



Review

Diffusion in polymeric systems—A review on free volume theory

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ABSTRACT

This review paper deals the history and development of various theories to predict the diffusion in polymeric systems. The basis and application of various theories with the prediction capabilities are discussed. The most commonly used theory is Vrentas and Duda free volume theory with excellent agreement with experimental data report so far. This theory predicts the data very accurately in rubbery region. However, few modifications have come up in this theory to predict the diffusion above the glass transition with a little success.

1. Introduction

In this era, there are lot of research and advancements have been done in the field of polymer engineering and technologies which enhances the versatility in the application of polymer materials ranging from home made to industries.

Polymer coatings are being produced in very large scale and find applications in each and every field of engineering. Polymeric coatings have numerous applications like magnetic tapes, storage devices, optical film and fiber, membrane and filters, multiphase gels, functional films, biomedical, controlled drug delivery, pharmaceutical products, food packaging, protective films, and decorative films etc [1–8]. Coatings are being made using polymers and applied using thinner. Combinations of thinner are being used to dilute the coating solution in order to get smooth and uniform surface morphology. Solvent should be cheap, environmental friendly and amenable for easy recovery from the coating without generating any production defects like blisters, cracks, wrinkles etc. These production defects can be controlled by minimizing the residual solvent(s) within the coating. The residual solvent in polymeric coating can be mathematically minimized by use of proper diffusion model and to use these modeled variables to get the real product without defects. The diffusion of penetrant in polymeric system is studies using free volume theory and there are so many free volume theories have appeared in the literature and these literatures are very scattered and not documented properly. This work summarizes all available free volume theories with their merits and demerits.

2. Various free volume theory models

Fujita [9] and Vrentas et al. [10] discussed free volume theories

named Fujita and Vrentas and Duda theory [11,12] and also gave the new evidence of Fujita – Kishimoto theory based on the composition dependency of the fractional free volume. Free volume is introduced such as the molecules travels in liquid have large freedom of motion comparable to solids and the molecules can be shifted thermally over a distance of macroscopic scale. This feature identifies the existence of holes or interstitial space for which each and every molecule can move freely and a measure of this quantity of free space.

The molecular mobility can be calculate using Cohen and Turnbull [13] expression for pure liquids-

$$\ln m = \ln m_0 - \gamma v_0/v_f$$

The mobility of either jumping unit is governed by average free volume per jumping unit as per Vrentas and Duda Theory [11,12]. The jumping unit mobility and its composition dependency can be calculated using pure component properties. Doolittle [14] proposed for viscosity of pure liquids, $\ln \eta = A' - B/f$, where A' and B are constants

Specific free volume of the solution is, $V_f = V - V_M$

Total number of jumping units, N is, $N = N_A(w_s/M_s + w_{pj}/M_{pj})$

Vrentas and Duda extended Cohen and Turnbull Theory and given expression for, m_s as following

$$\ln m_s = \ln m_{s0} - \gamma V_s M_s N / N_A V_f$$

Vrentas and Duda expression of V_m is given by

$$V_M = w_s V_{Ms}(0) \exp\left(\int_0^T \alpha_{cs} dT\right) + w_p V_{Mp}(0) \exp\left(\int_0^T \alpha_{cp} dT\right)$$

Relation between Fujita – Kishimoto theory [15] and Vrentas and Duda Theory [11,12] is

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Nomenclature

E_A, E_i	Activation energy
D_1	Solvent self diffusion coefficient
R	Universal gas constant
T	Temperature
f^{dyn}	Fractional free volume as defined by the fujita theory
f_s^{dyn}	Value of f^{dyn} for pure solvent
f_p^{dyn}	Value of f^{dyn} for pure polymer
V_f	Free volume as defined by the hole volume definition
V	Total volume of a system
V_o	Total core volume of molecules
f	Fractional free volume as defined by the hole volume definition
E	Constant in the Cohen-Turnbull equation
m	Mobility of a liquid molecule
γ	Numerical factor between 0.5 and 1
v_f	Free volume per jumping unit
ϕ_s	Volume fraction of solvent
$\tilde{\rho}$	Reduced mass density
ρ	Mass density
\hat{V}_{FH2}	Polymer specific hole free volume
\tilde{P}	Reduced pressure
\tilde{T}	Reduced temperature
Y	Transport property: D, η or λ
Ω	Weight fraction activity coefficient
φ	Volume fraction
ω	Weight fraction
x_i	Mole fraction of component i
c	Combinatorial property

