

## Crystallization of Poly(vinylidene fluoride)-SiO<sub>2</sub> Hybrid Composites Prepared by a Sol-gel Process

Jae Whan Cho\* and Kyung Il Sul

Department of Textile Engineering, Konkuk University, Seoul 143-701, Korea

(Received May 31, 2001; Revised June 16, 2001; Accepted June 25, 2001)

**Abstract:** Organic-inorganic hybrid composites consisting of poly(vinylidene fluoride) (PVDF) and SiO<sub>2</sub> were prepared through a sol-gel process and the crystallization behavior of PVDF in the presence of SiO<sub>2</sub> networks was investigated by spectroscopic, thermal and x-ray diffraction measurements. The hybrid composites obtained were relatively transparent, and brittleness increased with increasing content of tetraethoxysilane (TEOS). It was regarded from FT-IR and DSC thermal analyses that at least a certain interaction existed between PVDF molecules and the SiO<sub>2</sub> networks. X-ray diffraction measurements showed that all of the hybrid samples had a crystal structure of PVDF  $\gamma$ -phase. Fresh gel prepared from the sol-gel reaction showed a very weak x-ray diffraction peak near  $2\theta=21^\circ$  due to PVDF crystallization, and intensity increased gradually with time after gelation. The crystallization behavior of PVDF was strongly affected by the amount of SiO<sub>2</sub> networks. That is, SiO<sub>2</sub> content directly influenced preference and disturbance for crystallization. In polymer-rich hybrids, SiO<sub>2</sub> networks had a favorable effect on the extent of PVDF crystallization. In particular, the maximum percent crystallinity of PVDF occurred at the content of 3.7 wt% SiO<sub>2</sub> and was higher than that of pure PVDF. However, beyond about 10 wt% SiO<sub>2</sub>, the crystallization of PVDF was strongly confined.

**Keywords:** Poly(vinylidene fluoride), Organic-inorganic hybrids, Crystallization, SiO<sub>2</sub> networks

### Introduction

In recent years, advanced hybrid organic-inorganic composites [1-5] have attracted much attention because their properties are superior to those of the parent materials. Hybrids are prepared usually through a sol-gel process by incorporating organic polymers with alkoxysilanes, mainly tetramethoxy- or tetraethoxysilanes (TEOS). Hybrid materials may have a controllable combination of properties of both organic polymers and inorganic glasses. The organic component can enhance the toughness of brittle inorganic materials, whereas the inorganic network can increase scratch resistance and hardness of plastics. It is also possible to obtain optically transparent hybrids by properly controlling the reaction conditions of hydrolysis and condensation of TEOS in the presence of a preformed organic polymer. The optimized combination of the best properties of polymers and inorganic materials has been often obtained. Furthermore, polymers which have functional organic groups may also be introduced into the inorganic networks, and the resulting hybrids used for applications in many fields such as biomaterials, membranes, coatings, optics and electronics[6-9].

Poly(vinylidene fluoride) (PVDF) is a very attractive crystalline polymer[10,11], exhibiting ferroelectric, piezoelectric, and pyroelectric characteristics that have been explored in the development of electronic devices. There have been attempts at developing hybrid composites consisting of highly piezo- and pyroelectric ceramic material combined with PVDF or its copolymers in the hope of obtaining the properties of both polymer and ceramic. It was reported that

a superior effect in hybrid PVDF-SiO<sub>2</sub> composites such as a charge storage effect and stability[12] might be obtained. An electroactive effect in PVDF is attributed to its polar crystals, and thus its crystal structure and crystallinity play an important role in achieving well-developed piezoelectricity. However, though many investigations have been devoted to the understanding of crystallization behavior in pure PVDF and its blends, few have examined the crystallization of PVDF in hybrids with inorganic networks. An understanding of the crystallization behavior and structure development of PVDF in an inorganic network matrix is necessary before one can apply the organic-inorganic PVDF hybrids.

In this paper, the crystallization behavior of PVDF-SiO<sub>2</sub> hybrids prepared by the sol-gel process is investigated as a function of SiO<sub>2</sub> content.

