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Oxygen permeability of amylose and amylopectin films

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Abstract

The effects of water and glycerol contents on oxygen permeability of starch polymer films were investigated. Starch films were prepared of amylose and amylopectin by a casting technique and oxygen permeability was analysed at 20°C. Glycerol contents were 0, 10, 20 or 30% while water content varied from 8 to 36%. Under ambient humidity both amylose and amylopectin films were excellent oxygen barriers, as good as the commercial ethylene vinyl alcohol film which was studied as a reference material. It was observed that the film permeabilities were determined by water content; below 15% water both starch films were good oxygen barriers, above 20% water the barrier property was lost. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Amylose; Amylopectin films; Permeability

1. Introduction

Starches may be used as barriers for food protection and preservation or as carriers of various components used in food processing. When acting as barriers the film formation property of starches can be utilised, and their mechanical properties can be controlled by addition of plasticisers such as glycerol. One of the advantages of using edible hydrophilic films like starches for food protection is their ability to act as oxygen barriers.

Early investigation on film formation properties of starches was focused on amylose and amylomaize starches. Mainly the mechanical properties of the films were examined but also some permeability experiments were performed. Amylose film was observed to have very low oxygen permeability under dry conditions at 25°C (Rankin, Wolff, Davis & Rist, 1958). Films prepared of amylomaize starch were investigated without and with glycerol under varying relative humidities (rh), stored at 5 and at 25°C (Mark, Roth, Mehltretter & Rist, 1966). Below rh 100% oxygen was not observed to permeate the film, and only a small difference was found between the unplasticised and the plasticised films. Gas permeabilities of potato starch films embedded with low-density polyethylene (LDPE) have been studied more recently (Sala & Tomka, 1993). At low rh, potato starch film showed similar oxygen barrier characteristics to synthetic hydrophilic barriers, but with increasing water content the good property was gradually lost. In another study the permeabilities of gases (oxygen, carbon dioxide and nitrogen) across films prepared of potato, rice and wheat starches were analysed over a wide temperature range (Arvanitoyannis, Kalichevsky & Blanshard, 1994; Arvanitoyannis, Psomiadou & Nakayama, 1996). Gas diffusion was observed to increase with increasing temperature and water contents. Effects of glycerol, sorbitol and sugars were also analysed and it was observed that gas diffusion increased with increasing polyol or sugar content. A recently reported study focused on film formation conditions of amylose and amylopectin (Rindlav-Wetsling, Stading, Hermansson & Gatenholm, 1998). The rh during film drying at 23°C was varied from 20 to 90% and was observed not to affect the oxygen permeability. As compared to the amylopectin film the oxygen transport was somewhat lower in the amylose film.

We have earlier investigated processing and properties of starch films produced by extrusion technique (Forssell, Hulleman, Myllärinen, Moates & Parker, 1999; Forssell, Mikkilä, Moates & Parker, 1997) and mechanical as well as structural behaviour of amylose and amylopectin films prepared by a casting method (Myllärinen, Lahtinen, Seppälä & Forssell, in preparation; Myllärinen, Buleon, Lahtinen & Forssell, in preparation). In order to gain better understanding of the dependence of oxygen permeability on the structure of starch polymers and on plasticisers, a study on oxygen transport across thin films prepared of amylose and amylopectin was conducted.

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2. Materials and methods

2.1. Materials

Amylose was commercial isolated potato amylose from Sigma (A-0512) and amylopectin was waxy maize starch from National Starch & Chemical (Amioca). Glycerol used as plasticiser was from Merck (1.04093.1000).

Synthetic films were commercial, polyamide from Biaxis Oy and polyethene-laminated ethylene vinyl alcohol from Åkerlund & Rausing Oy (Finland).

2.2. Film preparation

Amylose and amylopectin were solubilized with glycerol (0, 10, 20 and 30% of dry weight) in water by heating with mixing in a pressure chamber to 140°C. After cooling to 90°C, the 1 and 2% solutions of amylose and amylopectin, respectively, were cast in Teflon moulds and dried at 75°C until films were formed and could be removed from the moulds.

