Article

Active Coatings Development Based on Chitosan/Polyvinyl Alcohol Polymeric Matrix Incorporated with Thymol Modified Activated Carbon Nanohybrids

Constantinos E. Salmas [1,*], Areti Leontiou [2], Eleni Kollia [3], Konstantinos Zaharioudakis [2], Anna Kopsacheili [3], Learda Avdylaj [3], Stavros Georgopoulos [2], Vassilios K. Karabagias [2], Andreas Karydis-Messinis [1], George Kehayias [2], Charalampos Proestos [3,*] and Aris E. Giannakas [2,*]

[1] Department of Material Science and Engineering, University of Ioannina, 45110 Ioannina, Greece; karydis.and@gmail.com
[2] Department of Food Science and Technology, University of Patras, 30100 Agrinio, Greece; aleontiu@upatras.gr (A.L.); zacharioudakis.k@upatras.gr (K.Z.); sgeorgop@upatras.gr (S.G.); vkarampagias@upatras.gr (V.K.K.); gkechagi@upatras.gr (G.K.)
[3] Laboratory of Food Chemistry, Department of Chemistry, National and Kapodistrian University of Athens Zografou, 15771 Athens, Greece; elenikollia@chem.uoa.gr (E.K.); akopsacheili@chem.uoa.gr (A.K.); leardaavdy@chem.uoa.gr (L.A.)
* Correspondence: ksalmas@uoi.gr (C.E.S.); harpro@chem.uoa.gr (C.P.); agiannakas@upatras.gr (A.E.G.)

Abstract: The food waste disposal to landfill practice contributes to the greenhouse problem due to the emission of gases such as methane into the atmosphere. Shelf life extension of food products and further valorization of food wastes such as the conversion to activated carbon are tested nowadays as alternative techniques. The development and use of biobased active coatings against food oxidation/bacterial deterioration is an environmentally friendly technique. In this study, a novel food active coating was successfully developed based on a chitosan (CS)/polyvinyl alcohol (PVOH) matrix activated with a nanohybrid of natural thymol (TO) adsorbed in activated carbon (AC) derived from spent coffee. The results have shown that, compared to the pure CS/PVOH polymeric matrix, the coating with 15 wt.% TO@AC nanohybrid concentration achieved a +23.5% Young's modulus value, a +20.1% ultimate strength value, an increased barrier of +50.2% for water and +74.0% for oxygen, a +69.0% antioxidant activity, an increased antibacterial activity of +5.5% against *Escherichia coli*, a +17.8% against *Salmonella enterica*, a +42.5% against *Staphylococcus aureus*, and a +2.5% against *Listeria monocytogenes*. A visual evaluation of this coating showed a delay in fresh bananas' enzymatic browning and a significant decrease in their weight loss. This indicates the potential extension of the fresh fruits' shelf life.

Keywords: shelf life; biomass valorization; spent coffee; activated carbon; thymol; chitosan; polyvinyl alcohol; nanohybrids; control release; active coatings; bananas preservation

check for updates

Citation: Salmas, C.E.; Leontiou, A.; Kollia, E.; Zaharioudakis, K.; Kopsacheili, A.; Avdylaj, L.; Georgopoulos, S.; Karabagias, V.K.; Karydis-Messinis, A.; Kehayias, G.; et al. Active Coatings Development Based on Chitosan/Polyvinyl Alcohol Polymeric Matrix Incorporated with Thymol Modified Activated Carbon Nanohybrids. *Coatings* **2023**, *13*, 1503. https://doi.org/10.3390/coatings13091503

Academic Editor: Domingo Martínez-Romero

Received: 27 July 2023
Revised: 16 August 2023
Accepted: 22 August 2023
Published: 25 August 2023

1. Introduction

Nowadays, a worldwide effort is being made to disengage the global economy from fossil fuels and their petrochemical derivatives [1–3]. One huge category of such derivatives is the petrochemical polymer plastics, which due to their non-biodegradable nature, contribute significantly to environmental pollution [1,4]. To reach a zero-carbon footprint, researchers suggest replacing fossil fuel-made polymers with biopolymers, which can be extracted or synthesized from biomass. The use of plastic polymers for packaging applications in the food industry is very common because of their flexible, rigid, or semi-rigid nature [5,6]. For a transition to a sustainable and "green" food industry, the researchers recommend the use of biobased polymers as food packaging materials [7–9]. Cellulose, starch, gelatin, alginate salts, and chitosan are some of the suggested natural abundant biopolymers that can replace the petrochemically derived polymers used in the food packaging industry [10–12]. Chitosan (CS) holds great potential for use in food packaging applications due to its non-toxicity, biodegradability, film-forming properties, gas barrier properties, and significant antibacterial activity against various food pathogens [13–16]. Moreover, it can be produced from chitin, which is the second most abundant biopolymer after cellulose and can be extracted from crustacean waste, such as crabs, shrimps, and crayfish [14].

Another significant global trend is food waste management, which can enforce sustainability and the green economy [17–21]. Large amounts of food are wasted due to the modern lifestyle, which increases the demand for the availability of all kinds of food throughout the year. The landfilling of food waste produces small quantities of methane via an aerobic decomposition stage and anaerobic conditions are established. In less than a year, food waste decomposition starts to be boosted by methane-producing bacteria, and larger quantities of methane are generated. The food supply chain is supported economically by higher added value products originating from food waste valorization. Active packaging could be a potentially sustainable solution to reduce food waste by increasing its preservation period and nutritional characteristics [22]. CS-based films have been suggested as promising fruit and vegetable coatings [23]. Because of their antibacterial properties and their controllable CO_2 and O_2 barrier properties, CS films could regulate fruit and vegetable respiration and extend their shelf life period. Polyvinyl alcohol (PVOH) is a synthetic water-soluble biodegradable polymer that incorporates excellently with CS, to develop CS/PVOH composites with enhanced tensile, barrier, and antibacterial properties [24]. On the other hand, essential oils (EO) and their derivatives are promising candidates to replace antioxidant and antibacterial additives used to preserve fruit and vegetables [25]. EO can be incorporated into a biopolymer such as CS creating bioactive hydrogels and, exhibiting controlled antioxidant and antibacterial activity, be used as fruit and vegetable active coatings [25,26]. To minimize the reduction of EO's antioxidant and antibacterial activity, because of their volatile nature, it is suggested that such bioactive compounds be adsorbed into nanocarriers such as montmorillonite and halloysites nanoclays [27,28]. Recently, natural zeolites were suggested as an alternative nanocarrier for such bioactive compounds, to control the release of EOs in active food packaging systems [29–31]. Under the same spirit, activated carbon (AC) could be a novel alternative nanocarrier and a controlled release platform for EOs in active packaging systems because it can be produced almost from all kinds of biomass and food waste, and due to its very high specific pore surface area [31].

Browning of raw fruits is a major problem in the food industry and is believed that it will be one of the main reasons for quality loss during after-harvest handling and processing. It will also be one of the main reasons for the dramatic increase in food waste [32]. Bananas are rich in nutritional components but are highly sensitive to enzymatic browning. Thus, is a particularly problematic fruit. This enzymatic browning reduces bananas' preservation time, deters consumers from purchasing them, and increases banana waste [33]. Last year's studies showed that CS-based active coatings could extend bananas' preservation period and protect them from enzymatic browning [34].

Recently, AC produced via the pyrolysis of spent coffee was modified with a thymol (TO)-rich fraction of thyme essential oil to create a TO@AC nanohybrid. The TO@AC nanohybrid was successfully incorporated into LDPE active packaging films [35]. Also, the CS/PVOH biodegradable composite matrix proved to be beneficial for the water/oxygen barrier, antioxidant, and antibacterial properties as compared to pure CS matrix [24,36]. In the present study, the as-prepared TO@AC nanohybrid was incorporated into a CS/PVOH matrix at 5, 10, and 15 wt.% contents to develop novel CS/PVOH/xTO@AC active films/coatings (where x = 5, 10, and 15) via a solution casting method. For comparison, pure AC from spent coffee was incorporated into a CS/PVOH matrix to develop CS/PVOH/xAC active film/coatings (where x = 5, 10, and 15). The as-prepared CS/PVOH/xAC and CS/PVOH films were characterized with XRD analysis, FTIR spectroscopy, and SEM images to investigate the relaxation and dispersion of the pure AC and TO@AC nanohybrid within the CS/PVOH matrix. Tensile, water/oxygen barrier properties were investigated, while total antioxidant activity and antibacterial properties against two Gram-positive and two Gram-negative food pathogens were studied. All these studied properties are crucial for such active coatings. To be novel, an active coating with potential use as active food coating should exhibit enhanced tensile strength, water/oxygen barrier properties, and significant antioxidant/antibacterial activity [23]. The most active CS/PVOH/xAC and CS/PVOH/xTO@AC films were successfully applied as coatings to extend the preservation time of fresh bananas. The overall study showed that these novel CS/PVOH/xAC and CS/PVOH/xTO@AC active films could potentially be used as fresh fruit and vegetable active coatings.

The innovation of this work is that by following the spirit of bioeconomy, a biodegradable active coating for the preservation of fresh fruits such as fresh bananas was first time developed. This new active packaging was developed by combining CS, which was derived from shellfish and crustacean byproducts, and AC, which was obtained from spent coffee, a water-soluble biopolymer such as PVOH, and TO which was a component of naturally available EOs.

