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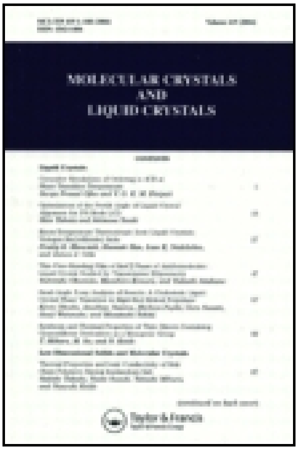

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Physical Properties of Multi-Walled Carbon Nanotube-Filled PVDF Composites Prepared by Melt Compounding

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Multi-walled carbon nanotube (MWNT)/Poly(vinylidene fluoride) (PVDF) composites with various loading levels (0.01 ~ 10 wt%) have been prepared by the simple melt-compounding approach. Morphology and electrical properties of the composites were investigated. The experimental percolation threshold for the electrical conductivity was estimated and clearly occurred between 2 and 2.5 wt%. MWNT/PVDF composites presented a shoulder posterior to the main melting peak and an increased endpoint of the peak. In the WAXD profiles, the incorporation of MWNT produced a larger shoulder at $2\theta = 20.7^\circ$ with increase in the loading levels, corresponding to the β-form crystal of PVDF. In the rheological properties, dynamic viscosity, the extent of shear thinning behaviors and relaxation time were notably increased with the MWNT content.

Keywords: β-form crystal; dynamic viscosity; electrical conductivity; multi-walled carbon nanotube; poly(vinylidene fluoride)

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) has attracted much attention because of its potential applications to high pyroelectric, piezoelectric, and ferroelectric materials. It is semicrystalline polymer with various crystal phases such as nonpolar α-phase, polar β-and γ-phase, depending on

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the crystallization condition [1]. It is well known that the β-phase is responsible for its favorable properties among them [2].

Carbon nanotube (CNT) exhibits unique physical properties including high electrical and thermal conductivity and tensile strength. Introduction of conducting fillers into the polymer has been extensively studied to provide the insulating polymer with the electrical conductivity. Until now, there have been many reports on CNT-reinforced polymer composites for various organic polymers such as polyethylene [3], polypropylene [4], poly(methyl methacrylate) [5], polystyrene [6], polyacrylonitrile [7,8], and poly(vinyl alcohol) [9,10]. However, there is little study on PVDF composites filled with CNT even though they can be applicable in various electronic devices. When the CNT is introduced into polymer, the favorable properties can be achieved at very low content in comparison with those of polymer composites filled with conventional sphere-shaped particles, such as graphite and carbon black. This is attributed to its high aspect ratio of 100–1000 and high specific surface areas. In addition, the geometry of CNT may result in a different flow behavior from that of conventional filled polymer. The rheological properties of polymeric system are closely associated with its processing. Thus, understanding the rheological properties of the composites gives significant clues to determining optimum condition of polymer processing. In this study, PVDF was melt-compounded with multi-walled carbon nanotube (MWNT) in various loading levels (0.01–10 wt%), and the physical properties of the composites were investigated in terms of electrical conductivity, rheology, thermal properties, and morphological properties.

EXPERIMENTAL

Materials

A commercial available SOLEF 1010 poly(vinylidene fluoride) (PVDF; Melt flow index = 6, 230°C, 5 kg) was obtained from Solvay, Inc. (Belgium) and high purity multiwalled-carbon nanotube (MWNT; purity = 95%, average diameter = $10 \sim 15$ nm, length = $10 \sim 20$ μm) was purchased from Iijin, Inc. (Korea). Polyoxyethylene octylphenylether (Triton X-100, Duksan Chemical Co., Korea), a non-ionic surfactant, was employed at a concentration of 0.9 wt% to produce good dispersion of MWNT by preventing the entanglement. The MWNT powder was surfactant-treated in toluene by ultrasonicating for 2 hrs. The toluene was then evaporated and the resultant surfactant-treated MWNT are vacuum-dried at 100°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 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 loading levels (X) of the nanocomposites ranged from 0.01 to 10 wt%, and they were coded PVDF-X.

Measurement of Physical Properties

Field emission scanning electron microscopic (FESEM; JEOL, JSM-6340F) observations were carried out on the surface of PVDF/MWNT composite in a sheet state. The surfaces of the samples were sputter-coated with a thin gold layer prior to scanning. The electrical conductivity of the composites was measured using a standard four-probe method. A Keithley 2400 sourcemeter was used to measure the I-V characteristics of the samples at room temperature. The thermal properties of PVDF/MWNT composites 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. 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. Dynamic rheological measurements were carried out with a mechanical spectrometer UDS 200 (Paar Physica). Parallel plate geometry with a diameter of 25 mm was employed. The plate gap and strain level were 1 mm and 5%, respectively. The frequency sweep tests were carried out in an oscillatory mode at 220°C.

