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A Model for Ceramic Membrane Formation by Dip-coating

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Abstract

The wet ceramic membrane formation on a porous substrate in the dip-coating process plays a key role for high quality separation layers of the asymmetric membranes. A model to quantitatively describe the membrane growth under a driving force of the capillary filtration is derived on the basis of the slip-casting model. As an example, α-Al_2O_3 microfiltration membranes were prepared by dip-coating. The influence of the dipping time on the membrane thickness was examined. The data for α-Al_2O_3 microfiltration membranes fit the predictions made by the model well. In addition, the results of γ-Al_2O_3 membranes demonstrate that this model is also valid for ultrafiltration membrane formation by dipping sols. © 1999 Elsevier Science Limited. All rights reserved

Keywords: dip-coating, slip casting model, Al_2O_3, membranes.

1 Introduction

The slip-casting process is one of common techniques used to fabricate ceramics with complex shapes from particle suspensions, in which a ceramic powder suspension is poured into a porous plaster mold of the desired shape.[1] Recently, this process has been extended to prepare ceramic asymmetric membranes, including porous ceramic filtration membranes and dense membranes.[2,3] When a dry porous substrate is dipped into a ceramic suspension and subsequently withdrawn from it, a wet and more or less dense cake of well-defined thickness can be formed on the substrate surface. After being dried and sintered, a ceramic membrane is achieved. The structure of the membrane, formed by this so-called 'dip-coating' process, plays a critical role in determining its properties. In principle, for example, the thickness of the coating by this process can be adjusted in the range of 100 nm to 100 μm. In fact, however, the minimum layer thickness should be of the order of the maximum in surface roughness to cover the substrate completely, in order to ensure the absence of defects related to the substrate surface roughness such as cracks and voids. Meanwhile the layer thickness should be as small as possible to obtain higher mass flux. So the thickness of the membrane must be carefully controlled for high quality. Therefore, it is necessary and important to quantitatively analyze the membrane formation process.

During the dip-coating process, a dry porous substrate contacts a suspension and the porous surface is wetted by the dispersion liquid. The capillary suction caused by the porous substrate drives ceramic particles to concentrate at the substrate–suspension boundary, and a wet membrane is formed if the particles cannot enter into the pores. In this capillary filtration, the driving force behind the fluid flow is the capillary suction pressure of the substrate, as in the slip casting process.[4–6] Thus, it is reasonable to develop a model for the membrane formation by dip-coating on the basis of the slip-casting model. Leenaars *et al.*[2] used the slip casting model to describe the gel formation process by dip-coating.[2] Their model derivation started with the volume of the liquid that has passed the gel layer on a kind of overall balance, and so it can not simply be implemented in the velocity equation (from Darcy's equation) for the liquid flowing through the layer. In addition, in their model the effect of porosity of substrate on the total driving force was neglected.

In this paper, a better model was developed to describe the wet membrane formation on the substrate during the dip-coating process. Then it was checked by the experimental results of alumina membranes prepared by dip-coating.

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2 A Model for the Membrane Formation

In general, there are two types of substrates, planar and tubular. The radial flow through a cylindrical substrate is quite different from the unidirectional flow encountered in flat substrate. Radial geometry leads to mathematical complexities not encountered in analysis of planar molds, because the pressure is not linear in terms of the radius and the pressure drop across the cake is not constant.[7] In most cases, however, the thickness of the cake on a porous tube is small compared to the curvature radius of the substrate surface and the filtration process can approximately be described as one-dimensional filtration, as schematically demonstrated in Fig. 1.

2.1 Velocity equation of the wet membrane formation

When a porous substrate is dipped into a ceramic suspension, a wet ceramic membrane begins to form at the whole surface of the substrate by the capillary suction pressure. The membrane and substrate are considered as incompressible. The structure of the wet membrane is assumed to be homogeneous. That means the solid volume fraction of the particles in the membrane is fixed during the dip-coating process. After dipping the time ($t+\mathrm{d}t$), the membrane with a thickness ($L_m+\mathrm{d}L_m$) is formed from a thickness ($L+\mathrm{d}L$) of the suspension. When $\mathrm{d}t\rightarrow 0$, $\mathrm{d}L_m\rightarrow 0$, and thus $\mathrm{d}L_m/\mathrm{d}t$ is the growth velocity of the membrane at the time t. The ceramic particles in this volume of suspension are considered to be retained in the membrane while the dispersion liquid passes through the membrane and into the pores of the substrate, as shown in Fig. 1.