2.3. Oxygen transport

Oxygen mass transfer rates were analysed by Mocon OX-Tran2/20 (USA) using a standard method (ASTM 3985). Film samples were double masked with aluminium foil masks leaving a circular uncovered film area of 5 cm^2. On one side of the film 100% oxygen gas was flowing, and on the other side nitrogen gas (98% N_2 and 2% H_2). Nitrogen gas was conducted to the coulometric sensor, and measurements were obtained when the steady state was reached. The relative humidity of both gases was controlled by humidifier and varied from 50 to 90%. The permeability analysis was not performed below rh 50% because starch films were cracking. Measurements were conducted at 20°C. Prior to experiments the films were conditioned for one week at rh 50% and at 20°C, and in the measuring cells at the desired rh for 6–10 h at low rh and for 24 h at high rh. To get the oxygen permeability the oxygen mass transfer rate obtained from the instrument in cm^3/m^2 24 h was multiplied by the thickness of the film and divided by the pressure difference of oxygen (101 kPa).

2.4. Water content

Water contents of the films were approximated from the water vapour sorption isotherms determined earlier (Myllärinen, Lahtinen et al., in preparation; Myllärinen, Buleon et al., in preparation).

2.5. Glycerol content

Glycerol contents of the films were determined by Shimadzu UV-1601 (Japan) spectrophotometer with a glycerol determination kit from Boehringer Mannheim (148 270).

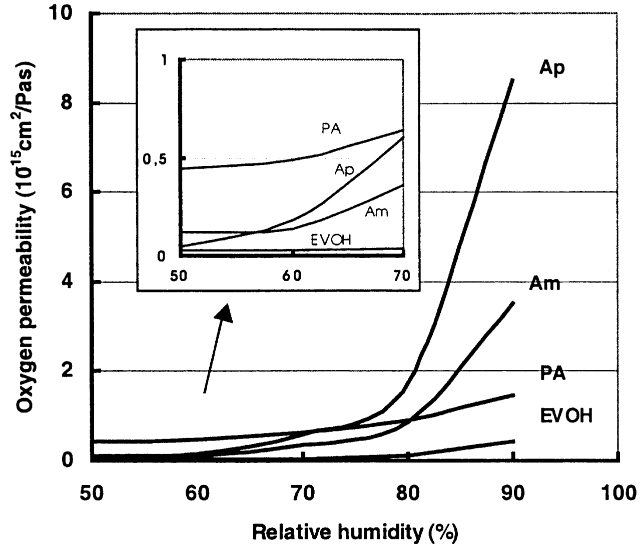

Fig. 1. Dependence of oxygen permeability on relative humidity at 20°C. Starch films made of amylose (AM) and amylopectin (AP) and the synthetic films ethylene vinyl alcohol (EVOH) and polyamide (PA).

3. Results and discussion

3.1. Comparison of starches with synthetic polymers

Analysis of oxygen permeability was first performed for starch films without glycerol. For comparison two commercial films, polyamide (PA) and ethylene vinyl alcohol (EVOH), the latter film laminated with polyethylene, were analysed under similar experimental conditions, which were applied for the starch films. Oxygen permeability was determined in the rh range from 50 to 90% and at 20°C. At ambient humidity both starch films were as good barriers as EVOH having permeabilities of about 10^{-16} cm^2/Pa s,

