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# Making PVF porous sponge with and without using the pore-forming agent—A comparison

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## ABSTRACT

Based on the formaldehyde hybrid reaction (*i.e.* acetalization) and the spinodal decomposition (SD) phase separation principle, the main purpose of the present study is to compare the physical properties of porous poly(vinyl formaldehyde) (PVF) sponges with and without the use of the pore-forming agent of wheat starch. Through the help of images taken by a scanning electron microscope, the effect of poly(vinyl alcohol) (PVA) concentration on the pore structure of the PVF sponges will be investigated in detail through the analyses of pore-size distribution, mechanical modulus and water adsorption capacities.

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## 1. Introduction

Porous poly(vinyl formaldehyde) (PVF) sponge is a well-known hydrophilic superabsorbent made conventionally by poly(vinyl alcohol) (PVA) and formaldehyde through the hybrid reaction (*i.e.* acetalization) when the suitable type of the pore-forming agent is employed [1–3]. Since the 1960s, because of their biodegradability, wheat starch is the common pore-forming agent used in the sponge-manufacturing industry (named as PVF/starch sponge below) 4–6. The PVF/starch sponges always possess the open cell type structure and become flexible and soft when wetted with water. Unfortunately, since those starch pore-forming agents were required to washed off in the final manufacture step, the wastewater discharged from the plant always contained a high COD (chemical oxygen demand) value which caused serious environmental pollution problem; *i.e.* because 1.0 mg/L of starch contributes 1.185 mg/L of COD in water, so its daily wastewater COD value was always higher than 10,000 mg/L as reported by a local Taiwan plant [7].

In order to resolve the above wastewater pollution problem, based on the spinodal decomposition (SD) principle, we had established a novel method to reduce this high COD value problem by preparing PVF porous sponge without using the pore-forming agent in our previous works (named as PVF/SD sponge below) [8]. SD is essentially a mechanism by which a solution of two or more components can separate into two coexisting phases with distinctly different chemical compositions and physical properties,

which can be illustrated on a ternary phase diagram exhibiting a miscibility gap [9]. In this diagram, phase separation occurs whenever a mixture transitions into the unstable region of this miscibility gap (*i.e.* the spinodal region), whose boundary is referred to as the binodal or coexistence curve (indicated by the miscibility gap with a dome shape as shown in Fig. 7 below). In our previous paper [8], through the help of microscopic video camera, the formation mechanism of PVF/SD sponges was successfully analyzed in terms of the SD principle which was dominated by the capillary drainage phenomenon. We found that the microstructural pores of those PVF/SD sponges all occur at the first few minutes of the acetalization reaction, and the close-cell type pore size decreases but its uniformity increases with the increase of PVA concentration [8]. Moreover, we also found that the daily averaged wastewater COD value of making those PVF/SD sponges can be decreased to 1500 mg/L as low as the case of making PVF sponges when silica particles were served as the pore-forming agent [7]. In order to evidence the advantage of using our novel method of manufacturing PVF/SD sponge, the physical properties of PVF/starch and PVF/SD sponges made by 9–11 wt% PVA of the same polymerization and hydrolysis degree will be compared systematically as follows.

## 2. Experimental

### 2.1. Materials

Different with our previous experiments where PVA with an averaged polymerization degree of 500 (BF-05; 99.3 wt%) was used as the raw material [7], the commercial PVA (BF-08; 99.3 wt%) with

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an average polymerization degree of 1700 and hydrolysis degree of 98.5–99.2 mol% were purchased from Chang-Chun Petrochemical Co., Ltd, Taiwan. All other reagents were of analytical grade.

#### 2.1.1. PVF/starch sponge synthesis when wheat starch served as the pore-forming agent

The reaction solution was prepared by adding 45 g of PVA in a 270 ml aqueous solution first, which was then mixed with a 50 ml dispersion containing 15 g wheat starches. The resulting mixture was heated up to 95 °C (about the gelatinization temperature of wheat starch [10]) for one hour while being stirred at a speed of 250 rpm to obtain a pasty aqueous mixed solution. The mixed solution was cooled gradually to 85 °C for two minutes and a 180 ml aqueous mixture containing 90 ml of 24 wt% formaldehyde solution and 30 ml of 50 wt% sulfuric acid was then added slowly, and the resulting mixture was mixed homogeneously while being stirred at a speed of 125 rpm in order to obtain a reaction solution containing 9 wt% PVA and 3.0 wt% wheat starch at 60 °C. Other reaction solutions containing 9.5, 10 and 11 wt% PVA and 3.0 wt% wheat starch were prepared by the same procedure with suitable amount of PVA added.

#### 2.1.2. PVF/SD sponge synthesis without using the pore-forming agent

The reaction solution was prepared by adding 60 g of PVA in a 380 ml aqueous solution first, which was then heated to 95 °C for one hour in order to dissolve the PVA completely. The resulting mixture was poured into a 5-l double-layer glass reactor pre-heated at 50 °C, which was equipped with a speed-controlled blender (IKA, T-25 digital, Germany) and a vacuum pump (ROCKER, Chemker-411, Taiwan) in a water-recirculating chiller (HSC, type 806, Taiwan). After mixing with a speed of 1000 rpm for 5 min at 0.2 atm, an aqueous solution containing 90 ml of 24 wt% formaldehyde solution and 30 ml of 50 wt% sulfuric acid was then added, and the resulting mixture was mixed homogeneously for another 5 min while being stirred at a speed of 250 rpm in order to obtain a reaction solution containing 9 wt% PVA. Other reaction solutions containing 9.5, 10 and 11 wt% PVA were prepared by the same procedure.

