

Preparation and Characterization of Poly(dimethyl amino ethyl methacrylate) Modified Poly(vinyl alcohol) Membrane by UV Radiation for the Permeation of 5-Fluorouracil

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ABSTRACT: Poly(vinyl alcohol) was modified by UV radiation with dimethyl amino ethyl methacrylate (DMAEMA) monomer to get poly(dimethyl amino ethyl methacrylate) modified poly(vinyl alcohol) (PVADMAEMA) membrane. The PVADMAEMA membranes were characterized by Fourier transform infrared spectroscopy. The tensile strength and elongation of PVADMAEMA membranes were measured by Universal Testing Machine. The results of X-ray diffraction (XRD) and differential scanning calorimetry (DSC) showed that (1) the crystalline area in PVADMAEMA decreased with increasing the content of poly(dimethyl amino ethyl methacrylate) in the membrane. (2) Only one glass transition temperature (T_g) was found for the various PVADMAEMA membranes. It means that poly(dimethyl amino ethyl methacrylate) and PVA are compatible in PVADMAEMA membrane. (3) The T_g of the membrane is reduced with increasing the content of poly(dimethyl amino ethyl methacrylate) in the membrane. The water

content on the PVADMAEMA membranes was determined. It was found that the water content on the PVADMAEMA membrane increased with increasing the content of poly(dimethyl amino ethyl methacrylate). The changes of properties enhanced the permeability of 5-Fluorouracil (5-Fu) through the PVADMAEMA membranes. A linear relationship between the permeability and the weight percent of poly(dimethyl amino ethyl methacrylate) in the PVADMAEMA membrane is found. It is expressed as P (cm/s) = $(9.6 \pm 0.4) \times 10^{-5} + (8.8 \pm 0.6) \times 10^{-5} W_x$, where P is the permeability of 5-Fu through the membrane and W_x is the weight percent of poly(dimethyl amino ethyl methacrylate) in the PVADMAEMA membrane. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3182–3188, 2012

Key words: poly(vinyl alcohol); poly(dimethyl amino ethyl methacrylate); permeability; 5-fluorouracil

INTRODUCTION

Because of the excellent properties such as high abrasion resistance, elongation, tensile strength, flexibility, chemical stability, easy processability to film, and high hydrophilicity, poly(vinyl alcohol) (PVA) is an attractive material for the use in many fields.^{1–36} For examples, the studies on diffusive permeability of solutes in poly(vinyl alcohol) (PVA) gel membranes and the application for separation have been reported.^{1–6} Because of the higher affinity for water compared to alcohols, PVA membrane was applied on pervaporation.⁷ Several studies showed that PVA membrane with the sulfonated acid could reduce methanol permeability.^{8–12} As the excellent properties, PVA is also modified and evaluated for the

applications of polymer electrolyte, Zn–air batteries, rechargeable Ni–MH batteries and direct methanol fuel cell.^{13–28} In addition, PVA is biocompatible and nontoxic, and exhibits minimal cell adhesion and protein absorption so PVA has been developed for biomedical applications.^{29–36}

The chemotherapy agent 5-Fu (fluorouracil) has been in use against cancer for about 40 years.³⁷ For cancer patients, the treatment with infusion method has higher response rate and is safer than the treatment with injection method. But the long-term usage with drip is inconvenience for patients. The catheter-related complications often occur by this treatment. The oral-style can provide the same pharmacokinetic effect as the treatment of infusion method and the usage is easy so the developments about the research with drug control release become important.

The cytotoxic anticancer drug often causes severe side effects because it does not act selectively on the target. To control the release rate of 5-Fu, chitosan/PVA blended hydrogel membranes can be used as the protective drug coatings. The permeability of 5-

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Fu through chitosan/PVA blended hydrogel membranes was evaluated in our previous study.³⁸

Hydrogels exhibit the ability to swell in water and retain a significant fraction of water within its structure without dissolving. It has physical properties similar to those of human tissues and possesses excellent tissue compatibility. A variety of synthetic and naturally derived materials may be used as hydrogels. Synthetic materials include poly(hydroxyethyl methacrylate), poly(dimethyl amino ethyl methacrylate), poly(vinyl alcohol), poly(ethylene glycol dimethacrylate), poly(ethylene oxide), poly(acrylic acid) and its derivatives, etc. Naturally derived hydrogels include agarose, alginate, chitosan, collagen, gelatin, and hyaluronic acid.

