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The effect of fatty acid content on water vapour and carbon dioxide transmissions of cellulose-based edible films

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Abstract

Water vapour and CO_2 transmissions of methyl cellulose (MC)-based edible films with varying amounts of the fatty acids, stearic acid (SA), palmitic acid (PA) and lauric acid (LA) were studied and the results were compared with those obtained for a film without added fatty acid. Water vapour transmission rate (WVTR), water vapour permeance (WVPN) and water vapour permeability (WVP) values of films were determined by measuring the amounts of water vapour transmitted through the film and then adsorbed on anhydrous $CaCl_2$ as a function of time, using a static method. A recently-developed static method which utilises ascarite to adsorb carbon dioxide transmitted through the film was employed for the determination of carbon dioxide transmission rate (CO_2TR), carbon dioxide permeance (CO_2PN) and carbon dioxide permeability (CO_2P) of films. Among the three fatty acids studied, SA was found to be the most effective in decreasing both the water vapour and the CO_2 transmissions of films. In general, it was observed that WVTR, WVPN and WVP values of films decreased with increasing fatty acid content in the film composition. CO_2 transmission parameters also decreased with increasing SA and PA contents but increased with increasing LA content of films.

Keywords: Edible films; Water vapour transmission; Carbon dioxide transmission; Fatty acids

1. Introduction

Studies on the development of edible films and coatings are receiving more attention as they lead to the extension of shelf-life of foods. Edible films are developed to control migration of moisture and to control respiratory exchange by selective gas permeability. Although the water vapour transmission of edible films has been extensively studied (Ayranci & Cetin, 1995; Gontard, Marchesseau, Cuq & Guilbert, 1995; Kamper & Fennema, 1984; McHugh, Aujard & Krochta, 1994), only a limited number of studies report on the carbon dioxide permeability of edible films (Gontard, Thibault, Cuq & Guilbert, 1996). Krochta (1992) reviewed some of the methods used for the measurement of oxygen and carbon dioxide permeabilities, together with water vapour permeability. Most of the methods are based on the standard method described in ASTM (1988) for oxygen gas transmission through the films. They involve a flowing O_2 or CO_2 stream on one side of the film and a flowing N_2 stream on the other side to carry the transmitted gas to the analyser. A coulometric sensor, an infrared sensor, a gas chromatograph or a dedicated oxygen or carbon dioxide analyser is used for monitoring. Recently, a new static method was developed to measure CO_2 transmission through edible films by Ayranci, Tunc and Etci (1999). It was an adoption of the static method described for measurement of water vapour transmission in ASTM (1993) with some modifications for CO_2. Once the reliable transmission measurements become possible, it is important to examine the factors affecting the water vapour or CO_2 transmissions, such as temperature, relative humidity and film composition. The effects of some of these factors on transmission parameters, especially on water vapour transmission, were investigated for some edible film systems (Avena-Bustillos & Krochta, 1993; Ayranci, Buyuktas & Cetin, 1997; Ayranci & Cetin, 1995; Kamper & Fennema, 1984).

The purpose of the present work was to examine the effects of stearic acid (SA), palmitic acid (PA) and lauric acid (LA) contents on water vapour and CO_2 transmission

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parameters of cellulose-based edible films. The transmission parameters determined were water vapour transmission rate (WVTR), water vapour permeance (WVPN), water vapour permeability (WVP), carbon dioxide transmission rate (CO_2TR), carbon dioxide permeance (CO_2PN) and carbon dioxide permeability (CO_2P).

2. Materials and methods

2.1. Materials

Methyl cellulose (MC), with an average molecular weight of 41 000, and polyethylene glycol (PEG), with an average molecular weight of 400, SA, PA, LA, anhydrous $CaCl_2$ and KCl were obtained from Sigma. Ascarite II was bought from Aldrich. CO_2 was obtained from a local gas supplier, HABAS. Ethanol was reagent grade and water was deionized.

