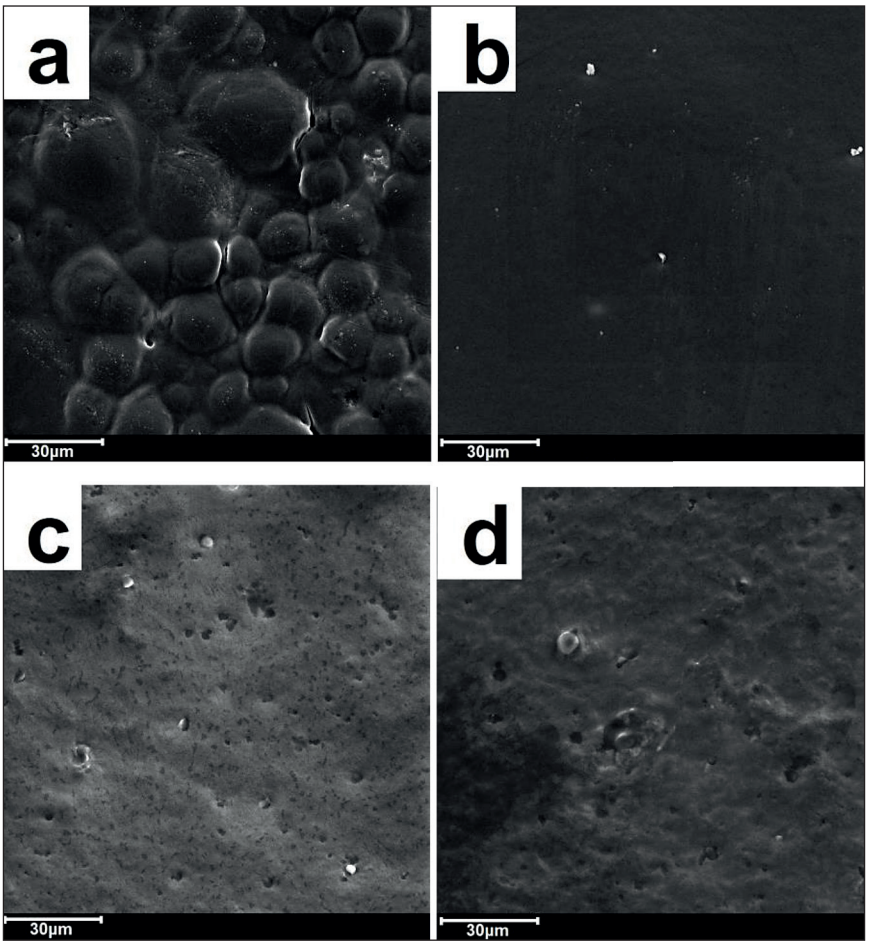

Figure 2. Microstructure images of the films surfaces (SEM): a) TPS/P; b) TPS/KA; c) TPS/BW; d) TPS/KABW.

homogenizing step to improve the microstructure homogeneity of beeswax modified cassava starch films. Ochoa et. al. [30] obtained continuous and homogeneous structures for modified corn starch-based films with the 1% w/w beeswax addition. The authors argued that the good incorporation of beeswax into the starch polymer matrix was due to the high energy emulsification process.

Mechanical properties

Tensile strength and elongation are two important properties of packaging materials/packaging films that determine their suitability to mechanical integrity of food support [31]. As it is shown at Figure 3 – TPS/P film samples were damaged with a relatively constant value of the failure strain of about 16%. A similar trend (relatively constant value of the failure strain) was noticed for films with KA+BW addition (TPS/KABW), where the failure strain ranged from 2 to 3%. It is observed that any additive used in the tested films resulted in a decrease of failure strain compared to the pure films. Depending on the type of addition, the values of the failure strain ranged from 1 to 5%.

Microstructure of the fractures showed no differences between the specimens after tensile test performed at different velocities of measurement head. TPS/P films fractures are characterized by the most smooth surface (Fig. 4a). The fractures of samples with KA and BW/KA addition (Fig. 4b and d) had layered structure with a visible rough surface with brittle fracture characteristic. The samples containing BW are characterized by some discontinuities in internal structure of the fractures Figure 4c and d, (marked with white arrows), as well as the presence of undissolved spherical residues of beeswax (Fig. 5d). The existence of a non-homogeneous structure leads to the weakening of the tensile properties, which is confirmed by [20, 27] and shown at Figure 3 for TPS/BW and TPS/KABW samples.