As the radiation, such as γ -ray or UV photografting or polymerization, provides a sterilization effect and no initiator is required for polymerization, no environmental pollution and biological toxic substances are generated. In our previous study,³⁹ we reported the grafting of dimethyl amino ethyl methacrylate (DMAEMA) onto the membrane of styrene-butadiene-styrene triblock copolymer by UV photografting without degassing. The graft copolymer was characterized and the absorption of fibrinogen and albumin onto membranes was performed to evaluate the biocompatibility of the graft copolymer membranes.

In this study poly(vinyl alcohol) modified by UV radiation with dimethyl amino ethyl methacrylate (DMAEMA) monomer to get poly(dimethyl amino ethyl methacrylate) modified poly(vinyl alcohol) (PVADMAEMA) membrane is reported. The PVADMAEMA membranes were characterized by FTIR. The thermal stability of the PVADMAEMA membrane was studied with differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The water content of distilled water on the PVADMAEMA membrane was determined. In addition, the permeation of 5-Fu through the PVADMAEMA membrane was also conducted.

MATERIALS AND METHODS

Materials

The chemicals used in this study were poly(vinyl alcohol) obtained from Sigma., ($M_w = 70,000$ – $100,000$ g), dimethyl amino ethyl methacrylate (DMAEMA) obtained from Acros. 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one from Ciba was used as photo-initiator. 5Fu was purchased from Sigma and used for permeation test.

Preparation of PVADMAEMA membranes

Totally, 10 wt % PVA solution was prepared by dissolving PVA in 85 °C distilled water with stirring

for 2 h. Various contents of DMAEMA monomer with 1 wt % photo-initiator dissolved in distilled water were added to the PVA solution to form 0, 20, 40, 60, 80, and 100% (w/w) mixture solutions with stirring for 0.5 h. The weight ratio between DMAEMA monomer and PVA is about 0/100, 20/80, 40/60, 60/40, 80/20, and 100/0, respectively. The mixture solutions were poured onto a clean Teflon surface and irradiated by UV light, the wavelength is 365 nm, without degassing at room temperature. After irradiation for about 30 min, the UV source was turned off and the mixture solutions were maintained at 50°C to keep the polymerization going and let the solvent evaporate until PVADMAEMA membranes were formed. The PVADMAEMA membranes were washed in n-hexane with ultrasonication to move unreacted DMAEMA monomer and followed by drying in a vacuum oven before use. The PVADMAEMA membranes were noted as PVA, PD82, PD64, PD46, PD28, and poly(DMAEMA) for the membranes prepared with weight ratio between DMAEMA monomer and PVA is about 0/100, 20/80, 40/60, 60/40, 80/20, and 100/0, respectively.

The chemical compositions of these membranes were characterized with Fourier transfer infrared spectra (FTIR, Bio-Rad/FTS165). Various PVADMAEMA membranes were cut into pieces measuring 50 mm \times 10 mm \times 0.5 mm. The stress-strain curve of the membranes was determined using the Universal Testing Machine (Hung Ta H1-9102). The thermal property was evaluated with DSC (Du Pont 2100 DSC V4 OB). The DSC was scanned at heating rate of 10°C /min. The X-ray diffraction curve for various samples was conducted with XRD (Siemens/D5005).

Measurement of water content on the PVADMAEMA membranes

The PVADMAEMA membrane was cut into 2 cm \times 2 cm and dried in a vacuum oven at 50°C for 12 h to determine its dry weight (W_d). Water content was measured by immersing the PVADMAEMA membrane in distilled water at 25°C. The wet weight with different immersion times (W_t) was determined by wiping off the surface water with a piece of filter paper. The absorbed water content was then calculated by

$$\text{Water content (W\%)} = (W_t - W_d) / W_t.$$

As swelling reaches equilibrium, water content approaches the saturated swelling and known as the equilibrium content, W_{eq} (%).

