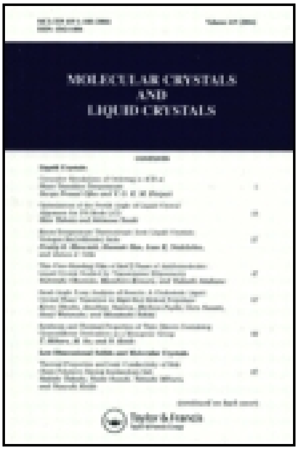

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# Crystal Structure and Ferroelectric Properties of Poly(vinylidene fluoride)-Carbon nano tube Nanocomposite Film

**Ji Seok Lee[1,2], Gwang Ho Kim[1,3], Woo Nyon Kim[3], Kyung Hwan Oh[2], Hyeong Tae Kim[1], Seung Sang Hwang[1], and Soon Man Hong[1]**
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*We investigated the effect of carbon nanotube on the crystal structure and mechanical/ferroelectric/piezoelectric properties based on poly(vinylidene fluoride) (PVDF) and carbon nano tube (CNT) composite film. The composite films were prepared by solution blending method, and the films were formed by hot-pressing. The contents of CNT were from 0.001 wt.% to 1 wt.%. For inducing piezoelectric beta-crystal structure, the hot-pressed nano composite films were drawn by 400% elongation. These samples were poled at high voltage and high temperature for polarization of the PVDF/CNT composite film. The beta-crystalline phase were increased with CNT contents, passing through the peak, and decreased. The structural changes depend on the CNT contents, drawing and poling conditions.*

**Keywords:** carbon nano tube; ferroelectric properties; nano-composite; poly(vinylidene fluoride)

## INTRODUCTION

For extensive ferroelectric and piezoelectric applications, various electroactive materials have been recently investigated [1]. Especially, PVDF and its copolymers show the largest piezoelectric

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and ferroelectric properties, and have been intensively researched by several researchers [2,3]. However, the potential of piezoelectric applications for PVDF is still limited because of their low coupling between electrical and mechanical properties and relatively low generated voltage and force.

There has been much effort to solve the problems such as uniform dispersion of nano-size ferroelectric ceramic particles in PVDF matrix and compatibility between them [4,5]. CNT has been recently utilized as the reinforcement for improving ferroelectric properties of some matrix [2,6,7]. These CNT based polymer composites can make high strength and extension due to its high tensile and mechanical properties. Furthermore, CNT can play a role of nuclei for rapid crystallization, so that it can generate much more β-phase crystal structure which plays an important role in acting piezoelectric and ferroelectric behaviors [8].

In this paper, the effect of introducing multi-walled carbon nanotube on the crystal structure, physical, ferroelectric and piezoelectric properties of PVDF/CNT nanocomposite films prepared by solution blending was studied with drawing and poling processes.

## EXPERIMENTAL

The materials were a commercial poly (vinylidene fluoride) (PVDF) and multiwalled-carbon nanotube (CNT). The PVDF was obtained from Solvay, Inc. (SOLEF 1010). CNT was purchased from Iljin Inc. The purity of CNT was 95%, and the average diameter was $10 \sim 15\,\mathrm{nm}$, and the length was $10 \sim 20\,\mu\mathrm{m}$. *N,N*-dimethylformamide (DMF), used as a solvent was supplied from Aldrich co. For enhancing the interfacial compatibility between PVDF and CNT, the surface of CNT was modified. The CNTs were first treated in a 3:1 $HNO_3/H_2SO_4$ solution and ultrasonicated in *N,N*-dimethylformamide (DMF). Then, the suspension of acid-treated CNTs in DMF was added to the PVDF-DMF solution. These PVDF/CNT/DMF solutions were washed in the distilled water, and the precipitated materials were dried. After drying, uniform films were obtained. The drawing procedure was conducted by an automatic drawing machine manufactured by our laboratory. The drawing rate was 1 mm/sec. After drawing, the poling procedures were carried out. The films were subjected to high electric fields by applying high voltage between the both sides of deposited electrodes in silicon oil bath with a DC high voltage supplier and high voltage amplifier (HY-150, Han young). Films were poled at electric fields up to 1.5 MV/cm at 100°C and the poling time was 30 min. For the poling process and the measurement of ferroelectric properties, aluminum electrodes were thermally evaporated onto both surfaces of the PVDF-CNT nano-composite film. ATR-Fourier Transform Infrared (ATR FT-IR) spectrum was obtained using Nicolet Magna 550 series II spectrometer (Midac) with an average of 200 scans in the $400 \sim 4000\,\mathrm{cm}^{-1}$. The crystal structure of nano-composites was studied by wide angle X-ray diffraction (WAXD) experiment carried out by Rigaku Denki with Ni-filtered Cu-Kα radiation at 40 kV and 100 mA. For the measurement of polarization, P-E hysteresis loop was obtained with a ferroelectric testing system (RT66A, Radiant Technology Precision) connected with a high voltage interface (Trek). A piezoelectric strain constant, $d_{31}$ and elastic modulus were measured using a Rheolograph Solid II (Toyoseiki) at 100 Hz.

