The effect of adding SiO$_2$ on the pore structure and the color fastness to washing of PVA sponge

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Abstract. The present study investigates the role of pore-forming SiO$_2$ particles on the pore structure, and color fastness following washing of a porous PVA sponge. We found that the SiO$_2$ micron particle consideration plays a decisive role on the pore-structural type and the color fastness. Moreover, the particles also influence the mechanical modulus and the water adsorption capacity.

1. Introduction

It is well known that porous Poly (vinyl formal) foams can be made by using hydrophilic chemicals of different grades of Poly (vinyl alcohol) (PVA) [1, 2]. PVA sponges are usually prepared by the condensation reaction (i.e. acetalization) between PVA and formaldehyde by using suitable pore-making agent under acidic condition. Different types of the pore-making agents, such as potato and wheat starches, and their content used in the acetalization process is the most important role in affecting the morphology and the resilience of the PVA sponge. Because of its availability from the food industry since the 1960s, wheat starch has been commonly used as the pore-making agent in the making of PVA sponges [3-5]. However, when those wheat starches of high COD value were washed out in the final step of manufacturing PVA sponges, the discharged wastewater always caused a serious environmental impact problem.

In order to minimize the above pollution problem, in recent years SiO$_2$ micron scale particles have been used as the pore-making agent to replace the wheat starch in making PVA sponge [6]. Since fine SiO$_2$ particles can be synthesized when sulfuric acid is added to the sodium silicate (i.e. water glass) solution [7, 8], so we had adopted sodium silicate solution derived SiO$_2$ micron particles as the pore-making agent when PVA sponges were manufactured under acidic condition (named as PVA/SiO$_2$ sponge below) [6]. When different contents of sodium silicate solution serving as the pore-making agent were mixed with 12 wt% PVA aqueous solution, a closed-cell type PVA/SiO$_2$ sponge was found in our previous work [9]. Because the water molecules cannot easily to go through the pore structure of close-cell type, we found that the adsorption rate of PVA/SiO$_2$ sponge for water molecules is not as good as those of open-cell type PVA/starch sponge, which adopted wheat starches as the pore-making agent as always (named as PVA/starch sponge below). However, we did find that the wastewater COD
(chemical oxygen demand) value for making PVA/SiO$_2$ sponge can be reduced efficiently [6].

Since we already proved that the content of PVA does affect the pore-structural type and the pore size when PVA/starch sponges were made, in order to improve the super-absorbent ability of those PVA/SiO$_2$ sponges made by using SiO$_2$ micron particles as the pore-making agent, the main purpose of the present paper is to see if it is possible to change the pore morphology of PVA/ SiO$_2$ sponges from the closed-cell type to the open-cell type when the raw material content of PVA is adjusted. Also, because those SiO$_2$ particles residue in the PVA polymer matrix perform a good ink receptivity, so their role on improving the sponge’s color fastness is investigated, too.

2. Experimental

2.1. Materials

The pure white PVA powders (BF-05; 99.3 wt%) was obtained from Chang-Chun Petrochemical Co., Ltd., Taiwan, whose averaged polymerization degree was 500 and the hydrolysis degree was 98.5-99.2 mol%. The sodium silicate solution was purchased from Rong Xiang Ind. Co., Ltd., Taiwan (EG, 50 wt%, Na$_2$O:SiO$_2$=1:1, CAS No. 6834-92-0). All reagents adopted in the present experiments were analytical grade.

2.2. Preparation of PVA/ SiO$_2$ sponge

In making the present PVA/SiO$_2$ porous sponges, the solutions of 12, 13 and 14 wt% of PVA and 0.1, 0.3 and 0.5 wt% of sodium silicate solution were adopted. The detailed experimental procedure can be found in our previous paper [6, 9].

2.3. Scanning electron microscope imaging

The porous structure of the present sponge was obtained using a scanning electron microscope (SEM, JSM-7000F, JEOL, Japan) at the operating voltage 15 KV. After coating with a thin layer of gold at 5.0 Pa and 20 mA for 80 seconds, the samples were then monitored by.

In addition to taking those SEM images, we also determined the glass transition temperature ($T_g$, Perkin-Elmer DSC Pyris-1), the Young’s modulus of tensile test (Instron, Model 4467) and the water adsorption capacity of PVA/ SiO$_2$ samples. The detailed analyze methods can be found in our previous papers, too [6, 9].

