# Synthesis and Characterization of Soluble Hybrids of Poly(vinyl pyrrolidone) or Its Copolymer

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**ABSTRACT:** The purpose of this study was to examine the properties and synthesis feasibility of water-soluble hybrids of poly(vinyl pyrrolidone) (PVP) or a PVP copolymer. PVP was first mixed with different concentrations of tetraethoxysilane (TEOS) to produce PVP/SiO$_2$ hybrids. Second, PVP/sodium polyacrylate (PAANa) copolymers were prepared and further developed into hybrids and then were analyzed and tested with methods such as Fourier transform infrared, NMR, X-ray spectroscopy, and scanning electron microscopy. According to the results of the experiments, the PVP polymer or its copolymer generated hydrogen bonding with the —OH group in SiO$_2$ with both PVP/SiO$_2$ and PVP–PAANa/SiO$_2$ hybrids. With an adequate concentration of TEOS, the hybrids exhibited increased heat resistance. Moreover, the roughness and holes in the hybrids increased with increasing TEOS concentration. However, when the TEOS concentration exceeded 6%, the roughness began to drop. Finally, all the hybrids were water-soluble but possessed inferior solubility when used with organic solvents. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2164–2170, 2006

**Key words:** hybrid; copolymer; X-ray; hydrogen bond; roughness

## INTRODUCTION

Nanomaterials constitute an innovative technology from which endless business opportunities have sprouted for the technology industry. Nanomaterials have had a tremendous impact on traditional industry, affecting the living environment of all human beings. The sol–gel process is one important method for producing nanomaterials. In the past, several scholars have produced materials using this method, which has broad applications in lenses, ceramics, optics, charged catalysts, and so forth.[1–8]

The sol–gel process is a commonly applied method for producing organic/inorganic hybrids. The basic process is as follows. An ester compound or metal alkoxide is dissolved in organic solvents to form a uniform solution, other ingredients are added, and hydrolysis and polycondensation are employed at a uniform temperature; a gel, which gradually forms during the aforementioned procedure, is further processed for the required material through dehydration and sintering. According to the material type, the sol–gel process can be divided into organic and inorganic processes. In the organic process, a metal organic alkoxide is used as the raw material to produce sol through hydrolysis and polycondensation, and further polycondensation is conducted to form the gel. The gel is then treated with an evaporation process to remove the solvents to form dry gels. At the same time, the homogeneous sol can be coated on different materials and heat-treated to form membranes and then extracted for fibers or powderized with different treatments. In the sol–gel process, the structure of the final product is initially formed in the solvent, and the follow-up engineering is directly related to the characteristics of the sol; therefore, the quality of the sol is extremely important. Factors affecting the sol quality include the water, catalyst, pH value, temperature, metal alkoxide, and concentrations and effects of the solvents.[9–12]

As a water-soluble polymer, poly(vinyl pyrrolidone) (PVP) possesses generic characteristics such as protection, adhesiveness, absorbency, solubilization, and condensation; its special features are excellent solubility, biological compatibility, and complexity. Additionally, PVP has low toxicity and is broadly used in areas such as medicine, food, cosmetics, and health-related domains.[13]

Because of the ease of modifying the chemical and physical characteristics of nanometer sol, the use of a modified nanometer gel enables considerable tailoring of the characteristics of the product. At the same time, if the modified nanometer materials can exist in a liquid form, this will greatly benefit the production process. Thus, this article, concerning related research, has been given the title "Synthesis and Characteriza-

tion of Soluble Hybrids of Poly(vinyl pyrrolidone) or Its Copolymer". First, we examine the production of the sol–gel, using different ratios of PVP and tetraethoxysilane (TEOS) with specific amounts of water and a catalyst. The sol–gel is then dehydrated to remove solvents and made into nanometer hybrids to produce related sol and hybrids with a PVP/sodium polyacrylate (PAANa) copolymer and TEOS. The effects on the properties of the hybrids with different ratios of PVP or its copolymer and TEOS are discussed further.