fv	Free-volume property
h	Hardcore molecular property
\hat{V}_i^*	Specific critical hole free volume of component i
\hat{V}_i^0	Specific volume of pure component i
ξ	Ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit
m_s	Molecular mobility
m_o	Constant having dimension of m
v_c	Volume of a minimum hole (or critical free volume)
E_v	Height of the potential barrier between equilibrium positions
$A_{\sigma,B}$	Constants
D_i^∞	Infinite-temperature diffusivity of species i
\bar{V}_{ij}^*	Critical volume of a species i jumping unit
\bar{V}_{ij}	Average hole free volume per jumping unit
\bar{V}_i	Partial molar volume of species i
D_{ik}^0	Infinite-dilution diffusivity of species i in k
$\hat{V}_{pen.}^*$	Molecular core volume
$D_{s,pen.}$	Self-diffusivity of penetrant molecule
$D_{0,pen.}$	Preexponential factor of penetrant molecule
M_i	Molecular weight of component i
N_A	Avogadro's number
s_i	Molecular surface area of component i
$V_{f,i}/\gamma$	Free volume of component i
ω_i	Weight fraction of component i
pen.	Penetrant molecule
η	coefficient of viscosity

$$\ln \frac{m_s(\phi_s)}{m_s(0)} = \frac{\bar{B}\bar{\beta}V\phi_s}{V(p)f_p^2 + \bar{\beta}f_pV\phi_s}$$

In Fujita Theory, the mobility of either jumping unit is governed by free volume per unit volume of solution through equation given below. He determined the temperature and composition dependence of f in actual polymer solutions from appropriate mobility data.

$$\ln m = A' - B/f$$

In a binary solution mono-dispersed polymer and pure solvent are present which were assumed as a single solvent molecule [16]. Doolittle [14] gave the expression of fraction free volume, $f = \frac{V_f}{V}$, where, V_f : free volume, V : volume of liquid, and $V_f = V - V_o$. The major drawback of Fujita theory was that there was no clear physical understanding for f^{dyn} , in contrast to f . The motion of jumping unit is given in terms of the quantity f^{dyn} which is indication of free space in polymeric system.

The Vrentas-Duda theory [11,12] showed theoretically that in a pure liquids mobility of a molecule is given by, $\ln m = E - \gamma \frac{v}{v_f}$. The Vrentas-Duda extended the Cohen-Turnbull theory [17] by adding critical hole free volume. This theory allows to calculate the jumping unit of polymer and solvent. The total free volume expression is given by $f^{\text{dyn}} = f_s^{\text{dyn}}\phi_s + f_p^{\text{dyn}}(1 - \phi_s)$, where f_s^{dyn} and f_p^{dyn} are the solvent and polymer free volumes respectively.

Vrentas and Duda [11,12] reevaluated free volume of diffusion and also determined the self-diffusion coefficient and specific free volume for the polymeric systems. In Polymer-solvent systems, the relation of mutual diffusion coefficient D and friction coefficient ζ_{12} are as follows:

$$D = \frac{M_2\rho_1\hat{V}_2}{N_A^2\zeta_{12}} \left(\frac{\partial\mu_1}{\partial\rho_1} \right)_{T,P} = \frac{M_1\rho_2\hat{V}_1}{N_A^2\zeta_{12}} \left(\frac{\partial\mu_2}{\partial\rho_2} \right)_{T,P}$$

Similarly, the self-diffusion coefficient D_1 and D_2 is correlated with the friction coefficients ζ_{11} , ζ_{12} , ζ_{22} are as follows:

$$D_1 = \frac{RT}{N_A^2(\rho_1\zeta_{11}/M_1 + \rho_2\zeta_{12}/M_2)}, D_2 = \frac{RT}{N_A^2(\rho_2\zeta_{22}/M_2 + \rho_1\zeta_{12}/M_1)}$$

The two parameter theory is dependent on the concentration of diffusion coefficient for dilute polymer solutions. They reconsidered the free volume theory and its parameters which are applied for diffusion in polymer solvent mixtures.

Humada et al. [18] have proposed the modification of Flory theory which is applicable in both poly (dimethylsiloxane) solvent system and poly (isobutylene) systems for determination of excess volume. In the binary mixture, Flory assumed that segments were random to be of equal molecular core volume. The segments of core volume in the binary mixture is as follows:

$$v^* = \sigma_1^2 v_1^* + 2\sigma_1\sigma_2 v_{12}^* + \sigma_2^2 v_2^*, \text{ where, } v_{12}^* = \zeta[(v_1^{*1/3} + v_2^{*1/3})/2]^3$$

For both poly (dimethylsiloxane) and poly (isobutylene) systems, the author found that the modified Flory theory can imitate the experimental values like χ , $\Delta H^m(\infty)$ and V^E/V^o .

Vrentas et al. [19,20] had performed validation of free volume and self-diffusion theories with the experimental data and found that experimental data favors Vrentas-Duda free volume theory [11,12] over the Paul version of the theory in most of the cases. In this work, the author has studied the theoretical and conceptual difference in both Paul version and Vrentas-Duda free volume theory [11,12]. They found that effect of temperature on diffusion energy is minor and given by Vrentas et al. [19] expression as following:

$$E_D = RT^2 \left(\frac{\gamma\xi\hat{V}_2^* (\partial\hat{V}_{FH}/\partial T)_P}{\hat{V}_{FH}^2} \right)$$

Paul theory [21] assumed that the free volume is randomly distributed among all units of mass in the solution. The following relation was suggested by Paul for solvent self-diffusion coefficients are as follows:

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