

Analytical, Nutritional and Clinical Methods Section

A method for the measurement of the oxygen permeability and the development of edible films to reduce the rate of oxidative reactions in fresh foods

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Abstract

A method involving the flow of O₂ and N₂ gasses from the two sides of an edible film coupled with a simple wet chemical analysis at the end, was developed to measure the oxygen permeability of edible films. The proposed method was employed to determine the oxygen permeability of methyl cellulose (MC)-based edible films of various composition with the aim of finding the optimum composition for minimising oxidative degradation of foods. The effects of the presence of stearic acid (SA), ascorbic acid (AA) and citric acid (CA), in varying amounts in the film composition, on the oxygen permeability (OP) of MC based edible films were examined. The OP increased with increasing SA content of the film and decreased with the inclusion of AA or CA in the film composition. The films, with various compositions and with the measured oxygen permeabilities, were then applied to mushrooms (*Agaricus bisporus*) and cauliflower (*Brassica botrytis*). It was found, from the analysis of these coated foods, that the coatings containing antioxidants slowed the browning reactions and reduced the vitamin C loss in both foods, the effects being greater in cauliflower. Moreover, the moisture loss of coated foods was less than that of uncoated.

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1. Introduction

The development of edible films to reduce the moisture transfer, the oxidation or the respiration in food systems is important to prolong the shelf-lives of foods. The measurements of permeabilities of stand-alone films to water vapour, oxygen and carbon dioxide are important tools for the development of edible films.

Oxygen is involved in many degradation reactions in foods, such as fat and oil rancidity, micro-organism growth, enzymatic browning and vitamin loss. Thus, many packaging strategies seek to exclude oxygen to protect the food product (Gontard, Thibault, Cuq, & Guilbert, 1996). On the other hand, the permeability to oxygen and carbon dioxide is essential for respiration in living tissues such as fresh fruits and vegetables. So, moderate barrier coatings are more appropriate. If a

coating with the appropriate permeability is chosen, a controlled respiratory exchange can be established and thus the preservation of fresh fruits and vegetables can be prolonged.

The main characteristics to consider in the selection of coating materials are their oxygen, carbon dioxide and water vapour permeabilities. The water vapour permeability (WVP) is the most extensively studied property of edible films (Ayranci, Buyuktas, & Cetin, 1997; Ayranci & Cetin, 1995; Gontard, Marchesseau, Cuq, & Guilbert, 1995; Kamper & Fennema, 1984; McHugh, Aujard, & Krochta, 1994) mainly because of the importance of the role of water in deteriorative reactions and partly because the ease of measurement. The correlation between moisture sorption isotherm and WVP of cellulose-based edible films was also sought (Ayranci, 1996). The measurement of oxygen and carbon dioxide permeabilities requires instruments which may not be easily available. Measurements are mostly based on the standard method described in ASTM (1988) for oxygen gas transmission through films. These

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methods involve a flowing an oxygen gas stream on one side of the film and a nitrogen stream, to carry the transmitted oxygen gas to the analyzer, on the other side. A coulometric sensor, an infrared sensor, a gas chromatograph or a dedicated oxygen analyser may be used for monitoring.

Park, Weller, Wergano, and Testin (1993) measured the oxygen permeabilities of methyl cellulose (MC) and hydroxypropyl methyl cellulose (HPC)-based edible films by the OX-TRAN 1000 system, operated according to the ASTM (1988) standard method. They found that the oxygen permeability (OP) of the films increased with the molecular weight of MC and HPC. In another work by Gennadios, Weller, and Testin (1993), the OP of corn zein, wheat gluten and wheat gluten/soy protein isolate films was measured at 7, 15, 25 and 35 °C by a method again based on ASTM (1988). The OP of all films was found to increase with temperature. It was also noted that the OP values of wheat gluten/soy protein isolate films were lower than those of other films. The degree of resistance of various lipid films to the oxygen transmission was measured with the aim of determining the influences of polymorphic forms of the lipid and of tempering, using the method of ASTM by Kester and Fennema (1989a, 1989b, 1989c). Greener and Fennema (1989) reported oxygen permeabilities of bilayer films prepared from methyl cellulose and beeswax measured by the same method. Another work on the oxygen transmission of a methyl cellulose-palmitic acid film was reported by Rico-Pena and Torres (1990).

In a recent work from our laboratory, a simple method was proposed for the measurement of CO₂ permeability (Ayranci, Tunc, & Etcı, 1999) and applied successfully to various cellulose-based edible films (Ayranci & Tunc, 2001).

In the present work, we introduce a method to measure the OP of edible films. The proposed method was applied to measure the OP of films of various composition with the aim of finding the optimum composition to minimise oxidative degradation of foods. Application of film solutions to fresh foods, such as mushrooms and cauliflower, and analysis of these foods for oxidative degradation, are also investigated.

2. Materials and methods

2.1. Materials

MC with an average molecular weight of 41 000, polyethylene glycol (PEG) with an average molecular weight of 400 and stearic acid (SA) were purchased from Sigma. Citric acid (CA), manganese(II) sulphate monohydrate, potassium iodide, sodium thiosulphate and sodium hydroxide were obtained from Merck. Oxygen gas was obtained from a local gas supplier,

HABAS. Ethanol was reagent grade and water was distilled.

Gallic acid, Folin and Ciocalteu phenol reagent, obtained from Sigma, and Na₂CO₃, obtained from Merck, were used for the analysis of phenol. (+) Catechin, purchased from Sigma, and phosphate buffer, obtained from Merck, were used in the polyphenol oxidase (PPO) activity measurements. Ascorbic acid (AA), purchased from Sigma, CuSO₄·5H₂O and H₂C₂O₄, obtained from Merck, were used for the analysis of vitamin C.