According to a mass balance, at the time t, the flux of the dispersion liquid passing through the membrane can be described as

$$Q=(\mathrm{d}L-\mathrm{d}L_m)/\mathrm{d}t \tag{1}$$

The same amount of the particles in the suspension with the thickness $\mathrm{d}L$ and in the membrane with the thickness $\mathrm{d}L_m$ gives

$$(\mathrm{d}L)\varphi_0=(\mathrm{d}L_m)\varphi_m \tag{2}$$

where φ_0 and φ_m are the volume fraction of the particles in the suspension and in the wet membrane, respectively. Combining eqns (1) and (2) gives

$$Q=\alpha\mathrm{d}L_m/\mathrm{d}t \tag{3}$$

where α is defined as

$$\alpha=(\varphi_0/\varphi_m)-1 \tag{4}$$

According to Darcy's law for the flow through a porous medium,[2] the flux of the liquid flow through the membrane at time t is

$$Q=\Delta P_m K_m/\eta L_m \tag{5}$$

where K_m is the permeability of the wet membrane (m^2), η is the viscosity of the dispersion liquid (continuous phase) (N m^{-2} s) and ΔP_m is the pressure drop across the membrane (N m^{-2}). Therefore, the velocity equation for the formation of the wet membrane can be obtained from eqns (3) and (5) as follows,

$$L_m\mathrm{d}L_m/\mathrm{d}t=\Delta P_m K_m/\alpha\eta \tag{6}$$

2.2 Pressure drop over the wet membrane (ΔP_m)

During the membrane formation, the total driving force (ΔP) is the average capillary suction pressure caused by all pores in the surface of the substrate. Assuming that the cylindrical pores with a radius R are homogeneously distributed in the porous substrate surface gives

$$\Delta P=n\left(\pi R^2\right)\Delta p/A=\varepsilon_S\Delta p \tag{7}$$

where n is the number of the cylindrical pores in the surface of the substrate; A is the area of the substrate surface (m^2); ε_S is the porosity of the substrate; Δp is the capillary pressure caused by a pore (N m^{-2}), which is,

$$\Delta p=2\gamma(\mathrm{Cos}\theta)/R=2\gamma/R \tag{8}$$

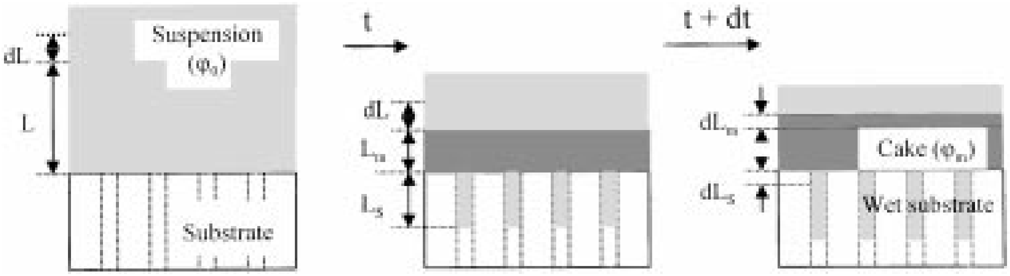

Fig. 1. Membrane formation process on a porous substrate by the capillary suction pressure.

where γ represents the surface tension of the liquid in the pores of the support (N m^{-1}); θ is the contact angle between the liquid and the solid surface and is assumed to be zero degree. From eqn (7), it is concluded that the total driving force for the membrane formation is smaller than the capillary pressure by each pore.

The total driving force (ΔP) is divided into two parts. One is the pressure over the membrane (ΔP_m) (N m^{-2}), which is used to drive the liquid pass through the membrane; The other for driving the liquid flow in the pores of the support is the pressure across the saturated substrate (ΔP_S) (N m^{-2}), as shown in Fig. 2. Thus,

$$\Delta P = \Delta P_m + \Delta P_S \tag{9}$$

At time t, the flux of the liquid through the membrane is the same as through the substrate, hence eqn (5) gives

$$\Delta P_m K_m / \eta L_m = \Delta P_S K_S / \eta L_S \tag{10}$$

where K_S is the permeability of the substrate (m^2) and L_S is the penetration depth of the liquid (m). Combining eqns (7), (9) and (10) gives

