

Modeling of Fuel Permeation in Multilayer Automotive Plastic Fuel Tanks

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Zohir Benrabah, Francis Thibault and Robert DiRaddo
NRC IMI

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ABSTRACT

A numerical simulation model for predicting the fuel hydrocarbon permeation as well as the barrier layer thickness optimization for multilayer plastic fuel tanks is presented. The diffusion model is based on Fick's laws of diffusion for a steady/unsteady state permeation regime through a multilayer polymeric wall under isothermal condition. A continuum approach based on an homogenization technique is used to model solvent diffusion through an n layer film. The hydrocarbon flux determination through the multilayer film is solved using homogenization techniques that ensure continuity of partial pressure at the polymer-polymer inter-diffusion interface. Since the pinch-off zone is known to be the major source of emission per unit area, a method has been developed to automatically detect it at the end of the extrusion blow molding process and the diffusion model is adapted to adequately evaluate the hydrocarbon permeation through this specific area. Finally a gradient-based algorithm has been implemented to get the optimal barrier layer thickness which satisfies the total hydrocarbon fuel emission constraint. The numerical validation in terms of hydrocarbon flux calculation under steady and non steady state is performed on academic case studies by comparing numerical predictions to the analytical ones. The illustration of the methodology and the gain in terms of weight and fuel permeation, during optimization iterations, will be presented for a plastic fuel tank (PFT) case study.

INTRODUCTION

The uses of PFT continue to grow in the automotive industry. One of the few drawbacks of PFTs with regard to steel or aluminum fuel tanks is that a fuel fraction may permeate

through a polymer material and cause hydrocarbon emissions. For environmental reasons the emissions have to be kept low to avoid smog and green house effects. Because of this, the government has regulated acceptable levels of evaporative fuel emissions for automotive PFT through the sealed housing evaporative determination (SHED) test. One of the methods used by the automotive industry to meet the SHED is by adding thin layers of a low permeability material such as Ethylene-vinyl alcohol (EVOH). These co-extruded multilayer blow molded fuel tanks are now commonly used. In general, the inner and outer layers of PFTs are made of virgin high-density polyethylene (HDPE), whereas the core of the sheet is made of HDPE regrind. To ensure good hydrocarbon barrier properties, the EVOH layer must be positioned in the core of the structure and cross-linked to the inner HDPE and regrind layer with adhesive tie layers of linear low-density polyethylene (LLDPE), to ensure the required adhesion between EVOH and HDPE [1-2]. With this material layers configuration, the low permeability criterion is achieved over most of the fuel tank surface. However it is still common practice in the thermoplastic forming industry to rely on trial and error to find the right configuration/ thickness of the barrier layer required to meet the SHED test. A tool that offers more efficient alternatives based on reliable predictive/virtual analysis of the fuel diffusion throughout multilayer blow molded parts could significantly shorten the design/development cycle by allowing the product prototypes to be analyzed and tested virtually. A first finite element based model that could help a designer to better understand barrier layer properties, was integrated in our BlowView¹ software [3]. The mathematical diffusion model adopted is based on Fick's steady state law to predict hydrocarbon diffusion through a multilayer polymeric wall. Promising

¹BlowView is an engineering simulation software developed at IMI-NRC that can handle extrusion blow molding, injection blow molding, stretch blow molding and thermoforming [4, 5, 6].

results in term of fuel flux and fuel permeation were obtained with this first version of BlowView.

The goal of this work is to generalize the previous permeability model to expand our predictive permeation capabilities for automotive PFTs to both steady and unsteady state regimes. The problem zone for automotive PFTs is the pinch-off zone where EVOH layers (or other barrier materials) are highly compressed and can ultimately vanish. Therefore, adequate prediction of fuel permeation in this specific area is of utmost importance. The pinch off zone is automatically detected at the end of the extrusion blow molding process and a modified diffusion model is applied that evaluates adequately the fuel permeation through this specific area under steady/unsteady states regime. Finally the fuel emissions test for PFT is analyzed for both steady and unsteady state via simulation and a sensitivity analysis is performed to show the impact of barrier layer percentage on fuel emissions.

