



## **CHAPTER IV**

### **INTERPOLYMER COMPLEXATION: A SIMPLE SYSTEM TO PRODUCE HYDROGEL AND AEROGEL**

#### **4.1 Abstract**

A model of interpolymer complex (IPC) hydrogel under physically crosslinked structure is proposed. The hydrogel prepared from the mixture of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) at various ratio by freezing-thawing proves to be an effective method. Freeze-drying of hydrogel is used as a procedure to convert hydrogel to aerogel. Heat treatment applied to hydrogel initiates the gel strength as clarified by increases in thermal stability. An increase of PVA crystallinity in IPC enhances the mechanical and thermal properties of the aerogel.

**Keywords:** Interpolymer complex; poly(vinyl alcohol); poly(acrylic acid); freezing-thawing; freeze drying; hydrogel; aerogel

## 4.2 Introduction

Hydrogels are three dimensional hydrophilic polymer networks which swell in water or biological fluids, and retain a large amount of fluids in the swollen state.<sup>1</sup> Hydrogels can be prepared by several techniques such as solution polymerization crosslinking, suspension polymerization, polymerization by irradiation, chemically crosslinked hydrogels and physically crosslinked hydrogels.<sup>2</sup> It should be noted that most of the chemical organic molecules to provide covalent crosslinking are toxic. An alternative way to form hydrogels is to apply the reversible ionic crosslinking or interpolymer complexes. In contrast to covalent crosslinking, no auxiliary molecules such as catalysts are required.<sup>3</sup>

For some polymers, particularly poly(vinyl alcohol) (PVA), hydrogel can be prepared by freezing and thawing of aqueous solution.<sup>4</sup> The preparation of pure PVA hydrogels using freezing and thawing techniques was prepared by varying PVA between 2.5 to 15 wt%. The PVA solutions were frozen at -20°C and thawed back to room temperature resulting in the formation of crystallites.<sup>5</sup> The possible factors related to the crystal formation are the concentration of PVA in solution, the freezing and thawing time. The crystal nucleuses are generated by freezing. During thawing, these nucleuses grow into crystals which act as crosslinking sites for polymer. Subsequent freezing produces regions of pure ice crystals to form and force sections of polymer molecules to come into “closer proximity”. The thawing process allows the “close proximity” molecules to realign and form crystalline phase.<sup>6</sup>

Inspired by the simplicity in preparing spongy-like aerogel by freeze-drying of physically crosslinked hydrogel in water-based system. Poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) are good candidates for producing interpolymer complex (IPC) hydrogels and aerogels. They are, to each other, proton-donating and proton-accepting macromolecules because of the oppositely charged with high hydrophilicity and highly biocompatibility, thermal stability and commercial availability.<sup>7</sup>

### 4.3 Experimental

**Materials** Poly(vinyl alcohol) 99% hydrolyzed with a molecular weight of 89,000-98,000, poly(acrylic acid) with an average molecular weight of 450,000 were supplied from Sigma-Aldrich Company and distilled water. All chemicals were used without further purification.

**Instruments and Equipments** The viscosity was measured by a Brookfield viscometer Model DV-III using spindle no. 21 at room temperature (25°C) and reported as centi-Poise (cP) at the highest %torque. The surface area, pore volume, and pore size were investigated using an Autosorp-1 gas sorption system (Quantachrome Corporation). Fourier transform infrared spectrophotometer (FTIR) spectrum was carried out by using a Nicolet/Nexus 670 with a 32 scans at a resolution of 4  $\text{cm}^{-1}$  in a frequency range of 4000-400  $\text{cm}^{-1}$ . Thermal characteristics of aerogel, including the melting temperature ( $T_m$ ) and heat of fusion ( $\Delta H_f$ ) were determined by a Perkin-Elmer DSC-7 instrument. The heating was carried out from 30°C to 300°C with a heating rate of 10°C/min in a  $\text{N}_2$  atmosphere. A thermo gravimetric analyzer was applied with  $\text{N}_2$  flow rate of 20 mL/min and a heating rate of 10°C/min from 30°C to 550°C. The morphology was studied by a JEOL/JSM 5200 at 15 kV. X-ray diffraction pattern of the aerogel were recorded at  $2\theta/\theta$  range of 5 degree to 25 degree by a RIGAKU RINT 2000 with  $\text{CuK}\alpha$  as an X-ray source. The operating condition is 40 kV and 30 mA with 5 degree/min scanning speed and scan step 0.2 degree using Ni filter. Tensile strength, Young's modulus and percentage elongation at break were measured by using a LLOYD Model LRX Mechanical Universal Testing Machine with a 500 N load cell, a crosshead speed of 10 mm/min and 15 mm gauge length.

**PVA/PAA Interpolymer Complex Solution** A 5 wt% aqueous solution of PVA was prepared by dissolving PVA in hot distilled water. The solution was left at room temperature before further mixing. A 5 wt% aqueous solution of PAA was prepared by dissolving PAA in distilled water and stirred at room temperature by a magnetic stirrer until the homogeneous solution was obtained. PAA solution was left overnight to eliminate the bubbles generated during stirring.