$$\Delta P_m = \frac{\varepsilon_S \Delta P}{1 + K_m L_S / K_S L_m} \tag{11}$$

During the entire time of t, a wet membrane with thickness L_m and a saturated substrate with length L_S are formed from a suspension with thickness L, and so the entire volume of the dispersion liquid through the membrane is equal to that of the liquid in the substrate,

$$L - L_m = \varepsilon_S L_S \tag{12}$$

The amount of the particles in the suspension is the same as in the membrane, hence

$$L\varphi_0 = L_m \varphi_m \tag{13}$$

Connecting eqns (12) and (13) gives

$$L_S / L_m = [(\varphi_0/\varphi_m) - 1]/\varepsilon_S = \alpha/\varepsilon_S \tag{14}$$

Combing eqns (9), (11) and (14) gives

$$\Delta P_m = \frac{2\varepsilon_S \gamma}{R(1 + K_m \alpha / K_S \varepsilon_S)} \tag{15}$$

Therefore, the pressure drop across the cake (ΔP_m) is invariable during the membrane formation.

2.3 Equation to describe the cake formation

Since ΔP_m, K_m, α and η are the constants, eqn (6) becomes

$$\mathrm{d}(L_m)^2 = (2\Delta P_m K_m / \alpha\eta)\mathrm{d}t \tag{16}$$

Integration under the boundary condition that $L_m = 0$ at $t = 0$ and elimination of ΔP_m with eqn (15) gives

$$L_m = 2\left[\frac{\varepsilon_S \gamma}{\eta\alpha R(1/K_m + \alpha/\varepsilon_S K_S)} t\right]^{1/2} \tag{17}$$

From eqn (17), we can conclude that when the same suspension and substrate are used, the thickness of the membrane during the filtration process is proportional to the square root of the dipping time, but is independent of the withdrawal speed. Certainly, this is a simplified model however, ignoring changes in the value of the contact angel, which is assumed to be always zero and ignoring concentration effects in the contact area between liquid and moving tube.

2.4 A simplified growth equation when $K_S \gg K_m$

Usually, the permeability of the substrate (K_S) is much bigger than that of the membrane (K_m), and eqn (11) becomes

$$\Delta P_m = \varepsilon_S \Delta p = \Delta P \tag{18}$$

That means that the pressure drop across the saturated substrate may be neglected and the total

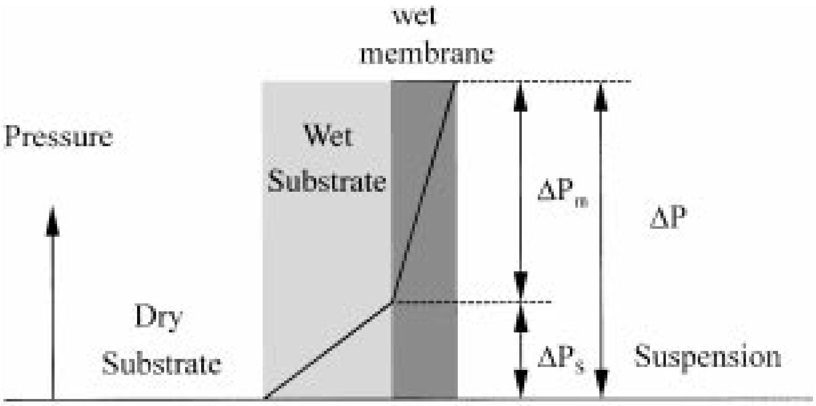

Fig. 2. Distribution of the pressure drop in the membrane formation.

driving force is applied on the wet membrane. Substituting ΔP_m in eqn (18) to eqn (16) gives a simplified equation for membrane growth as follows,

$$\mathrm{L}_m = 2\left(\frac{\varepsilon_\mathrm{S}\gamma K_m}{\eta\alpha R}\mathrm{t}\right)^{1/2} \tag{19}$$

This equation implies that during the dip-coating process, the porosity and pore diameter of substrates have much influence on the membrane formation, although their permeability has not. A substrate with larger number of smaller pores is good for the membrane formation. In addition, the structure of the wet membrane, and the properties of suspensions such as the solid volume fraction, the dispersion liquid viscosity and surface tension are also related to the formation.