THE PERMEATION MECHANISM

The permeation mechanism occurs in three main phases: The first phase is the absorption of the permeant (fuel) into the polymer that occurs at the upstream side of the polymer wall. The second phase is the diffusion of the permeant from the surface to the core of the polymer due to the concentration gradient. Finally the permeant desorbs on the downstream side of the membranes and is removed from the surface by evaporation to the surrounding air.

MATHEMATICAL MODEL

Given the inherently low diffusivity of plastics and the special geometrical configuration of a blow formed part which is relatively thin compared to their surface area, unilateral diffusion is usually assumed to be one dimensional through the thickness. The one-dimensional flux of the permeant transported through the polymer per unit area (A) and unit time (t) is given by Fick's first law [7-8]:

$$J = -D \frac{\partial C}{\partial x} \quad (1.a)$$

The diffusion equation for a constant diffusivity D is given by the following Fick's second law expression:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1.b)$$

where C is the liquid concentration in the polymer matrix, t is the time, and x the distance through the thickness. The initial and boundary conditions are:

$$t = 0 \quad 0 < x < h \quad C = C_0 \quad (2)$$

$$t > 0 \quad x = 0 \quad C = C_s \quad (3)$$

$$t > 0 \quad x = h \quad C = C_0 \quad (4)$$

The measurement of surface concentrations (C) is not always a simple task. From Henry's law (5) where S is Henry's solubility coefficient (the solubility coefficient of the permeant in the polymer) and p is the vapor pressure of the fuel.

$$C = S \cdot p \quad (5)$$

If the solubility S is assumed to be constant the flux (J) can be expressed in terms of the variation of the vapor pressure, p.

$$J = -P \frac{\partial p}{\partial x} \quad (6)$$

where P is the permeability defined as the product of the solubility and diffusivity coefficients of the material which obeys the Fick's law:

$$P = S \cdot D \quad (7)$$

The set of partial differential equations (1), (2), (3), (4) can be transformed as follows, [7, 8, 9, 10, 11]:

$$S \frac{\partial p}{\partial t} = P \frac{\partial^2 p}{\partial x^2} \quad (8)$$

$$t = 0 \quad 0 < x < h \quad p = p_0 \quad (9)$$

$$t > 0 \quad x = 0 \quad p = p_s \quad (10)$$

$$t > 0 \quad x = h \quad p = p_0 \quad (11)$$

where p_s is the saturated vapor pressure of the fuel.

PERMEATION THROUGH A MULTILAYER POLYMERIC WALL

The inter-diffusion variables and hydrocarbon flux determination through the multilayer polymeric materials is solved using homogenization techniques and by assuming

continuity of the partial pressure at the polymer/polymer inter-diffusion interface. The penetrate diffusivity and solubility for each layer are assumed to be constant.

STEADY-STATE PERMEATION

Steady state permeation produces a linear piecewise vapor pressure profile in each layer (green dashed line) as illustrated in [Figure 1](#).

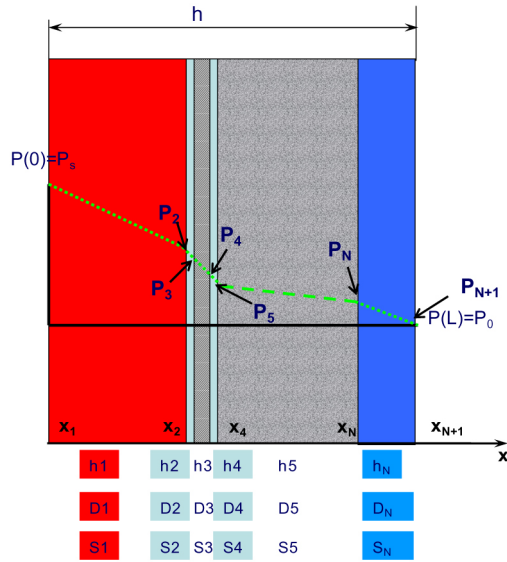


Figure 1. Schematic of n layer film for steady-state continuous saturated pressure profiles.

