JOURNAL OF Applied Polymer SCIENCE

A New Method of Preparing Superabsorbent PVF Porous Foam Through the Simultaneous Acidification of Water Glass Solution-Aspect of Environmental Protection

You-Im Chang,[1] Wei-You Cheng,[1] Larry Jang[2]
[1]Department of Chemical Engineering, Tunghai University, Taichung 40704, Taiwan
[2]Department of Chemical Engineering, California State University, Long Beach, California 90840
Correspondence to: Y.-I. Chang (E-mail: yichang@thu.edu.tw)

ABSTRACT: To reduce the wastewater pollution problem, silica particles that have resulted from simultaneous sulfuric acidification of water glass solution serve as the pore-forming agent for preparing superabsorbent PVF/SiO_2 foam in this study. This is a departure from the traditional porous PVF/starch foam's manufacture method. The pore structure of PVF/SiO_2 foam is very different from that of PVF/starch foam. The effect of the concentration of these pore-forming agents on the pore structure, mechanical modulus, and water adsorption capacity of PVF/starch and PVF/SiO_2 foams are investigated in this study. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39894.

KEYWORDS: hydrophilic polymers; manufacturing; porous materials

Received 21 June 2013; accepted 26 August 2013
DOI: 10.1002/app.39894

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a well-studied hydrophilic polymer with a good reputation in the superabsorbent polymer (SAP) industry.[1] PVA is a nontoxic and biodegradable polymer[2] that can be applied to synthesis porous poly(vinyl formal) (PVF) foam in different types of sponge products used in cleaning and washing processes.[3] Using sulfuric acid as catalyst and suitable pore-forming agent, the porous PVF foam was prepared through PVA and formaldehyde hybrid reaction (i.e., acetalization). The large interconnected pores endow the PVF foam with unique spongy morphology and good resilience, both of which are controlled by the type of pore-forming agent employed. Owing to its complete biodegradability, starch has been a common pore-forming agent used in the making of porous PVF foam since the 1960s.[4–7] It was reported that the averaged pore diameter of PVF foam varied from 30 to 60 μm when wheat-starch was used, and from 60 to 100 μm when potato-starch was used.[8,9] However, when those starch pore-forming agents were washed by water in the final manufacturing step of PVF foam, the high concentration of starch in the wastewater always caused serious environmental pollution problems because of its high COD value; that is, since 1.0 mg/L of starch contributes 1.185 mg/L of COD in water, so its wastewater COD value is as high as 10,000 mg/L as recorded by a local PVF foam manufacture plant located at Taichung industry park (see Figure 13 below). Therefore, the need for a non-polluting pore-forming agent to serve as a substitute for starch in the producing of PVF foam became an important issue in recent years. In this study, we adopt fine silica particles obtained directly from the acidification of water glass solution as the pore-forming agent used in the production of PVF foam, due to these particles' low cost and low environmental impact.

Traditionally, microsized silica particles have been synthesized by hydrolysis and the polycondensation reactions, while the intermediate of silane oxide is generated by the hydrolysis of alkyl silicates first (for example, through the titration of water glass solution from basic to acidic condition), followed by the condensation reaction to gradually form a three-dimensional silicon dioxide sample.[10,11] For nanosized silica particles, the standard procedure established by Stöber and Fink can be followed,[12] in which tetraethyl orthosilicate was served as the starting raw material. In making both microsized and nanosized silica particles, the particle size and its distribution are subjected to changes of many preparation parameters, such as the effects of the alkyl silicate concentration, pH value, reaction time, and temperature.[13,14] By using silica powders as the pore-forming agent, Sueoka et al.[7] incorporated these powders into PVA solution to make a microporous PVF membrane. They found that a PVF membrane with an average pore size of 0.01–50 μm can be produced, when those silica powders with uniform particle sizes within the range of 0.005–10 μm were employed. Their PVF membranes possessed a porosity of at least 60%. Since the porous PVF foam is prepared by the acetalization reaction through the mixing of PVA and formaldehyde under acidic condition, and fine silica particles can be synthesized simultaneously when sulfuric acid is added to the water glass solution, both procedures would benefit from the use of the water glass solution to produce silica particles as the pore-forming agent when PVF foam is made in this article.

A new method of preparing superabsorbent PVF porous foam through the simultaneous acidification of water glass solution to produce SiO_2 particles and PVF formation will be presented in this study. Properties of PVF foam made from wheat starch and from silica particle produced by water glass solution as the pore-forming agent will be compared. Additionally, the effect of their concentrations on the pore structure of the PVF foam will be investigated. Moreover, the water adsorption capacity of the PVF foams obtained by using these two pore-forming agents will be studied in detail through the analyses of pore size distribution, mechanical modulus, and thermal property.

EXPERIMENTAL

Materials

Commercial PVA (BF-05; 99.3 wt %) with averaged polymerization degree of 500 and hydrolysis degree of 98.5–99.2 mol % were obtained from Chang-Chun Petrochemical, Taiwan. The starch used in this study was unmodified native wheat starch purchased from Sigma-Aldrich USA (S5127, CAS No. 9005-25-8). The sodium silicates water glass solution was purchased from Nihon-Shiyaku, Japan (EG, 50 wt %, $Na_2O : SiO_2 = 1 : 1$, CAS No. 6834-92-0, which is free of surfactant molecules). Deionized water was used for the solvent of PVA. Other reagents, all of which were analytical grade, were used as received.

Synthesis of PVF Superabsorbent Foam

Wheat Starch Served as the Pore-Forming Agent (Named as PVF/Starch Foam Below). A dispersion of 5 g of wheat starch in 50 mL of water was first added to 270 mL of an aqueous solution containing 60 g of PVA. The resulting mixture was heated up to 95°C (about the gel point of wheat starch)[15] for 45 min while being stirred to obtain a pasty aqueous mixed solution. The mixed solution was then cooled to 85°C and 180 mL of an aqueous mixture containing 90 mL of 24 wt % formaldehyde solution and 30 mL of 50 wt % sulfuric acid was added, and the resulting mixture was mixed homogeneously while being stirred to obtaining a reaction solution containing 12 wt % PVA and 1.0 wt % wheat starch. Other reaction solutions containing 12 wt % PVA and 2.0–5.0 wt % wheat starch were prepared by the same procedure with suitable amount of wheat starch added.