For the TPS/BW films along with the increase of the deformation velocity, the material failure occurred at lower mean values of the failure stress compared to TPS/P films. On the other hand, for films with KA addition (TPS/KA), the samples breaking occurred at higher mean values of failure stress. For all tested films, an increase in the failure stress with the increase of the deformation velocity was noticed. For all kinds of analysed films, the value of the elastic modulus growth with the deformation velocity increase, was noted (Fig. 5).

The addition of KA and/or BW increases the average values of the modulus of elasticity – compared to TPS/P films. The greatest increase in the modulus of elasticity was observed for the TPS/KA films. For the lowest test

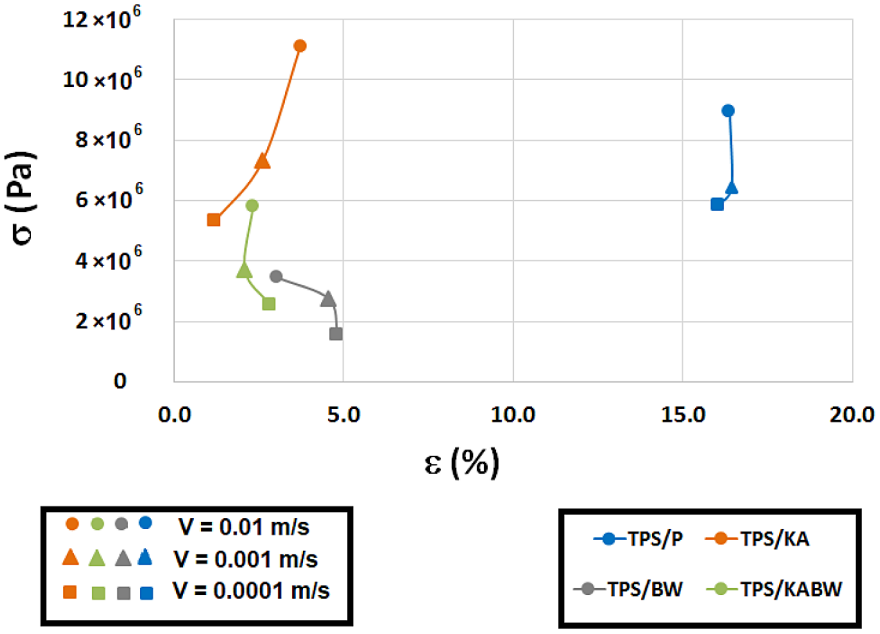

Figure 3. The relationship between failure stress, σ (Pa), and failure strain, ε (%), at different deformation velocities.