Permeation studies

Permeation studies were performed using side-by-side diffusion cells. Preswollen PVADMAEMA membranes were mounted between the two half-

cells of the donor cell and receptor cell. A solution with a 5-Fu concentration was added to the donor cell, and fresh buffer solution was added to the receptor cell. The entire content of the receptor cell was removed at regular time intervals and replaced with fresh buffer solution. To ensure constant temperature of the solution, water with constant temperature was pumped through the outer half-cells. An ultraviolet-visible light spectrophotometer (Ultrospec 1100 pro, Biochrom, Cambridge, UK) was used to measure the absorbance of the samples taken from the receptor half-cell. The 5-Fu concentration of each sample could be determined using a calibration curve derived from the absorbance of the known concentration of 5-Fu. The permeability coefficients, P (cm/s), were determined^{38,40} from the following equation.

$$-(V/2A) \ln[1 - 2(C_t/C_0)] = Pt, \quad (1)$$

where C_t is the solute concentration in the receptor cell at time t , C_0 is the initial 5-Fu concentration of the donor cell, V is volume of each half-cell, and A is the effective area of the membrane available for solute permeation. Linear regression was employed to calculate the permeability of 5-Fu through the membrane.

RESULTS AND DISCUSSION

Characterization of PVADMAEMA membranes

Figure 1 shows the absorption spectra of pure PVA, pure poly(DMAEMA), and various PVADMAEMA membranes, respectively. The FTIR spectrum of pure PVA membrane shows the absorption peaks at about 3256 cm^{-1} ($-\text{OH}$) and at about 1086 and 1415 cm^{-1} for the $-\text{C}-\text{O}$ group. In addition to the absorption peaks associated with pure PVA, the various PVADMAEMA membranes also had absorption peaks at about 2787 cm^{-1} for the third amino group. Since the unreacted DMAEMA is extracted with *n*-hexane, the presence of this absorption band confirms that PVADMAEMA was a copolymer. The results are similar to the study of our previous report.²¹ The monomers of DMAEMA are homogeneous dispersed in the PVA solution before preparing the copolymer. After the treatment of UV radiation, the free radical polymerization of DMAEMA monomers in the PVA matrix occurs and results in the formation of interpenetrating polymers with entanglements between PVA and polyDMAEMA.

From Figure 1, it is also found that the intensity of the peak at 2787 cm^{-1} increases with increasing the content of poly(DMAEMA) in the PVADMAEMA membranes. As polyvinyl alcohol is prepared by hydrolysis of poly(vinyl acetate), the degree of hydro-

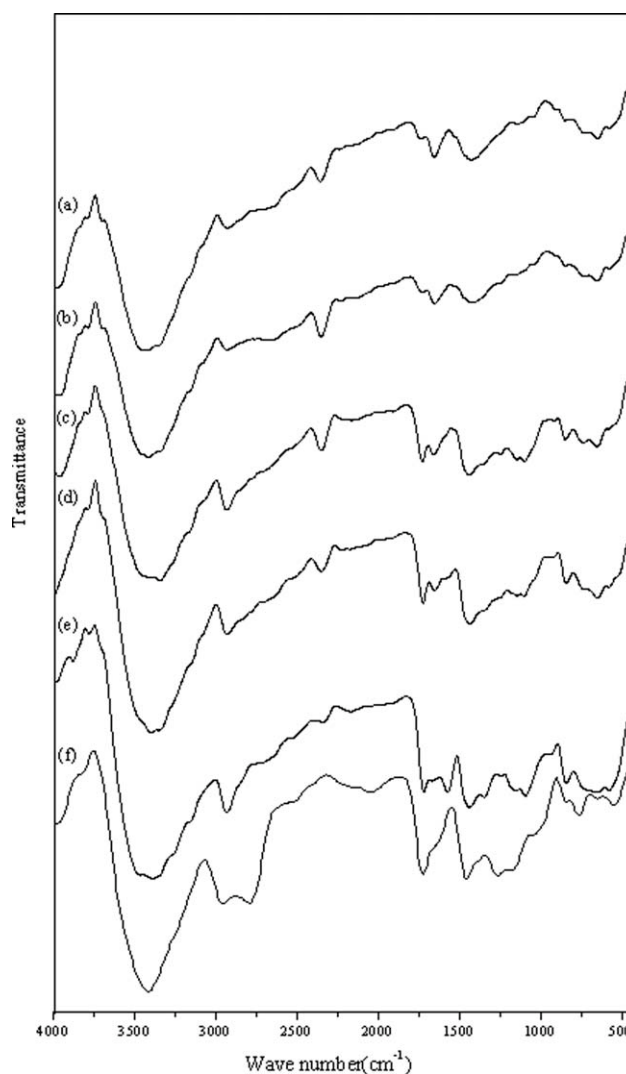


Figure 1 The FTIR spectra of various membranes: (a) pure PVA, (b) PD82, (c) PD64, (d) PD46, (e) PD28, and (f) pure poly(DMAEMA).