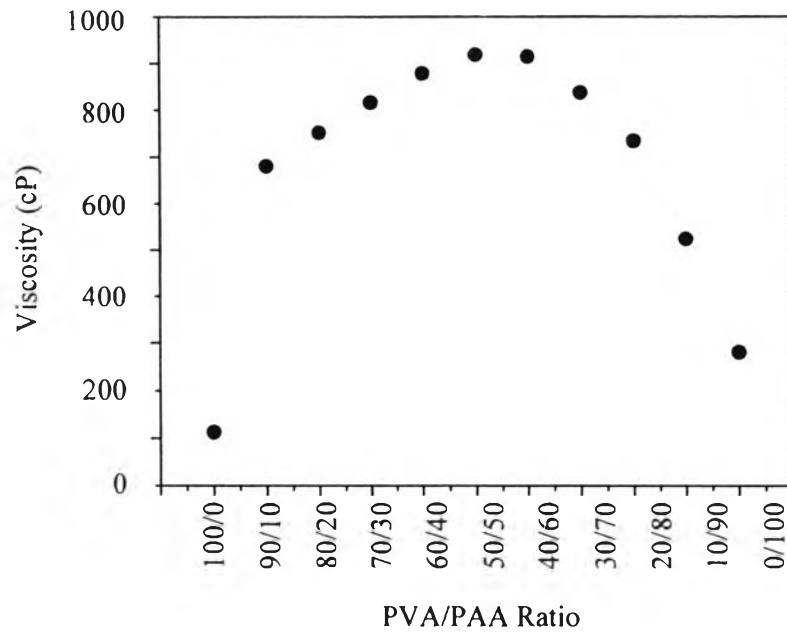
**Hydrogel Preparation by Freezing-thawing** PVA/PAA blends with 50/50, 60/40, 70/30, 80/20, 90/10, and 100/0 (v/v) ratios were prepared. Each blend was poured into polystyrene mold. Samples were submitted to seven freezing-thawing cycles to obtain hydrogels. Each cycle involved the lowering of the temperature to  $-40^{\circ}\text{C}$ , standing at this temperature for 2 h, and then rising the temperature to room temperature ( $25^{\circ}\text{C}$ ) for 1 h. The first cycle was left at  $-40^{\circ}\text{C}$  for 12 h. The obtained hydrogels were kept in the refrigerator.

**Aerogel Preparation** Hydrogel obtained from freezing-thawing was lyophilized to obtain aerogel. The mixtures of PVA and PAA with ratios of 50/50, 60/40, 70/30, 80/20, 90/10, and 100/0 (v/v) were also lyophilized and used as reference sample.

#### **4.4 Results and Discussion**

##### **Part I: Effect of Preparation Method and Heat Treatment on Aerogel Structural and Mechanical Properties.**

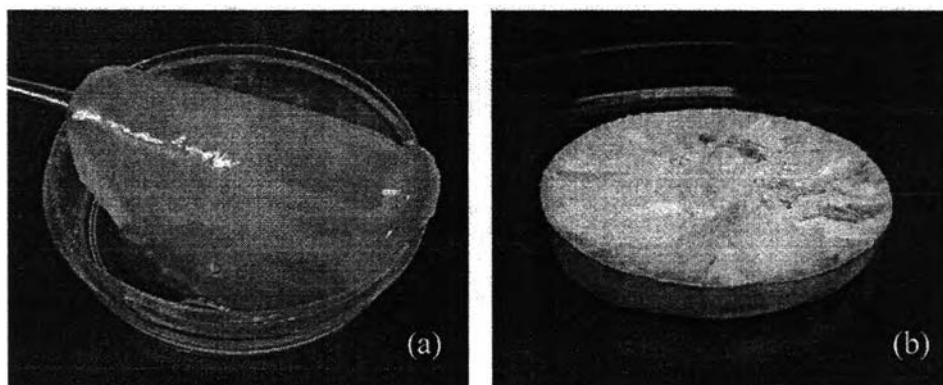
**Solution Viscosity** The shear viscosity of PVA (wt%), PAA (wt%) and PVA/PAA (wt%) mixtures at different volume fractions are shown in Figure 4.1. The viscosity sharply increases with small amount of PAA content. The highest viscosity is obtained from 50/50 mixing ratio of PVA/PAA mixture. This implied that the equal amount of different charged macromolecules give the highest intermolecular interaction. In this part, we selected 50/50 mixing ratio to study structural and mechanical properties.



**Figure 4.1** Viscosity of PVA/PAA mixtures at different volume fractions.

### Hydrogel and Aerogel Appearances

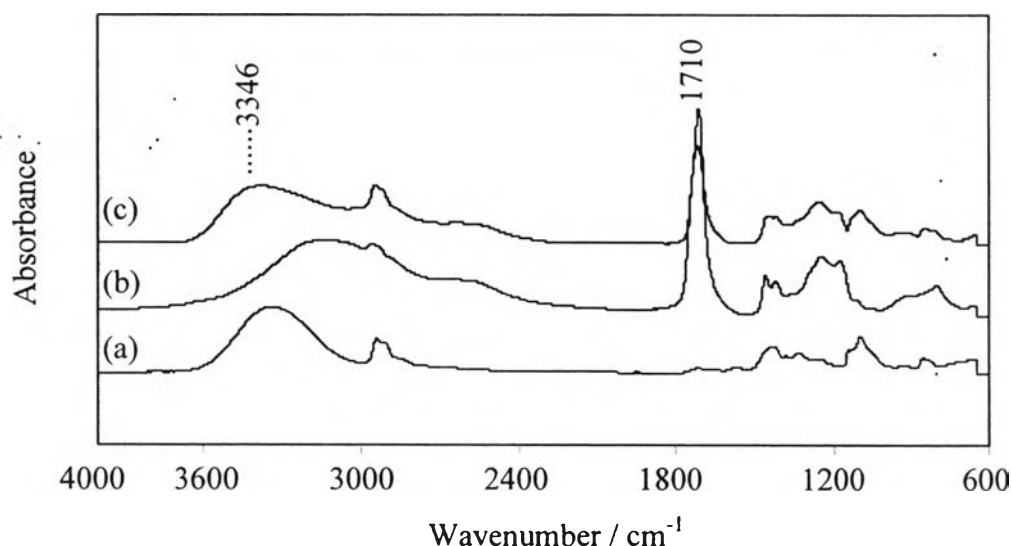
PVA/PAA mixtures were filled in polystyrene mold and the freezing-thawing were applied for 7 cycles. A soft and flexible hydrogel was obtained as shown in Figure 4.2(a). Figure 4.2(b) shows the aerogel obtained from freeze-drying of the hydrogel.