2.2. Preparation of films

Films were prepared as described by Ayranci and Cetin (1995). Three grams MC and 1.18 g PEG were dissolved in a solvent mixture of 33 ml water and 66 ml ethanol at about 60°C and the solution was homogenised with an Ultra-Turrax T25 homogeniser at 24 000 rpm for 5 min. After the addition of fatty acids in varying amounts, the solution was rehomogenised. In order to remove air bubbles or any dissolved air, the final solution was kept under vacuum in a Nuve EV 018 vacuum oven for about a day. It was then heated to 60°C and spread on 20×20 cm glass plates using a hand-operated plate coater of CAMAG thin-layer chromatography by adjusting its thickness to 0.5 mm. The spread films were dried in an oven for 25 min and then at room temperature for a day.

2.3. Measurement of water vapour transmission

Water vapour transmission of films was measured using the ASTM (1993) method. Special cups, with an average diameter of 3.9 cm and a depth of 1 cm, having a small platform at the top to seal the films, were constructed by a glassblower. After placing 3 g of anhydrous $CaCl_2$ in each cup, they were covered with edible films of varying composition. Films were cut into discs with a diameter slightly larger than the diameter of the cup and then sealed using melted paraffin. The cups were weighed with their contents and placed in a desiccator containing saturated KCl solution in a small beaker at the bottom. A small amount of solid KCl was left at the bottom of the saturated solution to ensure that the solution remained saturated at all times. Saturated KCl solution in the desiccator provides a constant relative humidity medium of 84.34% at 25°C. The desiccator was kept in a Sanyo MIR 152 incubator at 25.0±0.1°C. Cups were weighed every 24 h until a steady increase in weight was achieved.

2.4. Determination of water vapour transmission parameters

The amount of water vapour transferred through the films is calculated from the increasing weight of the cup kept in the desiccator and is plotted as a function of time. A linear variation in weight vs. time plot was taken as an indication of steady transfer rate and this was achieved around day 4 in most cases. The slope of this linear portion, calculated by applying least square analysis, was divided by the total area of the film exposed to transmission to obtain WVTR of each film.

WVPN was determined by dividing WVTR by water vapour pressure difference across the film. Water vapour pressure on the $CaCl_2$ side of the film was taken as zero. On the other side of the film, the water vapour pressure was calculated by multiplying the water activity in the desiccator with vapour pressure of pure water at 25°C.

WVP was obtained as the product of permeance and the film thickness.

2.5. Measurement of carbon dioxide transmission

Carbon dioxide transmission of films was measured according to the method described by Ayranci et al. (1999). The special cups constructed for water vapour transmission measurements were also suitable for CO_2 transmission measurements. Sufficient amounts of ascarite II to absorb CO_2 and anhydrous $CaCl_2$ to absorb water released during the reaction of CO_2 with ascarite II were placed in the cup. Separate preliminary experiments were carried out as described previously (Ayranci et al., 1999) to determine the required minimum amounts of these two materials. The film was sealed over the cup using melted paraffin. The sealed cup was weighed and placed in a vacuum desiccator over $CaCl_2$. The desiccator was kept in the incubator at 25.0±0.1°C. The valve of the desiccator was connected to a three-way system of stopcocks by a tube passing through a special port of the incubator. The three ways lead to a vacuum pump, a mercury manometer and a CO_2 gas cylinder.

CO_2 pressure inside the desiccator was adjusted in the following way: the vacuum valve was opened slowly in a controlled manner until the vacuum pressure reached the desired CO_2 pressure, as monitored by the manometer, keeping the desiccator and the manometer valves open and the CO_2 valve closed. Then, the vacuum valve was closed and the CO_2 valve was opened slowly in a controlled manner until the levels of mercury at the two manometer arms became the same. The CO_2 valve was then closed again. It should be noted that these measurements were carried out in the absence of water vapour. The anhydrous $CaCl_2$ at the bottom of the desiccator provides such a dry atmosphere. CO_2 transmitted through the film was absorbed by ascarite II in the cup and the water evolved during the reaction of CO_2 with ascarite II was held in the cup by the anhydrous $CaCl_2$ associated with the ascarite II. The small pressure decrease within the desiccator, due to loss of CO_2 by transmission and then absorption, was monitored from the manometer. This pressure loss was made up twice a day by opening the CO_2 valve in a controlled manner until the level of mercury in the two arms of the manometer were equal. It should be noted that the pressure reduction during the 12 h period was less than 0.67 kPa.