### Experimental

PVDF polymer (Aldrich co.,  $M_w=275,000$ ,  $M_n=107,000$ ) was used in this study. It was dissolved in dimethylformamide (DMF) at a 10 weight percent concentration. The homogeneous mixture was prepared from deionized water, hydrochloric acid, ethanol, and TEOS in a molar ratio of 2/0.01/7/1. Four different volumes of TEOS solution were added carefully to the 10 wt% PVDF solution, while stirring, to obtain four mixtures with different weight percentage of PVDF/TEOS (100/0, 90/10, 80/20, and 70/30), which were then stirred at 40°C for 2 h. The resulting homogeneous solution was cast at room temperature and was allowed to stand at 60°C for 24 hour for gelation. Finally, the gelled samples were slowly dried at room temperature for more than two weeks.

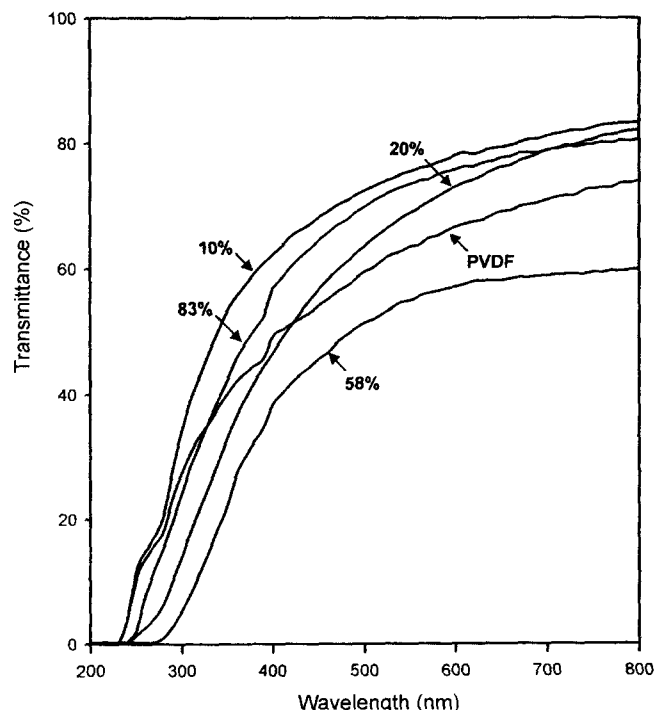
Fourier transform infrared (FT-IR) and ultra-visible (UV/

\*Corresponding author: jwcho@konkuk.ac.kr

VIS) spectra were obtained using Jasco FT-IR 300E and Shimadzu 160A UV/VIS spectroscopies, respectively. FT-IR measurements were performed using the attenuated total reflectance method. The surfaces of the hybrid films were examined using scanning electron microscopy (SEM), Alpha-25A. Differential scanning calorimetry (DSC) was performed on TA DSC 2010 under a nitrogen flow at a heating rate of 10°C/min. X-ray diffraction was carried out with Rigaku Rinter 2100 Series, using  $\text{CuK}\alpha$  radiation. Thermogravimetric analysis (TGA) was made from room temperature to 600°C using a TA TGA 2050 instrument with a heating rate of 10°C/min under nitrogen gas atmosphere.

### Results and Discussion

PVDF- $\text{SiO}_2$  hybrid films obtained via a sol-gel process were relatively transparent over the whole range studied; their homogeneity could be due to the dispersion of PVDF in the silica networks. Figure 1 shows the UV/VIS spectra measured for various samples about 55  $\mu\text{m}$  thick. A 10 wt% TEOS sample had a transmittance above 70% over a range of 400-800 nm, higher than that of pure PVDF film. Such a high transmittance in hybrid composites may be used as an initial criterion for the formation of a homogeneous phase of both inorganic and organic components. However, no clear dependence of light transmittance on TEOS content was shown. On the other hand, all hybrid films obtained were

