Polymer Journal, Vol. 24, No. 7, pp 689—692 (1992)

NOTES

# Preparation of Silica-Containing Polyvinylpyrrolidone Films by Sol–Gel Process

Atsushi MORIKAWA, Yoshitake IYOKU, Masa-aki KAKIMOTO, and Yoshio IMAI

*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan*

(Received November 20, 1991)

KEY WORDS Polyvinylpyrrolidone / Sol–Gel Process / Silica / Organic–Inorganic Hydrid Materials /

Recently, the sol–gel process has been paid attention as a preparative method for inorganic metal oxides under mild conditions, which consists of hydrolysis of metal alkoxides, followed by polycondensation.[1,2] An important advantage of this process for polymer chemistry is that starting metal alkoxides are essentially organic compounds, and can be mixed with organic polymers in an appropriate solution system. If the metal alkoxides are hydrolyzed and grown to metal oxides in such systems, new organic–inorganic hydrid materials can be successfully produced. Recently, silicon oxide (silica) and polymer hydrid materials have been systhesized from TEOS and the polymers such as poly(oxytetramethylene),[3-6] poly(oxyethylene),[7] sodium poly(4-styrene sulfonate),[8] perfluorosulfonic acid ionomer,[9,10] poly(ether ketone),[11] poly(dimethylsiloxane),[5,12,13] polysiloxane elastmers,[14-19] and polyoxazoline,[20,21] and polyimides.[22-24] Primary work of polyvinylpyrrolidone-silica hybrid materials was also reported.[25]

In this paper, we report the preparation of the silica polyvinylpyrrolidone (PVP) hydrid materials by the hydrolysis-polycondensation of TEOS in alcoholic aqueous solution of PVP.

## EXPERIMENTAL

### *Measurements*

IR and NMR spectra were measured with a JASCO FT/IR5000 spectrophotometer and a JEOL-FX90Q spectrometer, respectively. Thermogravimetry (TG) was performed with a Shimadzu thermal analyzer TGA-40M. Dynamic mechanical analysis (DMA) was performed with a Toyoseiki Rheograph Solid. Scanning electron micrograph (SEM) was obtained with a JEOL-T220 electron microscope, where the energy dispersion X-ray fluorescence analysis was performed with a Philips EDAX-9900 attachment.

### *Preparation of PVP-Silica Hybrid Films*

In a flask, 1.0 g of PVP ($M_w = 3.6 \times 10^5$) was dissolved in an equal volume mixture of water and ethanol. An appropriate amount of TEOS (see Table I) was added to the solution. After the solution was stirred at room temperature for 3 h, the homogeneous solution formed was cast onto a poly(ethylene terephthalate) (PET) film and dried overnight at 60°C.

## RESULTS AND DISCUSSION

The sol–gel reaction starting from TEOS was carried out under neutral condition in the solution of PVP dissolved in a mixture of water and ethanol (1 : 1 by volume). PVP-silica hybrid films were obtained simply by casting the solutions onto a PET film and drying at 60°C. The results of the preparation of the hybrid films with various silica content are summarized in Table I. The silica content denotes the value calculated assuming that the sol–gel reaction proceeded completely. All solutions before casting were homogeneous. Transparent hydrid films were obtained when the silica content was less than 8 wt%, whereas the films were heterogeneous and rather brittle in case of higher silica content. These films were generally strongly hygroscopic, and were not so easy to handle in the usual atmosphere.

**Table I.** Prepration of silica-containing PVP films

| No. | Water–Ethanol (50 : 50)/ml | PVP g | TEOS ml | $SiO_2$[a] % | Remarks[b] |
|---|---|---|---|---|---|
| 1 | 6 | 1 | 0 | 0 | homo |
| 2 | 6 | 1 | 0.08 | 2 | homo |
| 3 | 6 | 1 | 0.12 | 3 | homo |
| 4 | 6 | 1 | 0.16 | 4 | homo |
| 5 | 6 | 1 | 0.20 | 5 | homo |
| 6 | 6 | 1 | 0.24 | 6 | homo |
| 7 | 6 | 1 | 0.29 | 7 | homo |
| 8 | 6 | 1 | 0.33 | 8 | homo |
| 9 | 6 | 1 | 0.44 | 9 | hetero |

[a] Calculated as fully cured product.
[b] homo, homogeneous and transparent film; hetero, face separation was occurred.

