# The application of model equations to Non-Fickian diffusion observed in Fluoropolymers

Sangwha Lee

Dept. Chemical Engineering, Kyungwon University

San 65 Bokjung-Dong, Soojung-Gu, Seongnam City, Kyunggi-Do, Korea

## INTRODUCTION

The diffusional behavior of many non-solvents in glassy or semicrystalline polymers cannot be adequately described by a concentration-dependent form of Fick's law, especially when mass transfer is coupled with structural changes. Many mathematical models have been devised to interpret non-Fickian diffusion dominated by relaxation kinetics.

In formulation of non-Fickian diffusion mathematics, therefore, the most important factor to consider is how relaxation effects can influence the governing constitutive equation and boundary conditions. That is, relaxation parameters can be accommodated by variable boundary conditions or a modified continuity equation, or both, depending on specific systems and conditions (Frish, 1980).

Accoring to Astarita and Nicolais (1983), the model equations can be broadly categorized as continuous or discontinuous. Continuous model equations encompass phenomena where the structural change takes place gradually over the whole volume of the polymer sample (Crank, 1953; Long and Richman, 1961; Berens and Hopfenberg, 1978). On the other hand, discontinuous model equations deal with the phenomena where the morphological change appears to be abrupt (Li, 1984).

Four mathematical models with different relaxation parameters were applied to fit the anomalous sorption data observed in fluoropolymers (PVDF, ECTFE). The fitted result for PVDF-benzene sorption data is shown in Fig. 1.

## CONCLUSIONS

Based on the best-fit parameter values of various mathematical models, it was concluded that non-Fickian sorption data observed in fluoropolymers could not be fitted by well-known model equations. Crank model indicate that two different mechnisms are involved in sorption data of fluoropolymer-organic chemicals. First, Fickian diffusion with constant diffusion coefficient contributes the total mass uptake and secondly, relaxation mechanism is also involved. In contrast with crank's results, the fitted instantaneous diffusion coefficient was found not to be concentration-dependent and first-order rate coefficient was much less concentration dependent. Long and Richman model could not fit the data adequately with constant diffusion coefficient. This implies that diffusion coefficient is changed during sorption. Berens and Hopfenberg model based on the observation of sorption curves which consisted of quick Fickian diffusion followed by slow relaxation could not also produce good fits. The contributing fraction of Fickian diffusion was found to be

almost zero. This indicates that Fickian diffusion and relaxation process occurs simulataneously. Finally, Li model based on Case II mechnism could not produce good fits.
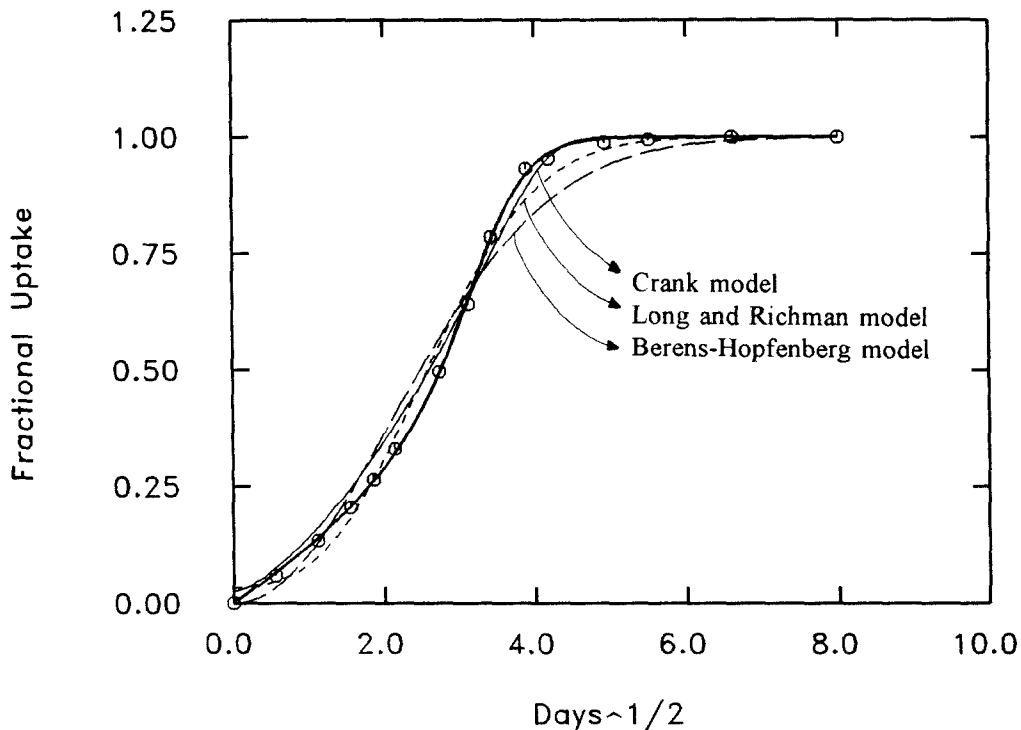


Fig.1 Model fitting of PVDF-benzene sorption data

## REFERENCES

Astarita, G., and L. Nicolais, "Physics and mathematics of Heat and Mass Transfer in POlymers," *Pure & Appl. Chem.*, **55**, 727 (1983).

Berens, A. R., and H. B. Hopfenberg, "Diffusion and Relaxation in Glassy Polymer Powders: 2. Separation of Diffusion and Relaxation Parameters," *Polymer*, **19**, 489 (1978).

Crank, J."A Theoretical Investigation of the Influence of Molecular Relaxation and Internal Stress on Diffusion in Polymers," *J. Polym. Sci.*, **11**,151 (1953).

Long, F. A., and D. Richman, "Concentration Gradients for Diffusion of Vapors on their Relation to Time Dependent Diffusion Phenomena," *J. Am. Chem. Soc.*, **82**, 513 (1960).

Frish, H. L., "Sorption and Transport in Glassy Polymers-A Review," *Polym. Eng. Sci.*, **20**, 2 (1980).