## RESULT AND DISCUSSION

FT-IR spectra of PVDF/CNT nanocomposite with various CNT contents are shown in Figure 1. The peaks of α-crystal phase were appeared at 615 and $765\,\mathrm{cm}^{-1}$, $797\,\mathrm{cm}^{-1}$ and $975\,\mathrm{cm}^{-1}$. On the other

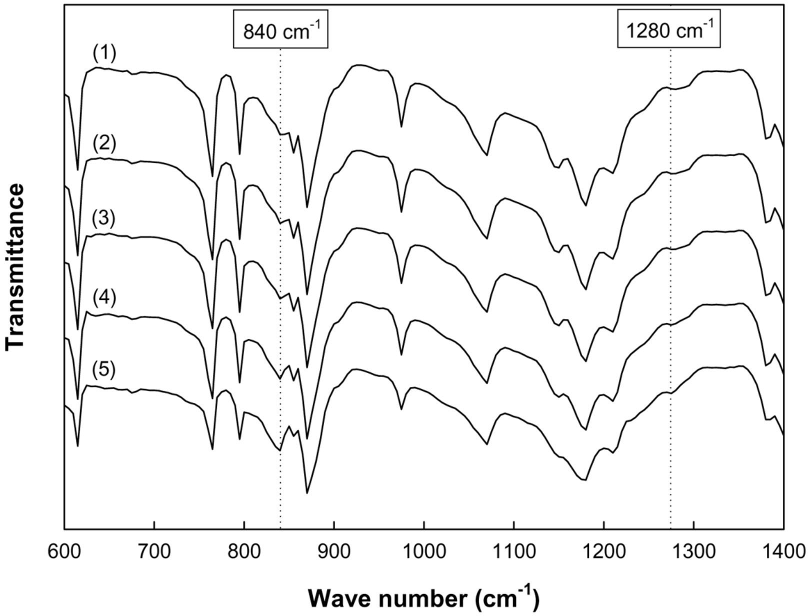

**FIGURE 1** FT-IR spectra of PVDF/CNT nano-composites with various CNT content. (1) PVDF; (2) PVDF/CNT-0.1 wt%; (3) PVDF/CNT-0.2 wt%; (4) PVDF/CNT-0.5 wt%; (5) PVDF/CNT-1.0 wt%.

hand, the peaks of β-crystal phase at 840 and 1280 $\text{cm}^{-1}$. Especially, the peak of β-phase at 840 $\text{cm}^{-1}$ increased with the amount of CNT and maximum peak was appeared in PVDF/CNT-0.1 wt% while the peaks of α-phase decreased at 615 and 765 $\text{cm}^{-1}$ [9]. It means adding CNT to PVDF affects the increase of β-phase. It was attributed to the fact that carbon nanotubes play a role of nuclei for crystallization and alter the kinetics of crystallization [8]. Thus, a relatively unstable and stretched β-phase crystal structure could be obtained by the rapid crystallization rate resulted from CNT. WAXD was performed to investigate the effect of CNT content on the structure of PVDF/CNT composites. Figure 2 describes the X-ray patterns for pure PVDF and drawn & poled PVDF/CNT nanocomposite films. As shown in Figure 2-(1), four characteristic diffraction peaks were observed at the diffraction angles ($2\theta$); 17.7, 18.5, 19.9, and 26.5°, which correspond to (100), (020), (110), and (021) reflections, respectively. All the peaks are assigned to the α-phase crystal with a non-polar TGTǦ (trans-gauche-trans-ǧauche) conformation which is the most stable structure. However, in the drawn & poled samples, the peaks of α-crystal decreased while those of β-crystal increased. Also, the two