The permeant profile in the polymer layers is obtained by solving the following boundary value problem [12].

$$D_i \cdot S_i \cdot \frac{\partial^2 p_i}{\partial x^2} = 0 \quad \text{where } i = 1, 2, \dots, N \quad (12)$$

with boundary conditions:

$$\begin{cases} p_j(x_{j+1}) = p_{j+1}(x_{j+1}) \\ S_j D_j \frac{\partial p_j}{\partial x} \Big|_{x_{j+1}} = S_{j+1} D_{j+1} \frac{\partial p_{j+1}}{\partial x} \Big|_{x_{j+1}} \end{cases} \quad \text{at } x = x_{j+1} \text{ where } j = 1, 2, \dots, N-1 \quad (13)$$

and

$$p_1 = p(x_1) = p_s \quad \text{at } x = x_1 = 0 \quad (\text{upstream side}) \quad (14)$$

$$p_{N+1} = p(x_{N+1}) = p_0 \quad \text{at } x = x_{N+1} = h \quad (\text{downstream side}) \quad (15)$$

The interlayer vapor pressure value p_j can be obtained by combining [equation \(12\)](#), [\(13\)](#), [\(14\)](#), [\(15\)](#), and will produce in the case of a constant diffusivity D_j and solubility S_j the following equation:

$$p_{j+1} = (p_{N+1} - p_1) \cdot \frac{R_{EQ}^j}{R_{EQ}} + p_1 \quad (16)$$

where

$$R_{EQ}^j = \sum_{i=1}^j \left(\frac{h_i}{S_i D_i} \right) \quad \text{for } j = 1, 2, 3, \dots, N \quad (17)$$

and

$$R_{EQ} = \sum_{i=1}^N \left(\frac{h_i}{S_i D_i} \right) \quad (18)$$

where h is the total thickness of the multilayer membrane and h_j the specified thickness of layer i .

The discontinuous fuel concentration at the inter-diffusion interface is obtained from [equation \(16\)](#):

For the left hand side of the inter-diffusion interface j :

$$C_j^{Left} = S_j \cdot p_j \quad \text{for } j = 2, 3, \dots, N \quad (19)$$

For the right hand side of the inter-diffusion interface j :

$$C_j^{Right} = S_{j+1} \cdot p_j \quad \text{for } j = 2, 3, \dots, N \quad (20)$$

The average concentration at the inter-diffusion interface is obtained by averaging the previous left and right quantities:

$$C_j^{av} = \frac{C_j^{Right} + C_j^{Left}}{2} \quad \text{for } j = 2, 3, \dots, N \quad (21)$$

The concentration at the upstream and downstream side of the polymer membranes is given respectively by the following equations:

$$C_1 = S_1 \cdot p_1 \quad \text{and} \quad C_{N+1} = S_N \cdot p_{N+1} \quad (22)$$

Applying an homogenization technique, assuming continuity of the partial pressure at the inter-diffusion interface, integrating [\(12\)](#) across the total local thickness of the gas tank

h , and interpolating between the two saturated vapor pressures, yields the following expression for the fuel permeation rate (FPR):

$$FPR = J = -\frac{P_{EQ}}{h} \cdot (p_{N+1} - p_1) \quad (23)$$

with

$$P_{EQ} = \frac{h}{R_{EQ}} = \frac{h}{\sum_{j=1}^n \frac{h_j}{D_j S_j}} \quad (24)$$

