Solvent diffusion in semicrystalline polymer films – An experimental and numerical study

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Introduction

In the manufacture of high-grade polymer films, careful design of individual process steps, not least drying of the liquid coating, is regularly required, increasing the demand for accurate and reliable information on solvent mass transport as well as phase equilibrium characteristics. At the same time, microstructure formation during processing and long-term structural stability may need to be addressed in order to ensure optimum film performance.

With the joint experimental and numerical characterisation of water transport in poly(vinyl alcohol) films, the present study is concerned with mass transfer and microstructure development in a technically relevant polymer whose semicrystalline morphology is governed by both thermal history and the presence of solvent.

Experimental

Film preparation

PVA films with high crystallinity and excellent transparency were prepared from a mixed aqueous/organic solvent via cyclic cooling and heating as described elsewhere [1, 2]. Upon cooling, partial PVA crystallisation is induced as, with temperature decreasing, molecular motion is increasingly

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[1] Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

restricted, thus promoting intermolecular interactions between adjacent polymer chains, leading to the formation of crystalline regions [3]. The resulting highly swollen films were dried for 24 h at 25°C under ambient humidity before further use.

Solvent uptake and crystallinity determination

The dynamics of the gas-phase sorption process were monitored experimentally via non-intrusive Inverse-Micro-Raman-Spectroscopy (IMRS) [4]. The obtained spectra provide quantitative information regarding both local solvent content and crystallinity, enabling the in-situ characterisation of polymer microstructure during the sorption process. To achieve the high spatial resolution of 2 - 3 µm, the incident laser beam is focussed into the sample via an oil immersion objective with a piezo focus providing for the exact vertical positioning of the laser focus.

For quantitative analysis, component-specific Raman bands are evaluated and modelled as the superposition of weighted pure component spectra [5]. Changes in crystallinity are reflected in the 1000 - 1150 cm^{-1} region where four bands are sensitive to the crystalline and amorphous states of PVA [6]. For calibration, spectral information was linked to crystallinity data obtained from density measurements. Densities were determined by flotation in anhydrous toluene/chloroform and converted via the densities of fully amorphous and fully crystalline PVA respectively [7].

Sorption studies

The progression of water diffusion into the crosslinked polymer film and the associated development of its semicrystalline structure were studied in a series of time-resolved measurements by means of the sorption cell depicted in Fig. 1. In order to create a stable thermal environment, the system is thermostated via a double jacket with gas-phase temperature controlled by continuous measurements. Water vapour activity in the presence of air is adjusted with an accuracy of $\Delta a_W < 0.001$, employing aqueous sodium chloride solutions of varying salt concentration. The reservoir containing the salt solution comprises two compartments which may be opened and closed individually so as to allow vapour-phase activity to be

varied without unduly affecting the equilibration process by disassembling the sorption cell. During measurements, the vapour phase is agitated by a compact fan to reduce the gas-phase mass transfer resistance, hence speeding up the sorption process.
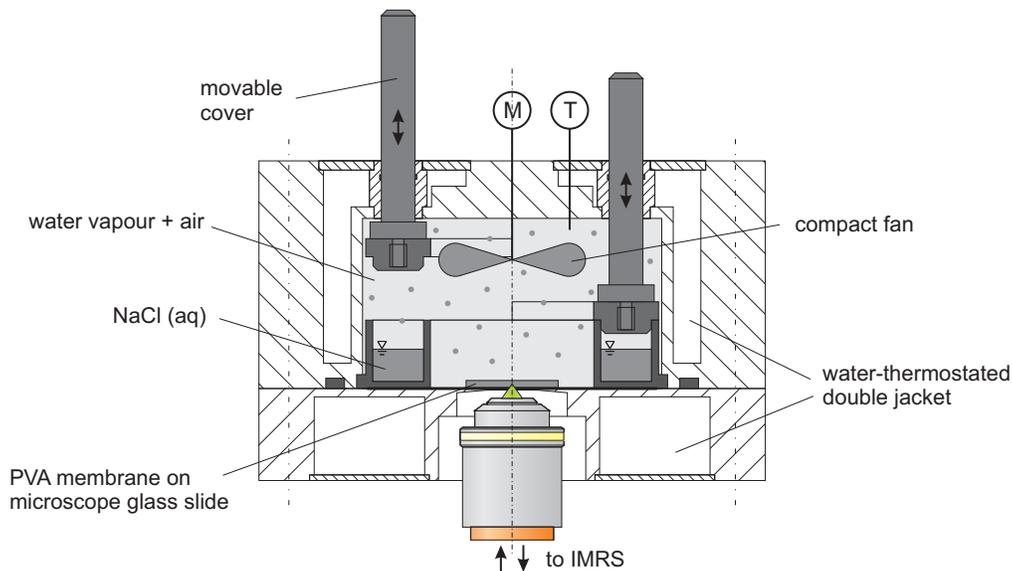
Figure 1: Experimental setup for the in-situ characterisation of water vapour sorption into semicrystalline PVA films at variable solvent activity.

Results and Discussion

Structural rearrangements in the presence of water seem to be governed by two opposing effects. Fig. 2 exemplarily shows the progression of crystallinity upon vapour-phase sorption at $a_W = 0.95$. The corresponding solvent uptake was evaluated numerically via the mass transport model proposed in [8] and is plotted for comparison. Thus, upon water uptake into the semicrystalline PVA film, the overall amount of crystalline material reduces and crystallinity initially decreases well below its equilibrium value, the time scale matching that of water uptake. As sorption proceeds, the solvent content of the film settles at its steady-state value. Structural rearrangements, however, are not yet completed and at virtually constant water content, crystallinity slowly rises towards its equilibrium value. The observed increase may be attributed to the enhanced segmental mobility in the presence of solvent, entailing three-dimensional ordering of polymer chains and thus the formation of new crystallites.

First results at periodically varying vapour-phase activity further suggest that the semicrystalline polymer structure and its behaviour in a humid environment are perceptibly influenced by manufacturing and polymer thermal history, most notably drying prior to the sorption process.
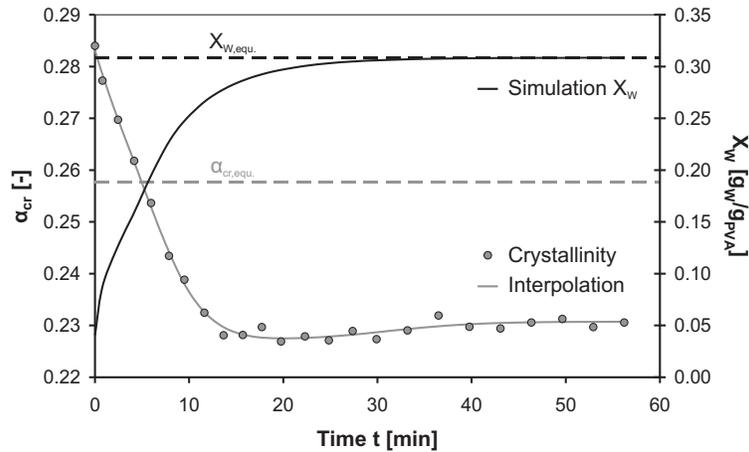
Figure 2: Progression of overall degree of crystallinity α_{cr} and corresponding water content X_W upon vapour-phase sorption into a semicrystalline PVA film. $a_W = 0.95$; $T = 25°C$.

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