2. Materials and Methods

2.1. Materials

Acros-Organics company (Zeel West Zone 2, Janssen Pharmaceuticalaan 3a, B2440, Geel, Belgium) was the supplier of high molecular weight, i.e., 100,000–300,000, Chitosan (CS). Thermo Scientific Chemicals Co., (168 Third Avenue, Waltham, MA, USA 02451) was the supplier for low molecular weight polyvinyl alcohol, hydrolyzed up to 86%–89%. Students' café of the University of Ioannina was the supplier for spent coffee which was converted to activated carbon (AC) via pyrolysis process and using KOH activator [37]. The produced AC exhibited a Brünaüer-Emmett-Teller (BET) surface area of 1372 m^2/g and a micropore volume fraction of 84.6% [37]. Sigma-Aldrich (Co., 3050 Spruce Street, St. Louis, MO, USA, 314-771-5765) was the supplier of acetic acid (CAS Number: 64-19-7).

2.2. Preparation of TO@AC Nanohybrid

Pure activated carbon was modified using thyme oil rich in thymol (TO) according to a recently developed and reported "green" distillation/adsorption process [35]. The TO fraction of the TO@AC nanohybrid was rather physiosorbed than chemisorbed with a concentration of 51 wt.% [35]. Physiosorbed TO molecules are released easier from the AC porous material and are more preferable for control release processes compared with chemisorbed molecules.

2.3. CS/PVOH/xAC and CS/PVOH/xTO@AC Films Preparation

For the preparation of CS/PVOH/xAC and CS/PVOH/xTO@AC films, a solution casting method was used [38]. Firstly, a 1 v/v in acetic acid 2 wt.% CS aquatic solution of was prepared and a 10 wt.% aquatic solution of PVOH [38,39]. For each film, 90 mL of the 2 wt.% CS solution and 12 mL of the 10 wt.% PVOH solution was mixed. In the obtained CS/PVOH solution 0.21 g, 0.44 g, and 0.71 g of AC or TO@AC powder was added to achieve 5, 10, and 15 wt.% AC and TO@AC final nominal content. All the CS/PVOH/xAC and CS/PVOH/xTO@AC mixtures were homogenized with stirring for 5 min at 18,000 rpm. Approximately 50 mL of obtained solutions were cast in two plastic Petri dishes with 10 cm diameter and dried at 25 °C for three-four days. The obtained CS/PVOH/xAC and CS/PVOH/xTO@AC (see Figure 1) were piled off from Petri dishes and stored at 25 °C and 50% RH for further use and characterization.

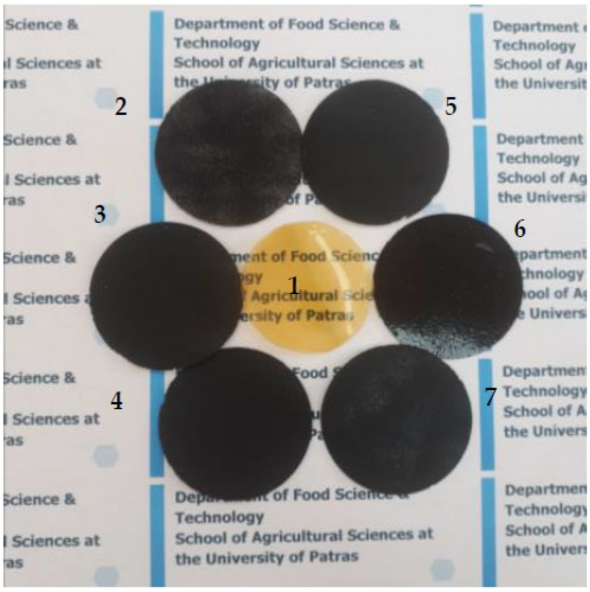

Figure 1. Obtained (1) pure CS/PVOH, (2) CS/PVOH/5AC, (3) CS/PVOH/10AC, (4) CS/PVOH/15AC, (5) CS/PVOH/5TO@AC, (6) CS/PVOH/10TO@AC, and (7) CS/PVOH/15TO@AC.

2.4. XRD Analysis of CS/PVOH/xAC and CS/PVOH/xTO@AC Films

The obtained CS/PVOH/xAC and CS/PVOH/xTO@AC films were characterized with XRD analysis by using a Brüker D8 Advance X-ray diffractometer instrument (Brüker, Analytical Instruments, S.A., Athens, Greece) and according to the experimental condition described recently [24].

2.5. FTIR Spectroscopy of CS/PVOH/xAC and CS/PVOH/xTO@AC Films

The relaxations of AC and TO@AC with CS/PVOH matrix were investigated with FTIR spectroscopy measurements. For the measurements, an FT/IR-6000 JASCO Fourier transform spectrometer (JASCO, Interlab, S.A., Athens, Greece) was employed according to the experimental conditions described recently [24].

2.6. Tensile Measurements of CS/PVOH/xAC and CS/PVOH/xTO@AC Films

Tensile properties of obtained CS/PVOH/xAC and CS/PVOH/xTO@AC films, as well as pure CS/PVOH, were carried out according to the ASTM D638 method and the methodology described recently [40]. For the tensile measurements, a Simantzü AX-G 5kNt instrument (Simandzu Asteriadis, S.A., Athens, Greece) was employed.

2.7. Water Vapor Transmission Rate Measurements and Water Diffusion Coefficient Calculation

The water vapor transmission rate (WVTR [g/(cm^2.s)]) for all obtained CS/PVOH/xAC and CS/PVOH/xTO@AC films, as well as pure CS/PVOH film was measured according to the ASTM E96/E 96M-05 method at 38 °C and 95% RH by using a handmade apparatus. The calculated WVTR values were transformed into water vapor diffusivity (D_{wv}) values according to the theory and equations described in detail in previous publications [30].

2.8. Oxygen Transmission Rate Measurements and Oxygen Permeability Calculation

Oxygen transmission rate (OTR) values (cc O_2/m^2/day) for all obtained CS/PVOH/xAC and CS/PVOH/xTO@AC films, as well as pure CS/PVOH film were measured according to the ASTM D 3985 method at 23 °C and 0% RH. For the measurements, an oxygen permeation analyzer (O.P.A., 8001, Systech Illinois Instruments Co., Johnsburg, IL, USA) was employed. From the measured OTR values the oxygen permeability coefficient values (PeO_2) were calculated according to the theory and equations provided in detail in previous publications [30].

2.9. Total Antioxidant Activity of CS/PVOH/xAC and CS/PVOH/xTO@AC Films

The total antioxidant activity of all CS/PVOH/xAC and CS/PVOH/xTO@AC films was estimated according to the diphenyl-1-picrylhydrazyl (DPPH) method. For the experiments, a 40 ppm ethanolic solution of DPPH stock solution was prepared. Inside a dark glass bottle, 10 mL of DPPH stock solution and 300 mg of each film were placed and incubated for 24 h. Sampling from the incubated DPPH solution was carried out at the beginning and after 24 h. The absorbance at 517 nm wavelength was measured using a Jasco V-530 UV-vis spectrophotometer. As a blank sample measurement, the absorbance value of a 10 mL DPPH ethanolic solution without film was measured at the same wavelength.

Equation (1) was used for the estimation of the % antioxidant activity after 24 h and incubation of films was calculated according to the following equation:

$$\%\ \text{Antioxidant activity} = (\text{Abs}_{\text{blank}} - \text{Abs}_{\text{sample}})/\text{Abs}_{\text{blank}} \times 100 \quad (1)$$

2.10. Antibacterial Activity Tests of CS/PVOH/xAC and CS/PVOH/xTO@AC Films

The antibacterial activity of the films was evaluated using the well diffusion method against four foodborne pathogenic bacteria. ELGO-DEMETER, Institute of Technology of Agricultural Products, which is located at Lykovryssi area, Athens, Attica, Greece is the provider of *Escherichia coli* (ATCC 25922), *Salmonella enterica* subsp. *enterica* (DSMZ 17420) (Gram-negative bacteria), *Staphylococcus aureus* (DSMZ 12463), and *Listeria monocytogenes* (DSMZ 27575) (Gram-positive bacteria) bacterial strains. These two gram+ and two gram- bacteria are four of the seven most frequently occurring foodborne pathogenic bacteria [41].

Experiments were started with cultivation of the bacterial strains in Mueller-Hinton broth at a temperature of 37 °C for 24 h. By facilitating growth, a bacterial concentration ranging between 10^7 and 10^8 colony-forming units per milliliter (CFU mL^{-1}) was obtained. These bacterial cultures were evenly spread on Mueller-Hinton agar plates by rotating the plates at 60-degree intervals. This technique increases the assurance of uniform growth of bacterial colonies.

Testing wells were made using a cork borer dipped in alcohol and flamed. This borer was cut into 6 mm wells into the agar surface of the plates. An amount of 100 μL of the antimicrobial suspensions, precursors of the final films, was used to fill up these wells. The plates were incubated overnight at 37 °C.

After the incubation period, the diameter of any clear zone surrounding the wells was measured using calipers. The clean zone diameter value was used for the estimation of the antimicrobial activity extension of the suspensions against the tested bacteria. Three repetitions of the entire experimental procedure were carried out to achieve a final consistent and reliable mean value.