Silica Particle Served as the Pore Forming Agent (Named as PVF/SiO_2 Foam Below). The reaction solution containing 12 wt % PVA and 0.05 wt % water glass solution produced silica particles was prepared in the same manner described above, with the exception that 1.0 mL of 1*M* NaOH and 0.5 g of water glass solution (50 wt % in sodium silicates) in 50 mL of water were added simultaneously after heating 270 mL of an aqueous solution containing 60 g of PVA for 45 min. The mixed solution was cooled to 85°C and titrated with 10 mL of 10 wt % sulfuric acid to pH 7.0 first, and then mixed with 170 mL of an aqueous mixture containing 90 mL of formaldehyde solution (24 wt %) and 30 mL of 50 wt % sulfuric acid. Other reaction solutions of containing 12 wt % PVA and 0.05–0.25 wt % water glass solution were prepared by the same procedure with suitable amount of water glass solution added.

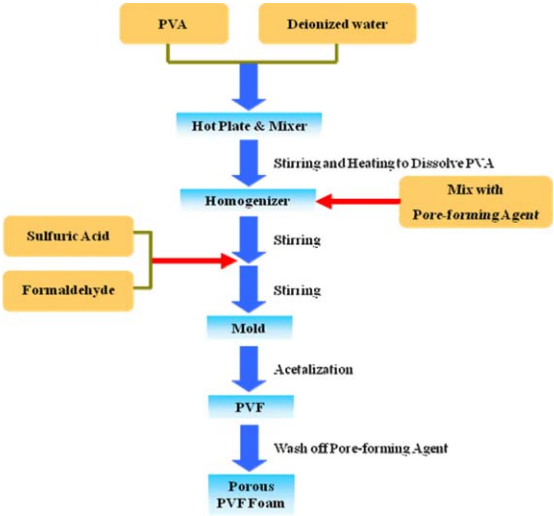


Figure 1. The flow sheet of the procedures for making PVF/starch and PVF/SiO2 foams. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Each of the above reaction solution was finally introduced to a hard plastic rectangular vessel with a dimension of 15 × 20 cm and 5 cm in height. The vessels were then put in a temperature-controlled oven to carry out the acetalization reaction at 60°C for 8 h. The resulting samples of porous PVF foam were washed thoroughly three times with deionized water associated with the supersonic machine to remove the remaining sulfuric acid, formaldehyde, and pore-forming agent of either the wheat starch or the silica particle. The flow sheet of the above procedures for making PVF/starch and PVF/SiO_2 foams are summarized in Figure 1.

Scanning Electron Microscope Imaging

To observe the pore size distribution of PVF/starch and PVF/SiO_2 foams, the samples were coated with a thin layer of gold (coating at 5.0 Pa and 20 mA for 80 s) and then monitored by a scanning electron microscope (SEM, JSM-7000F, JEOL, Japan) at a 15 KV accelerating voltage.

DSC and TGA Thermal Analyses

A Perkin-Elmer DSC Pyris-1 instrument was used to determine the glass transition temperature (T_g) of 5 mg of the PVF/starch and PVF/SiO_2 foam samples. The temperatures were scanned from 0 to 150°C with a heating rate of 20°C/min under nitrogen flow rate of 20 cm^3/min. The water adsorption capacity and the water desorption rate of the wet PVF/starch and PVF/SiO_2 foams were determined using DuPont TGA-Q50 thermal analyzer.[16] Under nitrogen flow rate of 100 cm^3/min, the water adsorption capacity of the wet PVF/starch and PVF/SiO_2 foams

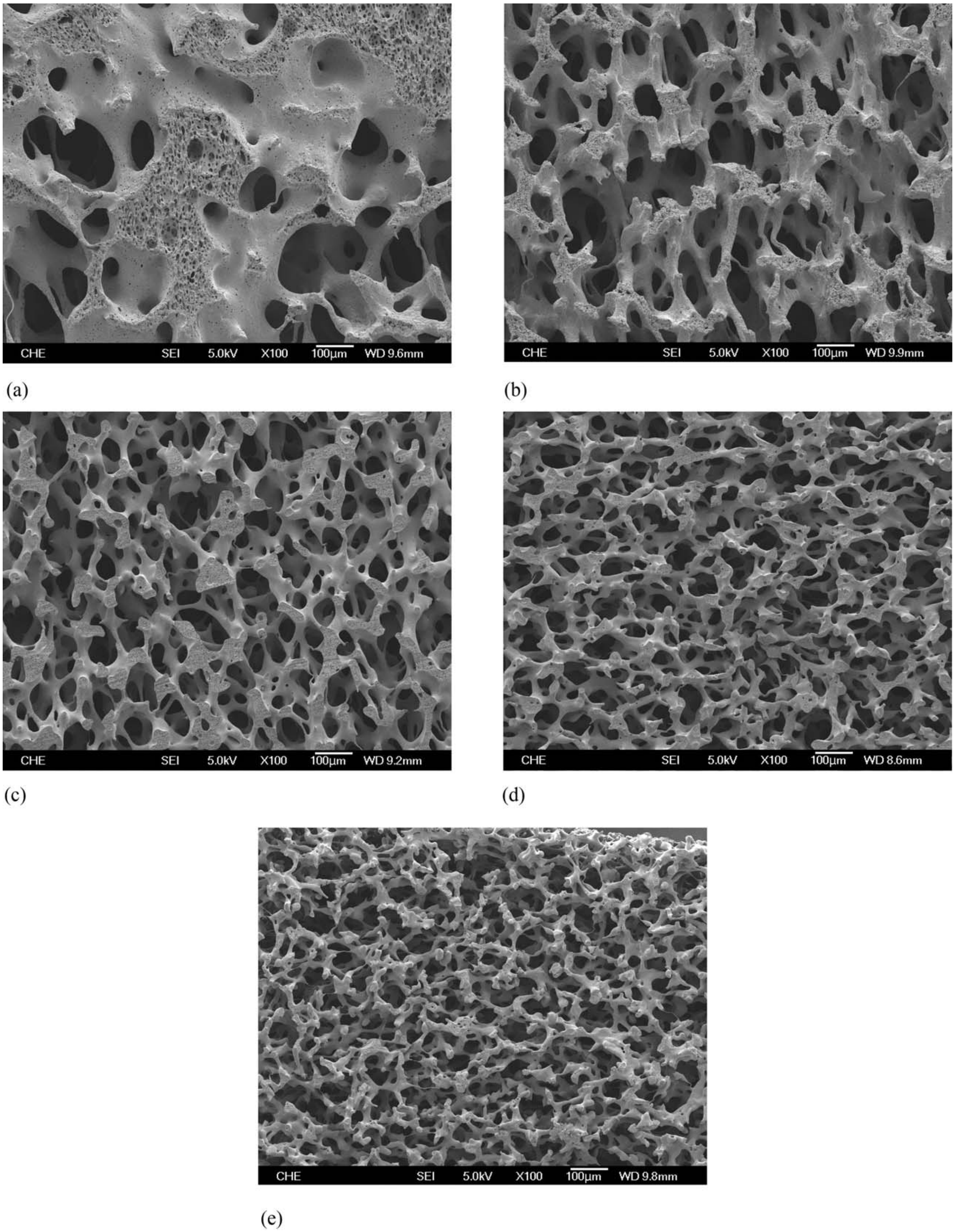


Figure 2. SEM pictures of the pore structure of PVF/starch foams obtained in this study, when different amounts of 1.0 (a), 2.0 (b), 3.0 (c), 4.0 (d), and 5.0 wt % (e) of wheat starch served as the pore-forming agent.