2.4. Color fastness to washing

Color fastness to washing is one of the most important parameters for testing the quality of PVA sponges from the viewpoint of consumers. In order to prove the ability of the present PVA/SiO$_2$ sponges to fasten various color dyes, at this point we adopt the AATCC 61-2010 test method to determine the loss of sponge and any change in the sponge’s color in the washing process and the possible staining of other garments (or lighter portion) that may be washed with it. In this test method, a six-multifibre swatch (acetate, cotton, nylon, polyester, acrylic and wool) is mechanically washed with the sample sponges for 45 minutes at 40±2°C in 0.37% WOB solution (without optical brighteners, 1993 AATCC standard reference detergent), along with #10 steel balls and 200 ml liquor in volume. The conventional PVA/starch sponges made by using the wheat starches as the pore-making agent are also adopted as the contrast samples in this test (i.e. its manufacture method can be found in our previous paper [6]).

3. Results and discussion

3.1. The pore morphology

The SEM pictures of the pore structures of PVA/SiO$_2$ sponges made at 12 wt% PVA and different content of 0.1, 0.3 and 0.5 wt% sodium silicate solution are shown in figures 1(a)-1(d). We can find that the PVA/SiO$_2$ sponges shown in these four pictures were all belong to a closed-cell type with
many micron voids of $2 \, \mu m$ in diameter appear on the pore walls. The SEM example of those SiO$_2$ micron particles resulted from the acidification of the sodium silicate solution is shown in figure 2, which illustrates that the average diameter of the present SiO$_2$ is about $2 \, \mu m$, too, hence we believe that those micron voids were made by those non-aggregated SiO$_2$ micron particles. As shown in figures 1(a)-1(d), the average diameter of those closed-cell type pores is 300 $\mu m$ (which is the same as in our previous paper [6, 9]), and the pore size of PVA/SiO$_2$ sponges was found only slightly increased when sodium silicate content is increased from 0.1 wt% to either 0.3 or 0.5 wt%. In addition to those silica particles dispersed in the PVA matrix which will reinforce the mechanic strength of sponges (see the tensile test results below), the aggregation of those SiO$_2$ particles reside in the aqueous solution associate with their surface adsorbed H$_2$O molecules and those water molecules condensed from acetalization is the main reason to cause this close-cell type pore structure [10].

![SEM pictures of PVA/SiO$_2$ sponges](image)

**Figure 1.** SEM pictures of PVA/SiO$_2$ sponges when different amounts of 0.1 (a), 0.3 (b) and 0.5 wt% (c) sodium silicate solutions are added in a 12 wt% PVA aqueous solution, respectively. (d) is the enlarged part of (c).

As shown in figures 3(a)-3(d), due to the increased PVA content, the average pore size of PVA sponge decreased from 300 $\mu m$ to 40 $\mu m$ when PVA content is increased from 12 wt% to 13 wt%. Fewer micron voids are observed on the pore walls under the contents of 0.1, 0.3 and 0.5 wt% sodium silicate solution as observed in these four pictures. When comparing with the pore type between
Figure 2. SEM picture of the SiO$_2$ micron particles obtained in the present experiments.

Figure 3. The pore structure SEM pictures of PVA/SiO$_2$ sponges when 0.1 (a), 0.3 (b) and 0.5 wt% (c) sodium silicate solutions are added in a 13 wt% PVA aqueous solution. (d) is the enlarged part of (c).
figures 1(a)-1(d) and figures 3(a)-3(d), it is interesting to note that more pores in figures 3(a)-3(d) become a more open type than those pores in figures 1(a)-1(d). Also, because of the formation of a larger silica aggregate, the pore size of the open part of those pores made by 13 wt% PVA increases with the increase of the content of sodium silicate solution. The same results are observed in figures 4(a)-4(d) when the PVA content is further increased to 14 wt%; i.e. the pore size of sponge can be further decreased but the open part of those pores increases with the increase of the sodium silicate solution content. Note that there is no micrometer void observed in figures 4(a)-4(d). By using the Image-Pro Plus software to measure the pore size distribution [11], the results for those sponges made by 13 and 14 wt% PVA are summarized in figure 5. It can be found that, instead of the proportions of those 10 \( \mu m \) voids appear on the pore walls of PVA/SiO\(_2\) sponges made by 13 wt% PVA, the pore sizes of those PVA sponges made by 14 wt% PVA all become increased and locate at 30, 40 and 50 \( \mu m \), respectively. This result proves that the pore structure of PVA/ SiO\(_2\) sponges can be changed from the close-cell type to the open-cell type when PVA content is increased from 13 to 14 wt%.