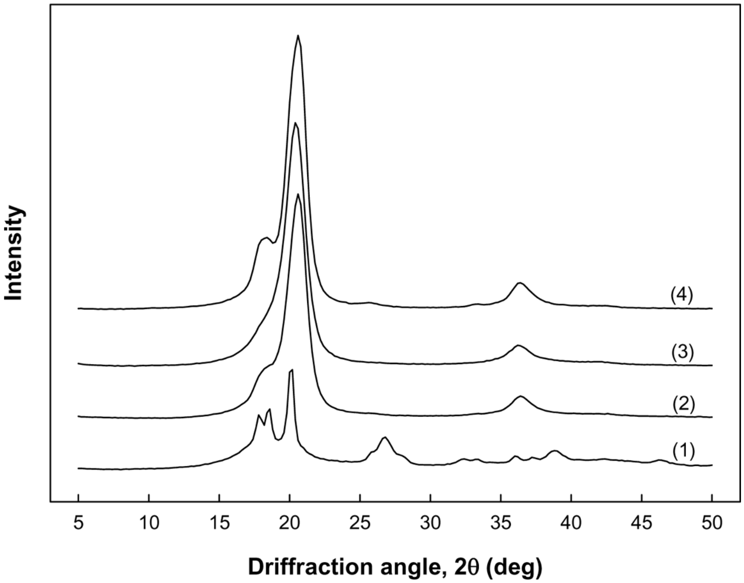

**FIGURE 2** X-ray diffraction spectra of PVDF/CNT nano-composites. (1) PVDF; (2) drawn & poled PVDF; (3) drawn & poled PVDF/CNT-0.2 wt%; (4) drawn & poled PVDF/CNT-1.0 wt%.

unique peaks obviously appeared at the diffraction angles ($2\theta$); 20.6 and 36.3°, which is assigned to (110) and (200) reflections, respectively. These peaks correspond to the β-phase crystal with a fully stretched all-trans planar zigzag conformation which is a relatively unstable structure. It means that the drawing process transfer α-crystal (monoclinic crystal) to β-crystal (orthorhombic crystal). Particularly, in the case of adding CNT, the amount of β-crystal were increased with CNT content up to 0.2 wt%-CNT. On the while, it decreased with CNT content over 0.2 wt%-CNT. This may be due to the fact that first, up to CNT content-0.2 wt%, the β-phase crystal increased due to the role of CNT as nuclei for the rapid crystallization through increasing crystalline rate. Second, over CNT content-0.2 wt%, although there was more β-phase due to an introduction of more amount of CNT, CNT could act as a role of hindrance in the extension of polymer chains at the drawing process.

Figure 3 shows the elastic modulus at the drawn direction with CNT content. The elastic modulus ($E_{31}$) linearly increased with CNT