lysis is not complete 100% during hydrolysis. A peak at about 1700 cm^{-1} for the $-\text{C}=\text{O}$ group was found in Figure 1(a). As pure poly(DMAEMA) is a kind of ester, the peak at about 1750 cm^{-1} was found in Figure 1(f). From Table I, it is found that the intensity ratio of the peak at about 2787 cm^{-1} over that at about 3256 cm^{-1} increases with increasing the poly(DMAEMA) content in PVADMAEMA membranes. The same tendency is also found for the intensity ratio of the peak at about 1750 cm^{-1} over that at about 3256 cm^{-1} .

The results of X-ray diffraction for the PVADMAEMA membranes were found in Figure 2. For pure PVA, the peak appears at about 19.78° (2θ). With increasing the content of poly(DMAEMA) in the PVADMAEMA membrane, the intensity of the peak decreases. DSC curves of the PVADMAEMA membranes were shown in Figure 3. A melting endothermic peak at about 225°C was shown in

TABLE I
The Relative Intensity Ratio of Absorbance at About 1750, 2787, and 3256 cm^{-1} of Various Membranes

Sample	Relative intensity ratio (%)	
	Ester group/ hydroxyl group	Amino group/ hydroxyl group
PVA	0	0
PD82	10	18
PD64	16	25
PD46	18	31
PD28	20	42

Figure 3, which is associated with the crystalline polymer fraction of PVA. After modification with DMAEMA by UV radiation, the temperature shifted to low temperature with increasing the content of poly(DMAEMA) in the PVADMAEMA membrane. With comparing the area of the endothermic peak of PVADMAEMA to that of PVA membranes, it means that the crystallinity in membrane is decreased after

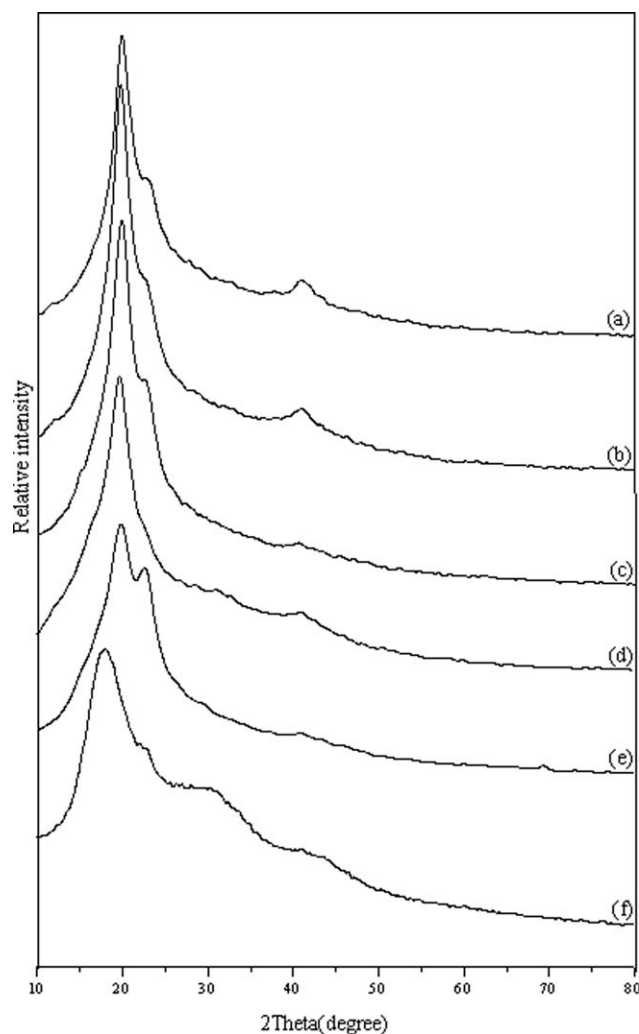


Figure 2 The XRD curves of various membranes: (a) pure PVA, (b) PD82, (c) PD64, (d) PD46, (e) PD28, and (f) pure poly(DMAEMA).

