

Hydrolysis Induced Formation of Macrovoids in Poly(methyl methacrylate)

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ABSTRACT: In the PMMA with saturated methanol and ethanol desorbed in the distilled water, because of the phase inversion, the macrovoids are produced. The size and the quantity of macrovoids near the surface layer are larger than those inside of the specimens. If the hydrolysis temperature is lower, the macrovoids formed tend to be of close-type. On the contrary, if the temperature is higher, there will be open-type macrovoids. Because of the occurrence of macrovoids, the size of which is smaller than the visible wavelength, the light will scatter, thereby reducing the transmittance of the specimens. The transmittance decreased as the hydrolysis temperature and hydrolysis time was increased.

This phenomenon is much obvious when using ethanol, instead of methanol, as the solvent. The scattering intensity of the specimens after hydrolysis is inversely proportional to the visible wavelength with an exponent, n , in the range from 0.03 to 2.40 for methanol and 0.02 to 0.15 for ethanol. The exponent is equal to 4 corresponding to the Rayleigh scattering. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3451–3465, 2006

Key words: PMMA; phase inversion; macrovoids; hydrolysis; transmittance

INTRODUCTION

The mass transport between polymer and the organic solvent is driven by the gradient of the chemical potential. When the organic solvent mass transforms into polymer, it will induce mechanical stress. This stress is gradually relaxed by swelling or by moving and redistributing molecular chains. The mass transport will proceed until the chemical potential and the mechanical stress are in equilibrium.^{1–3} Diffusion means small molecules enter the existed or dynamically formed free volume. Swelling is the movement of large quantity of molecular chains, which will increase the gaps between the molecular chains and then redistribute the free volume.² Alfrey et al.⁴ divides the mass transport between glassy polymer and the organic solvent into three categories: (1) Case I or Fickian diffusion, (2) Case II diffusion, and (3) Non-Fickian diffusion or anomalous diffusion. The solvent acts as a plasticizer between polymer chains. That is, it increases the movements of polymer chains, decreases the glass transition temperature, and causes swelling during

diffusion process, which leads to an increase in the volume.⁵

The membrane structure includes microstructure, composition, and macrovoid types. Different manufacturing processes of the polymer membrane will produce different types of the membrane structure. On the basis of the macrovoid types, the membrane structure can be distinguished into two types: the symmetric type and the asymmetric type.⁶ In the asymmetric type membrane, different sizes of macrovoids are unevenly distributed. It is formed with a top layer, 0.1–2- μm -dense skin layer, and a sub layer of porous matrix.⁷ The interface between the membrane making solution and the immersing solution of the nonsolvent produces a very thin but high concentration zone. This zone will be converted into the dense skin layer.⁸ The porous matrix is formed because the nonsolvent immersing solution comes into the membrane making solution, which causes the phase inversion. There are two major types of porous structures: the sponge-like structure and the finger-like structure.^{9,10}

There are four methods to manufacture the membrane: sintering, stretching, track etching, and phase inverting.¹¹ Among them, phase inversion method is to transform uniform polymer solution into polymer gel, and then solidify it into the complete membrane.¹² Commonly used phase inversion methods include immersion precipitation, precipitation by solvent evapo-

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ration, dry/wet process, thermal-induced phase separation, and precipitation from the vapor phase. Immersion precipitation method is to immerse the membrane making solution, which contains polymer solution, solvent, and nonsolvent, into the immersion solution, which is mainly nonsolvent. The polymer solution and the immersion solution, therefore, precede diffusion exchange and the solvent is extracted. The nonsolvent then diffused into the membrane making solution, which reduces the solubility of the polymer and causes phase inversion of the polymer solution. Therefore, the gel is desorbed from the membrane making solution, and solidified into a porous membrane. This method is usually used for making the asymmetric membrane.^{11,13,14} Because of the phase inversion, the membrane is porous. The vitalization rates of the solvent and the nonsolvent are the key point to the phase inversion.^{12,15,16} For the dry/wet process, after the membrane is cast, the solvent is volatilized under the constant temperature. Thereafter, the membrane is extracted with the nonsolvent. The formation of the dense skin layer depends on the volatilization time. This membrane making procedure combines dry and wet phase inversion methods.¹⁷

According to Lin et al.¹⁸ PMMA will turn from transparent to opaque when absorbing methanol. The degree of opacity is related to the amount of the absorbed solvent and the desorbing rate. With the observation of the cleavage surface of the specimens, it is found that the reduction of the transmittance to light results from the macrovoids of the specimens caused by swelling. If the size of the macrovoids is larger than the wavelength of incident visible light, reflective interference happened. On the contrary, if the sizes of the macrovoids are smaller than the wavelength of incident visible light, interference scattering happened and the transmittance is related to the wavelength. With the scattering theorem and the concept of fractal, some researchers^{19–22} have studied the irregular contours or the types and dimensions of fractal. Based on the research by Chou and Lee,²³ it is known that after absorbing a critical amount of solvents, because of the formation of light scattering related large macrovoids, the transmittance is reduced. Besides, the absorbed amount of solvent and the transmittance of specimens are in a linear relation with 2–3 transitions. The first transition happens when the swelling interfaces of both sides of the specimen meet. The second transition occurs only when absorbing the low concentration solvent and the transmittance will turn from increasing to decreasing mode. With the solvent treatment, the transmittance of the specimens will depend on the wavelength of the incident light. The swelling-induced macrovoids are regarded as the particulates that cause scattering. The scattering intensity and the wavelength of light are in an inverse proportion of n th order, and n is from 1.2 to 3.26. For Rayleigh's scat-

tering, surface scattering, n is equal to 4.²⁴ This difference indicates that the macrovoids possess fractal dimension. Besides, the composite molecules of the residual solvent will also affect light scattering, and hence influence the factor n .

The first part of this research involves using the PMMA plate to absorb solvent (methanol and ethanol) and then hydrolyzed into porous membrane. Under this procedure, the effects of the hydrolysis temperature and hydrolysis time of the specimens on the microvoid forming mechanism, and the types of macrovoids are discussed. The second part involves the study of the relationship between the transmittance of the porous membrane and the wavelength of the incident light.

EXPERIMENTAL

Material preparation

PMMA with inherent viscosity (0.237 dL/g) is used as the specimens. The thickness of the specimens is 2 mm. The dimension is cut to be $50 \times 20 \times 2$ mm³. Methanol and ethanol are reagent level solvents from J. T. Backer Co. Ltd. (USA) and Riedel-Dehaen Co. Ltd. (Germany) respectively.

Solvent absorption and hydrolysis

PMMA specimens and solvents are preheated to the working temperature. Thereafter, the specimens were immersed into 60°C solvents. Within the intervals, the specimens were taken out from the solvent system to measure the weight of the absorbed solvent with the help of a digital balance (± 0.1 mg) until they were saturated. When the specimens were saturated with solvent, they were quickly immersed into the 40–90°C distilled water system so as to be hydrolyzed for 3 h. Then, they were further hydrolyzed in the 60°C distilled water for 0.5–4 h. After that, the specimens were taken out in the atmosphere to be desorbed for 24 h until there is no weight change. Moreover, to further investigate the interaction between solvents of the polymer and distilled water during the hydrolysis process, saturated specimens were taken out from the 60°C solvent and desorbed under the air and the 40–90°C distilled water separately.

SEM observation

The completely hydrolyzed specimens were cleaved for SEM observation. To cleave the specimens, first a groove was carved on the surface, and then cleaved using a vise along the indent. To observe the microstructure of the cleavage surfaces, SEM of LEO-1530 was employed. Before the observation, the specimens were sputtered with gold to a thickness of ~ 2.5 nm.

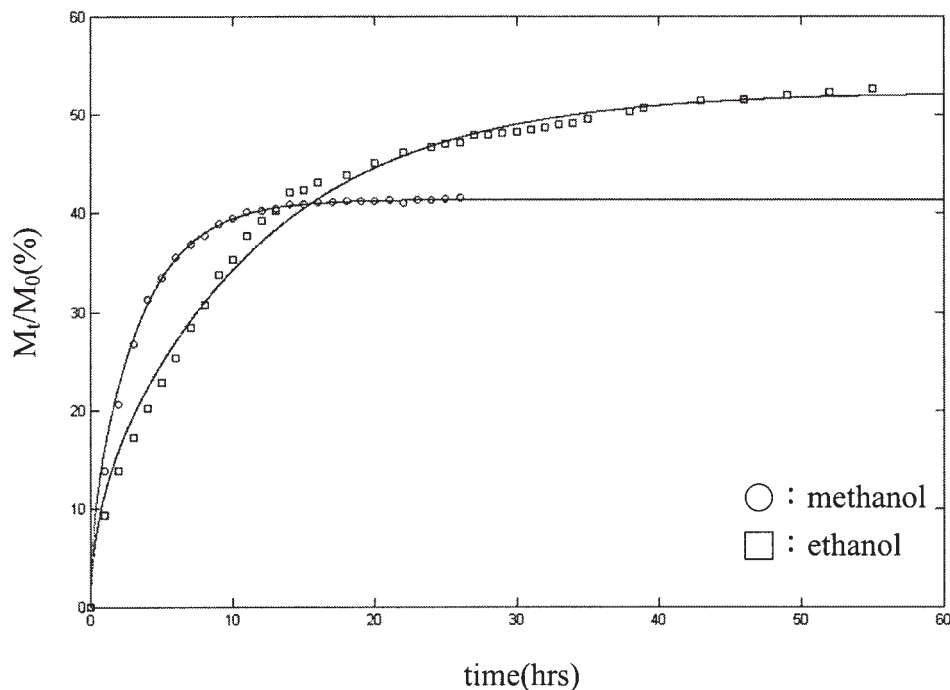


Figure 1 The mass transport of methanol and ethanol in PMMA at 60°C.