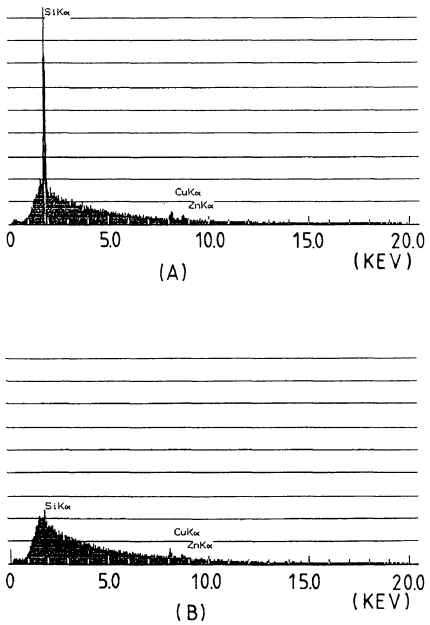


**Figure 1.** Energy dispersion X-ray spectra of (A) PVP-silica hybrid film (8 wt% silica) and (B) PVP film without silica. Background peaks should mainly arise from the sample holder.

Although the SEM photograph of the hybrid film (silica content 8 wt%) showed no remarkable structure, a strong peak corresponding to the Si atom was clearly detected in the energy dispersion X-ray spectrum of the hybrid film (Figure 1), which was measured at the same time as the SEM observation. Homogeneously dispersed particles of 0.1 $\mu$m diameter were observed by a transmission scanning microscopic photograph as shown in Figure 2.

The chemical structure of the hybrid films was confirmed by IR and NMR spectra. The IR spectrum of PVP-silica hybrid film (8 wt% silica) are shown in Figure 3. Characteristic absorptions of Si–O–Si were observed at 1035

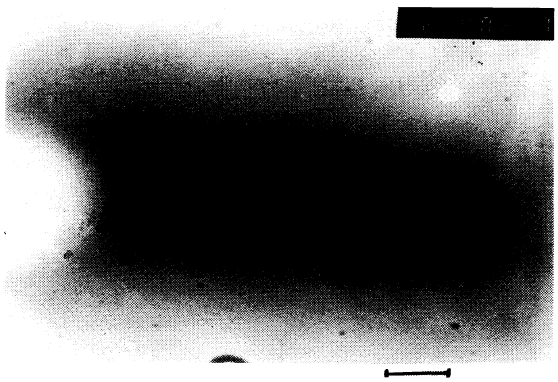

**Figure 2.** Transmission scanning microscopic photograph of PVP-silica hybrid film (8 wt% silica). Black bar indicates 0.5 mm.

