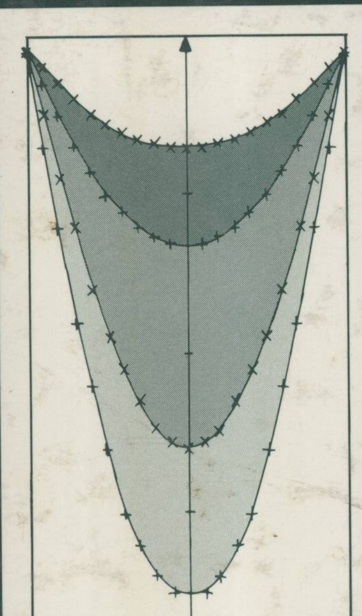

LIQUID TRANSPORT PROCESSES IN POLYMERIC MATERIALS

MODELING AND INDUSTRIAL APPLICATIONS

J.M. VERGNAUD

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Modeling and Industrial Applications

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Preface

This book, devoted to the modeling of liquid transport through various polymers, has several purposes.

First and foremost, the material presented here is concerned with the study of the processes of liquid transports which take place in various solids, and especially in polymers. The focus is to provide the reader with pertinent information on these processes. Through this, it is hoped that a better understanding of the process will be gained, before developing industrial applications in various fields. For example, applications of matter transports are considered in some cases:

- the decrease in the transport of liquid and plasticizer in the case of plasticized PVC in contact with various liquids.
- the control of the rate of delivery of a drug from dosage forms in the patient's stomach, or the rate of release of active agent in water in agricultural applications.

Special consideration is also given to the modeling of the process and to the lastest applications of computer simulation, frequently the only means of solving fundamental problems concerning matter transports through polymers. Emphasis is placed on the method used to build up numerical models, beginning with experiments carried out by using short tests and long real tests, and progressing through numerical analysis and computerization.

Experiments are necessary first to obtain a precise knowledge of the process, then to determine data such as diffusivities, the concentration dependency of diffusivities, and the capacity of absorption, by using short tests, and finally, to test the validity of the model with long real tests performed by varying the operational conditions.

Modeling generally obliges the user to carry out experiments in a more precise way and with more attention, because one has to write down the process and draw its various steps at the end of these experiments. When experimental results do not coincide well with the theoretical results, the model has to be improved, and sometimes the experiments have to be performed in a more precise way.

Numerical methods are built up by writing down the various steps of the process on the flowsheet, and by dealing with the mathematical treatment and numerical analysis. Numerical analysis is sometimes considered the art of making the assumptions and approximations which are necessary to transform differential equations into simple equations in common use by computers. It is then understandable that the best person to make these assumptions is the researcher who is responsible for the development of the process, because with a good knowledge of the process one will be obliged to focus in greater detail on these assumptions, and will try to find the best ones.

Numerical analysis has to be used when mathematical treatment is not capable of finding an analytical solution for the problem. In matter of diffusion, the mathematical treatment is powerful in only simple cases:

- when the diffusivity is constant.
- when the initial conditions are simple, for example, when the concentration of the diffusing substance is uniform in the solid.
- when the material is isotropic.
- when the boundary conditions are simple.

Numerical methods can be used in all cases because all the facts can be taken into account in the model: not only the various initial and boundary conditions, but also the concentration dependency of the diffusivity, as well as the various properties of the materials, isotropic or not.

Moreover, numerical models are of help for the user, bringing many advantages. As it is necessary to draw the process on the flowsheet with the various steps, parameters, and assumptions, researchers must be clear in their ideas, and this is of help for planning the work. After the validity of the model has been tested, a simple coincidence with something wrong in the process may appear when theoretical results coincide well with experiments. More experiements should be conducted under various conditions to make sure that the model describes the process properly in all cases.

As each parameter appears clearly in the model, the role played by all parameters can be determined by simulating the process. The optimization of the process in finding the best values for these parameters is then possible.

Modeling and simulation are often used in industrial applications. For instance, from experiments done on a laboratory scale, results in a full-scale plant process can be evaluated by calculation. In the case of polymeric devices, the dimensions of the device as well as the properties desirable for the polymers can be predicted by calculation in terms of the purpose.

Simulation of the process with the help of the model can help in predicting the behavior of large industrial samples without having to carry out tedious, costly, and time-consuming experiments on the real sample, and without detriment to the material, by using the data determined by short tests performed on small aliquot samples. Modeling is generally of help to reduce the number of experiments, and especially to determine the plan of the experiments necessary for the research.

The book is divided into three parts, and each part consists of many chapters.

The first part presents a general overview of the state of the mathematical treatment of diffusion. It is necessary for researchers to have good background knowledge of the mathematical treatment of diffusion equations to know when analytical solutions are available, and the conditions in which they are obtained, and to know how to determine the values of parameters in proper conditions. For instance, at least two ways can be used for determining the value of the diffusivity: (1) by using the square root dependency of the amount of diffusing substance with time, when this amount is low enough and thus for short times, and (2) by drawing the amount of diffusing substance in logarithmic form in terms of time, when this amount is high enough and thus for long times. Special attention is given to the assumptions made so as to obtain an analytical solution for the problem, because it is necessary to know exactly the conditions upon which the solution is given.