**Figure 4.2** Appearances of (a) hydrogel of PVA/PAA: 50/50 obtained from freezing-thawing, and (b) aerogel obtained from freeze-drying of (a).

### Structure and morphology of PVA/PAA complex

FTIR spectra were applied to identify the interactions in PVA/PAA blends as a function of blend composition. H-bonding interaction between two macromolecules has been proved by analysis of O-H and C=O stretching region in the FTIR spectra.<sup>8</sup> In this study, FTIR spectra are shown in Figure 4.3. PVA shows characteristic O-H stretching at  $3346\text{ cm}^{-1}$ . The absorption corresponding to the O-H stretching in PAA is a very broad band with  $\nu_{\text{max}} = 3117\text{ cm}^{-1}$  and C=O stretching at  $1710\text{ cm}^{-1}$ . These stretching were also observed in the spectra of PVA/PAA, indicating that all the O-H groups of PVA are not undergoing the crosslinking reaction with COOH group of PAA.

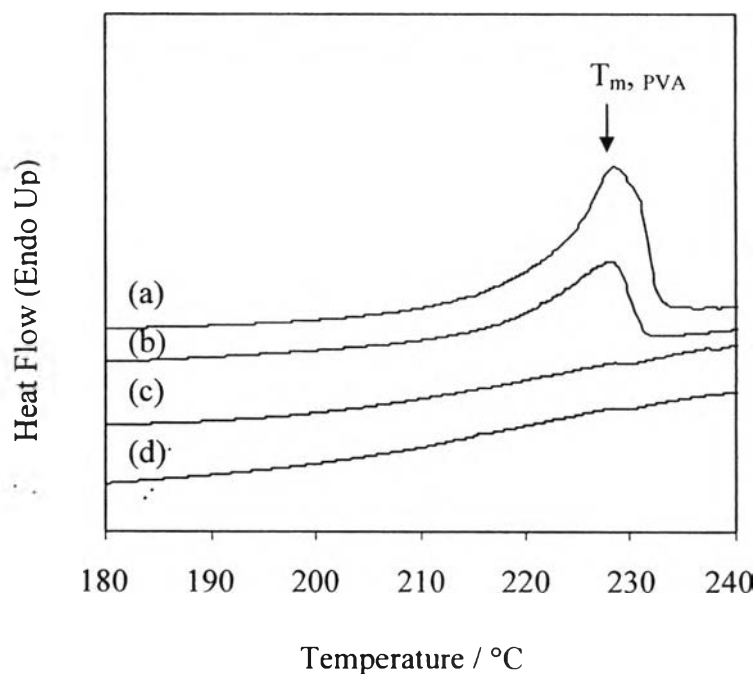


**Figure 4.3** FTIR spectra of; (a) PVA, (b) PAA, and (c) PVA/PAA films.

### Thermal Analysis

Figure 4.4 shows the melting temperature ( $T_m$ ) of PVA/PAA interpolymer complex as compared to that of pure PVA powder and pure PVA aerogel.  $T_m$  of PVA is reported in the range of  $220^\circ\text{C}$  to  $240^\circ\text{C}$  depending on the degree of hydrolyzed PVA.<sup>9</sup> The peak at  $227^\circ\text{C}$  in Figure 4.4 referred to the melting temperature of PVA. PVA/PAA complexes (Figure 4.4 (c) and (d)) from both preparation methods show no peak on DSC scans. The heat of fusion ( $\Delta H_f$ ) which can be calculated from area under  $T_m$  peak is found to be related to the degree of crystallinity of PVA.<sup>8</sup> It can be

concluded that PVA after mixing and forming complexation with PAA at equal mixing ratio loses ability to form crystals. As can be seen by  $T_m$  peak disappearance in PVA/PAA interpolymer complex both with/without freezing-thawing process applied.



**Figure 4.4** DSC thermograms of samples; (a) PVA powder, (b) PVA aerogel, (c) PVA/PAA aerogel prepared from freeze drying solution, and (d) PVA/PAA aerogel prepared from freeze drying hydrogel.

### Porous Network Characterization

**Table 4.1** Percent water uptake of PVA/PAA IPC aerogel and PVA aerogel obtained from freeze-drying of the mixing solution and freezing-thawing hydrogel

Samples	PVA/PAA from solution	PVA/PAA from hydrogel	PVA aerogel from solution	PVA aerogel from hydrogel
%water uptake	906	838	606	507

In order to prepare aerogel, freeze-drying or lyophilizing the solution or hydrogel was carried out. Here, solution of PVA (5 wt%) and the hydrogel obtained from freezing-thawing were used. The aerogel was evaluated by the porosity after the aerogel was swelled in water at 25°C for a week. Due to both of PVA and PAA are hydrophilic polymers, high %water uptake is obtained as expected. Table 4.1 shows an increase in %water uptake in PVA/PAA IPC aerogel as compared to the PVA aerogel obtained either from the solution or from the freezing-thawing hydrogel. This may be due to the disappearance of crystalline phase in PVA/PAA IPC as previously discussed in Figure 4.4. The smaller crystalline phase, the larger specific volume to retain the water in its structure will be obtained. Moreover, it was found that the PVA/PAA IPC and PVA aerogel obtained from freeze-drying of hydrogel have %water uptake slightly lower than the aerogel obtained from freeze-drying of mixing solution. This may be caused by close packing of IPC molecule during freezing-thawing process which will be discussed in Table 4.2.

