

## Notes

### ***Directional Permeability of Asymmetrically Oxidized Poly(L-methionine) Film to Oxygen Dissolved in Water***

#### **Synopsis**

The permeability of an asymmetrically oxidized poly(L-methionine) film to oxygen dissolved in water was examined. It was recognized that the permeability along an increasing gradient of oxidized methionine composition is higher than when the gradient is reversed. A qualitative analysis of this result was presented in terms of the oxygen solubilities into the film and water absorbed in the film.

Permeation of oxygen dissolved in water through synthetic polypeptide films is of special interest because of its importance as a biomedical material for contact lenses, artificial lungs,<sup>1</sup> and skin.<sup>2,3</sup> It has been reported that water in a polypeptide film affects greatly the permeability of the film to dissolved oxygen.<sup>4</sup> This is interpreted in terms of a plasticizing effect of water which increases a diffusion rate of oxygen. We studied the effect of oxidation of L-methionine containing copolypeptide films on the permeability to dissolved oxygen<sup>3</sup>: The oxidation introduces hydrophilic sulfoxide and/or sulfone groups into the film and the permeability increases according to the extent of the oxidation.

An asymmetrically oxidized poly(L-methionine) film, which is prepared by contacting only one side of the film to an aqueous hydrogen peroxide solution, has a relatively more hydrophilic surface on the oxidized side and less hydrophilic one on the other side; according to our previous studies,<sup>3,5</sup> the film is not a two-layered film consisting of a surface layer of oxidized methionine at the treated side and a layer of methionine at the other side, but a film with a decreasing composition gradient of oxidized methionine across the film. If the permeability of such films to a small molecule will be examined, one must take directional permeation behavior<sup>6</sup> into account. In fact, when the treated side of the asymmetrically oxidized film faces water vapor there is a higher flux of water than when the untreated side faces water vapor.<sup>5</sup>

In this report, we try to examine the permeability of the asymmetrically oxidized poly(L-methionine) film to oxygen dissolved in water.

Details of the preparation and characterization of poly(L-methionine) (PLM) were described elsewhere.<sup>3</sup> The oxidation was carried out at 20°C using a 30% H<sub>2</sub>O<sub>2</sub> aq solution. Only one side of a film was kept in contact with the H<sub>2</sub>O<sub>2</sub> solution.<sup>3,5</sup> The procedure of the permeation experiment was an oxygen electrode method cited in the literature.<sup>3</sup>

Table I shows the permeabilities in the temperature range of 5–40°C when the film was oxidized for 3 and 5 min. It is clear for both films oxidized for different time that the permeability when the untreated side is exposed to oxygen is higher than when the treated side is exposed. This phenomenon is opposite to that for water permeation through the similar film.<sup>5</sup>

TABLE I  
Permeability of Asymmetrically Oxidized Poly(L-Methionine) Film to Oxygen Dissolved in Water at Several Temperatures (10<sup>10</sup>cm<sup>3</sup>(S.T.P.)·cm/cm<sup>2</sup>·s·cm Hg)

Oxidation time	Side exposed to oxygen	Temperature (°C)							
		5	10	15	20	25	30	35	40
5	Treated	0.56	0.60	0.80	0.97	1.1	1.4	1.6	—
5	Untreated	0.78	0.88	0.90	1.2	1.3	1.6	1.7	—
3	Treated	—	0.50	0.63	0.69	0.96	1.2	—	1.6
3	Untreated	—	0.62	0.66	0.78	0.99	1.2	—	1.7

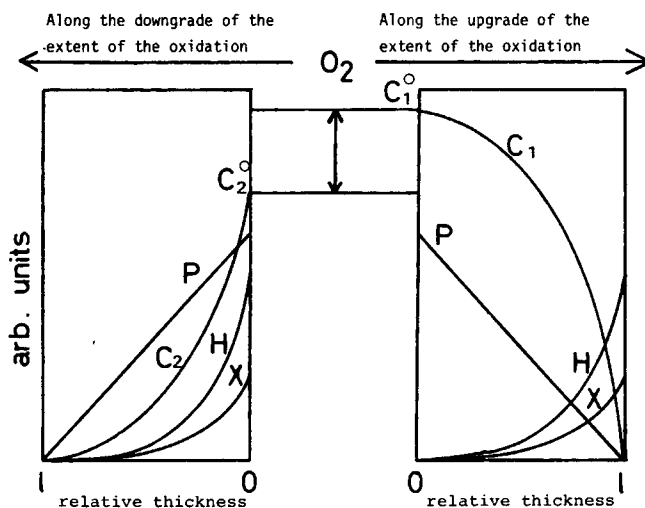


Fig. 1. Extent of oxidation ( $X$ ), degree of hydration ( $H$ ), oxygen partial pressure ( $P$ ), and oxygen concentrations ( $C_1$  and  $C_2$ ) vs. relative thickness.

In the case of water permeation, since the permeability coefficient is the product of the solubility and diffusion coefficient and the slight differences in diffusion coefficient for both flow directions due to slightly different chemical structures and the degree of hydration across the film are too small to affect the overall behavior, water solubility into the film is a main factor, and the solubility into the oxidized side is higher than that into the unoxidized side, as one can expect.

For the oxygen permeation, the differences in diffusion coefficients for both directions are assumed to be neglected as well as the above. However, the solubility coefficients at any point in the film are changing according to the extent of the oxidation and the hydration. Figure 1 shows a qualitative illustration for the changes of the extent of the oxidation ( $X$ ), the degree of the hydration ( $H$ ), oxygen partial pressure ( $P$ ), and oxygen concentration ( $C$ ) across the film. The oxygen concentrations in the film for two systems, that is, along the upgrade and downgrade of the hydration, are drawn in Figure 1 as  $C_1$  and  $C_2$ , respectively.  $C$  across the film is a function of  $P$  and the solubilities into PLM, oxidized PLM, and water. The solubility coefficient of oxygen into a PLM film in the dry state was reported as  $0.060 \text{ cm}^3(\text{S.T.P.})/\text{cm}^3\text{-cm Hg}$  at  $25^\circ\text{C}$  by Hirota et al.<sup>7</sup> and that into water is  $0.00037$  at  $25^\circ\text{C}$ .<sup>8</sup> Since the solubility into a oxidized PLM film is similar to that of a PLM film,  $C_1$  and  $C_2$  are greatly affected by the hydration: The more the hydration, the lower the concentration is.  $H$  of a PLM film is very low (below 2%),<sup>3,4</sup> and the oxygen concentration at the unoxidized surface, indicated as  $C_1^\circ$  in Figure 1, is assumed not to be so different from that in a PLM in the dry state.

In contrast with the above, the value of  $C_2^\circ$ , the oxygen concentration at the oxidized side, can be estimated to be below  $C_1^\circ$ . Therefore, the oxygen permeability along the upgrade of the extent of the oxidation is higher than along the downgrade.

A few reports<sup>9</sup> described that transport of low molecular weight vapors through a film with a gradient of structural composition from one surface to the another proceeded at a higher rate along the downgrade of a structure introduced than along the upgrade when the structure had an affinity for the vapors. In our case, however, the third component, water, has a great influence on the oxygen permeation. Then the permeation is peculiar, and higher permeation along the upgrade is observed.

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