Spectrum analysis

Hitachi U-3410/U-3420 spectrometer was used to measure the specimen transmittance of visible light (390–780 nm) under air at the room temperature (27°C). The scanning speed of the spectrometer was 1200 nm/min.

RESULTS AND DISCUSSION

Mass transport

For the mass transport of PMMA in methanol and ethanol, the relation between the solvent absorption ($M_t/M_0 \cdot 100\%$) and the change of the mass transport time is shown in Figure 1. M_0 is the weight of the specimens without absorbed solvent, and M_t is the weight of the specimens after absorbing solvent for time t . These data can be analyzed using a mass transport model proposed by Harmon et al.^{25,26} Their model assumed that the transport behavior accounts

for Case I and Case II diffusion. This line fits the experimental data very well. In this analysis model, the symmetric concentration gradient and the flux of the specimens with finite thickness are related to the absorption of the organic solvent and the mass transport time. This relation can be expressed in the following equation:

$$\frac{M_t}{M_\infty} = 1 - 2 \sum_{n=1}^{\infty} \frac{\lambda_n^2 (1 - 2 \cos \lambda_n) \exp\left(\frac{-v l}{2D}\right)}{\beta_n^4 \left(1 - \frac{2D}{v l} \cos^2 \lambda_n\right)} \times \exp\left(-\beta_n^2 \frac{Dt}{l^2}\right) \quad (1)$$

where M_t is the weight gained after time t , M_∞ the weight gained after the specimen is saturated, D the diffusion coefficient of Case I, v the velocity of Case II,

TABLE I
Diffusion Coefficient (D) for Case I, Velocity (v) of Case II, and the Equilibrium Solvent Content (ESC) in Methanol and Ethanol/PMMA

Solvent	Solvent characteristic		D (10^8 cm ² /s)	V (10^6 cm ² /s)	ESC (%)
	Solubility parameter (Cal/cm ³) ^{1/2}	Boiling temperature (°C)			
Methanol	14.3	64.7	21.7	5.9	41.4
Ethanol	12.9	78.2	6.8	2.9	52.4

The solubility parameter of PMMA is 9.2.

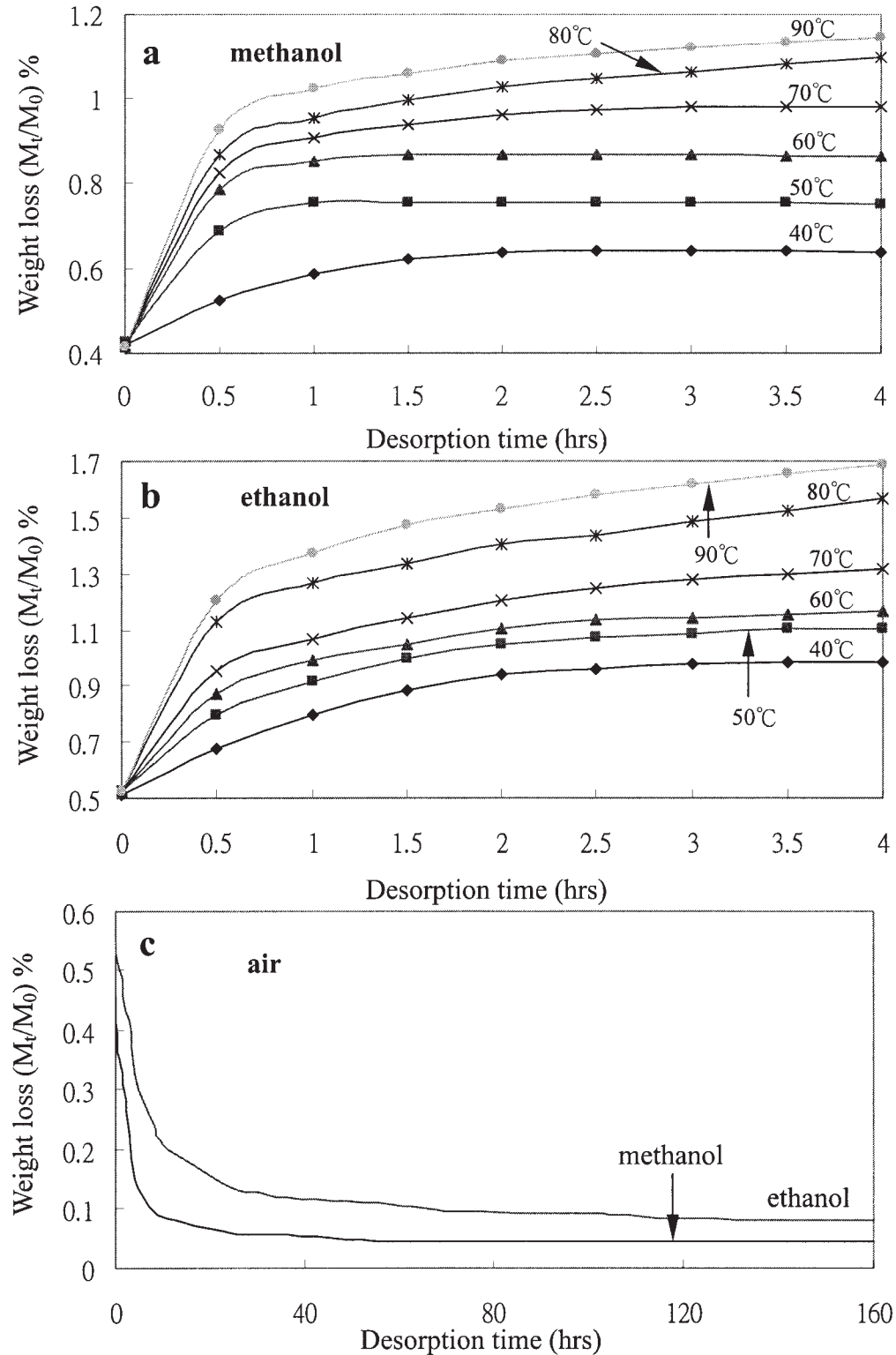


Figure 2 The weight loss for PMMA with saturated (a) methanol and (b) ethanol desorbed in the 40–90°C distilled water and (c) under air.

$2l$ the thickness of the specimen, λ_n the positive real solution of the following equation

$$\lambda_n = \frac{vl}{2D} \tan \lambda_n$$

$$\beta_n^2 = \frac{v^2 l^2}{4D^2} + \lambda_n^2$$

In Table I, the equilibrium coefficients of PMMA absorbing methanol and ethanol are provided. These

TABLE II
Values of the Volume Change ($V-V_0/V_0$), Density (ρ), and Void Ratio ($\rho_0-\rho/\rho$) of the PMMA with Methanol and Ethanol Desorbed in the 40–90°C Distilled Water

Solvent	Hydrolysis temperature (°C)	$V - V_0/V_0 \times 100\%$	$\rho \times 10^{-3}$ (g/mm ²)	$\rho_0 - \rho/\rho_0 \times 100\%$
Methanol	40	88.4	0.61	47.0
	50	92.8	0.60	47.8
	60	101.6	0.57	50.4
	70	110.3	0.55	52.2
	80	116.0	0.53	53.9
	90	119.8	0.52	54.8
Ethanol	40	118.1	0.53	53.1
	50	147.1	0.47	59.1
	60	204.4	0.38	67.0
	70	244.9	0.33	71.3
	80	251.4	0.32	72.2
	90	269.0	0.31	73.0

coefficients include the diffusion coefficient (D), the velocity (v) of Case II, and the equilibrium solvent content (ESC). The ESC of the system is defined as the equilibrium weight of solvent in the specimen divided by the weight of the virgin specimen. The diffusion coefficient and the velocity of Case II for the methanol system are larger than those of the ethanol system. The physical meaning of this is that the time of the methanol system to reach saturation is shorter than that of the ethanol system. In addition, for the PMMA with saturated solvent, the amount of solvent absorbed in the ethanol system is more than that in the methanol system. This is because the solubility parameter for the methanol system is not as close to that of PMMA as the solubility parameter of the ethanol system is.