Mushrooms were obtained from ANT-BUZ Gıda ve Tarım Ürünleri San. Tic. A.Ş. and cauliflower was from a local bazaar.

2.2. Preparation of films

MC (3 g) was dissolved in a solvent mixture of 66 ml ethanol and 33 ml water. After the addition of 1 ml PEG, the solution was homogenised with an homogeniser at 24 000 rev min⁻¹ for 5 min. It was re-homogenised after the addition of fatty acid and other additives. The final solution was kept in a vacuum oven at 80 °C for about 5 h in order to remove air bubbles or dissolved air. It was then spread on 20×20 cm glass plates by adjusting the hand-operated thin layer chromatography plate coater to 0.5 mm thickness. The spread films were dried at 60 °C in an oven for 25 min and then at room temperature for 1 day.

2.3. Measurement of the OP

An edible film was sealed between two specially designed glass cups, each having a diameter of 4 cm and a depth of 5 cm (Fig. 1). Both cups have two channels. Oxygen enters to the cup on one side of the film from one channel and leaves from the other with a controlled flow rate to keep the oxygen pressure constant in that compartment. The cup on the other side of the film was purged by a stream of nitrogen entering from one channel and leaving from the other. This nitrogen acted as a carrier for oxygen permeated from the other side of the film to the wet analysis system (Fig. 1). Up to the wet analysis system, the design was mainly based on the ASTM standard (1988). A modification was made to the O₂ analysis and a classical wet analysis, based on the well-known method of iodimetry was applied for the determination of the amount of permeated O₂, instead of using an oxygen analyser as in the ASTM standard, which uses a coulometric sensor.

The mixture of N₂ and permeated O₂ was passed from the wet system for a known period of time. Then the wet system, which originally contained aqueous manganese(II) sulphate and alkaline iodide solution, was analysed for O₂ (Vogel, 1989). It is well known that manganese(II) hydroxide is rapidly and quantitatively

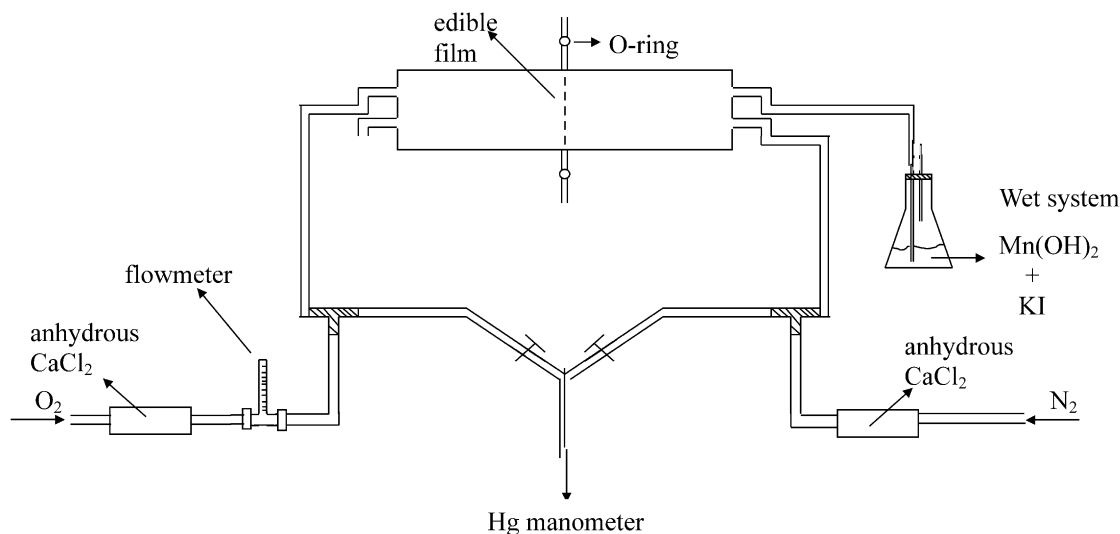
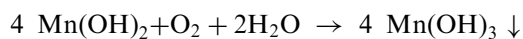
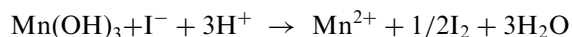


Fig. 1. Schematic of the apparatus used to measure oxygen permeability of edible films.

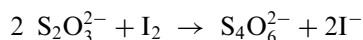
converted to manganese(III) hydroxide with oxygen by the following reaction:



The brown precipitate formed was dissolved on acidification and allowed to oxidise iodide ions present in the system quantitatively to iodine ;



The liberated iodine could then be titrated with a standard thiosulphate solution;



A blank titration was carried out to determine any oxygen pre-dissolved in the wet system. The stoichiometry indicated that 1 mol of dissolved oxygen required 4 mol of thiosulphate.

The OP of the film was then calculated by Eq. (1);

$$\text{OP} = \frac{m \cdot d}{A \cdot t \cdot \Delta P} \quad (1)$$

where m is the mass of O_2 permeated through the film with a thickness of d and an area of A over the measured time interval t . ΔP is the difference in O_2 pressure between the two sides of the film. The pressure on the O_2 side of the film (Fig. 1) was kept at 1 atm by controlling the flow of pure O_2 purged to this compartment and by measuring its pressure with a Hg manometer (Fig. 1). The O_2 pressure on the N_2 side of the film was assumed to be zero, since any O_2 permeated through the film was continuously swept to the wet system for analysis at the end. So, ΔP was taken as 1 atm.

The OP of various edible films were determined according to the method described above at 25 ± 1 °C and 0% relative humidity. Both O_2 and N_2 gases were dried by passing through a gas drying column containing anhydrous calcium chloride before entering the system (Fig. 1). Prior to the permeability measurements, films were also conditioned in a desiccator over anhydrous calcium chloride for 1 day.

