Effect of infrared laser irradiation on the piezoelectric properties of the TiO_2 coated MWCNT reinforced PVDF film

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Abstract

The β-phase poly (vinylidene fluoride) (PVDF) exhibits excellent piezoelectric properties compared to other crystalline polymers, because it has the special chain arrangement inducing the largest dipole moment in crystalline phase. However, it is still necessary to increase all-trans conformation to apply PVDF polymer as sensing material. In the infrared region, the natural frequency of the PVDF molecular structure can induce transition from TGTG to TTTT-type molecular chain because energy of infrared vibration can generate resonance with rotational-vibrational energy of molecules and the addition of TiO_2 coated multi-walled carbon nanotube (MWCNT) can lead to hydrogen bond between the F atom on PVDF and hydroxyl group on the TiO_2 coated MWCNT due to difference of the electronegativity. In addition, induced all-trans molecular chain can be easily adsorbed on the TiO_2 coated MWCNT surface and act as nucleating agents for the crystallization of PVDF chains.

In this study, we investigated piezoelectric property of the TiO_2 coated MWCNT reinforced PVDF film by generating molecular vibration at specific infrared frequency ranges. The crystal structure and morphology of the film were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). The piezoelectric coefficient of d33 was measured by d33 meter.

1. Introduction

Poly(vinylidene fluoride) (PVDF) is semi-crystalline thermoplastic fluoropolymer which exhibits at least four different polymorphs distinguished as α, β, γ, and δ forms. Among the these four crystalline forms, β form is known to be a crystalline structure with high spontaneous polarization because chain conformation of the polar β phase has all-trans planar zigzag structure consisting of a TT-type chain [1-2]. Thus, PVDF with a high content of β phase shows the superior piezoelectric and ferroelectric properties. Due to these properties, PVDF is widely used as material for sensing strain and deformation in applications such as sensors, actuators, generators, transducers among polymeric materials [3]. To apply PVDF as piezoelectric material, enhancing the β-phase content within the PVDF is an important factor.

In order to obtain the poly(vinylidene fluoride) (PVDF) films with enhanced β-phase content, mechanical stretching and poling processs are generally used to induce the α to β phase transformation. A different approach to improve the β-phase of PVDF is the addition of various particles such as carbon nanotubes (CNTs), TiO_2, clay, hydrated ionic salt, or ferrite nanoparticles. Among these materials, carbon nanotube(CNTs) have received significant attention in a field of research for coating of particular material on its surface [4]. In the case of the TiO_2 (titanium dioxide), possesses three

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crystalline structures such as anatase, rutile, and brookite and it can be attatched on the surface using carbon nanotubes as a support. TiO_2 with anatase crystalline structures has hydroxyl groups on its surface and can interact with F atoms on the PVDF through the hydrogen bond. Thus, TiO_2 composed of anatase crystalline structures can exhibit surprisingly large effect to improve the β crystal structure by coating on carbon nanotubes with high specific surface area [5].

Infrared radiation can be used for inducing the molecular vibrations corresponding to the natural frequency of the PVDF able to increase the chemical bond between the PVDF chain and TiO_2 coated multiwalled carbon nanotube.The infrared is divided into three regions; the near-, mid- and far-infrared, among the infrared regions, The mid-infrared are related to the rotational-vibrational mode of molecular in the wavenumber range of 4,000 to 400 cm^{-1} (wavelengths 2.5 to 25 µm). Crystalline structure of PVDF chains has natural frequency with specific vibrational mode in the mid-infrared region. When the mid-infrared source was irradiated to PVDF, molecules of the PVDF absorb IR source that corresponds to the natural frequency and can occur molecular vibrations.

In this work, MWCNTs were coated with anatase TiO_2 nanoparticles by hydrothermal process and Infrared radiation was applied to TiO_2 coated MWCNT/PVDF solution to enhance the interaction between the TiO_2 coated MWCNT nanoparticles and F atoms of PVDF.

2. Experimental

2.1. Materials

PVDF pellets (kynar 720, Arkema, France) were mixed with N,N-dimethyl formamide (DMF, Junsei Chemical Co.,Ltd. Japan). Both Nitric acid (HNO_3) and Hydrogen peroxide (H_2O_2) were used for functionalization of Multi-wall carbon nanotube (CM-95, Hanhwa Nanotech., Korea). ($TiCl_4$)titanium tetrachloride (99%, Junsei Chemical Co.,Ltd.Japan) was used as TiO_2 precursor.

