



On the diffusion phenomenon of solvent within polymeric coatings: Development of a new model



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ABSTRACT

Diffusion phenomenon of solvent molecules within the polymeric coatings has a great influence on their properties. To study this phenomenon, a new semi-empirical model was developed using the combination of a theoretical model proposed based on the Fick's second law of diffusion with the empirical technique of coating capacitance measurement. The proposed model has both a simple form and high ability to deal with the diffusion behavior over the whole of immersion time. Additionally, the parameters of the diffusion coefficient and the type (Fickian or non-Fickian) were precisely calculated by fitting of the proposed model to the literature experimental data. According to this modeling approach, the diffusion coefficient has no constant value and reduces over the immersion time.

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1. Introduction

Once a polymeric coating is exposed by a solution environment, the solvent molecules penetrate within the coating structure. This phenomenon can affect on the physical properties of coating such as electrical [1,2] and its anticorrosion behavior [2]. So far, investigating the water uptake of polymeric coatings has been attracted a great deal of interest in many studies [1,3–6] in them, the water uptake of coatings has been commonly determined by measurement of the electrical properties such as the dielectric constant. In this regard, the earliest work was made by Hartshorn [7] who proposed a mixing rule equation relating the water content to the dielectric constant of a coating as the following:

$$\varepsilon_t = \varepsilon_c^{V_c} \varepsilon_a^{V_a} \varepsilon_w^{V_w} \quad (1)$$

in this equation, the parameters of ε and V are the dielectric constant and volume fraction, respectively and subtitles denote as c : dry coating, a : air, w : water as a representative of solution components and t : instant of immersion time.

Frequently, researchers have utilized the parameter of coating capacitance instead of the dielectric constant in Eq. (1) due to readily measurement of the capacitance property during immersion

time. However, these two parameters are related to each other by the following well-known equation: [2,8]

$$C_t = \frac{\varepsilon_t \varepsilon_0 A_s}{L} \quad (2)$$

where C_t is the coating capacitance at an instant of immersion time, ε_0 the dielectric constant of vacuum ($8.854 \times 10^{-12} \text{ Fm}^{-2}$), A_s the coating surface area and L the thickness of coating. In this context, an applied coating is simulated as an electrical element of capacitance [9]. Furthermore, it has been generally accepted that the change of coating capacitance value during the immersion time is arisen from the variation of the dielectric constant under penetration of solution molecules within a coating [1].

Based on this approach, several correlations have been proposed for relating the solution content of coating to its capacitance. Early, Brasher and Kingsbury (in 1954) [6], suggested the following correlation to estimate the water content of coating:

$$V_w = \frac{\log(C_t/C_0)}{\log \varepsilon_w} \quad (3)$$

where C_0 is the coating capacitance at the initial time of immersion. Later, Castela et al. [1] introduced a relation for a binary system consists of coating and water as:

$$V_w = \frac{C_t - C_0}{C_w - C_0} \quad (4)$$

However the estimation of water content is convenient by using the capacitance technique, it is actually time consuming for all over the immersion time. Moreover, it provides no information

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Nomenclature

A	Fickian diffusion parameter
A_s	Surface area of coating (m^2)
C_0	Capacitance of dry film (F)
C_∞	Capacitance of saturated film (F)
C_t	Capacitance of coating in an instance time (F)
D	Diffusion coefficient (cm^2/s)
D_{ave}	Average diffusion coefficient for the proposed model (cm^2/s)
K	Non-Fickian diffusion parameter
$K'(t)$	Non-Fickian diffusion function of immersion time
$K'(T)$	Non-Fickian diffusion function of reduced immersion time
L	Thickness of coating (m)
M_∞	Amounts of solvent accumulated in coating till saturation point (kg)
M_t	Total amounts of solvent accumulated within coating till an instance time t (kg)
n	Exponent of diffusion
T	Reduced immersion time
t	An instant of immersion time (s)
t_{sat}	Saturation time (s)
V_a	Volume fraction of air
V_c	Volume fraction of coating
V_w	Volume fraction of water
$V_{w\infty}$	Volume fraction of water at saturation point