## EXPERIMENTAL

### Materials

We used PVP, hydrochloric acid, sodium hydroxide, acrylic acid (AA; reagent grade; Wako Pure Chemical Industry Co., Japan), ammonium persulfate, isopropyl alcohol (IPA; reagent-grade; Panreac Quimicasa), tetraethoxysilane (TEOS), and N-methyl-2-pyrolidine (reagent-grade; Acros, United States). We also used glycerol, ammonium persulphate, dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF), which were all reagent-grade (purchased from the Shimallu Pure Chemicals, Japan).

### Methods

PVP/SiO$_2$ hybrid synthesis

PVP (6 g) was first absorbed in 35 mL of IPA and stirred to form a uniform solution. Adequate amounts of TEOS were added to dissolve 35 mL of IPA and 3.6 mL of 0.05$N$ HCl, stirred to form a uniform solution, and then mixed with the aforementioned solution at room temperature. It was then stirred for 3 h, with half of the IPA contents being retrieved and heated until they were sufficiently dehydrated to acquire the hybrids. The other half of the contents remained in the solvent form.

PVP/PAANa copolymer synthesis

Resultants of AA (60 g) was neutralized with an NaOH solution (27.2 g of NaOH dissolved in 78 g of water at pH 7) and cooled to room temperature; then, the solution was diluted with water to 50%. PVP (5 g), 20 g of AANa, 0.2 g of glycerin, and 0.05 g of ammonium persulfate were placed into the reaction chamber one by one (except for the initiator), stirred, and injected with helium for 20 min. This mixture was heated to 40°C, and then the initiator was added; polymerization was begun for 2 h under nitrogen gas. Gradually, the temperature was increased to 70°C, and the polymerization process was started for another 2 h to produce the PVP/PAANa copolymer.

PVP–PAANa/SiO$_2$ hybrid synthesis

First, a TEOS solution was prepared (as described in the previous step), and adequate quantities of the synthesized copolymer were obtained to be mixed with the TEOS solution. The mixture was stirred for 2 h to produce the sol. Half was retrieved, and IPA was heated until it was sufficiently dehydrated to acquire the hybrid. The other half remained in the solvent form.

### Analysis and Measurement

The copolymer and hybrid were immersed in ethanol twice for 24 h each before measurement and then were dehydrated and purified. The measurement and analysis for the evaluation of the functional group, heat weight loss, surface morphology, $^{13}$C and $^{29}$Si absorption, surface roughness, crystal structure, and so forth were conducted individually with a Bio-Rad Digilab FTS-200 Micro Fourier transform infrared (Micro-FTIR) spectrometer, a DuPont 2200 thermogravimetric analyzer inflowing nitrogen (60 cm$^3$/min) at a heating rate of 20°C/min, a JEOL 5610 scanning electron microscope (Japan), a Bruker Avance 40 NMR spectrometer (Germany), a Seiko SPA 300 HV atomic force microscope (Japan), and a Rigaku Rint 2500 X-ray diffraction spectrometer (Japan). The measurement of the solubility was conducted individually with different solvents, such as water, IPA, THF, NMP, and DMSO. The solubility was tested after a certain period of stirring.

## RESULTS AND DISCUSSIONS

### FTIR

Figure 1(a) shows that PVP has a clear absorption spectrum at 1655 cm$^{-1}$, which is the absorption spectrum for amide and is an excitation/absorption spectrum combined with the $>$C$=$O and C—N groups.[14] Because this is a combined effort, it is smaller than the pure $>$C$=$O absorption spectrum (1750–1700 cm$^{-1}$). The clear C$=$O group absorption spectra of the three PVP/SiO$_2$ hybrids at different weight ratios [Fig. 1(b–d)] at 1651, 1647, and 1646 cm$^{-1}$ also gradually shift toward the low-frequency region with an increase in the TEOS weight ratio. Clear absorption spectra are also shown at 1144, 1094, and 1059 cm$^{-1}$, which are the absorption spectra for the Si—O—Si group, confirming the existence of the synthesized PVP/SiO$_2$ hybrid. Because of the shifting of the absorption spectra for the PVP $>$C$=$O group between the two, on the basis of reports written by several scholars,[15–17] this allows the identification of the existence of hydrogen bonding.