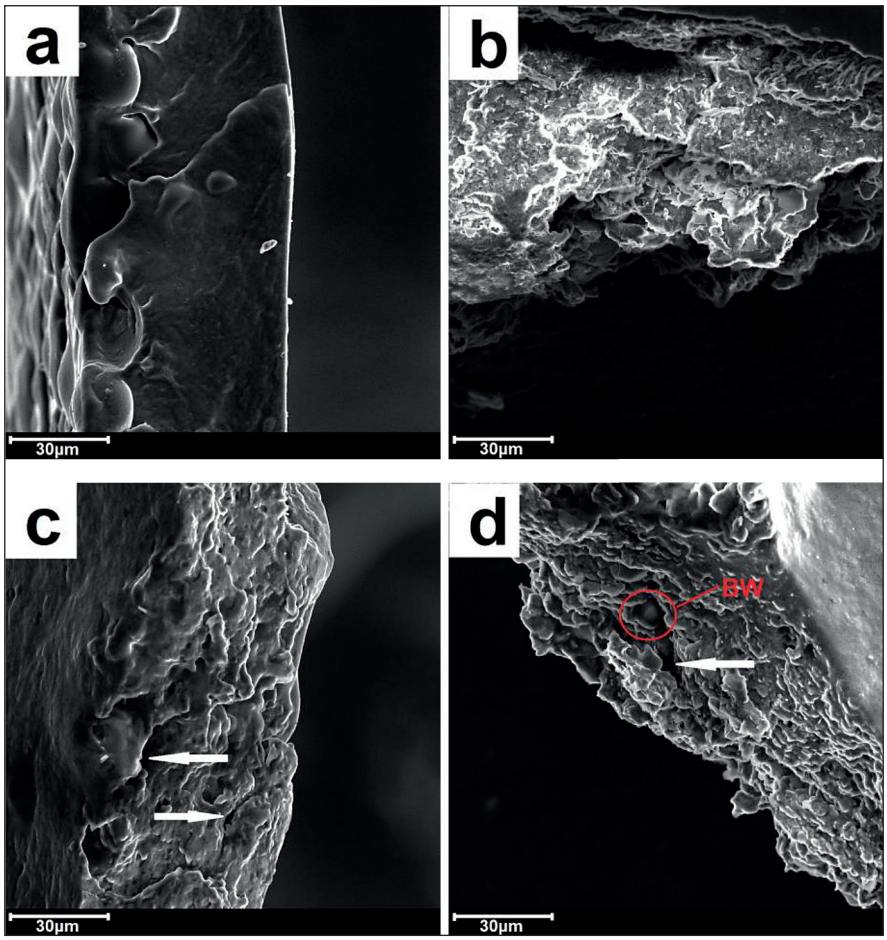

Figure 4. Representative SEM observations of the fractures: (a) TPS/P; (b) TPS/KA; (c) TPS/BW; (d) TPS/KABW.

velocity (V = 0.0001 m/s), these results are consistent with the results of [19] who noted (for V = 8.33 ×10^{-6} m/s) the lower tensile strength for samples made with the kaolin clay addition (5% w/w), compared to pure TPS films. The authors observed a decrease of values (tensile strength and Young's modulus) with an increased amount of kaolin clay addition. With a higher percentage of kaolin clay an increase in the percentage of polymer chains to be intercalated was observed

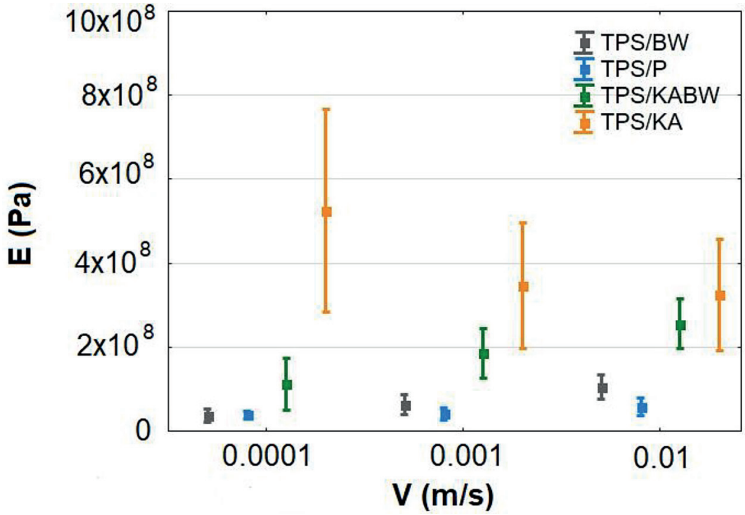

Figure 5. The dependence of the modulus of elasticity (E), on the deformation velocity (V).

(according to [19]). The authors pointed out that the phenomenon of decreasing the concentration of the non-incorporated polymer chains might be a main factor weakening of the mechanical properties of films. Further diffraction analysis is necessary to confirm or exclude this phenomenon for our results. Other hand, reduction of tensile strength and tensile strain values of the starch/BW blends described also the study [20]. The authors suggested that these phenomena is a result of low compatibility of starch (as a hydrophilic material) and BW (hydrophobic) and lead to formation of heterogeneous film structure along with the presence of discontinuities in the polymer network.

