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An Investigation of Microstructural Characteristics of Contact-Lens Polymers

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Abstract

The free volume and gas permeability in several contact-lens samples have been measured as part of a space commercialization program. Free volume was measured by using positron lifetime spectroscopy, while permeability for O_2, N_2, and CO_2 gases was measured by using mass spectrometry and polarography. Permeability for all gases increases with the mean free-volume cell size in the test samples. As might be expected, the samples with the highest free-volume fraction also exhibit the lowest Rockwell hardness number. An interesting corollary of this study is the finding that the presence of fluorine atoms in the lens chemical structure inhibits the filling up of the free-volume cells. This is expected to allow the lenses to breathe freely while in actual use.

Introduction

Contact lenses are widely used by a large segment of the U.S. population, particularly the younger generation. Primary qualifications of a good contact-lens polymer are softness, wettability, and high permeability for water and for N_2, O_2, and CO_2 gases. The ability to develop good contact-lens materials demands an understanding of the relationships between the chemical structures of the polymers and their gas permeabilities and other physical properties.

Careful studies of gas transport in polymers below their glass transition temperatures (ref. 1) indicate that the usual Henry's law has to be modified as follows:

$$C = K_D p + C_H \left(\frac{bp}{1 + bp} \right) \tag{1a}$$

where

C	concentration of penetrant gas dissolved in polymer, $\frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3 \text{ polymer}}$
K_D	solubility coefficient for penetrant gas, $\frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3 \text{ polymer} \cdot \text{atm}}$
p	gas pressure at solution equilibrium, atm
C_H	Langmuir mode concentration of sorbed gas or gas population in microvoids, $\frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3 \text{ polymer}}$
b	gas affinity parameter, atm^{-1}

The first term in equation (1a) represents the usual Henry mode of sorption in solids. The second term is attributed to sorption in microvoids normally present in all glassy polymers. This modified form of Henry's law is known as the dual sorption model, because there are two different modes of sorption in the glassy polymers. Equation (1a) can be simplified as follows:

$$\left. \begin{aligned} C &= K_D p + C_H bp \qquad (bp << 1) \\ &= (K_D + C_H b)p \\ &= K'_D p \end{aligned} \right\} \tag{1b}$$

Similarly, the generalized form of Fick's law in glassy polymers (ref. 2) takes the following form:

$$N = -D_D \frac{dC_D}{dx} - D_H \frac{dC_H}{dx} \tag{2a}$$

where

N	rate of gas transfer per unit area
D_D	Fick's diffusion coefficient
C_D	Henry's concentration of sorbed gas
D_H	diffusion coefficient for gas trapped in microvoids ($D_H < D_D$)
C_H	gas population in microvoids ($C_H < C_D$)

Equation (2a) can be simplified as follows:

$$\left. \begin{aligned} N &= -D'_D \frac{d}{dx}(C_D + C_H) \\ &= -D'_D \frac{dC'}{dx} \end{aligned} \right\} \tag{2b}$$

The molecules sorbed by the Henry's law mode and the Langmuir mechanism are in equilibrium with each other. The Langmuir molecules have less diffusional mobility than the Henry molecules. Since permeability P is the product of the solubility coefficient K_D and the diffusion coefficient D, it is expected that P in glassy polymers will change with the free volumes. We have measured free volumes in several contact-lens samples using positron annihilation spectroscopy. (See ref. 3.) We have also measured permeabilities for O_2, N_2, and CO_2 gases in these samples. The results and their interpretations are discussed in this paper.