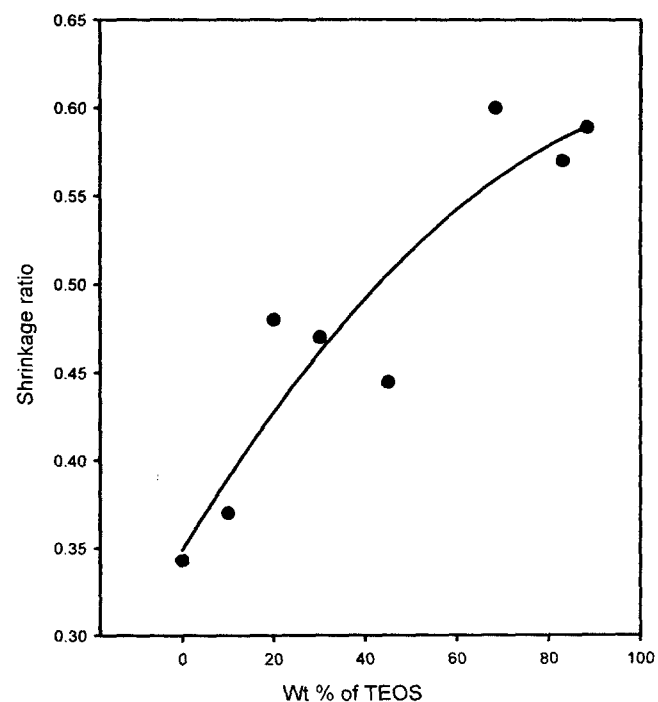


**Figure 1.** UV/VIS spectra of pure PVDF film and PVDF- $\text{SiO}_2$  hybrid films.

hard, and their brittleness increased with increasing TEOS content.

The hybrid gels shrunk considerably during drying after the sol-gel reaction. The shrinkage ratio, which was obtained by measuring the diameter of the hybrid gels before and after shrinkage, increased with increasing the TEOS content as shown in Figure 2. The shrinkage ratio of the 83% TEOS hybrid film was about 1.7 times as large as that of pure PVDF film. This shrinkage may have resulted from either removal of solvent during drying or gelation due to formation of inorganic networks. However, considering that the pure PVDF film has a shrinkage ratio of 34%, it seems that the shrinkage for hybrid films should be ascribed primarily to the gelation, that is, the formation of silica networks[13].

FT-IR spectra of the hybrid films and the pure PVDF film are shown in Figure 3. The characteristic absorption bands for asymmetric Si-O-Si stretching and Si-OH stretching [14,15] appear near 1072  $\text{cm}^{-1}$  and 960  $\text{cm}^{-1}$ , respectively, in all hybrid samples. Pure PVDF film shows no absorption band near 960  $\text{cm}^{-1}$ . Typical pure PVDF bands are near 480  $\text{cm}^{-1}$  and 540  $\text{cm}^{-1}$  due to  $\text{CF}_2$  bending, and near 1175  $\text{cm}^{-1}$  due to  $\text{CF}_2$  symmetric stretching[16]. In the spectra of composite films, both characteristic FT-IR bands for  $\text{SiO}_2$  and PVDF are present, indicating that hybridization was done via sol-gel reaction. In particular, as the TEOS content increases, the band peak at 960  $\text{cm}^{-1}$  shifts toward the lower wavenumber. This reflects the existence of at least a certain



**Figure 2.** Shrinkage ratio of hybrid films versus TEOS content.

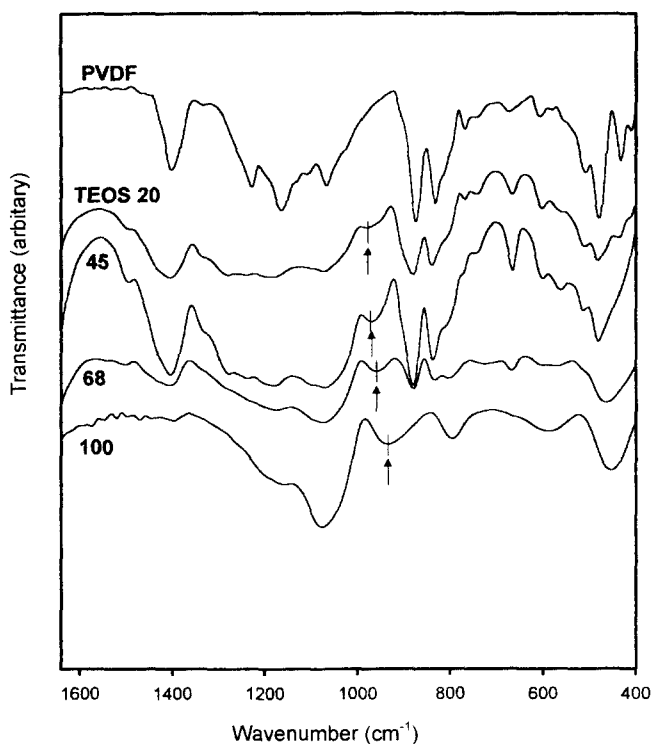


Figure 3. FT-IR spectra of pure PVDF and PVDF-SiO<sub>2</sub> hybrid films.

