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SHORT COMMUNICATION

P. Peterková
L'. Lapčík Jr

Determination of the diffusion coefficient of water into atelocollagen type I thin films by attenuated total reflection Fourier transform infrared spectroscopy

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P. Peterková
Faculty of Chemistry
Technical University of Brno
Purkyňova 118, 612 00 Brno
Czech Republic

L'. Lapčík Jr (✉)
Institute of Physics and Material
Engineering, Faculty of Technology
Technical University of Brno
Nám. T.G. Masaryka 275, 762 72 Zlín
Czech Republic

Abstract The diffusion coefficient of water into thin polymer layers of glutar aldehyde cross-linked atelocollagen type I matrix (sample 1, the typical layer thickness was about 0.065×10^{-3} m) at 23 °C was 1.142×10^{-10} m^2 s^{-1}. At twice the concentration of the cross-linking agent (sample 2) the diffusion coefficient was 2.795×10^{-10} m^2 s^{-1}. This increase was attributed to the more ordered morphology and the creation of ordered microvoids in the film. A larger surface area is then available for the transport of diffusing molecules, allowing a higher penetration rate of the solvent.

Key words Atelocollagen type I · Attenuated total reflection · Fourier transform infrared spectroscopy · Diffusion coefficient · Thin films

Introduction

At the present time, surface modification of the synthetic polymer materials used in a wide range of medical applications (e.g. implants, storage of body fluids, contact lenses, etc.) enhances the durability as well as the quality and the comfort of the final application [1–3].

Atelocollagen type I is a fibrillar collagen composed of two polypeptide chains, α_1 and α_2. It occurs in many biologically important organs, in the skin, tendons, bones and blood vessels. Collagen polypeptide chains contain repeating tripeptide units: (Gly-X-Y)$_n$, where X and Y are imino acids, mainly proline and 4-hydroxyproline, which constitute about 20% of all residues in collagen [4].

In the present work the diffusion coefficients of chemically cross-linked atelocollagen type I thin films were determined by the attenuated total reflection Fourier transform IR (ATR FTIR) technique. The values were compared with diffusion coefficients determined by measuring the kinetics of swelling of HYPRO Sorb, a macroscopic spongelike collagen.

Materials and methods

Atelocollagen type I was extracted form bovine tendon (HYPRO Sorb collagen sponge, HYPRO, Otrokovice, Czech Republic) and dissolved in 0.2 M sodium hydroxide (Lachema, Brno). For cross-linking 50 w/w glutar aldehyde (GTA) was used (UCARCIDE 250 Antimicrobial, Union Carbide). A solution of 2 w/w atelocollagen type I dissolved in 0.2 M NaOH cross-linked with GTA at the following concentrations: sample 1 – 0.5 w/w, sample 2 – 1.0 w/w. sample 3 was the original HYPRO Sorb collagen sponge.

A Nicolet Impact 400 FTIR spectrometer was used for collecting the IR spectra. The measurement was performed using the ATR technique on a ZnSe crystal-based horizontal accessory kit (Spectra Physics) with OMNIC and 3DIRS operating systems (Nicolet).

Film preparation

The films were prepared by casting the solution on the ATR crystal in three layers (each sample addition was of 500 μl, total sample volume deposited was 1500 μl) and the solution was allowed to evaporate. The samples were conditioned in a constant humidity chamber for 2 days prior to the measurement (samples 1, and 2).

Calculation of the diffusion coefficient from ATR FTIR spectroscopy

The method for measuring the diffusion coefficient of thin layers using the ATR method was described by Van Alsten [5]. The time dependence of the evolution of the characteristic IR absorption bands during penetration of the solvent through the polymer film deposited on the ATR crystal is measured. From Fick's law for small solvent molecules the diffusion coefficient (D) is calculated according to the formula

$$\frac{A_t}{A_\infty} = 1 - \frac{8}{\pi\lambda}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\frac{1}{\frac{2}{\lambda}+\frac{(2n+1)^2\pi^2\lambda}{8L^2}}\exp\left(\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right) , \quad (1)$$

where A_t is the absorbance at time t, A_∞ is the equilibrium absorbance after total solvent penetration, n is the number of measurements, L is the thickness of the polymer film (0.065×10^{-3} m) and λ is the penetration depth (typically 2.5–5 μm [5]). The thickness of the polymer film was measured using a micrometer screw. For the measurement 900 μl water was spread uniformly on the surface of the sample and, simultaneously, the IR spectra recording was started.