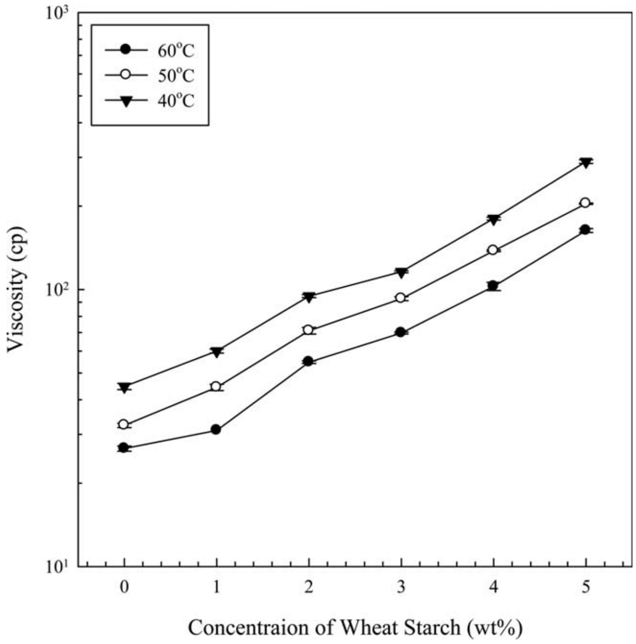


Figure 3. The viscosity of the reaction solution mixed with PVA and starch versus the concentration of wheat starch at different temperatures of 40, 50, and 60°C.

was calculated from the weight loss at 100°C when each 20 mg sample was heated from room temperature to 600°C with a heating rate of 10°C/min, and the water desorption rate was determined when each sample was heated at 50°C for 50 min, respectively.

Tensile Test

An Instron Universal Test Machine (Model 4467) was adopted to measure the Young's modulus of PVF/starch and PVF/SiO_2 foams with 25 wt % water content according to the standard procedure described by ASTM D638-99. The cross-head load was 100 Newton and the extending speed was 20 mm/min. The modulus values of the foam samples were determined by the average of six values.

RESULTS AND DISCUSSION

The Pore Structures of PVF/Starch and PVF/SiO_2 Foams

Figure 2(a–e) show the SEM pictures of the pore structures of PVF/starch foams, when various amounts (1.0, 2.0, 3.0, 4.0, and 5.0 wt %) of wheat starch served as the pore-forming agent under the same concentration of 12 wt % PVA and acetalization reaction at 60°C for 8 h. The pore structures of PVF/starch foams shown in Figure 2(a–e) belong to an open-cell type, and a higher porosity but smaller pore size can be obtained when the concentration of wheat starch concentration is increased from 1.0 to 5.0 wt %. The average pore size is found to be 80 μm when 1.0 wt % of wheat starch is added, and 50 μm when 5.0 wt % of wheat starch is added. This result is due in large part to the increased viscosity of the reaction solution when the concentration of wheat starch is increased. As shown in Figure 3, the viscosity of the reaction solution mixed with PVA and starch increases with the increase of either starch concentration or solution temperature. Since the reaction solutions of this study were all prepared at 95°C when various concentrations of wheat starch were added to the aqueous PVA solution, the molecules of wheat starch are completely gelatinized and swollen under this temperature. Consequently, the gelatinized molecules of wheat starch will increase the solution's viscosity. Since the high viscosity of the reaction solution will help those starch molecules to suspend in the solution and prevent their sedimentation behavior during the 8-h acetalization period, the increased viscosity as shown in Figure 3 causes higher porosity but smaller pore size when the concentration of wheat starch is increased.

Figure 4(a–e) show the SEM pictures of the pore structure of PVF/SiO_2 foams obtained when different concentrations of 0.05, 0.1, 0.15, 0.2, and 0.25 wt % water glass solution served as the pore-forming agent, under the same concentration of 12 wt % PVA as the acetalization reaction proceeded at 60°C for 8 h. It was found that the pore structures of PVF/SiO_2 foams shown in Figure 4(a–e) belong to a closed-cell type but with many micrometer voids existing on the pore walls. The average diameter of those closed-cell type pores are as big as 400 μm, and the porosity and pore size of PVF/SiO_2 foams only increase slightly when silica particle concentration is increased from 0.05 to 0.25 wt %. As acetalization proceeds, since the affinity between PVF and H_2O molecules of aqueous solution decreases, so many H_2O molecules become unbounded from the PVF. Because the hydrophilic surfaces of silica particles can preferentially adsorb those unbounded H_2O molecules and those water molecules condensed from the acetalization reaction, and those adsorbed water molecules will consequently accelerate the aggregation rate of silica particles, the aggregates of silica particle gradually become bigger as reaction proceeds, which will finally cause a closed-cell type pore structure as observed in Figure 4(a–e). In addition, it was found that there were many micrometer voids left on the pore walls when the PVF/SiO_2 foams were washed thoroughly with water in the final step. Figure 5 shows an example of the SEM picture of sodium silicate particle size distribution obtained at pH 7.0 when 0.15 wt % of silica particles were added to 12 wt % PVA aqueous solution. In our experiments, we found that most silica particles aggregate together through their hydrophilic surfaces with those unbounded H_2O molecules and those water molecules condensed from the acetalization reaction. However, because of the inherent difficulty for agitating those silica particles homogeneously within the viscous PVF solution (i.e., their aggregation rates did not reach the final equilibrium stage completely), there were still few silica particles left alone in the PVF polymer matrix, which made micrometer voids as observed in Figure 4(a–e). Also, because the particle sizes of those silica particles are smaller than 1.0 μm (i.e., with an averaged diameter of 0.8 μm as shown in Figure 5), we believe that the micrometer voids existing on the pore walls as observed in Figure 4(a–e) were made by those nonaggregate silica particles associated with their surface water molecules (i.e., see an example of the enlarge part of Figure 4(c) illustrates at Figure 6).