As indicated in Figure 2(e), the PVP/PAANa copolymer has a clear C$=$O group absorption spectrum at
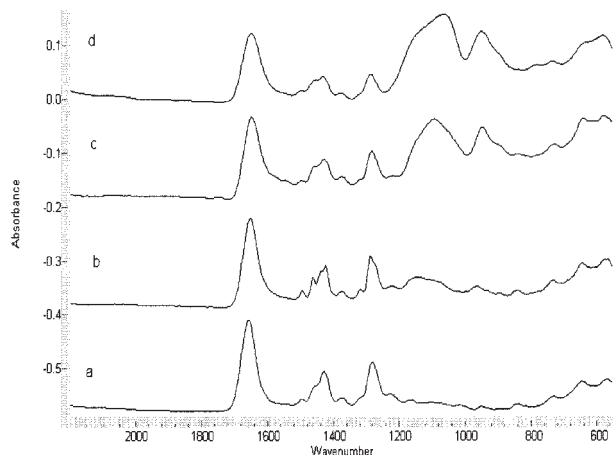
**Figure 1** FTIR of PVP/SiO$_2$ hybrids synthesized with different TEOS concentrations: (a) 0, (b) 3, (c) 9, and (d) 15%.



**Figure 3** $^{13}$C-NMR spectra of hybrids [(a–c) PVP/SiO$_2$ and (d–f) PVP–PAANa/SiO$_2$] with different TEOS concentrations: (a,d) 0, (b,e) 3, and (c,f) 9%.

1651 cm$^{-1}$ and a —COOM absorption spectrum at 1562 cm$^{-1}$, which is unique in a PAANa polymer. As shown in Figure 2(f–h), the PVP–PAANa/SiO$_2$ hybrids with three different weight ratios have clear and individual C=O group absorption spectra at 1650, 1648, and 1647 cm$^{-1}$. They are also shifted toward the low-frequency region with an increase in the TEOS concentration with the COOM group absorption spectra at 1555, 1563, and 1562 cm$^{-1}$ and the Si—O—Si group absorption spectra at 1109, 1099, and 1088 cm$^{-1}$.

## NMR

### $^{13}$C-NMR analysis

$^{13}$C-NMR analysis can be used as a chemical deviation method for examining $^{13}$C in polymer compound microstructures (e.g., stereoregularity, comonomer sequence distribution, and defective structures).[18] As
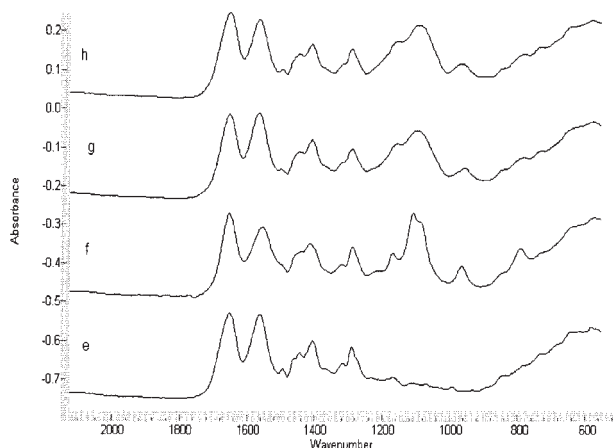


**Figure 2** FTIR of PVP–PAANa/SiO$_2$ hybrids synthesized with different TEOS concentrations: (e) 0, (f) 3, (g) 9, and (h) 15%.
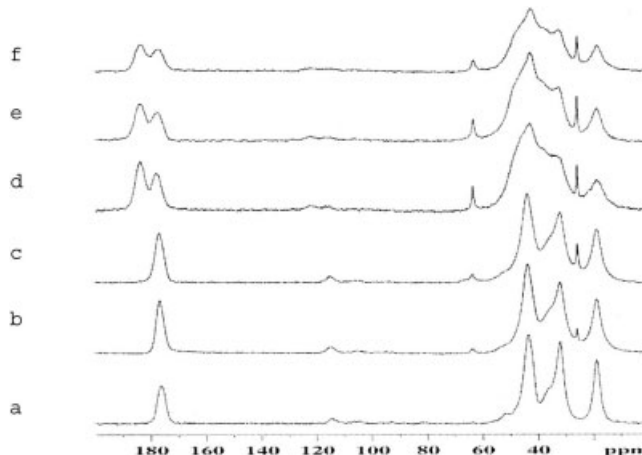
indicated in Figure 3(a), PVP has a C=O group absorption spectrum at 177.191 ppm. As observed in Figure 3(b,c), the PVP/SiO$_2$ hybrids with two different weight ratios have individual C=O group absorption spectra at 178.335 and 178.476 ppm, which indicate that hydrogen bonding has occurred in the PVP C=O group and SiO$_2$ —OH group resulting from the shifting in the $^{13}$C-NMR spectra for specific groups moving toward the high-frequency area.[19–21]