2.4. Measurement of the film thickness

The film thickness was measured with a hand-held micrometer having a sensitivity of 0.001 mm. This measurement was carried out at the end of the permeability test to avoid the effect of mechanical damage that could be caused on the film during the thickness measurement. The thickness was measured at various locations (at least five) of the film and then an average value was calculated.

2.5. Comparison of the OP results obtained by the present method with those reported in literature

The data on OP, determined by ASTM methods in the literature, are reported at varying conditions of temperature, film thickness, film composition and relative humidity. It should be recognised that it is very difficult to match all these conditions exactly for OP measurements in different laboratories to compare or test the results obtained by a new method. However, a reasonable comparison can be made between the reported OP data and the data obtained in this work, under slightly different conditions, in order to seek support for the validity of the method.

Rico-Pena and Torres' (1990) OP data, reported for a film with a composition of PA:MC:PEG in 3:9:1 ratio,

was taken as the first reference to compare with the results obtained in the present method. The film used in the reference work had a thickness of 54 μm and its OP was measured at 24 °C and 0% relative humidity as $0.52 \times 10^{-9} \text{ g d}^{-1} \text{ Pa}^{-1} \text{ m}^{-1}$. The film prepared in the present work, for comparison purposes, had the same composition. Its OP was measured at the same temperature and relative humidity. However, the thickness of the film could only be adjusted to 42 μm which is 12 μm thinner than Rico-Pena and Torres' film. The measured OP was $(0.82 \pm 0.05) \times 10^{-9} \text{ g d}^{-1} \text{ Pa}^{-1} \text{ m}^{-1}$ which has the same order of magnitude but is greater than Rico-Pena and Torres' reported value. The difference is believed to originate from the difference in thickness of the two films. It was reported by Park and Chinnan (1990) that O_2 and CO_2 permeabilities of protein based films increase with decreasing thickness.

The second selected reference OP was reported by Park and Chinnan (1990) for a film with a composition of MC:PEG in 9:1 ratio and with a thickness of 40 μm . The OP of this film was found to be $0.21 \times 10^{-9} \text{ g d}^{-1} \text{ Pa}^{-1} \text{ m}^{-1}$ at 30 °C and 0% relative humidity. The control film prepared in the present work had the same composition and the same thickness. Its OP was measured at 29 °C and 0% relative humidity as $(0.52 \pm 0.03) \times 10^{-9} \text{ g d}^{-1} \text{ Pa}^{-1} \text{ m}^{-1}$, which again has the same order of magnitude but is greater than the reported result of Park and Chinnan. This time the difference in conditions seems to be only in temperature and that is only 1 °C, which can not explain the large difference observed in OP values. This large difference can only be attributed to the origin of MC used in the film preparation. The MC used in the present work has an average molecular weight of 41 000. Unfortunately, the molecular weight of MC used by Park and Chinnan was not reported. It might be different. Ayranci et al. (1997) found the effective molecular weight of MC on WVP of MC-based edible films to be especially important above 41 000.

The OP values of edible films measured with the proposed method, in the present work, have the same order of magnitude as those reported in the literature. Some differences may arise due to the differences in conditions of measurements and composition or thickness of the films. It is noteworthy that the OP values determined with the proposed method, for a series of films, show the same trend even if there are some differences in absolute values from those in literature.

2.6. Coating procedure

Mushrooms and cauliflowers were selected as model systems for the application of coating formulations for several reasons. They are susceptible to browning, contain sufficient vitamin C, the loss of which can be studied, they are easily available and coatings can easily be applied. Whole mushrooms and cuts of cauliflowers

were used for coating. Fresh foods were dipped completely into the coating solutions, whose compositions are given in Table 1, for about 5 s at room temperature (and then taken out). This process was repeated twice. Then the coating was dried with the help of a fan.

Coated and uncoated foods were kept in a Sanyo MIR 152 incubator (Japan) at 25 °C and 84% relative humidity until analysis for water loss, colour, vitamin C, polyphenol oxidase activity and total phenol content as a function of time.

2.7. Measurement of water loss

The coated and uncoated fresh mushrooms and cauliflower were weighed to the nearest 0.1 mg and kept in an incubator at 25 °C for 5–8 days. Weighings of foods were repeated every 24 h in order to determine the moisture loss as a function of time.

2.8. Colour measurement

The lightness (*L* value) of mushrooms was determined using a Minolta CR-200 colorimeter. Colour measurement of cauliflower was not possible with a colorimeter due to the non-smooth surface. So, their colour change could only be followed by eye.

2.9. Vitamin C determination

The concentration of vitamin C in foods was determined by a spectrophotometric method (Sawyer, Heineman, & Beebe, 1984). Ten grams of food was homogenised in about 100 ml, 4% $\text{H}_2\text{C}_2\text{O}_4$ solution. The mixture was filtered and diluted to a certain volume with 4% $\text{H}_2\text{C}_2\text{O}_4$.

For the calibration process, the standard solutions were prepared from 100 $\mu\text{g ml}^{-1}$ AA solution in 4% $\text{H}_2\text{C}_2\text{O}_4$. 1 ml of 50 $\mu\text{g ml}^{-1}$ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution (pH = 6) was added to each standard solution and then their absorbance values were recorded at 249 nm as a function of AA concentration.

