Computers and Chemical Engineering 50 (2013) 152–183

Contents lists available at SciVerse ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

Finite element solution of coupled-partial differential and ordinary equations in multicomponent polymeric coatings

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ARTICLE INFO

Article history:
Received 11 July 2012
Received in revised form 25 October 2012
Accepted 31 October 2012
Available online 20 November 2012

Keywords:
Coupled partial differential equations
MATLAB solution
Multicomponent polymeric coatings
Free volume theory
Galerkin's method of finite elements

ABSTRACT

Mass transport equations in multicomponent polymeric coatings are nonlinear coupled partial differential equations. These equations were solved using Galerkin's method of finite elements which converts them to ordinary differential equations. Residuals were made orthogonal by using quadratic basis functions. Non-uniform elements were used to capture steep concentration gradient near the top of the coating. Finite element formulation has been solved using ode15s of MATLAB. Results are in very good agreement with the earlier results using different solution techniques.

1. Introduction

Diffusion is usually the rate controlling step during transport in many polymer solvent systems. Fick's law of diffusion, states that the flux of a diffusing component at a location equals the product of diffusion coefficient and its concentration gradient there. For polymer solvent systems, the diffusion coefficient is a strong function of temperature and concentration. Free volume theory (Vrentas & Duda, 1977a, 1977b) describes this function accurately for several systems involving one polymer and one solvent.

Flux of the solvent at a location in multicomponent systems is determined by not only its concentration gradient but also those of others. The diffusion coefficient of the solvent, which combines with its own concentration gradient is called main-term coefficient and those that combine with gradient for other solvents are called cross-term coefficients. In fact, to describe diffusion in a N-component system, $(N-1)^2$ mutual diffusion coefficients are needed.

Recently, a unified theory (Price & Romdhane, 2003) is proposed of which the existing theories are special cases. They showed that the theories predict almost same average concentration of solvent in a drying ternary coating. But, they could predict different concentration profile of the solvent inside the coating. Such profiles are important in coatings that phase separate during drying.

Transport equations in multicomponent polymer–solvent–solvent systems are non-linear coupled partial differential equations. This paper deals with the solution scheme and the optimization of free-volume parameter required for diffusion models.

2. Governing equations

Fig. 1 shows the schematic of a drying ternary coating that has been cast on impermeable substrate. As the solvent reaches the surface from the bottom, it evaporates into air. As solvents depart, the coating shrinks with time. There is no mass transfer through the substrate; hence flux of both the solvents is zero at the substrate. The coating is heated from both the top and bottom sides.

2.1. Mass transport

The rate of change of concentration of solvent 1 equals gradient of flux, which is due to its own concentration gradient and that of solvent 2.

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http://dx.doi.org/10.1016/j.compchemeng.2012.10.015

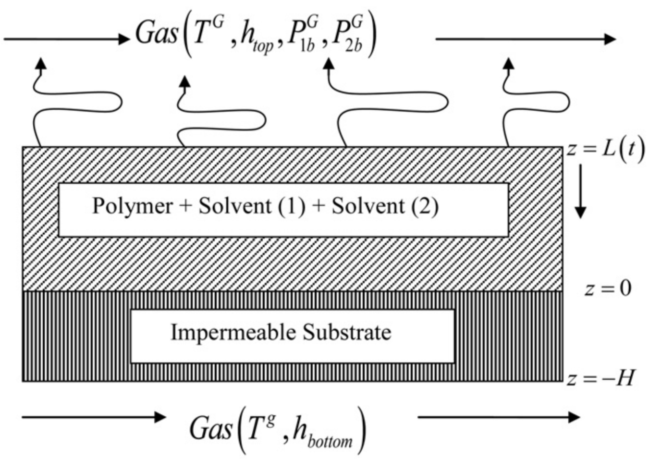

Fig. 1. Schematic of a drying coating.