Each of the above reaction solutions with the volume of 300 ml was finally poured into a polypropylene made rectangular vessel with a dimension of 10 cm × 20 cm and 5 cm in height. These vessels were then put in a temperature-controlled oven to execute the acetalization reaction at 60 °C for eight hours. The resulting PVF sponges were washed thoroughly with pure water for three times in order to remove the unreacted sulfuric acid and formaldehyde, and to wash off the pore-forming agent of wheat starches when PVF/starch sponges were manufactured.

#### 2.2. Determination of the conversion rate of formaldehyde

In determining the conversion rate of formaldehyde obtained in the present acetalization reaction, the residual concentrations of formaldehyde at different reaction times were determined by the UV-visible spectrophotometry (Standard method No. JIS-L-1041:2011) [11]. At which, the samples diluted with various amounts of distilled water were titrated by 2, 4-pentanedione (*i.e.* 0.2 wt%) to form 3, 5-diacetyl-1, 4-hydroxylutone in the presence of excessive ammonium acetate (*i.e.* 15 g per 250 mL), which is yellow in color and has a maximum absorbance at 412 nm.

#### 2.3. Scanning electron microscope imaging

After coating the samples with a thin layer of gold at 5.0 Pa and 20 mA for 80 s, the SEM pictures of the present porous PVF

sponges were monitored by a scanning electron microscope (JSM-7000F, JEOL, Japan) at a 15 kV accelerating voltage in the present experiments.

#### 2.4. DSC and TGA thermal analyses

The glass transition temperature ( $T_g$ ) of the present PVF sponges (weight in 5 mg) was scanned from 0 °C to 150 °C by using a Perkin-Elmer DSC Pyris-1 instrument. A heating rate of 20 °C/min under a nitrogen flow rate of 20 cm<sup>3</sup>/min was chosen as the measurement condition. The water adsorption capacity and the water desorption rate of the present PVF sponges were determined by using a DuPont TGA-Q50 thermal analyzer under a nitrogen flow rate of 100 cm<sup>3</sup>/min, respectively. The water adsorption capacity of the sponge samples were calculated from the weight loss at 100 °C (*i.e.* the boiling temperature of water) when each 20 mg sample was heated from room temperature to 200 °C with a heating rate of 10 °C/min, and the time-dependent water retention of sponges was determined when each sample was heated at a constant temperature of 50 °C for 50 min in TGA analyzer [8].

#### 2.5. Tensile test

The Young's modulus of PVA sponges with 25 wt% water content was measured by an Instron Universal Test Machine (Model 4467) according to the standard procedure described by ASTM D638-99. The 100 Newton cross-head load with an extending speed of 20 mm/min was adopted in the measurements. The modulus values of the sponge samples were determined by the average of six values.

### 3. Results and discussion

#### 3.1. The pore structures of PVF/starch sponges

Fig. 1(a)–(d) shows the SEM pictures of the pore structures of PVF/starch sponges, when various amounts (9, 9.5, 10 and 11 wt%) of PVA reacted with 50 wt% sulfuric acid (*i.e.* acetalization reaction) for eight hours at 60 °C. The pore structures of PVF/starch sponges shown in Fig. 1(a)–(d) belong to an open-cell type, and a smaller pore size but greater wall thickness can be obtained when the concentration of PVA concentration is increased from 9 to 11 wt%. By using the Image-Pro Plus software [12], the pore area analyzing examples of PVF/starch sponges are shown in Fig. 2(a)–(d) (*i.e.* based on the three magnitudes of ×50, ×100 and ×300 SEM pictures). For the PVF/starch sponges made by 9 wt% PVA, as shown in Fig. 2(a), the highest intensity of 14.3% locates at pore area of  $2.7 \times 10^2 \mu\text{m}^2$  accompanying with a smaller intensity of 6.6% around  $10^3 \mu\text{m}^2$  and of 8% around  $10^4 \mu\text{m}^2$  pore area, respectively. However for those PVF/starch sponges made by 9.5% PVA as shown in Fig. 2(b), the intensity of the peak located at  $2.7 \times 10^2 \mu\text{m}^2$  pore area increases to 20.5% and at  $10^3 \mu\text{m}^2$  increases to 12%, but decreases to 6% at  $10^4 \mu\text{m}^2$  pore area. Same increase tendency is observed in Fig. 2(c) when those PVF/starch sponges made by 10% PVA, where the intensity locates at  $2.7 \times 10^2 \mu\text{m}^2$  pore area increases to 21.5% and at  $10^3 \mu\text{m}^2$  increases to 13.5%, respectively. When the concentration of PVA is further increased to 11 wt%, as shown in Fig. 2(d), the intensity locates at  $2.7 \times 10^2 \mu\text{m}^2$  pore area increases from 21.5% to 29 % but at  $10^3 \mu\text{m}^2$  decreases from 13.5% to 12% for those PVF/starch sponges. The increased concentration of PVA reactants is the major cause of this result; the higher the concentration of PVA, the smaller the pore size. Since the affinity between PVA and H<sub>2</sub>O molecules decreases as acetalization proceeds, many H<sub>2</sub>O molecules become unbounded from the hybrid PVA-formaldehyde polymer matrix (*i.e.* PVF). Consequently, those unbounded water molecules will coalesce with

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