2.10. Polyphenoloxidase activity

Polyphenoloxidase (PPO) activity was determined according to the procedure described by Zemel, Sims,

Table 1
Compositions of the coating solutions applied to mushrooms and cauliflower

Coating no.	Ethanol/water (ml/ml)	MC (g)	PEG (ml)	SA (g)	Antioxidant (g)
1	66/33	3	1	–	–
2	66/33	3	1	0.6	–
3	66/33	3	1	0.6	0.5 AA
4	66/33	3	1	0.6	0.5 CA

Marshall, and Balaban (1990). Food juice was extracted by pressing about 10 g of food. The PPO activity was assayed in a mixture of 1.2 ml 0.05 M phosphate buffer (pH=6.9), 1.7 ml 0.05 M (+) catechin and 0.1 ml of food juice at 25 °C. The increase in absorbance at 420 nm was followed for 4 min by a UV-160A Shimadzu spectrophotometer

2.11. Total phenol determination

Total phenol content was determined by the Folin–Ciocalteu method (Spanos & Wrolstad, 1990). Food juice, extracted by pressing the food, was filtered through a 0.45- μ m membrane filter. A 0.1 ml aliquot of the clear solution was mixed with 5.0 ml 0.2 N Folin–Ciocalteu reagent, 4.0 ml of saturated sodium carbonate and 0.9 ml of distilled water. After 2 h, the absorbance was recorded at 765 nm. Total phenol content was then determined using a calibration curve prepared with gallic acid, and the results reported as mg/l.

3. Results and discussion

3.1. The effect of antioxidants on the OP of edible films containing SA

Fatty acids, such as SA, LA and PA, being edible and having hydrophobic character, are used in coating formulations as water vapour barrier materials. In previous work we had found SA to be more effective than LA and PA for decreasing WVP of cellulose-based edible films (Ayranci & Tunc, 1997, 2001). Therefore, it was of interest to see how the OP of these films was affected by the SA content. The OP values of MC-based edible films, containing varying amounts of SA in their composition, were determined by the method developed in the present work, as described earlier, and are given in Table 2, together with film thickness values.

The general trend is that the OP increases with increasing SA content of the film. This may be attributed to the formation of holes in the crystal structure of edible films as the SA content increases. These holes, which are especially formed above 15 g SA/100 g MC,

Table 2
The SA content, the thickness and the OP values of edible films at 25 °C and 0% RH

SA content g (100 g MC) ⁻¹	Thickness 10 ⁵ m	OP 10 ⁹ g d ⁻¹ Pa ⁻¹ m ⁻¹
0.0	1.86±0.00	6.8±0.4
5.0	1.93±0.03	5.2±0.2
15	2.10±0.01	7.7±0.9
25	1.88±0.04	8.6±0.3
40	2.00±0.00	14±1

may facilitate the permeation of oxygen. A similar result was also reported by Park et al. (1993). They found the OP values of laminated films to increase with increasing fatty acid content of the film.

There seems to be a paradox here. Increasing the SA content of the film increases the desired water vapour barrier property but decreases the oxygen barrier property which is not so desirable. In order to improve the oxygen barrier property together with the water vapour barrier property, some antioxidants, such as AA and CA, could be added to the film composition, together with SA. Being antioxidants, AA or CA are expected to lower the OP of films.

Varying amounts of AA and CA were included in the film composition containing a fixed amount of SA (20 g/100 g MC), in order to examine their effects on the OP of the films. The antioxidant content, the thickness and the OP values of these films are given in Table 3.

It is clear from Table 3 that OP values of films decrease with both AA and CA contents. The only exception to this trend is at 16.7 g CA/100 g MC content. The OP values of this film were found to be slightly larger than that of the film with 3.33 g CA/100 g MC. The two antioxidants show similar effects in improving the oxygen barrier property of the films.

3.2. The effects of coating on water loss of fresh foods

The water loss of mushrooms, with coatings of varying composition, given in Table 1, and of uncoated ones, as a function of time, are shown in Fig. 2. In the coating formulations, an intermediate SA content of 20 g/100 g MC (which is equivalent to 0.6 g/3 g MC) and the highest examined CA or AA content of 16.7 g/100 g MC (which is equivalent to 0.5 g/3 g MC) were maintained according to the results presented above in Section 3.1. The % water losses of uncoated mushrooms are 3.86, 14.7 and 19.7 at the end of first, third and fifth days, respectively. Mushrooms with coatings of varying

Table 3
The antioxidant content, the thickness and the OP values of edible films containing 20 g SA/100 g MC at 25 °C and 0% RH

Antioxidant content g (100 g MC) ⁻¹	Thickness 10 ⁵ m	OP 10 ⁹ g d ⁻¹ Pa ⁻¹ m ⁻¹
<i>AA</i>		
0.33	1.9±0.2	8.3±0.2
1.67	1.87±0.03	6.5±0.1
3.33	1.8±0.0	5.8±0.2
16.67	1.80±0.02	4.5±0.2
<i>CA</i>		
0.33	1.68±0.0	6.4±0.3
1.67	1.57±0.03	5.39±0.03
3.33	1.49±0.01	3.9±0.2
16.67	1.62±0.02	4.7±0.2

composition have lower % water loss than uncoated ones, the effect of lowering the water loss being the greatest with the coating containing only SA (coating 2) as an additive. This is an expected result, due to the hydrophobicity provided to the coating by SA. The coating without SA (coating 1) is the least efficient in reducing water loss of mushrooms. The inclusion of AA and CA, in addition to SA in the coating formulation (coating 3 and coating 4), lowers the hydrophobicity of the coatings. Thus, mushrooms with these coatings have slightly larger water losses than those with the coating containing only SA (Fig. 2).

The % water losses of cauliflower with the same coatings (Table 1) and of uncoated ones, as a function of time, are given in Fig. 3. The trends seen for cauliflower are very similar to those for mushrooms, for example water loss is the highest for uncoated cauliflower and the lowest for cauliflower with the coating containing only SA (coating 2).