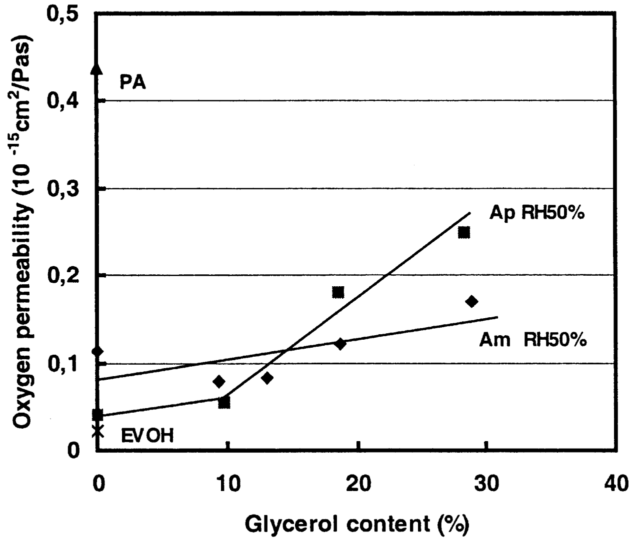

Fig. 2. Dependence of oxygen permeability on glycerol content at 20°C. Symbols are the same as in Fig. 1.

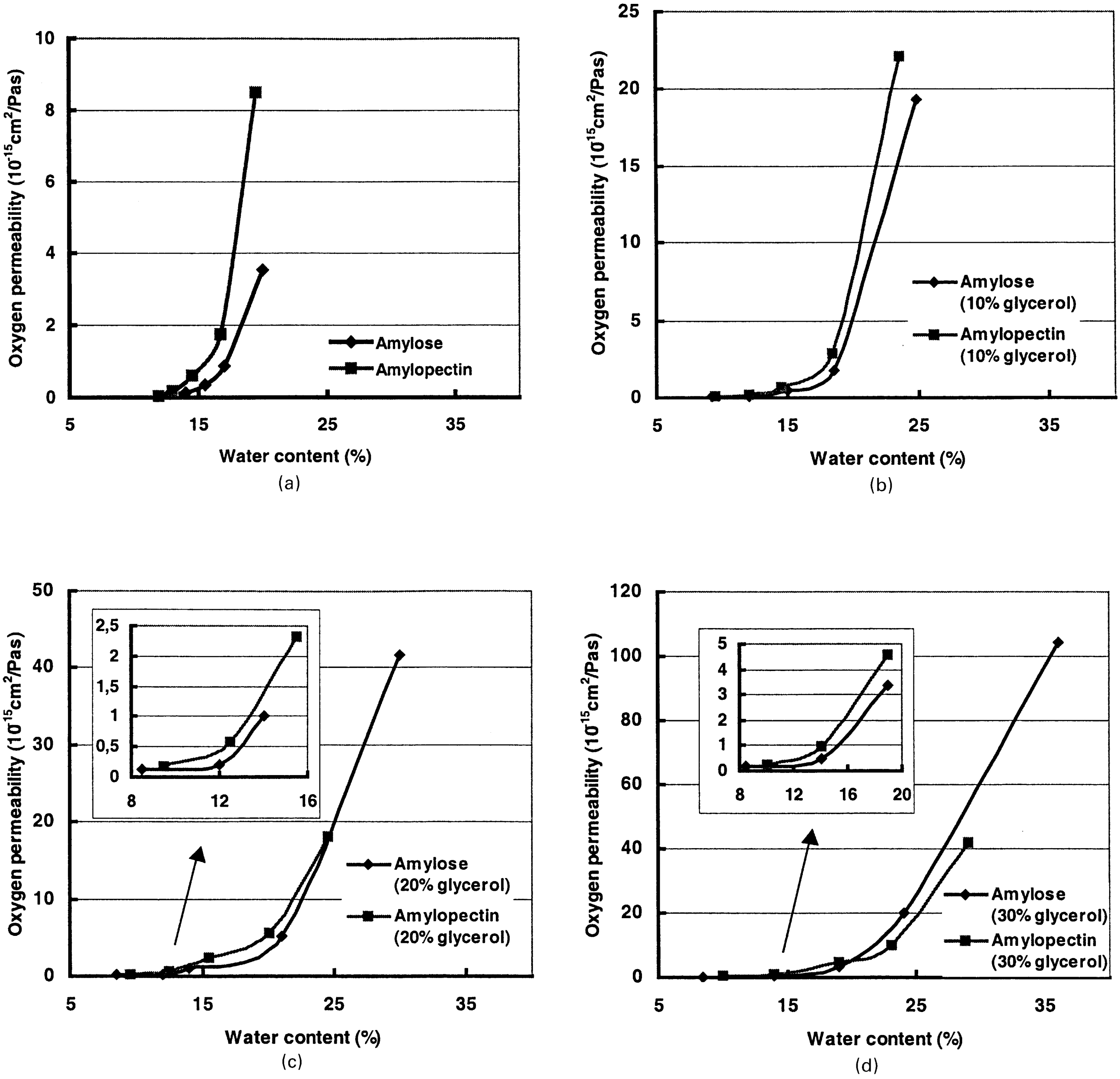

Fig. 3. Effect of water content on oxygen permeability of starch films at 20°C. Glycerol contents are (a) 0, (b) 10, (c) 20 and (d) 30%.

but at higher rh a difference was detected (Fig. 1). Above rh 70% permeabilities of the starch films started to increase, and at rh 90% both starch films were significantly more permeable to oxygen than the synthetic films. When comparing starch films with each other, the film prepared of amylopectin was more permeable at high humidities. Thus the environmental humidity affected more the behaviour of the starch films than that of the synthetic films.

3.2. Effect of starch structure, glycerol and water contents

The effect of glycerol content on the oxygen permeability of the starch films was examined at rh 50% and at 20°C. The changes observed under these conditions can be regarded to be due to variation in the glycerol content and starch polymer structure only because based on measured water sorption isotherms earlier the water contents of the starch films were independent of the glycerol content (Myllärinen, Lahtinen et al., in preparation; Myllärinen, Buleon et al., in preparation). The permeability of the amylopectin film increased with increasing glycerol content above 10% glycerol (Fig. 2). Permeability of the amylose film was practically independent of the glycerol content having a value of about 10^{-16} cm^2/Pa s. Without glycerol the film prepared of amylopectin was a better barrier but from the highly plasticised films the amylose film was less permeable. For comparison the measured permeabilities of the synthetic films are shown in the *y*-axis of Fig. 2. It can be concluded that at rh 50% and at 20°C starch films prepared of amylose or amylopectin were good oxygen barriers, non-plasticised films as good as EVOH, and that glycerol and starch polymer structure did not affect the permeability much.