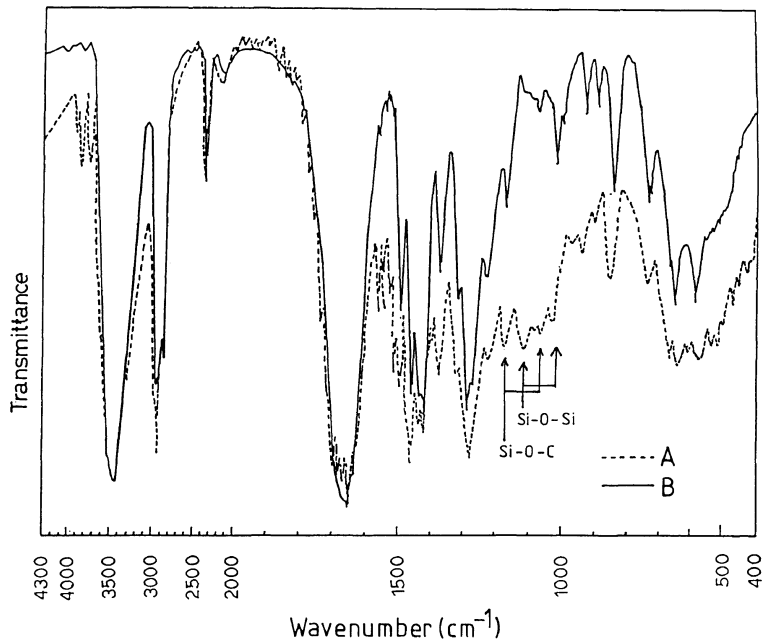


**Figure 3.** IR spectra of (A) PVP-silica hybrid film (8 wt% silica) and (B) PVP film without silica.

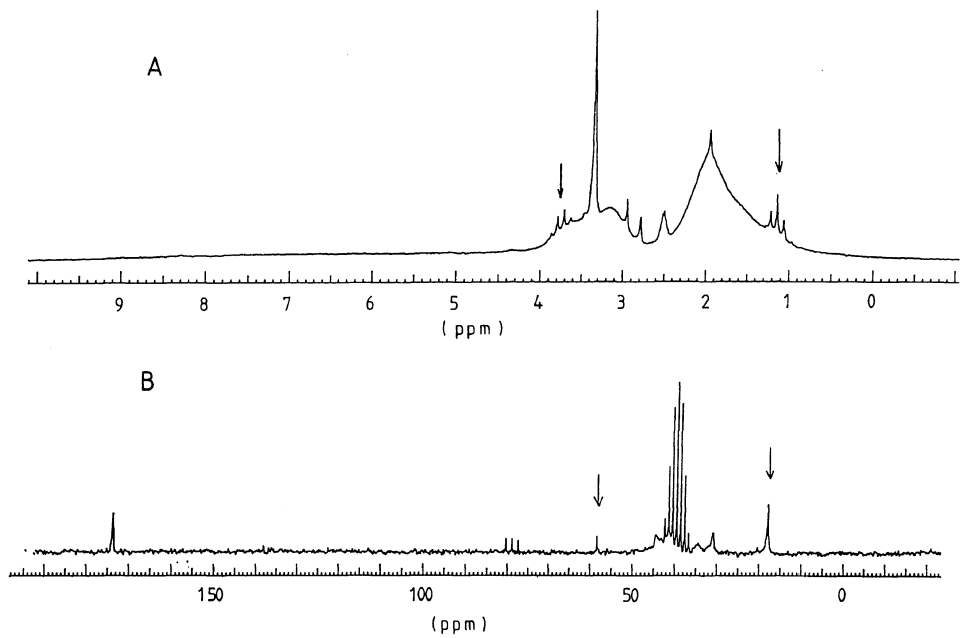


**Figure 4.** a) $^{1}H$ NMR and b) $^{13}C$ NMR spectra of PVP-silica hybrid material (8 wt% silica) measured in DMSO-$d_6$.

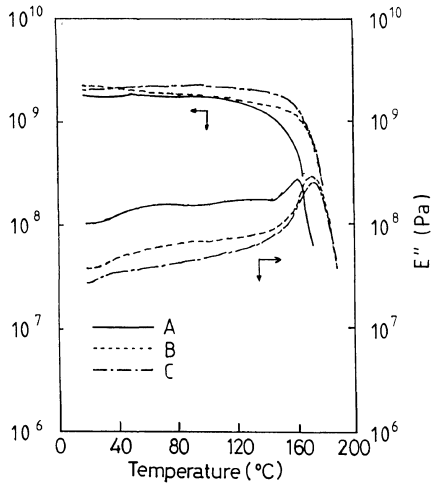


**Figure 5.** DMA curves of PVP-silica hybrid films: (A) without silica; (B) 4 wt% silica; (C) 8 wt% silica.

and 1178 $cm^{-1}$, and those of Si–O–C at 1087 and 1140 $cm^{-1}$. As shown in Figure 4, small peaks corresponding to the ethyl group were observed at 1.2 and 3.8 ppm, and 18 and 58 ppm, in the $^{1}H$ NMR and $^{13}C$ NMR spectra, respectively. These results suggest that the PVP-silica hybrid films contain a small amount of ethoxy groups not hydrolyzed under the present conditions.