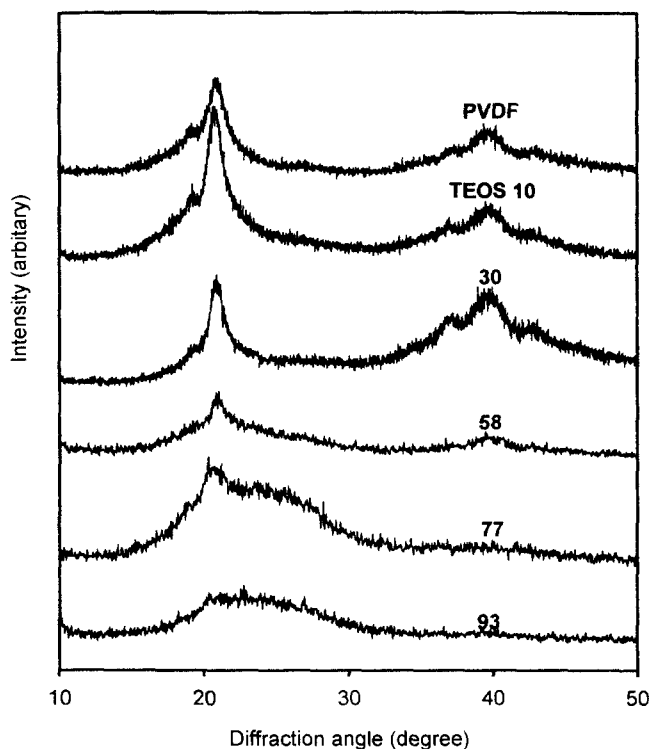


Figure 4. X-ray diffractograms of pure PVDF and PVDF-SiO<sub>2</sub> hybrid films.

interaction between PVDF molecules and SiO<sub>2</sub> networks. The presence of such interaction seems to be attributed to the formation of relatively homogeneous film with some hardness.

Figure 4 shows the x-ray diffraction patterns of hybrid films as well as pure PVDF film. The crystal structure of composite films did not change even after the formation of SiO<sub>2</sub> networks. The crystalline peaks of pure PVDF appear near  $2\theta=21^\circ$  and  $40^\circ$ , which characterizes the  $\gamma$ -PVDF crystalline phases[17,18]. The diffraction intensity at each characteristic peak varies with the TEOS content even though there is little change in the crystal structure. This implies that the crystallinity of PVDF is affected by the TEOS content. In particular, the hybrids sample, including high TEOS content of 93 wt%, shows the diffraction pattern similar to nearly amorphous halo. On the other hand, Figure 5 is a good representation of the influence of time after the initial gelation on x-ray diffraction curves of the gels. The fresh gel shows a very weak diffraction peak near  $2\theta=21^\circ$ , indicating that the fresh gel contains only a slight amount of crystallites. As the time after the initial gelation increased, the x-ray diffraction intensity became stronger due to the gradual increase in crystallization of gels. At the same time, the lattice space due to  $2\theta=21^\circ$  tended to decrease with the time after gelation. This means that the molecular packing in the crystallization of gels continues to become more stable during drying.

