Supporting Information

Organic liquid impregnation behavior into nanofibrous membranes: quantitative analysis of the effects of structural parameters

Ikuo Uematsu†‡*, Tomomichi Naka‡, Yoko Tokuno‡, Yasutada Nakagawa‡,

and Hidetoshi Matsumoto†‡*

†Department of Materials Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

‡Corporate Manufacturing Engineering Center, Toshiba Corporation, 33 Shin-Isogo-Cho, Isogo-ku, Yokohama 235-0017, Japan

*Address correspondence to ikuo.uematsu@toshiba.co.jp and matsumoto.h.ac@m.titech.ac.jp
Time-resolved liquid contact angle measurements and determination of impregnation velocity.

Figure S1. Schematic of the measurement for liquid impregnation into the NF membrane.

At the measured impregnation time ($t$) required for the contact angle to reach zero degrees after the deposition of the droplet, the cylindrical liquid permeation (wetting) region is always formed for the NF membranes (see Figure S1). Here we put a NF membrane on a glass substrate. At the $t$ [sec] after the deposition of the droplet, we observed the top and bottom surfaces of the NF membranes. The typical images of both the surfaces of the NF membranes are shown in Figure S2. The circular wetting areas of both the surfaces are almost same. Therefore, we determined the apparent impregnation velocity ($v$) of organic liquid into porous NF membranes as follows. At $t$, the apparent permeation volume reaches the droplet volume divided by the apparent membrane porosity ($\varepsilon$). Therefore, the apparent permeation volume can be expressed by $(v \times t)^2 \times \pi \times L_c$. $L_c$ is the membrane thickness. Consequently, $v$ is given as follows:

$$v = \sqrt{\frac{\text{droplet volume}}{(\varepsilon \times L_c \times \pi) / t}} \quad (S1)$$
Figure S2. The typical images of wetting area on the both surfaces of the PAI-2 NF membranes. (a) Top surface view and (b) bottom surface one.

The intrinsic contact angle of the fiber materials.

To investigate the intrinsic contact angle of the fiber materials used in this work, the smooth and flat thin films were prepared by spin-coating from the fiber materials. The organic liquid contact angles of spin-coated films were measured by the sessile drop method using a DropMaster 500 (Kyowa Interface Science Co., Japan) at approximately 25 °C. An organic liquid (EMC) droplet with a volume of 0.2 μL was used as the probe liquid. The samples were prepared by spin-coating from the DMAc solutions of PAIs. The reference cellulose nonwoven membrane, Nanobes-2, cannot be dissolved in solvents, so the samples were prepared by spin-coating from 10 wt% CMC aqueous solution. The intrinsic organic solvent (EMC) contact angles (θ) of PAIs and CMC are 3.3-6.6° and 5°, respectively.
Effect of the structural parameters on liquid impregnation velocity into NF membranes.

**Figure S3.** (a) The relationship between the impregnation velocity ($v$) and porosity ($\epsilon$) of NF membranes.

(b) The relationship between the impregnation velocity ($v$) and average fiber diameter ($\delta_0$) of NF membranes.
Kozeny-Carman equation for NF membranes.

We used the Kozeny-Carman equation, which is a differential equation commonly used for liquid impregnation into porous media for the calculation of the impregnation velocity \( v \) into NF membranes.

The D’Arcy law, which describes the flow of a fluid through a porous medium, is given as follows:

\[
K = \frac{Q/A}{\Delta P/h} = \frac{U_e}{\Delta P/h} = \frac{\varepsilon U}{\Delta P/h} \quad (S2)
\]

where \( K \) is the permeability; \( Q \) is the flow rate; \( \Delta P \) is the pressure difference across the porous medium; \( A \) and \( h \) are the cross-section area and thickness of the porous medium, respectively; \( U_e \) and \( U \) are the apparent and real flow velocities, respectively; and \( \varepsilon \) is the porosity of the porous medium.

From the Poiseuille equation, the flow rate per unit area can be written as:

\[
\frac{Q_c}{\pi (d_c/2)^2} = \frac{\Delta P}{8 \eta h} \left(\frac{d_c}{2}\right)^2 \quad (S3)
\]

where \( d_c \) is an average pore diameter of the porous medium.