RESULTS AND DISCUSSION

FESEM microphographs of pristine MWNT and the surface of PVDF/MWNT composites 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 [11,12]. The diameters of the MWNT are approximately $10 \sim 30$ nm, with a length of several micrometers, implying a high aspect ratio for the MWNT. From the SEM microphotograph of the fractured PVDF/MWNT composite, it can be seen that MWNT form entangled structures in the PVDF matrix. However, the MWNT is uniformly dispersed in the PVDF matrix, despite some aggregated MWNT structures. In addition, a great amount of naked MWNT on the surface are observed at a high loading level. This may be associated with the

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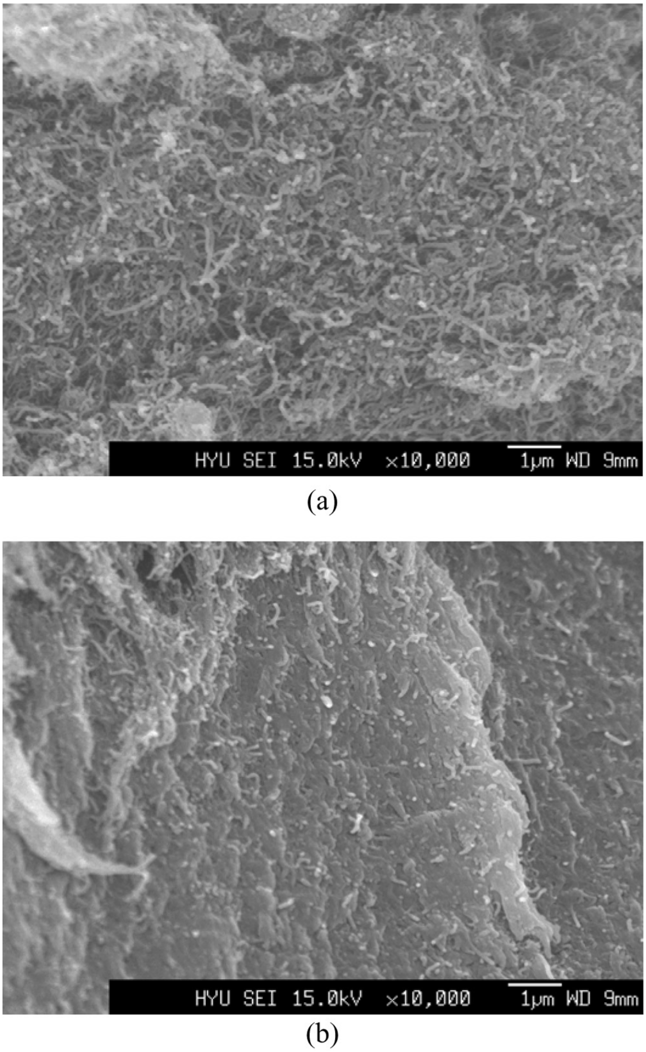

FIGURE 1 FESEM micrographs of (a) pristine MWNT and (b) surface of PVDF composites with 10 wt% MWNT.

absence of specific interfacial interaction between PVDF chain and MWNT. Thus, the MWNT might act as a defect within the composite when the load is applied.

It is well known that the presence of MWNT in the polymer matrix provide the nonconductible polymer with the electrical conductivity. We herein investigated the effect of MWNT concentration on the

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electrical conductivity of PVDF. As shown in Table 1, we also observed that the conductivity shows the typical percolation behavior for PVDF/MWNT composites between 2 and 2.5 wt% and reaches 2.42×10^0 S/cm at 10 wt% MWNT loading, 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 composition. However, above 5 wt%, additional incorporation of MWNT does not significantly alter the electrical conductivity. This indicates that there is conductivity saturation from a critical loading level because of the formation of an infinite cluster [13].

WAXD was used to observe the effect of MWNT content on the microstructure of PVDF resin. Figure 2 describes the WAXD patterns for pure PVDF and PVDF/MWNT composites. 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 composites exhibit decreased peaks for α-phase crystal from 0.5 wt% loading. In addition to the features associated with α-phase crystal, the introduction of MWNT produces a shoulder at a 2θ value of 20.7° and it is clearer with increasing the MWNT content. This is attributed to the formation of β-phase crystal which has all-trans conformation. It is recognized that the β-phase, the most polar among other crystals, exhibits piezoelectric, pyroelectric, and ferroelectric properties and it is typically obtained by stretching and electric polling [2]. This implies that the incorporation of alien particle can be considered as a method to increase those properties of PVDF.