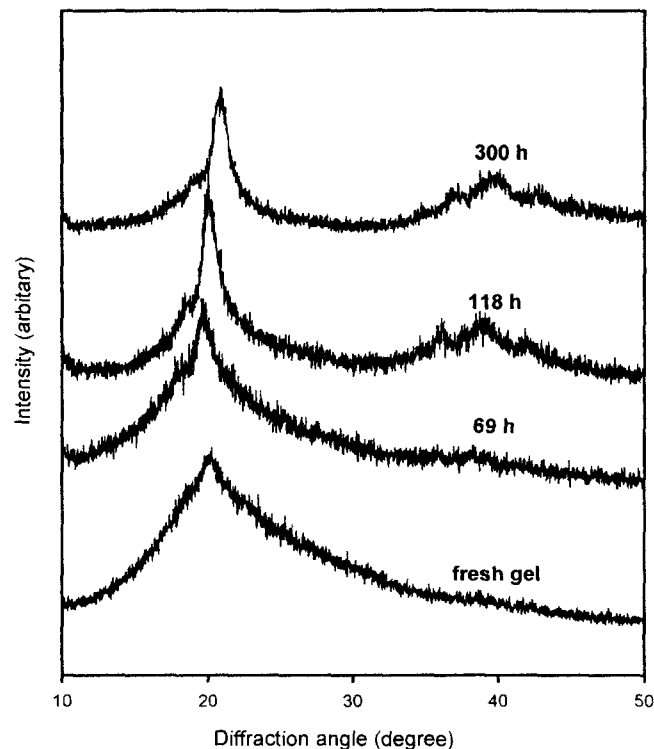
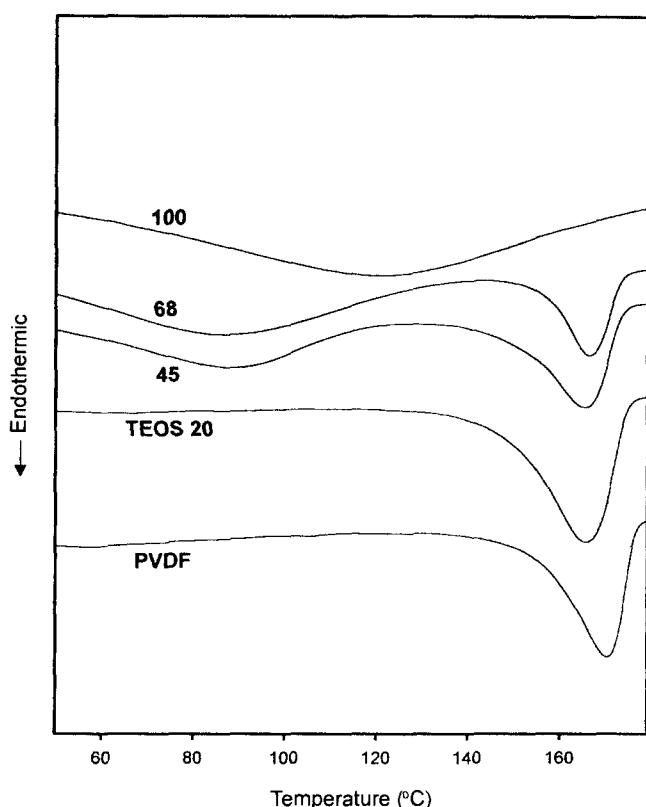
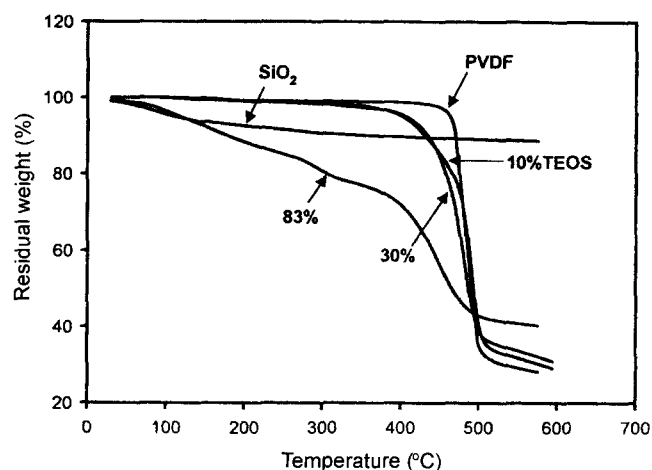


Figure 5. X-ray diffractograms of fresh hybrid gels and three time periods after gelation.



**Figure 6.** DSC thermograms of pure PVDF and PVDF-SiO<sub>2</sub> hybrid films.

Figure 6 shows the DSC thermograms for pure PVDF and PVDF-SiO<sub>2</sub> hybrids. The melting temperature of pure PVDF is shifted from 170°C to a slightly lower temperature as the TEOS content increases. Such a melting point depression may be ascribed to the existence of a certain organic-inorganic molecular interaction due to the hybridization of PVDF with SiO<sub>2</sub>, as described in the previous FT-IR measurements. A very broad endothermic peak, which appeared over a wide temperature range of 90-120, is due to a loss of adsorbed water upon the formation of SiO<sub>2</sub> networks by the hydrolysis-condensation[19]. On the other hand, the hybridization of PVDF with SiO<sub>2</sub> is responsible for a change in the heat of fusion from 71.2 J/g of pure PVDF to 83.7 J/g of 20% TEOS. This indicates that PVDF crystallization can be well enhanced even in the hybrids with SiO<sub>2</sub> networks. However, in estimating the crystallinity of PVDF, it should be noted that the heat of fusion obtained from DSC measurement is not an actual one due to pure PVDF alone, but the value for the total weight, including both polymer and SiO<sub>2</sub>[20,21]. Considering the pure weight of the polymer only, the actual heat of fusion should be calculated from the measured heat of fusion and the weight fraction of SiO<sub>2</sub>, which is known from the TGA results. That is, the percent crystallinity ( $\chi$ ) can be determined from the



