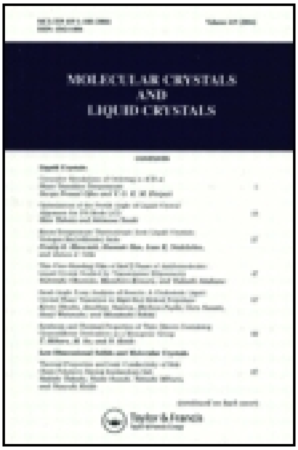

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Influence of High Contents of Silver Nanoparticles on the Physical Properties of Poly(Vinylidene Fluoride)

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Silver (Ag) nanoparticles were incorporated into poly(vinylidene fluoride) (PVDF) up to 90 wt% (15.3 vol%) via melt mixing. The addition of Ag nanoparticles slightly increased the crystallization temperature and heat of crystallization of PVDF by 1.2°C and 5.1 J/g at 90 wt% loading, respectively. In the thermal degradation behaviors, high contents of Ag nanoparticles more than 50 wt% induced a negative effect on the thermal stability of the matrix by decreasing the onset temperature of the degradation as much as 40°C. Thermal conductivity was slightly increased with Ag content up to 5 wt%, but further addition of Ag induced a notable increase because of the high thermal conductivity of Ag nanoparticles. In the WAXD (Wide Angle X-ray Diffraction) patterns, all the samples presented only α-phase crystal regardless of Ag loading. Both tensile strength and elongation at break were decreased from 5 wt% loading with increasing Ag content.

Keywords: poly(vinylidene fluoride); silver nanoparticles; tensile properties; thermal conductivity; thermal properties

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INTRODUCTION

The incorporation of metal/inorganic nanoparticles into a polymer matrix has attracted a great deal of interests in the research and industrial fields because the composites with tailored properties desired for particular application or to cover up the drawbacks of the physical properties of polymer can be created. These nanocomposites exhibit high transparency, high gas barrier properties, excellent solvent-resistance and flame-retardancy, improved mechanical properties, and low thermal expansion coefficient [1–5]. Further, these benefits can be achieved at a relatively low concentration in comparison to conventional micro-scale filled composites because of the extraordinary high specific surface area of the nanoparticles [6].

PVDF is a semi-crystalline polymer exhibiting many favorable properties such as piezoelectric and pyroelectric characteristics, good chemical resistance, and high mechanical properties [7–10]. This enables PVDF to be applied in the electronic devices and membrane for separation. Inclusion of Ag nanoparticles is expected to impart electromagnetic shielding properties, discharging of static electricity, and bacterial killing to polymers. As for the fabrication of PVDF, wet process has been usually employed, which requires some environmentally unfriendly additives and toxic solvents. Thus, the method to fabricate the PVDF in a melt state should be developed. The formation of nanocomposites via melt compounding is the most convenient and economical way of obtaining hybrid plastic materials, in particular, highly concentrated polymer composites [11].

Some properties such as electrical conductivity and electromagnetic wave absorption are endowed at a high loading level of metal nanoparticles because the nanoparticles are required to constitute continuous phase in the polymer matrix. However, there have been few reports on the highly concentrated polymer composites with metal nanoparticles. In this study, hybridization of PVDF with silver nanoparticles (0.1–90 wt%) was carried out by melt mixing and the effects of incorporating silver nanoparticles on the physical properties of PVDF were discussed, including thermal, morphological, and tensile properties.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride) pellet (PVDF; density = 1.78 g/cm^3, melt flow index = 6) was supplied by Solvay, Inc., Belgium. Round silver (Ag) nanoparticles (purity: 99.99%, NTbase Co., Korea) were incorporated as a fine powder, whose average size and density were 150 nm and 10.49 g/cm^3, respectively. The titanate coupling agent neoalkoxy, tri(dioctylpyrophosphato) titanate, LICA-38 (Kenrich Petrochemicals Inc., Bayonne, NJ) was employed to improve the dispersion by reducing the agglomeration of Ag nanoparticles in the matrix. The agent was first dispersed in toluene at 0.4 wt% on the basis of Ag prior to the addition of Ag nanopowder. The solutions were vigorously stirred and ultrasonicated for 30 min. The toluene was then evaporated at 100°C and the treated powders were vacuum-dried at 80°C for 24 hrs to remove the residual toluene completely. The PVDF was also vacuum dried at 80°C for 24 hrs prior to melt mixing. The PVDF and Ag nanoparticles were dry mixed via tumbling in a bottle, and then the premixture was melt-blended in an internal mixer (Haake Rheomix 600) for 10 min at 220°C at a rotor speed of 60 rpm. The contents (X) of Ag nanoparticles in PVDF matrix were 0.1, 1, 5, 10, 20, 50, 70, and 90% by weight (15.3% by volume), and they were coded PVDF-X.