Symbols

b	gas affinity parameter, atm^{-1}
C	concentration of penetrant gas dissolved in polymer, $\frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3 \text{ polymer}}$

C_D Henry's concentration of sorbed gas

C_H Langmuir mode concentration of sorbed gas or gas population in microvoids, $\frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3 \text{ polymer}}$

C_S structural constant

D diffusion coefficient

D_D Fick's diffusion coefficient

D_H diffusion coefficient for gas trapped in microvoids, $D_H < D_D$

f free-volume fraction, percent

I_3 relative intensity of longest component lifetime, percent

K_D solubility coefficient for penetrant gas, $\frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3 \text{ polymer} \cdot \text{atm}}$

N rate of gas transfer per unit area

P permeability $(K_D D)$, $\left[\frac{\text{cm}^3 \text{ (test gas at STP)}}{\text{cm}^3 \text{ polymer} \cdot \text{mm Hg}} \frac{\text{cm}^2}{\text{sec}}\right] \times 10^{-11}$

p gas pressure at solution equilibrium, atm

R microvoid radius, nm

R_0 $R + 0.1656$, nm

V_f microvoid volume or free-volume, A^3

v/o saturation moisture content by volume percent

w/o saturation moisture content by weight percent

α Rockwell hardness number

τ_3 longest component lifetime

Experimental Procedures

Contact-Lens Samples

The test samples were copolymers of silicone methacrylate and methyl methacrylate monomers crosslinked by a difunctional monomer. Their physical properties are summarized in table I. The last two columns list the respective saturation moisture content by weight percent (w/o) and volume percent (v/o). These values were obtained by immersing the samples in distilled water at 80°C till their weight became constant. The first three samples had increasing amounts of silicone methacrylate monomer but no fluorine. The last three samples had increasing amounts of silicone methacrylate as well as fluorinated acrylate monomers. These samples were provided by Paragon Optical. The samples for gas permeability measurements were fabricated to match the commercial contact-lens geometry. Mass spectrometry and polarography were both used to measure gas permeabilities in these samples. (See ref. 4.)

Positron Lifetime Measurements

Positron lifetime measurements were made by using a standard fast-fast coincidence measurement technique. Samples for positron annihilation spectroscopy (PAS) measurements were obtained in the form of 1-cm-diameter rods from which 2-mm-thick discs were cut for positron lifetime measurements. A 50-μC Na^{22} positron source was sandwiched between the test discs, and the spectra were accumulated for 6 to 8 hours. This counting time produced total counts of about 2×10^6 in each spectrum. The time resolution of the lifetime system was 250 psec. Figure 1 shows a typical lifetime spectrum in contact-lens samples. The lifetime spectra were analyzed using the computer program (ref. 5) for analyzing positron lifetime spectra (PAPLS) and the POSFIT-EXTENDED program (ref. 6).

Experimental Results

The permeability measurements for O_2, N_2, and CO_2 gases in various test samples were measured at 21°C and 35°C. The results obtained by mass spectrometry are summarized in table II.

The positron lifetime spectra were analyzed into three components, from 0.2 to 5.0 nsec, for each sample. The results are summarized in table III. Only the longest component lifetimes τ_3 and their relative intensity values I_3 are listed, since only the orthopositronium quench rates relate directly to the free-volume cell sizes (ref. 7), as seen from the following equation:

$$\frac{1}{2\tau_3} = 1 - \frac{R}{R_0} + \frac{1}{2\pi}\left(\sin\frac{2\pi R}{R_0}\right) \tag{3}$$

where

τ_3 longest component lifetime, nsec

R microvoid radius, nm

R_0 $(R + 0.1656)$, nm

The microvoid volume is given by $\frac{4}{3}\pi R^3$.

The free-volume fraction f can be calculated as follows:

$$f = C_S I_3 V_f \tag{4}$$

where

C_S	structural constant
I_3	intensity of longest component lifetime, percent
V_f	microvoid volume

The structural constant has been calculated by equating saturation moisture content in volume percent of Paraperm 02 sample with its free-volume fraction, that is,

$$\left.\begin{aligned} C_S(27.8)132 &= 1.71 \\ C_S &= 4.66 \times 10^{-4} \end{aligned}\right\} \quad (5)$$

The free-volume fraction in the remaining contact-lens samples has been calculated by assuming that the value of the structural constant C_S is the same for all the samples.