Hydrolysis

The weight losses for the PMMA with saturated solvent and desorbed in the 40–90°C distilled water [Figs. 2(a) and 2(b)] and under air [Fig. 2(c)] are provided. It is shown that the weight loss under air decreases as hydrolysis time increases until there is no weight change. The initial hydrolysis rate in the methanol system is larger than that in the ethanol system. However, hydrolysis in distilled water is quite different. The weight increases, not decreases, with the increase in hydrolysis temperature and time. This is because hydrolysis of the organic solvent was impeded by distilled water. In addition, for the PMMA with saturated solvent, the effective glass transition temperature becomes low,²³ which relatively increases distilled water diffusion into the specimen. Furthermore, at a higher hydrolysis temperature, the mass transport temperature in hydrolysis process is raised again more slowly, which causes more distilled water getting into the specimens, hence increasing the weight. In the whole hydrolysis process, when the

transport temperature of PMMA is raised again to be higher than the hydrolysis temperature, the distilled water difficultly enters into the specimen. That is, the

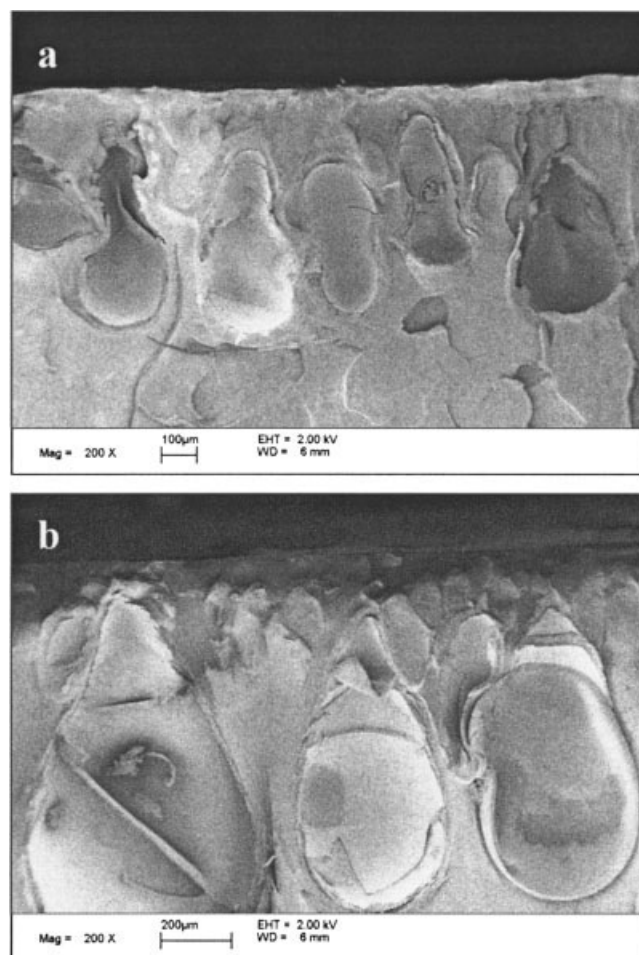


Figure 3 SEM morphology of the near surface of the PMMA with saturated methanol desorbed in 60°C distilled water for (a) 0.5 h and (b) 4 h hydrolysis time.

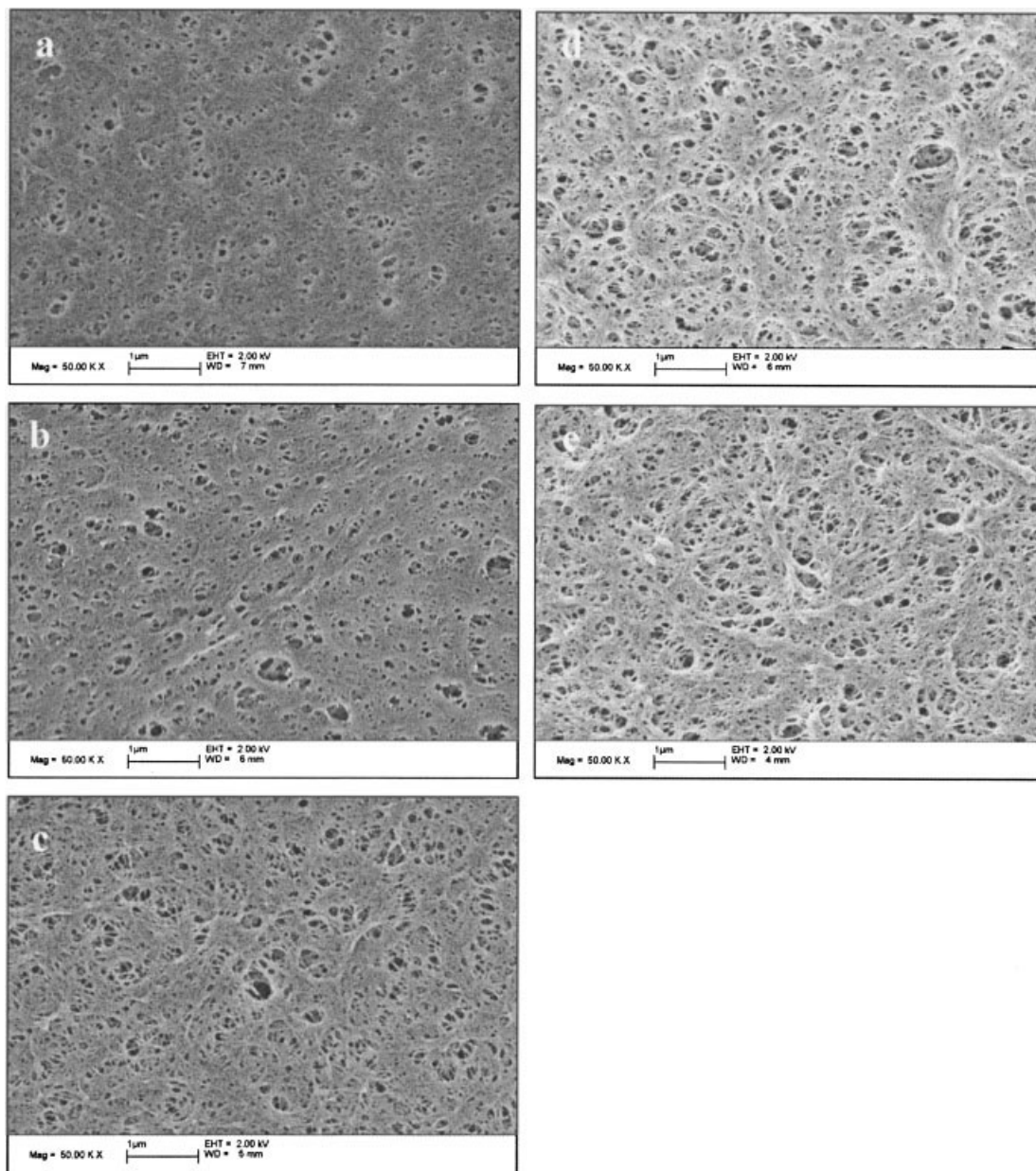


Figure 4 SEM morphology of the inside of the oval-shaped macrovoids in the near surface of the PMMA with saturated methanol desorbed in 60°C distilled water at different hydrolysis time durations: (a) 0.5 h, (b) 1.0 h, (c) 2.0 h, (d) 3.0 h, and (e) 4.0 h.

weight is then unchanged. As to the ethanol system, the required amount of absorbed organic solvent for the PMMA to be saturated and the effective glass transition temperature are less than those of the methanol system. Therefore, the time of the mass transport of distilled water to PMMA is longer, which makes for more distilled water into the specimen. The volume change ($V - V_0 / V_0$), density (ρ) and void ratio ($\rho_0 - \rho / \rho$) of the PMMA with saturated solvent desorbed in the 40–90°C distilled water are shown in Table II; these factors increase as the hydrolysis temperature increases. Besides, the increments of these factors in the ethanol system are larger than those in the methanol system.