Determination of the diffusion coefficient by measuring the kinetics of swelling

For the calculation of the diffusion coefficient the time dependence of the amount of the solvent absorbed per unit amount of the sample studied (Q_t) was determined [6]:

$$\frac{Q_t}{Q_\infty} = \left(\frac{4}{L}\right)\left(\frac{Dt}{\pi}\right)^{0.5} + \text{integration constant} , \quad (2)$$

where Q_∞ is the equilibrium amount of water absorbed per unit amount of the sample, L is the sample thickness and t is the swelling time. The amount of water absorbed was determined by the volumetric method. The measurements were repeated five times at 23 °C with sample 3. The swelling coefficient (α) was determined from the mass differences:

$$\alpha = \frac{m_\infty - m_0}{m_0} , \quad (3)$$

where m_∞ and m_0 are mass of the sample after and before equilibrium swelling.

Results and discussion

A typical pattern of the time dependence of the ATR FTIR spectra during penetration of water into the biopolymer film is shown in Fig. 1. For the calculation of the diffusion coefficient the area of the broad absorption band at a wavenumber of 3390 cm^{-1} was used. This is characteristic of the antisymmetric stretching vibrations of the hydroxyl groups of water present in the structure of the thin film [7]. The spectra were of medium resolution between 4000 and 2800 cm^{-1} because of the relatively high rate of swelling. Due to the very thin layer thickness, contact between the ZnSe crystal and the deposited polymer film became worth. The absorption peak area was not affected by background noise (the area of the background region was less than 1% of the total band area). The increase in the peak area related to the OH antisymmetric stretching mode is shown in Fig. 2. The plateau region is attributed to the equilibrium swelling. The diffusion coefficients determined by the ATR technique are summarized in Table 1.

For comparison, the diffusion coefficient of water into the original atelocollagen type I sponge (sample 3)

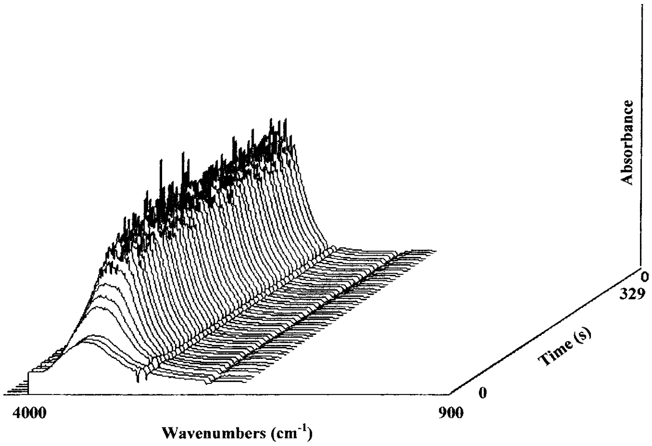

Fig. 1 A typical pattern of the measured time dependence of attenuated total reflection Fourier transform IR (ATR FTIR) spectra (region characteristic of the antisymmetric stretching vibrations of OH groups of water) during swelling of water into the thin biopolymer film