2.2. Fabrication of TiO_2 coated multiwalled carbon nanotube

For functionalization of MWCNTs, chemical oxidation was conducted using two acid treatments. First treatment was initiated by HNO_3 and H_2O_2 treatment was carried out in sequential. MWCNT was added to the acid solution and the mixture was stirred, followed by sonication treatment performed for 4h. Then it was filtered and washed by deionized water. The slurry were finally to obtained after drying in conventional oven at 120 ℃ for 4h. Afterwards, both functionalized MWCNTs and $TiCl_4$ was added into 1M HCl solutions. The mixture were ultrasound for 2h and then was neutralized by ammonia solution (5M). After stirring in hydrolysis temperature range of 80 ℃ for 3h, the products were washed by deionized water and dried at 100 °C for 1 h. Finally, to fabricate TiO_2 coated onto MWCNTs, TiO_2-MWCNT nanocomposite was heated at 500°C in N_2 medium for 2h using the chemical vapor deposition (CVD).

2.3. Fabrication of TiO_2 coated MWCNT/PVDF film composites

TiO_2 coated MWCNT/PVDF film composites was formed by solvent casting method. First, PVDF pellets was dissolved in DMF solvent at 60 ℃ for 4h to yield a 20 wt.%. TiO_2 coated MWCNT particles was added to neat PVDF solution and then the suspension was stirred by paste mixer for 15 min and ultrasonically treated for 30min. The light from IR source was introduced to TiO_2 coated MWCNT dispersed PVDF solution to generate the molecular vibration of PVDF. Distance between the IR source and TiO_2 coated MWCNT/PVDF solution is maintained at least 30cm to prevent the solidification of the solution by IR adiation. The IR irradiation time was applied in the range of 10 minutes to 30 minutes.

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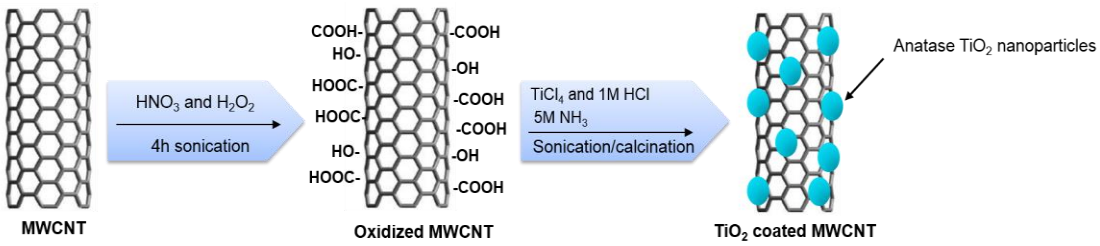

Figure 1. The schematic of fabrication of TiO_2 coated MWCNT

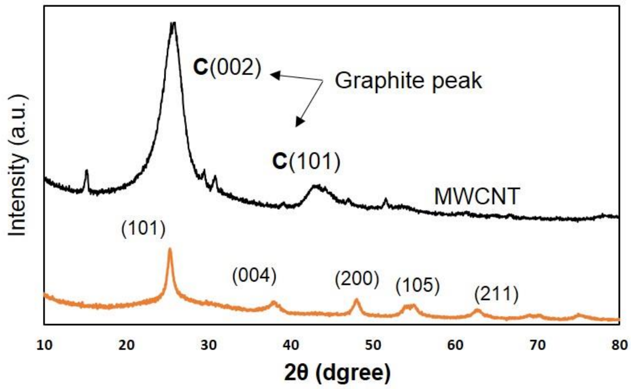

Figure 2. XRD patterns of neat MWCNT and TiO_2 coated MWCNT.

2.5. Corona poling process of TiO_2 coated MWCNT/PVDF film composites

The electrical poling of the TiO_2 coated MWCNT/PVDF film composites was performed by a corona discharge to enhance the piezoelectricity of film composites. The metal needle tip was used as the electrode and the distance between the needle tip and the film composites is 1 cm. At first, corona poling process is maintained at 100 ℃ for 30 min and then temperature drop from the 100 ℃ to room temperature for 45 min. In the entire process, electric field used is 4MV/cm.

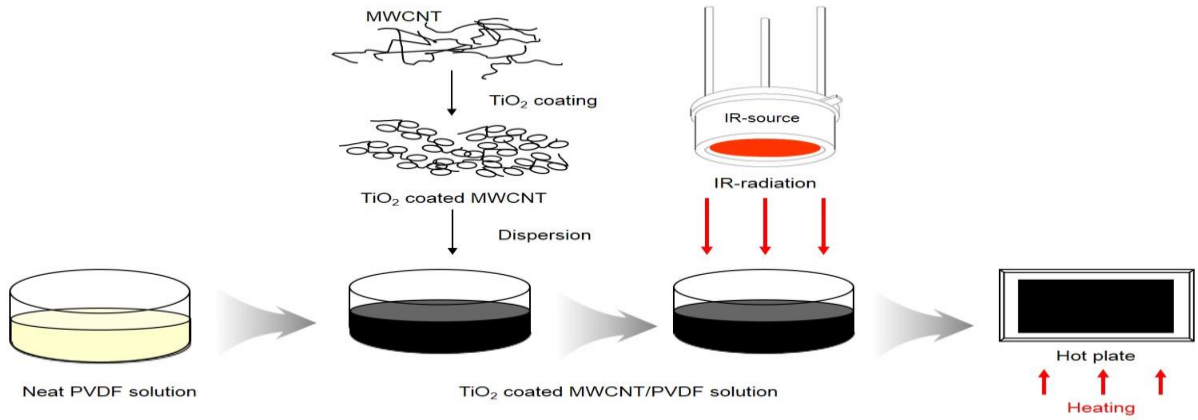

Figure 3. The schematic of fabrication of TiO_2 coated MWCNT/PVDF film composites.