2.11. Application in Fresh Bananas Preservation

For the application of the obtained CS/PVOH/xAC and CS/PVOH/xTO@AC films as banana coating, the following procedure was followed. With the procedure described hereabove in Section 2.3, 1000 mL of pure CS/PVOH, CS/PVOH/15AC, and CS/PVOH/15TO@AC hydrogel coatings were prepared. Next, twelve (12) banana samples without diseases and pests, mechanical damage, and the same maturity were selected from a local fruit market. The samples were divided into four groups with three bananas each. The first group with three bananas was the uncoated group. The second group with three bananas was the group coated with CS/PVOH coating. The third group with three bananas was the group coated with CS/PVOH/15AC coating and the fourth group with three bananas was the group coated with the CS/PVOH/15TO@AC coating. Bananas were coated, immersing them in the obtained 1000 mL hydrogel solutions of pure CS/PVOH, CS/PVOH/15AC, and CS/PVOH/15TO@AC for 1 min. Then, all the coated and the uncoated bananas were stored in room conditions (15–20 °C and 65% mean relative humidity (RH)) for 8 d. Then, the quality changes in bananas at 0, 1, 2, 3, 4, 5, 6, 7, and 8 d of storage were monitored by taking photos and measuring the weight loss of them.

2.12. Statistical Analysis

Experimental values obtained by three repetitions of characterization measurements, i.e., tensile, water/oxygen barrier, antioxidant activity, antibacterial activity, and weight loss of fresh bananas, were treated using the statistical software IBM, SPSS version 25 (IBM Corp., Armonk, NY, USA). The mean values achieved after the statistical treatment are presented in Tables 1–3, Figures 5 and 8. Values after the plus/minus (±) sign correspond to standard deviation considering a confidence interval of C.I. = 95%. The statistical inequality between mean values of properties was checked via a hypothesis test routine assuming a statistical significance level of $p = 0.05$. The after-test rejected assumption of normality imposed by the non-parametric Kruskal-Wallis method for hypothesis test. Statistically equal mean values are indicated in tables with the same superscript index.

3. Results

3.1. XRD Analysis of CS/PVOH/xAC, CS/PVOH/xTO@AC Films

In Figure 2, the XRD plots of pure CS/PVOH film as well as of all CS/PVOH/xAC and all CS/PVOH/xTO@AC films are observed in the range of 2 theta from 2° to 30°.

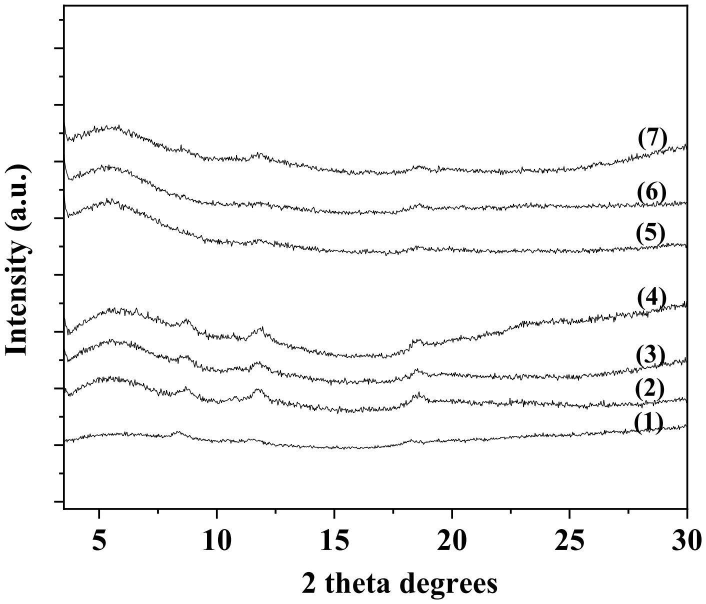

Figure 2. XRD plots of (1) CS/PVOH, (2) CS/PVOH/5AC (3) CS/PVOH/10AC, (4) CS/PVOH /15AC, (5) CS/PVOH /5TO@AC, (6) CS/PVOH/10TO@AC, and (7) CS/PVOH /15TO@AC obtained films.

In the XRD plots of pure CS/PVOH composite film (see line (1) in Figure 1), broad peaks at around 8.5°, 11.5°, and 18.5° are observed. Peaks at 8.5° and 11.5° indicate the CS's hydrated crystallite structure because of the insertion of water molecules in the CS's crystal lattice [36]. The third peak at 18.5° is assigned to the CS's regular crystal lattice [36]. As it was mentioned recently, the peaks at 8.5°, 11.5°, and 18.5° indicate that PVOH enhances the hydrated structure of CS [24,36].

In the case of CS/PVOH/xAC films, the peaks at 8.5°, 11.5°, and 18.5° (see plot lines (2), (3), and (4) in Figure 2) are slightly increased in comparison to the pure CS/PVOH film. On the contrary, in the case of CS/PVOH/xTOAC films, the same peaks at 8.5°, 11.5°, and 18.5° (see plot lines (5), (6), and (7) in Figure 2) almost disappeared. This suggests higher miscibility and dispersion of modified TO@AC nanohybrid as compared to pure AC with CS/PVOH matrix.

3.2. FTIR Spectroscopy of CS/PVOH/xAC, CS/PVOH/xTO@AC Films

FTIR spectra of all obtained CS/PVOH/xAC and CS/PVOH/xTO@AC films, as well as the pure CS/PVOH film, are plotted in Figure 3.

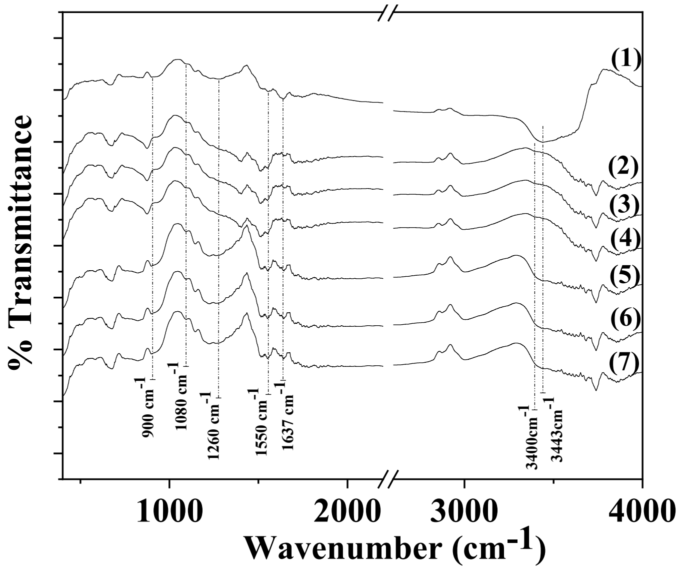

Figure 3. FTIR plots of (1) CS/PVOH, (2) CS/PVOH/5NZ (3) CS/PVOH/10NZ, (4) CS/PVOH /15NZ, (5) CS/PVOH /5TO@NZ, (6) CS/PVOH/10TO@NZ, and (7) CS/PVOH /15TO@NZ obtained films.

In the FTIR plot of the pure CS/PVOH film (see line (1) in Figure 3) there are obtained reflections of both CS and PVOH polymers. The large band at 3443 cm^{-1} is assigned to the stretching vibration of hydroxyl groups of both CS and PVOH [29]. At 3400 cm^{-1} is assigned the primary stretching vibration of amino groups of CS [29]. The reflections at 1637, 1550, 1260, 1080, and 900 cm^{-1} are redshift of C-H stretching, C-O stretching, N-H bending, and O-H stretching of CS due to the strong relaxation with PVOH chains [42]. In the case of both CS/PVOH/xAC (see lines (2), (3), and (4) in Figure 3) and CS/PVOH/xTO@AC (see lines (5), (6), and (7) in Figure 3) FTIR plots the characteristic reflections of AC are observed in advance to CS/PVOH matrix reflections. The band at 1260 cm^{-1} is assigned to the stretching vibration of the C-O groups. The band with a maximum of about 3420–3440 cm^{-1} is assigned to the O-H stretching mode of hydroxyl groups of the adsorbed water molecules [37]. With a careful glance at the CS/PVOH/xAC and CS/PVOH/xTO@AC FTIR plot, the result is that, in the case of CS/PVOH/xTO@AC, the reflection at 1260 cm^{-1} increased, implying a bigger relaxation and interplay between CS/PVOH N-H groups and TO@AC C-O groups. In advance in the case of CS/PVOH/xTO@AC FTIR plots, the reflection of the primary stretching vibration of amino groups of CS at 3400 cm^{-1} is more intense than in the case of CS/PVOH/xAC FTIR plots where the same reflection almost disappeared. This is also implying the higher relaxation of N-H groups of the CS/PVOH matrix with the O-H groups of the TO@AC nanohybrid.

Thus, by both XRD analysis and FTIR spectroscopy it resulted in the higher dispersion and relaxation of TO@AC nanohybrid with CS/PVOH matrix in comparison to pure AC with CS/PVOH matrix.