3.3. The effects of coating on browning of fresh foods

L value (lightness) of a food product, determined by a colorimeter, is a measure of the degree of browning of that product. An *L* value of 100 means white colour, zero absorbance and 100% transmittance. *L* value decreases below 100 with increasing degree of browning of the product. *L* values of uncoated mushrooms, and of mushrooms with coatings of varying compositions (Table 1) as a function of time, are given in Fig. 4.

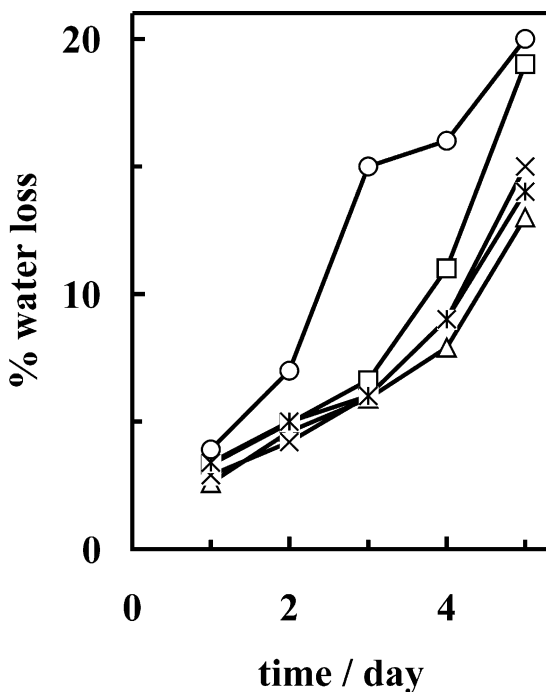


Fig. 2. Water loss of uncoated mushrooms (○) and mushrooms with coating 1 (□), coating 2 (△), coating 3 (×) and coating 4 (⊗) as a function of time at 25 °C and 84% RH.

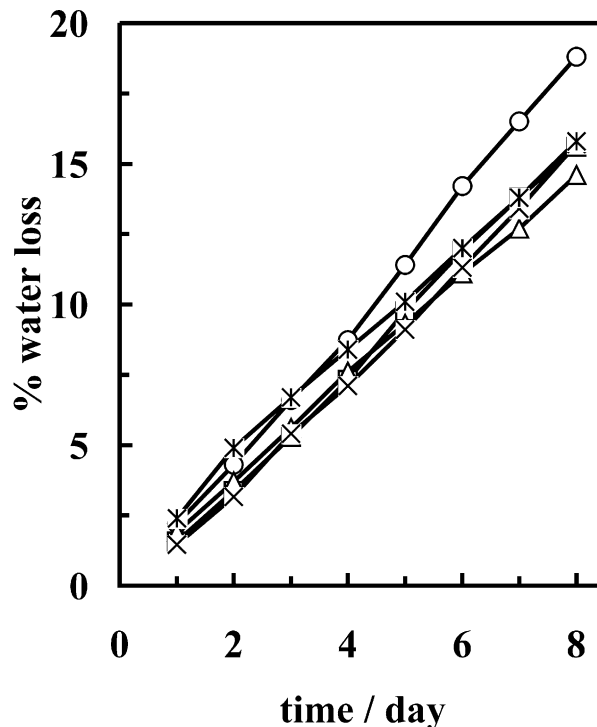


Fig. 3. Water loss of uncoated cauliflower (○) and cauliflower with coating 1 (□), coating 2 (△), coating 3 (×) and coating 4 (⊗) as a function of time at 25 °C and 84% RH.

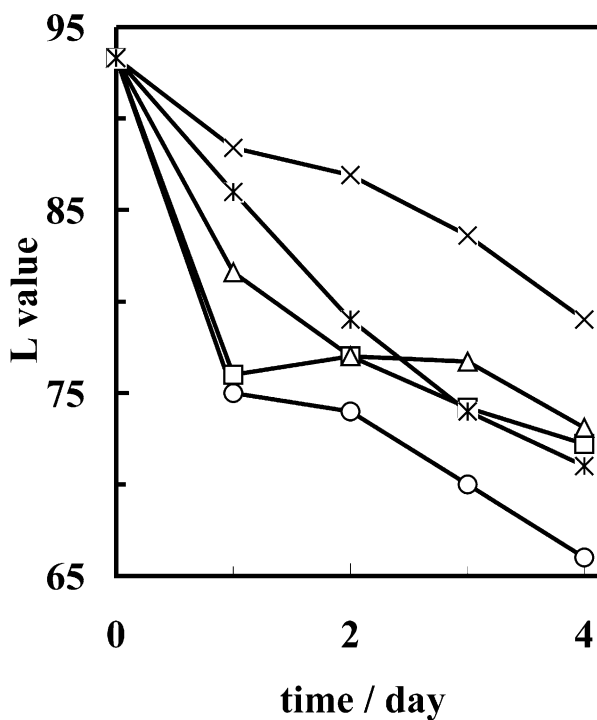


Fig. 4. *L* values of uncoated mushrooms (○) and mushrooms with coating 1 (□), coating 2 (△), coating 3 (×) and coating 4 (⊗) as a function of time at 25 °C and 84% RH.

Uncoated mushrooms had the lowest L values throughout the whole period of 4 days. The highest L values were maintained by mushrooms with the coating containing SA and AA (coating 3) during the same working period. So, it can be concluded that coating 3 is the most effective in preventing the browning of fresh mushrooms. The second most effective film appears to be coating 4, the one containing CA (Fig. 4).