The weight increase in the cup and its contents was measured at 24 h intervals using a balance with a sensitivity of 0.1 mg. Weighings were completed in the shortest possible period, usually less than 5 min. The whole system was reset as described above after each weighing.

2.6. Determination of carbon dioxide transmission parameters

The amount of CO_2 transferred through the films was determined from the increase in weight of the cup kept in the desiccator. This was plotted as a function of time. A linear variation in weight vs. time, indicating a steady transfer rate, was achieved within 4 days in most cases. The CO_2TR of the film was obtained by dividing the slope of this linear portion, calculated by applying least square analysis, by the total area of the film exposed to transmission.

CO_2PN was determined as the ratio of CO_2TR to the CO_2 pressure difference between the two sides of the film. Ascarite II was assumed to have absorbed all the CO_2 inside the cup, so the CO_2 pressure on that side was taken as zero. Thus, the CO_2 pressure difference between the two sides is simply the pressure within the desiccator that has been kept reasonably constant. Finally, CO_2P was determined by multiplying CO_2PN by the average thickness of the film.

2.7. Measurements of the film thickness

The film thickness was measured with a Mitutoyo M820-25 hand-held micrometer having a sensitivity of 0.001 mm. Measurements were made at different places (at least five) of the film and then an average value was calculated.

3. Results and discussion

3.1. Water vapour transmission

WVTR and WVPN values of films with varying fatty acid contents are given in Table 1 where the film thicknesses are also included. The parameters for the film without any fatty acid are given in the first row of the table. The measurements were made at least in duplicate and the average values together with standard deviations were recorded. It is recognised that some of the data have considerably high standard deviations (as high as 20% of the mean value for a few data). However, we believe that the mean values still demonstrate the general trends in transmission behaviour of films. WVP values were also determined for these films. When the three water vapour transmission parameters were plotted as a function of fatty acid content of films, they all showed similar trends. In order to show this trend graphically, the variation of WVP with fatty acid content is given in Fig. 1. WVP is probably the most informative parameter since it takes both the water vapour pressure difference between the two sides of the film and the film thickness into account. The data presented in Fig. 1 and Table 1 show that the average values of WVTR, WVPN and WVP decrease with increasing fatty acid content of the film. This is mainly due to the hydrophobicity of fatty acids present in the film composition. It is notable that the decrease in transmission parameters is the most significant for films with SA. For example, even at the lowest SA content level studied, i.e. 5 g SA/100 g MC, the WVP of the film drops by about 40% compared to WVP of the film without fatty acid (Fig. 1). At the same level of LA or PA, the decrease in WVP is not that significant. On the other hand, WVTR and WVPN values of films with LA and PA drop considerably at this fatty acid content level (Table 1). This difference is probably a result of the film thickness factor considered only in WVP determination.

The WVTR and WVPN values of films with PA lie between those of films with LA and SA (Table 1). The same behaviour is observed for WVP values with the exception at 25 g/100 g MC fatty acid content where WVP of the film with PA goes slightly above that of the film with LA (Fig. 1). This must again be related to the thickness factor, since it was observed only in the WVP behaviour. Beside the irregularity observed at this particular point, at any fixed fatty acid content all three transmission parameters of films decrease, according to the type of fatty acid they contain, in the order of LA, PA and SA. This behaviour can be explained by the increase in hydrophobicity of fatty acid with increasing chain length in the order of LA (C_{12}), PA (C_{16}) and SA (C_{18}). Furthermore, the chain mobility of fatty acids, which helps transmission of water vapour, decreases in the same order.

