Spoliation of Fluoroperm Rigid Gas Permeable Contact Lens by Sodium Chloride: A Positron Annihilation Study

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ABSTRACT: The interaction of sodium chloride with Fluoroperm92 contact lens has been investigated using several techniques. Results indicate adhesion of sodium chloride to the methacrylate and fluorine sites of the lens resulting to zones of excess salt concentration. Na^+ and Cl^- ions appear to be pushed toward the polymer by water molecules, which favor the bulk water structures. Further inference is that lens with more free water leads to localized spots of drying resulting to sites for lipid deposition and lens spoilage. The changes in refractive index of the lens due to salt adhesion correlate well with the free volume. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 112: 372–380, 2009

Key words: rigid gas permeable lens; sodium chloride; free volume; positron lifetime; refractive index

INTRODUCTION

The use of biomaterials within the body as replacement prostheses has seen a rapid rise over the recent years. The biocompatibility of the given material depends on many factors, related to both the host and implanted material. To date, the biomaterial to receive the greatest clinical exposure is the contact lens material. Although soft contact lenses are very common now-a-days, rigid gas permeable (RGP) lenses still continue to be a valuable lens wear option for a large number of patients. One of the greatest benefits of RGPs is their stellar optical quality. RGPs are the lens of choice for irregular corneas, keratoconus, and many postsurgical cases. Even though the availability and stability of soft toric lenses have grown dramatically, RGPs are still preferred lenses for correcting astigmatism.

One of the major problems of the contact lenses is that they are susceptible to spoilage from constituents of the tear film, which include a wide variety of proteins, lipids, glucose, mucins, and mineral salts.[1,2] At extreme levels of build-up, these deposits are associated with diminished visual acuity[3] and a feeling of dryness and discomfort.[4] Deposits can ultimately lead to more serious clinical conditions such as hypersensitivity reactions and giant papillary conjunctivitis.[5] Moreover, these deposits potentially increase the risk of bacterial attachment through wide range of interactions and competitive processes. The adsorption of tear derived substances at the contact lens surface is the overall result of various types of interactions between different components present, that is, the chemical composition, surface charge, nature of the medium (tears), specially sodium chloride, and many other solutes present in tears.[6] However, the relative importance of the different components of deposited films to these clinical effects remains largely unknown.

Spoliation of contact lenses, being one of the major clinical problems, has been extensively investigated over the past 3 decades. Bontempo and Rapp[7] examined rigid gas permeable (RGP) lenses and found that these materials generally deposit more lipid than many soft lens materials. When RGP lenses were further examined for lipid and protein interactions on the lens surface, different interactions were found.[7] There is an interesting study by Cowell et al.[8] who observed an increase in adhesion of salt with increase in sodium chloride concentration. Although it is generally agreed that the spoliation of contact lenses must be a result of interaction between polymers and primary tear components, the involvement of the these inorganic ions of tear, in the initial stages of the deposit formation has never been satisfactorily explained. In this study, with an interest to understand the interaction of sodium chloride, which contributes to salinity of tears, with that of an RGP lens, has been undertaken through sorption study of sodium chloride in Fluoroperm92 (FP92), an RGP contact lens material. FP is an

important semisoft contact lens material, whose chemical name is *Fluorosilicone acrylate*. It has silicone methacrylate as well as fluorinated acrylate monomer. It is known that sodium chloride or other deposits like lipids, protein are associated with the loss of optical transparency of these lens materials. The particular optical property of interest of lenses is the refractive index, which is related to the polarizability of the lens material. Therefore, understanding the interaction of sodium chloride tear component at the molecular level with regard to how it influences this optical property becomes foremost important in the design and application of contact lens materials. The important aspect of this study is that an attempt has been made to connect the interaction described above in terms of the nanosized free volume holes present in the lens material to loss of optical transparency. The free volume holes are open spaces evolved because of molecular architecture and chain arrangement and are characterized as low electron density regions, existing mainly in the amorphous domains of the polymer system.[9] The free volume as a material parameter has been successfully used in explaining several of the polymer properties.[9,10] To enunciate the versatility of this method, we mention only a few of the interesting studies carried out using this technique: structural relaxation of polyethylene teraphthalate and polycarbonate,[11–13] permeability of gases, water and solute in polymers,[14–17] polymers containing silver nanoparticles,[18] ageing studies on polymers[10] etc. For the transport of small molecules, the free volume holes serve as pathways for diffusion. One of the most versatile experimental methods used by many researchers to measure this nanometer sized free volume cavities and their content in a polymer is undoubtedly positron lifetime spectroscopy (PLS). We have used this novel technique to explore the possible interaction of sodium chloride solute with FP92 contact lens biopolymer, by monitoring the changes in its free volume size and number density as NaCl being diffused into the system. Further, to know how the sodium chloride influences the nature of water in the lens material, we have made a comparative study of water sorption in the same sample. Sorption kinetics of water and sodium chloride was carried out by the standard gravimetric method. To supplement positron results, energy dispersive X-ray spectroscopy (EDS) for elemental analysis was carried out.