Kozeny used an average hydraulic radius, \( r_H \), instead of \( d_c \).

Therefore, eq. S2 can be rewritten as follows:

\[
U = \frac{r_H^2 \Delta P}{k_0 \eta h_0} \quad (S4)
\]

where \( k_0 \) is the constant; and \( h_0 \) is the real flow distance.
The average hydraulic radius, $r_H$, can be written by the following equation by using the real specific surface area per unit volume of a porous medium, $S_p (= S/(1 - \varepsilon))$. $S$ is the apparent surface area per unit volume of a porous medium.

$$r_H = \frac{\varepsilon}{S} = \frac{\varepsilon}{S_p(1-\varepsilon)} \quad (S5)$$

Therefore, the following equation is obtained by substituting eq S4 for eq S5.

$$U = \frac{\varepsilon^2 \Delta P}{k_0(1-\varepsilon)^2 S_p^2 \eta h_0} \quad (S6)$$

By using the apparent flow distance, $h$, the apparent flow velocity, $U_e$ can be written as:

$$U_e = \frac{v_\varepsilon}{h_0/h} = \frac{\varepsilon^3 \Delta P}{k_0(1-\varepsilon)^2 S_p^2 \eta h_0(h_0/h)} = \frac{\varepsilon^3 \Delta P}{k_0(h_0/h)^2(1-\varepsilon)^2 S_p^2 \eta h} = \frac{\varepsilon^3 \Delta P}{k(1-\varepsilon)^2 S_p^2 \eta h} \quad (S7, \text{Kozeny-Carman equation})$$

where $k = k_0(h_0/h)^2 = k_0 f^2$ and $f$ is the tortuosity.

For simplification of the calculation, we adopted a model NF membrane composed of aligned fibers as the first-approximated structural model, as shown in Figure S4, instead of the prepared NF membranes with random nonwoven and interconnected pore structures. We calculated the $\nu$-value of the model NF membranes along three directions: cross-section, side, and surface.
Figure S4. Schematic of the model NF membrane composed of aligned fibers.\(^2\) (a) Directions of liquid impregnation into the model NF membrane. (b) The cross-sectional and side views of the model NF membrane.

The arithmetic mean capillary pressure \(P_{TA}\) along three directions can be obtained as follows:\(^2\)

\[
P_{TA} = \frac{P_{T1} + P_{T2} + P_{T3}}{3} = \frac{32(1-\varepsilon)\gammaL\cos\theta}{3\pi\delta_0\epsilon} \quad (S8)
\]

where

\[
P_{T1} = \frac{16(1-\varepsilon)\gammaL\cos\theta}{\pi\delta_0\epsilon} \quad \text{(from cross section)}
\]

\[
P_{T2} = \frac{8(1-\varepsilon)\gammaL\cos\theta}{\pi\delta_0\epsilon} \quad \text{(from side)}
\]

\[
P_{T3} = \frac{8(1-\varepsilon)\gammaL\cos\theta}{\pi\delta_0\epsilon} \quad \text{(from surface)}
\]
The pressure difference in the Kozeny-Carman equation ($\Delta P$) can be written by using the arithmetic mean capillary pressure ($P_{TA}$) and the gravity difference of the ascending liquid ($\rho gh$):

$$\Delta P = P_{TA} - \rho gh \quad (S9)$$

The liquid impregnation velocity ($v$) induced by the capillary pressure,

$$v = \frac{dh}{dt} = \frac{\varepsilon^3 \Delta P}{k(1-\varepsilon)^2 S_p^2 \eta h} = \frac{\varepsilon^3}{k(1-\varepsilon)^2 S_p^2 \eta h} \left\{ \frac{32(1-\varepsilon) \gamma_L \cos \theta}{3\pi \delta_0 \varepsilon \rho g} \right\} - \rho gh$$

$$= \frac{\varepsilon^3 \rho g}{k(1-\varepsilon)^2 S_p^2 \eta h} \left\{ \frac{32(1-\varepsilon) \gamma_L \cos \theta}{3\pi \delta_0 \varepsilon \rho g} - h \right\} \quad (S10)$$