SA, possessing the longest hydrocarbon chain, is the most hydrophobic and has the lowest chain mobility among the three fatty acids studied. Therefore, films with SA have the lowest water vapour transmission parameters. It should be noted that, in a recent work from this laboratory (Ayranci & Tunc, 1997), cellulose-based

Table 1
Composition, thickness, WVTR and WVPN values of edible films at 25°C

Fatty acid content (g fatty acid/100 g MC)	Thickness (10^5 m)	WVTR (g day^{-1} m^{-2})	WVPN (g day^{-1} m^{-2} Pa^{-1})
No fatty acid	1.57±0.05	520±20	0.19±0.01
LA 5	1.89±0.03	410±20	0.16±0.01
15	1.67±0.05	400±20	0.15±0.01
25	1.56±0.01	370±20	0.14±0.00
40	1.73±0.07	312±6	0.12±0.00
PA 5	2.0±0.1	390±60	0.15±0.02
15	1.75±0.05	370±50	0.14±0.02
25	1.2±0.2	310±60	0.12±0.02
40	1.98±0.04	161±8	0.06±0.00
SA 5	1.8±0.3	274±4	0.10±0.00
15	1.62±0.01	210±10	0.08±0.00
25	1.69±0.02	250±10	0.09±0.00
40	1.80±0.04	160±20	0.06±0.01

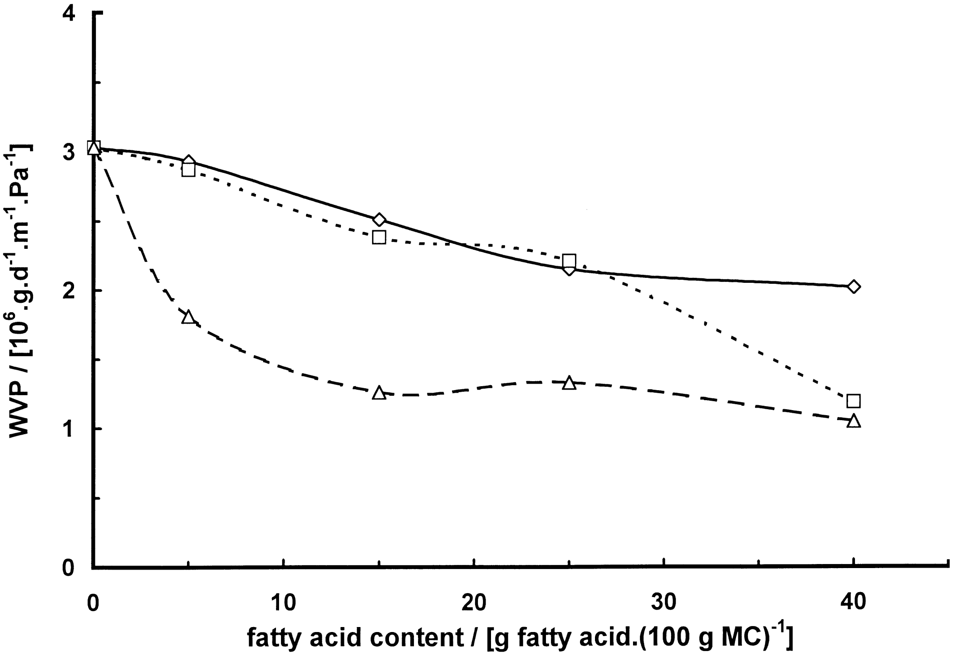

Fig. 1. WVP as a function of fatty acid content of edible film with LA (◇), PA (□) and SA (△).

edible films with SA were found to be more effective than those containing LA or PA in reducing the moisture loss when they were applied to fresh beans and strawberries.

3.2. Carbon dioxide transmission

CO_2TR and CO_2PN values of films with varying fatty acid contents are given in Table 2. The corresponding values for the film without any fatty acid and all the average film thickness values are also included in the table. The measurements were again made at least in duplicate and the average values, together with standard deviations, were recorded. Although the standard deviations are quite high for a few data points, it is believed that the general trends in transmission behaviour of films are still well demonstrated. All three CO_2 transmission parameters show similar trends when plotted as a function of fatty acid content. In order to show this graphically, the variation of CO_2P with fatty acid content is given in Fig. 2. It may again be recalled that CO_2P is probably the most informative transmission parameter as it takes both the CO_2 pressure difference between the two sides of the film and the film thickness into account.