Microstructure

The cleavage surface of the PMMA with saturated 60°C methanol desorbed in the 60°C distilled water at different hydrolysis time durations are shown in Figure 3. It can be seen that near the surface of the specimens, there are oval-shaped macrovoids formed. The major axis of the macrovoids is parallel to the direction of the mass transport of the solvent. The size of the macrovoids is proportional to the hydrolysis time, and is from $\sim 500 \mu\text{m}$ in the major axis and $250 \mu\text{m}$ in the minor axis at the time of 0.5 h [Fig. 3(a)] to $\sim 900\text{--}500 \mu\text{m}$ respectively, at the time of 4 h [Fig. 3(b)]. The magnified micrographs of the oval-shaped macrovoids from hydrolysis time of

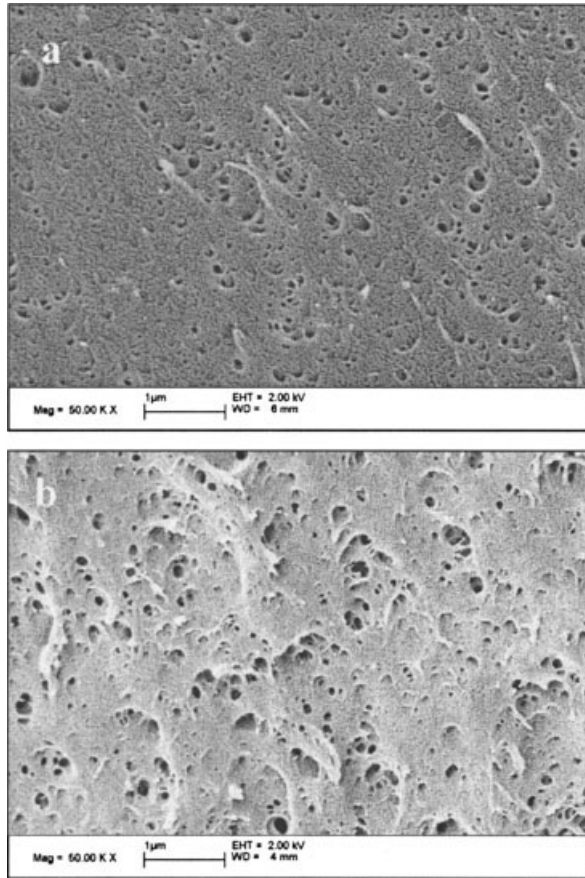


Figure 5 SEM morphology of the inside of the PMMA with saturated methanol desorbed in 60°C distilled water at (a) 0.5 h and (b) 4.0 h hydrolysis time.

0.5–4.0 h are shown in Figure 4. The voids are open-type, and the size and the quantity of the voids increase as the hydrolysis time increases. Inside of the specimen, the voids are close-type and the size is also proportional to the hydrolysis time (Fig. 5).

The cleavage surfaces of the PMMA with saturated methanol desorbed in distilled water were viewed at different hydrolysis temperatures. In the 40°C distilled water, no oval-shaped macrovoid occurred near the surface of the specimen. In the 50–70°C distilled water, there are oval-shaped macrovoids formed near the surface of the specimens. And for the PMMA desorbed in the 80–90°C distilled water, the shape of the macrovoids becomes sponge-like, as shown in Figure 6. Inside of the specimen, the macrovoids are close-type and the quantity of the macrovoids increases as the hydrolysis temperature increases in the 40–80°C distilled water. However, for the PMMA desorbed in 90°C distilled water, the macrovoids become open-type, as shown in Figure 7.

The cleavage surface of the PMMA with saturated ethanol desorbed in 60°C distilled water were observed at different hydrolysis time durations. Near the surface of the specimens, there are oval-shaped mac-

rovoids formed. The size of the macrovoids is proportional to the hydrolysis time, and is from $\sim 550 \mu\text{m}$ in the major axis and $200 \mu\text{m}$ in the minor axis at the time of 0.5 h to ~ 1200 and $550 \mu\text{m}$ respectively, at the time of 4 h. By comparing the methanol system and the ethanol system, under the same hydrolysis time, the macrovoids near the surface of the ethanol-saturated specimens are bigger, especially after desorbed for a longer time. The oval-shaped macrovoids near the surface of the PMMA are open-type, as shown in Figure 8. Inside the specimens, these macrovoids are close-type and their size and quantity increase as the hydrolysis time increases, as shown in Figure 9.

The cleavage surface of the PMMA with saturated ethanol desorbed in 40–90°C distilled water were analyzed. When the hydrolysis temperature is 40–60°C, open oval-shaped macrovoids are formed near the surface of the specimens. The void ratio increases as the hydrolysis temperature increases. However, for specimens desorbed in the 70–90°C distilled water, the macrovoids become sponge-like. Inside of the specimens, these macrovoids are close-type when desorbed in the 40–70°C distilled water, and open-type when desorbed in the 80–90°C distilled water. The quantity, size, and void ratio increase as the hydrolysis temperature increases, as shown in Figure 10.

Forming mechanism of macrovoids

For the PMMA with saturated solvent (methanol and ethanol) desorbed in the 40–90°C distilled water, when the organic solvent diffuses outside the specimens, the effective glass transition temperature is raised again. And the distilled water comes into the specimen at the mean time. During hydrolysis process, the solvent is confronted with distilled water

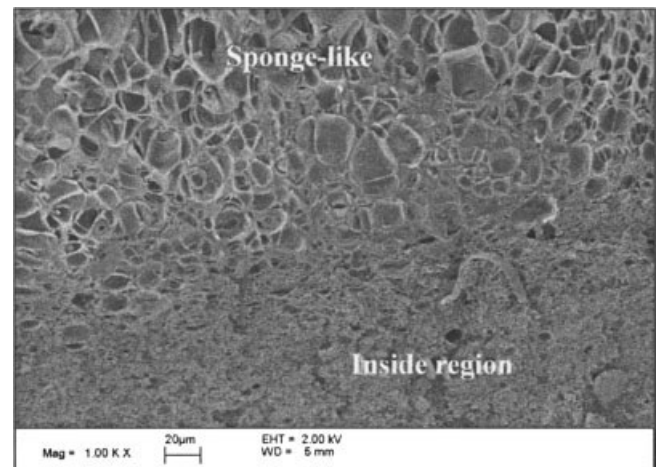


Figure 6 SEM morphology of near surface of the PMMA with saturated methanol desorbed in the 90°C distilled water.

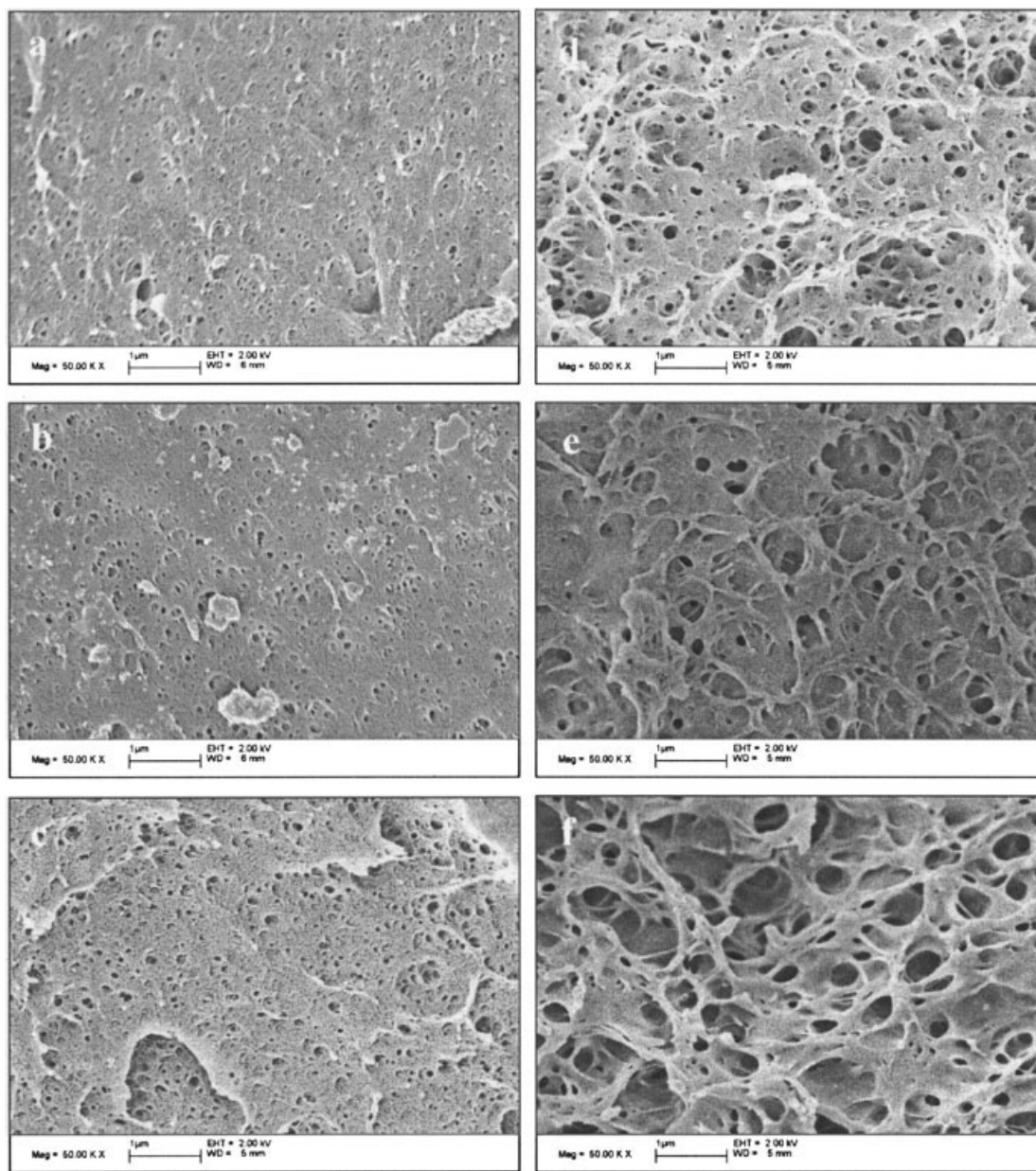


Figure 7 SEM morphology of the inside of the PMMA with saturated methanol desorbed in the distilled water at different hydrolysis temperatures: (a) 40°C, (b) 50°C, (c) 60°C, (d) 70°C, (e) 80°C, and (f) 90°C.

