Investigation of glycerol and sorbitol effect to the cinnamon essential oil incorporated corn or rice starch based edible films

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Corn or rice starch based, cinnamon essential oil incorporated, and plasticized with glycerol and/or sorbitol, eco-friendly, biodegradable edible films have been produced successfully. The effects of glycerol, sorbitol and cinnamon essential oil on the physical and barrier properties (colour parameters, moisture content, water solubility, water vapour transmission rate of corn and rice starch edible films have been investigated. Corn starch composite films plasticized with glycerol and rice starch composite films plasticized with sorbitol, have demonstrated high colour change. The composite films have lower moisture contents. The control films containing only glycerol as plasticizer have higher moisture content than the control films containing only sorbitol. Glycerol is found to be a more suitable plasticizer for starch films as lower water vapour transmission rate values are preferred in the food industry and the composite rice starch films, has the highest water solubility. The interaction of film components has been evaluated by Fourier transform infrared spectroscopy.

Keywords: Cinnamon essential oil, Edible film, Glycerol, Sorbitol, Starch

Introduction

Since plastic products are not biodegradable, they cause environmental pollution when thrown away randomly. For this reason, the use of single-use plastic products has been limited in many countries, and the production of eco-friendly, biodegradable, edible films is increasing. Starch is one of the most preferred natural edible film raw materials being cheap, renewable, biodegradable and always available material. It is known that wheat, cassava, potato, corn, rice and quinoa starches have good film forming properties. Starch is formed from amylose and amylopectin. The film forming properties of starches with high amylose content are much better than those of starches with low amylose content because the linear chains that can interact with the hydrogen bond in the amylose content, enable the starch to form a film. Therefore, corn and rice starches, having high amylose, can be utilized as a raw material in the edible films production. The edible coating can preserve the food against various microbial pollutants, increase the shelf life, decrease deterioration effect, reduce lipid oxidation and moisture loss of foods. Plant essential oils are natural agents, which can be incorporated into the edible films. They are attractive additives for the food industry due to their antimicrobial and antioxidant properties. Essential oils also affect the physical, optical and structural properties of edible films such as water vapour permeability, optical, structural, tensile etc. cinnamon essential oil (CEO) addition can protect and prolong the shelf life of food. In this study, glycerol, sorbitol and CEO influences on the physical and barrier properties of produced corn and rice starch edible films were studied.

Experimental Section

Materials
Corn and rice starch used in this study were buying from regional bazaars in Istanbul, Turkey. Glycerol was buying from Merck (Germany), sodium alginate from AFG Bioscience (USA), D-sorbitol from Carlo Erba (France) and CEO from Arifoğlu (Turkey).

Preparation of corn and rice starch based edible films
Edible films were prepared by casting method. 3 g corn or rice starch and 0.50 g sodium alginate were dissolved in distilled water (100 mL) using varied amount of glycerol and/or sorbitol (0, 0.35, 0.5, 0.65,
1 g) to determine its plasticizing effect. Then 0.5 mL CEO was added to the resulting mixtures to obtain composite films. The mixtures of corn and rice starch based edible films (CSCEO1, CSCEO2, CSCEO3, CSCEO4, CSCEO5 and RSCEO1, RSCEO2, RSCEO3, RSCEO4, and RSCEO5, respectively) were mixed in a magnetic stirrer (500 rpm, 60 min and 60°C). The film solutions were stirred with the Bandelin Sonopuls HD 2070 (20 kHz) model ultrasonic probe (Bandelin electronic GmbH & Co. KG, Berlin, Germany) for 10 min to obtain more homogeneous films. They were stirred in an ultrasonic water bath (Isolab, Wertheim, Germany) (50°C, 10 min.) up to the mixtures were fully solubilized. The film solutions were put in 10 cm diameter Petri dishes and drying at 50°C for 24 h. The control films (without CEO) of corn and rice starch based edible films (CS1, CS2, CS3, CS4, CS5 and RS1, RS2, RS3, RS4, RS5, respectively) were also produced employing the same conditions. Last, the films were robbed and placed in a desiccator after cooling.