Mass balance for solvent 1:

$$\frac{\partial c_1}{\partial t} = \frac{\partial}{\partial z}\left(D_{11}\frac{\partial c_1}{\partial z}\right) + \frac{\partial}{\partial z}\left(D_{12}\frac{\partial c_2}{\partial z}\right) \tag{1}$$

Mass balance for solvent 2:

$$\frac{\partial c_2}{\partial t} = \frac{\partial}{\partial z}\left(D_{21}\frac{\partial c_1}{\partial z}\right) + \frac{\partial}{\partial z}\left(D_{22}\frac{\partial c_2}{\partial z}\right) \tag{2}$$

The reference velocity is chosen to be volume average velocity because it is shown to be equal to zero if there is no change in volume on mixing [4].

c_i, is the concentration of solvent i, t is the time, z, is the thickness of the coatings at anytime, D_{11} and D_{22} are main-term diffusion coefficients that characterize transport due to solvents own concentration gradient, D_{12} and D_{21} are cross-term diffusion coefficients that characterize transport due to other solvents concentration gradient.

Mutual diffusion coefficients were calculated using multicomponent diffusion models. There are several models available to relate self-diffusion coefficient to mutual diffusion coefficient (Alsoy & Duda, 1999; Dabral, 1999; Price & Romdhane, 2003; Zielinski & Hanley, 1999). In this work only Alsoy and Duda model has been used and given in Table 1.

Self diffusion coefficients were calculated using Vrentas and Duda (1977a, 1977b) free volume theory:

$$D_i = D_{0i}\exp\left(-\frac{\sum_{j=1}^{3}\omega_j \hat{V}_j^*(\xi_{i3}/\xi_{j3})}{\hat{V}_{FH}/\gamma}\right) \tag{3}$$

$$\xi_{i3} = \frac{\text{critical molar volume of a jumping unit of component } i}{\text{critical molar volume of the jumping unit of the polymer}}$$

$\xi_{i3} = \frac{\hat{V}_i^* M_{ji}}{\hat{V}_3^* M_{j3}}$ (Vrentas, Duda, & Ling, 1984), and

The hole free volume is given by:

$$\frac{\hat{V}_{FH}}{\gamma} = \frac{K_{11}}{\gamma}\omega_1(K_{21} + T - T_{g1}) + \frac{K_{12}}{\gamma}\omega_2(K_{22} + T - T_{g2}) + \frac{K_{13}}{\gamma}\omega_3(K_{23} + T - T_{g3}) \tag{4}$$

ω_j: mass fraction of component j

$\left(\frac{K_{11}}{\gamma}, K_{21} - T_{g1}\right)$ and $\left(\frac{K_{12}}{\gamma}, K_{22} - T_{g2}\right)$ are free volume parameters for solvent 1 and solvent two respectively

$\frac{K_{13}}{\gamma}, K_{23} - T_{g3}$: are free volume parameters for polymer

Table 1
Four cases for diffusion coefficients of ternary polymer solvent systems (Alsoy & Duda, 1999).

Case	D_{11}	D_{12}	D_{21}	D_{22}
1	$D_1\left[\frac{\partial \ln a_1}{\partial \ln c_1}\right]$	$\frac{c_1}{c_2}D_1\left[\frac{\partial \ln a_1}{\partial \ln c_2}\right]$	$\frac{c_2}{c_1}D_2\left[\frac{\partial \ln a_2}{\partial \ln c_1}\right]$	$D_2\left[\frac{\partial \ln a_2}{\partial \ln c_2}\right]$
2	$D_1\left[\frac{\partial \ln a_1}{\partial \ln c_1}\right]$	0	0	$D_2\left[\frac{\partial \ln a_2}{\partial \ln c_2}\right]$
3	D_1	0	0	D_2
4	$D_1c_1(1-c_1\hat{V}_1)\left[\frac{\partial \ln a_1}{\partial c_1}\right]$ $-D_2c_1c_2\hat{V}_2\left[\frac{\partial \ln a_2}{\partial c_1}\right]$	$D_1c_1(1-c_1\hat{V}_1)\left[\frac{\partial \ln a_1}{\partial c_2}\right]$ $-D_2c_1c_2\hat{V}_2\left[\frac{\partial \ln a_2}{\partial c_2}\right]$	$D_2c_2(1-c_2\hat{V}_2)\left[\frac{\partial \ln a_2}{\partial c_1}\right]$ $-D_1c_1c_2\hat{V}_1\left[\frac{\partial \ln a_1}{\partial c_1}\right]$	$D_2c_2(1-c_2\hat{V}_2)\left[\frac{\partial \ln a_2}{\partial c_2}\right]$ $-D_1c_1c_2\hat{V}_1\left[\frac{\partial \ln a_1}{\partial c_2}\right]$