TABLE 1 Variation of the Electrical Conductivity of PVDF and PVDF/MWNT Composites with MWNT Content

Material	Electrical conductivity (S/cm)
PVDF	1×10^{-14}
PVDF/MWNT 0.01	1×10^{-14}
PVDF/MWNT 0.1	1×10^{-14}
PVDF/MWNT 0.5	1×10^{-14}
PVDF/MWNT 1.0	1×10^{-14}
PVDF/MWNT 2.0	1×10^{-14}
PVDF/MWNT 2.5	9.06×10^{-7}
PVDF/MWNT 5.0	2.39×10^{-1}
PVDF/MWNT 7.0	8.35×10^{-1}
PVDF/MWNT 10.0	2.42×10^{0}

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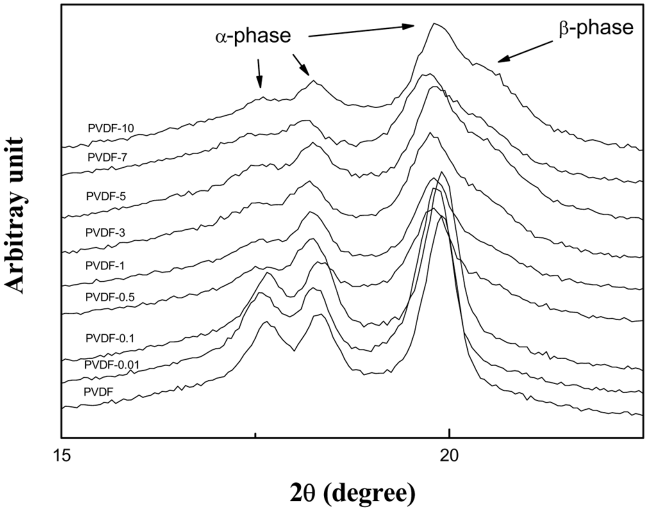

FIGURE 2 WAXD patterns of PVDF and PVDF/MWNT composites.

The heating scan thermograms of PVDF and PVDF/MWNT composite are shown in Figure 3. The samples give the main melting peak at ca. 172°C irrespective of the presence of MWNT. However, the

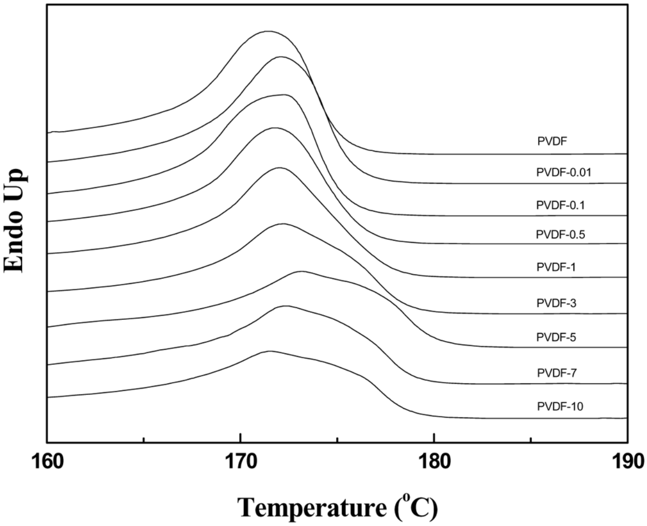

FIGURE 3 DSC heating scan thermograms of PVDF and PVDF/MWNT composites.

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TABLE 2 Crystallization Temperature of PVDF and PVDF/MWNT Composites at a Cooling Rate of 10°C/min

Material	Crystallization temperature (°C)
PVDF	142.60
PVDF/MWNT 0.01	142.49
PVDF/MWNT 0.1	142.42
PVDF/MWNT 0.5	145.85
PVDF/MWNT 1.0	146.80
PVDF/MWNT 3.0	147.83
PVDF/MWNT 5.0	148.07
PVDF/MWNT 7.0	148.49
PVDF/MWNT 10.0	148.50

addition of MWNT more than 3 wt% produces the shoulder posterior to the main melting peak and an increased endpoint of the peak. This phenomenon is attributed to the presence of two morphologically different crystallites. The β-phase crystal with all-trans conformation gives higher endotherm than the α-phase crystal with TGTG conformation. This is in good agreement with WAWD results. On the other hand, as shown in Table 2, up to 0.1 wt% loading of MWNT, it has little effect on the crystallization temperature (T_c) of PVDF, but further addition increases T_c, from 142.4 to 148.5°C, with increasing the loading level. This suggests that MWNT acts as a nucleation agent for PVDF above a critical loading level.