The orientation of molecules or groups of atoms within the molecule influences the polarizability of the molecule and a change in molecular orientation in turn influences the *o*-Ps lifetime. Story[19] suggested that the *o*-Ps lifetimes in a number of plastic materials may be correlated with their dielectric constants. Later, Gray et al.[20] succeeded in theoretically correlating the quenching cross section of ortho positronium (*o*-Ps) in *n*-alkanes with electron polarizability of the molecule. There are studies directly correlating polarizability with density and other such physical parameters through Lorenz-Lorentz equation,[21] but no attempt was made to correlate free volume and polarizability of the medium, particularly in case of contact lens polymers. For this, we have made use of long arm spectrometer of Brewster's angle method to measure the changes in refractive index in the lens material on sodium chloride sorption. The molar refraction was calculated from refractive index using Lorenz-Lorentz equation to correlate the *o*-Ps quenching cross section, deduced from experimentally measured *o*-Ps lifetime. This would provide some insight into the influence of free volume on refractive index of the lens material especially for the sodium chloride sorbed one.

MATERIALS AND METHODS

Sample details

Fluoroperm92 contact lens samples manufactured from Paragon Vision Sciences were procured commercially for this work. FP92 has a specific gravity of 1.1, refractive index of 1.453, glass transition temperature T_g of 110°C, and light transmittance of ~ 95%. "92" refers to its oxygen permeability or Dk. For sorption and positron lifetime measurements, samples of size 1.1-mm thick and 15-mm diameter circular discs with smooth surface were used.

Sorption measurements

Prior to each sorption measurement, the samples were dried for several hours in a vacuum oven at 90°C. The dry weight of the sample was recorded on a Sartorius Basic BA110 S digital balance, (German make), with a precision of ± 0.1 mg. The samples were then soaked in sodium chloride solution of $0.5M$ for a known interval of sorption time. After this, they were removed from the solution, blotted to remove excess moisture and salt from the surface, and weighed again. The samples were then used in the positron lifetime measurements. The sorption experiment was continued until the weight gain reached a constant value, which was taken as the equilibrium mass uptake. A similar procedure was followed for sorption of distilled water in the same sample.[17]

Positron lifetime measurements

Positron lifetime measurements were carried out using a standard fast–fast coincidence system with conically shaped BaF_2 scintillators, coupled to photomultiplier tubes of type XP2020/Q with quartz window as detectors. The coincidence lifetime

spectrometer has a time resolution of 220 ps. All measurements were made at room temperature. The source-sample geometry was used for positron lifetime measurements. Typical spectrum accumulation time was 2 h with a 17 μCi Na^{22} positron source, which provided good counting statistics with more than 10^6 counts under each spectrum. The instrumental time resolution and source correction terms were obtained from the lifetime spectrum of well-annealed aluminum, using the program RESOLUTION.[22] The lifetime spectra so acquired were analyzed into three lifetime components using PATFIT-88 computer program,[22] resulting in better χ^2 values and standard deviations.

Energy dispersive X-ray spectroscopic measurements

To identify the elemental composition, the lens sample soaked in sodium chloride solution for more than 2 days was air dried before subjected to EDS measurements. Virgin sample was also subjected to EDS study in the same way. The EDS measurements for the samples were done using the LEICA S 440I scanning electron microscope equipped with an Oxford EDX attachment.

Refractive index measurements

The refractive index of the lens material at different time intervals of sodium chloride sorption was measured by Brewster's angle method. Helium-Neon red laser of wavelength 632.8 nm was used as the source. Several trials of measurements were carried with an accuracy of 0.001 and the average values reported.

RESULTS

Sorption results

To understand the sorption mechanism, we have invoked Fick's second law of diffusion,[23]

$$\frac{\delta C_d}{\delta t} = D \frac{\delta^2 C_d}{\delta x^2} \tag{1}$$

where C_d is the concentration of the diffusing species, t is the sorption time, and ($\delta C_d / \delta x$) is the concentration gradient. Cranck's solution[24] for this equation in a plane sheet of the sample of thickness L with surfaces maintained at constant concentration is given by

$$Q_t = \left(\frac{M_t}{M_\infty}\right)$$
$$= 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{\frac{-(2n+1)^2\pi^2 Dt}{L^2}\right\} \tag{2}$$

where M_t is the mass uptake at time t, M_∞ is the equilibrium mass uptake, and D is the diffusion coefficient. This equation holds well for the conditions of an infinite plane sheet maintained at a constant concentration. Because the ratio of surface area to thickness of the experimental sample turns out to be very high compared with the thickness, it can be approximated to an infinite plane sheet. The ratio (M_t/M_∞) in eq. (2) is the quantity experimentally measured and expressed as

$$Q_t = \frac{(W_t - W_d)}{(W_\infty - W_d)} \tag{3}$$

where W_d is the weight of the dry sample, W_t is the weight of the sample that has been soaked in water/solution for a time t, and W_∞ is the weight of the sample in the final stages of sorption. The ratio Q_t is evaluated according to the above equation with the measured values of W_t, W_d, and W_∞. A widely used approximation is the rule that at short times (up to $Q_t = 0.5$), the amount of substance diffused is proportional to square root of the time of sorption, which is also known as the square-root-of-time-law or Stefan's approximation[24,25] and is given by