The porosity of both PVF/starch and PVF/SiO_2 foams were analyzed by the Image-Pro Plus software.[17] Two sets of the analyzed examples of PVF/starch and PVF/SiO_2 foams are

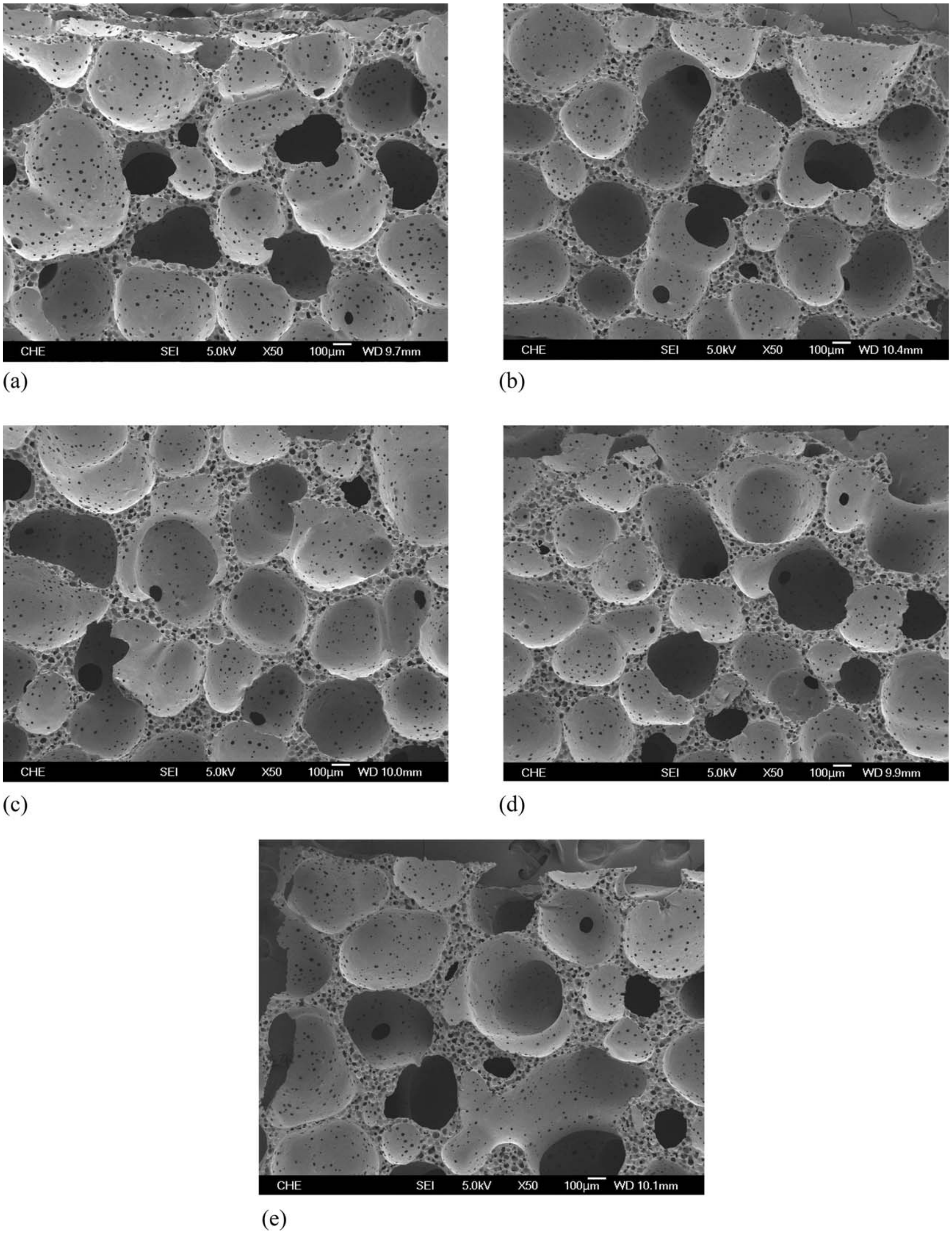


Figure 4. SEM pictures of the pore structure of PVF/SiO_2 foams obtained in this study, when various amounts of 0.05 (a), 0.1 (b), 0.15 (c), 0.2 (d), and 0.25 wt % (e) of silica particles served as the pore-forming agent.

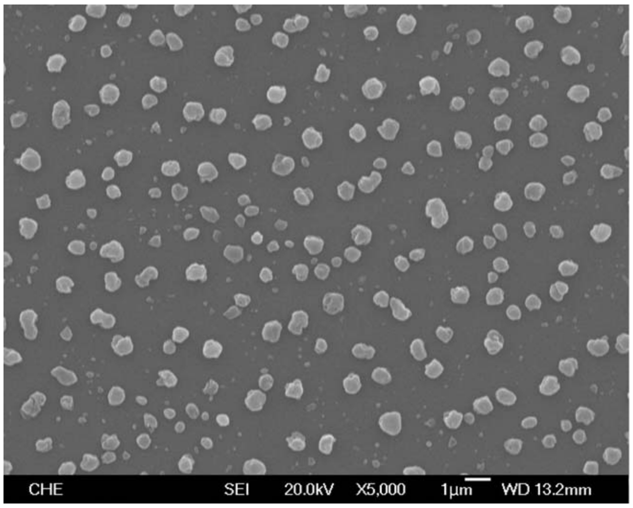


Figure 5. SEM picture of the particle size distribution of sodium silicates obtained at pH 7.0 when 0.15 wt % of silica particle was added in 12 wt % PVA aqueous solution.

shown in Figures 7(a,b) and 8(a,b), respectively. For PVF/starch foams, as shown in Figure 7(a,b), the intensity of large pore area (10^4-10^5 μm^2) for 1.0 wt % wheat starch is higher than that of 5.0 wt % wheat starch, which owns double intensity in small pore area of 10^3 μm^2. This result coincides with the SEM observation of Figure 2(a,e) that a higher porosity with smaller pore size can be obtained when wheat starch concentration is increased from 1.0 to 5.0 wt %. Conversely, as shown in Figure 8(a,b), the intensity of the large pore area of 10^5 μm^2 only increases slightly when silica particle concentration is increased from 0.05 to 0.25 wt %, which coincides with SEM results obtained in Figure 4(a,e). By using the Image-Pro Plus software, the calculated porosities of PVF/starch and PVF/SiO_2 foams are shown in Figure 9. It can be found that the porosity of PVF/starch can increase from 77 to 82% when the wheat starch concentration increases from 1.0 to 5.0 wt %, and that the porosity of PVF/SiO_2 foams (80–82%) is always higher than that of PVF/starch foams obtained. This PVF/SiO_2 foams own larger pore size and higher porosity than that of PVF membranes reported by Sueoka et al.[7] where the silica powders were served as the pore-forming agent.

