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# Enhanced Mechanical and Dielectric Properties of Poly(vinylidene fluoride)/Polyurethane/Multi-walled Carbon Nanotube Nanocomposites

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**Abstract:** Multi-walled carbon nanotubes (MWNTs) nanocomposites with the polymer matrix composed of blends of poly(vinylidene fluoride) (PVDF) and polyurethane (PU) were prepared via functionalization of 3,4,5-triflouroaniline (TFA) on MWNTs. The MWNTs/polymer nanocomposites showed a dominantly enhanced elongation due to incorporation of PU molecules in PVDF matrix and the improved MWNTs dispersion in the polymer matrix resulting from functionalization of MWNTs with TFA. The functionalization of TFA on MWNTs was confirmed by the measurements of Raman, FT-IR spectra, SEM, and TEM images. In addition, the dielectric constant of nanocomposites increased with an increase of TFA-functionalized MWNTs in PVDF/PU/MWNTs nanocomposites. The polymer blend nanocomposites incorporating MWNTs may be available as an alternative potential route for the actuator materials.

**Keywords:** Nanocomposite, Carbon nanotube, Mechanical property, Dielectric constant

## Introduction

Polymer electroactive actuators have received much attention due to their high light weight, processability, energy density, and high electromechanical coupling efficiency compared to the inorganic actuators [1-4]. These include electrically conducting polymers, ferroelectric polymers, electrostrictive polymers, dielectric polymers, and etc. Of all the electroactive polymer actuators, dielectric elastomers show the largest actuation areal strain though high electric fields are required to achieve it. Dielectric elastomers are usually prepared from chemically crosslinked homopolymers such as acrylic and silicone elastomer and physically crosslinked copolymers such as polyurethane block copolymers.

Polymer composites with high dielectric properties may be more desirable for use in application of dielectric elastomers because they can enhance the dielectric properties of polymers by incorporating the ceramic, semiconducting fillers, and silver nanoparticles [5-7]. However there has been still deterioration in thermal stability and mechanical properties for most elastomer-based polymers and their composites. As an alternative method of preparing the dielectric elastomer actuator materials, the polymer blends incorporating the nanomaterials such as carbon nanotubes (CNTs) may be desirable. Since CNTs have the extraordinary electrical, thermal and mechanical properties [8,9], the CNT/polymer nanocomposites make it possible to obtain high dielectric materials using CNT functionalization [10,11] with high dielectric molecules.

In this study, the polymer blend/CNT nanocomposites composed of poly(vinylidene fluoride) (PVDF) and polyurethane (PU) were employed. PVDF is a typical ferroelectric polymer and thermally stable [12,13]. For enhancing the dielectric properties of materials, CNTs are functionalized with the high dielectric molecules. The analysis of mechanical and dielectric properties as well as CNT functionalization and the morphology of nanocomposites are investigated as a function of polymer blend ratio and CNT content.

## Experimental

### Materials

The multi-walled carbon nanotubes (MWNTs, Iljin Nanotech, Korea) were used in this study. Their diameter and length were about 10-20 nm and 20 μm, respectively. PVDF ($M_w$=530,000 g/mol, Sigma Aldrich Co.), commercial PU chips synthesized from 4,4-methylenebis(phenylisocyanate) (MDI), poly(tetramethylene glycol) (PTMG), 1,4-butanediol (BD) (SK Company, Korea) by mole ratio of (MDI:PTMG: BD=39:52:9), and 3,4,5-trifluoroaniline (TFA, TCI) were used in this study.

### Functionalization of MWNTs

MWNTs (0.5 mmol of carbon) and TFA (4 equiv/mol of carbon) were dispersed in *o*-dichlorobenzene (ODCB) using horn sonication for 15 min. The MWNTs/ODCB/TFA solution was dissolved in acetonitrile in a two-necked flask with a reflux condenser and a magnetic stirrer bar to obtain the homogeneous solution. Then isoamyl nitrite (4.8 equiv/mol of carbon) was slowly added to the solution, and they were heated to 60 °C with continuous stirring for 24 h under nitrogen atmosphere. The resulting product was washed with an excess amount of dimethylformamide (DMF) to get TFA-functionalized MWNTs (TFA-MWNTs) (Figure 1).