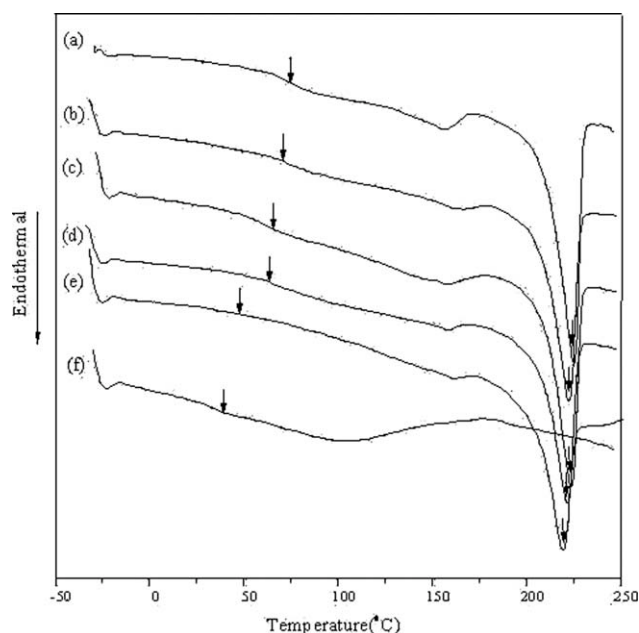


Figure 3 The DSC curves of various membranes: (a) pure PVA, (b) PD82, (c) PD64, (d) PD46, (e) PD28, and (f) pure poly(DMAEMA).

modification with DMAEMA monomer by UV radiation, which is confirmed by the results of XRD in Figure 2. The results are similar to the study of our previous report²¹; the crystallinity in the modified PVA membrane would decrease with increasing the content of amorphous polymer in the modified PVA membrane. Because of the formation of interpenetrating polymer chain of poly(DMAEMA) in the modified PVA membrane, the crystalline area of the modified PVA membrane was destroyed by comparing with the pure PVA.²¹

The glass transition temperature is about 75°C and 38°C for pure PVA and poly(DMAEMA), respectively (Fig. 3). There is only one glass transition temperature for various PVADMAEMA membranes (Table II). It means that PVA and poly(DMAEMA) are compatible in the PVADMAEMA membrane. As the glass transition temperature of poly(DMAEMA) is lower than that of PVA, the glass transition temperature of PVADMAEMA decreases with increasing the content of poly(DMAEMA) in the PVADMAEMA membrane. To predict the relationship between the

TABLE II
The T_g and T_m of Various Membranes

Sample	T_g (°C)	T_m (°C)
PVA	74.81	225.13
PD82	70.85	222.56
PD64	66.20	223.78
PD46	63.53	221.74
PD28	48.68	216.97
Poly(DMAEMA)	38.24	—

TABLE III
The Glass Transition Temperature of Various PVADMAEMA Membranes Calculated from eqs. (2) and (3) and the Relative Ratio Between the Calculated Temperature and Measured Temperature from the Results of DSC

Sample	Glass transition temperature (K)		Relative ratio (T_{gc}/T_{gm}) ^a	
	Eq. 2	Eq. 3	Eq. 2	Eq. 3
PVA	347.81	347.81	1	1
PD82	345.4	345.16	1.0045	1.0038
PD64	342	341.59	1.0083	1.0068
PD46	339.56	338.8	1.009	1.0067
PD28	328	327.47	1.0196	1.018
Poly(DMAEMA)	311.24	311.24	1.0	1.0

^a T_{gm} , the glass transition temperature obtained from the results of DSC; T_{gc} , the glass transition temperature obtained from the calculation of eqs. (2) or (3).

glass transition temperature and mol % of PVA and poly(DMAEMA) content, two different equations were assumed as follows:

$$T_g(\text{K}) = \Sigma(T_{gi} \times \text{mol}_i\%), \quad (2)$$

$$1/T_g(\text{K}^{-1}) = \Sigma(\text{mol}_i\%/T_{gi}). \quad (3)$$

Based on eq. (2), the glass transition temperature for PD82 was calculated as follows:

$$\begin{aligned} T_g &= (74.81 + 273) \times (80/44) / [(80/44) + (20/157)] \\ &\quad + (38.24 + 273) \times (20/157) / [(80/44) + (20/157)] \\ &= 345.4 \end{aligned}$$

Based on eq. (3), the glass transition temperature for PD82 was calculated as follows:

$$\begin{aligned} 1/T_g &= \{(80/44) / [(80/44) + (20/157)]\} / (74.81 + 273) \\ &\quad + \{(20/157) / [(80/44) + (20/157)]\} / (38.24 + 273) \\ &= 1/345.16 \end{aligned}$$

Based on both eqs. (2) and (3), the glass transition temperature calculated for various PVADMAEMA membranes were shown in Table III. It is found that these experimental results are actually close to the results calculated from both eqs. (2) and (3).