entering at the surface of the specimen; it becomes hydrotropic addition, which causes phase inversion and the formation of oval-shaped macrovoids. Nevertheless, as the effective glass transition temperature is raised again higher than the hydrolysis temperature, the macrovoids stop growing. On the contrary, for the PMMA desorbed in air, because the solvent is diffused quickly from the inside of the specimen, there is not enough time for the macrovoids to be formed.

Effects of hydrolysis temperature and types of solvent on shapes of macrovoids

From Table II, it is known that the volume change and void ratio increase as the hydrolysis temperature in-

creases. This is because when the hydrolysis temperature is higher, more macrovoids are formed (Figs. 3–10). In Figure 11, the thickness change of specimens is observed. For the methanol system, the specimens are obviously thicker when the hydrolysis temperature is around 50–70°C. For the ethanol system, when the hydrolysis temperature reaches 40°C, the thickness increases. However, when the hydrolysis temperature is higher than 70°C, the increase slows down. It can be explained that at this temperature, there are oval-shaped macrovoids formed at the surfaces of the specimens, which change the dimension dramatically. The formation of oval-shaped macrovoids is because the higher hydrolysis temperature helps the mass trans-

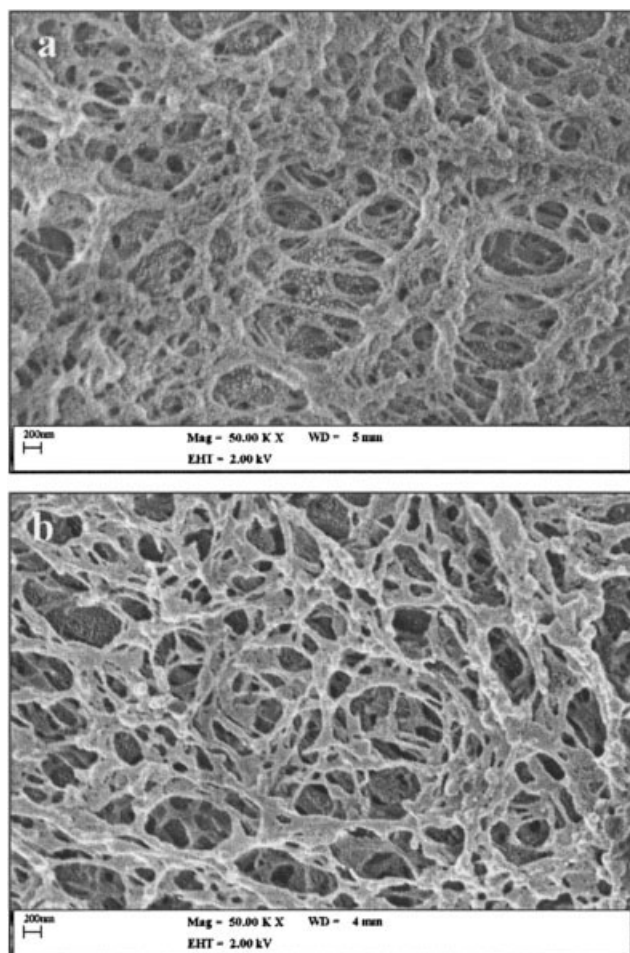


Figure 8 SEM morphology of the inside of the macrovoids in the near surface of the PMMA with saturated ethanol desorbed in 60°C distilled water for (a) 0.5 h and (b) 4 h hydrolysis time.

port of distilled water to the specimens and obscures the diffusion of the organic solvent from the specimens, that is, keeps the organic solvent staying inside the specimens longer and allows the macrovoids enough time to grow. When the organic solvent and mass-transformed distilled water confront at the surface, they converge into hydrotropic addition. As the mass transport continues, the converging continues, which increases the size of the macrovoids. After the effective glass transition temperature of the polymer near the converging area of hydrotropic addition is raised again higher than the hydrolysis temperature, the macrovoids stop growing. For PMMA in methanol system, comparing with PMMA in ethanol system, the amount of solvent absorbed is smaller and the glass transition temperature is lower, and thus the mass transport is much assisted. Consequently, the quantity of distilled water gathered in the specimen surface is more in the ethanol system, which leads to bigger oval-shaped macrovoids being produced. The diffus-

ing rate of methanol away from PMMA is higher than that of ethanol. The low hydrolysis temperature works as a coolant for the 60°C solvent saturated specimens. Because of the differences in dissolution coefficients, hot water is not easy to get into the specimens and interact with the solvent; thus, the macrovoids cannot be quickly shaped and then shrink gradually. Therefore, only few or no effective macrovoids are formed near the surface of the specimens. On the other hand, because of the mass transport of solvents and distilled water, the concentration gradient (or driving force) of hydrolysis is reduced, which slows down the organic solvent from moving out of the specimens. For the methanol system, when the specimens were desorbed in the 40°C distilled water, because the hydrolysis temperature is low, the mass transport of distilled water into the specimens is hampered, which makes methanol easy to come out of the specimens. In this mechanism, only few close macrovoids exist. In addition, when the effective glass transition temperature is lower than the hydrolysis temperature, there will not be enough time for the macrovoids inside the specimens to grow. At 50–60°C hydrolysis temperature, the oval-shaped macrovoids near the surfaces of the specimens are crosslinked (like nets). It can be explained that the oval-shaped macrovoids are where the solvent and distilled water gathered. As the solvent mass transforms to this region, the effective glass transition temperature is lower, which makes it possible for the macrovoids to grow. In the 70°C distilled water, the size of the oval-shaped macrovoids is bigger, and the reason is that the high hydrolysis temperature slows down the rate of effective glass transition temperature. At 80°C hydrolysis temperature, there is no clustered oval-shaped macrovoids formed. Because the hydrolysis temperature is higher, the surface of the membrane allows more water to come in; thus, the size of the macrovoids is bigger than that when desorbed in low hydrolysis temperatures. At 90°C hydrolysis temperature, the macrovoids are open and crosslinked. It is because at this higher hydrolysis temperature, the regaining time of the effective glass transition temperatures at the inner and outer layers of the specimens are about the same. In other words, after the effective glass transition temperature of the specimens regains higher than the hydrolysis temperature, there is still a great quantity of solvent remaining inside the specimens which are of higher hydrolysis temperature.

The macrovoid structure of the specimens in the ethanol system is similar to that in the methanol system. However, when the hydrolysis temperature reaches 80°C, the macrovoids inside the specimens are crosslinked, unlike in the methanol system, in which crosslinked macrovoids are not formed until the hydrolysis temperature reaches 90°C. This is because the solubility parameter of ethanol is much closer to that