Three chapters are considered in the first part:

- A plane sheet of solid with a diffusing substance in contact with the two faces, the diffusion being conducted under transient or stationary conditions.
- A cylinder, either of infinite length or of finite length. The case of the hollow cylinder is also considered.
- The sphere is also studied, this shape being of interest for various applications.

Two cases of interest are described:

- When the solid is in perfect contact with the liquid by considering a large volume or a finite volume of liquid. Absorption and desorption of the liquid are studied.
- When the solid is in contact with the diffusing substance in a vapor state or with atmosphere, enabling the condensation or evaporation of the substance on the surface which diffuses through the solid.

The second part looks at the concept of numerical analysis in order to accustom researchers to this new way of working. Explicit numerical methods are essentially developed, because they are easily used with microcomputers.

Chapter 4 presents examples of numerical analysis in the case of plane sheets, when diffusion proceeds within the solid with constant or concentration-dependent diffusivities, by using various conditions on the surface.

Chapter 5 describes the numerical treatment for cylinders of infinite and finite length, as well as for hollow cylinders of infinite and finite length (tubing, annulus), when the diffusivity is constant or concentration dependent.

Chapter 6 traces the development of numerical analysis for solid and hollow spheres, with constant and concentration-dependent diffusivities.

Chapter 7 deals with the numerical analysis in the case of three-dimensional transports of matter with various main diffusivities along the three main directions of diffusion.

In the second part, two cases of interest are emphasized:

- When the solid is in perfect contact with the diffusing substance in liquid state, and then the concentration of the liquid on the surface reaches equilibrium as soon as the process starts.
- When the diffusing substance evaporates or condenses from or on the surface, the rate of transport being proportional to the difference between the concentration on the surface and the concentration at equilibrium.

The third part examines various approaches of studies of matter transports controlled by diffusion with different materials and liquids. Chapters 8 through 13 discuss each of the various problems, moving through the difficulties of experiments and calculation, and finally showing industrial applications.

Chapter 8 shows the complexity of the matter transport taking place between plasticized PVC and various liquids, and how powerful the numerical methods are to provide good knowledge of the process. Two matter transports are observed, with the liquid entering the PVC enabling the plasticizer to leave the polymer. Moreover, the kinetics of absorption of the liquid exhibit a maximum. And finally, the diffusivities for each of these two liquids are expressed in terms of the concentrations of the plasticizer and liquid, in such a way that these diffusivities are connected with each other. The knowledge obtained from experiments and models enables one to describe a method of preparation of flexible plasticized PVC with low matter transports.

Chapter 9 deals with the problems of absorption and desorption of liquids with rubber samples of various shapes: sheets, cylinders, tubings, and annuli. From experiments performed with thin sheets made of the same material, the data obtained such as the diffusivity and capacity of absorption (or desorption) are successfully used with the help of models to predict the behavior of large real rubber devices of various shapes.

Chapter 10 focuses on the problems of drug delivery for curing the patient, and the preparation and study of dosage forms able to deliver a drug in the stomach at a constant rate. Simple plane and spherical devices obtained by dispersing the drug in biocompatible polymers are studied, the result being that the liquid enters the polymer, dissolves the drug, and then enables the drug to diffuse through the liquid located in the polymer. More complex devices, consisting of a core and shell with defined properties, are built in order to obtain constant rates of delivery.

Chapter 11 discusses the problem of release of an active agent (insecticide, for example) in water, with application in agriculture. As constant rate of release is desirable for the agent, devices made of a core and shell with special properties are prepared and studied. As for the previous chapter with drug delivery, all parameters characterizing the core and shell (dimensions, nature, and properties of the materials) are determined with the help of the model.

Chapter 12 examines the drying of coatings, which is controlled by diffusion of the solvent through the coating and evaporation on the surface. The problem is not simple, because of the concentration-dependent diffusivity and of the presence of various layers. Nevertheless, the models are able to describe the process and to predict the kinetics of drying for coatings made of one and many layers.

Chapter 13 studies the absorption and desorption of moisture by wood samples of various sizes with one-, two-, and three-dimensional transports. All data, such as the three main diffusivities and their dependency with moisture concentration, and the capacity of absorption (amount of moisture absorbed at equilibrium), are determined in a rather fast way by using thin sheets of wood cut along the main axes of diffusion. The models tested are then able to describe the process of absorption and desorption of moisture, whether the conditions of the surrounding atmosphere are constant or programmed relative humidity, and whatever the shape of the wood samples.

As this book is essentially of practical use, no long literature survey is developed concerning the various theories elaborated on the diffusion of liquids through polymers or wood. In the case of rubber and rubbery materials, the essential results from these theories are summarized, as far as they are of practical use.

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Contents