From the data summarized in tables II and III, it is evident that permeability values and the free-volume cell sizes in the test samples are strongly interrelated. This, of course, is not surprising in view of the arguments supporting equations (1a) and (2a). The results for oxygen are illustrated in figure 2. Even though the presence of microvoids affects both the solubility coefficient K_D and the diffusion coefficient D, the latter coefficient is more directly affected. A comparison of the data summarized in tables I and III brings out an interesting feature. If we look at the ratio of free-volume fraction to saturation moisture content, it increases from 1.0 to 2.7 as we go from sample 1 to sample 6. This result is quite consistent with the chemical structure of the strongly cross-linked silicone acrylate copolymers. The silicone content increased in samples 1 to 6, but samples 4 to 6 also had increasing amounts of fluoroacrylates. Thus, while sample 1 had no fluorine, the fluorine content of sample 6 was reasonably high (approximately 7 percent by weight). The presence of fluorine in one of the monomers making up the contact lens apparently interferes with the entry of moisture into the free-volume cells. (See ref. 3.)

The Rockwell hardness numbers (ref. 8) of the contact-lens samples were also measured. The results are summarized in table IV and are illustrated in figure 3. It is apparent that α decreases linearly with increased free-volume fraction. As expected, sample 6, which has the highest free-volume fraction, also has the lowest Rockwell hardness number.

Concluding Remarks

The following conclusions can be drawn from the results presented herein:

1. The free-volume fraction in contact-lens samples containing fluorine atoms is the highest, but they pick up the least amount of moisture. This implies that the free-volume cells in these samples, which play an important role in gas and vapor transport through the contact lens, will not be flooded with the eye fluids when in use. This process will facilitate "breathing" by, as well as cleansing of, the lenses during use.
2. The fluorine-containing lens samples are the softest, as would be anticipated on the basis of their high free-volume fraction.
3. The permeability of the lens samples increases with the free-volume cell sizes. This increase confirms the validity of the dual sorption model in glassy polymers below their transition temperatures.

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Table I. Summary of Contact-Lens Sample Properties

Sample	Description	Density, g/cm^3	Refractive index	Saturation moisture content, percent by— Weight	Volume
1	Paraperm 02	1.12	1.480	1.55	1.71
2	Paraperm 02^+	1.09	1.475	1.69	1.81
3	Paraperm EW	1.07	1.475	1.40	1.48
4	Fluoroperm 30	1.14	1.475	1.12	1.26
5	Fluoroperm 60	1.15	1.473	0.86	0.98
6	Fluoroperm 90	1.10	1.471	0.87	0.95

Table II. Permeability of O_2, N_2, and CO_2 Gases in Contact-Lens Samples

Sample	Permeability, P, of test gas at— 21°C O_2	21°C N_2	21°C CO_2	35°C O_2	35°C N_2	35°C CO_2
1	15.8 ± 0.9	9.3 ± 0.6	95.0 ± 3.6	32.8 ± 2.2	17.9 ± 2.3	129.0 ± 3.2
2	31.4 ± 1.1	10.3 ± 1.8	257.5 ± 2.8	64.6 ± 3.1	31.5 ± 1.7	272.0 ± 4.6
3	45.3 ± 0.9	15.5 ± 1.1	348.5 ± 6.8	76.9 ± 1.6	37.0 ± 2.3	414.5 ± 6.0
4	40.2 ± 2.0	(*a*)	(*a*)	41.4 ± 2.0	(*a*)	(*a*)
5	60.0 ± 2.0	(*a*)	(*a*)	63.4 ± 2.0	(*a*)	(*a*)
6	68.3 ± 1.1	32.0 ± 1.0	498.5 ± 7.2	109.0 ± 1.1	55.2 ± 2.6	561.5 ± 14.6

[a] Only O_2 permeability data are available.