Measurement of Physical Properties

The thermal properties were investigated using differential scanning calorimeter (DSC 2010; TA instrument, Dupont) in a nitrogen atmosphere. The cooling scan was performed at 10°C/min. The samples were held at 220°C in the molten state for 5 min to eliminate the previous thermal history prior to the cooling scan.

The thermal stability was evaluated using thermogravimetric analyzer (TGA; TA Instruments, SDT2950). The heating scan was carried out to 700°C at 10°C/min in a nitrogen atmosphere.

Thermal conductivity was measured at room temperature by TC Probe (Mathis Instrumentals Ltd.). Test specimens were in the form of rectangular whose dimensions were 3 mm × 30 mm with a thickness of 0.4 mm. The average of two measurements was taken as data.

The crystal structure was determined by wide angle x-ray diffraction (WAXD), using a Rigaku Denki (D/MAX-2000) with nickel filtered CuKα radiation of 40 kV and 100 mA. Scanning was carried out on the equator in the 2θ angle ranging from 5 to 60° at a scan speed of 5°/min.

The tensile tests were performed at room temperature using an Instron tensile tester model 4465. The dog-bone shaped specimens (ASTM D638 Type V) were used. The crosshead speed and the gauge length were 2 mm/min and 25 mm, respectively.

The morphology of tensile fractured surfaces for PVDF nano composite was examined using a field emission scanning electron microscope (FESEM; JEOL, JSM-6340F). The surfaces were sputter-coated with a thin gold layer to avoid charging prior to scanning.

RESULTS AND DISCUSSION

To investigate the effect of Ag nanoparticle addition on the crystallization of PVDF, DSC studies were performed. The cooling scan thermograms of PVDF and its nanocomposites with Ag are shown in Figure 1. The Ag nanoparticles increase the crystallization temperature with the loading level from 142.4 to 143.6°C even though the increasing extent is extremely small. In addition, the PVDF/Ag nanocomposites exhibit an increased degree of crystallinity with Ag content from 47.0 to 52.1 J/g. This indicates that the nanoparticles may act as a nucleating agent to some degree and produce heterogeneous nucleation.

Figure 2 presents the effects of Ag nanoparticles on the thermal degradation process of PVDF. When the comparing the onset temperature (T_{10}) of the degradation at which 10% degradation occurs, up to 20 wt% Ag content, it does not have large effect on T_{10} ranging from 472 to 476°C. However, further incorporation of Ag nanoparticles induces a negative effect on the thermal stability of PVDF matrix by decreasing T_{10} to 435°C. The presence of high contents of Ag nanoparticles seems to facilitate the thermal decomposition of PVDF matrix which may be attributed to their high thermal conductivity.

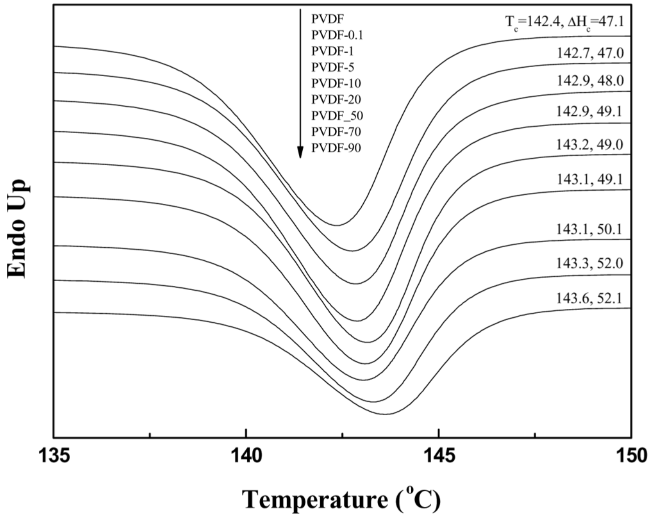

FIGURE 1 DSC cooling scan thermograms of PVDF and PVDF/Ag nanocomposites. Maximum crystallization temperature (T_c) and heat of crystallization ($\triangle H_c$) are indicated. The value of $\triangle H_c$ is normalized with Ag content.