Dynamic mechanical analysis was performed on the obtained films (Figure 5). The storage modulus of the films as well as the glass transition temperature increased with increasing silica content.

In conclusion, the PVP-silica hybrid films were readily prepared by the sol–gel process. The obtained films containing less than 8 wt% of silica had well dispersed silica particles. However, the results of the IR and NMR spectroscopies indicated that the hydrolysis and condensation of TEOS were incomplete. This must arise from low cure temperature because of less thermal stability of the matrix polymer, PVP.

*Acknowledgment.* The authors are grateful to Toshiba Silicone Co., Ltd. for gift of silicon reagents.

## REFERENCES

1. D. R. Ulrich, *Chemtech*, 242 (1988).
2. L. L. Hench and J. K. West, *Chem. Rev.*, **90**, 33 (1990).
3. D. Ravaine, A. Seminel, Y. Charbouillot, and M. Vincens, *J. Non-Cryst. Solids*, **82**, 210 (1986).
4. H-H. Huang and G. L. Wilkes, *Polym. Bull.*, **18**, 455 (1987).
5. R. H. Glaser and G. L. Wilkes, *Polym. Bull.*, **19**, 51 (1988).
6. H-H. Huang, G. L. Wilkes, and J. C. Carlson, *Polymer*, **30**, 2001 (1989).
7. M. Fujita and K. Honda, *Polym. Commun.*, **30**, 200 (1989).
8. K. Nakanishi and N. Soga, *J. Non-Cryst. Solids*, **108**, 157 (1989).
9. K. A. Mauritz and R. M. Warren, *Macromolecules*, **22**, 1730 (1989).
10. I. D. Stefanithis and K. A. Mauritz, *Macromolecules*, **23**, 2397 (1990).
11. J. L. W. Noell, G. L. Wilkes, D. K. Mohantly, and J. E. MacGrath, *J. Appl. Polym. Sci.*, **40**, 1177 (1990).
12. H-H. Huang, B. Oriler, and L. Wilkes, *Polym. Bull.*, **14**, 557 (1985).
13. H-H. Huang, B. Orier, and G. L. Wilkes, *Macromolecules*, **20**, 1322 (1987).
14. Y.-P. Ning, M.-Y. Tang, C.-Y. Jiang, J. E. Mark, and W. C. Roth, *J. Appl. Polym. Sci.*, **29**, 3209 (1984).
15. J. E. Mark, C.-Y. Jiang, and M.-Y. Tang, *Macromolecules*, **17**, 2613 (1984).
16. C.-Y. Jiang and J. E. Mark, *Makromol. Chem.*, **185**, 2609 (1984).
17. Y.-P. Ning and J. E. Mark, *J. Appl. Polym. Sci.*, **30**, 3519 (1985).
18. J. E. Mark, Y.-P. Ning, C.-Y. Jiang, M.-Y. Tang and W. C. Roth, *Polymer*, **26**, 2069 (1985).
19. G. S. Sur and J. E. Mark, *Makromol. Chem.*, **187**, 2861 (1986).
20. Y. Chujo, E. Ihara, H. Ihara, and T. Saeguse, *Macromolecules*, **22**, 2040 (1989).
21. Y. Chujo, E. Ihara, S. Kure, K. Suzuki, and T. Saegusa, *Polym. Prepr.*, **31**, 59 (1990).
22. A. Morikawa, Y. Iyoku, M. Kakimoto, and Y. Imai, *Polym. J.*, **1991**, (1991).
23. M. Spinu, A. Brennan, J. Rancourt, G. L. Wilkes, and J. E. McGrath, *Mater. Res. Soc. Symp. Proc.*, **175**, 179 (1990).
24. M. Nandi, J. A. Conklin, L. Salvati, Jr., and A. Sen, *Chem. Mater.*, **3**, 201 (1991).
25. S. Kure, R. Jordan, Y. Chujo, and T. Saegusa, *Polym. Prepr. Jpn.*, **39**, 329 (1990).