As mentioned in the experimental part, the browning of coated and uncoated cauliflower could only be followed by eye as a function of time because it was not possible to measure L values due to roughness of the surfaces. Again, minimum degree of browning was observed for cauliflower with coatings containing CA or AA (coating 3 and 4) throughout the 12-day observation period. Browning of uncoated cauliflower began on the fourth or fifth days and its extent increased with time.

3.4. The effects of coating on vitamin C content, polyphenoloxidase activity and total phenol content of fresh foods

The resistance provided by the coatings for the vitamin C loss of mushrooms and cauliflower was followed by measuring the vitamin C contents of these foods without coating and with coatings of varying compositions. The results are given in Fig. 5 for mushrooms and in Fig. 6 for cauliflower.

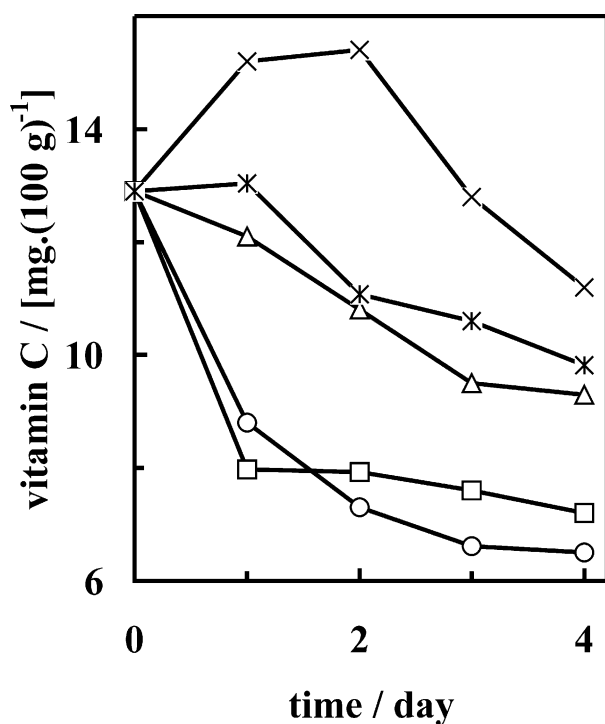


Fig. 5. Vitamin C contents of uncoated mushrooms (○) and mushrooms with coating 1 (□), coating 2 (Δ), coating 3 (X) and coating 4 (X) as a function of time at 25 °C and 84% RH.

An increase in the vitamin C content was observed for mushrooms with coating 3 (with AA) on the first and second days (Fig. 5). This may result from the diffusion of AA present in the coating composition to the mushrooms in the first 2 days. After the second day, vitamin C contents of these mushrooms started to decrease. Percentage vitamin C loss of uncoated mushrooms was 49.8, and those of mushrooms with coatings 1, 2 and 4 were 43.9, 27.9 and 23.9, respectively, at the end of fourth day. It is evident that the coatings with CA or AA are the most effective in preserving the vitamin C content of mushrooms. This can be attributed to the low oxygen permeability of these coatings (Table 3) compared with the others. Keeping oxygen away from the food delays the deteriorative oxidation reactions of vitamin C. Mushrooms without coating or with coatings containing only MC and PEG (coating 1) maintained the lowest vitamin C content throughout the working period of 4 days (Fig. 5).

It is noteworthy that the oxidation of ascorbic acid to dehydroascorbic acid does not represent the loss of vitamin C, as both forms have the vitamin property. The loss of vitamin C, here, represents the conversion of dehydroascorbic acid to diketogulonic acid by further oxidation (Rai & Saxena, 1988).

The variation in vitamin C content of cauliflower, as a function of time, given in Fig. 6, showed trends similar to those of mushrooms. Again, coatings with AA or CA

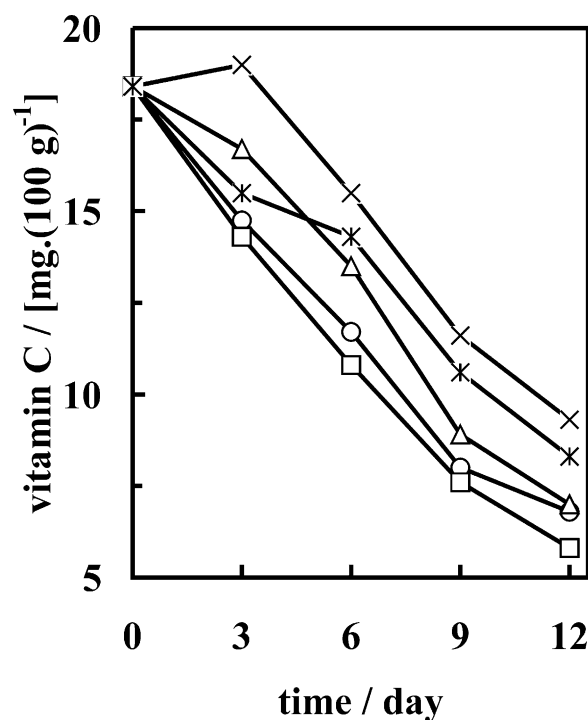


Fig. 6. Vitamin C contents of uncoated cauliflower (○) and cauliflower with coating 1 (□), coating 2 (Δ), coating 3 (X) and coating 4 (X) as a function of time at 25 °C and 84% RH.

(coatings 3 and 4) were the most effective in preserving vitamin C content of cauliflower.

PPO activity and total phenol contents of foods are considered to be a measure of the degree of oxidation reactions. Oxidation increases with PPO activity since PPO acts as a catalyst in oxidation reactions. Similarly, increase in total phenol content indicates an increase in oxidation, since phenolic compounds are products of oxidation reactions.

