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Morphology and Physical Properties of Binary Blend Based on PVDF and Multi-Walled Carbon Nanotube

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Summary: Semicrystalline Poly(vinylidene fluoride)(PVDF) was melt blended by multi-walled carbon nanotube (MWNT) at various contents (0.01 ∼ 5 wt%) using internal mixer. The relationships between morphology and physical properties based on PVDF and MWNT were investigated. As the MWNT content is increased, the apparent supercooling required for PVDF crystallization and the size of spherulites in PVDF decrease. In the WAXD profiles, the incorporation of MWNT produced a large shoulder at $2\theta = 20.7^\circ$ with increasing the MWNT content, corresponding to the polar β-form crystal of PVDF. The experimental percolation threshold for the electrical conductivity in PVDF was estimated and clearly occured between 2 and 2.5 wt%. Similar tendency was also observed in thermal conductivity and permittivity.

Keywords: electrical conductivity; Multi-walled carbon nanotube; permittivity.; poly(vinylidene fluoride); Supercooling

Introduction

Incorporation of conductivity filler such as MWNT(multi-wall carbon nanotubes) into the organic polymers holds promise for preparing an important class of new high performance hybrid materials.[1–4] The great aspect ratio of MWNT may give rise to a high degree of specific surface area between polymer and MWNT, leading to high barrier properties and electrical conductivity. Poly(vinylidene fluoride) (PVDF) has attracted much attention because of its potential applications to high pyroelectric, piezoelectric, and ferroelectric materials. In the PVDF blend containing inorganic nanoparticles, PVDF chains are confined by the dispersed nanoparticle resulting in different crystallization behaviors and structures.

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In this study, the relationships between the morphology and electrical properties based on semicrystalline PVDF and MWNT by melt compounding were investigated.

Expermental Part

Materials

A commercial SOLEF 1010 poly(vinylidene fluoride) (PVDF; Melt flow index = 6, 230 °C, 5 kg) was supplied from Solvay, Inc. (Belgium) and high purity multiwalled-carbon nanotube (MWNT; purity = 95%, average diameter = 10 ∼ 15 nm, length = 10 ∼ 20 μm) was supplied from Iijin, Inc. (Korea). Pristine MWNTs were heated up to 550 °C in air and held at 550 °C for 1 hr. PVDF was also vacuum dried at 80 °C for 24 hr prior to melt mixing. PVDF and MWNT were dry mixed via tumbling in a bottle, and then the mixture 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 PVDF/MWNT blends ranged from 0.01 to 5 wt%, and they were coded PVDF-X.

Measurement of Physical Properties

The thermal properties of PVDF/MWNT blends were investigated using differential scanning calorimeter (DSC 2010; TA instrument, Dupont) in a nitrogen atmosphere. Heating or 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 cooling scan.

The polarized optical texture of PVDF/MWNT blends was observed by a Leitz Ortholux II microscope equipped with a hesting stage and a programmable PID temperature controller model 350. The radial growth rate of PVDF were observed by the same microscope. Wide angle X-ray diffraction (WAXD) experiment was performed by a Rigaku Denki with Ni-filtered CuKα radiation at 40 kV and 100 mA. Scanning was carried out at a scan speed of 5 °/min. Field emission scanning electron microscopic (FESEM; JEOL, JSM-6340F) observations were carried out on the surface of PVDF/MWNT blend in a sheet state. The surfaces of the samples were sputter-coated with a thin gold layer prior to scanning. Electrical conductivity measurement was performed using the four-probe method to eliminate the effect of contact resistance. A Keithley 2400 digital multimeter equipped with a YEW 2553 DSC DC voltage current standard (YEW Electronics, Japen) was used to measure the I–V characteristics of the samples at room temperature. Thermal conductivity was measured using TC probe (Mathis Instrumental Ltd). Dielectric measurements were performed on a frequency response analysis system using broadband dielectric analyzer (Novocontrol GmbH, Germany) with a frequency range from 10^{-1} to 10^{4} KHz.

Results and Discussion

FESEM micrographs of pristine MWNT and the surface of 97/3 PVDF/MWNT blends are presented in Figure 1.

