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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Mechanisms of non-Fickian Micromolecular Diffusion in Glassy Polymer Films: Analysis of Experimental Sorption and Concurrent Dilation Kinetics in the Light of a Differential Swelling Stress Model

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1. Introduction

Non-Fickian sorption kinetics of organic vapors in glassy polymer films may physically be attributed to (i) slow volume viscous relaxations (VVR) of the swelling polymer, and/or (ii) internal differential swelling stresses (DSS), generated by the non-uniform distribution of concentration (and thus non-uniform tendency of longitudinal swelling) during the one-dimensional diffusion process [1, 2]. The DSS mechanism enables interpretation of both sorption kinetics and the kinetics of parallel longitudinal swelling of the polymeric film [1, 2].

Here we present results on sorption (S) kinetics of methylene chloride (MC) vapor in cellulose acetate (CA) films, supplemented by the kinetics of parallel longitudinal dilation (LD) and thickness dilation (TD). On the basis of DSS modelling [1-2], the S-LD kinetic correlations provide evidence of the presence of DSS, as well as information on the viscoelastic properties of the swelling polymer. The corresponding TS kinetic data give further insight on the corresponding anisotropic volume swelling.

2. Results

Fig. 1 displays examples of sorption kinetics obtained from a series of absorption-desorption cycles, each one starting from dry CA film (p_i=0, C_i~0) and covering progressively higher concentration intervals ΔC. For the lowest ΔC experiment, the coincidence of the absorption curves of two films of different thickness L, on a $t^{1/2}/L$ scale, excludes the presence of VVR effects and points to DSS as the only possible cause of the observed non-Fickian sorption kinetics. Evidence of the presence of VVR effects appears only at higher ΔCs, in the form of a thickness effect on a $t^{1/2}/L$ scale. In all cases, the operation of the DDS mechanism is revealed by the corresponding kinetics of dimensional changes, shown in the example of Fig. 2 as fractional longitudinal ($\Delta H_t/\Delta H_{\infty o}$) and thickness ($\Delta L_t/\Delta L_\infty$) dilation. At the initial stages of the sorption process, longitudinal dilation is prevented by the compressive DSS exerted by the glassy core on the outer swollen regions, leading to anisotropic volume swelling through predominant thickness dilation. Eventually, as the concentration becomes more uniform during the sorption process, the said stresses decay and the film returns to its original shape by contracting in the thickness direction. The fact that the calculated volume swelling ($\Delta V_t/\Delta V_\infty$) initially lags behind weight gain (Q_t/Q_∞), should be attributed to sorption of

MC in pre-existing holes that constitute the excess free volume of the initially dry polymer, effected without substantial dilation

The S-LD correlations for all absorption experiments of Fig.1, pertaining to the thicker film, are shown in Fig. 3.The substantial negative deviations of absorption-dilation plots from linearity constitute direct evidence of the existence of DSS of significant magnitude in the presence of plasticization effects (concentration dependence of the modulus of elasticity *E* or of the stress relaxation time τ); while the small deviation exhibited by the corresponding desorption-contraction plot are diagnostic of non linear viscoelastic behaviour (*E* and τ dependent on stress) [2,3].

3. Conclusions

The sorption-longitudinal dilation kinetic correlations can be used as a diagnostic tool for identifying the viscoelastic behaviour of the glassy polymer in response to the DSS operating during a sorption experiment.

4. References

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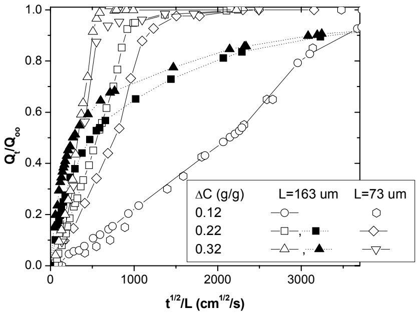

Fig. 1: Kinetics of fractional amount (Q_t/Q_∞) of MC absorbed (open points) or desorbed (filled points) in initially dry CA films, subjected to series of sorption runs covering progressively increasing concentration intervals Δ*C*.

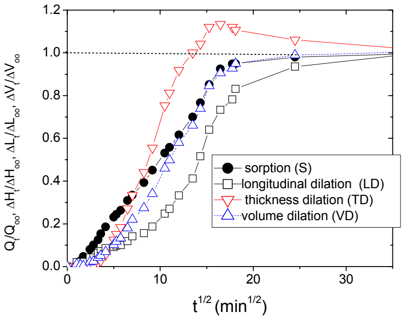

Fig. 2: Kinetics of MC sorption (●) in, and concurrent longitudinal (□), thickness (▽) and volume (△) dilation kinetics of, a CA film with *L*=163 μm subjected to an absorption run with C_i~0 and Δ*C*~0.12 g/g.

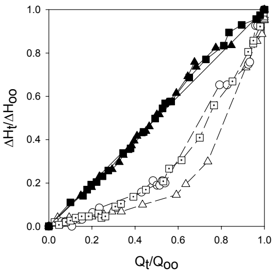

Fig. 3: Correlation of sorption-concurrent longitudinal dilation (S-LD) kinetics for the sorption experiments shown in Fig. 1. Notation as in Fig. 1.