Figure 4 shows the relationship between the tensile strength and strain for the various PVADMAEMA membranes. The stress of pure PVA was higher than those of PVADMAEMA membranes. With increasing the poly(DMAEMA) content in PVADMAEMA membranes, the tensile strength decreased but the strain increased (Table IV). This can be explained as follows. (1) The existence of the crystalline fractions in pure PVA and a glass transition at about 75°C were found in Figure 3(a). (2)

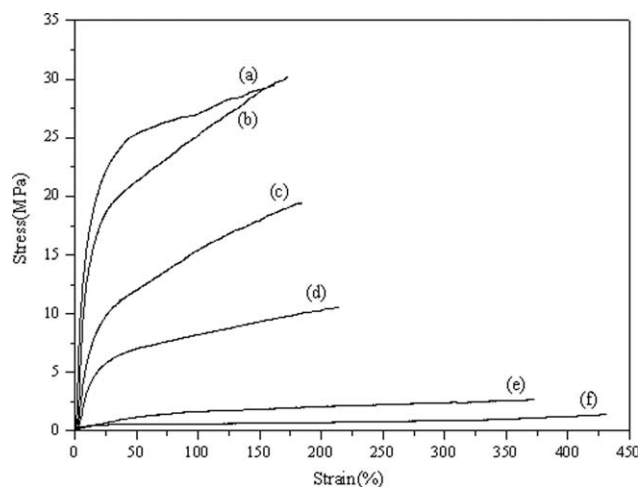


Figure 4 The stress-strain curves of various membranes: (a) pure PVA, (b) PD82, (c) PD64, (d) PD46, (e) PD28, and (f) pure poly(DMAEMA).

Crystalline fraction does not exist in the pure poly(DMAEMA) and a low glass transition temperature at about 38°C was found in Figure 3(f). (3) With increasing poly(DMAEMA) content in membrane, the relative crystalline fraction in PVADMAEMA membrane decreased, which results in the decreasing of the tensile strength and increasing of the elongation at breaking.

Water content and permeability of 5-Fu through PVADMAEMA membranes

Figure 5 shows the relationship between water content and the soaking time at 25°C for various PVADMAEMA membranes. The water content increased with the soaking time initially and then leveled off. The water content in the PVADMAEMA membrane also increased with increasing the content of poly(DMAEMA) in the PVADMAEMA membranes. Poly(DMAEMA) is soluble in water, whereas PVA is insoluble in water at 25°C. When the content of poly(DMAEMA) in the PVADMAEMA is higher than 60%, the PVADMAEMA collapses after immersed in water at 25°C.

To study the permeability coefficient of 5-Fu through the membrane, the plot of $-(V/2A)\ln[1 -$

TABLE IV
The Tensile Strength and Elongation of Various Membranes

Sample	Tensile strength (MPa)	Elongation (%)
PVA	33.6 ± 5.7	181.4 ± 8.4
PD82	32.2 ± 2.8	184.1 ± 1.8
PD64	19.4 ± 0.1	191.0 ± 9.6
PD46	11.5 ± 1.3	201.9 ± 17.5
PD28	2.5 ± 0.3	382.2 ± 2.6
Poly(DMAEMA)	1.5 ± 0.2	447.1 ± 9.9

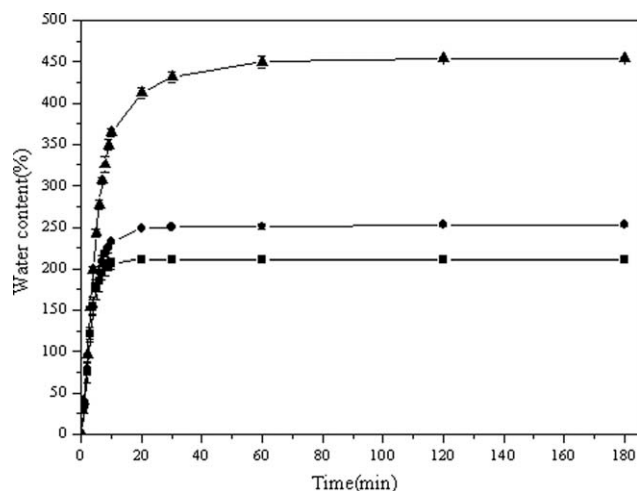


Figure 5 The water content for (■) pure PVA, (●) PD82, and (▲) PD64.