Figure 3(b–f) presents the $^{13}$C-NMR spectra for PVP/SiO$_2$ and PVP–PAANa/SiO$_2$ hybrids with different TEOS concentrations. As shown in Figure 3(b,c), PVP/SiO$_2$ hybrids with different concentrations individually demonstrate C=O group absorption spectra at 178.335 and 178.476 ppm. As can be observed in Figure 4(d–f), PVP–PAANa/SiO$_2$ hybrids with three different weight ratios individually demonstrate C=O group absorption spectra at 178.674, 178.725, and 178.748 ppm and also at 183.916, 183.444, and 183.875 ppm. This was formed by C=O within the PAANa —COONa group, verifying the copolymerization reaction between PVP and PAANa.

### $^{29}$Si-NMR analysis

Figure 4 presents the $^{29}$Si-NMR spectra for PVP/SiO$_2$ and PVP–PAANa/SiO$_2$ hybrids synthesized with different TEOS concentrations. As indicated in Figure 4(a,b), the PVP/SiO$_2$ hybrids with different weight ratios individually demonstrate absorption spectra at $-99.045$ and $-97.501$ ppm. In Figure 4(c,d), the PVP–PAANa/SiO$_2$ hybrids with different weight ratios also reveal absorption spectra at $-100.54$ and $-107.59$ ppm. These are the absorption spectra for SiO$_2$ after the TEOS reaction, indicating a shift to a higher frequency in the absorption spectra with an increase in TEOS.
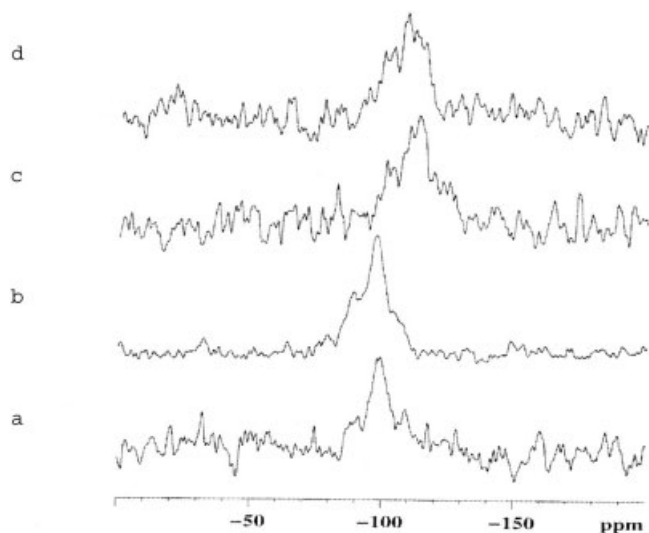
**Figure 4** $^{29}$Si-NMR spectra of hybrids [(a,b) PVP/SiO$_2$ and (c,d) PVP–PAANa/SiO$_2$] with different TEOS concentrations: (a,c) 3 and (b,d) 9%.

## X-ray analysis

As shown in Figure 5, the crystallinity of the hybrid does not change with an increase in the TEOS concentration but is related to the copolymerization of PAANa. Because of the copolymerization with PAANa, a weakening of the peaks for the original PVP at $2\theta$ = 11 and 22 without any change in location indicates that the original PVP crystallinity is lower because of PAANa copolymerization.

