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Ultrasonic Characterization of the Kinetics of Water Sorption in Hydrogels

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SUMMARY: A complex mechanism characterizes the water uptake kinetics in hydrogels, as a consequence of the strong structural changes occurring in the material during the sorption process. Water acts as a plasticizer, reducing the glass transition temperature of the polymer below the sorption temperature and determining a glass transition in the polymer. In this study the changes in the ultrasonic attenuation and velocity in semicrystalline Poly-vinyl-alcohol (PVA) hydrogel films during water sorption are measured by a pulse-echo system. The ultrasonic wave propagation is applied to monitor the position of the swollen/unswollen fronts and to the measurement of velocity and attenuation. The structural changes in PVA hydrogels, monitored by Wide Angle X-ray Diffractometry (WAXD), performed during the sorption process, are correlated with the ultrasonic data.

Introduction

Water sorption in dry hydrogel films is responsible of the swelling of the glassy matrix in correspondence of two fronts moving from the sample boundaries towards the center and separating a glassy core from two external rubbery regions. Water acts as a plasticizer, reducing the glass transition temperature (T_g) of the polymer below the sorption temperature and determining a glass transition in the polymer [1,2]. The propagation of ultrasonic waves through the hydrogel during water sorption is characterized by reflections at the glassy-rubbery fronts as well as absorption in correspondence of the swollen-unswollen fronts undergoing a glass transition. In this study the changes in the ultrasonic attenuation and velocity in Poly-vinyl-alcohol (PVA) hydrogels are measured during water sorption by a pulse-echo system. In particular, the pulse-echo technique is applied to monitor the position of the swollen/unswollen fronts during water sorption. The evolution of the attenuation is analyzed in terms of reflections on macroscopic discontinuities and absorption mechanisms [3]. The structural changes in PVA hydrogels, monitored by Wide Angle X-ray Diffractometry (WAXD), performed during the sorption process, are correlated with the ultrasonic data.

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Experimental

The PVA, Polyviol G2810, kindly provided Wacker, is characterized by a degree of hydrolysis of 0.98 and a M_n= 72000. PVA films are prepared drying a diluted solution (9% by weight) at 30 °C layer by layer up to a thickness between 1 and 1.5 mm.

After drying the samples under vacuum at 50 °C for 36 h, water sorption is obtained by immersion of the samples in distilled water (used also as coupling fluid for ultrasonic waves transmission) at a constant temperature of 25 °C. Since the samples are characterized by a thin film geometry (aspect ratio larger than 20:1), a one-dimensional water sorption process is assumed. The longitudinal velocity, the ultrasonic wave attenuation and the thickness of the sample are simultaneously measured during the water sorption, according with the apparatus geometry of Fig. 1. Ultrasonic measurements are obtained by pulse-echo technique at 20 Mhz by using a Panametrics 560A1 - ST system connected with an oscilloscope Philips PM3323. Thickness is measured using a Thermo-Mechanical Analyzer (TMA) 402 Netzsch.

Wide Angle X-ray Diffractometry (WAXD) is performed with a standard instrument XRD-Philips equipped with a CuKα source. Diffraction patterns are collected on PVA samples in dry and saturated conditions in the 2θ range 10°-60° and at different sorption times between 16° and 23°. For each measurement, the sample is removed from water and analyzed. In this

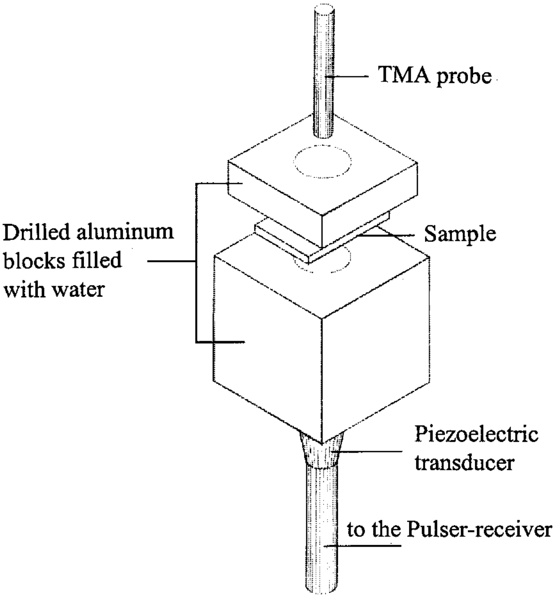

Figure 1. Sketch of the experimental apparatus for simultaneous TMA and ultrasonic measurements

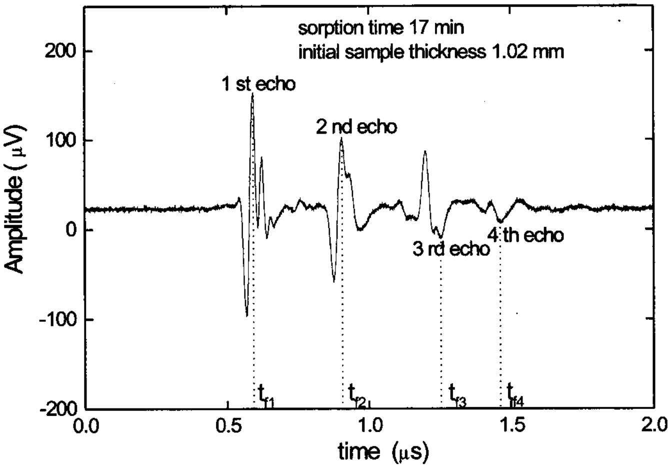

Figure 2. Multiple reflections of ultrasonic waves recorded by an oscilloscope during water sorption in PVA film.

range, the changes of the major diffraction peak, occuring at 19.3° (plane 110), are observed in only 3 min, limiting in this way the time during which the sample is kept in air during the measurement.