$$Q_t = 4\left(\frac{Dt}{\pi L^2}\right)^{1/2} \tag{4}$$

This approximation is derived under the assumption that the diffusion coefficient (D) is a constant. A plot of this ratio ($M_t/M_\infty = Q_t$) versus square root of sorption time ($t^{1/2}$) is generally referred to as the sorption curve, and D can be calculated from the slope of the initial linear portion of the curve. The diffusion coefficient can also be calculated from the late-time approximation of eq. (2) taking $n = 0$ which results to

$$Q_t = 1 - \frac{8}{\pi^2} \exp\left(-\frac{D\pi^2 t}{L^2}\right) \tag{5}$$

According to the solvent diffusion rate and polymer relaxation rate, Alfrey et al.,[26] proposed a classification: Fickian (Case I) and non-Fickian (Case II and anomalous) diffusions. A Fickian diffusion rate is characterized by a solvent diffusion rate slower than the polymer relaxation rate and is proportional to the square root of time. In Case II diffusion, the solvent diffusion rate is faster than the polymer relaxation rate. In anomalous diffusion, the solvent diffusion rate and the polymer relaxation rates are about the same order of magnitude and characterized by a fast, Fickian sorption followed by slow, non-Fickian behavior. The water and sodium sorption curves are plotted and shown in Figures 1 and 2, respectively, and these results are discussed in detail in the discussion section.
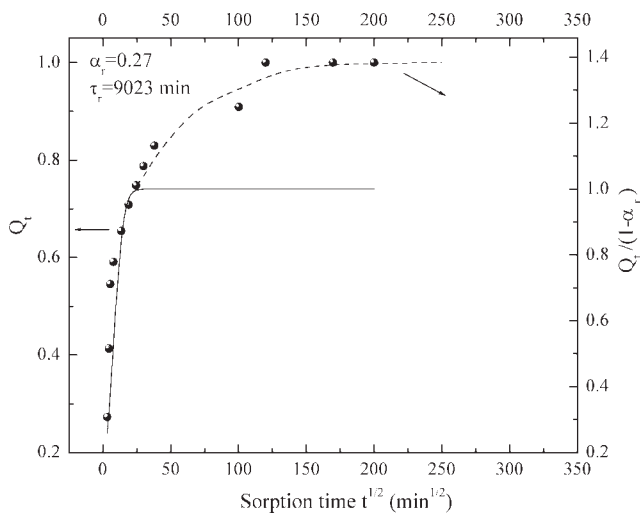
Figure 1 Water sorption—Variation of Q_t and $Q_t/(1-\alpha_r)$ as a function of square root of sorption time, $t^{1/2}$. (●) represent the experimental points; (−) is fit to Berens and Hopfenberg model.

PLS results

All the measured positron lifetime spectra were resolved into three lifetime components τ_1, τ_2, and τ_3 with intensities I_1, I_2, and I_3, respectively. Generally, the attribution of these lifetime components is as follows: The shortest lifetime component τ_1 with intensity I_1 is attributed to p-Ps and free positron annihilations. The intermediate lifetime component τ_2 with intensity I_2 is usually considered as a result of annihilation of positrons trapped at the defects present in the crystalline regions or at the crystalline-amorphous interface regions of the medium. The longest-lived component τ_3 with intensity I_3 is due to pick-off annihilation of the o-Ps in the free volume sites present mainly in the amorphous regions of the polymer matrix. A simple relation developed by Nakanishi et al.[27–29] relates o-Ps lifetime I_3 to the free volume hole size. In this model, positronium atom is assumed to be localized in a spherical potential well having an infinite potential barrier of radius R_0 with an electron layer in the region $R < r < R_0$. According to this model, the relation between τ_3 and the free volume hole or cavity radius R is given by

$$(\tau_3)^{-1} = 2\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]\text{ns}^{-1} \quad (6)$$

where $R_0 = R + \delta R$ and δR is a fitting parameter. By fitting Eq. (6) with τ_3 values for known hole sizes in porous materials like zeolites and other molecular media, a value of $\delta R = 0.1657$ nm was obtained. It has been verified that this value of δR also holds good for the present lifetime value in FP lens material. Hence, with this value of δR, the free volume

radius R has been calculated from Eq. (6), and the average size of the free volume holes V_f is evaluated as $V_f = (4/3)\pi R^3$. The fractional free volume or the free volume content (F_v) can then be estimated as

$$F_v = C V_f I_3 \quad (7)$$

where C is a constant, V_f and I_3 are the parameters described above. The parameter C has to be estimated from an independent experiment. Because we have not measured the C value, in this case, we use the relative fractional free volume defined as $F_{vR} = V_f I_3$ to understand the changes in free volume fraction.

The changes in free volume parameters in case of water and sodium chloride sorption in FP92 contact lens biopolymer are compared in Figures 3 and 4. Figure 3(a,b) present the variation of τ_3 and V_f as a function of sorption time for water and sodium chloride, respectively, while Figure 4(a,b) present the variation of free volume fraction and o-Ps intensity with sorption time.