UNSTEADY-STATE PERMEATION

Under unsteady-state permeation condition, the analytical expression of the FPR is adapted from [12]:

$$FPR = J(t, x) = -\frac{P_{EQ} \cdot (p_{N+1} - p_1)}{h} + P_{EQ} \cdot \frac{n\pi}{h} \cdot \frac{2}{h} \sum_{n=1}^{\infty} \exp\left[-D_{EQ} \frac{n^2 \pi^2}{h^2} t\right] \times \cos\left[\frac{n\pi}{h} x\right] \times \int_0^L p_0 \sin\left[\frac{n\pi}{h} x\right] dx + P_{EQ} \cdot \frac{2}{h} \sum_{n=1}^{\infty} \exp\left[-D_{EQ} \frac{n^2 \pi^2}{h^2} t\right] \times \cos\left[\frac{n\pi}{h} x\right] \times \left(p_{N+1} \cos\left[\frac{n\pi}{h} x\right] - p_1\right) \quad (25)$$

with

$$D_{EQ} = \frac{h}{\sum_{j=1}^n \frac{h_j}{D_j}} \quad (26)$$

Note that as time t increases (steady state), the expression for the FPR (25) simplifies to (23).

From the FPR expression, the Fuel Mass Rate (FMR) that permeates through a wall of polymeric membrane area A at the downstream side in time t , is given by the following expressions:

$$FMR = \frac{dM(t, x=h)}{dt} = \int_A J(t, x) \cdot dA = A \cdot J(t, x=h) \quad (27)$$

FINITE ELEMENT FORMULATION

For a thin walled container such as a PFT, all of the previous inter-diffusion variables i.e. p_j , C_j as well as the expression for FPR and MFR are directly applied within each finite element mesh of the co-extruded fuel tank shell.

Therefore for each shell element e with area A_e we can define the quantities below:

$$p_{j+1}^e = (p_{n+1} - p_1) \cdot \frac{R_{EQ}^j}{R_{EQ}} + p_1 \quad (28)$$

where

$$R_{EQ}^j = \sum_{i=1}^j \left(\frac{h_i^e}{S_i D_i} \right) \quad \text{for } j = 1, 2, \dots, N \quad (29a)$$

$$R_{EQ} = \sum_{i=1}^N \left(\frac{h_i^e}{S_i D_i} \right) \quad \text{for } j = 1, 2, \dots, N \quad (29b)$$

and

$$C_j^{Left} = S_j \cdot p_j^e \quad \text{for } j = 2, \dots, N \quad (30a)$$

$$C_j^{Right} = S_{j+1} \cdot p_j \quad \text{for } j = 2, \dots, N \quad (30b)$$

$$C_j^{av} = \frac{C_j^{Right} + C_j^{Left}}{2} \quad \text{for } j = 2, \dots, N \quad (30c)$$

The elementary FPR is given by:

$$FPR^e = J^e(t, x) = \frac{P_{EQ} \cdot (p_{N+1} - p_1)}{h} + P_{EQ}^e \cdot \frac{n\pi}{h} \cdot \frac{2}{h} \sum_{n=1}^{\infty} \exp\left[-D_{EQ}^e \left(\frac{n\pi}{h^e}\right)^2 t\right] \times \cos\left[\frac{n\pi}{h^e} x\right] \times \int_0^L p_0 \sin\left[\frac{n\pi}{h^e} x\right] dx + P_{EQ}^e \cdot \frac{2}{h} \sum_{n=1}^{\infty} \exp\left[-D_{EQ}^e \left(\frac{n\pi}{h^e}\right)^2 t\right] \times \cos\left[\frac{n\pi}{h^e} x\right] \times \left(p_{N+1} \cos\left[\frac{n\pi}{h^e} x\right] - p_1\right) \quad (31)$$

with

$$P_{EQ}^e = \frac{h^e}{\sum_{j=1}^n \frac{h_j^e}{D_j S_j}} \quad \text{and} \quad D_{EQ}^e = \frac{h^e}{\sum_{j=1}^n \frac{h_j^e}{D_j}} \quad (32)$$

h^e and h_j^e being respectively the total thickness and the thickness of layer j for the current finite element e .