MWNT exhibits highly curved and random coiled features, which may be attributed to hydrogen bonding and van der Waals attractive interactions between carbon nanotubes.[5,6] The diameters of the MWNT were approximately 10 ~ 30 nm, with a length of several micrometers, implying a high aspect ratio for the MWNT. From the SEM microphotograph of the fractured PVDF/MWNT blends, it can be seen that MWNT forms entangled structures in the PVDF matrix. However, the MWNT were uniformly dispersed in the PVDF matrix, despite some aggregated MWNT structures.

In addition, a great amount of naked MWNT on the surface are observed with increasing the MWNT content. This may be associated with the absence of specific interfacial interaction between PVDF chain and MWNT.

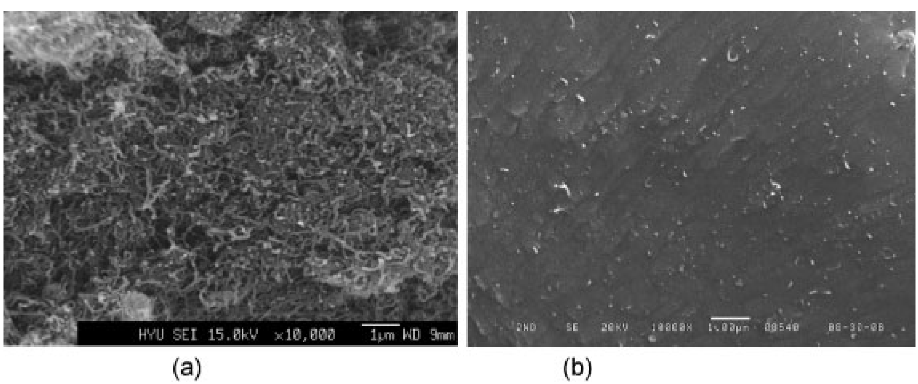

Figure 1.
FESEM micrographs surface (a) pristine MWNT (b) PVDF/MWNT blends with 3 wt%.

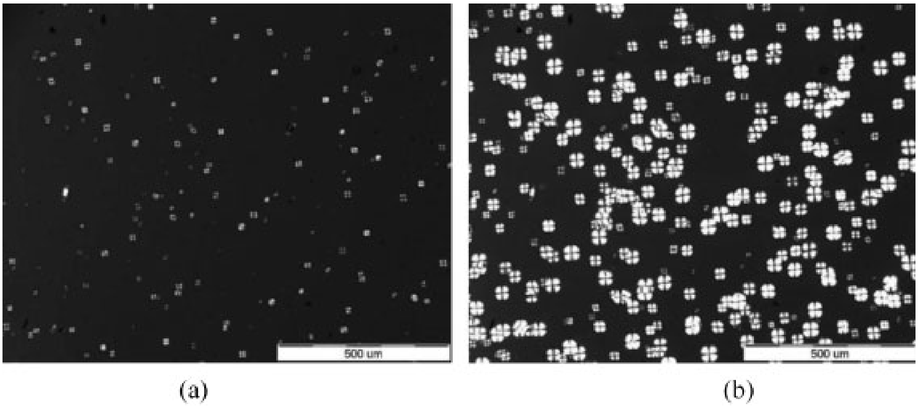

Figure 2.
Polarized optical micrographs of PVDF resin taken during isothermal crystallization at 160 °C after different crystallization times. (a) 11 min (b) 20 min.

Crystallization behaviors of PVDF/MWNT blends can be directly seen by observing the crystal morphology. Using the polarized optical microscope equipped with a hot stage, crystal morphology and radial growth behavior of spherulites were observed. Figures 2 and 3 show polarized optical micrographs of PVDF/MWNT blends, isothermally crystallized at 160 °C. The morphologies are totally different from each other.

Figures 2 and 3 show a well developed spherulite, later limited by several adjacent ones, typical crystalline structure of PVDF. Grain spherulitic structures containing a nucleated PVDF are observed with increasing the content of MWNT and crystallization time. This means that MWNT can be used as a nucleating agent. The melt crystallization exotherms of PVDF and PVDF/MWNT blend systems were observed during the cooling stage, as shown in Table 1.