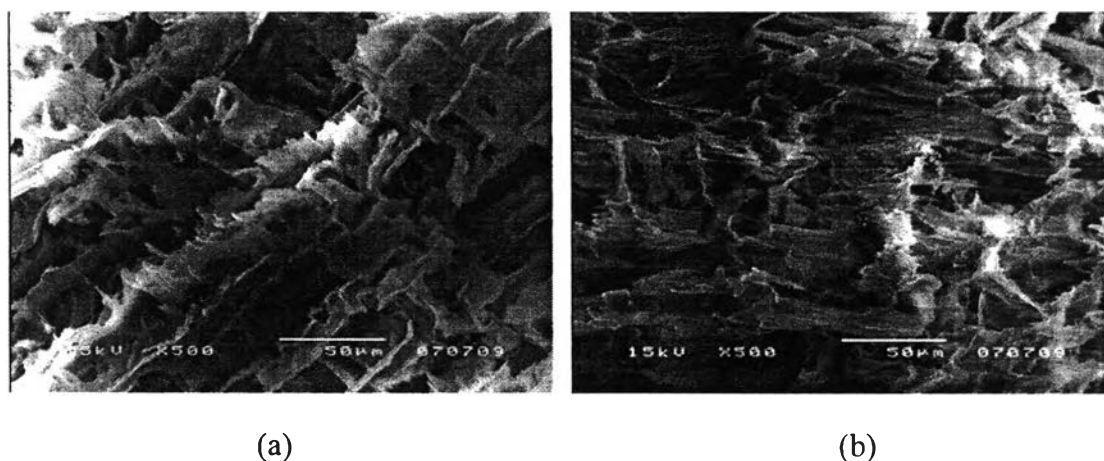
**Table 4.2** Surface area and pore volume

Samples	Surface area (m <sup>2</sup> /g)	Total pore volume (cc/g)
PVA/PAA aerogel from freeze-drying of mixing solution	5.254	0.0849
PVA/PAA aerogel from freeze-drying of freezing-thawing hydrogel	2.991	0.1071

The characteristic of the pores was further investigated by BET in terms of surface areas and pore volume. Table 4.2 shows that the aerogel obtained from PVA/PAA solution has higher surface area and lower pore volume than the aerogel obtained from freezing-thawing hydrogel. This may be because of close packing of IPC molecules during freezing-thawing process. At this process, the ice crystals grow and push the polymer molecules to come closer and pack together. Comparing with



surface area obtained from cellulose aerogel prepared by super critical CO<sub>2</sub> drying, larger surface area (400-500 m<sup>2</sup>/g) than PVA/PAA aerogels is observed.<sup>10</sup>



**Figure 4.5** SEM micrographs of the PVA/PAA aerogel observed at 15kV of; (a) the aerogel obtained from freeze drying of PVA/PAA solution ( $\times 500$ ), and (b) the aerogel obtained from PVA/PAA freezing-thawing hydrogel ( $\times 500$ ).

SEM was applied to observe the morphology of the aerogel obtained from different preparation method. Figure 4.5 shows the porous structure of PVA/PAA aerogel. This implies to the successful in preparing PVA/PAA porous materials. The holes in this figure represent the ice crystal formation which was then removed by freeze-drying process.

### **Mechanical Properties of Aerogel**

The mechanical properties of the aerogels were evaluated based on tensile strength, tensile modulus and %elongation at break. Table 4.3 summarizes the tensile properties of the PVA/PAA aerogel obtained from freeze drying PVA/PAA solution and PVA/PAA freezing-thawing hydrogel. Here, the hydrogel was obtained from seven freezing-thawing cycles. The aerogel from the freeze-thawed hydrogel shows the higher tensile strength as compared to the aerogel from the solution. This refers the interpolymer network between two polymer chains which bring the close packing structure.