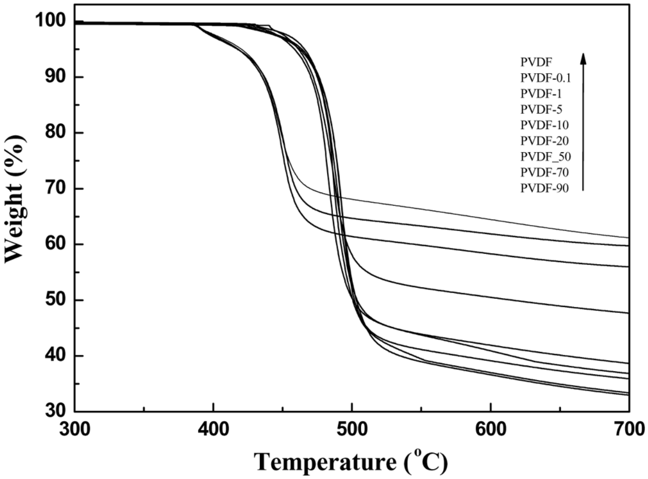

FIGURE 2 TGA thermograms of PVDF and PVDF/Ag nanocomposites.

In addition, the residual weight is increased with the Ag content, as expected.

Figure 3 presents the effects of Ag nanoparticles on the thermal conductivity of PVDF. Thermal conductivity is increased with Ag content because of the high thermal conductivity of Ag nanoparticles. Up to 5 wt% thermal conductivity is slightly increased with Ag content,

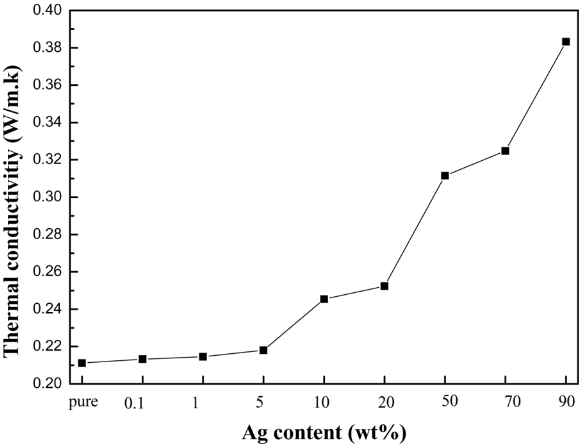

FIGURE 3 Variation of thermal conductivity of PVDF and PVDF/Ag nanocomposites with Ag content.

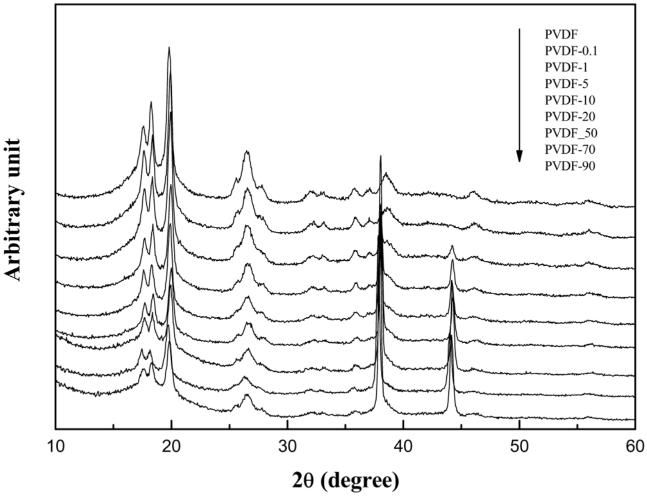

FIGURE 4 WAXD patterns of PVDF and PVDF/Ag nanocomposites.

but further addition produces a notable increase of thermal conductivity. This suggests that the conductive paths of Ag nanoparticles in the PVDF matrix begin to form above the loading level.