During the subsequent drying and sintering process, the membrane shrinks only in the direction perpendicular to the membrane (or substrate) because of the strain caused by the substrate. According to a weight balance, if the ceramic particles keep up unchanged during the next process, the thickness of the sintered membrane $L_{m,\mathrm{sintered}}$ can be expressed as

$$L_{m,\mathrm{sintered}} = \left(\frac{\varphi_m}{1-\varepsilon_m}\right)L_m = \beta L_m \tag{20}$$

where ε_m is the porosity of the sintered membrane; β is defined as

$$\beta = \varphi_m/(1-\varepsilon_m) \tag{21}$$

Substituting L_m in eqn (19) to eqn (20) gives

$$\mathrm{L}_{m,\mathrm{sintered}} = 2\beta\left(\frac{\varepsilon_\mathrm{S}\gamma K_m}{\eta\alpha \mathrm{Rt}}\right)^{1/2} \tag{22}$$

3 Experimental Procedure

A stable aqueous α-Al_2O_3 suspension was prepared by mixing α-Al_2O_3 powders with the deflocculant (PAA) and binder (PVA), and ball-milling for 10 h. The preparation of microfiltration membranes on the inside of a porous tubular α-Al_2O_3 substrate was performed by pouring the aqueous alumina suspension into the tube. The porous alumina tubular substrates with an average pore diameter of 2·2 μm and porosity of 44% were self-made by extrusion. After contacting the different time, the substrates were withdrawn from the suspension. Then the wet membranes were dried at the room temperature and sintered at 1400°C for 2 h.

The average surface area of α-Al_2O_3 powders was measured by standard BET N_2 adsorption and the porosity of sintered membrane by a mercury porosimetry. The thickness of the sintered membranes is determined by the following equation

$$L_{m,\mathrm{sintered}} = (m_2 - m_1)/\rho A(1-\varepsilon_m) \tag{23}$$

where m_1 and m_2 are the weight of the substrate before and after dip-coating and sintering (g), respectively. ρ is the theoretical density of the membrane (g cm^{-3}). A is the surface area of the membrane (m^2), approximate to that of the inner tube.

4 Results and Discussion

4.1 The influence of the dipping time on the membrane thickness

A same suspension with a solid concentration of 10 wt% was used. The dipping time was in the range of 9~64 s, but the different withdrawal speeds were examined. The withdrawal speed for a series of samples A is faster than that for B. The results given in Fig. 3 show that the membrane thickness increases linearly with the square root of the dipping time when the time is less than 64 s. This linear relation is in agreement with the model derived above.

It is noted that the two lines in Fig. 3 are nearly parallel with each other. This also well fits the model. Those two series of data were obtained by using the same suspension and substrate, although the different withdrawal speeds were selected. According to eqn (19), the withdrawal speed has no relation to the membrane formation caused by capillary filtration, so the two lines have the same slope.

In addition, the lines do not pass through the origin. This is because that during withdrawal from the dispersion an adhering dispersion layer is retained as a result of the drag force exerted by the substrate. This is so-called film-coating mechanism. The thickness of this layer adhered increases with

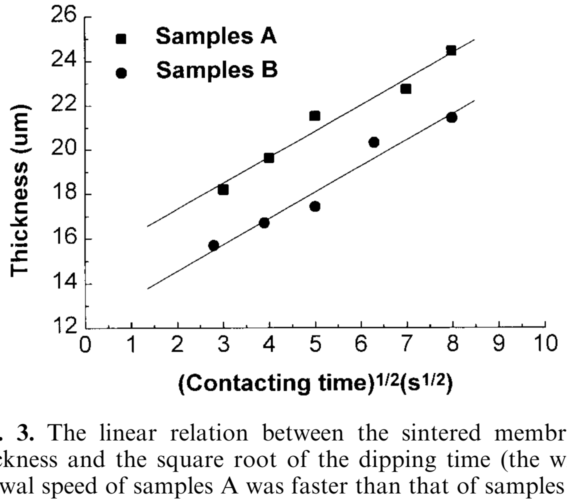

Fig. 3. The linear relation between the sintered membrane thickness and the square root of the dipping time (the withdrawal speed of samples A was faster than that of samples B).

the withdrawal speed and dispersion viscosity, but is not dependent to the dipping time.[2] The thickness of this layer is the intersection of lines with the vertical axis. The value of the line A at the vertical axis is bigger than that of the line B because of the faster withdrawal speed.

