350d Dual Mode Transport with Finite Hole-Filling Kinetics in Glassy Polymers

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FTIR-ATR spectroscopy, applied to the study of diffusion in polymer films, has been shown to be a reliable technique for measuring the diffusion coefficient for small molecules from either the vapor or liquid phase in polymers. A unique feature of this technique is its ability to measure concentration at a particular location, namely the interface between the polymer film and the ATR crystal. As a result, it can uncover physical phenomena that can be masked by integral techniques, such as gravimetry and membrane permeation. Recently, using the system acetonitrile in glassy cellulose acetate, the rate at which acetonitrile reached the polymer-ATR interface was longer than predicted from a simple Fickian model, even though the system appears to exhibit Fickian behavior from gravimetric experiments. In addition, desorption experiments exhibit considerably longer "diffusion" time scales when compared to those during sorption.

To explain this behavior, the assumption of local equilibrium in the dual mode transport model was relaxed to include finite rates at which the holes fill and empty during both sorption and desorption. The resulting model fits the experimental data well with physically realistic parameters. This modeling approach could improve our understanding of residual solvent removal from films, organic vapor perturbations in gas separation membranes, and response times in polymer-based sensors.