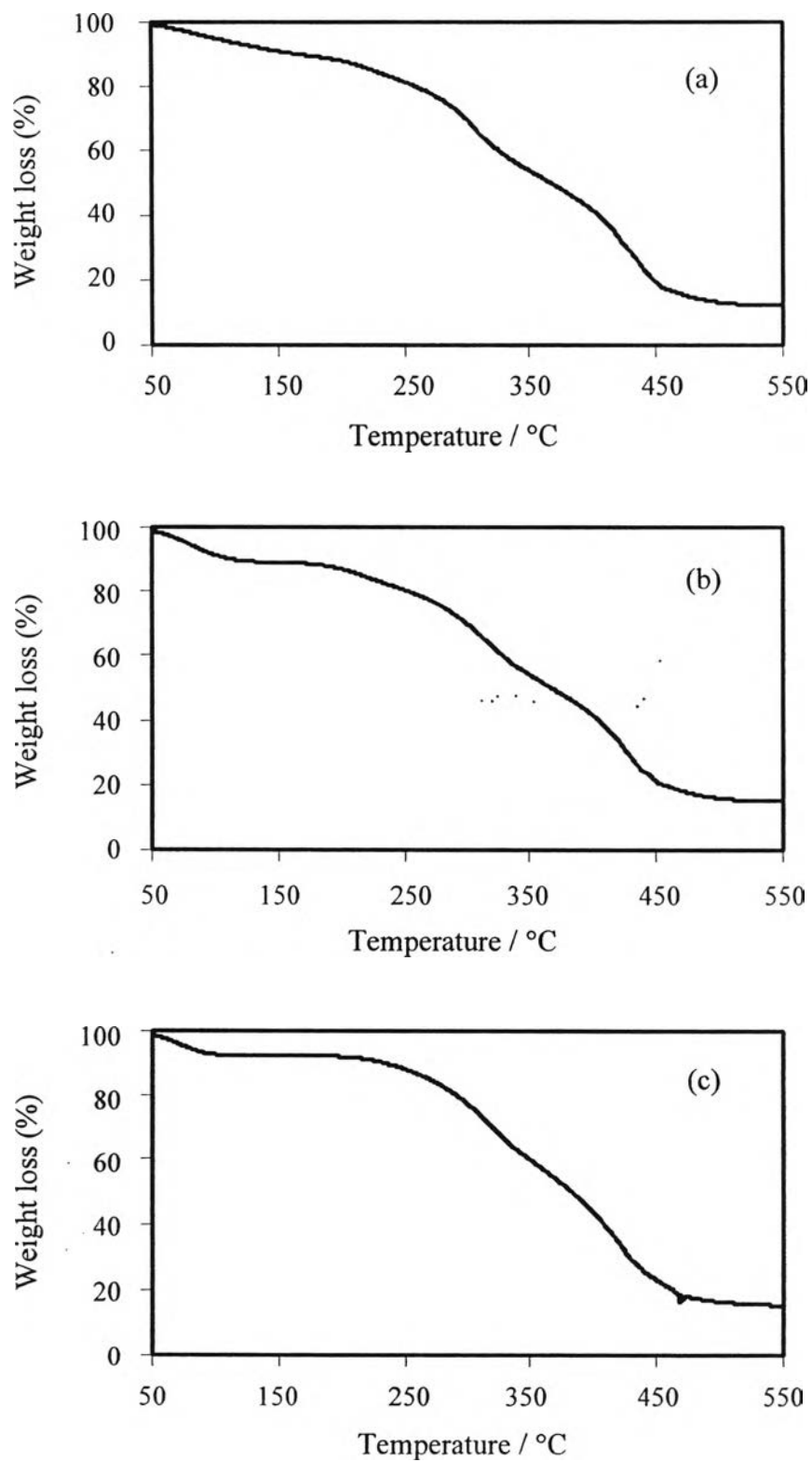
**Table 4.3** Mechanical properties of PVA/PAA aerogels

Samples	Tensile Strength (MPa)	Young's Modulus (kPa)	Elongation at break (%)
PVA/PAA aerogel from freeze-drying of mixing solution	0.24	9.18	26
PVA/PAA aerogel from freeze-drying of freezing-thawing hydrogel	0.38	12.98	30

#### **Enhancement of Aerogel Properties by Heat-treatment**

The study on crosslinking reaction of PVA with PAA by heat treatment was reported by heating PVA/PAA blended film (PVA/PAA = 8/2) at 200°C for 20 min. PAA was selected as a crosslinking reagent because it has a functional carboxyl group to react with hydroxyl group of PVA. FTIR analysis shows the degradation of PVA rather than esterification, resulting in low degree of crosslinking reaction.<sup>11</sup> In this study, TGA was used to characterize thermal stability of heat-treated aerogel.

Figure 4.6 shows the thermal stability of heat treated PVA/PAA IPC aerogel as compared to no heat treatment applied IPC aerogel. The weight loss for 10% starting from 60°C to 100°C refers to the moisture content. The first degradation step is from 300°C to 350°C. The differential thermo gravimetric (DTG) peaks of; (a) no heat treated, (b) heat treatment at 100°C, 40 min, and (c) heat treatment at 180°C, 10 min are 305°C, 318°C, 320°C, respectively. This implies that the heat treatment can enhance the thermal stability of the aerogel due to the higher degradation temperature.

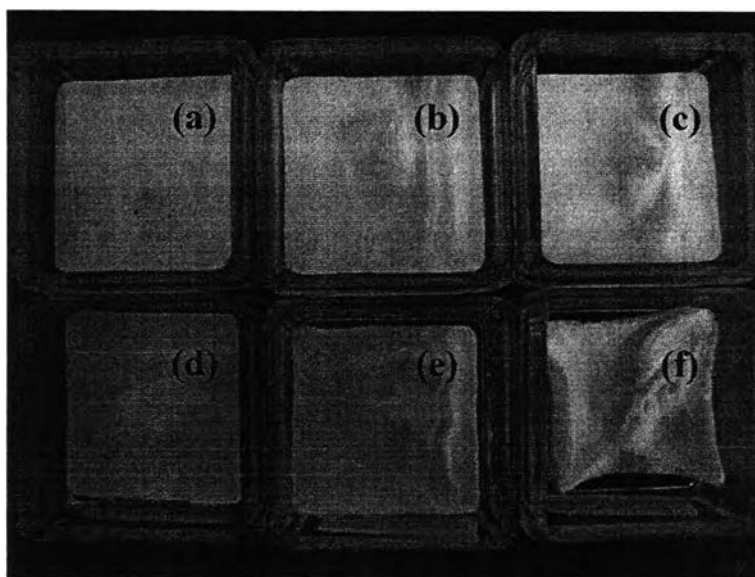


**Figure 4.6** TGA thermograms of PVA/PAA IPC aerogel; (a) no heat treatment applied, (b) heat treatment at 100 °C, 40 min, and (c) heat treatment at 180 °C, 10 min.