Energy dispersive X-ray spectroscopic results

The EDS results are presented in Figure 5. Figure 5(a) depicts the EDS spectrum for virgin FP92 lens and Figure 5(b) is the EDS scan of the lens sample soaked in sodium chloride solution to saturation.

Refractive index results

The measured refractive index "n" and the corresponding o-Ps lifetime τ_3 in the lens sample soaked in sodium chloride solution for different time intervals of soaking are plotted and shown in Figure 6(a).
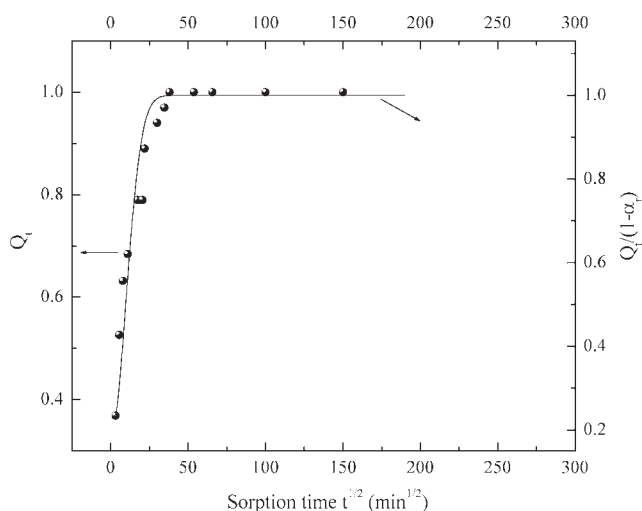

Figure 2 Sodium chloride sorption—Variation of Q_t and $Q_t/(1-\alpha_r)$ as a function of square root of sorption time, $t^{1/2}$. (−) is a fit to Part I of Eq. (4).
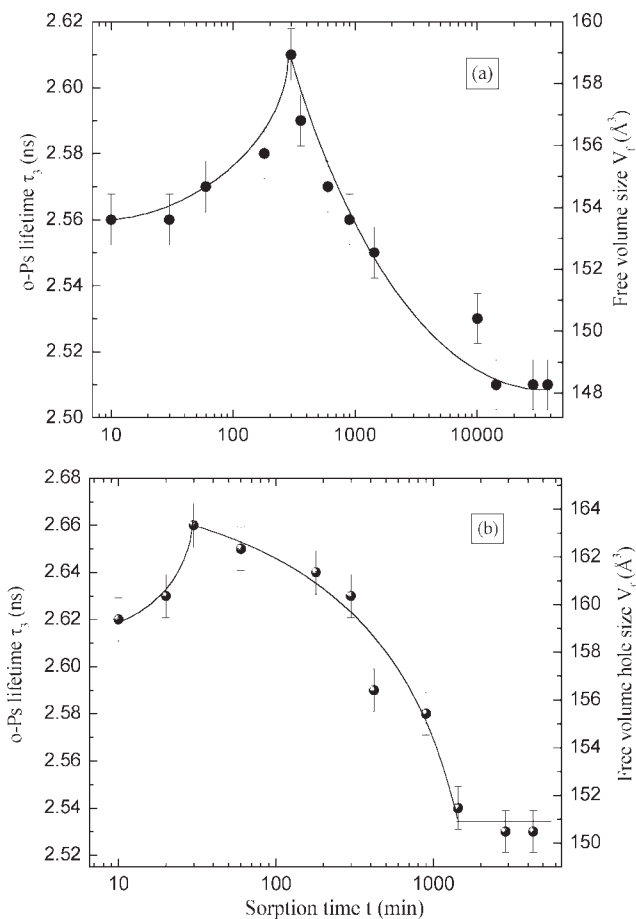
Figure 3 (a) Water sorption—Variation of o-Ps lifetime τ_3 and free volume hole size V_f as a function of sorption time. (Solid line is to guide the eye). (b) Sodium chloride sorption—Variation of o-Ps lifetime τ_3 and free volume hole size V_f as a function of sorption time. (Solid line is to guide the eye).

DISCUSSION

From the water sorption curve (Fig. 1), we see at short times, the mass uptake Q_t increases linearly with $t^{1/2}$ indicating the diffusion is Fickian, but at longer times, the maximum uptake exhibits a protracted asymptotic approach toward equilibrium, suggesting that, water sorption is non-Fickian.[16] In an experimental situation, it is hard to reach equilibrium condition and as such, we consider the final sorbed mass that remains more or less constant within the experimental errors as pseudo- equilibrium mass uptake and this is used to construct the sorption curves. From the initial linear portion of this sorption curve, the diffusion coefficient D was calculated. It should be noted that, the usual mass uptake equation at a constant concentration [eq. (5)] given by Crank seems to be inadequate to fit the experimental data. For such non-Fickian sorption curves, the initial linear portion represents the diffusion-controlled sorption and the nonlinear portion

represents the relaxation-controlled sorption. The initial linear portion of the sorption curve may be used to estimate the diffusion coefficient even when the total sorption does not follow the Fickian model.[30] The best fitted value for Fickian diffusion coefficient, D for water sorption in FP92 turns out to be 4.48×10^{-6} cm^2 s^{-1}.