3.3. Tensile Properties CS/PVOH/xAC, CS/PVOH/xTO@AC Films

In Figure 4, the representative stress-strain curves of all CS/PVOH/xAC and CS/PVOH/xTO@AC films, as well as of the pure CS/PVOH film, are plotted for comparison. From these stress-strain curves, the Young's (E) modulus, ultimate tensile strength (σ_{uts}), and % strain at break (ε_b) have been calculated and listed in Table 1. From the calculated values of the Young's (E) modulus, the ultimate tensile strength (σ_{uts}), and % strain at break (ε_b) the effect of the addition of both pure AC and modified TO@AC nanohybrid in the CS/PVOH matrix is estimated. Higher ultimate strength values of obtained CS/PVOH/xAC and CS/PVOH/xTO@AC films are favorable for the application of such nanocomposites as coatings.

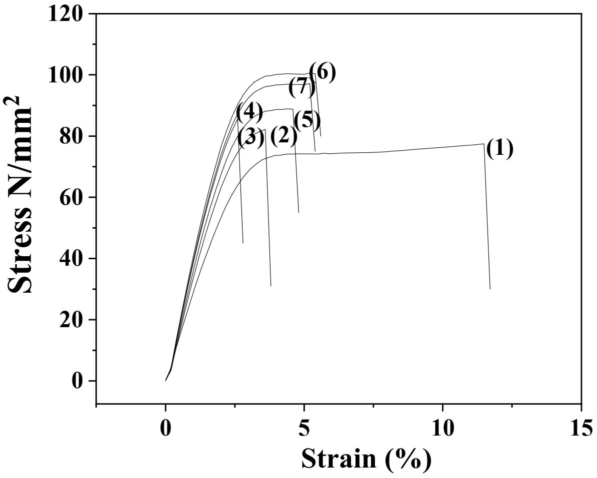

Figure 4. Stress-strain curves of (1) CS/PVOH, (2) CS/PVOH/5AC (3) CS/PVOH/10AC, (4) CS/PVOH /15AC, (5) CS/PVOH /5TO@AC, (6) CS/PVOH/10TO@AC, and (7) CS/PVOH /15TO@AC obtained films.

Table 1. Calculated values of Young's (E) modulus, ultimate tensile strength (σ_{uts}), and % strain at break (ε_b).

Sample Code Name	E	σ_{uts}	ε%
CS/PVOH	2249.3(100.3)	71.2(1.8)	11.8(0.9)
CS/PVOH/5AC	2511.0(43.0)	79.0(5.7)	4.1(0.7)
CS/PVOH/10AC	2881.3(63.2)	86.1(6.1)	3.4(0.1)
CS/PVOH/15AC	2789.0(64.4)	82.1(4.5)	5.4(0.9)
CS/PVOH/5TO@AC	2692.0(54.2)	81.8(7.4)	5.2(1.5)
CS/PVOH10TO@AC	3041.3(79.2)	104.3(8.0)	6.1(0.9)
CS/PVOH/15TO@AC	2938.5(60.5)	88.0(6.1)	5.9(0.8)

As is obtained from the Young's (E) modulus, ultimate tensile strength (σ_{uts}), and % strain at break (ε_b) values of Table 1, the addition of both pure AC and modified TO@AC nanohybrids in the CS/PVOH matrix enhanced the tensile stress and strength values while reducing the elongation at break values of all CS/PVOH/xAC and CS/PVOH/xTO@AC films. Higher stress and ultimate strength values are obtained for all CS/PVOH/xTO@AC films in comparison to CS/PVOH/xAC films. The film with the highest stress and ultimate strength is the CS/PVOH10TO@AC film.

3.4. Water-Oxygen Barrier Properties of CS/PVOH/xAC, CS/PVOH/xTO@AC Films

The obtained water vapor transmission rate (WVTR) and the oxygen transmission rate (OTR) values for all CS/PVOH/xAC and CS/PVOH/xTO@AC films as well as pure CS/PVOH film are listed in Table 2. From these values, the water diffusivity (D_w) and the oxygen diffusivity (PeO_2) values are calculated and are listed in Table 2 for comparison.

As is obtained from Table 2, both pure AC and modified TO@AC nanohybrids decrease the D_w and PeO_2 values of obtained films. The higher the AC and TO@AC wt.% content, the lower the obtained D_w and PeO_2 values. The TO@AC nanohybrid succeeded to decrease farther than the obtained D_w and PeO_2 values than pure AC. This result is correlated with the higher dispersion and relaxation of the TO@AC nanohybrid shown hereabove in the XRD analysis and FTIR spectrometry measurements.

Table 2. Film thickness, water vapor transmission rate (WVTR), water diffusivity (D), oxygen transmission rate (OTR), and oxygen diffusivity (PeO_2) values of pure CS/PVOH film as well as CS/PVOH/HNT and CS/PVOH/TO@HNT films.

Sample Code Name	Water Vapor Transmission Rate Film Thickness (mm)	Water Vapor Transmission Rate (10^{-6} g/cm^2.s)	Diffusion Coefficient (10^{-4} cm^2/s)	Oxygen Transmission Rate Film Thickness (mm)	Oxygen Transmission Rate (mL/m^2.day)	PeO_2 (10^{-7} cm^2/s)
CS/PVOH	0.14 ± 0.01	1.339 ± 0.024	4.36 ± 0.11	0.15 ± 0.01	38.20 ± 1.91	5.73 ± 0.29
CS/PVOH/5AC	0.15 ± 0.01	1.240 ± 0.025	4.32 ± 0.11	0.15 ± 0.01	19.10 ± 0.96	2.87 ± 0.14
CS/PVOH/10AC	0.17 ± 0.01	0.896 ± 0.021	3.53 ± 0.10	0.09 ± 0.01	27.50 ± 1.38	2.48 ± 0.12
CS/PVOH/15AC	0.16 ± 0.01	0.924 ± 0.014	3.43 ± 0.07	0.16 ± 0.01	10.10 ± 0.51	1.62 ± 0.08
CS/PVOH/5TO@AC	0.12 ± 0.01	0.902 ± 0.018	3.18 ± 0.07	0.14 ± 0.01	18.50 ± 0.93	2.59 ± 0.13
CS/PVOH/10TO@AC	0.13 ± 0.01	0.735 ± 0.017	2.99 ± 0.09	0.10 ± 0.01	17.50 ± 0.88	1.75 ± 0.09
CS/PVOH/15TO@AC	0.14 ± 0.01	0.802 ± 0.012	2.17 ± 0.09	0.15 ± 0.01	10.30 ± 0.50	1.49 ± 0.07

3.5. Total Antioxidant Activity of CS/PVOH/xAC and CS/PVOH/xTO@AC Films

The % total antioxidant activity of all CS/PVOH/xAC and CS/PVOH/xTO@AC films as well as pure CS/PVOH after 24 h of incubation are plotted in Figure 5. As it was expected, pure CS/PVOH and all CS/PVOH/xAC films showed small values of total antioxidant activity due to the presence of CS, which is known to have antioxidant activity [43]. For CS/PVOH/xTO@AC films, a significant % total antioxidant activity values are obtained due to the presence of TO molecules [44]. As the wt.% content of TO@AC use increased, the obtained % total antioxidant activity values increased further. It must also be underlined that the values obtained here for CS/PVOH/xTO@AC are much higher than the values reported recently for CS/PVOH/xTO@AC films with the same method, implying the superiority of AC against HNT as TO molecule nanocarriers for control release applications [45].

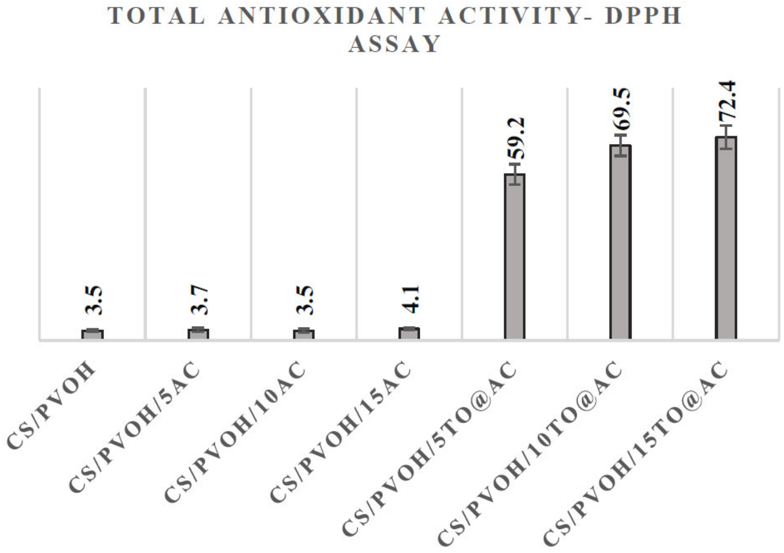

Figure 5. % Total antioxidant activity of all obtained CS/PVOH/xAC and CS/PVOH/xTO@AC films.

3.6. Antibacterial Properties of CS/PVOH/xAC and CS/PVOH/xTO@AC Films Agar Diffusion Test

The antibacterial activity of various film materials against four bacterial strains (*E. coli*, *S. aureus*, *S. enterica*, and *L. monocytogenes*) was investigated in this study. The films tested included CS, CS/PVOH, CS/PVOH/5AC, CS/PVOH/10AC, CS/PVOH/15AC, CS/PVOH/5TO@AC, CS/PVOH/10TO@AC, and CS/PVOH/15TO@AC. The inhibitory activity of the film materials against the bacteria was determined by measuring the clear zone diameters. The results showed varying levels of antibacterial activity among the film materials, indicating the potential for improved efficacy through the addition of specific components.