**Figure 7.** TGA curves of pure PVDF and PVDF-SiO<sub>2</sub> hybrid films.

following equation:

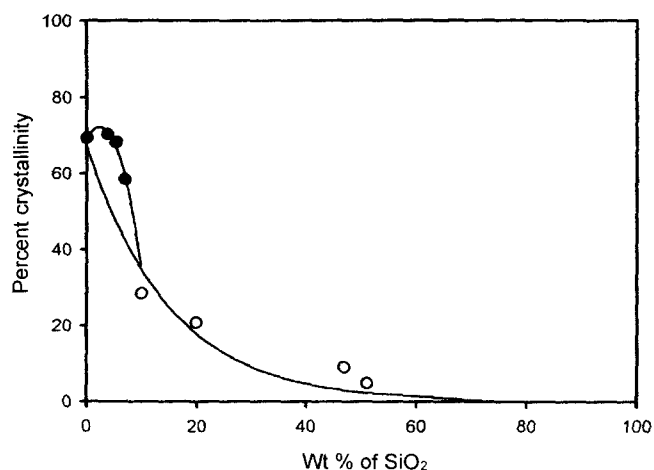
$$\chi = \Delta H_m / (W \Delta H_m^0) \times 100 \quad (1)$$

where  $\Delta H_m$  is the experimental heat of fusion,  $\Delta H_m^0$  is an equilibrium heat of fusion for a completely crystalline PVDF, and  $W$  is the PVDF weight fraction in the PVDF-SiO<sub>2</sub> hybrids. A value of 104.7 J/g[22] was used for  $\Delta H_m^0$ . TGA measurements were performed in order to determine the weight fraction of PVDF preserved in each sample. Figure 7 shows a major weight loss of composite films at the onset temperature of about 450°C, which is attributed to the decomposition of the polymer. Pure SiO<sub>2</sub> film does not present any abrupt decrease in weight, and a slight decrease at approximately 100°C appears due to the removal of water which had been absorbed and then lost[19]. In the hybrid samples, the weight retained after decomposition is dependent on the polymer content. The weight residue of composites at 570°C increases with increasing TEOS content. Based on this, the amounts of SiO<sub>2</sub> formed in the composites can be determined[21,22]. Their calculated results are listed in Table 1.

The relationship between percent crystallinity and wt% of

**Table 1.** SiO<sub>2</sub> content and percent crystallinity of samples used in this study

Wt% of TEOS	Wt% of SiO <sub>2</sub>	Heat of fusion (J/g)	Percent crystallinity
0	0	72.9	69.4
10	3.7	73.9	70.4
20	5.3	71.6	68.2
30	6.9	61.4	58.5
68	9.9	30.0	28.5
83	19.8	21.8	20.8
88	46.9	18.0	9.1
93	51	5.1	4.9



**Figure 8.** Effect of wt% of SiO<sub>2</sub> on the percent crystallinity of PVDF-SiO<sub>2</sub> hybrid films.

SiO<sub>2</sub> is plotted in Figure 8. It is interesting that the hybrid composite with SiO<sub>2</sub> of 3.7 wt%, which corresponds to 10 wt% TEOS, had a slightly higher crystallinity than that of pure PVDF. However, as the SiO<sub>2</sub> content increased, the percent crystallinity decreased greatly, and zero crystallinity appeared near 65 wt% SiO<sub>2</sub>. These results indicate that SiO<sub>2</sub> content influences preference and disturbance for crystallization. Therefore, two curves for percent crystallinity data can be drawn as shown in Figure 8. Beyond about 10 wt% of SiO<sub>2</sub>, the crystallization of PVDF was strongly confined, similar to poly(ethylene oxide)-SiO<sub>2</sub> hybrids[23]. However, the crystallization of PVDF at SiO<sub>2</sub> content less than 10 wt% indicates that the existence of SiO<sub>2</sub> had a favorable effect on the extent of the PVDF crystallization. That is, a small amount of SiO<sub>2</sub> networks led to the increase in polymer crystallinity as reported often in crystalline polymer blends or composites[24,25].