However, for a complete understanding of the diffusion kinetics in such cases, Berens and Hopfenberg[31] model has been extensively used and described in our earlier works.[15–17] We have also dealt with the non-Fickian nature of water sorption and its causes in this work.[17] According to this, the physical properties of the contact lens polymers are governed by the state of water within them. A water molecule is liable to be bound to a polymer or trapped in a small space formed within the polymer, which is the free volume site. Water molecules form a continuous hydrogen-bonded network containing
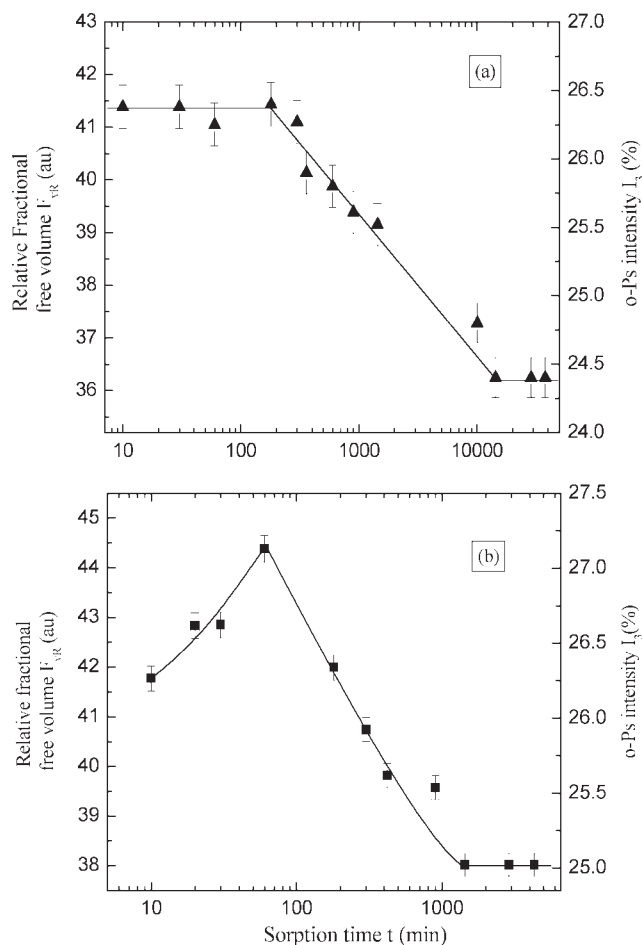

Figure 4 (a) Water sorption—Variation of relative fractional free volume F_{vR} and o-Ps intensity I_3 as a function of sorption time. (Solid line is to guide the eye). (b) Sodium chloride sorption–Variation of relative fractional free volume F_{vR} and o-Ps intensity I_3 as a function of sorption time. (Solid line is to guide the eye).
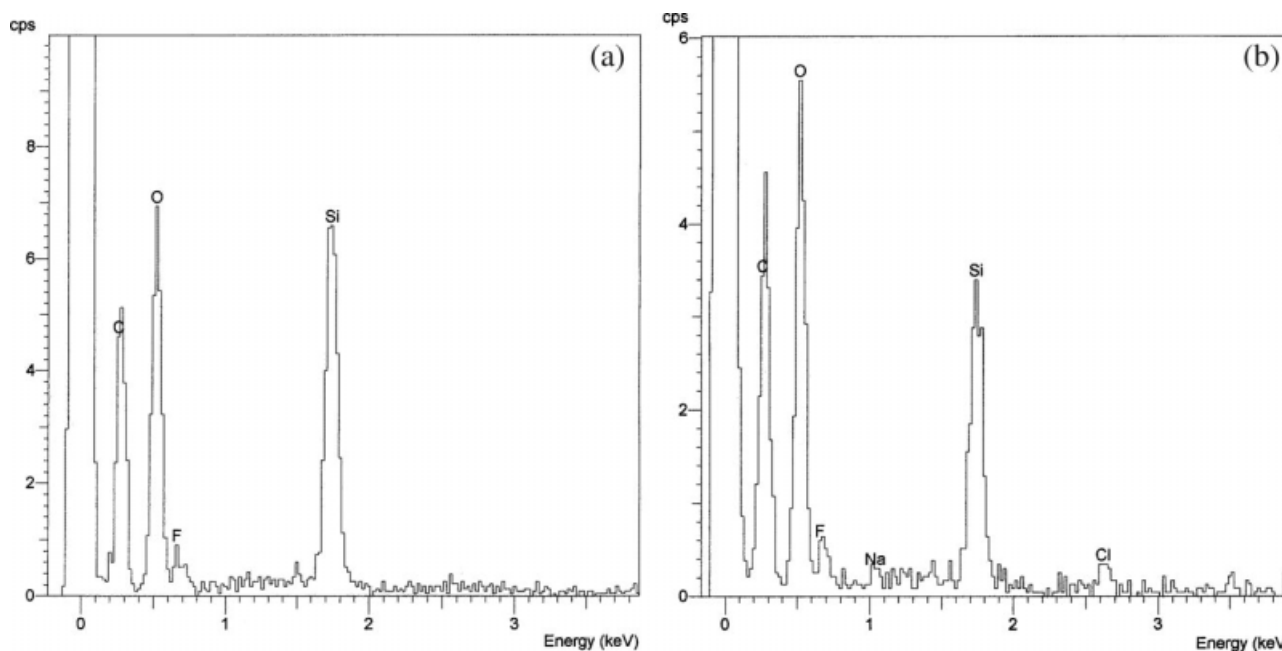
Figure 5 (a) EDS plot of Virgin FP92. Both Na and Cl peaks are absent. (b) EDS plot of FP92 soaked in sodium chloride solution for saturation time of 2 days. Both Na and Cl peaks are present.