## Thermogravimetric analysis (TGA)

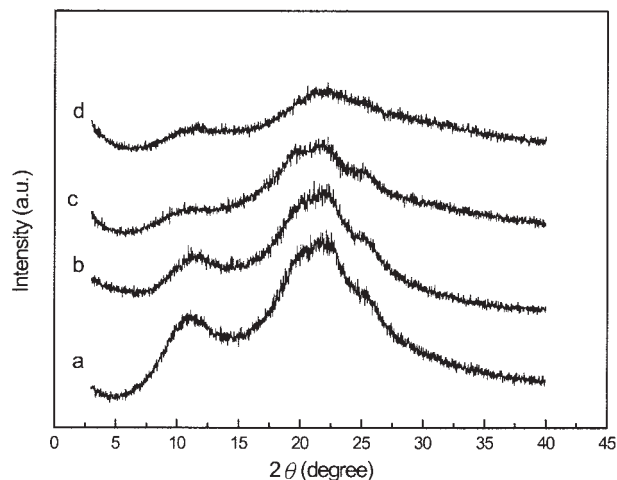Figure 6 and Table I display TGA spectra and related data for PVP and PVP/SiO$_2$ hybrids. Figure 6(b0) is



**Figure 5** X-ray spectra of hybrids [(a,b) PVP/SiO$_2$ and (c,d) PVP–PAANa/SiO$_2$] with different TEOS concentrations: (a,c) 0 and (b,d) 9%.
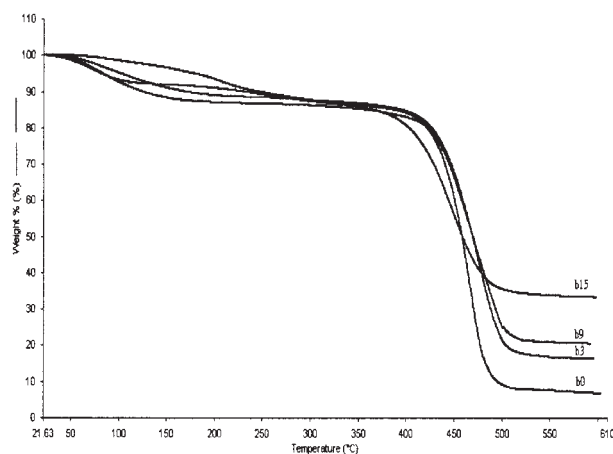


**Figure 6** TGA of PVP and PVP/SiO$_2$ hybrids with different TEOS concentrations: (b0) 0, (b3) 3, (b9) 9, and (b15) 15%.

the curve for pure PVP. As indicated in the table, the initial decomposition temperature for PVP is 439.724°C with a decomposition rate of $-1.543\%/°C$ for fast decomposition. When the decomposition temperature reaches 500°C, only 9.162% of the hybrid is left. Figure 6(b3,b9,b15) shows TGA spectra for PVP/SiO$_2$ hybrids synthesized with different TEOS concentrations (3, 9, and 15%). The initial decomposition temperature decreases with an increase in the TEOS concentration, and this is due to the minute amount of water present in the hybrids from a polycondensation reaction. Another reason for this is the residue of Si(OH)$_4$ in the hybrid pending polycondensation, with the decomposition rate gradually decreasing, whereas the hybrid residue gradually increased. This proves that indirect hydrogen bonding occurs between inorganic SiO$_2$ and the copolymer after the PVP and TEOS reaction starts to form a mesh structure, causing the increase in the hybrid heat resistance.

Second, as indicated in Table I, the initial decomposition temperature for PVP–PAANa is 426.921°C with a decomposition rate of $-0.946\%/°C$. When the decomposition temperature reaches 500°C, the residue concentration is 22.388%. The initial decomposition temperature, decomposition rate, and residues for PVP–PAANa/SiO$_2$ hybrids synthesized with different TEOS concentrations are all superior to those of pure PVP; this indicates that the addition of SiO$_2$ successfully elevates the thermal stability for PVP.