### Conclusions

Relatively transparent PVDF-SiO<sub>2</sub> hybrid films were obtained by a sol-gel process and brittleness was directly related to TEOS content. It was found that at least a certain interaction between PVDF molecules and SiO<sub>2</sub> networks might exist based on FT-IR and DSC thermal analyses. X-ray diffraction measurements showed that all the hybrid samples displayed a crystal structure of PVDF  $\gamma$ -phase, and the x-ray diffraction peak near  $2\theta=21^\circ$  for fresh hybrid gels increased with increasing time after gelation. SiO<sub>2</sub> content directly influences preference and disturbance for crystallization. In particular, the percent crystallinity of PVDF showed a maximum value at the content of 3.7 wt% SiO<sub>2</sub>, which is higher than that of pure PVDF. However, beyond about 10 wt% SiO<sub>2</sub>, the crystallization of PVDF was strongly confined. Consequently, the crystallization behavior

of PVDF was strongly affected by the amount of SiO<sub>2</sub> networks.

### Acknowledgement

The author gratefully acknowledges financial support from the Korea Science and Engineering Foundation (Grant no. 981-1107-039-2).

### References

1. U. Schuber, N. Husing, and A. Lorenz, *Chem. Mater.*, **7**, 2010 (1995).
2. P. Judeinstein and C. Sanchez, *J. Mater. Chem.*, **6**, 511 (1996).
3. J. E. Mark, C. Y. C. Lee, and P. A. Bianconi, "Hybrid Organic-Inorganic Composites", American Chemical Society, Washington, 1995.
4. H. Schmidt, *J. Non-Cryst. Solids*, **73**, 681 (1985).
5. J. Wen and G. Wilkes, *Chem. Mater.*, **8**, 1667 (1996).
6. K. G. Neoh, K. K. Tan, P. L. Goh, S. W. Huang, E. T. Kang, and K. L. Tan, *Polymer*, **40**, 887 (1999).
7. P. N. Prasad, *Polymer*, **32**, 1746 (1991).
8. R. Zusman, C. Rottman, M. Ottololenghi, and D. Avnir, *J. Non-Cryst. Solids*, **122**, 107 (1990).
9. Y. Imai, K. Naka, and Y. Chujo, *Macromolecules*, **31**, 532 (1998).
10. A. J. Lovinger, "Poly(vinylidene fluoride) in Developments in Crystalline Polymers-1", (D. C. Bassett Ed.), Chap. 5, Applied Science Publishers, London, 1982.
11. J. S. Kim and S. Y. Kim, *J. Korean Fiber Soc.*, **29**, 59 (1992).
12. D. Yang and W. Bei, "Conference Record of the 1996 IEEE International Symposium on Electrical Insulation", Montreal, p.854, 1996.
13. C. J. Brinker and G. W. Scherer, "Sol-Gel Science: the Physics and Chemistry of Sol-Gel Processing", Chap. 6, Academic Press, Boston, 1990.
14. M. Guglielmi, G. Brusatin, G. Facchin, and M. Gleria, *J. Mater. Res.*, **11**, 2029 (1996).
15. A. Bertoluzza, C. Fagnano, V. Gottardi, and M. Guglielmi, *J. Non-Cryst. Solids*, **48**, 117 (1982).
16. K. Tashiro, M. Kobayashi, and H. Tadokora, *Macromolecules*, **14**, 1757 (1981).
17. S. Weinhold, M. H. Litt, and J. B. Lando, *Macromolecules*, **13**, 1178 (1980).
18. M. Kobayashi, K. Tashiro, and H. Tadokora, *Macromolecules*, **8**, 158 (1975).
19. A. Duran, C. Serna, V. Fornes, and J. M. F. Navarro, *J. Non-Cryst. Solids*, **82**, 69 (1986).
20. Z. Liu, P. Marechal, and R. Jerome, *Polymer*, **38**, 4925 (1997).
21. J. W. Cho and K. I. Sul, *Polymer*, **42**, 727 (2001).
22. K. Nakagawa and Y. Ishida, *J. Polym. Sci., Polym. Phys.*,

- 11**, 2153 (1973).
23. S. Jiang, D. Yu, X. Ji, L. An, and B. Jiang, *Polymer*, **41**, 2041 (2000).
24. B. E. Tiganis, R. A. Shanks, and Y. Long, *ANTEC'96*, **2**, 1744 (1996).
25. Z. Liu, P. Marechal, and R. Jerome, *Polymer*, **38**, 4925 (1997).