predominantly four or five mutually associated molecules per cluster and many strained or broken hydrogen bonds.[32] To describe the structure and dynamics of water in the polymer environment, different terms are favored by polymer chemists. As described by Pedley and Tighe,[33] bound water or tightly-bound water is usually associated with water molecules, which have direct hydrogen bonding with the polar groups of the polymer matrix, or water molecules that strongly interact with ionic residues of the polymer matrix. Free or bulk water refers to water molecules, which do not interact with the polymer matrix. The water in FP92, after diffusion, forms the bound water molecules through

hydrogen bond, diffuse as cluster of molecules resulting to a rather slow intake and swelling. As we know, the phenomenon of swelling depends on the forces of interaction between the solvent molecules and the polymer segments. The penetrated water molecules establish polar attractive forces with the polymer chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segmental mobility, thereby accommodating more water, which leads to swelling in case of pure water sorption in FP92.[15,16,34]

The change in diffusion kinetics of water in the presence of sodium chloride is shown in Figure 2. The curve is linear during the early stages of
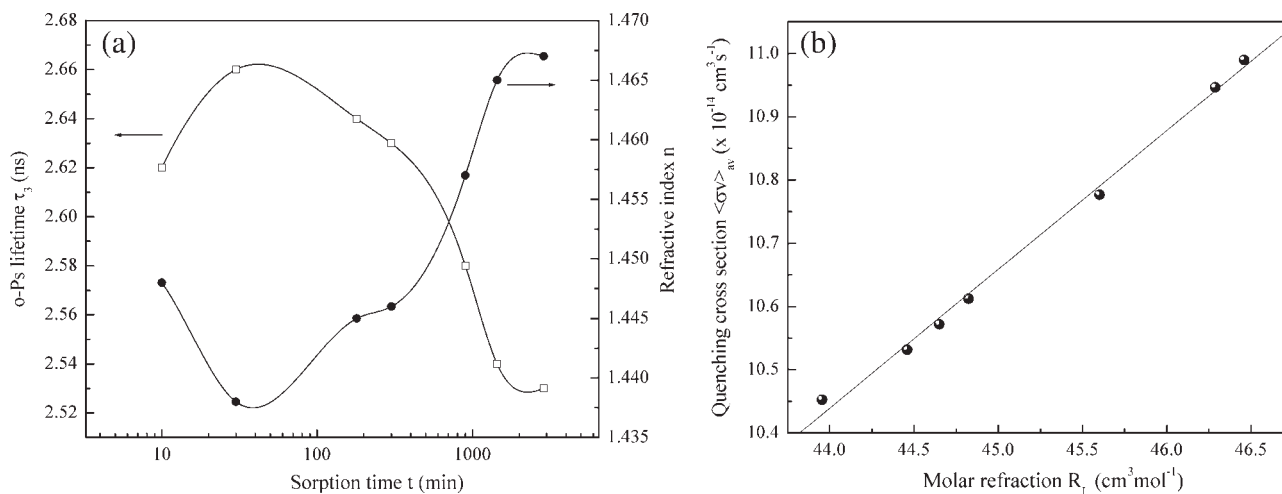

Figure 6 (a) Variation of refractive index n and o-Ps lifetime τ_3 as a function of sorption time. (Solid line is to guide the eye). (b) Variation of quenching cross section σv as a function of molar refraction R_L. (Solid line is linear regression fit).

sorption and levels off at longer times. This is the characteristic of Fickian diffusion. Therefore, unlike pure water, sodium chloride diffusion follows a Fickian type diffusion,[25,35] with a constant diffusion coefficient $D = 4.23 \times 10^{-7}$ cm^2 s^{-1}. Further, using the glass transition temperature (T_g) values of FP92 (110°C) and water (-135°C) in the Gordon-Taylor equation,[36] we found that the T_g of polymer-penetrant system reduces below environmental temperature in the presence of sorbed water, thus justifying Fickian diffusion.