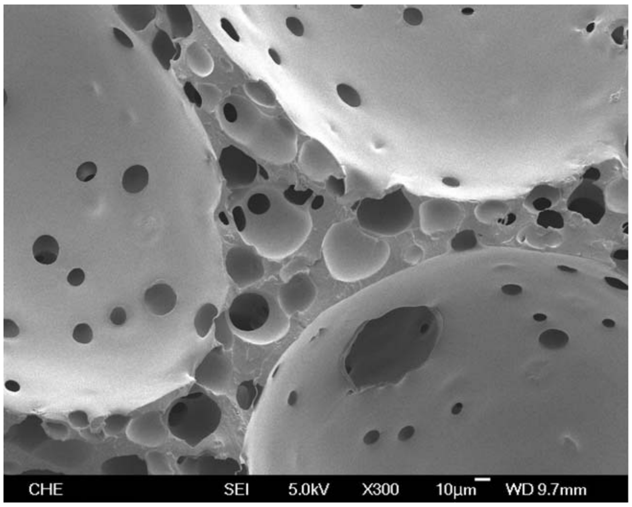


Figure 6. The enlarge part of Figure 4(c).

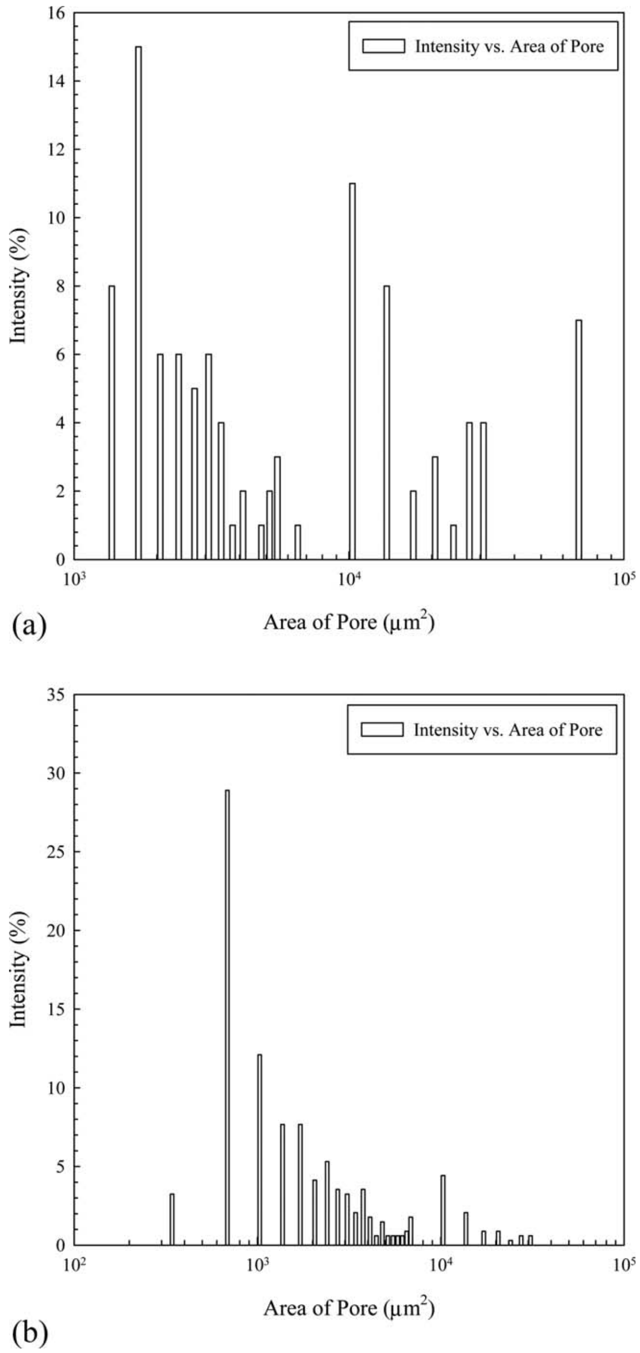
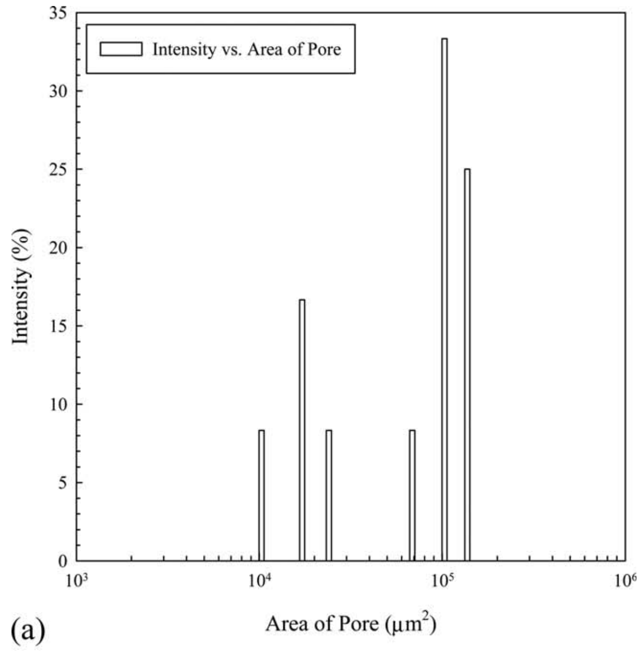


Figure 7. The pore area distribution of PVF/starch foams analyzed by using the Image-Pro Plus software,[17] when 1.0 wt % (a) and 5.0 wt % (b) of wheat starch were served as the pore-forming agent.

Glass Transition Temperature Tg of PVF/Starch and PVF/SiO$_2$ Foams

From the results of DSC analyses of PVF/starch and PVF/SiO_2 foams, we found that their glass transition temperatures T_g are all located at 70°C and remain unchanged, when different



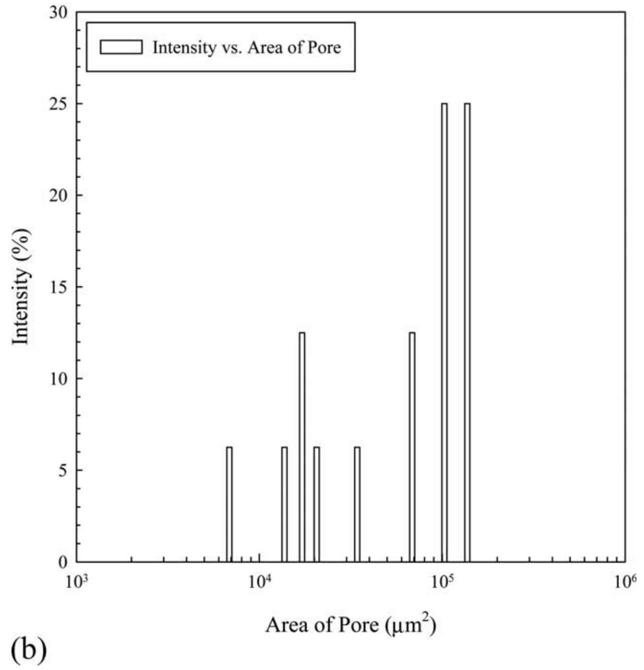


Figure 8. The pore area distribution of PVF/SiO_2 foams analyzed by using the Image-Pro Plus software,[17] when 0.05 wt % (a) and 0.25 wt % (b) of silica particles were served as the pore-forming agent.