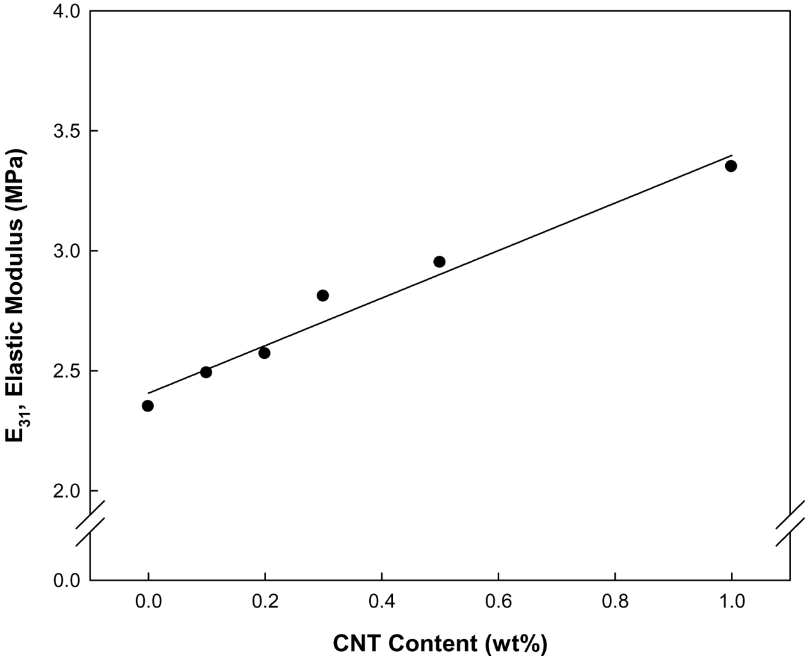

**FIGURE 3** Elastic modulus of drawn and poled PVDF/CNT composites with CNT contents at the drawn direction (31-mode).

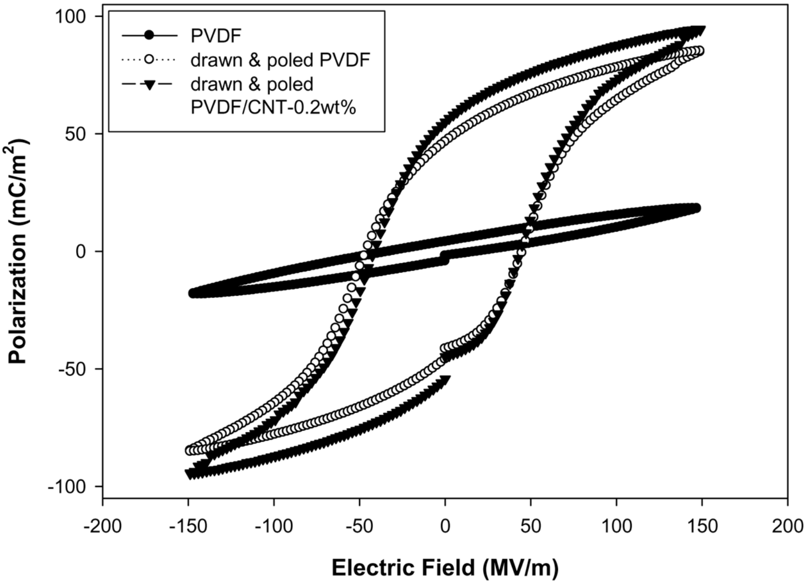

**FIGURE 4** P-E hysteresis loop of PVDF and PVDF/CNT nanocomposites film.

content. This means that CNT played a role as reinforcements in the PVDF/CNT composites [8–10].

As shown in Figure 4, the P-E hysteresis loop was investigated to measure the ferroelectric properties. The voltage was applied to the both of two sides of PVDF/CNT nanocomposites up to 150 MV/cm. While the remanent polarization ($P_r$) of pure PVDF was very low, that of drawn & poled PVDF/CNT-0.2 wt% had the highest value. Herein, several facts are worthy of note: (1) while $E_{31}$ increased in the elastic modulus at the drawn direction, the value of remanent polarization was not shown as the same behavior. (2) The Pr value increased up to 0.2 wt%-CNT, and then decreased. It can be explained by the fact that adding more CNT over 0.2 wt% in PVDF/CNT composites interferes with the development of β-phase crystal in drawing process.

Using a rheovibron (Rheograph solid II, Toyoseki), the piezoelectric strain constant ($d_{31}$) was measured in the 31-drawn direction. As shown in Figure 5, the maximum value of piezoelectric strain constant in 31-direction which largely depends on the β-phase crystal structure and the polarization of the materials also came out at 0.2 wt%-CNT content. After passing through the highest value, it decreased with CNT content. It is interesting to note that the addition of proper

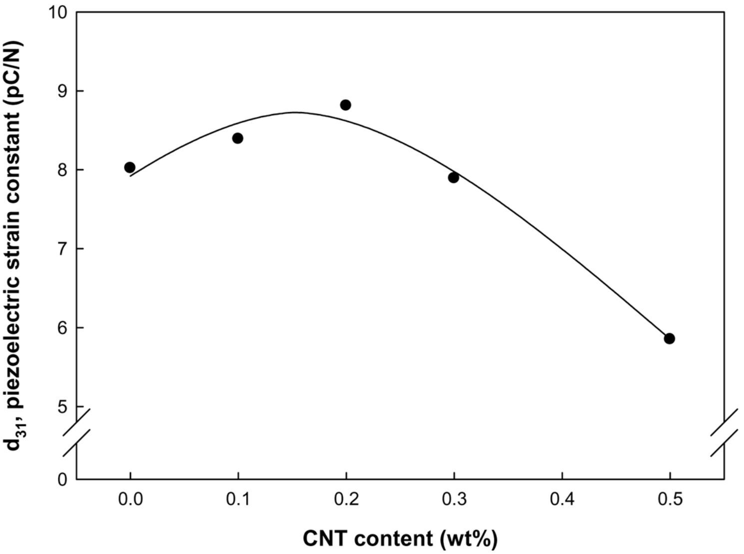

**FIGURE 5** D31-piezoelectric strain constant of drawn and poled PVDF/CNT composites with CNT content.

amount of CNT into the PVDF matrix makes it possible to satisfy not only a good elastic modulus but also a high piezoelectricity although both of them are inversely proportional to each other. (See the following equations)

$$d_{ij} = \left[\frac{\partial \varepsilon_j}{\partial E_j}\right]_{\sigma=} \left[\frac{\partial D_i}{\partial \sigma_i}\right]_E$$

$$d_{ij} \sim \varepsilon_j \sim \frac{1}{e_j}$$

$d_{ij}$: piezoelectric strain constant; $E_j$: strain; $\sigma_i$: stress; E: electric field; $D_i$: electric displacement; $e_j$: elastic modulus.

## CONCLUSIONS

In this study, we attempted to investigate the effect of carbon nanotube on the crystal structure and mechanical/ferroelectric/piezoelectric properties on the PVDF/CNT nanocomposite film. CNT in the PVDF polymer matrix played a role of nuclei for crystallization, leading to developing β-phase crystal as well as having higher elastic modulus. However, in case of drawn & poled PVDF/CNT nanocomposite film, the ferroelectric and piezoelectric properties such as the value of remanent polarization and piezoelectric constants ($d_{31}$) had a peak value, at the content of 0.2 wt%-CNT. Therefore, we could find an optimum content of carbon nanotube for a good mechanical properties and high ferroelectric/piezoelectric properties.

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