Table 3 and Figure 6 provide an assessment of the antibacterial effectiveness of the studied nano-reinforced CS/PVOH-based packaging films.

Table 3. Antimicrobial activity of active films against food pathogenic bacteria *E. coli*, *S. aureus*, *S. enterica*, and *L. monocytogenes*.

Film Material	***E. coli***	***S. aureus***	***S. enterica***	***L. monocytogenes***
	Inhibition [1] (Diameter of Clear Zone)	**Inhibition [1] (Diameter of Clear Zone)**	**Inhibition [1] (Diameter of Clear Zone)**	**Inhibition [1] (Diameter of Clear Zone)**
CS	3.07 ± 0.22^{a}	3.56 ± 0.43^{a}	3.40 ± 0.32^{a}	2.03 ± 0.26^{a}
CS/PVOH	3.63 ± 0.35^{ab}	3.72 ± 0.25^{ab}	3.49 ± 0.11^{ab}	3.78 ± 0.52^{ab}
CS/PVOH/5AC	0 ± 0^{c}	0 ± 0^{c}	0 ± 0^{c}	0 ± 0^{ac}
CS/PVOH/10AC	0 ± 0^{c}	0 ± 0^{c}	0 ± 0^{c}	0 ± 0^{ac}
CS/PVOH/15AC	0 ± 0^{c}	0 ± 0^{c}	0 ± 0^{c}	0 ± 0^{ac}
CS/PVOH/5TO@AC	3.08 ± 0.26^{abd}	5.43 ± 0.49^{abd}	4.13 ± 0.68^{abd}	2.66 ± 0.36^{a}
CS/PVOH/10TO@AC	3.10 ± 0.29^{abd}	3.63 ± 0.46^{abd}	3.00 ± 0.16^{abd}	3.44 ± 0.30^{ad}
CS/PVOH/15TO@AC	3.84 ± 0.60^{abd}	4.53 ± 0.36^{abd}	6.07 ± 0.18^{e}	3.86 ± 0.91^{ad}

[1] Inhibitory zone surrounding wells measured in mm after the subtraction of the well diameter (6 mm). Results expressed as mean ± standard deviation ($n = 3$). Means in the same column baring different superscript letters are significantly different ($p < 0.5$).

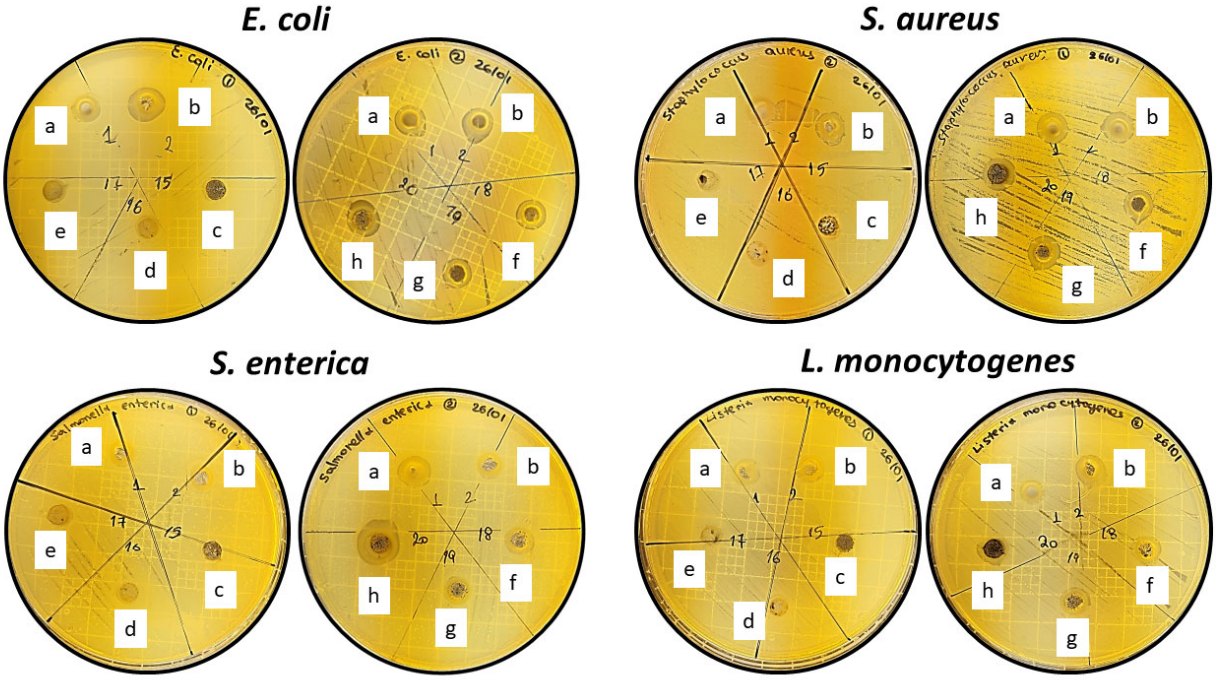

Figure 6. Petri dish images of (a) CS, (b) CS/PVOH, (c) CS/PVOH 5%AC, (d) CS/PVOH 10%AC, (e) CS/PVOH 15%AC, (f) CS/PVOH/5TO@AC, (g) CS/PVOH/10TO@AC, (h) CS/PVOH/15TO@AC films against *E. coli*, *S. aureus*, *S. enterica*, and *L. monocytogenes*.

The results indicate that the film material composed of CS exhibits some antimicrobial activity against the tested bacteria, with varying levels of effectiveness. Notably, it demonstrates moderate inhibition against *S. aureus* and *S. enterica*, while displaying lower activity against *L. monocytogenes*. However, its efficacy against *E. coli* is relatively limited. CS is known for its antibacterial effects against a wide range of bacteria. This property is attributed to its cationic characteristics, specifically the positively charged ammonium (NH_4^+) groups that interact with the negatively charged elements of bacterial cell walls. Furthermore, the importance of chitosan's cationic nature in contributing to its antibacterial activity has been emphasized by Giannakas et al. (2022) and Unuabonah et al. (2018) [24,46].

The CS/PVOH film material displayed diverse antibacterial activity depending on the bacterial strain, with the greatest inhibitory activity against *L. monocytogenes*. Moreover, CS/PVOH films showed comparable inhibitory activity to CS against *S. aureus* and *S. enterica.* This suggests that the addition of PVOH to CS enhances the film's ability to inhibit bacterial growth.

On the other hand, the film materials containing AC in various concentrations (CS/PVOH/5AC, CS/PVOH/10AC, and CS/PVOH/15AC) show no antimicrobial activity against any of the tested bacteria. This indicates that the inclusion of activated carbon in the film formulation does not contribute to its antimicrobial properties.

However, when TO complexed with AC (TO@AC) is incorporated into the CS/PVOH film material, the antimicrobial activity is notably improved.

The clear zone diameters ranged from 2.66 to 6.07, with the highest inhibition observed against *S. enterica*. Specifically, the presence of 5% TO@AC enhances the film's effectiveness against *S. aureus* and *S. enterica.* Increasing the concentration of TO@AC to 10% and 15% in CS/PVOH films displayed varying degrees of inhibitory activity against the bacteria, with CS/PVOH/15% TO@AC demonstrating the highest inhibitory activity against *S. enterica*, followed by *S. aureus*. The results clearly demonstrate an increased inhibitory effect on bacterial growth with higher concentrations of TO@AC nanohybrids. The results of the statistical analysis revealed significant differences in the antibacterial activity of the film materials against the tested bacteria ($p < 0.05$) and Tukey HSD post hoc comparisons were conducted to identify the specific differences.

For the tested bacteria, pairwise comparisons showed that all CS/PVOH films containing TO@AC in different concentrations exhibited significantly higher inhibitory activity compared to CS/PVOH films incorporated only with AC ($p < 0.05$). In the case of *S. enterica*, the CS/PVOH/15% TO@AC film displayed the highest inhibitory activity, with significant differences observed when compared to all the tested materials ($p < 0.05$). These statistical results confirm that the addition of thyme oil complexed with activated carbon (TO@AC) significantly enhances the antibacterial activity of the CS/PVOH films, particularly against *S. aureus* and *S. enterica.*

AC, also known as activated charcoal, is a highly porous form of carbon that has various applications due to its adsorption properties. It is extensively utilized in the field of air pollution control and wastewater treatment for the removal of various pollutants. This is primarily attributed to its remarkable characteristics, such as large surface area and high adsorption capacity.

While AC is commonly used for its ability to remove impurities, toxins, and odors, its antimicrobial activity against bacteria is limited. A notable concern associated with AC is the formation of biofilm on carbon particles by bacteria, leading to increased resistance to disinfection processes and the potential for the carbon itself to act as a source of bacterial contamination [47,48].

AC primarily works by adsorbing (binding) substances to its porous surface. As mentioned before, it can effectively remove organic compounds, toxins, and certain gases through this adsorption process. However, its ability to kill or inhibit the growth of bacteria is not significant. The porous structure of AC provides a large surface area for bacteria to attach to, but it does not possess inherent antimicrobial properties. The adsorption process can physically trap bacteria within the carbon's pores, preventing them from spreading. This property is utilized in certain applications, such as water and air filters, to remove bacteria and improve cleanliness. However, it is important to note that activated carbon alone does not actively kill bacteria [49].