![Figure 4](image1.png)

**Figure 4.** The pore structure SEM pictures of PVA/SiO\(_2\) sponges when 0.1 (a), 0.3 (b) and 0.5 wt% (c) sodium silicate solutions are added in a 14 wt% PVA aqueous solution. (d) is the enlarged part of (c).

The above results can be explained by the fact that, as illustrated by the schematic diagram of figure 6, since the drainage velocity of PVA polymer between two water bubbles in 13 wt% PVA solution is faster than that in 14 wt% PVA solution due to its increased viscosity, therefore a larger pore size but thinner pore wall can be induced in PVA sponge made by 13 wt% than that made 14...
wt% PVA. This result is evidenced by the examples of the enlarged SEM pictures shown in figures 3(d) and 4(d) where PVA content is fixed at 13 and 14 wt%, respectively, for the case of adding 0.5 wt% sodium silicate solution.

![Image](image1.png)

**Figure 5.** The pore-size distribution of PVA/SiO$_2$ sponges analyzed by using the Image-Pro Plus software [11], when 0.1, 0.3 and 0.5 wt% sodium silicate solutions are added in the 13 wt% and 14 wt% PVA aqueous solution, respectively.

![Image](image2.png)

**Figure 6.** The schematic diagram illustrates the drainage phenomenon of PVA polymer occurred in the pore walls of PVA/SiO$_2$ sponges. In this figure, the SiO$_2$ micron particles are represented by the dots as shown by the black color. The capillary pressure difference between PVA polymer and plateau borders (i.e. at positions of inter-film contact) leads to rapid PVA wall thinning (over pressure is indicated by +, low pressure by −).

3.2. DSC analysis
From the DSC analysis results, we found that $T_g$ of the present PVA/SiO$_2$ sponges made by different PVA and sodium silicate contents are all fixed at 70°C. This result indicates that the present SiO$_2$ particles do not affect the hybrid bond formation between PVA and formaldehyde molecules as acetalization proceeds.

3.3. Mechanical property
From the slope of the strain-stress curves obtained from the tensile test, the Young’s modulus of
present PVA/SiO$_2$ sponges can be determined (i.e. based on the five times of measurements) and the results are shown in figure 7. It can be found that the Young’s modulus of PVA/SiO$_2$ sponges increases as PVA content increases. Also, under the same content of PVA, the sponge’s modulus increases with the increase of the sodium silicate solution content. The reinforcement role played by those silica particles dispersed in the PVA matrix is believed to be the primary cause of this result [12, 13].

**Figure 7.** The mechanical modulus of PVA/SiO$_2$ sponges made by 12, 13 and 14 wt% PVA, respectively, when 0.1, 0.3 and 0.5 wt% of sodium silicate solution are added.

**Figure 8.** The water adsorption capacity of PVA/SiO$_2$ sponges made by 12, 13 and 14 wt% PVA, respectively, when 0.1, 0.3 and 0.5 wt% of sodium silicate solutions are added.

### 3.4. The water adsorption capacity and the water desorption rate

The water adsorption capacity of the present PVA/SiO$_2$ sponges was determined from the loss of the sample weight at 100°C by using TGA, when 20 mg of dry sample was inserted into 100 mL water for
one minute. As shown in figure 8, there is an 84% weight loss of water (therefore the water adsorption capacity) obtained for the 12 wt% PVA made sponge when 0.1 wt% sodium silicate solution was added. The same value of 84% was also obtained for other PVA/ SiO$_2$ samples when 0.3 and 0.5 wt% sodium silicate solution was added, respectively. Hence, the water adsorption capacity of the present sponge is determined by its PVA content and that it is not affected by the added sodium silicate solution [9]. However, because of the less amount of water can be adsorbed in those smaller but become more open type pores than those close type but bigger pores of 12 wt% PVA made sponge, an average 80% water adsorption capacity was obtained for those 13 and 14 wt% PVA made PVA/SiO$_2$ sponges. These water adsorption capacities of 80 and 84% water weight meet the requirement of superabsorbent [1]. This conclusion can be evidenced by the temporal water retention curves as shown in figures 9(a)-9(c) when the present sponge samples were heated at 50°C in TGA for 50 minutes (i.e. since the value of 16 wt% water retention is always reached after heating 30 minutes at 50°C for all of curves shown in figures 9(a)-9(c). The water desorption rates of the sponges can be therefore determined by the slopes of those temporal water retention curves. Since more open-type pores can be obtained for those sponges made by increased PVA as shown in figures 4(a)-4(d), which will drive those water molecules to go through pores easier, hence the water desorption rates of 14 wt% PVA made sponges are always higher than those sponges made by 12 and 13 wt% PVA.