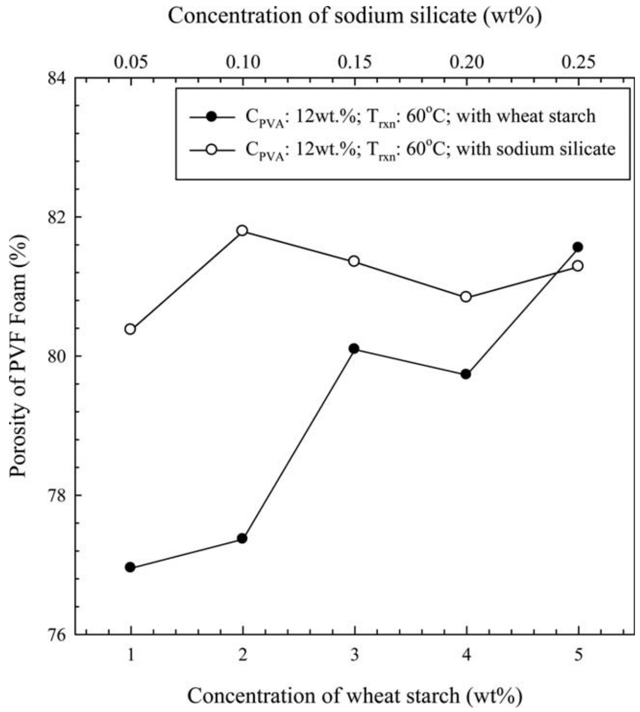


Figure 9. The porosity of PVF/starch and of PVF/SiO_2 foams, when different concentrations of wheat starch and silica particles were served as the pore-forming agent, respectively.

amounts of either wheat starch or silica particle served as the pore forming agent. This result indicates that those pore-foaming agents of either wheat starch or silica particle do not affect the hybrid bond formation between PVA and formaldehyde molecules as acetalization proceeds.

Young's Modulus of PVF/Starch and PVF/SiO_2 Foams

The Young's modulus of PVF/starch and PVF/SiO_2 foams can be determined from the slope of the strain-stress curves of foam samples chosen by the average value of six tensile tests. Figure 10(a) shows the Young's modulus of PVF/starch foams when 1.0–5.0 wt % of wheat starch served as the pore-forming agent, and that the Young's modulus of PVF/starch foams decreases as the concentration of wheat starch increases; that is, decreases from 0.20 to 0.09 Mpa as wheat starch increases from 1.0 to 5.0 wt %. Because a foam of higher porosity but smaller pore size can be obtained when the concentration of wheat starch is increased from 1.0 to 5.0 wt %, which will lower the mass content per unit volume of PVF foam and consequently make thinner pore walls as shown in Figure 2(a–e), the foam's modulus decreases with the increase of wheat starch concentration. However, the porosity and pore size of for PVF/SiO_2 foams change only slightly as observed in Figure 4(a–e), hence their modulus values vary only between 0.13 and 0.14 Mpa as shown in Figure 10(b) when 0.05–0.25 wt % of silica particles served as the pore-forming agent.

Water Adsorption Capacity and Water Desorption Rate of the Wet PVF/Starch and PVF/SiO_2 Foams

To behave as an SAP, since the water adsorption capacity of PVF foam is one of the most import properties needed to be identified, therefore we have tested it as follows. After inserting the dry sample foams (i.e., 20 mg per piece) into 100 mL water for 1 min, by taking the average value of six pieces, the water adsorption capacity of the wet PVF/starch and PVF/SiO_2 foams can be determined from the TGA curves of sample weight loss at 100°C. As shown in Figure 11, there is an 84% weight loss of water at 100°C from PVF/starch foam, which was made by 12 wt % PVA and 1.0 wt % wheat starch. The same value of 84% water weight loss at 100°C was obtained for other PVF/starch samples with 2.0, 3.0, 4.0, and 5.0 wt %

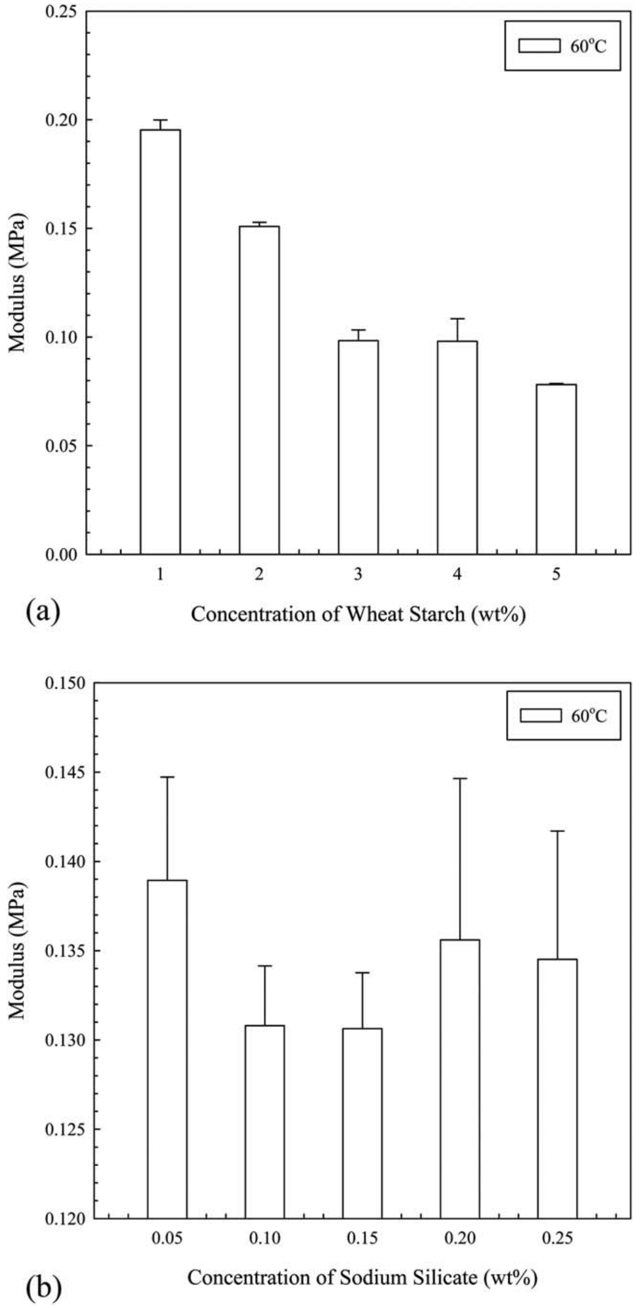


Figure 10. The Young's modulus of PVF/starch and PVF/SiO_2 foams, when different concentrations of wheat starch (a) and silica particles (b) were served as the pore-forming agent, respectively.

