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Recent advances in materials science and synthetic chemistry have led to the development and design of new classes of polymeric materials with desirable and beneficial properties. They are of enormous importance in many industrial and military situations. Most of these materials have features not well understood scientifically and not explainable with current standard equations of motion. We have been looking at several classes of these polymers with the intent of developing the nonlinear models for the study of transport by and through them. The models are then applied to specific new technological problems necessitating the development of new asymptotic, perturbation and numerical techniques for their solutions.

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Dr. Arje Nachman
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Dear Arje:

Final Technical Report
Air Force Grant AFOSR-87-0270
15 July 1987 - 14 December 1988

Recent advances in materials science and synthetic chemistry have led to the development and design of new classes of polymeric materials with desirable and beneficial properties. They are of enormous importance in many industrial and military situations. Most of these materials have features not well understood scientifically and not explainable with current standard equations of motion. We have been looking at several classes of these polymers with the intent of developing the nonlinear models for the study of transport by and through them. The models are then applied to specific new technological problems necessitating the development of new asymptotic, perturbation and numerical techniques for their solutions.

The work is being carried out by Professor Donald S. Cohen and his graduate students. Several problems are being studied jointly with Professor Thomas Erneux of Northwestern University and with the scientific computation and applied math group headed by Dr. Andrew B. White of Los Alamos National Laboratory.

We have developed a comprehensive model for diffusion and stress in polymers to account for the non-Fickian effects observed in the transition from the glassy to the rubbery phase. We have employed this theory to model several different problems involving absorption and/or desorption in polymer slabs, membranes, and encapsulating devices.

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Dr. Arje Nachman/May 2, 1989

Our basic theory recognizes that a diffusion penetrant (gaseous or liquid) induces a differential strain in the polymer host. Thus, we incorporate a visco-elastic flux into our model to account for the experimental observations. Depending on the polymer-penetrant combination different response laws must be used. We have been successful in accounting for several aspects of so-called Case II diffusion and the phenomenon of diffusive overshoot. We are continuing along these lines to look at moisture seepage and gaseous membrane problems in encapsulating devices, material failure as a result of cracks initiated by diffusive penetration, and materials problems associated with pharmaceuticals.

Sincerely yours,

Donald S. Cohen

Donald S. Cohen
Professor and Executive Officer
for Applied Mathematics

DSC/ss
enclosures

cc: Kathleen L. Wetherell/AFOSR (w/enc.)
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Thesis Abstract

A Model For Stress-Driven Diffusion In Polymers

Robert W. Cox

California Institute of Technology

Penetration of solvents into polymers is sometimes characterized by steep concentration gradients that move into the polymer and last for long times. The behavior of these fronts cannot be explained by standard diffusion equations, even with concentration dependent diffusion coefficients. The addition of stress terms to the diffusive flux can produce such progressive fronts. Model equations are proposed that include solvent flux due to stress gradients in addition to the Fickian flux. The stress in turn obeys a concentration dependent evolution equation.

The model equations are analyzed in the limit of small diffusivity for the problem of penetration into a semi-finite medium. Provided that the coefficient functions obey certain monotonicity conditions, the solvent concentration profile is shown to have a steep front that progress into the medium. A formula governing the progression of the front is developed. After the front decays away, the long time behavior of the solution is shown to be a similarity solution. Two techniques for approximating the solvent concentration and the front position are presented. The first approximation method is a series expansion: formulas are given for the initial speed and deceleration of the front. The second approximation method uses a portion of the long time similarity solution to represent the short time solution behind the front.

The addition of a convective term to the solvent flux is shown to raise the possibility of a traveling wave solution. The existence of the traveling wave solution is shown for certain types of coefficient functions. The way the initial front speed evolves onto the traveling wave speed is sketched out.

Publications

1. D.S. Cohen and T. Erneux, Free boundary problems in controlled release pharmaceuticals.
 1. Diffusion in glassy polymers, SIAM J. Appl. Math., 48 (1988) 1451-1465.
2. Donald S. Cohen and T. Erneux, Free boundary problems in controlled release pharmaceuticals.
 2. Swelling controlled release. SIAM J. Appl. Math., 48 (1988) 1466-1474.
3. R.W. Cox, Shocks in a model for stress-driven diffusion, to appear SIAM J. Appl. Math.

Manuscripts In Preparation

1. D.S. Cohen and A.B. White, Sharp fronts due to diffusion and stress at the glass transition in polymers, to be submitted to J. Polymer Science: Physics Edition.
2. D.S. Cohen and R.W. Cox, A mathematical model for stress-driven diffusion in polymers, to be submitted to J. Polymer Science: Physics Edition.

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