## Part II: Effect of PAA Content on Crystallinity and Mechanical Properties Based on Freezing-thawing Technique.

Although the aerogel obtained from freeze drying of freeze-thawed PVA/PAA hydrogel at 50/50 blending ratio in part-I has sufficient mechanical strength, the hydrogel forming ability is not satisfactory and the mechanical properties should be further improved. The study on mechanical and film forming properties improvement of PVA/PAA semi- and interpenetrating network membranes was done by increasing PVA content.<sup>12</sup> Based on this concept, PVA content was varied from 50/50 to 100/0 (PVA/PAA).

The appearance of aerogels obtained from various blending ratios is shown in Figure 4.7. The increase in PVA content aerogel showed more shrinking and distortion. At PVA/PAA more than 80/20 (v/v), aerogel started to shrink which may cause by crystalline phase formation which was confirmed by WAXD and DSC.



**Figure 4.7** Aerogel appearances at; (a) 50/50, (b) 60/40, (c) 70/30, (d) 80/20, (e) 90/10, and (f) 100/0 PVA/PAA blending ratio.

### Mechanical Properties

Table 4.4 shows that an increase in PVA content in the interpolymer complex aerogel, the tensile strength and modulus increases while the percent elongation at break fluctuates. This might be due to the increase in polymer chain packing as a consequence of freezing-thawing. Yokoyama et al. reported that PVA forms crystalline phase as a result of freeze-thaw effect.<sup>13</sup>

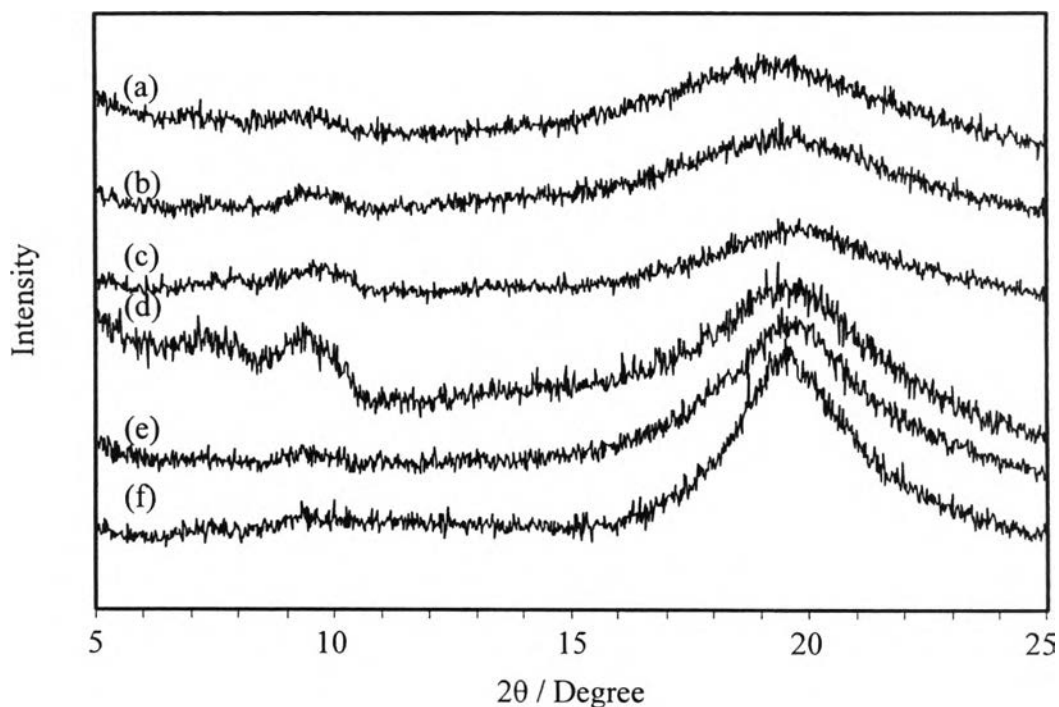
**Table 4.4** Mechanical properties of IPC prepared by freezing-thawing method

Samples (PVA/PAA)	Tensile Strength (MPa)	Tensile Modulus (kPa)	Elongation at break (%)
50/50	0.30	7.52	44
60/40	0.43	6.22	73
70/30	0.58	8.96	66
80/20	1.00	18.03	72
90/10	1.23	21.86	65
100/0	1.22	15.53	87

### Mechanical Properties Enhancement by Crystallinity of PVA

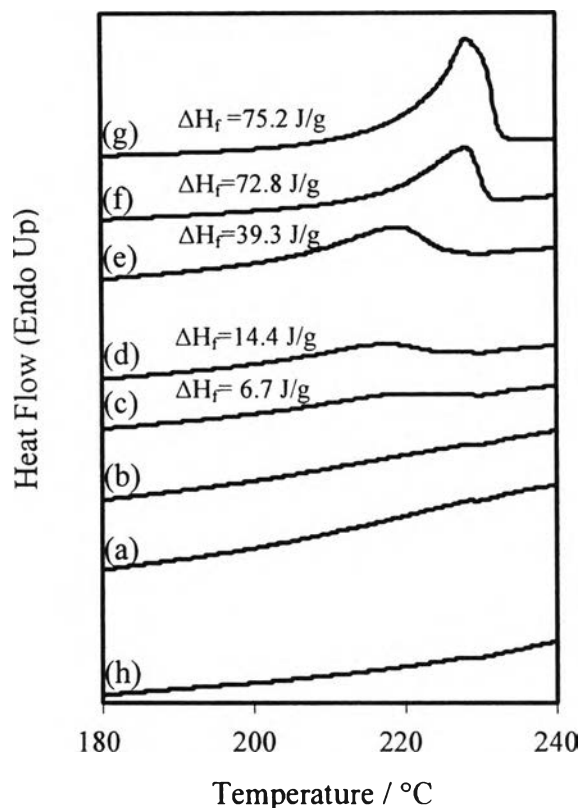
The study on PVA/PAA semi- and interpenetrating network pervaporation membranes was studied by Ruckenstein.<sup>12</sup> The presence of PVA improves the mechanical and film forming properties. In this work, effect of PVA content to aerogel strength was studied.