Also from Table I, for the hybrid acquired after the involvement of AANa in the copolymerization, the decomposition rate is slower, and the residue and initial decomposition temperature rise with an increase in the TEOS concentration. This could be the result of a better mesh structure in the copolymer and superior expansibility in the synthesized PVP–PAANa/SiO$_2$ together with the involvement of AANa in the copolymerization reaction causing a further

**TABLE I**
**Thermal Properties of PVP and PVP/SiO$_2$ Hybrids Materials**

| Hybrid | TEOS concentration (%) | Properties | | |
|---|---|---|---|---|
| | | Initial decomposition temperature (°C) | Decomposition rate (%/°C) | Residue (%)[a] |
| PVP/SiO$_2$ | 0 | 439.724 | −1.543 | 9.162 |
| | 3 | 426.985 | −1.011 | 21.741 |
| | 9 | 424.296 | −0.843 | 25.359 |
| | 15 | 413.027 | −0.649 | 35.594 |
| PVP–PAANa/SiO$_2$ | 0 | 426.921 | −0.466 | 32.388 |
| | 3 | 443.167 | −0.823 | 34.489 |
| | 9 | 448.441 | −0.619 | 39.530 |
| | 15 | 438.366 | −0.753 | 40.749 |

[a] Residue when heated to 500°C.

TEOS reaction. However, an excessive TEOS concentration might cause SiO$_2$ to be unevenly distributed in the organic phase, causing a minor drop in the initial decomposition temperature.

### Scanning electron microscopy (SEM)

Figure 7(a–c) shows a swift and shiny surface, whereas SiO$_2$ particles and holes can be seen in Figure 7(d). This proves that the holes and particles increase with an increase in the TEOS concentration. SiO$_2$ particles exist in Figure 7(e), but the surface is swift and shiny. Holes and SiO$_2$ particles exist in Figure 7(f). Half of the surface in Figure 7(g) is full of SiO$_2$ particles and some holes, whereas the SiO$_2$ particles and holes overwhelm the overall surface in Figure 7(h).

Figure 7(a–d) presents PVP hybrids, whereas Figure 7(e–h) presents PVP hybrids. A comparison of the two shows that PVP copolymer hybrids have far larger and more holes than PVP hybrids with an increase in SiO$_2$ particles. This is due to the crosslink-type copol-

ymer formed with the copolymerization reaction between poly(acrylic acid, sodium salt) and PVP. The existence of PAANa results in contact between the copolymer and the water molecules, causing expansion that produces a loosening in the structure. The resulting surface is a cloglike structure with more SiO$_2$ causing SiO$_2$ particles to be congested, leading to the obvious shrinkage of the space between the particles.

### Atomic force microscopy (AFM)

Figure 8 shows AFM images for PVP/SiO$_2$ and PVP–PAANa/SiO$_2$ hybrids synthesized with different TEOS concentrations. The roughness values of Figure 8(a–d) are 1.369, 1.419, 3.127 and 1.682 nm, with a roughness range of 1–4. The roughness values for Figure 8(e–h) are 3.264, 6.705, 16.45, and 2.261 nm, with a roughness range of 3–17; the roughness increases with an increase in the TEOS concentration. The maximum roughness is reached when the TEOS concentration is 6%. When the TEOS
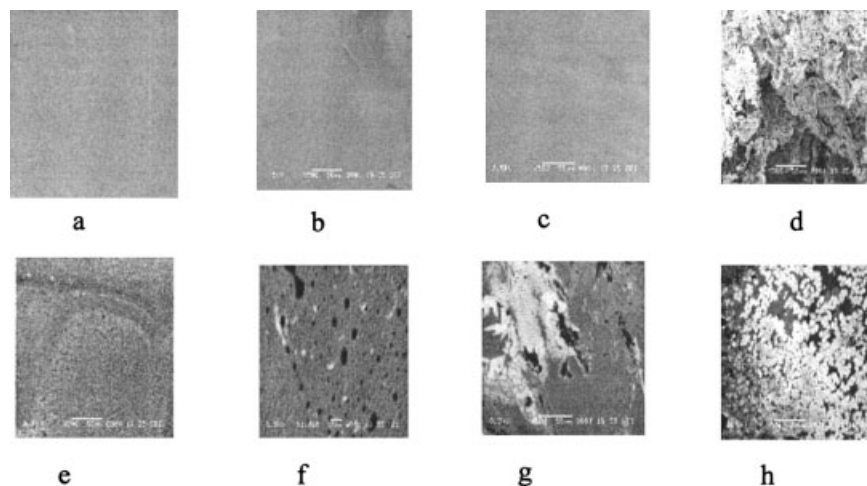