Characterization of films

Perkin Elmer Spectrum One Fourier transform infrared spectroscopy (FTIR) spectrometer (Waltham, MA, USA) was used for chemical structure analysis of the films. A handheld colorimeter (PCE-CSM 1; PCE Instruments UK Ltd., Southampton Hampshire, United Kingdom) was used for colour parameters analyses. L* values demonstrate the lightness or darkness, the positive a* values demonstrate redness, the negative a* values demonstrate greenness, the positive b* values demonstrate yellowness, the negative b* values demonstrate blueness in Hunter colour system. Total colour changes (ΔE) were calculated using the following equation:

\[ \Delta E = \sqrt{L_0 - L}^2 + a_0 - a)^2 + (b_0 - b)^2 \]  

(1)

Where \( L_0, a_0 \) and \( b_0 \) are the colour values of the control films and \( L, a \) and \( b \) are the colour values of the produced films. Moisture content of the films was determined according to AOAC Standard Method 19th edition defined by Wardak et al. and Lim et al. with slight modification. Edible films were cut to 3 × 3 cm and dried at 105 ± 2°C for 24 h using a hot air oven. Before \( M_0 \) (initial weight) and after \( M_1 \) (dry weight) drying, the weight loss of the edible films was measured as water content until constant weight was reached.

\[ \% \text{ Moisture} = \frac{M_0 - M_1}{M_0} \times 100 \]  

(2)

Water vapour transmission rate of the film samples was determined by the gravimetric analysis method based on ASTM E96-80 method. The films were dried in a hot air oven at 105 ± 2°C for 24 h until they attain a constant weight. Then the test tubes were filled with 5 g of silica gel, the mouth of the tubes was closed with the film sample dried in the oven and surrounded with paraffin. The prepared samples were weighed every 24 h for 5 days and the WVTR was calculated according to the formula given below:

\[ \text{WVTR} = \frac{\Delta W}{A} \]  

(3)

Where \( \Delta W \) = the amount of water transferred (g) per unit time (s), and \( A \) = the exposed area (m²).

Water solubility of the films was calculated as described by Pellá et al. and Ekramian et al. with slight modification. The film samples were dried in a hot air oven at 90 ± 2°C for 24 h. Square-shaped samples (2 cm²) were cut and then were weighed. 10 mL of distilled water was added to the weighed samples and mixed at 100 rpm at room temperature (22±0.5°C) for 6 h. The unsolvable part of the film samples was filtered, dried at 90 ± 2°C for 24 h, and weighed. Water solubility was calculated using the following equation:

\[ \text{Water solubility (%)} = \frac{W_1 - W_2}{W_1} \times 100 \]  

(4)

Where \( W_1 \) = dry weight and \( W_2 \) = dry weight of the insoluble fraction of the film.

Results and Discussion

Fourier transform infrared spectroscopy (FTIR)

Different function groups of edible control and composite films were detected by FTIR to observe the interactions between different components. FTIR spectra of the corn starch control films (Fig. 1), corn starch composite films (Fig. 2), rice starch control films (Fig. 3) and rice starch composite films (Fig. 4) are shown in Figs 1-4. The broad bands containing a peak around 3270-3293 cm⁻¹ correspond to vibrations of O-H group belong to starch, glycerol, sorbitol, and water through hydrogen bonding. The peaks close to 2854-2932 cm⁻¹ show C-H stretching vibrations of O-H group belong to starch, glycerol, sorbitol, and water through hydrogen bonding. The peaks close to 2854-2932 cm⁻¹ show C-H stretching vibrations of CEO, starch, glycerol, sorbitol, and sodium alginate and CH₂ stretching vibration of the pure CEO. After the CEO addition, the amplitude of these peaks increased. This may be due to a strong hydrogen bond formation between edible film and CEO. The adsorption bands around 1601-1607 cm⁻¹ and 1769-1770 cm⁻¹ correspond
Fig. 1 — FTIR spectra of CS control films