The dynamic viscosity (η') of pure PVDF and the PVDF/MWNT composites at 220°C as a function of frequency is shown in Figure 4. η' decreases with increasing frequency indicating a non-Newtonian behavior over the frequency range investigated. The shear thinning behavior observed in the PVDF/MWNT composites may be attributed to the orientation of the rigid molecular chains in the composites during the applied shear force. The increase of η' with MWNT content is more significant at low frequency compared with high frequency, and this effect is reduced with increasing frequency because of the strong shear thinning behavior induced by incorporating MWNT. This may be explained that the constraining influence of MWNT on the mobility of polymer chain becomes weak under high shear. In addition, the irregular decrease in the η' with increasing frequency indicates pseudoplastic characteristics of the PVDF/MWNT composites because of random orientation and entangled molecules in this composite system.

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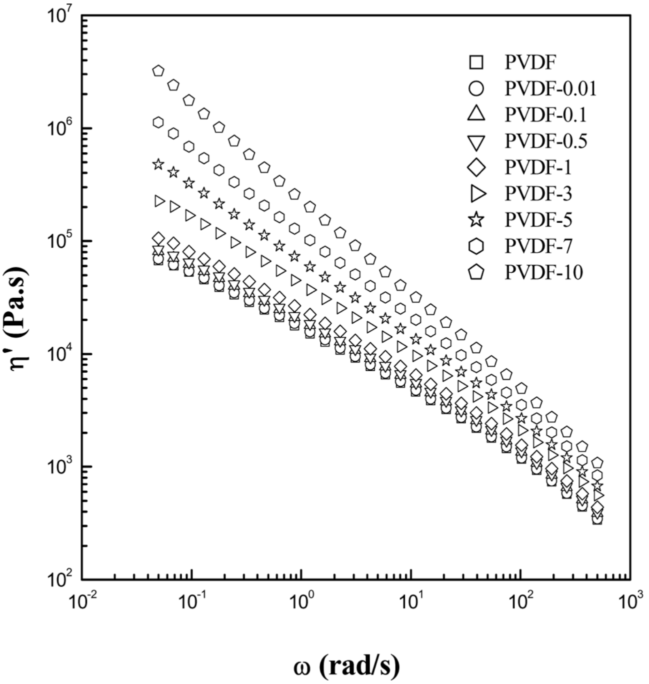

FIGURE 4 η' curve of PVDF and PVDF/MWNT composites at 220°C.

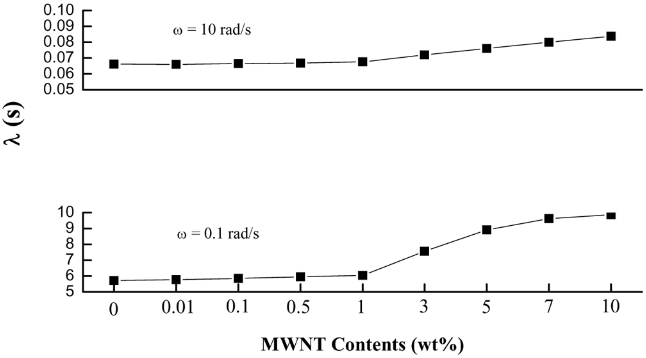

FIGURE 5 Variation of the λ of PVDF and PVDF/MWNT composites at two frequencies.

The relaxation behavior of PVDF chain is also affected by the presence of MWNT. For the polymeric systems, relaxation time (λ) under dynamic shear can be calculated as follows [14],

$$\begin{aligned} J' &= G'/(|\eta^*|\omega)^2 \\ \lambda &= J'|\eta^*| \end{aligned} \tag{1}$$

where λ is relaxation time, η^* complex viscosity, and J′ compliance. Figure 5 displays the dependence of the λ on MWNT content at two frequencies. PVDF composites present an increased λ at the higher content of MWNT. This suggests that the MWNT in the matrix impedes the chain mobility leading an increase of the chain rigidity, as previously mentioned.

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CONCLUSIONS

MWNT in the PVDF matrix constrained the mobility of polymer chain, leading to an increased viscosity and relaxation time with increasing the MWNT content. However, their increasing extent became small at high frequency because the orientation effects of the polymer molecules prevail. The incorporation of MWNT gave rise to the transformation of the crystallites from the α-form to β-form, resulting in high melting behavior. Thus, PVDF/MWNT composites are expected to be used extensively in piezoelectric, pyroelectric, and ferroelectric applications, which are associated with the β-form crystal.

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