Based on the above, AC seems it may have the ability to limit the migration properties of an antimicrobial agent through adsorption. When an antimicrobial agent is incorporated or impregnated into activated carbon, the activated carbon's porous structure physically traps and binds the antimicrobial agent, preventing or limiting its release into the surrounding environment. In the present work, the antimicrobial activity of chitosan is completely lost when it is incorporated into activated carbon. This suggests that the specific characteristics of chitosan and its interaction with activated carbon may lead to the loss of its antimicrobial properties.

There could be several reasons why chitosan loses its antimicrobial activity when incorporated into activated carbon. One possibility is that the adsorption process of chitosan onto activated carbon might alter its chemical structure or inhibit its interaction with microorganisms, thereby diminishing its antimicrobial effectiveness. Another reason could be related to the pore size or surface chemistry of the activated carbon. If the pore size of the activated carbon is not suitable for retaining chitosan or if the surface chemistry of the activated carbon hinders the interaction between chitosan and microorganisms, it could lead to a loss of antimicrobial activity.

However, our results demonstrated an increase in antimicrobial activity when thyme oil was incorporated into the CS/AC matrix. The presence of thyme oil led to a notable enhancement in the inhibitory effect against *S. aureus* and *S. enterica*. The antimicrobial efficacy observed suggests a synergistic effect between the constituents of the composite matrix, particularly chitosan, activated carbon, and thyme oil.

It is worth noting that the effectiveness of activated carbon in limiting the migration properties of an antimicrobial agent can vary depending on the specific characteristics of the antimicrobial agent and the properties of the activated carbon. In the case of chitosan, further investigation and experimentation would be required to understand why its antimicrobial activity is completely lost when incorporated into activated carbon.

In this study, CS served as the base material for the film, and its inherent antibacterial activity likely played a crucial role in controlling microbial growth, which was further amplified by the addition of thymol-modified activated carbon (TO@AC). The incorporation of specific components, such as thyme oil, can enhance the antibacterial efficacy of CS/PVOH films. However, the addition of activated carbon did not exhibit any inhibitory effects on the tested bacteria. These findings emphasize the need to optimize formulations and concentrations to maximize the antibacterial activity of film materials for various applications, including food packaging and biomedical devices. Azmi et al. (2022) provide insights into the various factors influencing the antibacterial properties of clay, which may be a significant avenue for future exploration if considering clay-based nanohybrids for antimicrobial applications [50].

3.7. Visual Evaluation of the Obtained Active Coatings against Enzymatic Browning of Fresh Bananas

The Figure 7 photos represent the evolution during the experimental period of 8 days of the uncoated bananas and of the bananas that were coated by immersing them in CS/PVOH, CS/PVOH15AC, and CS/PVOH/15TO@AC hydrogel solution for 1 min. It must be mentioned that the CS/PVOH15AC and CS/PVOH/15TO@AC samples were chosen to apply as banana coatings as they were shown to have the highest water/oxygen barrier properties and the highest antioxidant activity. At first glance, it is obvious that all the CS/PVOH, CS/PVOH15AC, and CS/PVOH/15TO@AC coatings succeeded to protect bananas from enzymatic browning in comparison to uncoated bananas [32]. This result is probably due to the CS/PVOH and CS/PVOH/15AC hydrogel coatings probably succeeded in protecting the fresh bananas from enzymatic browning growth. With a more careful glance, it is obtained that CS/PVOH/15AC and CS/PVOH/15TO@AC coatings succeeded in more effectively protecting the bananas from enzymatic browning. The extension of life duration was confirmed only by visible observations, and it was around 2 to 3 days longer for bananas coated with CS/PVOH/15AC and CS/PVOH/15TO@AC coatings as compared to the respective uncoated bananas and bananas coated with pure CS/PVOH coating.

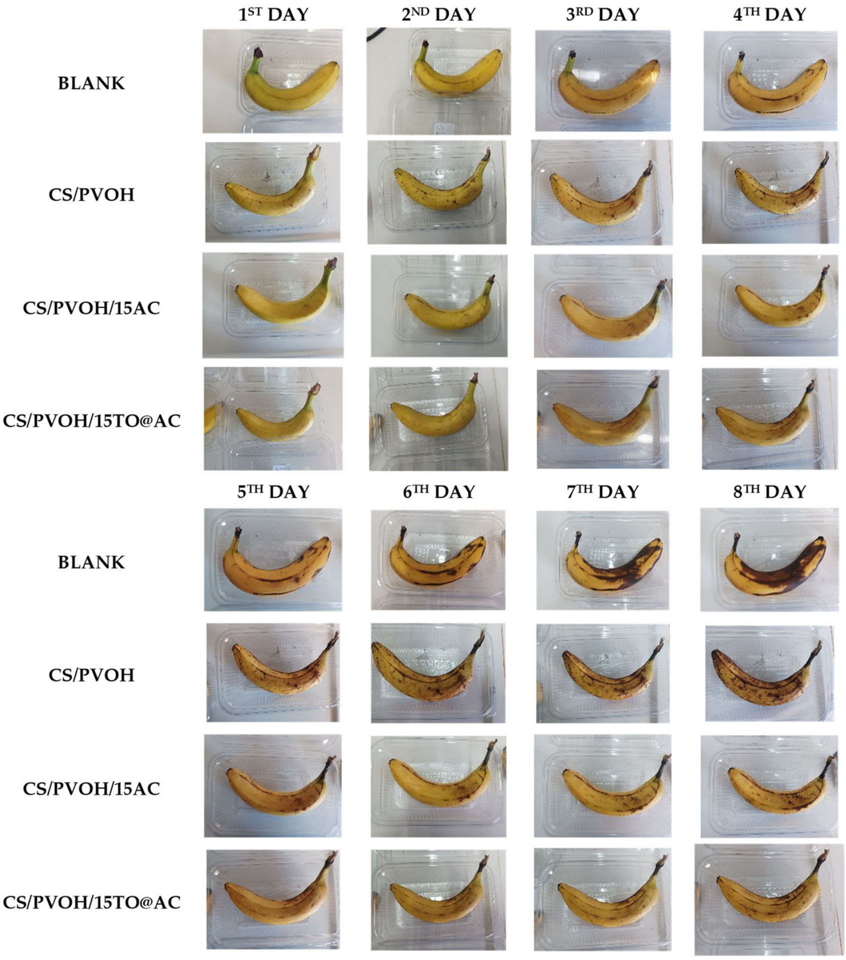

Figure 7. Photos during the experimental period of 8 d of the uncoated bananas and bananas coated with CS/PVOH, CS/PVOH15AC, and CS/PVOH/15TO@AC coatings.

In Figure 8, the average values of % weight loss of uncoated and uncoated bananas are plotted. It is obvious that the group of bananas coated with the CS/PVOH/15TO@AC coating exhibited a lower % weight loss during the experimental period of 8 days. The group of bananas coated with the CS/PVOH/15AC coating exhibited higher % weight loss values than bananas coated with the CS/PVOH/15TO@AC coating, but much lower % weight loss values than bananas coated with the CS/PVOH coating. So, it is concluded that the % weight loss values sequence the following trend:

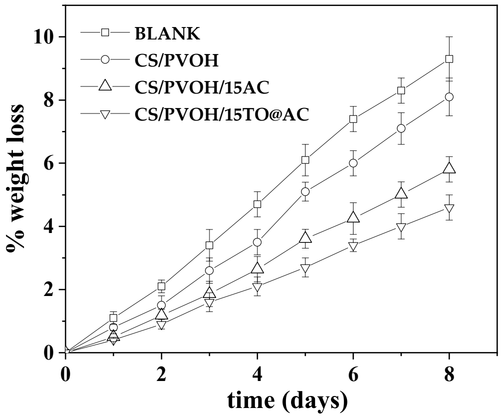

Figure 8. Average % weight loss values of uncoated bananas and bananas coated with CS/PVOH, CS/PVOH/15AC, and CS/PVOH/15TO@AC coatings.

Uncoated bananas > CS/PVOH-coated bananas > CS/PVOH/15AC-coated bananas > CS/PVOH/15TO@AC-coated bananas. The results of % weight loss of fresh bananas during the 8-day period of storage agree with the results of the visual evaluation of active coating in the protection of fresh bananas against the enzymatic browning deterioration process.

4. Conclusions

As was shown hereabove from all the results of the analytical measurements studied, the well-known CS/PVOH matrix can be transformed into a very promising active film/coating by the addition of pure AC and TO@AC nanohybrids. As it was shown, both pure AC and TO@AC nanohybrids were homogenously added in the CS/PVOH matrix in content varying from 5 to 15 wt.% and resulted in CS/PVOH/xAC and CS/PVOH/xTO@AC films with higher tensile and water/oxygen barrier properties. TO@AC nanohybrid was shown to achieve higher dispersion in the CS/PVOH matrix than pure AC and thus the obtained CS/PVOH/xTO@AC films resulted in higher water/oxygen barrier properties than the CS/PVOH/xAC films. The addition of TO@AC led to the significant antioxidant activity of all obtained CS/PVOH/xTO@AC active films/coatings. In advance, it was reported for the first time that AC addition deactivates the antibacterial activity of the CS/PVOH matrix while the addition of TO@AC nanohybrid resulted in enhanced antibacterial activity against four bacterial strains (*E. coli*, *S. aureus*, *S. enterica*, and *L. monocytogenes*) as compared to the CS/PVOH matrix.