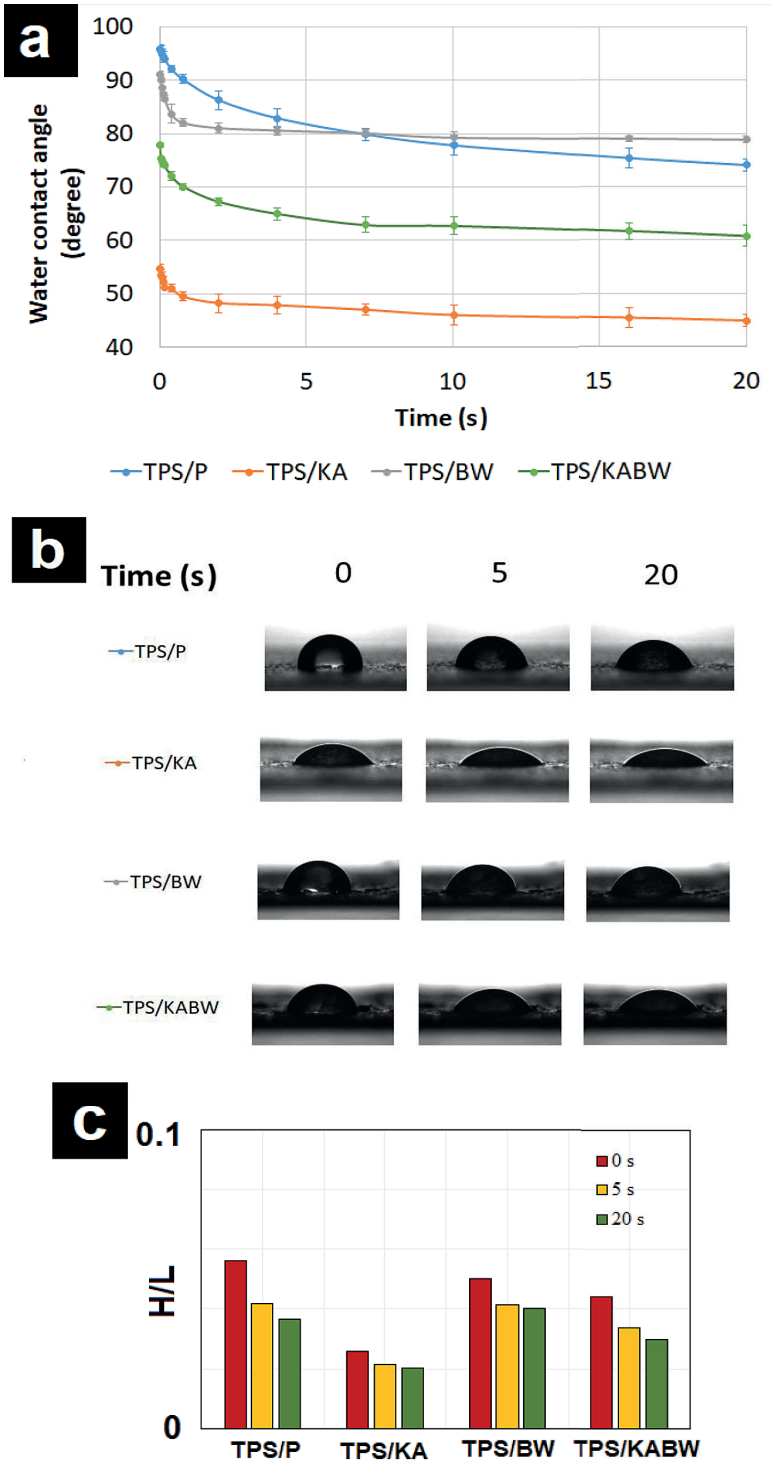

Figure 6. Shape (a) behavior (b-c) of water drops on the tested films as a function of time.

Surface characterization

The shape and behavior of water drops on the tested films as a function of time is shown at Figure 6. The highest initial value of water contact angle (WCA), measured immediately after drop contact with the surface of starch films, was noted for TPS/P (approximately 96°). For TPS/BW films, the initial WCA reached approximately 91°. Much lower values of the initial WCA angles were obtained for TPS/KABW films (about 78°) and TPS/KA films (about 55°) – Fig. 6a.