Results and discussion

The multiple reflections occurring in a PVA hydrogel during water sorption, as recorded by the oscilloscope, are reported in Fig. 2. The amplitude of the reflected waves is shown as a function of the flight time (representing the time that the wave pulse needs to reach a discontinuity and to return back to the transducer). In this figure four echoes are clearly shown. The reflections observed in Fig. 2 occur during water sorption at the sample boundaries and at the two moving swollen/unswollen interfaces. The first one occurs at the sample boundary when the ultrasonic pulse goes from the water into the sample. The two fronts between the rubbery and the glassy regions are responsible for the second and third reflection of the ultrasonic waves. Finally, the fourth echo is observed at the sample boundary on the opposite side of the transducer. As the two swollen/unswollen front moves towards the center of the sample, the second and third reflection overlap and cannot be distinguished anymore when the glassy core disappears. The overall ultrasonic velocity (V_l) throughout the sample is calculated using the time of flight of the first and last echo (t_{f1}, t_{f4}) and the actual thickness obtained from TMA measurements (d(t)):

$$V_l = 2d(t)/(t_{f4} - t_{f1}) \qquad (1)$$

V_l is compared in Fig. 3 with the velocity in the swollen rubbery region (V_{l12}). This velocity, calculated before the glassy core disappears, is obtained using the time of flight of the first and second echo of Fig. 2 (t_{fl}, t_{f2}) according with Eq. 1. However, the thickness of the rubbery region cannot be directly measured and is calculated assuming that the swollen-unswollen front moves as a function of the square root of the sorption time 3). This assumption, based on a Fickian behaviour of water sorption in the rubbery hydrogel 1-3), leads to a constant value, corresponding to that one measured after the glassy core is disappeared. This behaviour, usually observed in weight gain experiments, is usually explained assuming that the water dissolution in the swollen rubbery matrix, governed by a Fickian behaviour is the rate limiting step 1-3).

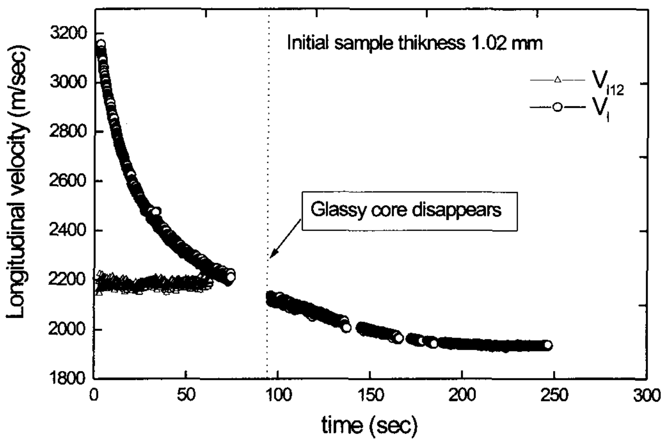

Figure 3. Ultrasonic velocity during water sorption in a PVA sample

The WAXD measurements indicate that the intensity of the peak at 19.3° (110) decreases rapidly as water is absorbed. As also observed by Hodge et al. 4) the angular position of the (110) diffraction peak, and thus the spacing of these planes in the crystals, is unaltered during water uptake, indicating that the crystallites are not swollen by the diffusing solvent. A rough estimate of the evolution of relative fraction of crystallinity, X_c, for the same sample analyzed by ultrasonic wave propagation, is obtained by WAXD analysis collecting diffraction spectra in a limited angular range during water sorption. A significant simplification in the calculation of X_c must be introduced for two reasons:

- the presence of water in the amorphous alters the nature of the amorphous region in a manner specific to the amount and state of water present$^{4)}$.
- the diffraction patterns are measured in a few minutes and in a small range of angles, in order limit the desorption of water that may be eventually accompanied by recrystallization phenomena during the measurements.

Then X_c is estimated as the ratio between the height of diffraction peak at 19.3° normalized to the peak height observed at the same angle for the dry sample. X_c is compared in Fig. 4 with the fraction of glassy unswollen (X_g) core as measured by the positions of the second end third reflections in Fig. 2. X_g is obtained as the ratio between the thickness of the glassy core and the total thickness. An analysis of Fig. 4 reveals that crystallites dissolve in the swollen portion of the polymer at a rate lower than the rate of advancement of swollen-unswollen fronts. As shown in Fig. 4, a residual relative fraction of crystallinity of about 25% is still present in the swollen polymer when the glassy core is disappeared. Therefore, as shown in Fig. 3, when the glassy core disappears, the ultrasonic velocity still decreases as a consequence of either a further uptake of water in the swollen polymer either for the dissolution of the residual crystalline phase.