The variation of PPO activity as a function of time is given in Fig. 7 for mushrooms with and without coating, and in Fig. 8 for cauliflower with and without coating. In general there was an increase in PPO activity with time for all samples. However, it is clear that mushrooms and cauliflower with coatings containing AA or CA (coatings 3 and 4) maintained the lowest PPO activity compared to those which were uncoated or coated with other coatings. It should also be noted that there was a direct relation between the PPO activity and the degree of browning.

The variation of total phenol content of only mushrooms with time could be followed and the results are presented in Fig. 9. Again, the effectiveness of coatings 3 and 4 (with AA and CA) in preserving mushrooms against oxidation could clearly be seen in this figure.

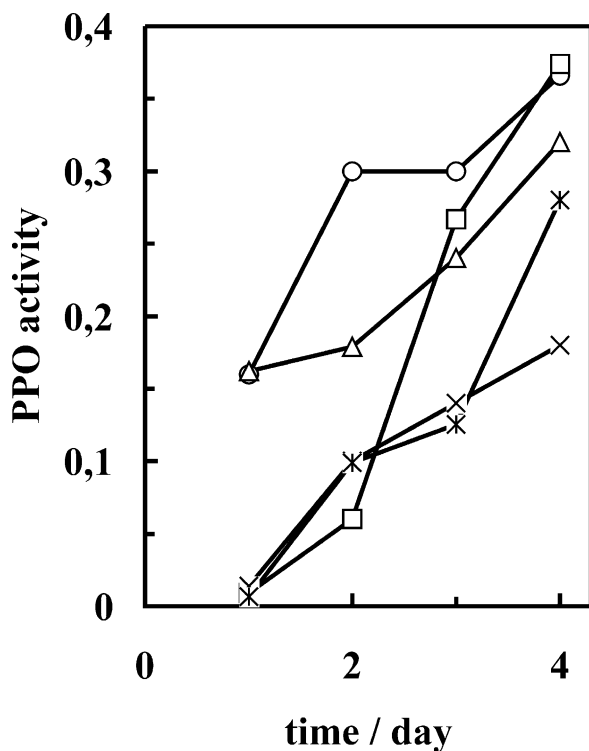


Fig. 7. PPO activity of uncoated mushrooms (○) and mushrooms with coating 1 (□), coating 2 (△), coating 3 (×) and coating 4 (×) as a function of time at 25 °C and 84% RH.

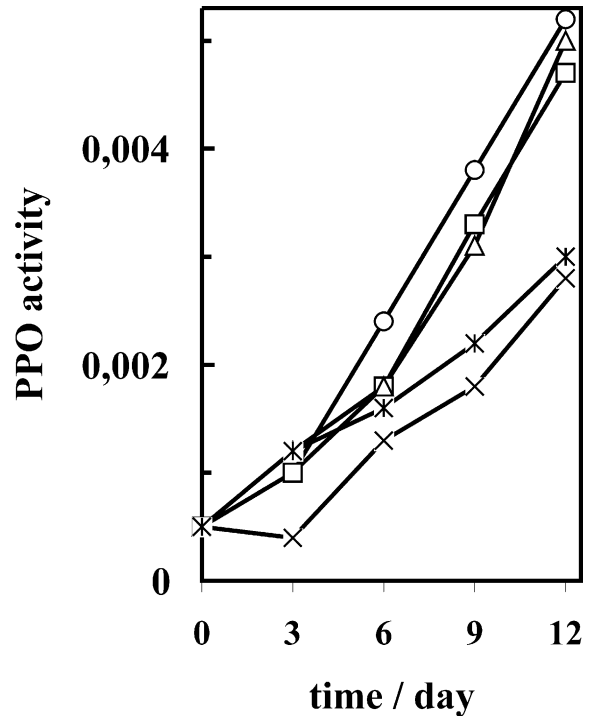


Fig. 8. PPO activity of uncoated cauliflower (○) and cauliflower with coating 1 (□), coating 2 (△), coating 3 (×) and coating 4 (×) as a function of time at 25 °C and 84% RH.

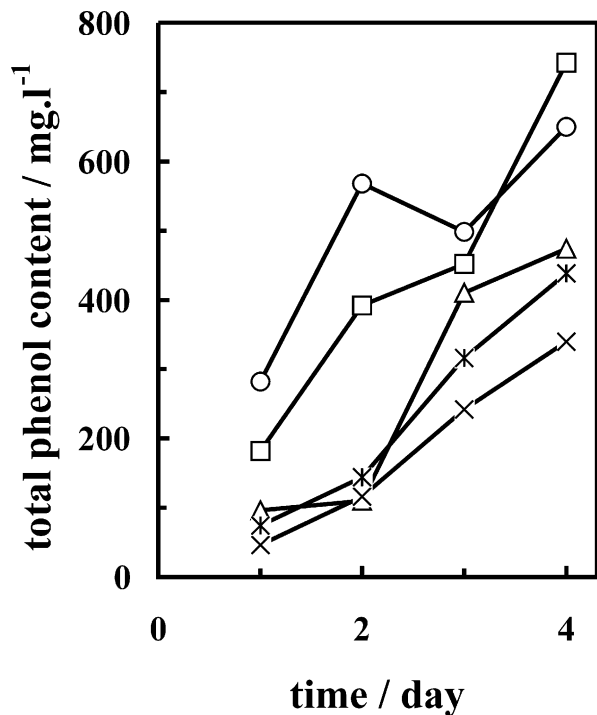


Fig. 9. Total phenol content of uncoated mushrooms (○) and mushrooms with coating 1 (□), coating 2 (△), coating 3 (×) and coating 4 (×) as a function of time at 25 °C and 84% RH.