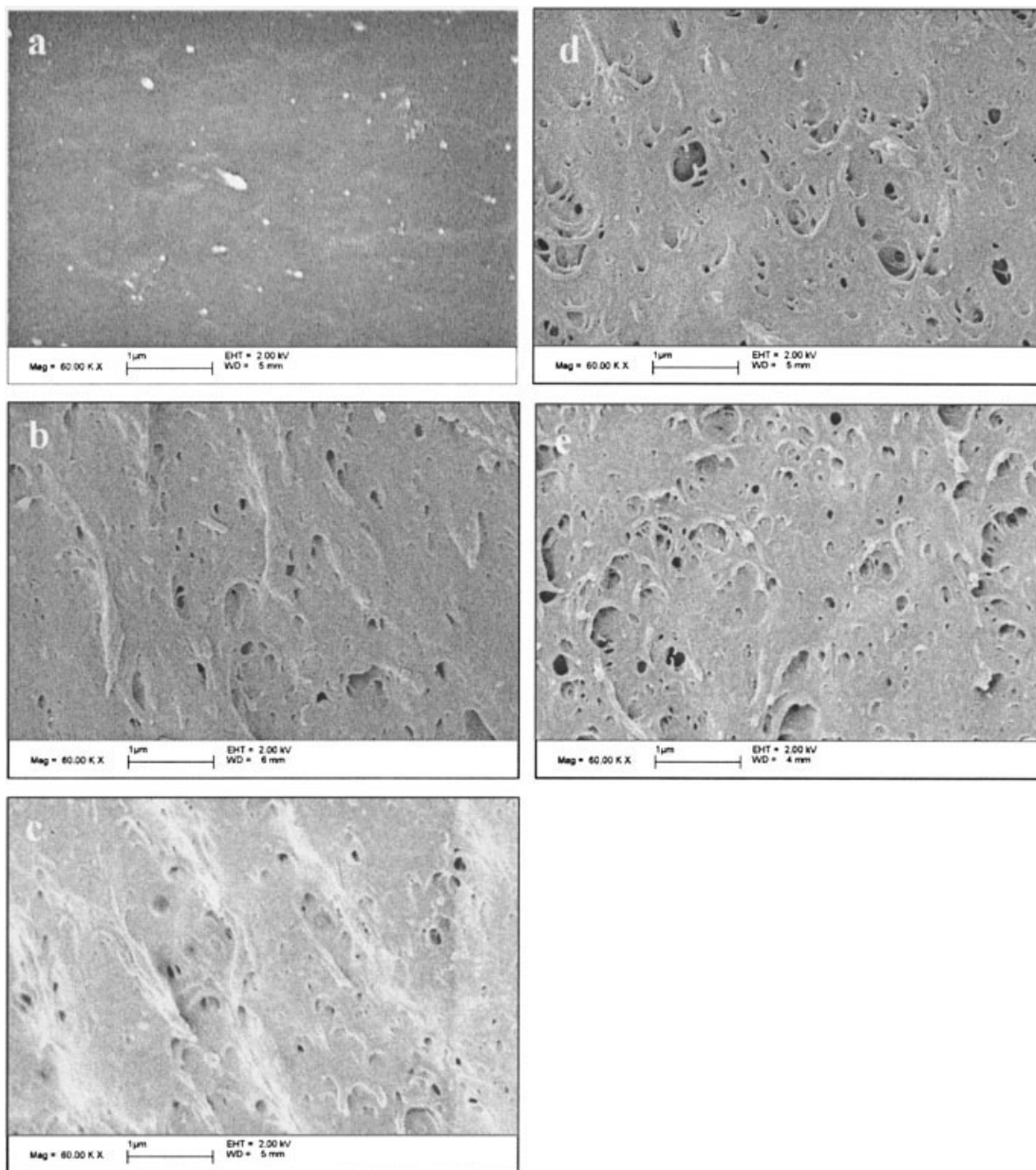


Figure 9 SEM morphology of the inside of the specimen with saturated methanol desorbed in 60°C distilled water at different hydrolysis time durations: (a) 0.5 h, (b) 1.0 h, (c) 2.0 h, (d) 3.0 h, and (e) 4.0 h.

of PMMA. Therefore, more ethanol solvent stays inside the PMMA specimens. In addition, $T_{g_{eff}}$ of ethanol is lower. Thus, after hydrolysis, the macrovoids inside or on the outer layers of the specimens are larger, and the big macrovoids where the solvent gathered are crosslinked.

Relation of transmittance and macrovoids

Originally, PMMA is transparent to light; however, after absorbing methanol or ethanol to saturation and then desorbed in the 40–90°C distilled water, the specimens turn from transparent to opaque, as shown in

Figure 12. Lin et al.^{18,27} pointed out that after absorbing methanol and cooling in the furnace or under air, PMMA would become opaque. This is because the macrovoids are enlarged by solvent during the solvent uptake and shrunken during hydrolysis, and the size of macrovoids smaller than the visible wavelength causes light scattering, thus preventing light from passing through the specimens. Moreover, because distilled water interacts with the solvent, phase inversion happens at the surface layer of the specimens and macrovoids are formed. There is little solvent gathered in the macrovoids, and hence the macrovoids are shaped at the same time. On the other hand, the

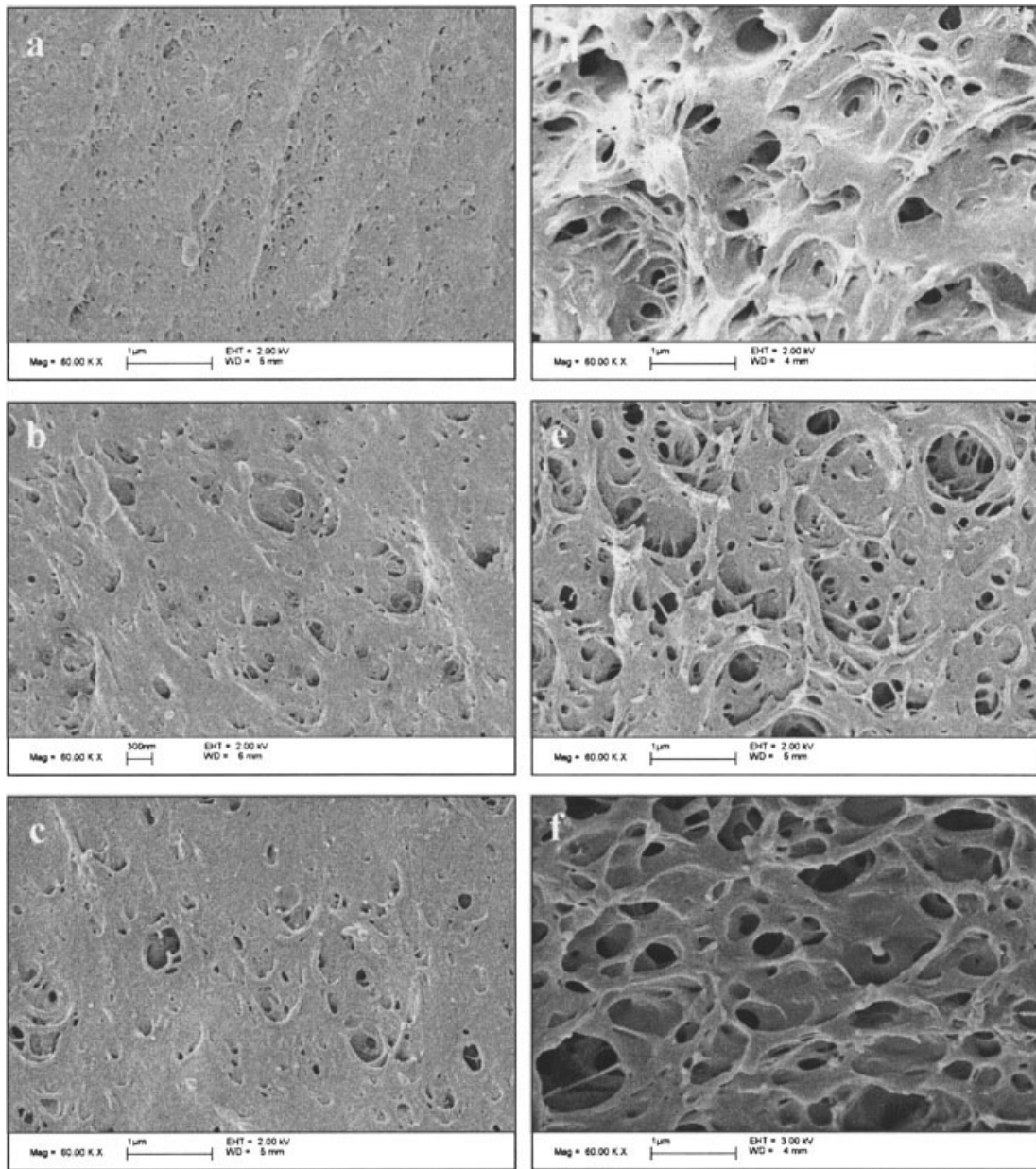


Figure 10 SEM morphology of the inside of the PMMA with saturated ethanol desorbed in the distilled water at different hydrolysis temperatures: (a) 40°C, (b) 50°C, (c) 60°C, (d) 70°C, (e) 80°C, and (f) 90°C.

macrovoids forming mechanism inside the specimens is similar to that under furnace cooling, which is from nucleation to growing. During the growing process of macrovoids, the solvent mass transforms into the free volume of PMMA, which increases the gaps between polymer molecule chains and leads to a decrease in the bonding forces (van der Waals force and mechanical locking force) between molecular chains. Therefore, the effective glass transition temperature, $T_{g_{eff}}$ is lowered and the plasticization of the macrovoids occurred. The macrovoids are then swelled and moistened. After the solvent comes into the macrovoids and enlarges the macrovoids, if PMMA desorbs under air,

the macrovoids cannot shrink completely. Hence, after $T_{g_{eff}}$ is raised again to approach its original temperature (104°C), there will be light-scattering macrovoids formed in the original solvent filled space. When the light travels into the PMMA specimens, besides passing directly through the specimens, it will continuously reflect and scatter between the macrovoids at the nonregular surfaces. The produced reflected light can be regarded as another incident light. As the gap between macrovoids gets smaller, the intensity of scattering becomes stronger, and the specimen becomes more opaque. The relations between the transmittance and the wavelength of PMMA saturated with metha-