It is to be noted that addition of a solute to polymer matrix perturbs the possibility of water cluster formation as reported earlier.[37,38] As the sorption kinetics in FP92 changes from non-Fickian in case of pure water sorption to Fickian because of the addition of sodium chloride solute, we infer that the possibility of formation of the clustered structure of water is prevented by the solute sodium chloride. Furthermore, water diffusion reaches saturation in 10 days, whereas sodium chloride diffusion saturates just in a day. This significant difference in equilibrium mass uptake can also be attributed to the influence of sodium chloride solute. The NaCl in water makes the polymer to absorb water in a very short time and equilibrate the osmotic pressure. This increase in osmotic pressure on addition of sodium chloride, and its influence on the water structure in the present contact lens polymer matrix can be further understood from positron results.

The influence of water sorption on the free volume parameters in case of few lens systems including FP92 were analyzed in detail in our earlier works.[16,17] Therefore, we prefer to describe only sodium chloride sorption related changes in free volume parameters in the present lens system in comparison with water sorption explained earlier.[17] The o-Ps lifetime value of FP92 in its dry state is found to be 2.56 ns, which correspond to free volume size, 153.6 Å^3. With sorption, we observe about 50 ps increase in τ_3 in the initial stages of water sorption [Fig. 3(a)], whereas 100 ps increase in τ_3 can be seen in sodium chloride sorption [Fig. 3(b)]. In terms of free volume size, an increase is 5.4 Å^3 for water diffusion, whereas it is almost double in case of sodium chloride intake, that is, 10.6 Å^3. It is also important to note that the time taken to attain maximum value in free volume size was 300 min in water, whereas it took just 30 min in sodium chloride sorption. In case of water sorption, F_{vR} and I_3 show constancy in the beginning and later it decreases (after 300 min) [Fig. 4(a)]. On the other hand, F_{vR} and I_3 show initial increase and then decrease in NaCl case [Fig. 4(b)]. After 30 min of sodium chloride mass uptake, τ_3 and V_f decreased by 130 ps and 13.7 Å^3, respectively, whereas for water sorption, this decrease is only 100 ps and 10.6 Å^3.

We propose this rapid decrease in free volume parameters in case of NaCl sorption in comparison with water sorption, to the adhesion of sodium chloride onto the polymer chain segments. The adhesion results in increased osmotic pressure and hence faster mass uptake. Supporting evidence to this proposition can be found in the literature.[39]

The following mechanism may be in place to explain the effect of ions of sodium chloride on the structure of water and the resulting increase in osmotic pressure. Several studies in the past suggest that ions directly interact with macromolecules by binding to their hydrophilic groups,[40] and few other studies suggest that indirect interaction is also possible with the polymer through perturbation of the water environment or by induction of changes in hydrogen bonding of water to the polar groups of the polymers.[41] The difference in the behavior of different ions in aqueous solutions is related to their surface charge densities.[42] Small ions of high surface charge density bind water molecules strongly relative to the strength of water–water interactions in the bulk. Large or relatively large ions of low surface charge density bind water molecules weakly relative to water–water interactions. Livney et al.,[43] have observed that Na$_2$SO$_4$ reduced the osmotic pressure of dextran, whereas NaCl and NaSCN increased it. They relate this difference in the behavior of different ions in aqueous solutions to their surface charge density. Accordingly, SO$_4^{-2}$, which has a high surface charge density, forms a complex of tightly bound water molecules around it. Such high charge density ions, especially anions reduce the electron-pair acceptability of their adjacent water molecules, thus destabilizing their hydrogen bonds and lowering the osmotic pressure of the polymer. Contrary to Na$_2$SO$_4$ solution, NaCl and NaSCN solution increased the osmotic pressure of dextran, due to their low charge density.[43] There is another possible explanation from Collin's work.[42] According to him, ions of low charge density adsorb onto hydrophilic sites of the polymer by releasing the weakly bound hydration shell water molecules, both their own and those of the polymer, allowing them to form more favorable bulk water. Although FP92 is hydrophobic because of the silicone part, it has fluorine and methacrylic part which increase wettability (hydrophilic). Hence these are more probable sites for the adhesion of sodium and chloride ions. Relatively large, low charge density ions such as Na$^+$ and Cl$^-$, increase the osmotic pressure and demonstrate a positive excess because they are pushed toward the polymer by the water molecules, which energetically favor the bulk water structures.[43] Adhesion of ions at these sites results to decreasing the free volume size and its number density to a large extent in comparison with water sorption case.

It has also been observed that zones of excess salt concentration form around the polymer segments.[39,43] This results in the reduced chemical potential of water, in overlapping excess zones of adjacent polymer chains; thereby a water potential gradient is established which serves as a driving force for water diffusion into these overlap zones, i.e., increased rate of water diffusion occurs. In effect, sodium chloride salt adsorbs to the contact lens polymer chains, releasing the bound water molecules, thus increasing the free water (bulk water) content in the lens.