Fig. 2 — FTIR spectra of CS composite films

Fig. 3 — FTIR spectra of RS control films

Fig. 4 — FTIR spectra of RS composite films
to the hydrogen bonding of -OH groups in starch structure, and the peak at around 1745 cm\(^{-1}\) displays the presence of C=O bonds in aldehydes. Characteristic absorption peak at 1650 cm\(^{-1}\) is associated with aldehyde carbonyl (C=O stretching vibration). The peaks around 1550 cm\(^{-1}\) are related to the aromatic ring (C=O skeleton vibration). The adsorption bands around 1408-1411 cm\(^{-1}\) are attributed to the C-O-H bending vibration. The bands around 1021-1076 cm\(^{-1}\) are characteristic adsorption bands of C-O-H stretching vibration and C-O-C stretching vibration. The FTIR spectra show typical C-O stretching signals corresponding to sodium alginate at 1246 cm\(^{-1}\). The bands around 1150 and 996 cm\(^{-1}\) are associated to C-O bands which are related to the interactions between starch molecules and plasticizers (glycerol and sorbitol)\(^{1,15,10,12,29-34}\). The absorption peaks of CEO appeared at around 1413 cm\(^{-1}\) and 1241 cm\(^{-1}\) that correspond to the stretching vibrations of C=C and -OH of aromatic compounds. The peaks at around 1150 cm\(^{-1}\) are related to the C-O deformation vibration. The band at around 750 cm\(^{-1}\) indicates the presence of aromatic C=C. The CEO has some specific peaks complying with phenyl group of cinnamaldehyde, at 522, 928, 996, 1077 cm\(^{-1}\)\(^{17,35-37}\). The FTIR spectra show that corn and rice starch control and composite films have similar peaks, demonstrating that corn or rice starch has good compatibility with CEO, glycerol and sorbitol.

Colour of the film

The colour of the film is one of the fundamental criteria that determine their effective use in food packaging applications\(^{19}\). The colour parameter of the CEO added corn or rice starch based edible films were given in Table 1. Colour parameters L*, a*, b* and total colour difference (ΔE) values were affected using glycerol and/or sorbitol as plasticizers. Moreover, CEO incorporation caused colour change in the produced films. The colour parameters (L*, a*, b* and total colour difference (ΔE)), are given in Table 1. It was observed that the L* value (brightness) increased after the incorporation of CEO in composite films. This change can be due to non-enzymatic browning reactions caused by high drying temperatures\(^{8}\). The CEO addition resulted in an increase in greenness (a*), only the a* values of the films RS-1 and RS-5 increased, tending to the red. The b* values of CS-1 and RS-5 were increased, tending to the yellow, however there was a reduction in yellowness (b*) values of the other films\(^{17}\). It was seen that after CEO addition, corn starch based edible films plasticized with glycerol and rice starch based edible films plasticized with sorbitol, demonstrated high colour change.

Moisture content

The moisture content of the control and composite, corn and rice starch edible films were given in Table 2. Moisture content of CEO added composite films is lower than the control films. This is because essential oils, due to their hydrophobic nature, increase the water barrier properties of edible films and reduce their water absorption capacity. It was observed that the control films containing only glycerol as plasticizer had higher moisture content than the control films containing only sorbitol. This can be caused by the hygroscopic character of glycerol. High moisture content films (CS1 and RS1 in this study), being stretch and elastic, can be used in different food areas\(^{4,10,25,31}\).