Water drastically affected the oxygen transport, which was observed by measuring the permeabilities at different rh (50–90%). The analysed permeability was plotted as a function of the water content, which was taken from the earlier reported sorption isotherms for starch films (Myllärinen, Lahtinen et al., in preparation; Myllärinen, Buleon et al., in preparation). The overall behaviour of the amylose and amylopectin films was very similar (Fig. 3) and the main observation was that the films lost their barrier property entirely when the water content was above 20% (Fig. 4). Even if oxygen permeability increased with increasing water content, the films with water content below 15% were good oxygen barriers (permeability less than 10^{-5} cm^2/Pa s). Thus the films plasticised with a high amount of glycerol transported oxygen easily mainly due to their high water contents.

The oxygen permeabilities obtained in this study are in good agreement with the earlier reported results for starches. In a recent investigation plasticised amylose and amylopectin films having about 30% glycerol were studied, and oxygen permeability at rh 50% was measured (Rindlav-Wetsling et al., 1998). The observed permeabilities for amylose and amylopectin films were 7 and 14×10^{-16} cm^2/Pa s, respectively. These are close to our results, which for the highly plastised amylose and amylopectin films were 1.5 and 2.5×10^{-16} cm^2/Pa s, respectively (rh 50% and 20°C). Our results are also in agreement with non-plasticised cornstarch films examined earlier (Arvanitoyannis et al., 1996). However, as compared with our study the reported permeabilities for cornstarch films increased much more with increasing glycerol content.