Due to the naturally more stable character of cauliflower than mushrooms, against deterioration, the level of total phenol content of cauliflower was either undetectable or very low during the storage period of about 12 days. For example, the total phenol content of cauliflower, with coatings 2, 3 and 4 was undetectably low at the end of the 12th day, that of those with coating 1 was as low as 60 mg l⁻¹ at the end of the 9th day and that of those which were uncoated was 258 mg l⁻¹ at the end of the 12th day.

4. Conclusions

A method developed in this work for the measurement of the OP of edible films, based on a wet analysis, after transporting the permeated oxygen into the wet system, was found to be successful in determining oxygen permeabilities of various methylcellulose-based edible films. It was found that inclusion of AA and CA in the film composition decreased the OP of stand-alone films. Also, the coatings containing, AA or CA, applied to mushrooms and cauliflower slowed down the browning reactions, as well as PPO activity and vitamin-C losses of these foods.

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References

- ASTM. (1988). *Standard test method for oxygen gas transmission rate through plastic film and sheeting using coulometric sensor*. Designation: D3985 (pp. 656–661).
- Ayranci, E. (1996). Moisture sorption of cellulose based edible films. *Nahrung*, 40, 274–276.
- Ayranci, E., Buyuktas, B. S., & Cetin, E. E. (1997). The effect of molecular weight of constituents on properties of cellulose-based edible films. *Lebensmittel Wissenschaft und Technologie*, 30, 101–104.
- Ayranci, E., & Cetin, E. (1995). The effect of protein isolate of pistacia terebinthus L on moisture transfer properties of cellulose-based edible films. *Lebensmittel Wissenschaft und Technologie*, 28, 241–244.
- Ayranci, E., & Tunc, S. (1997). Cellulose based edible films and their effects on fresh beans and strawberries. *Zeitschrift fuer Lebensmittel-Untersuchung und Forschung A*, 205, 470–473.
- Ayranci, E., & Tunc, S. (2001). The effect of fatty acid content on water vapour and carbon dioxide transmission of cellulose-based edible films. *Food Chemistry*, 72, 231–236.
- Ayranci, E., Tunc, S., & Etcı, A. (1999). The measurement of carbon dioxide transmission of edible films by a static method. *Journal of the Science of Food and Agriculture*, 79, 1033–1037.
- Gennadios, A., Weller, C. L., & Testin, R. F. (1993). Temperature effect on oxygen permeability of edible protein-based films. *Journal of Food Science*, 58, 212–214.
- Greener, I. K., & Fennema, O. (1989). Barrier properties and surface characteristics of edible, bilayer films. *Journal of Food Science*, 54, 1393–1399.
- Gontard, N., Marchesseau, S., Cuq, C. L., & Guilbert, S. (1995). Water vapour permeability of edible bilayer films of wheat gluten and lipids. *International Journal of Food Science and Technology*, 30, 49–56.
- Gontard, N., Thibault, R., Cuq, B., & Guilbert, S. (1996). Influence of relative humidity and film composition on oxygen and carbon dioxide permeabilities of edible films. *Journal of Agricultural and Food Chemistry*, 44, 1064–1069.
- Kamper, S. L., & Fennema, O. (1984). Water vapour permeability of edible, fatty acid, bilayer film. *Journal of Food Science*, 49, 1482–1485.
- Kester, J. J., & Fennema, O. (1989a). Resistance of lipid films to oxygen transmission. *Journal of The American Oil Chemists' Society*, 66, 1129–1138.
- Kester, J. J., & Fennema, O. (1989b). The influence of polymorphic form on oxygen and water vapour transmission through lipid films. *Journal of The American Oil Chemists' Society*, 66, 1147–1153.
- Kester, J. J., & Fennema, O. (1989c). Tempering influence on oxygen and water vapour transmission through a stearyl alcohol film. *Journal of The American Oil Chemists' Society*, 66, 1154–1157.
- McHugh, T. H., Aujard, J. F., & Krochta, J. M. (1994). Plasticised whey protein edible films: water vapour permeability properties. *Journal of Food Science*, 59, 416–419.
- Park, H. J., & Chinnan, M. S. (1990). *Properties of edible coatings for fruits and vegetables*. ASAE paper no. 90-6510. St. Joseph, MI: American Society of Agricultural Engineers.
- Park, H. J., Weller, C. L., Wergano, P. J., & Testin, R. F. (1993). Permeability and mechanical properties of cellulose-based edible films. *Journal of Food Science*, 58, 1361–1364.
- Rai, R. D., & Saxena, S. (1988). Effect of storage temperature on vitamin C content of Mushrooms (*agaricus bisporus*). *Current Science*, April, 20, 57–434–435.
- Rico-Pena, D. C., & Torres, J. A. (1990). Oxygen transmission rate of an edible methyl cellulose-palmitic acid film. *Journal of Food Process Engineering*, 13, 125–133.
- Sawyer, D. T., Heineman, W. R., & Beebe, J. M. (1984). *Chemistry experiments for instrumental methods*. New York: Wiley.
- Spanos, G. A., & Wrolstad, R. E. (1990). Influence of processing and storage on the phenolic composition of Thompson seedless grape juice. *Journal of Agricultural and Food Chemistry*, 38, 1565–1571.
- Vogel, A. I. (1989). *Vogel's textbook of quantitative chemical analysis (Revisors)* G. H. Jeffery, J. Bassett, J. Mendham, R. C. Denney (pp. 395–396). London: Longman.
- Zemel, G. P., Sims, C. A., Marshall, M. R., & Balaban, M. (1990). Low pH inactivation of polyphenoloxidase in apple juice. *Journal of Food Science*, 55, 562–564.