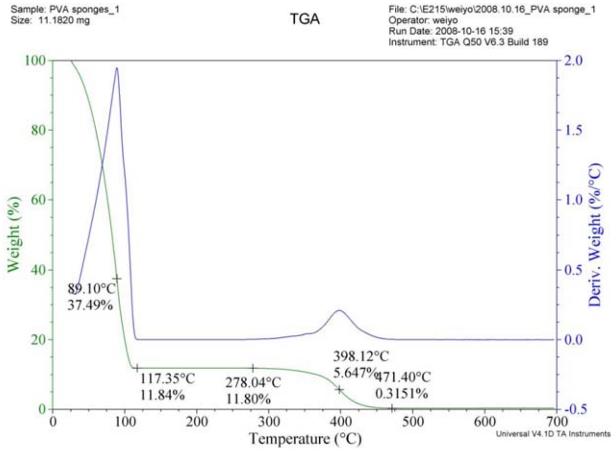


Figure 11. TGA curves of PVF/starch foam made of 12 wt % PVA when 1.0 wt % wheat starch was served as the pore-forming agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wheat starch. This value of 84% water weight loss was also obtained for those PVF/SiO_2 foams when different amounts of 0.05–0.25 wt % silica particles were served as the pore-forming agent. This 84% water adsorption capacity obtained for both PVF/starch and PVF/SiO_2 foams meets the requirement of SAP.[3] In addition, because the PVA concentration for all PVF/starch and PVF/SiO_2 foams was kept at 12 wt %, the amounts of hydroxyl group remaining on the PVF after acetalization are all the same for these two foams, and hence we believe that the water adsorption capacity of the present PVF foams is determined by the PVA concentration and not affected by the amounts of either starch or silica particle added. This conclusion is supported by the curves of water retention as shown in Figure 12(a,b) when the PVF samples were heated in TGA at 50°C for 50 min (because the value of 16 wt % water retention is always reached for all of PVF samples after heating 30 min at 50°C as shown in Figure 11). From the slopes of those water retention curves shown in Figure 12(a,b), the water desorption rates of all PVF/starch and PVF/SiO_2 foams can be determined. Since the porosities of PVF/starch foams increase with the increase of starch concentration, the rank of their water desorption rates is $5.0 > 4.0 > 3.0 > 2.0$ wt % as shown in Figure 12(a). The water desorption rate of 1.0 wt % is greater than that of the 2.0 wt % starch added is due to the nonuniform pore size distribution in PVF/starch foam as observed in Figure 2(a). Since the porosities of PVF/SiO_2 foams increase only slightly at 0.25 wt % water glass, the corresponding water desorption rates remained unchanged when 0.05–0.2 wt % silica particles were added and increased when 0.25 wt % silica particle was added. Comparing the slopes of those TGA curves of 5.0 wt % wheat starch and of 0.25 wt % silica particle as shown in Figure 12(a,b), because of its open-cell type pore structure as shown in Figure 2(a–e), so the water desorption rate of PVF/starch foam is always higher than that of PVF/SiO_2 foam with a closed-cell type pore structure as shown in Figure 4(a–e).

Low Wastewater COD Impact

The present PVF/SiO_2 foam exhibits excellent water adsorption capacity being at least as good as that of PVF/starch foam. Also because of its low environmental impact when silica particles produced from water glass solution were served as the pore forming agent, a local PVF manufacture plant has employed this new method in its production line since July 2012. The wastewater COD values before entering the conventional wastewater treatment process (i.e., activated sludge method) equipped in the plant were recorded in Figure 13. It is found that the daily averaged wastewater COD value of

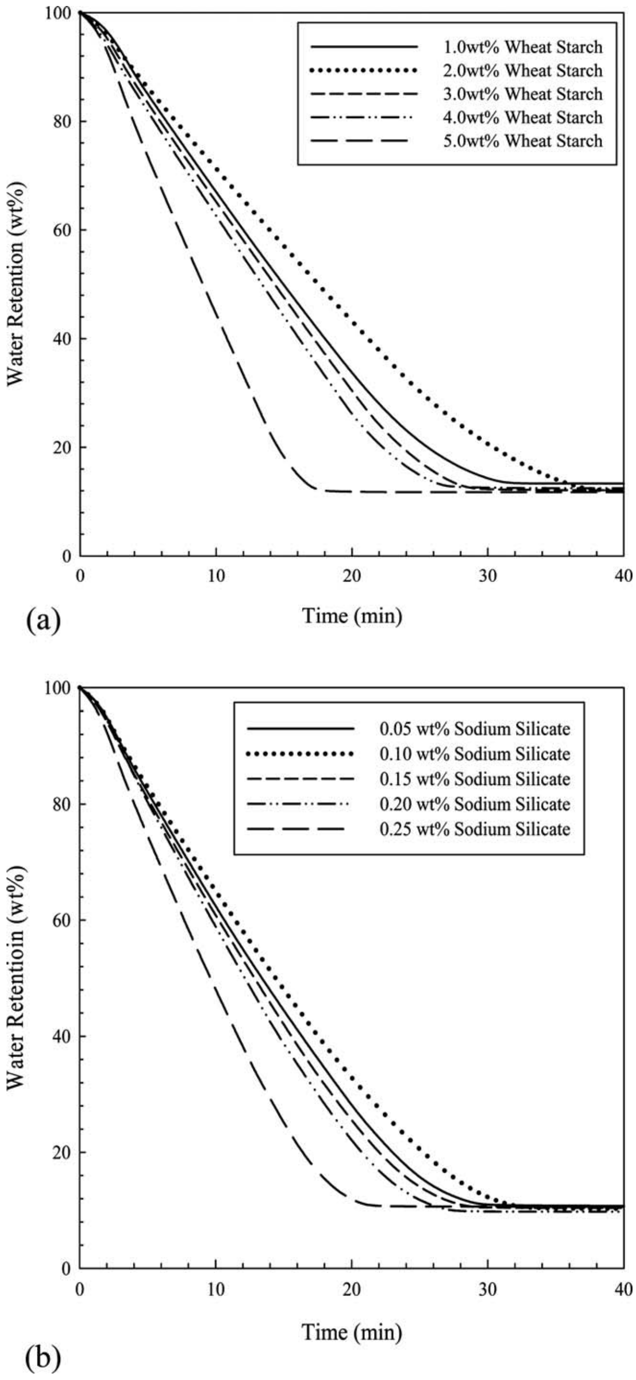


Figure 12. The water retention curves of PVF/starch foams (a) and PVF/SiO_2 foams (b), when the PVF samples were heated at 50°C for 50 min, respectively.

making PVF/SiO_2 foam is as low as 1500 mg/L, which is much lower than that of making PVF/starch foam, and therefore, its wastewater can be easily treated in the downstream wastewater treatment process of the plant. Note that, to avoid the health problem caused by those silica particles produced from water glass solution, its wastewater was also filtered through the membranes equipped in the plant wastewater treatment process.