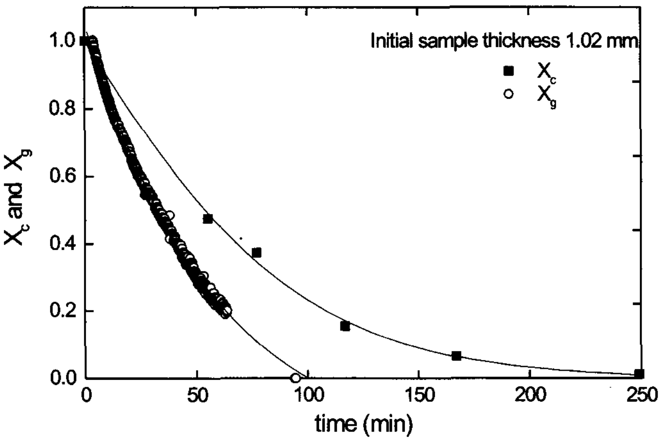

Figure 4. Comparison between the rate of dissolution of crytallites and the rate of disappearance of the glassy core during water sorption in a PVA sample.

The total attenuation (α_t) is calculated as a function of the amplitude of the first and last echo (A_1, A_4) and the actual thickness:

$$\alpha_t = [-\ln(A_4/A_1)]/2d(t) \qquad (2)$$

α_t is the sum of energy losses due to three contributions: α_r, the attenuation caused by reflections on macroscopic discontinuities, α_a, the attenuation caused by molecular absorption mechanisms in a viscoelastic material (for example at the glass transition), α_s , the attenuation caused by scattering if microporosities are present in the material. The last contribution may be neglected in an homogeneous material like a hydrogel. On the other hand, α_r results from the multiple reflections at the sample boundaries and at the swollen unswollen interfaces and may be calculated as a function of the reflection factor, $R_{i,j}$, at each interface between two materials i and *j*:

$$\alpha_r = \ln[f(R_{i,j})]/2d(t) \qquad (3)$$

$$R_{i,j} = \frac{Z_j - Z_i}{Z_j + Z_i} \quad \text{where} \quad Z_i = \rho_i V_{li} \quad Z_j = \rho_j V_{lj} \qquad (4)$$

In Eq. 4 ρ represnts the sample density and in Eq. 3 the function $f(R_{i,j})$ is obtained following a standard procedure $^{5)}$ as also reported in a previous paper [3]. α_a is calculated as α_s = α_t(measured) - α_r(calculated). The contributions of α_r and α_a to the total attenuation are compared in Fig. 5.

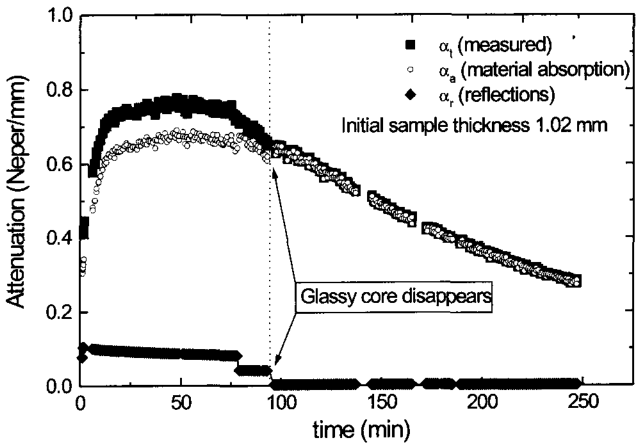

Figure 5. Absorption and reflection contributions to the total measured attenuation.

The evolution of α_t is dominated by the contribution of absorption, attributed to the glass transition occurring at the swollen-unswollen fronts. The initial increase of α_a up to a constant value corresponds to the development of two moving regions of constant thickness, undergoing to a glass transition and crossing the sample from the boundaries toward the center. The thickness of these regions is lower than the half thickness of the sample. When the glassy core disappears, as detected by reflections on the oscilloscope, the glass-rubber transition is completed throughout the thickness and water is absorbed only in the swollen matrix up to saturation. Finally the ultrasonic attenuation decreases to a final value lower than the initial one as the acoustic impedances of the water and of the swollen hydrogel become very close.

Conclusions

In this work, the longitudinal velocity, the ultrasonic wave attenuation and the thickness of PVA hydrogels, are simultaneously measured during the water sorption in an experimental set-up, properly developed. The pulse-echo technique is exploited in order to determine the position of the swollen-unswollen fronts and the ultrasonic velocity during sorption. The evolution of attenuation, analyzed in terms of reflections and absorption mechanisms, is dominated by the effects of the glass transition occurring at the moving fronts. The comparison of WAXD and ultrasonic data indicated that the crystallites dissolution proceeds at a lower rate than the swelling of the glassy core.

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