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2.5. Characterization of TiO_2 coated MWCNT/PVDF film composites

The phase transformation of PVDF was analyzed by FT-IR (Fourier Transform Infrared Spectrometer, Spectrum GX, PerkinElmer Inc, USA) in the range of wavenumbers from 400 to 4000 cm^{-1} . Verification of crystalline structure and crystallinity was performed by MP-XRD (Multi-Purpose High Performance X-ray Diffractomete, X'pert Powder, PANalytical Ltd., Netherlands) using the Cu Kα(λ=1.54Å) at the diffraction angle from 5 to 50° and DSC (Differential scanning calorimetry, Q20, TA Instruments Ltd., USA) with a heating rate of 10℃/min from 30 ℃ to 200 ℃.
The d33 value of piezoelectric constant of TiO_2 coated MWCNT/PVDF film composites was measured by d33 meter (YE2730A, Yangzhou, China).

3. Result and discussion

3.1. Charcterization of TiO_2 coated MWCNT

Figure 2 shows the XRD patterns of neat MWCNT and TiO_2 coated MWCNT. The main characteristic peaks of neat MWCNTs were observed at 25.9° (002), and 43° (001). In the case of the TiO_2 coated MWCNT, five distinct peaks such as 25.3° (101), 38° (004), 48.1° (200), 55.2° (105), 62.5° (211) were detected. These peaks present formation of anatase TiO_2 on the MWCNT surface .

3.2. Characterization of TiO_2 coated MWCNT/PVDF film composites`

Figure 4 shows the XRD patterns for neat PVDF and MWCNT/PVDF film composite and TiO_2 coated MWCNT/PVDF film composites. With the addition of TiO_2 coated MWCNT/PVDF film composites, the intensity of β-phase characteristic peak was enhanced.

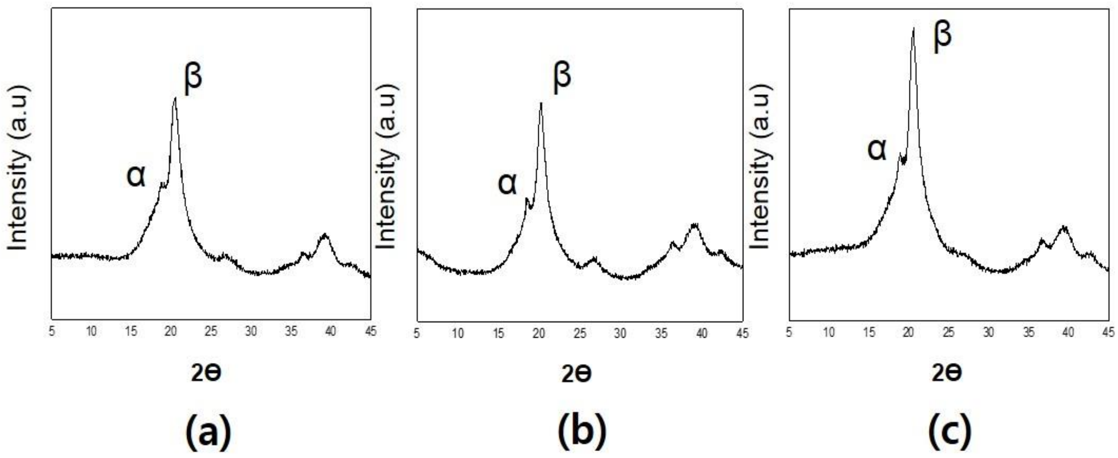

Figure 4. XRD patterns of ; (a) Neat PVDF, (b) MWCNT//PVDF film composites, (c) TiO_2 coated MWCNT/PVDF film composites

4. Conclusion

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In this study, TiO_2 coated MWCNT/PVDF film composites were fabricated by using solvent casting and enhancement of β-phase content was induced through the IR radiation on TiO_2 coated MWCNT/PVDF solution. Base on the results, the following conclusions were obtained.

- From the XRD analycis, Anatase TiO_2 nanoparticles was attatched on the MWCNT surface.
- From the XRD analysis, It was confirmed that addition of TiO_2 coated MWCNT affects on enhancing the β-crystal structure

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