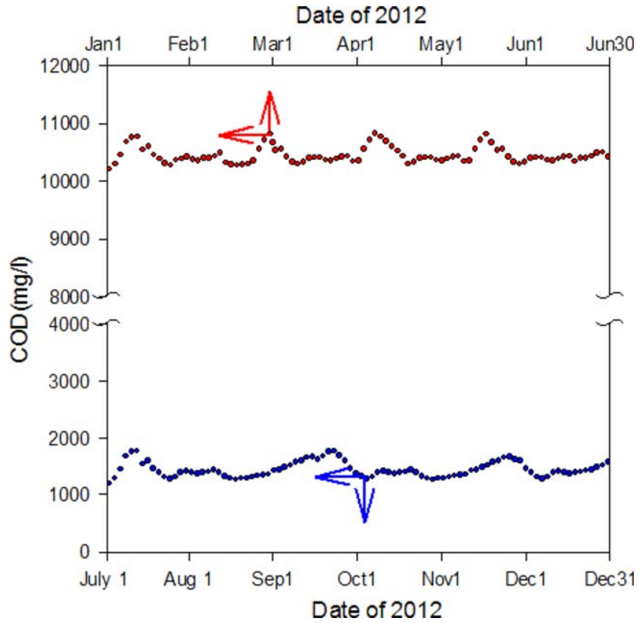


Figure 13. The daily wastewater COD values of 2012 as recorded by a local PVF foam manufacture plant located at Taichung industry park, whose wastewater discharge amount is 50,000 liters per day. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSION

To reduce the wastewater pollution problem, instead of using wheat starch as the pore-forming agent, a new method of preparing superabsorbent PVF/SiO_2 porous foam through the simultaneous acidification of water glass solution is presented in this study. After conducting our analysis with the help of the data of SEM, DSC, TGA, stress-strain, and water contents, we have arrived at seven conclusions: (1) The pore structure of PVF/starch foams belongs to an open-cell type and the pore structure of PVF/SiO_2 foams belongs to a closed-cell type. (2) Higher porosity but smaller pore size PVF/starch foams can be obtained when the concentration of wheat starch is increased, and the porosity and pore size of PVF/SiO_2 foams increase only slightly when the concentration of water glass solution is increased. (3) The porosity of PVF/SiO_2 foams is always higher than that of PVF/starch foam. (4) The present PVF/SiO_2 foams possess larger pore size and higher porosity than those of the PVF membranes reported by Sueoka et al.[7] where the silica powders were served as the pore–forming agent. The unchanged T_g indicates that the pore-foaming agent of either wheat starch or silica particle will not affect the hybrid bonds formatted through the acetalization reaction. (5) The Young's modulus of PVF/starch foams decreases with the increase of wheat starch concentration, and the Young's modulus of PVF/SiO_2 foams will not be affected by the concentration of silica particles produced by the water glass solution. (6) Because the PVA concentration was fixed at 12 wt % when preparing foam samples, the water adsorption capacity of the PVF/starch and PVF/SiO_2 foams obtained in this study are not affected by the concentrations of either wheat starch or silica particle when they are served as the pore-forming agent. (7) The water desorption rates of PVF/starch foams increase with the increase of wheat starch concentration, however, the water desorption rates of PVF/SiO_2 foams remain largely unchanged when different concentrations of silica particles produced by the acidification of water glass solution served as the pore-forming agent in this study.

Finally, since its wastewater COD value can be largely decreased, so the present new method of making PVF/SiO_2 foams can reduce its environmental impact efficiently.

ACKNOWLEDGMENTS

The financial support received from the National Science Council of Taiwan, research grant no. NSC 99-2221-E-029-021-MY3, is greatly appreciated.

REFERENCES

1. Kabiri, K.; Omidian, H.; Hashemi, S. A.; Zohuriaan-Mehr, M. *J. Eur. Polym. J.* **2003**, *39*, 1341.
2. Chiellini, E.; Corti, A.; D'Antone, S.; Solaro, R. *Prog. Polym. Sci. (Elsevier)*, **2003**, *28*, 963.
3. Buchhlz, F. L.; Graham, T. Modern Superabsorbent Polymer Technology, Wiley-VCH: New York, **1997.**
4. Wilson, C. L. U.S. Pat. 2, *609*, *347* (**1952**).
5. Kern, W.; Schulz, R. C.; Braun, D. *J. Polym. Sci.* **1960**, *48*, 91.
6. Nishimura, H.; Sata, S. U.S. Pat. 3, *663*, *470* (**1972**).
7. Sueoka, A.; Okamoto, T.; Ohmori, A.; Kawai, S.; Ueda, M. U.S. Pat. 4, *279*, *752* (**1981**).
8. BeMiller, J. N.; Whistler, R. L. Starch: Chemistry and Technology, 3rd ed.; Academic press: New York, **2009**.
9. Wilson, J. D.; Bechtel, D. B.; Todd, T. C.; Seib, P. A. *Cereal Chem.* **2006**, *83*, 259.
10. Brinker, C. J.; Scherer, G. W. Sol-Gel Science: The Physics And Chemistry Of Sol-Gel Processing; Academic Press: New York, **1990**.
11. Bergna, H. E. The Colloid Chemistry Of Silica, Advances In Chemistry Series No. 234; American Chemical Society: Washington DC, **1994**.
12. Stöber, W.; Fink, A. *J. Colloid Interface Sci.* **1986**, *26*, 62.
13. Lee, Y. K.; Yoon, Y. R.; Rhee, H. K. *Colloids Surf. A* **2000**, *173*, 109.
14. Wang, X. D.; Shen, Z. X.; Sang, T.; Cheng, X. B.; Li, M. F.; Chen, L. Y.; Wang, Z. S. *J. Colloid Interface Sci.* **2010**, *341*, 23.
15. Eliasson, A. C.; Karlsson, R. *Starch*, **1983**, *35*, 130.
16. Plieva, F. M.; Karlsson, M.; Aguilar, M. R.; Gomez, D.; Mikhalovsky, S.; Galaev I. Y.; Mattiasson, B. *J. Appl. Polym. Sci.* **2006**, *100*, 1057.
17. Image-Pro Plus, version 4.5, Media Cybernetics, Bethesda, Maryland, **2001**.