The melt crystallization temperature (T_{mc}) of PVDF increased with increasing the MWNT content because the MWNT phases dispersed finely within the PVDF matrix promotes heterogeneous nucleation.[7,8] On the other hand, MWNT enhances the crystallization rate. The gradual decrease in apparent supercooling ($\Delta T = T_p – T_o$; T_p is the onset temperature of

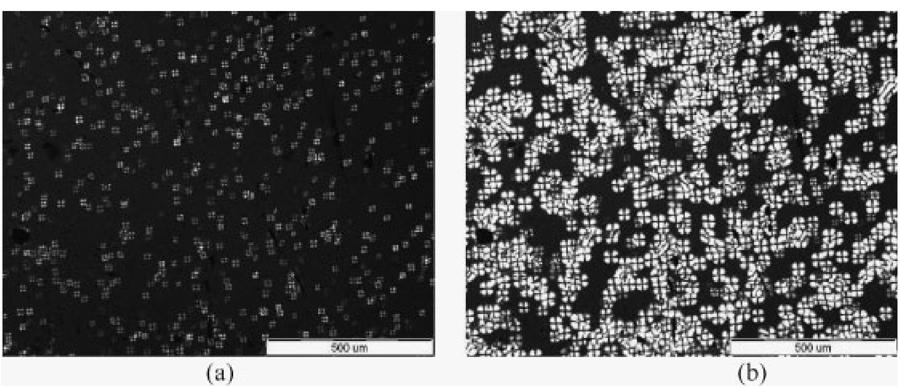

Figure 3.
Polarized optical micrographs of PVDF/MWNT blends with 0.1 wt% MWNT during isothermal crystallization at 160 °C after different crystallization times (a) 11 min (b) 20 min.

Table 1.
Thermal properties of several PVDF/MWNT blends.

CNT	T_m a)	T_m b)	T_{mc} c)	T_{mc} d)	ΔT e)
%	°C	°C	°C	°C	°C
0	172.3	177.9	142.4	148.3	24.0
0.01	172.5	178.5	142.4	148.6	23.9
0.1	172.6	178.8	142.4	148.8	23.8
0.5	172.6	180.0	145.8	151.1	21.5
1	172.6	181.1	146.8	151.6	21.0
3	172.8	181.4	147.8	152.4	20.4
5	173.1	182.1	147.9	152.8	20.3

a) T_m: Onset temperature of melting;
b) T_m: Melting peak temperature;
c) T_{mc}: Crystallization peak temperature;
d) T_{mc}: Onset temperature of crystallization;
e) ΔT: Degree of supercooling.

melting and T_o is the onset temperature of crystallization) further supports the validity of this explanation.

The apparent supercooling required for initiating crystallization was 24 °C for pure PVDF. However, it decreased to 20.3 °C with increasing the MWNT content as shown in Table 1.[9,10]

WAXD was used to observe the effect of MWNT content on the microstructure of PVDF resin. Figure 4 describes the WAXD patterns for pure PVDF and PVDF/MWNT blends.

Within a given range of scattering angles, three characteristic diffraction peaks appear at $2\theta = 17.7$, 18.4, and 19.9°, which correspond to (100), (020), and (110) reflections, respectively.

This is assigned to the α–phase crystal which has a non-polar trans-gauche-trans-gauche (TGTG) conformation. PVDF/MWNT blends exhibit decreased peaks for α–phase crystal from 0.5 wt% content. In addition to the features associated with α–phase crystal, the introduction of MWNT produces a shoulder at a 2θ value of 20.7°

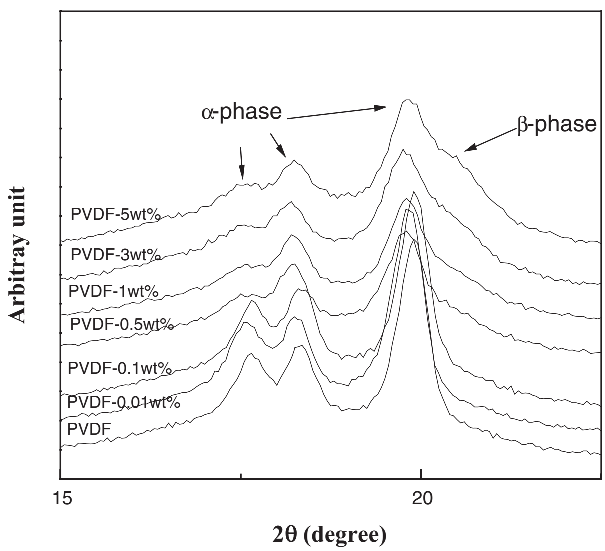

Figure 4.
WAXD patterns of PVDF and PVDF/MWNT blends.

and it is clearer with increasing the MWNT content. This is attributed to the formation of β–phase crystal, the most polar among other crystals.