X-ray diffraction is also used to measure the nature of polymer and extent of crystallinity present in the polymer sample. Figure 4.8 shows the sharpen peak when PVA content increases. This implied that the more PVA content the more crystallinity.



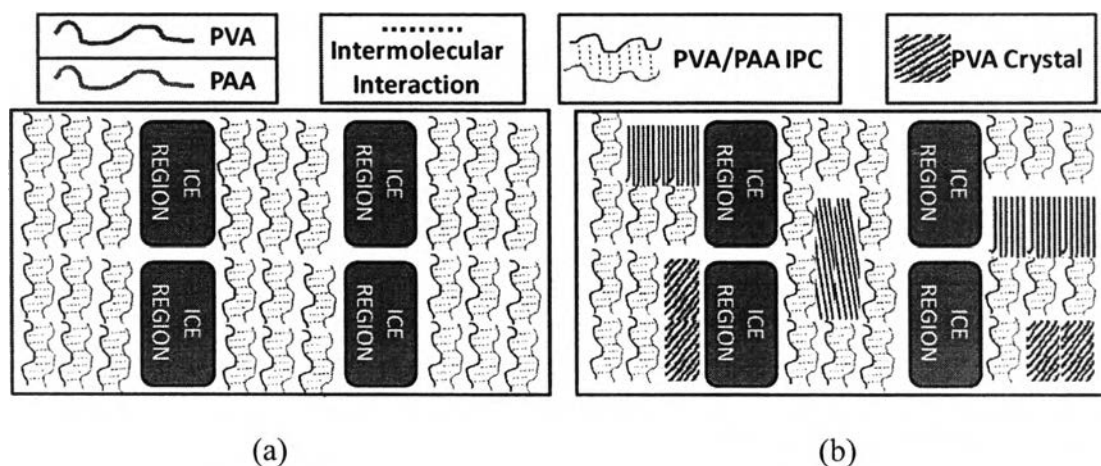
**Figure 4.8** WAXD patterns of; (a) 50/50, (b) 60/40, (c) 70/30, (d) 80/20, (e) 90/10, and (f) 100/0 PVA/PAA blending ratio.

Differential scanning calorimetry (DSC) is also used to clarify and determine the crystallinity in the complex aerogels. Figure 4.9 clearly shows that PVA content effects the crystallinity of PVA/PAA interpolymer complex as shown by area under  $T_m$  peak at temperature range between 220°C-230°C. The heat of fusion ( $\Delta H_f$ ) which implies to crystallinity of IPC aerogel can be obtained from program calculation. The heat of fusion can be started to detect at PVA/PAA blending ratio of 70/30 and gradually increase as PVA content increases.



**Figure 4.9** DSC thermograms of; (a) 50/50, (b) 60/40, (c) 70/30, (d) 80/20, (e) 90/10, (f) 100/0 PVA/PAA blending ratio, (g) PVA powder, and (h) PAA powder.

Yokoyama et al. proposed mechanism of PVA crystal formation that the gelling ability involved in freezing-thawing method was related to segregation mechanism<sup>13</sup> but the mechanism of gellation in PVA/PAA IPC hydrogel still unclear. Based on Yokoyama's concept, the gelation mechanism of IPC hydrogel is proposed in Scheme 4.1. At PVA/PAA blending ratio at 50/50 (Scheme 4.1(a)) PVA, which is known to be a semi-crystalline polymer, interact and form H-bonding with PAA until there is no free-PVA left to realign and form crystal. The increase in PVA content (Scheme 4.1(b)) shows partial part of PVA that is not interact with PAA undergo realignment and form crystalline regions. These crystalline parts cause the enhancement in mechanical properties of aerogels confirmed by WAXD and DSC.

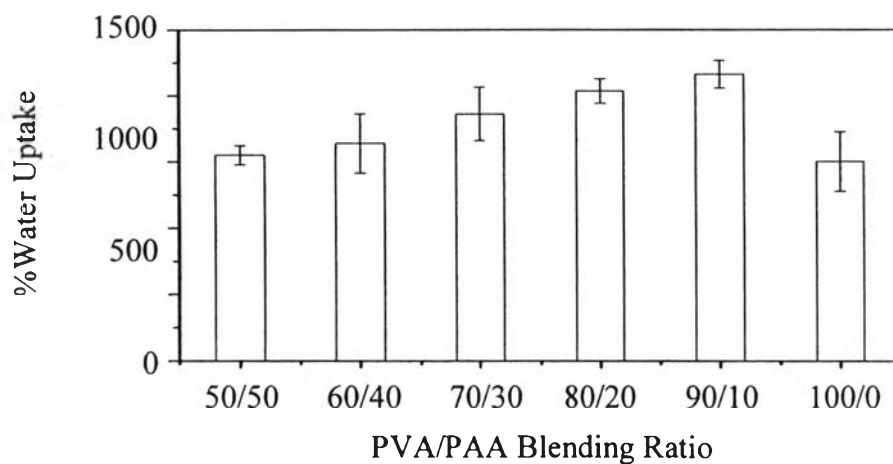


**Scheme 4.1** Schematic of freezing-thawing technique and the induction of; (a) close packing of interpolymer complex at PVA/PAA blending ratio equal to 1, and (b) interpolymer complex and phase separation of crystalline polymer when PVA/PAA blending ratio is higher than 1.