When investigating the permeabilities shown in Fig. 3 in more detail at rh 90% it was noticed that the permeability of the amylose film increased with increasing glycerol content, but the amylopectin film with 20% glycerol was somewhat less permeable to oxygen than the film with 10% glycerol. Furthermore, the highly plasticised amylopectin films were less permeable to oxygen than the corresponding amylose films (rh 90%). In synthetic polymers increase in crystallinity usually means decrease in gas permeability (Rogers, 1985). The observed lower permeability in the amylopectin films in the present study may thus be explained by crystallisation, which could have occurred in the more plasticised amylopectin films. This assumption is, however, not wholly in agreement with the earlier reported studies concerning starch films, in which crystallisation either has decreased or has not at all affected the oxygen permeability (Arvanitoyannis et al., 1996; Rindlav-Wetsling et al., 1998). When comparing the oxygen permeabilities of starch films with those of other biopolymer films such as whey proteins, the permeabilities are close to each other. The protein films were plasticised with glycerol and sorbitol and the reported permeabilities analysed at rh 50% and at 23°C were changing from 1 to 88×10^{-16} cm^2/Pa s (Chen, 1995). Water and glycerol were also shown to affect the permeability of whey protein and wheat gluten films similarly as demonstrated in this study for the starch films, but a more detailed comparison is difficult because results were plotted against rh and not against water content (Gontard, Thibault, Cuq & Guilbert, 1996; McHugh & Krochta, 1994).

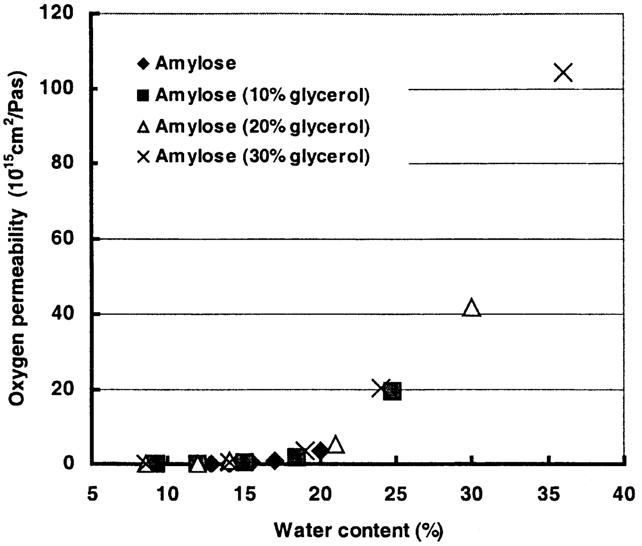

Fig. 4. Effect of water content on oxygen permeability of amylose films with different glycerol contents. Same data as in Fig. 3 for the amylose film but plotted in another way.

All hydrophilic polymer films such as EVOH lose their gas barrier property when stored under high humidity (Iwanami & Hirai, 1983). This was also the case for starch films examined in the present study. In order to permeate a film, oxygen has to dissolve into the film material and to diffuse across the film (Rogers, 1985). Under high humidities the starch films contained enough water so that part of it was able to freeze near 0°C (Myllärinen, Lahtinen et al., in preparation; Myllärinen, Buleon et al., in preparation). Water is also known to plasticise starch polymers. Thus both the solubility of oxygen may have been increased and the diffusion process may have been facilitated by the more mobile polymer chains. Permeabilities were very similar for both amylose and amylopectin, which indicated that the differences in the amylose and amylopectin film structures (Myllärinen, Lahtinen et al., in preparation; Myllärinen, Buleon et al., in preparation) did not affect oxygen permeability.

4. Conclusions

Oxygen permeability of the glycerol-plasticised starch films at constant temperature depended on the water content of the film. If the water content was below 15% the films were good oxygen barriers, but when the water content rose above 20% the barrier property was lost. The increase in the permeability occurred most likely because of increase in the polymer chain mobility, which facilitated the transport process. Structures of the starch polymers did not affect the oxygen transport indicating the very similar chemical nature of the starchy polymers, and perhaps their similar interactions with water. Both starch polymers plasticised with water only were very good oxygen barriers, under ambient humidity as good as EVOH. The obtained results support also a suggestion that under dry conditions, oxygen permeability of glycerol-plasticised starch films are really low.

Acknowledgements

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