It is well known that dispersion state of MWNT in the polymer matrix provide the nanoconductible polymer with the conductivity.

We herein investigated the effect of MWNT content on the electrical conductivity, permittivity and thermal conductivity of PVDF. The variation in electrical conductivity of PVDF filled with MWNTs is given in Figure 5 as a function of the MWNTs content in the polymer matrix. The MWNTs content is expressed as the content of MWNTs to PVDF matrix. The electrical conductivity of the PVDF blends was proportionally dependent on the content of MWNTs (conductivity of MWNT: 75 S/cm).

The electrical conductivity was increased from 10^{-14} to 10^{0} S/cm with increasing the content from 0 to 5 wt%. However, when the content of MWNTs went over 5 wt% the electrical conductivity was almost independent of the MWNTs content. As a result, the conductivity did not increase with a further raise of filler content.

We observed that the electrical conductivity shows the typical percolation behavior for PVDF/MWNT blends between 2 and 2.5 wt% and reaches 10^{0} S/cm at 5 wt% MWNT content, which is ca. 14 orders of magnitude higher than that (10^{-14} S/cm) of pure PVDF. This indicates that a nanotube network in the polymer matrix forms from the percolation content. However, above 5 wt%, additional incorporation of MWNT does not significantly alter the electrical conductivity, which is a measure of long range movements of charge carrier.[11] This indicates that there is conductivity saturation from a critical content because of formation of an infinite cluster.[12] Similar tendency was also observed in thermal conductivity above 3wt% of MWNT, as shown in Figure 6.

Figure 7 shows the permittivity behaviors with various MWNT contents. Dielectric constants are improved with increasing the content of MWNT. Ionic conduction phenomena are slightly observed above 5 wt% of MWNT. These results implied that the PVDF resin filled with MWNTs could be prospective EMI shield material since we can enhance the conductivity and permittivity by controlling the content of MWNT.

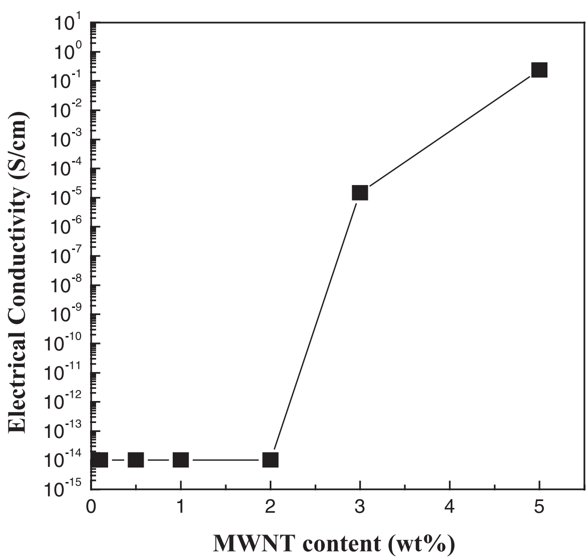

Figure 5.
Variation of the electrical conductivity of PVDF and PVDF/MWNT blends with MWNT content.

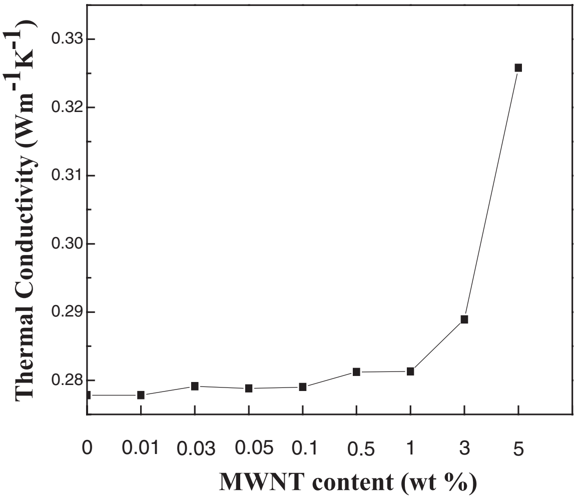

Figure 6.
Variation of the thermal conductivity of PVDF and PVDF/MWNT blends with MWNT content.