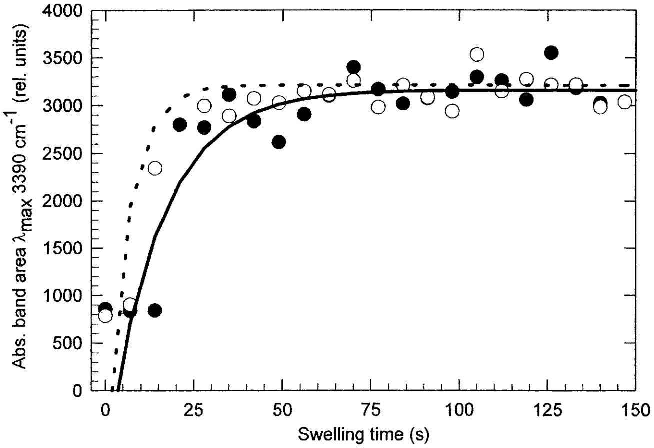

Fig. 2 Time dependence of the change in the area of the ATR FTIR absorption band (at λ_{max} 3390 cm^{-1} of the OH antisymmetric stretching vibration bands) during penetration of water into the atelocollagen type I thin film at 23 °C: *filled circles* – sample 1; *open circles* – sample 2. The *lines* are best fits of Eq. (1) using the parameters given in Table 1

Table 1 Diffusion coefficients of water molecules into the atelocollagen type I thin films studied at 23 °C as determined by the attenuated total reflection Fourier transform IR technique

Sample	Film thickness, L ($10^{-3} \times$ m)	Diffusion coefficient, D ($10^{-10} \times$ m^2 s^{-1})
Sample 1	0.065	1.142
Sample 2	0.063	2.795

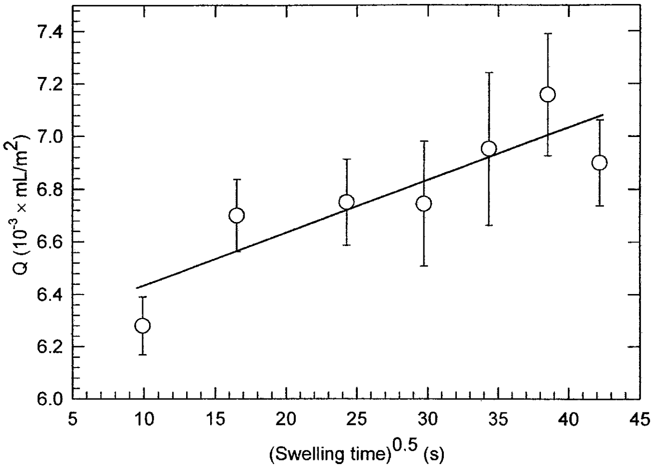

Fig. 3 Dependence of the amount of water absorbed per unit amount of sample 3 (*Q*) as a function of the square root of the swelling time as determined by the volumetric method (each measurement was repeated five times) at 23 °C. The *line* is the best fit of Eq. (2)

was measured by the water uptake of the sample (volumetric method). A typical linear pattern was observed for the square-root time dependence (Eq. 2) (Fig. 3). The diffusion coefficient was 3.7×10^{-7} m^2 s^{-1}, determined at a degree of swelling of 66.7%. With a higher degree of cross-linking (sample 2) the diffusion coefficient increased to 2.795×10^{-10} m^2 s^{-1}. This surprising result can be explained by the increased order of the microstructure of the thin layers. A more ordered morphology would create ordered microvoids in the film and increase the surface area, allowing a higher penetration rate of the solvent. The higher diffusion coefficient of water into the spongelike collagen foam (3.7×10^{-7} m^2 s^{-1}) with a higher total surface area available for solvent penetration supports our hypothesis.

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References

1. Kingshott P, Griesser HJ (1999) Curr Opin Solid State Mater Sci 4:403–412
2. Lapčík L, Jr, Lapčík L, De Smedt S, Demeester J, Chabreček P (1998) Chem Rev 98:2663–2684
3. Peterková P, Lapčík Jr L' (2000) Chem Listy 94:371–379
4. Nagarajan V, Kamitori S, Okuyama K (1998) J Biochem 124:1117–1123
5. Van Alsten JG (1995) TRIP 3:272–276
6. Crank J (1956) The mathematics of diffusion. Clarendon, Oxford
7. Lide DR (1999) In: Lide DR (ed), CRC handbook of chemistry and physics, 80th edn 1999–2000. CRC, Boca Raton, p 9–77