**Figure 7** SEM images of hybrids [(a–d) PVP/SiO$_2$ and (e–h) PVP–PAANa/SiO$_2$] synthesized with different TEOS concentrations: (a,e) 0, (b,f) 1.5, (c,g) 9, and (d,h) 15%.
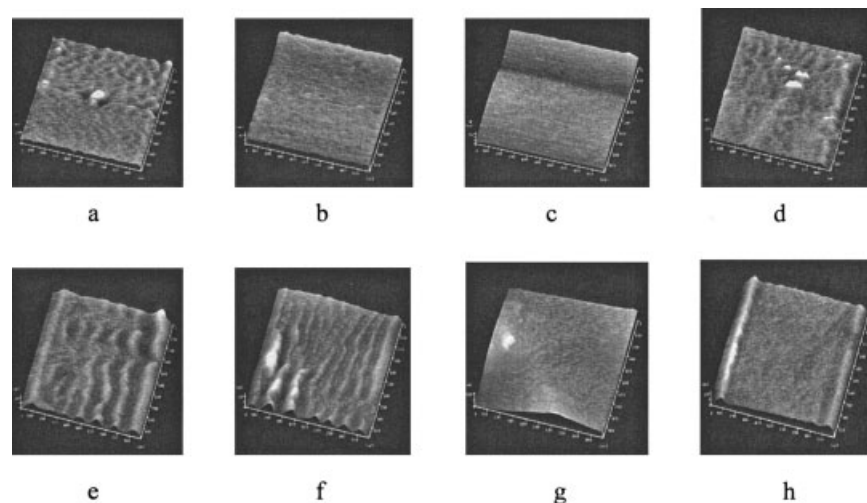
**Figure 8** AFM images of (a–d) PVP/SiO$_2$ and (e–h) PVP–PAANa/SiO$_2$ hybrids synthesized with different TEOS concentrations: (a,e) 0, (b,f) 1.5, (c,g) 9, and (d,h) 15%. The root mean square (RMS) values were (a) 1.369, (b) 1.419, (c) 3.127, (d) 1.682, (e) 3.264, (f) 6.705, (g) 16.45, and (h) 2.261.

concentration exceeds 6%, the hybrid roughness begins to drop. A possible reason for this is the clearer polycondensation, with the overdose of TEOS causing a tighter crosslink mesh structure and smaller particles with smaller roughness. A comparison of the two types of hybrids shows that the surface roughness of the hybrid made from the copolymer is larger than that of the hybrid made from the PVP polymer. The reasons for this are stated in the last section.

## Solubility

Table II indicates the solubility of different solvents for PVP/SiO$_2$ and PVP–PAANa/SiO$_2$ hybrids produced with different TEOS concentrations. The PVP/SiO$_2$ hybrid has better solubility in water and DMSO than in IPA and NMP. This is due to the polar deficiencies in both chemicals, with insolubility in THF. Furthermore, data from the table show that the PVP–PAANa/SiO$_2$ hybrids are water-soluble but insoluble in other organic solvents. This is due to their ease of solubility in water by PAANa but not in all organic solvents such as THF, IPA, and NMP. Nonpolar-to-polar esters, ethylene glycols, and so forth are all insoluble in PAANa.[22] Besides, all other hybrids have excellent solubility, except for PVP/SiO$_2$ hybrids with greater than 12% TEOS concentrations in water. This is due to the fact that the mesh structure within the organic phase is tighter when a higher TEOS concentration exists. For the PVP–PAANa/SiO$_2$ hybrids,

**TABLE II**
**Solubility of PVP/SiO$_2$ and PVP–PAANa/SiO$_2$ Hybrids**

| Hybrid | TEOS concentration (%) | Solvent | | | | |
|---|---|---|---|---|---|---|
| | | Water | IPA | THF | NMP | DMSO |
| PVP/SiO$_2$ | 0 | + | + | − | + | + |
| | 1.5 | + | − | − | + | + |
| | 3 | + | − | − | + | + |
| | 6 | + | − | − | + | + |
| | 9 | + | − | − | + − | + |
| | 12 | + − | − | − | − | + |
| | 15 | + − | − | − | − | + − |
| PVP–PAANa/SiO$_2$ | 0 | + | − | − | − | − |
| | 1.5 | + | − | − | − | − |
| | 3 | + | − | − | − | − |
| | 6 | + | − | − | − | − |
| | 9 | + | − | − | − | − |
| | 12 | + | − | − | − | − |
| | 15 | + | − | − | − | − |