The clinical observations show that change in free to bound water ratio lead to many physiological complications. In our previous article,[17] we had undertaken a comparative study of water and glucose sorption in the same FP92 RGP lens biopolymer with a view to understand the complexities in diabetic lens wearers. We found from this study that, excess glucose in tears increases the free water content in the lens and lenses with more free water are prone to complications like lens dehydration and corneal desiccation.[17]

It has been shown that rigid gas permeable lenses generally deposit more lipid than many soft lens materials. Hart [44] proposed that nodular deposits responsible for lens spoliation were due to localized spots of drying, resulting in hydrophobic areas which attract lipids. From the above analogy, we perceive that there is an increase of free water due to adhesion of the salt and the lens with more free water is prone to lens dehydration.[38] Because of this, many spots of drying may grow up. So these localized spots of drying may result in hydrophobic sites that attract lipids, hence leading to spoliation of the lens. This rationalization is in conformity with the work of Cowell et al.,[8] who observed an increase in adhesion with increase in sodium chloride concentration.

The above inference is also well reflected from EDS results. Figure 5(b) signs the presence of sodium (Na) (1.52%) and chloride (Cl) (2.05%) ions very clearly. Therefore, this proves beyond doubt the adhesion of sodium and chloride ions to the polymer chains mainly methacrylate and fluorine sites.

Various relationships have been proposed to relate the refractive index "n" of the materials to their physical and chemical structure. The famous and well known equation in such cases is the Lorenz-Lorentz equation[45,46]

$$\left(\frac{n^2-1}{n^2+2}\right)\frac{M_o}{\rho} = \frac{N_A\alpha}{3\varepsilon_o} = R_L \qquad (8)$$

where M_o is the molecular weight of the polymer repeat unit, ρ is the polymer density, N_A is Avoga-dro's number, ε_o is the permittivity of free space and α is the polarizability. R_L is called molar refraction that depends upon the polarizability of the molecules. Therefore a change in polarizability results to change in refractive index, which is an important material parameter for lens materials. The polarizability in turn depends on several factors such as density ρ, crosslinking, free volume and chemical coupling. However, we find no attempt made earlier to correlate free volume to this optical parameter n. The refractive index results as can be seen from Figure 6(a), n and τ_3 show exactly the opposite trend. To understand the correlation between n and τ_3 [Fig. 6(a)], the molar refractions R_L were calculated from their measured indices of refraction using eq. (8). The o-Ps quenching cross sections were determined from the measured o-Ps lifetimes τ_3 according to

$$\langle\sigma v\rangle_{av} = \left(\frac{M_o}{\rho N_A}\right)\left(\frac{1}{\tau_3}\right)cm^3 s^{-1} \qquad (9)$$

$<\sigma v>_{av}$ is plotted against R_L and shown in Figure 6(b). Evidently $<\sigma v>_{av}$ varies linearly with R_L and the first order linear regression describes the data well:

$$\langle\sigma v\rangle_{av} = 0.2193 + 0.7923\,R_L$$
$$(r^2 = 0.998;\ \text{solid line Fig 6b}) \qquad (10)$$

This clearly shows that there is a direct correlation between the polarizability of the system and the free volume. From Figure 6(a), we see that except for the initial sorption time, n increases as the o-Ps lifetime decreases. In the absence of theoretical attempts to connect these two quantities, the present data clearly points that we can empirically connect these two important parameters of the lens sytem. The plausible explanation we could offer at the moment is, as the concentration of Na^+ and Cl^- ions increases, free volume hole size decreases. The adhesion of these ions certainly brings about molecular orientation changes at the sites of adhesion. Therefore, the overall polarizability gets altered hence the refractive index and the free volume. From the power calculation using the conventional lens maker's formula keeping the radii of curvature constant, we notice that there is change in power from 0.75 Dioptres when the refractive index of the lens is 1.453–1.96 Dioptres when the refractive index changes to 1.467. This obviously directs the patient to change the contact lens as it becomes unusable.

CONCLUSIONS

The influence of sodium chloride on lens spoilage has been studied. The positron lifetime results reflect appreciable changes in free volume parameters on sodium chloride sorption in comparison with the

water sorption. There is 10.6 Å^3 increase in free volume size of the lens (with NaCl), which is almost double compared to 5.4 Å^3 in case of water sorption. After 30 min of sodium chloride mass uptake, τ_3 and V_f decreased by 130 ps and 13.7 Å^3, respectively, whereas for water sorption, this decrease is only 100 ps and 10.6 Å^3 that too after 300 min of sorption time. These changes are well correlated with changes in diffusion behavior of the two. Pure water diffusion reaches equilibrium mass uptake in 10 days, whereas sodium chloride diffusion reaches equilibrium mass uptake just in a day. This faster equilibrium mass uptake and rapid decrease in free volume parameters in case of NaCl sorption is attributed to the adhesion of sodium chloride onto the polymer chain segments. The relatively large, low charge density ions of Na$^+$ and Cl$^-$ increase the osmotic pressure and demonstrate a positive excess which energetically favor the bulk water structures. In the light of evidences that lens with more free water lead to lens dehydration, we propose that such lenses with more free water result in localized spots of drying, resulting in hydrophobic areas which are more probable sites for lipid deposition and hence lens spoilage. The most important lens property viz. the refractive index correlates well with free volume and hence the influence of NaCl on its change. Considering the ensuing discomfort to the lens wearer upon loss of transparency and associated pathologic complications, this study may provide some useful hints in solving such problems in the development of good biocompatible contact lens materials.

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