The WCA changes dynamic were the greatest within the first 5 s of measurement. In this time interval, the initial WCA were reduced by 14.6% (TPS/P), 12.1% (TPS/BW), 17.9% (TPS/KABW) and 13.6% (TPS/KA) – (Fig. 6a and b). It is worth mentioning that while the initial hydrophobicity of films with beeswax (TPS/BW) was lower compared to TPS/P, TPS/BW represents higher WCA values in time. In addition, a decrease in the droplet height to length ratio (H/L) (Fig. 6c) was observed, indicating the advantage of the liquid spreading over the penetration process. The changes in liquid volume did not exceed 3.7% (Table 2), with the highest dynamic observed for TPS/KA sample.

In the time interval from 5 to 20 s, changes dynamic of WCA, H/L ratio and liquid volume started to decrease. The WCA change was the highest for samples without additives (TPS/P), approximately 9.8%, with the changes in H/L and liquid volume reaching 12.07% and 1.76% respectively. In this case, the final value of WCA turned out to be lower than TPS/BW films (74° and 79°, respectively).

The water contact angle is a primary indicator of polymer materials' wettability properties [26]. When WCA is lower than 90°, a biopolymer can be considered hydrophilic, and hydrophobic when is higher than 90° [17, 32]. Initial contact angle values are primarily dependent on the chemical nature of the surface. According to Białopiotrowicz [33], during the film forming process, the most hydrophobic and branched parts of the amylopectin chain are directed outwards in the form of a gel film, which determines the initial wettability of the material. This explains the similar and high initial contact angle values obtained for TPS/P and TPS/BW and suggests a hydrophobic nature of both films. The composition of waxes may affect the hydrophobicity of starch-based film. Waxes contain special resins, higher fatty acids, wax esters of higher hydroxy alcohols, as well as long-chain alkanes of the strongest hydrophobicity [34]. Cheng et al. [35] showed that depending on waxes composition, they increase the water resistance and film surface hydrophobicity to a different extent. The Authors stated that the addition of beeswax significantly improved the surface hydrophobicity and WCA of starch gell films due to the wax crystal particles formed on the film surface.

The kaolinite addition usually increased the starch-based films' wettability [36, 37]. In line with Ashaduzzaman et al. [36] the interaction between the layered kaolinite and hydrophilic polymer chains produces intercalated films due to the penetration of the polymer into the interlayer region of the clay. Naturally occurring kaolin is hydrophilic and a key factor for this property is the surface hydroxyl groups of the octahedral surface [37]. Moreover, in the case of absorbing substrates, including those based on starch, complete stability of deposited drop is generally not achieved [38]. As some authors point out [39–41], this is the result of partial absorption of the liquid into the substrate, which reduces the contact angle. Our studies showed that the liquid spreading over the surface rather than absorbing into the material dominate for starch-based films with kaolinite. Typically, liquid absorption increases and contact angle decreases with increasing porosity [42, 43], pore size [44], and material permeability [41]. Kwaśniewska et al. [19], stated that increasing kaolin concentration in the biopolymer matrix led to enhanced surface roughness and wettability of the film composites surfaces.

Table 2. Drop volume change in 0–20 s.

Time (s)	Drop volume (m^3)			
	TPS/P	TPS/KA	TPS/BW	TPS/KABW
0	$1.99 \times 10^{-9} \pm 0.06$	$1.59 \times 10^{-9} \pm 0.02$	$1.64 \times 10^{-9} \pm 0.03$	$1.56 \times 10^{-9} \pm 0.02$
5	$1.94 \times 10^{-9} \pm 0.08$	$1.54 \times 10^{-9} \pm 0.02$	$1.63 \times 10^{-9} \pm 0.03$	$1.51 \times 10^{-9} \pm 0.03$
20	$1.90 \times 10^{-9} \pm 0.10$	$1.50 \times 10^{-9} \pm 0.02$	$1.60 \times 10^{-9} \pm 0.03$	$1.46 \times 10^{-9} \pm 0.03$