Therefore,

$$v = \frac{dh}{dt} = (\beta - h) \frac{\alpha}{h} \quad (S11)$$

where

$$\alpha = \frac{\varepsilon^3 \rho g}{k(1-\varepsilon)^2 S_p^2 \eta}$$

$$\beta = \frac{32(1-\varepsilon)^2 \gamma_L \cos \theta}{3\pi \delta_0 \varepsilon \rho g}$$

Herein, the influences of the thickness of the membranes and surface free energy of the fiber materials are negligible because the thickness is fixed at 20 $\mu$m and the liquid contact angles of the materials used here are 3.3-6.6°.

The following equation for the relationship between the liquid impregnation velocity ($v$) and the structural parameters of the NF membranes is derived under the assumption that the “impregnation depth
in nonwoven fibrous membrane $(h)$" is “the ascending height of porous media” in the original Kozeny-Carman equation.

$$v = \frac{dh}{dt} = (\beta - h) \frac{\alpha}{h} \quad (S11)$$

where

$$\alpha = \frac{\epsilon^3 \rho_L g}{k(1 - \epsilon)^2 S_p^2 \eta}$$

$$\beta = \frac{32(1 - \epsilon)^2 \gamma_L \cos \theta}{3\pi \delta_0 \epsilon \rho_L g}$$

$\epsilon$: membrane porosity, $\delta_0$: fiber diameter, $\rho_L$: liquid density, $\eta$: liquid viscosity, $\gamma_L$: liquid surface tension, $\theta$: intrinsic contact angle of the fiber material, $g$: gravitational acceleration, $k$: Carman constant $(= 2 \times 4^3 \epsilon/(3 \times 3\pi^2))$, $S_p$: specific surface area $(S_p = S/V = \pi \delta_0 L/\{((\delta_0)^2/4)\pi L\} = 4/\delta_0)$, $S$: surface area of fiber, $V$: volume of nanofiber).

Integration of eq S11 gives eq S12.

$$\frac{h}{h - \beta} dh = -\alpha dt$$

Then,

$$\left(\frac{h - \beta}{h - \beta} + \frac{\beta}{h - \beta}\right) dh = -\alpha dt$$

$$h - h_0 + \beta(\ln|h - \beta| - \ln|h_0 - \beta|) = -\alpha(t - t_0) \quad (S12)$$
Given that the initial values are $h_0 = 0$ and $t_0 = 0$, eq S13 is derived.

$$t = \frac{\beta}{\alpha} \left( \ln \beta - \ln(\beta - h) \right) - \frac{h}{\alpha} \quad (S13)$$

This equation is the Washburn equation for capillary ascent.

When eq S11 is discretized, the equation for the impregnation depth $h_n$ becomes eq 14 and the numerical integration gives eq S15. In this study, $h_n$ was determined by calculating the depth $dh_n$ that the liquid penetrates in 0.01 sec and adding $dh_n$ to $h_{n-1}$, which is the depth before 0.01 sec.

$$h_n = ((\beta - h_{n-1})/h_{n-1}) \Delta t + h_{n-1} \quad (S14)$$

$$h_n = \sum_{i=1}^{n} ((\beta - h_{i-1})/h_{i-1}) \Delta t) + h_0 \quad (S15)$$

Therefore, $v$ is given as follows:

$$\frac{h_n - h_0}{(n-1)\Delta t} = \sum_{i=1}^{n-1} ((\beta - h_{i-1})/h_{i-1}) \Delta t) \quad ((n-1)\Delta t) \quad (S16)$$

To consider the influence of the porosity ($\varepsilon$) and fiber diameter ($\delta_0$) on the impregnation velocity ($v$), the following relations are obtained by expressing $\alpha$ and $\beta$ using $\varepsilon$ and $\delta_0$.

$$\alpha \propto \varepsilon, \quad \alpha \propto \delta_0^2, \quad \beta \propto \varepsilon, \quad \beta \propto \delta_0^{-1} \quad (S17)$$

By substituting the relation $S_p = 4/\delta_0$ into eq S16, the following relations are obtained.