Water vapor transmission rate (WVTR)

WVTR is one of the most important characteristics of edible film, as a good edible film must prevent moisture transfer among the food and the environment. Water causes spoilage reactions on edible films. So, a packaging material should have suitable moisture content to preserve food quality during storage. Water vapour depends to the hydrophobicity/hydrophilicity ratio of the film and transferred by the hydrophilic section. In this study, the difference on the hydrophilicity of the glycerol and sorbitol and the interaction between the plasticizers, essential oil (CEO) and starch (corn or rice starch) have a significant effect on the WVTR of films. The CEO addition reduces the WVTR significantly and the difference in WVTR could be contributed by the hydrophilic behavior of glycerol or sorbitol. The results of WVTR are given in Table 2. The WVTR of control films were higher than the WVTR of composite films. The WVTR of corn starch

| Table 1 — Colour parameters of edible films |
|-----------|--------|--------|--------|--------|
| Film      | ΔL     | ΔA     | ΔB     | ΔE     |
| CS-1      | 13.44  | -2.96  | 4.8    | 14.57515695 |
| CS-2      | 4.37   | -0.28  | -6.02  | 7.444172217  |
| CS-3      | 26.49  | -0.44  | -2.29  | 26.59243877  |
| CS-4      | 3.99   | -1.44  | -2.94  | 5.161133596  |
| CS-5      | 17.81  | -2.95  | -6.99  | 19.35868539  |
| RS-1      | 11.02  | 0.84   | -1.92  | 11.21750418  |
| RS-2      | 1.22   | -0.06  | -1.58  | 1.997097894  |
| RS-3      | 13.46  | -0.31  | -6.17  | 14.81001688  |
| RS 4      | 14.58  | -1.2   | -5.96  | 15.79677182  |
| RS -5     | 0.84   | 0.11   | 0.37   | 0.92444578   |
Composite films decreased between 53 to 16%, and the WVTR of rice starch composite films decreased between 37 to 10% after CEO addition. The WVTR values of corn starch edible film was 12.43 g/(s.m²) when only glycerol was used as the plasticizer and it was 19.65 g/(s.m²) when only sorbitol was used as the plasticizer. The WVTR values of rice starch edible film was 16.31 g/(s.m²) when only glycerol was used as the plasticizer and it was 17.75 g/(s.m²) when only sorbitol was used as the plasticizer. Higher WVTR was observed with the incorporation of sorbitol into starch films compared to glycerol. It was observed that sorbitol plasticized films had higher permeability than glycerol plasticized films. Glycerol was found to be a more suitable plasticizer for starch films as lower WVTR values are preferred in the food industry.

Water solubility
Water solubility is a significant parameter for the applicability of the film, to the foods with high water activity. High solubility is needed, when the films are consumed with the product at the same time and it also determines the biodegradability of films when utilized for packaging. The addition of CEO, with glycerol and/or sorbitol as a plasticizer, decreased the water solubility of the corn starch films while enhancing the water solubility of the rice starch films. The reaction between hydrophobic CEO components and hydroxyl groups of edible films, decreased the hydroxyl groups interaction with water molecules and caused to less solubility of the corn starch films. The water solubility values of corn and rice starch control and composite films are given in Table 2. The water solubility of corn starch control films is ranged from 45.71% to 60.95%, while that of rice starch edible films is ranged from 45.38% to 58.32%. The water solubilities of corn starch composite films are ranged from 24.39% to 36.33%, and rice starch edible films are ranged from 60.08% to 80.47%. It was seen that the composite rice starch films, has the highest water solubility.

Conclusion
This study shows that corn or rice starch based, CEO added, glycerol and/or sorbitol plasticized edible films were produced successfully. The structures of the produced edible films were examined using FTIR to observe the interactions between the different components and it was seen that corn and rice starch have good compatibility with CEO, glycerol and sorbitol. It was seen that after CEO addition, corn starch based edible films plasticized with glycerol and rice starch based edible films plasticized with sorbitol, demonstrated high colour changes. Moisture content of CEO added composite films is lower than control films. This is because hydrophobic nature of the essential oils, which increase the water barrier properties of edible films and reduce their water absorption capacity. The CEO addition reduces the WVTR importantly and the difference in WVTR could be contributed by the hydrophilic behavior of glycerol or sorbitol. The addition of CEO, with glycerol and/or sorbitol as a plasticizer, decreased the water solubility of the corn starch films while increasing the water solubility of the rice starch films. In the continuation of this study, the antimicrobial properties of the produced edible films and their potential for use as packaging materials can be explored.

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References