Greek

α	Model constant
β	Model constant
ϵ_0	Dielectric constant of vacuum (8.854×10^{-12} F/m)
ϵ_a	Dielectric constant of air
ϵ_c	Dielectric constant of coating
ϵ_t	Total dielectric constant
ϵ_w	Dielectric constant of water
ρ	Density of water (gr/cm^3)

Acronyms

CM	Continuous model
DM	Discrete model
DWC	Dimensionless water content

Subscripts

a	Air
c	Coating
w	Water

about the diffusion parameters. Therefore, some of researchers have applied the modeling approach of diffusion phenomenon within a coating [10–13]. Traditionally, the modeling approach has been developed based on the Fick's second law and the general solution after applying the appropriate boundary and initial conditions leads to the following equation: [8,11]

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{L^2} \right)^{0.5} \times \left(\frac{1}{\pi^{0.5}} + 2 \sum_{n=0}^{\infty} (-1)^n \operatorname{erf} \frac{nL}{2(Dt)^{0.5}} \right) \quad (5)$$

where the terms of M_t and M_∞ represent the total amounts of solvent accumulated in the coating till the immersion time of t and infinite (i.e. saturation time), respectively and the parameter D is the diffusion coefficient. In the present work, the ratio of M_t/M_∞ is defined as a new parameter namely dimensionless water content (DWC). The exponent of 0.5 for the term of Dt/L^2 in the right hand

side of Eq. (5) indicates the Fickian type of diffusion [14]. However, the diffusion phenomenon in polymeric coatings often deviates from the Fickian behavior termed as non-Fickian diffusion [8,13]. The main reason of this behavior is related to increase of coating volume by solvent penetration termed as “swelling” phenomenon which has been less considered [8].

The main purpose of the present work is to develop a new model based on the combination of theoretical modeling and capacitance measurement approaches. The proposed model helps to simulate the diffusion behavior of an immersed coating and determine the diffusion coefficient and type of diffusion (Fickian or non-Fickian) during whole of immersion time.

2. Modeling development

2.1. Theoretical background

As previously mentioned, Eq. (5) is a general solution of diffusion phenomenon based on the Fick's second law but it is rather complex and inconvenient to use. In some studies [8,13], Eq. (5) has been utilized in a simplified form when the value of DWC is less than 0.6 as following:

$$\frac{M_t}{M_\infty} = At^{0.5} \quad (6)$$

where A is defined by the following relation:

$$A = \frac{4}{\pi^{0.5}} \left(\frac{D}{L^2} \right)^{0.5} \quad (7)$$

In this situation, to describe both Fickian and non Fickian diffusion, Eq. (7) has been used in a general form as [8,12]:

$$\frac{M_t}{M_\infty} = Kt^n \quad (8)$$

where n is the diffusion exponent attributed to the type of diffusion as Fickian ($n=0.5$) or non-Fickian ($n \neq 0.5$) behavior and parameter K is a parameter which is a function of thickness and diffusion coefficient of coating [15]. Accordingly, one of the most important work on the prediction of water content has been made by Bellucci and Nicodemo [8] who introduced two models termed as discrete model (DM) and continuous model (CM). In the DM model, a uniform distribution of water concentration has been assumed within a coating for each instant of immersion time which corresponds mainly to the condition of a thin polymeric layer as:

$$\frac{C_t}{C_0} = 1 + 2.3 \log(\epsilon_w) \frac{KV_{w\infty}}{M_\infty} t^n \quad (9)$$

where $V_{w\infty}$ is the volume fraction of water at the saturation time.

On the contrary, in the CM model the concentration of water has not been considered uniform which is more applicable for a thick polymeric layer:

$$\frac{1}{C_t} = \frac{1}{C_0} \left[1 - \frac{2.3 \log(\epsilon_w) K t^n}{\rho A_s L} \right] \quad (10)$$

where ρ is the density of water.

Nevertheless, these models have a major limitation of usage when the DWC value is greater than 0.6 especially near the saturation state. While, required time for variation of DWC from 0.6 to 1 (i.e. saturation state) may be considerably longer than that for variation of DWC from 0 up to 0.6.

2.2. Development of a new model

Based on the previous concepts, it implies to divide the whole of immersion time from initial to saturation point into two distinct parts as schematically exhibited in Fig. 1. As it is evident, the DWC

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