$$v \propto \varepsilon^2, \quad v \propto \delta_0 \quad (S18)$$

Eqs S11, S17, and S18 clearly show that the impregnation velocity ($v$) and depth ($h_n$) are proportional to the square of the porosity ($\varepsilon^2$), the fiber diameter ($\delta_0$), and the cosine of the contact angle of the fiber
material \((\cos \theta)\). In other words, the impregnation velocity increases with an increase in the porosity and the fiber diameter. In this study, we used the fiber materials with low intrinsic contact angles \((\theta)\) of 3.3-6.6\(^{\circ}\). Therefore, the chemical effect of the fiber materials on the liquid impregnation velocity \((v)\) is negligible.

The deviation of equation 7.

By substituting the relations, \(v \propto \varepsilon^2, v \propto \delta_0\) (eq S18), into eq 6 in the main text, the following relation is obtained.

\[
\delta = \left(\frac{\pi \delta_0^2}{4(1-\varepsilon)}\right)^{1/2} \propto \left(\frac{\pi v^2}{4(1-v^{1/2})}\right)^{1/2}
\]

Then, the relation between \(\delta\) and \(v\) is extracted.

\[
\delta \propto \left(\frac{v^2}{\nu^{1/2}}\right)^{1/2} = \left(v^{3/2}\right)^{1/2} = v^{3/4}
\]

Finally, the following relation between \(v_n\) and \(\delta_n\) is obtained.

\[
v_n \propto \delta_n^{4/3} \quad n = 1, 2 \quad \text{(eq 7 in the main text)}
\]
Multivariate statistical analysis

To improve the accuracy of our multivariate statistical analysis, the data for one NF membrane with a thin diameter ($\delta_0 \pm \sigma = 230 \pm 92$ nm, $\varepsilon = 90 \pm 2\%$, $v = 6.0 \pm 10$ mm/s) was used in addition to the data shown in Table 1. The additional NF membrane was prepared from poly(vinylidene fluoride) (PVDF), because it is difficult to prepare a NF membrane with a thin diameter from PAIs. The intrinsic organic solvent (EMC) contact angles ($\theta$) of PVDF was $4.6^\circ$, which is similar to the $\theta$-values of PAIs ($3.3-6.6^\circ$). Therefore, we think that the chemical effect of fiber materials on the liquid impregnation velocity is negligible.

The parameters used for our analysis ranged from 230 to 912 nm for the average fiber diameter ($\delta_0$), from 86 to 92% for the porosity ($\varepsilon$), and from 64 to 438 nm for the standard deviation of the fiber diameter ($\sigma$). These conditions are from the values measured for the NF membranes shown in Table 1 and the additional PVDF NF membrane. The analysis was carried out under the condition that the correlation coefficient ($R^2$) between the calculated and experimental values is close to 1. The $p$-values obtained from error analysis for all the input parameters are less than 0.05. As a result of our analysis, the following equation was obtained.

$$v = -1.04 \times 10^2 + 1.40 \times 10^{-4} \cdot \varepsilon + 3.12 \times 10^{-5} \cdot \delta_0 - 3.91 \times 10^{-5} \cdot \sigma + (\varepsilon - 77.9) \cdot (4.95 \times 10^{-7} \cdot (\sigma - 2.40 \times 10^2))$$

(S18)
REFERENCES

(1) Carman, P. C. Fluid Flow through Granular Beds. *Trans. Inst. Chem. Eng.* **1937**, *15*, 150.

(2) Koishi, M.; Uematsu, K. Eds. *Basics and Application of Impregnation Technology in Nanotechnology*. Age; Technosystem Co., Ltd.: Tokyo, 2007, Chapter 3.

(3) Uematsu, K.; Koishi, M. Kinetic Studies on Liquid Penetration in Polyester Nonwoven Fabric. *J. Colloid Interface Sci.* **1984**, *101*, 37.

(4) Flury, B.; Riedwyl, H. *Multivariate Statistics: A Practical Approach*, Chapman & Hall, Ltd.: London, 1988.

(5) Miller, A. J. *Subset Selection in Regression*, Chapman & Hall, Ltd: Boca Ranton, 1990.