WAXD was used to observe the effect of Ag content on the microstructure of PVDF resin. As shown in WAXD profiles of Figure 4, the peaks at $2\theta = 17.6$, 18.3, 19.8, 26.5, and 38.5° refer to the diffractions in the (100), (020), (110), (021), and (002) planes of PVDF, respectively [12]. These are distinctive features of the nonpolar α-form crystal of PVDF without the trace of polar β-form crystals. It is well known that the melt crystallization of PVDF at atmosphere pressure yields the α-form structure [13–14]. The spectra of the nanocomposite present neither new peak nor peak shift in comparison with those of pure PVDF indicating that Ag nanoparticles have little influence on the crystalline morphology of PVDF over the loading level examined. That is, Ag-filled PVDF nanocomposites consist of two phase structures, i.e., polymer and nanoparticle. In addition, the diffraction peaks at $2\theta = 38.2$ and 44.4°, representing (111) and (200) planes of Ag, respectively, are observed from 1 wt% loading and then get more prominent with increasing Ag content.

Figure 5 shows the variation of stress-strain (SS) curves with the content of Ag nanoparticles. The PVDF and PVDF/Ag nanocomposites exhibit clearly a yield behavior and then plateau region, where the stress is little dependent on the displacement, to a high elongation. However, the incorporation of Ag nanoparticles more than 5 wt%

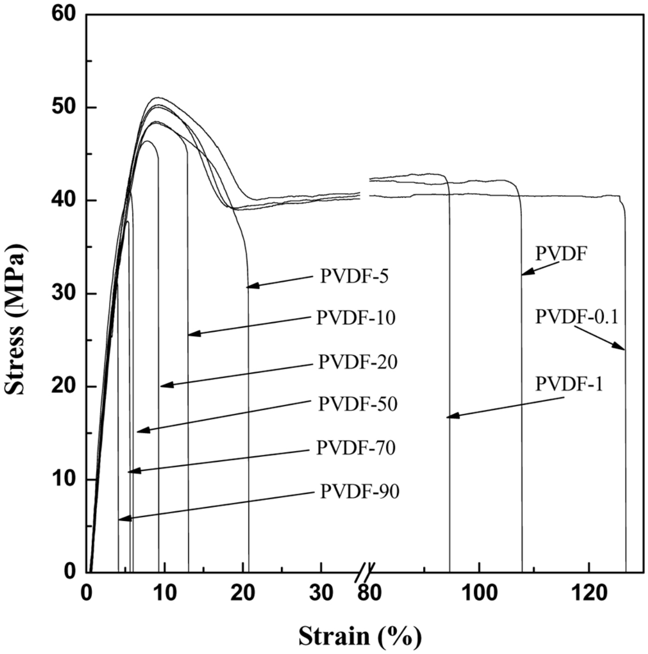

FIGURE 5 Stress-strain (SS) curves of PVDF and PVDF/Ag nanocomposites.

vanishes the plateau region in the curves, indicative of a decrease of the ductile properties of PVDF. That is, the composites become brittle with increasing Ag content because of the stress concentration effect of Ag nanoparticles. Tensile strength remains little changed up to 1 wt% Ag loading, after which it is decreased with increasing Ag content. An increased heterogeneity in the PVDF matrix with Ag content seems to introduce premature flaws in the system, which serves to lower the stress required to fracture. Thus, the weak point is increased progressively with filler fraction leading to a low tensile strength. At a low content of 0.1 wt% Ag nanoparticles increase elongation at break by ca. 18% but the addition more than 5 wt% decrease it abruptly with increasing the loading level. The Ag nanoparticles play a role in stopping crack growth at a small fraction of the nanoparticles leading to greater elongation at break than that of the unfilled PVDF. However, at a high loading level, the polymer chain fills the agglomerate of the nanoparticles. Thus, the entrapped polymer is immobilized and cannot deform as part of the matrix. This less deformable matrix results in a decrease of elongation at break. The significant reduction of elongation at break leads to the less toughnable properties from 5 wt% loading.