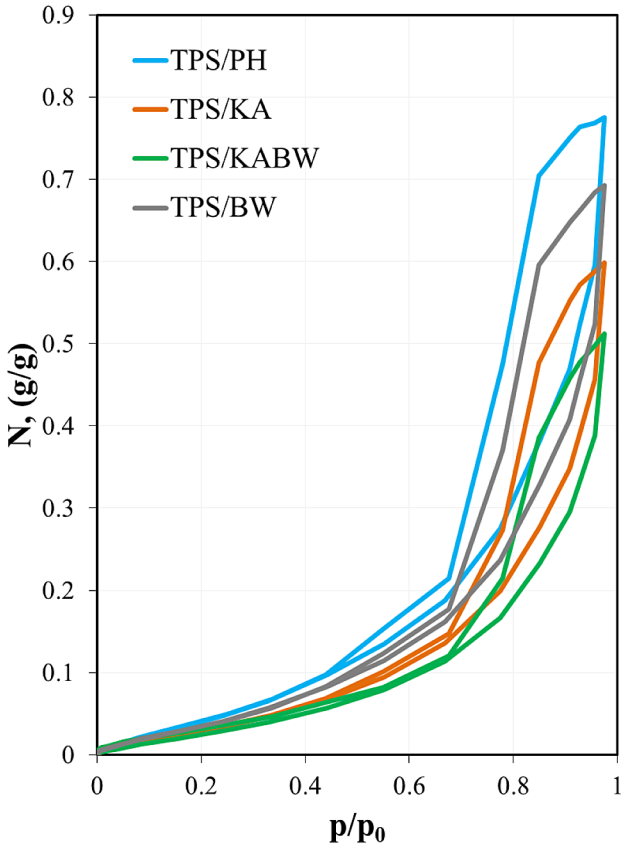

Figure 7. Water vapor sorption/desorption isotherms of the analyzed thermoplastic starch films.

Figure 7 presents water vapor sorption isotherms measured by the gravimetric method. For all analyzed samples isotherms were similar in shape without plateau effect at high water activity values. According to Brunauer et al. [21] classification they match to the type II characteristic for non-porous or macroporous adsorbents [45]. Sorption data showed that the highest adsorption was observed for TPS/P, while the addition of KA and BW decreased the adsorption quantity, and the size of hysteresis loops (Fig. 7). Hysteresis loops are generally associated with the filling and emptying of mesoporous [46] and have often been identified with specific pore structure. In food products hysteresis may also reflect conformation rearrangements influencing availability of polar sites [47]. The specific surface area is an essential parameter to quantify interaction processes at the gas-liquid-solid interface [48]. The greatest values of specific surface area (Table 3) were obtained for TPS/P samples. This could resulted from chemical nature of starch films that containing polar hydroxyl groups derived from glucose [2, 49]. These groups constitute strong adsorption centers for water vapor molecules. In contrast, BW wax is known as good water repellent material which affects wettability and higroscopicity [20, 49]. In line with [50], addition of BW significantly reduced moisture absorption rate in edible films based on gelatin. In the case of TPS/KA water could be partly adsorbed in pores or onto the external surfaces of kaolinite particles. However, kaolinite as a non – expanding clay, exhibits specific surface area ranging only from 10 to 40 m^2/g [51], which is several times less compared to the SSA of a pure starch film.

Table 3. Specific surface area (SSA) and maximum moisture content calculated from sorption isotherms data.

Specification	TPS/P	TPS/KA	TPS/BW	TPS/KABW
SSA (m^2/g)	208.46 ± 1.70	148.70 ± 1.13	171.79 ± 1.29	126.65 ± 1.67
Moisture content (g/g)	0.75 ± 0.03	0.60 ± 0.01	0.51 ± 0.02	0.69 ± 0.01

CONCLUSIONS

In study TPS films with beeswax and kaolinite addition were manufactured using the casting method. Structural and physical properties of films were investigated using microstructural observations, wettability, and water sorption isotherms determination. Additionally, the tensile tests were carried out under static load conditions at three different deformation velocities. The addition of kaolinite to the film matrix improved the homogeneity of the microstructure and increased the tensile strength and modulus of elasticity of TPS films. Beeswax films showed lower dynamics of the contact angle decrease, which proved their good water barrier properties. However, satisfying miscibility between the TPS matrix and beeswax was achieved, which resulted in a reduction in the tensile strength of beeswax film.

Our study confirmed composite kaolinite/beeswax films prospective for packaging applications. Further work is required to improve the quality of the films based on a combination of thermoplastic starch matrix and KA and BW additives to optimize their barrier and mechanical properties.

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