Table III. Summary of Positron Lifetime Results in Contact-Lens Samples

Sample	Positron component parameters		V_f, A^3	Free-volume fraction, f, percent
	Lifetime, τ_3, psec	Intensity, I_3, percent		
1	2364 ± 16	27.8	132	1.71
2	2477 ± 18	30.0	144	2.01
3	2583 ± 20	27.8	155	2.01
4	2586 ± 17	28.7	155	2.07
5	2711 ± 17	29.8	169	2.34
6	2795 ± 24	30.5	178	2.53

Table IV. Summary of Free-Volume Fraction and Rockwell Hardness Numbers for Contact-Lens Samples

Sample	Free-volume fraction, f, percent	Rockwell hardness number,[a] α
1	1.71	107.5 ± 0.8
2	2.01	(b)
3	2.01	93.3 ± 1.0
4	2.07	99.0 ± .5
5	2.34	90.6 ± .5
6	2.53	79.5 ± 1.4

[a]Scale: L
Indenter diameter: 6.3500 ± 0.0025 mm
Minor load: 10 kg
Major load: 60 kg
[b]Sample 2 was not available in appropriate size for hardness testing.

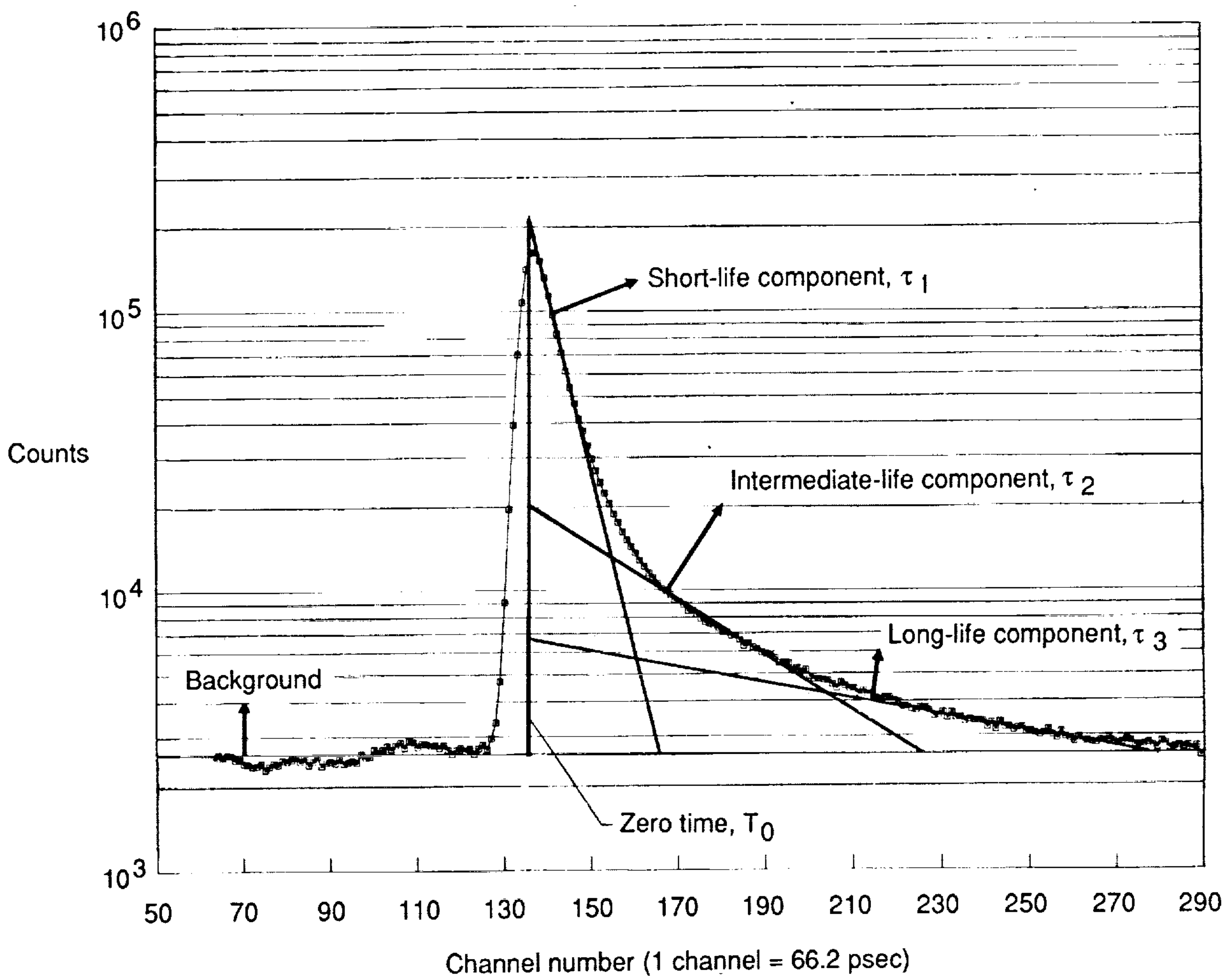

Figure 1. Typical spectrum in polyacrylate polymers.

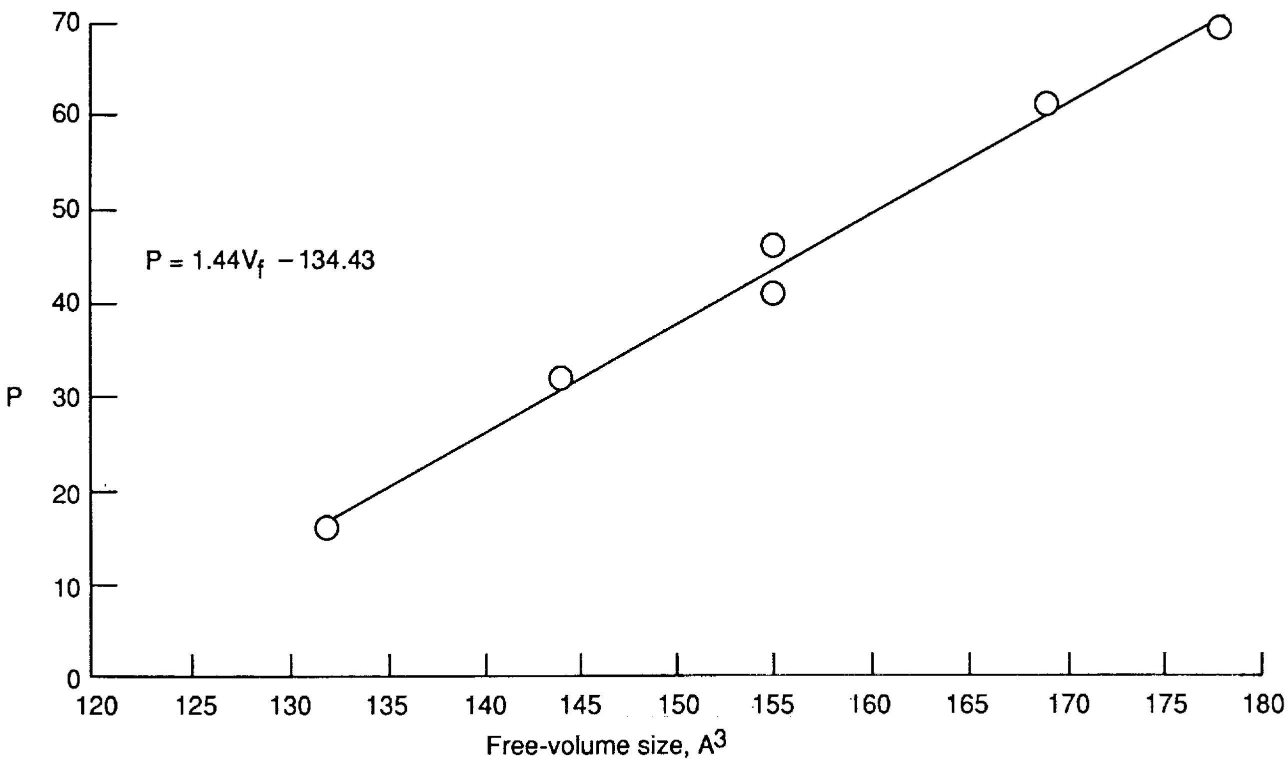

Figure 2. Permeability of O_2 versus free-volume size.