![Figure 9](image.png)

**Figure 9.** The temporal water retentions of PVA/SiO$_2$ sponges made by 12 (a), 13 (b) and 14 wt% (c) PVA, respectively, when 0.1, 0.3 and 0.5 wt% of sodium silicate solutions are added.

3.5. Test results of Color fastness to washing
One of the test results are summarized in table 1, where the PVA/SiO$_2$ sponges were manufactured by 13 wt% PVA and 0.3 wt% sodium silicate solutions and the PVA/starch sponges were manufactured by 10 wt% PVA and 3.0 wt% wheat starch. The concentrations of dyes employed in those sample sponges were all fixed at 0.05 wt%. It can be found that the PVA/SiO$_2$ sponges own a better fastness on navy-blue and crimson dyes (marked by the red color), and therefore on the darker colored dyes than that of the PVA/starch sponges. The good ink receptivity of those SiO$_2$ particles residue in the PVA/SiO$_2$ polymer matrix is the major reason to improve sponge’s color fastness.

**Table 1.** The test results of color fastness to washing for the present PVA/starch and PVA/SiO$_2$ sponges.

| Sample   | Change in shade | Staining of Acetate | Staining of Cotton | Staining of Nylon | Staining of Polyester | Staining of Acrylic | Staining of Wool |
|----------|-----------------|---------------------|--------------------|-------------------|-----------------------|---------------------|-----------------|
| (1)      | Grade 4.5       | Grade 4.0           | Grade 4.0          | Grade 4.0         | Grade 4.5             | Grade 4.5           | Grade 4.5       |
| (2)      | Grade 4.5       | Grade 4.5           | Grade 4.5          | Grade 4.0         | Grade 4.5             | Grade 4.5           | Grade 4.5       |
| (3)      | Grade 4.5       | Grade 4.5           | Grade 4.5          | Grade 4.0         | Grade 4.5             | Grade 4.5           | Grade 4.5       |
| (4)      | Grade 4.5       | Grade 4.5           | Grade 4.5          | Grade 4.0         | Grade 4.5             | Grade 4.5           | Grade 4.5       |
| (5)      | Grade 4.5       | Grade 4.5           | Grade 4.5          | Grade 4.0         | Grade 4.5             | Grade 4.5           | Grade 4.5       |

*Sample (1): PVA/SiO$_2$ sponge+Navy blue dye; Sample (2): PVA/SiO$_2$ sponge+Purple dye; Sample (3): PVA/SiO$_2$ sponge+Green dye; Sample (4): PVA/SiO$_2$ sponge+Yellow dye; Sample (5): PVA/SiO$_2$ sponge+Crimson dye; Sample (6): PVA/starch sponge+Navy blue dye; Sample (7): PVA/starch sponge+Purple dye; Sample (8): PVA/starch sponge+Green dye; Sample (9): PVA/starch sponge+Yellow dye; Sample (10): PVA/starch sponge+Crimson dye.*

4. Conclusion

Accompanying with the method of preparing 12, 13 and 14 wt% PVA made porous PVA/SiO$_2$ sponge through the simultaneous acidifications of 0.1, 0.3 and 0.5 wt% sodium silicate solutions, respectively, the effect of their contents on the sponge’s pore-structural type are investigated in the present paper. With the help of the analyses of SEM, the tensile test and the water adsorption capacity, there are five conclusions can be obtained: (1) The pore-structural type of sponges can be changed from the closed-cell type to the open-cell type when PVA content is increased from 12 to 14 wt%, especially when 0.5
wt% sodium silicate solution was served as the pore-making agent. (2) The pore size of PVA decreases with the increase of PVA content, but the the open part of those pores increases with the content of sodium silicate solution. (3) The unchanged $T_g$ indicates that the present sodium silicate solution does not involve in the formation of the hybrid bonds through the acetalization between PVA and formaldehyde. (4) The sponge’s modulus increases with the increase of PVA content. Also, under the same PVA content, the sponge’s modulus can be reinforced with the increase of the sodium silicate content. (5) Even with the same water adsorption capacity, but because more pores become opened, the water desorption rates of 14 wt% PVA made sponges are always higher than those sponges made by 12 and 13 wt% PVA, when different contents of sodium silicate solution were added in the present study. (6) Finally, but not at least, from the test results of color fastness to washing, we find that the present PVA/SiO$_2$ sponges own a better fastness on the darker colored dyes than that of the conventional PVA/starch sponges.

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