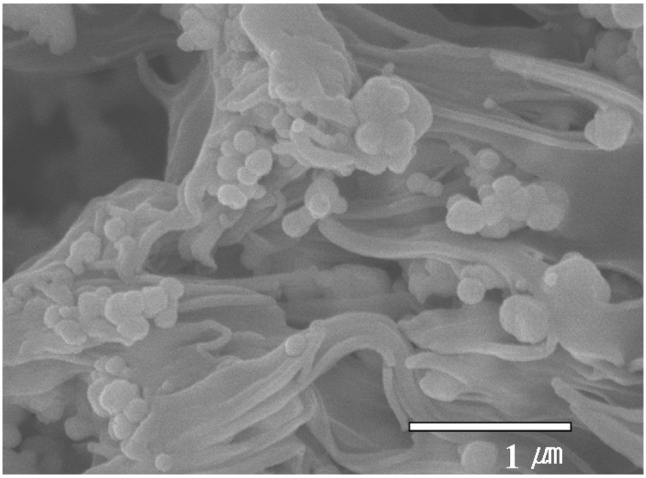

FIGURE 6 FESEM images of tensile-fractured surface of PVDF filled with 70 wt% Ag.

The variation of tensile properties with Ag content is confirmed by morphology of the fractured surfaces to represent the interfacial structure between polymer matrix and nanoparticle. The FESEM images of PVDF-70 display the poor adhesion between them, as shown in Figure 6. The micrograph shows the clean surface of Ag nanoparticles at the fracture surface and the separation of some Ag nanoparticles from the PVDF matrix. This may be associated with absence of specific interfacial interaction and the stiffness of Ag nanoparticles. Thus, Ag nanoparticles can act as defects within the material under applied loads and consequently be sites for cracking and subsequent fracture.

CONCLUSIONS

The presence of Ag nanoparticles increases slightly both crystallization temperature and heat of crystallization of PVDF even at a high content of 90 wt%, representing a low efficiency of the heterogeneous nucleation. Thermal conductivity is slightly increased with Ag content, but above 5 wt% loading, a notable increase of thermal conductivity is observed. In the WAXD (Wide Angle X-ray Diffraction) patterns, all the samples present only α-phase crystal regardless of Ag loading. It is well known that the β-phase is responsible for pyroelectric and piezoelectric properties of PVDF. Thus, it is necessary to control the processing condition if considering the application of the composites in electronic device. FESEM images of tensile fractured surface display the clean surface of Ag nanoparticles and its separation from the PVDF matrix, which seems to be attributed to the weak association between PVDF chain and Ag nanoparticles. This results in a notable decrease of tensile strength and elongation at break at a high Ag loading.

REFERENCES

[1] Yeh, J. M., Liou, S. J., Lai, C. Y., & Wu, P. C. (2002). *Chem. Mater.*, *14*, 154.

[2] Kim, T. H., Jang, L. W., Lee, D. C., Choi, H. J., & Jhon, M. S. (2002). *Macromol. Rapid Commun.*, *23*, 191.

[3] Sun, T. & Garces, M. (2002). *Adv. Mater.*, *14*, 128.

[4] Saujanya, C. & Radhakrishnan, S. (2001). *Polymer*, *42*, 6723.

[5] Zhu, H. & Wilkie, C. A. (2000). *Polym. Int.*, *49*, 1158.

[6] Zilg, C., Reichert, P., Dietsche, F., Engelhardt, T., & Mülhaupt, R. (1998). *Kunststoffe*, *88*, 1812.

[7] Du, C. H., Zhu, B. K., & Xu, Y. Y. (2005). *Macromol. Mater. Eng.*, *290*, 786.

[8] Xiao, D. Q. & Lang, S. B. (1989). *IEEE Trans. Elec. Insul.*, *24*, 503.

[9] Newman, B. A., Yoon, C. H., Pae, K. D., & Scheinbeim, J. I. (1979). *J. Appl. Phys.*, *50*, 6095.

[10] Nagai, M., Nakamura, K., Uehara, H., Kanamoto, T., Takahashi, Y., & Furukawa, T. (1999). *J. Polym. Sci. Part B: Polym. Phys.*, *37*, 2549.

[11] Wang, H., Elkovitch, M., Lee, L. J., & Koelling, K. W. (2000). ANTEC 2000, May 7–11, vol. II, Society of Plastics Engineers: New York, p. 2402.

[12] Laroche, G., Lafrance, C. P., Prud'homme, R. E., & Guidoin, R. (1998). *J. Biomed. Mater. Res.*, *39*, 184.

[13] Park, Y. J., Kang, Y. S., & Park, C. (2005). *Eur. Polym. J.*, *41*, 1002.

[14] Wang, J., Li, H., Liu, J., Duan, Y., Jiang, S., & Yan, S. (2003). *J. Am. Chem. Soc.*, *125*, 1496.