+, soluble; + −, partially insoluble; −, insoluble.

even though there is the possible existence of a tight mesh structure, their solubility in water is superior because PAANa is very water-soluble.

## CONCLUSIONS

The purpose of this study has been to examine the synthesis and characterization of water-soluble hybrids of PVP or its copolymer, and the following conclusions have been drawn from the results:

1. On the basis of an analysis of FTIR and NMR, PVP or its copolymer within PVP/SiO$_2$ and PVP–PAANa/SiO$_2$ hybrids will generate hydrogen bonding with the —OH group in SiO$_2$.

2. The thermal resistance of hybrids produced with adequate TEOS concentrations increases, with better heat resistance performance from the copolymer than the PVP polymer.

3. With respect to the surface morphology, the roughness and holes of the hybrids will increase with an increase in the TEOS concentration, but when the TEOS concentration exceeds 6%, the roughness will start to decrease with a decrease in holes and with the particles gradually changing into clogs.

4. All hybrids are water-soluble but have inferior solubility in organic solvents, especially hybrids produced from the PVP copolymer, which is insoluble in organic solvents.

## References

1. Hench, L. L.; West, J. K. Chem Rev 1990, 90, 33.
2. Bahulekar, R. V.; Prabhune, A. A.; Sivaraman, H.; Ponrathnam, S. Polymer 1993, 34, 163.
3. Johnson, J. D. W. Am Ceram Soc Bull 1985, 64, 1597.
4. Rabinson, E. M. J Mater Sci 1982, 20, 4259.
5. Brinker, C. J.; Scherer, G. W. Sol–Gel Science; Academic: New York, 1989.
6. Toki, M.; Miyashita, S.; Takeuchi, T.; Kanbe, S.; Kochi, A. J Non-Cryst Solids 1988, 100, 479.
7. Hench, L. L.; Wilson, M. J. R.; Balaban, C.; Nogues, J. L. Sol–Gel Processing of Large Silica Optics, Proceedings of the 4th International Conference on Ultrastructure Processing of Ceramics, Glasses and Hybrids, Tucson, AZ, 1989.
8. Zarzycki, J. J Sol-Gel Sci Technol 1997, 8, 17.
9. Ro, J. C.; Chung, I. J. J Non-Cryst Solids 1991, 130, 8.
10. Gadalla, A. M.; Yun, S. J. J Non-Cryst Solids 1992, 143, 121.
11. Brinker, C. J. J Non-Cryst Solids 1988, 100, 31.
12. Arriagada, J. F.; Osseo-Asare, K. J. Colloid Interface Sci 1995, 170, 8.
13. Liao, Z. H. Water-Soluble Polymer; Chemical Industry: Beijing, 1998; pp 1 and 586.
14. Chalapathi, V. V.; Ramiah, K. V. Curr Sci 1968, 16, 453.
15. Zhang, X.; Takegoshi, K.; Hikichi, K. Macromolecules 1992, 25, 2336.
16. Zhang, X.; Takegoshi, K.; Hikichi, K. Polymer 1992, 33, 712.
17. Bovey, F. A. High-Resolution NMR of Macromolecules; Academic: New York, 1972.
18. Zhang, X.; Takegoshi, K.; Hickichi, K. Macromolecules 1992, 25, 2336.
19. Qin, C.; Pries, A. T. N.; Belifore, L. A. Polym Commun 1992, 31, 177.
20. Miyoshi, T.; Takeqoshi, K.; Hikichi, K. Polymer 1992, 38, 2315.
21. Mayhias, L. J. Solid State NMR of Polymers; Plenum: New York, 1988.
22. Shiao, H. R. Applied Chemistry; NCTU: Taiwan, 2002.