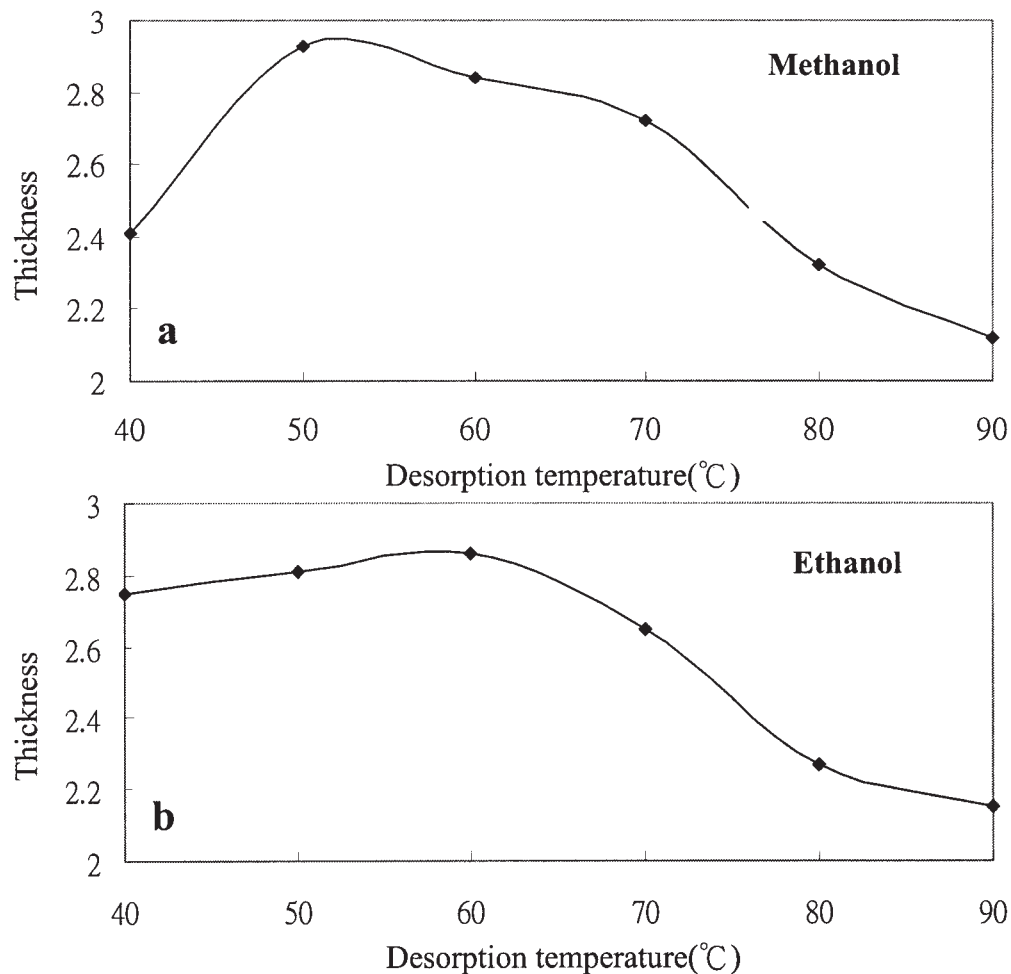


Figure 11 The thickness change for PMMA with saturated (a) methanol and (b) ethanol desorbed in the distilled water at different hydrolysis temperatures.

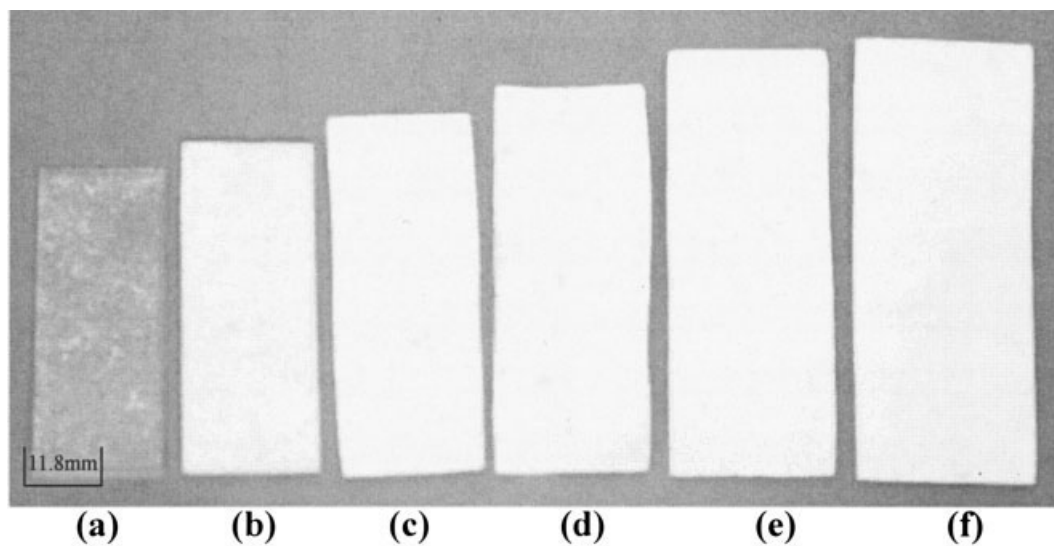


Figure 12 OM morphology of the PMMA with saturated ethanol desorbed in the distilled water at different hydrolysis temperatures: (a) 40°C, (b) 50°C, (c) 60°C, (d) 70°C, (e) 80°C, and (f) 90°C.

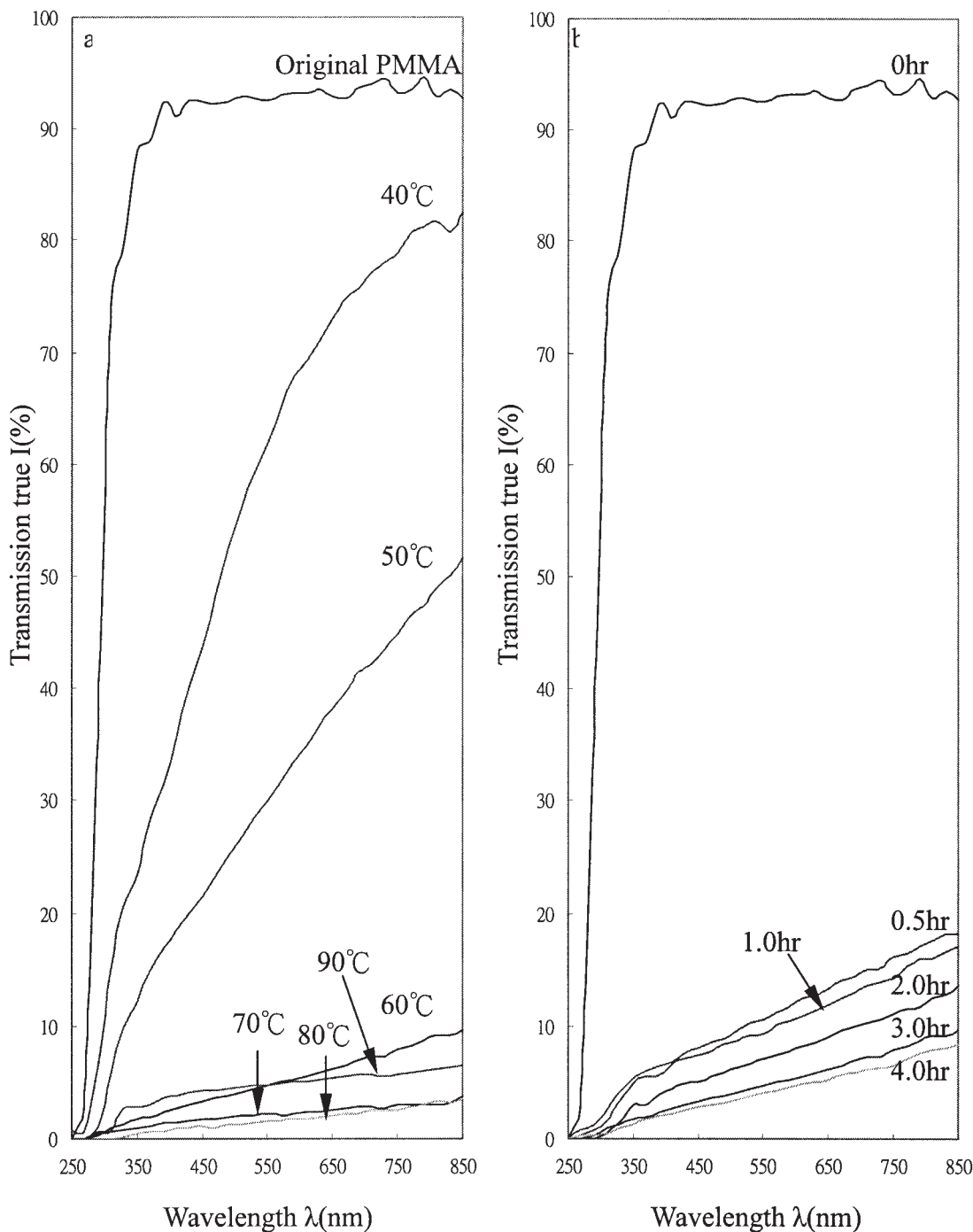


Figure 13 Plot of transmittance *versus* wavelength λ in the range 250–850 nm in the 60°C methanol system at various (a) hydrolysis temperatures; and (b) hydrolysis time durations.