The overall conclusion is that the active coating CS/PVOH/15TGO@AC exhibited a 23.5% higher Young's modulus value, a 20.1% higher ultimate strength value, a 50.2% higher water barrier, a 74.0% higher oxygen barrier, a 69.0% higher antioxidant activity, a 5.5% higher antibacterial activity against *Escherichia coli*, a 17.8% higher antibacterial activity against *Salmonella enterica*, a 42.5% higher antibacterial activity against *Staphylococcus aureus*, and a 2.5% higher antibacterial activity against *Listeria monocytogenes* as compared to the pure CS/PVOH matrix. This active coating has been shown to slow down the enzymatic browning and weight loss of fresh bananas in accordance with the antioxidant activity and oxygen barrier. The antimicrobial activity is not in perfect agreement with these results because the enzymatic browning is an oxidation reaction mechanism. Thus, this novel material could potentially be used as an active coating to extend the shelf life of fresh fruits. A continuation of this work could be the future investigation of the mechanisms that are underlying the observed improvements in the coating's performance, to contribute to its practical application.

Author Contributions: Synthesis experiment design, A.E.G., C.P. and C.E.S.; paper writing, A.E.G., C.P., E.K., K.Z. and C.E.S.; overall evaluation of this work, A.E.G. and C.E.S.; experimental data analysis and interpretation, A.E.G., C.E.S. and C.P.; XRD, FTIR, tensile measurements, antioxidant activity, WVTR, OTR experimental measurements, and fresh bananas packaging test, A.E.G., A.L., K.Z., S.G., V.K.K., A.K.-M., G.K. and C.E.S.; antimicrobial activity tests, E.K., A.K., L.A., K.Z. and C.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The datasets generated for this study are available on request to the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Luckachan, G.E.; Pillai, C.K.S. Biodegradable Polymers—A Review on Recent Trends and Emerging Perspectives. *J. Polym. Environ.* **2011**, *19*, 637–676. [CrossRef]
2. Viaggi, D. Agricultural Waste Management and Valorisation in the Context of the Circular Bioeconomy: Exploring the Potential of Biomass Value Webs. *Curr. Opin. Environ. Sci. Health* **2022**, *27*, 100356. [CrossRef]
3. Clark, J.H.; Farmer, T.J.; Hunt, A.J.; Sherwood, J. Opportunities for Bio-Based Solvents Created as Petrochemical and Fuel Products Transition towards Renewable Resources. *Int. J. Mol. Sci.* **2015**, *16*, 17101–17159. [CrossRef] [PubMed]
4. Samir, A.; Ashour, F.H.; Hakim, A.A.A.; Bassyouni, M. Recent Advances in Biodegradable Polymers for Sustainable Applications. *npj Mater. Degrad.* **2022**, *6*, 68. [CrossRef]
5. Ahmed, M.W.; Haque, M.A.; Mohibbullah, M.; Khan, M.S.I.; Islam, M.A.; Mondal, M.H.T.; Ahmmed, R. A Review on Active Packaging for Quality and Safety of Foods: Current Trends, Applications, Prospects and Challenges. *Food Packag. Shelf Life* **2022**, *33*, 100913. [CrossRef]
6. Ahari, H.; Soufiani, S.P. Smart and Active Food Packaging: Insights in Novel Food Packaging. *Front. Microbiol.* **2021**, *12*, 657233. [CrossRef]
7. Holden, N.M.; White, E.P.; Lange, M.C.; Oldfield, T.L. Review of the Sustainability of Food Systems and Transition Using the Internet of Food. *npj Sci. Food* **2018**, *2*, 18. [CrossRef]
8. Nemat, B.; Razzaghi, M.; Bolton, K.; Rousta, K. The Role of Food Packaging Design in Consumer Recycling Behavior—A Literature Review. *Sustainability* **2019**, *11*, 4350. [CrossRef]
9. Mahmud, N.; Islam, J.; Tahergorabi, R. Marine Biopolymers: Applications in Food Packaging. *Processes* **2021**, *9*, 2245. [CrossRef]
10. Rabnawaz, M.; Wyman, I.; Auras, R.; Cheng, S. A Roadmap towards Green Packaging: The Current Status and Future Outlook for Polyesters in the Packaging Industry. *Green Chem.* **2017**, *19*, 4737–4753. [CrossRef]
11. Gupta, S.; Sharma, S.; Kumar Nadda, A.; Saad Bala Husain, M.; Gupta, A. Biopolymers from Waste Biomass and Its Applications in the Cosmetic Industry: A Review. *Mater. Today Proc.* **2022**, *68*, 873–879. [CrossRef]
12. Mangaraj, S.; Yadav, A.; Bal, L.M.; Dash, S.K.; Mahanti, N.K. Application of Biodegradable Polymers in Food Packaging Industry: A Comprehensive Review. *J. Package Technol. Res.* **2019**, *3*, 77–96. [CrossRef]
13. Aider, M. Chitosan Application for Active Bio-Based Films Production and Potential in the Food Industry: Review. *LWT—Food Sci. Technol.* **2010**, *43*, 837–842. [CrossRef]
14. Cazón, P.; Vázquez, M. Applications of Chitosan as Food Packaging Materials. In *Sustainable Agriculture Reviews 36: Chitin and Chitosan: Applications in Food, Agriculture, Pharmacy, Medicine and Wastewater Treatment*; Crini, G., Lichtfouse, E., Eds.; Sustainable Agriculture Reviews; Springer International Publishing: Cham, Switzerland, 2019; pp. 81–123. ISBN 978-3-030-16581-9.
15. Elsabee, M.Z.; Abdou, E.S. Chitosan Based Edible Films and Coatings: A Review. *Mater. Sci. Eng. C* **2013**, *33*, 1819–1841. [CrossRef] [PubMed]
16. Goy, R.C.; de Britto, D.; Assis, O.B.G. A Review of the Antimicrobial Activity of Chitosan. *Polímeros* **2009**, *19*, 241–247. [CrossRef]
17. Ananno, A.A.; Masud, M.H.; Chowdhury, S.A.; Dabnichki, P.; Ahmed, N.; Arefin, A.M.E. Sustainable Food Waste Management Model for Bangladesh. *Sustain. Prod. Consum.* **2021**, *27*, 35–51. [CrossRef]
18. Huang, I.Y.; Manning, L.; James, K.L.; Grigoriadis, V.; Millington, A.; Wood, V.; Ward, S. Food Waste Management: A Review of Retailers' Business Practices and Their Implications for Sustainable Value. *J. Clean. Prod.* **2021**, *285*, 125484. [CrossRef]
19. Girotto, F.; Alibardi, L.; Cossu, R. Food Waste Generation and Industrial Uses: A Review. *Waste Manag.* **2015**, *45*, 32–41. [CrossRef]
20. Thi, N.B.D.; Kumar, G.; Lin, C.-Y. An Overview of Food Waste Management in Developing Countries: Current Status and Future Perspective. *J. Environ. Manag.* **2015**, *157*, 220–229. [CrossRef]
21. Kibler, K.M.; Reinhart, D.; Hawkins, C.; Motlagh, A.M.; Wright, J. Food Waste and the Food-Energy-Water Nexus: A Review of Food Waste Management Alternatives. *Waste Manag.* **2018**, *74*, 52–62. [CrossRef]
22. Soltani Firouz, M.; Mohi-Alden, K.; Omid, M. A Critical Review on Intelligent and Active Packaging in the Food Industry: Research and Development. *Food Res. Int.* **2021**, *141*, 110113. [CrossRef]
23. Wu, J.; Zhang, L.; Fan, K. Recent Advances in Polysaccharide-Based Edible Coatings for Preservation of Fruits and Vegetables: A Review. *Crit. Rev. Food Sci. Nutr.* **2022**, 1–16. [CrossRef] [PubMed]
24. Giannakas, A.E.; Salmas, C.E.; Moschovas, D.; Baikousi, M.; Kollia, E.; Tsigkou, V.; Karakassides, A.; Leontiou, A.; Kehayias, G.; Avgeropoulos, A.; et al. Nanocomposite Film Development Based on Chitosan/Polyvinyl Alcohol Using ZnO@Montmorillonite and ZnO@Halloysite Hybrid Nanostructures for Active Food Packaging Applications. *Nanomaterials* **2022**, *12*, 1843. [CrossRef] [PubMed]
25. Carpena, M.; Nuñez-Estevez, B.; Soria-Lopez, A.; Garcia-Oliveira, P.; Prieto, M.A. Essential Oils and Their Application on Active Packaging Systems: A Review. *Resources* **2021**, *10*, 7. [CrossRef]
26. Yılmaz, G.E.; Göktürk, I.; Ovezova, M.; Yılmaz, F.; Kılıç, S.; Denizli, A. Antimicrobial Nanomaterials: A Review. *Hygiene* **2023**, *3*, 269–290. [CrossRef]
27. de Oliveira, L.H.; Trigueiro, P.; Souza, J.S.N.; de Carvalho, M.S.; Osajima, J.A.; da Silva-Filho, E.C.; Fonseca, M.G. Montmorillonite with Essential Oils as Antimicrobial Agents, Packaging, Repellents, and Insecticides: An Overview. *Colloids Surf. B Biointerfaces* **2022**, *209*, 112186. [CrossRef] [PubMed]