#### Porous Network Characterization

The network porosity of the aerogel was achieved by analyzing the equilibrium swelling at 25°C for 1 week or until the constant weight. Figure 4.10 shows an increase in %water uptake in PVA/PAA complex as PVA content increases. From the definition of super-absorbance material, the material should retain water molecules inside its structure over 1000% of its dried weight, the PVA/PAA IPC obtained from our method might be classified as a super-absorbance. The high %water uptake in 90/10 blending ratio might come from the significant pores of the aerogel after some part of PAA dissolving out after swollen in water. In the case of 50/50 ratio, PAA forms interpolymer complex effectively with PVA as a result, the dissolution of PAA is not significant.



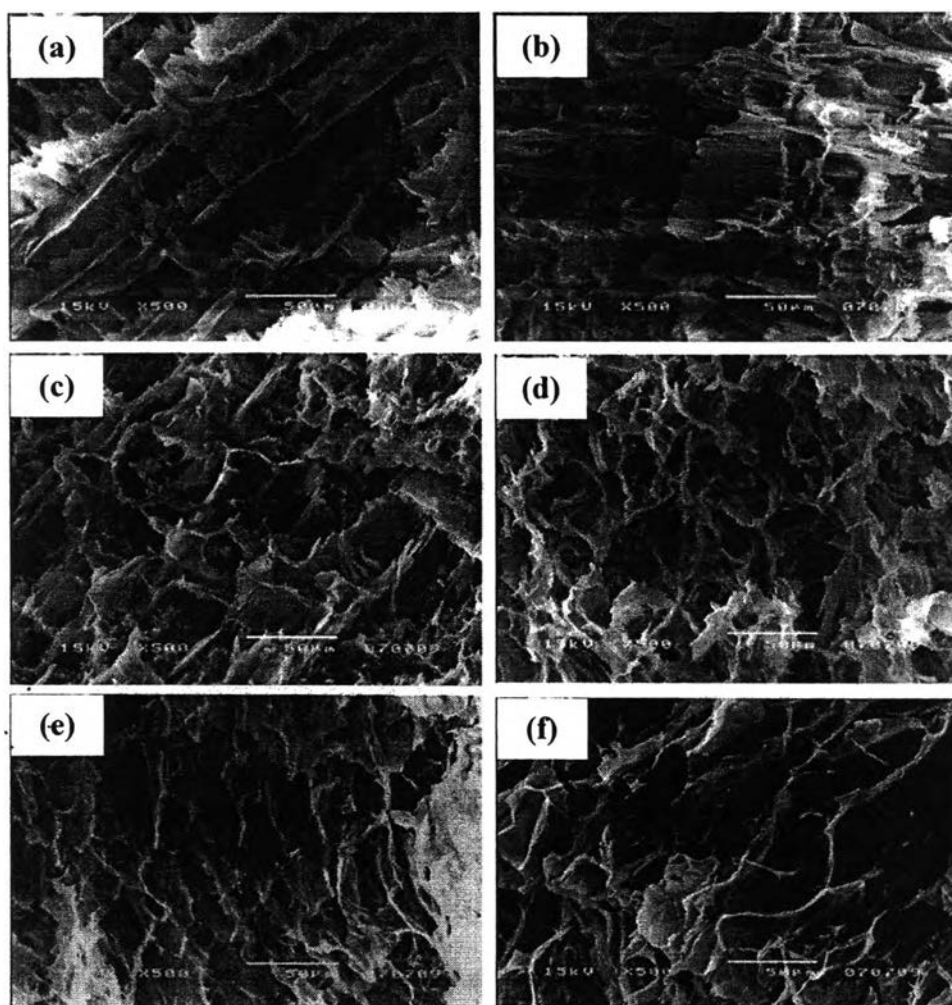


**Figure 4.10** Swelling ratio of PVA/PAA IPC aerogels at various blending ratio.

Table 4.5 summarizes the surface areas and pore volumes. The surface area is in the range between 4.60 to 6.45  $\text{m}^2/\text{g}$  while pore volume is between 0.05 to 0.25  $\text{cc}/\text{g}$ . Figure 4.11 confirms the porous structure and morphology in aerogels. For Figure 4.11(a), and (b), the dense aerogel texture can be observed when the content of PVA increases, the aerogel shows significant hollow structure as seen in case of Figure 4.11(c)-(f).

**Table 4.5** Surface area and pore volume

PVA/PAA Bending Ratio	Surface area ( $\text{m}^2/\text{g}$ )	Total pore volume ( $\text{cc}/\text{g}$ )
50/50	4.60	0.07
60/40	5.26	0.25
70/30	4.95	0.11
80/20	6.45	0.23
90/10	5.22	0.07
100/0	5.66	0.05



**Figure 4.11** SEM micrographs at 15kV ( $\times 500$ ) of; (a) 50/50, (b) 60/40, (c) 70/30, (d) 80/20, (e) 90/10, and (f) 100/0 PVA/PAA blending ratio.

#### 4.5 Conclusions

Interpolymer complex of PVA/PAA in this study was prepared in water-based system. The aerogel could be produced by a simple mixing polymer solution at equal volume fraction following by freezing the solution and freeze drying to get the aerogel. Several freezing-thawing cycles on mixing solution gave the physically crosslinked hydrogel. Freezing the hydrogel followed by freeze drying gave the aerogel. Heat treatment was found to enhance the thermal stability of the aerogel by picking aerogel from freezing-thawing technique. Moreover, an increasing in PVA

content enhances mechanical properties of aerogel by PVA crystalline phase formation.

#### 4.6 References

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