$(2C_t/C_0)]$ versus time of permeation is displayed. Straight lines were obtained for all of membranes and can be described by eq. (1). The regression results of $-(V/2A)\ln[1-2(C_t/C_0)]$ versus time (min) for 5-Fu through various membranes were shown in Table V. The permeability in the PVADMAEMA membrane increased with increasing the content of poly(DMAEMA) in the PVADMAEMA membranes. As mentioned in our previous study,³² solute transport through PVA hydrogel can be considered as pore mechanism. It means that permeation of solute in the pore model is expected to occur primarily via the bulk-like water within the hydrogel. As shown in Figure 5, water content increased with poly(DMAEMA) content in the PVADMAEMA membranes. Therefore, the permeability of 5-Fu through the PVADMAEMA membranes can be explained by water content which is based on the free volume theory of diffusion.^{40,41}

In general, the crystallinity of PVA can affect the permeability of 5-Fu through the PVADMAEMA membranes. From the study of DSC and XRD (Figs. 2 and 3), the crystallinity in the PVADMAEMA membranes was decreased by UV radiation with DMAEMA monomer. Thus the permeability of 5-Fu

TABLE V
Regression Result of $-(V/2A)\ln[1-2C_t/C_0]$ Versus Time (min) for 5-Fu Through Various Membranes

Sample	Formula	R^2	S.D. ^a
PVA	$Y = 576.3 \times 10^{-5} X$	0.999	35.3×10^{-5}
P D91	$Y = 625.4 \times 10^{-5} X$	0.999	22×10^{-5}
P D82	$Y = 674.5 \times 10^{-5} X$	0.999	9.2×10^{-5}
P D73	$Y = 730.7 \times 10^{-5} X$	0.999	11.2×10^{-5}
PD64	$Y = 787.0 \times 10^{-5} X$	0.999	13.2×10^{-5}

^a Standard deviation.

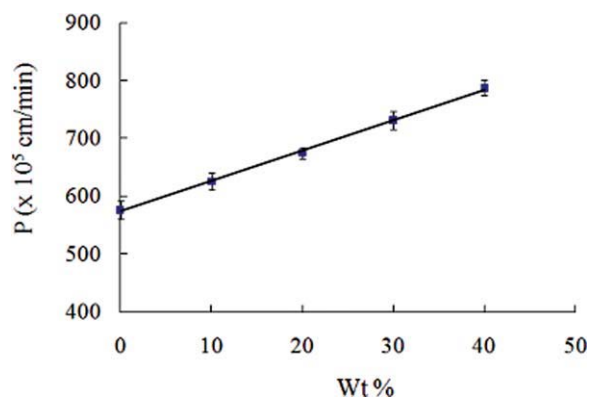


Figure 6 The relationship between permeability of 5-Fu and weight percent of poly(DMAEMA).

through the PVADMAEMA membrane increased with decreasing the crystallinity in membrane. A linear relationship between the permeability and the weight percent of poly(DMAEMA) in the PVADMAEMA membrane is found (Fig. 6). It is expressed as P (cm/s) = $(9.6 \pm 0.4) \times 10^{-5} + (8.8 \pm 0.6) \times 10^{-5} W_x$. Where P is the permeability of 5-Fu through the membrane and W_x is the weight percent of poly(DMAEMA) in the PVADMAEMA membrane.

CONCLUSION

PVADMAEMA membranes with different content of poly(DMAEMA) were prepared in this study. As there is only one glass transition temperature (T_g) for the various PVADMAEMA membranes, it means that poly(DMAEMA) and PVA are compatible in PVADMAEMA membrane. A relationship between glass transition temperature and mole percent of component can be found by eqs. (2) and (3). By comparing with pure PVA, the crystallinity of PVADMAEMA decreases with increasing the content of poly(DMAEMA) in the membrane and enhances the permeability of 5-Fu through PVADMAEMA membranes.

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