4.2 Quantitative calculation of the membrane thickness

The linear relation between the membrane thickness and the square root of the dipping time found in Fig. 3 implies that the structure of the wet membrane is homogeneous. In general, the porosity of the cake is 0·4~0·5 for a dense packing of powders and 0·3~0·4 for a dense random packing when coating with a colloidally stable suspension containing no aggregates or agglomerates. Haerle *et al.*[8] examined the structure of the undried cake prepared from a fully deflocculated slip. The volume fraction of voids in the cake was 0·425 by an ultrasonic monitoring system, and (0·44 ± 0·06) by dimensional measurements. So φ_m is reasonably assumed in the range of 0·5~0·6.

The permeability of the wet membrane (or substrate) was determined by the following equation

$$K = \frac{\varepsilon^3}{K_0 K_\tau S_V^2 (1-\varepsilon)^2} \tag{24}$$

where K_0 is a particle shape factor and K_τ accounts for the tortuosity of the porous medium. The product of K_0 and K_τ was generally put at about 5 for particle packings. S_V is the surface area of the particles per volume solids (m^{-1}). ε is the porosity of the porous medium. We calculated the permeability of the wet membrane by taking 8·52 $m^2\ g^{-1}$ for the specific surface area and 3·97 $g\ cm^{-3}$ for the theoretical density of α-Al_2O_3 powder used. They were $8{\cdot}74\times10^{-17}$, $5{\cdot}27\times10^{-17}$ and $3{\cdot}11\times10^{-17}\,m^2$ for φ_m of 50, 55 and 60%, respectively, as listed in Table 1. For the porous substrate, the K_S value is calculated to be $2{\cdot}14\times10^{-14}\,m^2$, three magnitude larger than the K_S value. Hence, the sintered membrane thickness can be calculated with eqn (22).

In this work, the calculation is performed for the alumina substrate, taking $1{\cdot}1\times10^{-6}$ m for R and 0·44 for ε_S. The viscosity of the values of the dispersion liquid (continuous phase) at 24°C were measured to be $\eta = 83\times10^{-3}\,N\,m^{-2}\,s$. For aqueous polymer thickeners γ may be $40{\sim}50\times10^{-3}\,N\,m^{-1}$, so a surface tension of $45\times10^{-3}\,N\,m^{-1}$ is selected. The φ_0 value for the suspension is 2·52%. A porosity of 35% for the sintered α-Al_2O_3 membrane was measured. The results of the calculation given in Table 1 and Fig. 4 show that the data for the alumina microfiltration membrane by dip coating fit the values predicated by the model well, if the adhering layer by film coating is considered and the volume of particles in the wet membrane is assumed to be 0·5~0·6.

4.3 Further checks on the validity of the model

Significantly, it was found that the model is also valid for the ultrafiltration membrane formation by dipping sols. The data by Leenaars[2] were taken for the calculation. This calculation was performed for type 1 support withdrawn from the sols after 60 s. The gelling concentration was determined by his experiments to be 11~13 mole l^{-1}. Because the boehmite sols are changed into γ-Al_2O_3 during calcining, the calcined membrane thickness was obtained from a mole balance of Al ions. The results were given in Table 2. It shows that the calculated membrane thickness is close to the experimental values. It was also found that the calculated value of the pressure drop on the membrane (ΔP_m), 11·4 bar for the gelling concentration

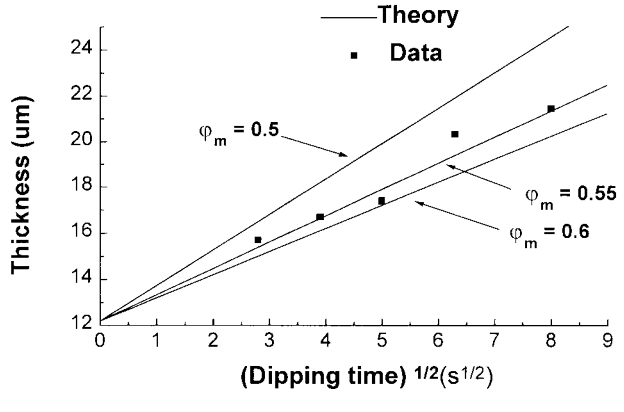

Fig. 4. The model has fit to the data for α-Al_2O_3 microfiltration membrane formation.