nol and ethanol and then desorbed at different hydrolysis temperatures for different times are shown in Figure 13 and Figure 14. Transmittance decreases as the hydrolysis temperature and time increase. The logarithmic relations of the scattering intensity and the wavelengths are linearly dependant. The relation is defined using the equation $I_s = a\lambda^{-n}$, where a and n are constant. Both parameters a and n are calculated

using the equation and listed in Table III. The exponent, n , is in the range from 0.03 to 2.40 for the methanol system and 0.02 to 0.15 for the ethanol system, at different hydrolysis temperatures and time durations. It decreases with the increase in the hydrolysis temperature and time. According to Rayleigh, the scattering intensity is proportional to the square of electric field arising from particulate, whose size is smaller

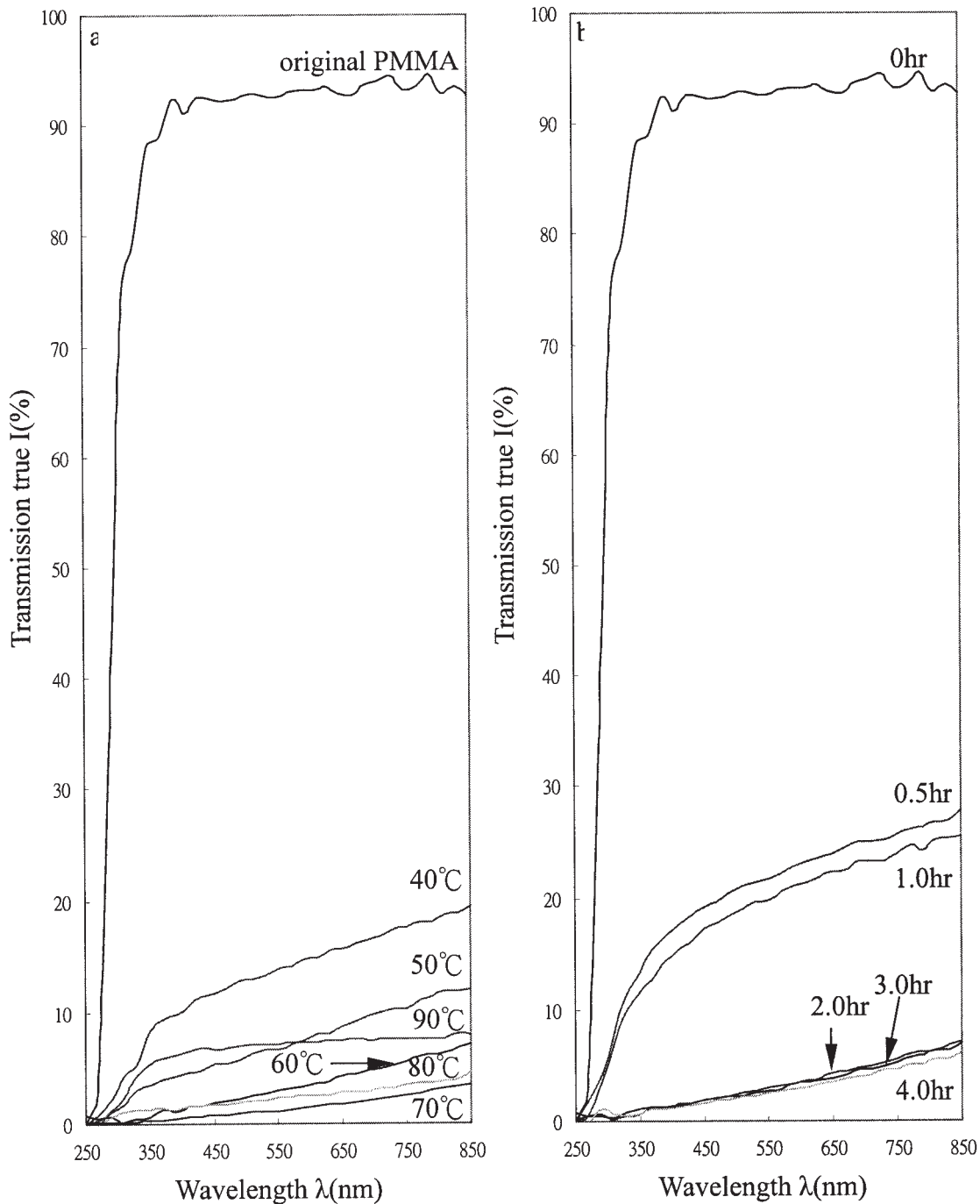


Figure 14 Plot of transmittance versus wavelength λ in the range 250–850 nm in the 60°C ethanol system at various (a) hydrolysis temperatures; and (b) hydrolysis time durations.

than the visible wavelength.²⁴ The electric field due to particulate scattering is inversely proportional to the square of visible wavelength when the surface of particulate is considered. The scattering intensity is proportional to λ^{-4} . The exponent, n , smaller than 4 may be due to the fractal surface macrovoids.^{19–22} The fractal surface dimension of a macrovoid is $n/2$. The dependence of scattering intensity upon light wave-

length arises from the different obstructive efficiency of the small particulate to various light wavelengths. It is known that methanol and virgin PMMA are transparent in the visible range, i.e., transmittance is above 90%. For the specimen with saturated methanol and ethanol desorbed in the distilled water, the dependence of scattering intensity upon visible wavelength is only attributed to the macrovoids. The macrovoids

TABLE III
Values of Constant a and Exponent n in $I_s = a\lambda^{-n}$
Related to Hydrolysis Temperature and Solvent

	a		n	
	Methanol	Ethanol	Methanol	Ethanol
Hydrolysis temperature (°C)				
40	6.06	0.32	2.40	0.15
50	1.99	0.28	0.80	0.12
60	0.24	0.18	0.11	0.08
70	0.04	0.11	0.03	0.05
80	0.04	0.07	0.04	0.04
90	0.05	0.01	0.04	0.02
Hydrolysis time (h)				
0.5	0.45	0.37	0.20	0.21
1.0	0.40	0.38	0.17	0.19
2.0	0.34	0.19	0.15	0.08
3.0	0.244	0.18	0.11	0.08
4.0	0.204	0.16	0.09	0.07

in the PMMA are considered as small particulates to scatter the visible light.

CONCLUSIONS

The conclusions are as follows:

1. For the PMMA with saturated solvent desorbed in the distilled water, the weight of the specimens increases as the hydrolysis time and temperature increase until the specimens are saturated. The weight gained in the ethanol system is greater than that in the methanol system.
2. In the PMMA with saturated methanol desorbed in 60°C distilled water (methanol system), there are oval-shaped macrovoids formed on the surface layer of the specimens. The macrovoids are close-type. However, after the specimens were desorbed in 90°C distilled water, there are sponge-like macrovoids formed on the surface of the specimens. Except PMMA desorbed in the 90°C distilled water in which the macrovoids are of open-hole type, they are all close-type macrovoids and the size and quantity of them increase as the hydrolysis temperature and time increase.
3. In the PMMA with saturated ethanol desorbed in the 40–60°C distilled water (the ethanol system), the macrovoids formed on the surface layers of the specimens are oval-shaped and the holes are of open-type. The void ratio increases

as the hydrolysis time increases. For PMMA desorbed in 70–90°C distilled water, the macrovoids on the surface layers are sponge-like. For the macrovoids inside the specimens, when hydrolysis temperature is 40–60°C, the holes are close-type; however, when hydrolysis temperature is 70–90°C, they are of open-hole type.

4. The reduction of transmittance, which is induced by light scattering, increases as the hydrolysis temperature and time increase. The reduction in the ethanol system is more obvious than that in the methanol system.

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