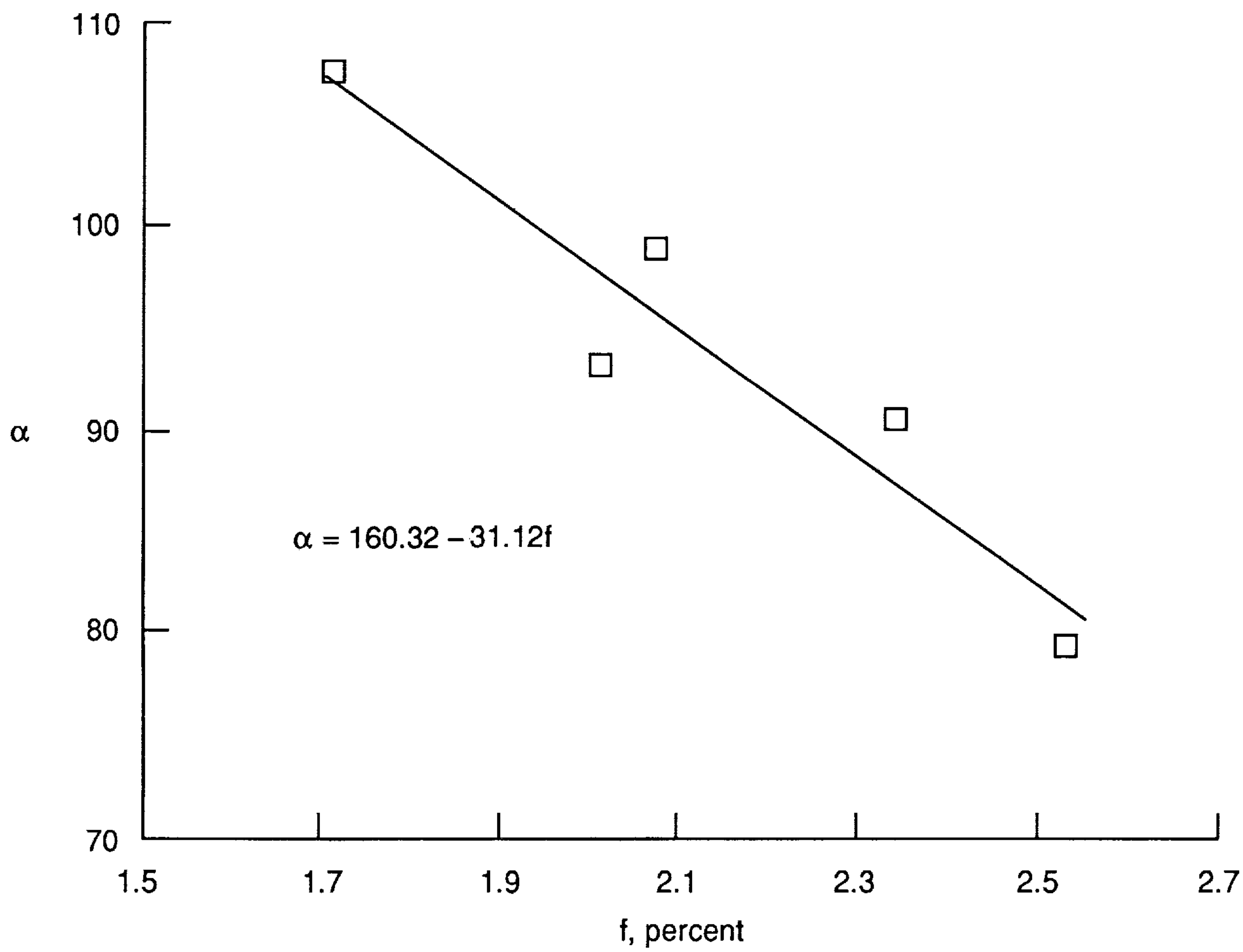

Figure 3. Rockwell hardness number versus free-volume fraction.

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15. Supplementary Notes

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