Table 1. Calculations of α-Al_2O_3 microfiltration membrane thickness[a]

φ_m (vol%)	$K_m\times10^{-17}$ (m^2)	α	$L_{m,sintered}$ (μm)	Sintered membrane thickness (μm)	
				Calculated[b]	Experimental
50	8·74	18·8	5·98	18·2	16·7
55	5·27	20·8	4·86	17·1	16·7
60	3·11	22·8	4·21	16·1	16·7

[a] Dipping time of 15 s for the samples B, $1{\cdot}1\times10^{-6}$ m for R, 0·44 for ε_S, $45\times10^{-3}\,Nm^{-1}$ and $83\times10^{-3}\,Nm^{-2}\,s$ for γ and η.
[b] After a correction of 12·2 μm caused by film-coating.

Table 2. Calculations of γ-Al$_2$O$_3$ ultrafiltration membrane thickness[a]

Concentration (mole l^{-1})	φ_m	$K_m \times 10^{-19}$ (m^2)	$\Delta P_m \times 10^5$ (Nm^{-2})	L_m (μm)	*Thickness calcined (μm)*	
					Calculated[b]	*Experimental*[c]
11	0·26	9·92	11·4	129	35·4	35
13	0·30	6·57	11·4	97·1	30·9	35

[a] 6×10^{-8} m for R, 0·46 for ε_S, $72{\cdot}8\times10^{-3}$ Nm^{-1} and 10^{-3} Nm^{-2}s for γ and η.
[b] After adding the thickness of 0·8 μm caused by film coating.
[c] Experimental values by Leenaars.[2]

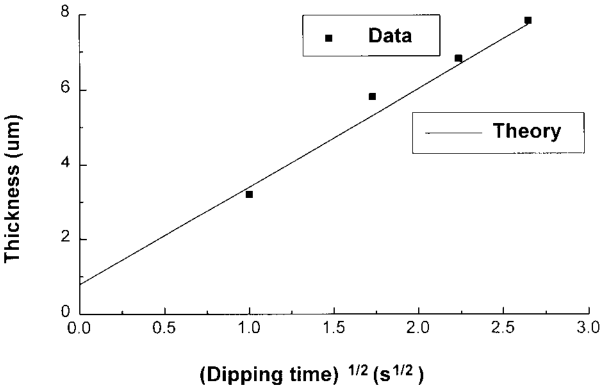

Fig. 5. The model also has best fit to the data[2] for γ-Al$_2$O$_3$ ultrafiltration membrane formation (type 2 support, sols with 1·22 mole Boehmite l^{-1} and gelling concentration for 12 mole l^{-1}).

11~13 mole l^{-1}, has good agreement with the experimental results of 12 bar by Leenaars.[2]

In addition, a theoretical line was obtained from the model in order to demonstrate the validity clearly, as shown in Fig. 5. It indeed appears that the data by Leenaars have the best fit to this model.

5 Conclusions

A model to quantitatively describe the wet membrane formation process on a porous substrate by the capillary filtration during the dip-coating process is derived on the basis of the slip-casting model. The growth equation for the wet supported membrane formed by the capillary filtration mechanism can be expressed as

$$L_m = 2\left[\frac{\varepsilon_S \gamma}{\eta \alpha R(1/K_m + \alpha/\varepsilon_S K_S)} t\right]^{1/2}$$

When the permeability of the substrate is much larger than that of the membrane, the pressure drop over the wet substrate can be neglected and hence the simplified growth equation is given as

$$L_m = 2\left(\frac{\varepsilon_S \gamma K_m}{\eta \alpha R} t\right)^{1/2}$$

This equation shows that when the suspension and substrate are fixed, the membrane thickness, contributed by the capillary filtration, increases linearly with the square root of the dipping time and does not change with the withdrawal speed of the substrate. It also implies that the structures of the porous substrate and the wet membrane, and the properties of the suspension have close relation to the membrane-formation process. As an example to check the model, α-Al$_2$O$_3$ microfiltration membranes were prepared by a dip-coating procedure. The data for the microfiltration membrane formation were in good agreement with the model. In addition, the experimental data by Leenaars were found to have accordance with the model, which demonstrates that this model also fit to the ultrafiltration membrane formation on a porous substrate by a dipping sols procedure.

Acknowledgements

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