It can be seen from Table 2 and Fig. 2 that LA behaves differently from the other two fatty acids in affecting CO_2 transmission of films. Films with LA have higher CO_2TR, CO_2PN and CO_2P than the film without fatty acid. This can be explained by the shorter hydrocarbon chain length of LA than that of PA and SA. This property makes attraction forces between LA molecules

Table 2
Composition, thickness, CO_2TR and CO_2PN values of edible films at 25°C and 2.1×10^4 Pa CO_2 pressure

Fatty acid content g fatty acid /100 g MC	Thickness (10^5 m)	CO_2TR (g day^{-1} m^{-2})	CO_2PN (10^3 g day^{-1} m^{-2} Pa^{-1})
No fatty acid	1.4±0.1	53±6	2.5±0.3
LA 5	1.6±0.0	62±6	2.9±0.3
15	1.5±0.1	71±5	3.4±0.2
25	1.5±0.0	69±21	3±1
40	1.7±0.1	65±20	3±1
PA 5	1.7±0.0	39.9±0.6	1.9±0.0
15	1.8±0.2	26±5	1.2±0.2
25	2.0±0.0	34±3	1.6±0.1
40	2.4±0.1	32±4	1.5±0.2
SA 5	1.4±0.1	30±5	1.4±0.3
15	1.4±0.0	15±1	0.7±0.1
25	1.7±0.2	15±1	0.7±0.1
40	1.3±0.0	15.1±0.5	0.7±0.2

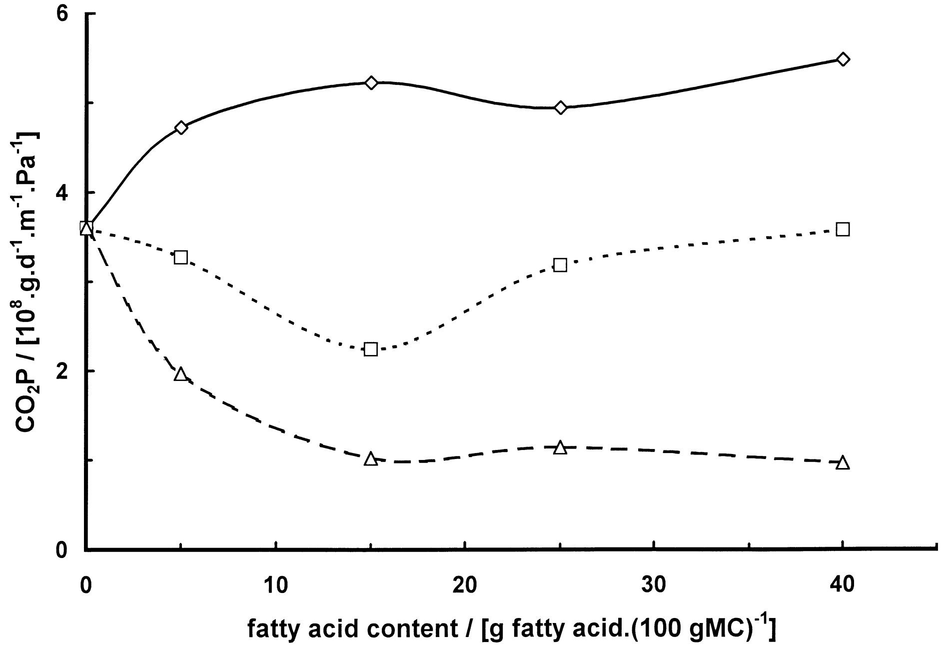

Fig. 2. CO_2P as a function of fatty acid content of edible film with LA (◇), PA (□) and SA (△).

weaker. Thus, CO_2 can permeate easily through the films containing LA. The greater chain mobility of LA may help facilitate this transmission process.

CO_2 transmission parameters for films containing PA and SA are lower than those for the film without fatty acid (Fig. 2 and Table 2). When PA and SA are compared with each other in lowering the CO_2 transmission of films, it can be seen that SA is more effective in this respect.

It can be concluded that, among the three fatty acids studied, SA is the most effective in reducing both the water vapour and the CO_2 transmissions of edible films. This reduction is steep up to 15 g SA/100 g MC level, after which transmission parameters seems to be little affected from the SA content.

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