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Permeation of gases in polymers: parameter identification and nonlinear regression analysis

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Abstract

In numerous previous studies it has been shown that the permeability of gases in polymers depends strongly on the polymer structure, on the gas type, as well as on the conditions of temperature and pressure. The theoretical models that have been proposed and developed in the literature, describe the transport mechanism of molecular species in polymers by diffusion involving a concentration-dependent diffusion coefficient. However, the exact form of this dependency and exact information on the diffusion coefficient and on the solubility coefficient are not always available in the literature, in particular in extreme conditions like in the case of protective polymer coatings for flexible offshore pipes where the temperature and pressure of the diffusing gas can be very high.

Using experimental data from permeation experiments on particularly developed experimental devices at the Institut Français du Pétrole (IFP) we are able to study this dependency and have produced a method which allows to identify the parameters in the model from this data. Mathematically, this leads to a nonlinear least-squares optimisation problem with constraints in the form of partial differential equations (PDEs), which we will concentrate on in this paper. In particular, we will focus on the statistical analysis of the results and give confidence intervals for the estimated parameters. We will also present tests to check whether the assumptions on our model are appropriate and to identify whether the introduction of a concentration-dependent diffusion coefficient is necessary for particular pairs of gas and polymer and at certain temperatures and pressures. We will demonstrate the performance of our method and the statistical analysis of the results on some data obtained with the experimental devices at the IFP.

Keywords: Gas permeation; Semi-crystalline polymers; Mathematical modelling; Gas transport parameters; Confidence regions

1. Introduction

Polymer materials are often used for their good barrier properties, for instance in a number of important practical applications such as food packaging, protective coating, selective barriers for the separation of gases, etc. In the oil environment, one of the main functions of polymers concerns the leak-proof (inner sheath of flexible offshore pipes, O-rings, gas or fuel tanks, selective membranes). In that case and especially in flexible pipes for petroleum transport, materials are in contact with gases at high temperature and high pressure. It is essential to understand some events such as the blistering of the inner sheaths of a flexible pipe (caused by gas absorption in the polymer followed by an explosive decompression), or the corrosion of the metal armour (caused by the diffusion of corrosive gases through the polymer sheath). By developing experimental techniques to study the permeation of gases through thermoplastic polymers at very high pressures and temperatures, we hope to gain a better understanding of the underlying transport phenomena under real conditions.

At the Institut Français du Pétrole (IFP) specific devices have been developed to determine gas transport coefficients in polymers under those extreme conditions [1–7]. They are

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based on a continuous measure of pressure accumulation in a closed receiving chamber and have already been described in detail elsewhere [2]. Recently, a new experiment for measuring mixed gas permeation through thermoplastic polymer membranes has been developed. The technique involves a gas chromatograph as the selective detector for monitoring the variation in penetrant concentration when the gases permeate through the membrane; for details, see [8]. The same set-up can also be used for conducting single gas permeation experiments. The main advantage of this technique is the much better accuracy of the measurements due to the better sensitivity of the detector system.

Using the data obtained with these experimental devices we will describe in the present paper a method based on least-squares optimisation to identify the parameters in a nonlinear diffusion model which describes well the permeation of high-pressure high-temperature gases in semi-crystalline polymers. All the numerical calculations were carried out using MATLAB [9] and they have been included in the software package PermGas for the identification of gas transport parameters from permeation data which is currently being developed at the IFP. Similar methods have already been described in [4,5]. However, here we apply for the first time a rigorous nonlinear regression analysis to check the validity of the proposed model and to determine confidence regions for the identified model parameters. Moreover, in contrast to [4,5] the method which we propose here avoids the use of an estimate for the time-lag which introduces unnecessarily additional numerical error.

In a series of papers Ash et al. [10,11] have also studied nonlinear diffusion models for the permeation of gases in polymers. However, they mainly analyse the form of the permeation curves for different theoretical models of the diffusion coefficient and do not concentrate on the identification of specific model parameters from actual experimental data.

For a more exhaustive literature review on nonlinear diffusion models for the permeation of gases in polymers see [1,10–13] and the references therein.

The paper is organised as follows. At first we recall in Section 2 some of the theory of permeation of gases through polymers and describe our experimental devices. Then we formulate the mathematical models and describe their solution in Sections 3 and 4. We describe the parameter identification in Section 5 and recall some basic tools of nonlinear regression analysis in Section 6. Finally we finish with a series of numerical results from real case studies in Section 7 and conclude in Section 8.

2. Gas permeation theory and the experimental devices

At the molecular level, the understanding of the mechanisms governing the transport of small molecules through polymer membranes is still far from satisfactory. In general, gas permeation in a polymer can be defined as the property of this material to be penetrated and crossed by the gas molecules. It is described by a solution–diffusion mechanism. At a given temperature, the transport of a gas molecule through a homogeneous polymer matrix can be illustrated as a three step process [12]: condensation and solution of the penetrating gas at one surface of the membrane, followed by diffusion through it under the influence of the applied driving force (pressure which corresponds to a concentration gradient) and finally evaporation at the other surface to the gaseous state [14]. All three steps depend on the characteristics of the membrane material and of the penetrant, and have been studied separately with various sorption and diffusion models in the literature (see, for example [1,12,13,15–17]).

Let us now describe the gas transport parameters which we are interested in. The permeability coefficient P is defined to be the product of the solubility coefficient S and the diffusion coefficient D, i.e.

$$P = DS. \tag{2.1}$$

Diffusion is the process by which a small molecule (organic liquid, vapour, gas, etc.) is transferred in the polymer matrix due to random molecular motions. The diffusion coefficient D is a kinetic term that reflects the mobility of the penetrating gas in the polymer phase. The solubility coefficient on the other hand has a thermodynamic origin and depends on the penetrant–polymer interactions as well as on the gas condensability. It is related to the concentration C of the gas dissolved in the polymer and on the gas pressure p. In its simplest form this relationship is expressed in the following form:

$$C = Sp. \tag{2.2}$$

The units which we will use for these quantities are $\mathrm{cm}^2\,\mathrm{s}^{-1}$ for the diffusion coefficient D, $\mathrm{cm}^3\,(\mathrm{STP})\,\mathrm{cm}^{-3}$ for the concentration C and $\mathrm{cm}^3\,(\mathrm{STP})\,\mathrm{bar}^{-1}\,\mathrm{cm}^{-3}$ for the solubility S. Consequently P is expressed in $\mathrm{cm}^3\,(\mathrm{STP})\,\mathrm{bar}^{-1}\,\mathrm{cm}^{-1}\,\mathrm{s}^{-1}$.

Gas transport through semi-crystalline polymers is in general studied following the idea of the two-phase model proposed and developed in [18]. Indeed, for isotropic high-density polyethylene (HDPE) with spherulitic structures, these authors have shown that the sorption and the diffusion takes place exclusively in the amorphous regions. The crystalline zones act as excluded volumes for the sorption process and are impermeable barriers for the diffusion process. Moreover, their existence does not seem to influence the sorption mode in the amorphous phase. We will not extend on that point and on later investigations that have been carried out in [19]. Thus, in the following, the two polymers considered in this paper, polyethylene (HDPE) and polyvinylidene uoride (PVDF), are treated as materials consisting of two phases, namely the impermeable crystalline phase and the permeable amorphous matrix. The latter is in fact rubbery since the test temperature T lies between the glass transition temperature T_g and the melting point T_m.