28. Saucedo-Zuñiga, J.N.; Sánchez-Valdes, S.; Ramírez-Vargas, E.; Guillen, L.; Ramos-deValle, L.F.; Graciano-Verdugo, A.; Uribe-Calderón, J.A.; Valera-Zaragoza, M.; Lozano-Ramírez, T.; Rodríguez-González, J.A.; et al. Controlled Release of Essential Oils Using Laminar Nanoclay and Porous Halloysite/Essential Oil Composites in a Multilayer Film Reservoir. *Microporous Mesoporous Mater.* **2021**, *316*, 110882. [CrossRef]
29. Eroglu, N.; Emekci, M.; Athanassiou, C.G. Applications of Natural Zeolites on Agriculture and Food Production. *J. Sci. Food Agric.* **2017**, *97*, 3487–3499. [CrossRef] [PubMed]
30. Giannakas, A.E.; Salmas, C.E.; Moschovas, D.; Zaharioudakis, K.; Georgopoulos, S.; Asimakopoulos, G.; Aktypis, A.; Proestos, C.; Karakassides, A.; Avgeropoulos, A.; et al. The Increase of Soft Cheese Shelf-Life Packaged with Edible Films Based on Novel Hybrid Nanostructures. *Gels* **2022**, *8*, 539. [CrossRef]
31. Chaemsanit, S.; Matan, N.; Matan, N. Activated Carbon for Food Packaging Application: Review. *Walailak J. Sci. Technol.* **2018**, *15*, 255–271. [CrossRef]
32. Quevedo, R.; Díaz, O.; Ronceros, B.; Pedreschi, F.; Aguilera, J.M. Description of the Kinetic Enzymatic Browning in Banana (Musa Cavendish) Slices Using Non-Uniform Color Information from Digital Images. *Food Res. Int.* **2009**, *42*, 1309–1314. [CrossRef]
33. Kaewjumpol, G.; Srisamlee, S.; Beckles, D.M.; Luengwilai, K. Enzymatic Browning in Banana Blossoms and Techniques for Its Reduction. *Horticulturae* **2021**, *7*, 373. [CrossRef]
34. Hu, D.; Liu, X.; Qin, Y.; Yan, J.; Li, J.; Yang, Q. A Novel Edible Packaging Film Based on Chitosan Incorporated with Persimmon Peel Extract for the Postharvest Preservation of Banana. *Food Qual. Saf.* **2022**, *6*, fyac028. [CrossRef]
35. Giannakas, A.E.; Karabagias, V.K.; Moschovas, D.; Leontiou, A.; Karabagias, I.K.; Georgopoulos, S.; Karydis-Messinis, A.; Zaharioudakis, K.; Andritsos, N.; Kehayias, G.; et al. Thymol@activated Carbon Nanohybrid for Low-Density Polyethylene-Based Active Packaging Films for Pork Fillets' Shelf-Life Extension. *Foods* **2023**, *12*, 2590. [CrossRef] [PubMed]
36. Salmas, C.E.; Giannakas, A.E.; Baikousi, M.; Kollia, E.; Tsigkou, V.; Proestos, C. Effect of Copper and Titanium-Exchanged Montmorillonite Nanostructures on the Packaging Performance of Chitosan/Poly-Vinyl-Alcohol-Based Active Packaging Nanocomposite Films. *Foods* **2021**, *10*, 3038. [CrossRef] [PubMed]
37. Asimakopoulos, G.; Baikousi, M.; Kostas, V.; Papantoniou, M.; Bourlinos, A.B.; Zbořil, R.; Karakassides, M.A.; Salmas, C.E. Nanoporous Activated Carbon Derived via Pyrolysis Process of Spent Coffee: Structural Characterization. Investigation of Its Use for Hexavalent Chromium Removal. *Appl. Sci.* **2020**, *10*, 8812. [CrossRef]
38. Salmas, C.E.; Giannakas, A.E.; Moschovas, D.; Kollia, E.; Georgopoulos, S.; Gioti, C.; Leontiou, A.; Avgeropoulos, A.; Kopsacheili, A.; Avdylaj, L.; et al. Kiwi Fruits Preservation Using Novel Edible Active Coatings Based on Rich Thymol Halloysite Nanostructures and Chitosan/Polyvinyl Alcohol Gels. *Gels* **2022**, *8*, 823. [CrossRef]
39. Salmas, C.E.; Kollia, E.; Avdylaj, L.; Kopsacheili, A.; Zaharioudakis, K.; Georgopoulos, S.; Leontiou, A.; Katerinopoulou, K.; Kehayias, G.; Karakassides, A.; et al. Thymol@Natural Zeolite Nanohybrids for Chitosan/Poly-Vinyl-Alcohol Based Hydrogels Applied as Active Pads for Strawberries Preservation. *Gels* **2023**, *9*, 570. [CrossRef]
40. Salmas, C.E.; Giannakas, A.E.; Karabagias, V.K.; Moschovas, D.; Karabagias, I.K.; Gioti, C.; Georgopoulos, S.; Leontiou, A.; Kehayias, G.; Avgeropoulos, A.; et al. Development and Evaluation of a Novel-Thymol@Natural-Zeolite/Low-Density-Polyethylene Active Packaging Film: Applications for Pork Fillets Preservation. *Antioxidants* **2023**, *12*, 523. [CrossRef]
41. Bintsis, T. Foodborne Pathogens. *AIMS Microbiol.* **2017**, *3*, 529–563. [CrossRef]
42. John, J.; Noorjan, N.; Gurumurthy, S.C.; Ramaprasad, A.T. Chitosan-Polyvinyl Alcohol Blend as Beta-Ray Attenuator. *Mater. Today Proc.* **2022**, *66*, 2109–2114. [CrossRef]
43. Ngo, D.-H.; Kim, S.-K. Chapter Two—Antioxidant Effects of Chitin, Chitosan, and Their Derivatives. In *Advances in Food and Nutrition Research*; Kim, S.-K., Ed.; Marine Carbohydrates: Fundamentals and Applications, Part B; Academic Press: Cambridge, MA, USA, 2014; Volume 73, pp. 15–31.
44. Sallam, M.F.; Ahmed, H.M.S.; Diab, K.A.; El-Nekeety, A.A.; Abdel-Aziem, S.H.; Sharaf, H.A.; Abdel-Wahhab, M.A. Improvement of the Antioxidant Activity of Thyme Essential Oil against Biosynthesized Titanium Dioxide Nanoparticles-Induced Oxidative Stress, DNA Damage, and Disturbances in Gene Expression in Vivo. *J. Trace Elem. Med. Biol.* **2022**, *73*, 127024. [CrossRef] [PubMed]
45. Giannakas, A.E.; Salmas, C.E.; Moschovas, D.; Karabagias, V.K.; Karabagias, I.K.; Baikousi, M.; Georgopoulos, S.; Leontiou, A.; Katerinopoulou, K.; Zafeiropoulos, N.E.; et al. Development, Characterization, and Evaluation as Food Active Packaging of Low-Density-Polyethylene-Based Films Incorporated with Rich in Thymol Halloysite Nanohybrid for Fresh "Scaloppini" Type Pork Meat Fillets Preservation. *Polymers* **2023**, *15*, 282. [CrossRef]
46. Unuabonah, E.I.; Ugwuja, C.G.; Omorogie, M.O.; Adewuyi, A.; Oladoja, N.A. Clays for Efficient Disinfection of Bacteria in Water. *Appl. Clay Sci.* **2018**, *151*, 211–223. [CrossRef]
47. Shi, Z.; Neoh, K.G.; Kang, E.T. Antibacterial and Adsorption Characteristics of Activated Carbon Functionalized with Quaternary Ammonium Moieties. *Ind. Eng. Chem. Res.* **2007**, *46*, 439–445. Available online: https://pubs.acs.org/doi/10.1021/ie0608096 (accessed on 10 August 2023). [CrossRef]
48. Stewart, M.H.; Wolfe, R.L.; Means, E.G. Assessment of the Bacteriological Activity Associated with Granular Activated Carbon Treatment of Drinking Water. *Appl. Environ. Microbiol.* **2023**, *56*, 3822–3829. Available online: https://journals.asm.org/doi/10.1128/aem.56.12.3822-3829.1990 (accessed on 17 July 2023). [CrossRef]

49. Burchacka, E.; Pstrowska, K.; Beran, E.; Fałtynowicz, H.; Chojnacka, K.; Kułażyński, M. Antibacterial Agents Adsorbed on Active Carbon: A New Approach for *S. aureus* and *E. coli* Pathogen Elimination. *Pathogens* **2021**, *10*, 1066. Available online: https://www.mdpi.com/2076-0817/10/8/1066 (accessed on 17 July 2023). [CrossRef] [PubMed]
50. Azmi, N.N.; Mahyudin, N.A.; Wan Omar, W.H.; Mahmud Ab Rashid, N.-K.; Ishak, C.F.; Abdullah, A.H.; Sharples, G.J. Antibacterial Activity of Clay Soils against Food-Borne Salmonella Typhimurium and Staphylococcus Aureus. *Molecules* **2022**, *27*, 170. [CrossRef]