Conclusions

We have investigated the relationships among morphology and physical properties based on PVDF and MWNT by melt compounding.

With increasing the MWNT content, supercooling required for PVDF crystallization and the size of spherulites in PVDF decrease. The incorporation of MWNT gave rise to the transformation of the crystallites from the nonpolar α-form to polar β-form.

The experimental percolation threshold for the electrical conductivity in PVDF was estimated and clearly occured between 2

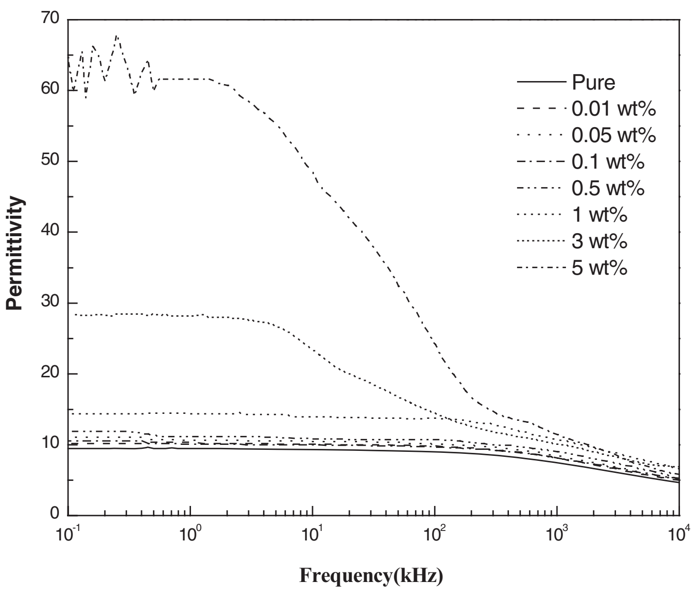

Figure 7.
Variation of the permittivity of PVDF and PVDF/MWNT blends with MWNT content.

and 2.5 wt%. Similar tendency was also observed in thermal conductivity and permittivity. This indicates that there is conductivity saturation from a critical content. Thus, PVDF/MWNT blends are expected to be used extensively in piezoelectric, pyroelectric, and ferroelectric applications, which are associated with the β-form crystal.

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[1] Y. Zou, Y. Feng, L. Wang, X. Liu, *Carbon* **2004**, *42*, 271.
[2] B. G. Min, T. V. Sreekumar, T. Uchida, S. Kumar, *Carbon* **2004**, *43*, 599.
[3] T. Furukawa, *Key Eng. Mater.* **1994**, *92–93*, 15.
[4] T. Furukawa, M. Date, E. Fukada, *J. Appl. Phys.* **1980**, *51*, 1135.
[5] T. Ebbesen, *Carbon Nanotubes; Preparation and Properties*, CRC Press, New York **1997**.
[6] S. N. Li, Z. M. Li, M. B. Yang, Z. Q. Hu, R. Huang, *Mater Lett.* **2004**, *58*, 3967.
[7] S. M. Hong, B. C. Kim, K.U. Kim, I. J. Chung, *Polymer J.* **1992**, *24*, 727.
[8] G. P. Desio, L. Rebenfeld, *J. Appl. Polym. Sci.* **1990**, *39*, 825.
[9] V. M. Nadkarni, J. P. Jog, *J. Appl. Polym. Sci.* **1986**, *32*, 5817.
[10] Y. Lee, R. S. Porteer, *Polym. Eng. Sci.* **1986**, *26*, 633.
[11] P. Potschke, S. M. Dudkin, I. Alig, *Polymer* **2003**, *44*, 5023
[12] R. Kotsilkova, D. Nesheva, I. Nedkov, E. Krusteva, S. Stavrev, *J. Appl. Polym. Sci.* **2004**, *92*, 2220.