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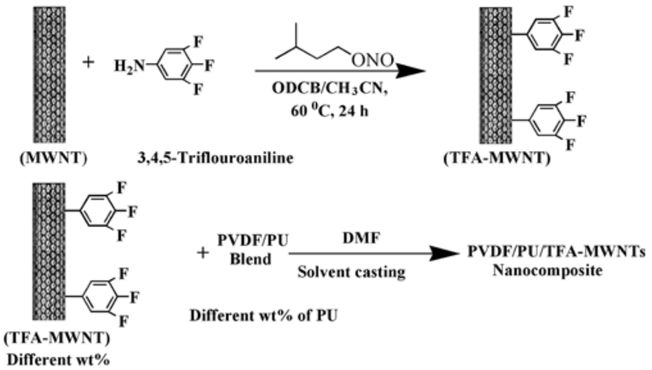

**Figure 1.** Scheme of CNT functionalization with 3,4,5-trifluoroaniline.

**Table 1.** Compounding formulation of PVDF/PU/TFA-MWNTs nanocomposites

| Sample code | PVDF (wt%) | PU (wt%) | TFA-MWNTs (wt%) |
|---|---|---|---|
| PVDF/TFA-MWNTs1% | 99 | 0 | 1 |
| PVDF/PU2%/TFA-MWNTs1% | 97 | 2 | 1 |
| PVDF/PU4%/TFA-MWNTs1% | 95 | 4 | 1 |
| PVDF/PU6%/TFA-MWNTs1% | 93 | 6 | 1 |

### Preparation of TFA-MWNTs/Polymer Composites

PVDF/PU/TFA-MWNTs nanocomposites films were prepared by solvent casting using DMF as solvent with varying TFA content MWNTs up to 1 wt% as well as the composition of PVDF and PU within 6 wt% PU. The cast films were used after removing the solvent completely in a hot drying oven. The average thickness of obtained films was approximately 0.1 mm. The compounding formulation of PVDF/PU/MWNTs nanocomposites is presented in Table 1.

### Characterization

Raman spectroscopy (Kaiser Holo Lab 5000 System 633 nm Ar-ion laser line, Japan) was used to investigate the functionalization of the MWNTs. Fourier transform infrared (FT-IR) spectroscopic measurements were performed using a Jasco FT-IR 300E device. The surface morphology of pristine and functionalized MWNTs was observed by transmission electron microscopy (TEM, JEM 2100F, JEOL, Japan). The cross-sectional morphology of the nanocomposites was observed with field emission scanning electron microscope (FE-SEM, S-4300SE, Hitachi). The mechanical properties of nanocomposites were measured at an elongation rate of 10 mm/min at room temperature using tensile tester machine (Instron 4468). The dielectric constants of samples were measured with dielectric analyzer (Broadband Dielectric Analyzer, Novocontrol GmbH, Germany) in a frequency range of $10^{-1}$ to $10^{7}$ Hz.

## Results and Discussion

TFA-functionalized MWNTs were employed for enhancing the mechanical and dielectric properties of PVDF/PU blends as dielectric elastomer actuator materials in this study, where TFA was acted as the dielectric fillers. Firstly to confirm the synthesis of TFA-functionalized MWNTs, Raman spectroscopic measurements were performed. Figure 2 shows Raman spectra for pristine and TFA-functionalized MWNTs. There are seen two characteristic peaks at 1575 $cm^{-1}$ (G band) and 1350 $cm^{-1}$ (D band) [14] for both pristine and functionalized MWNTs in the Raman spectra. The D band is corresponded to the defect sites in the hexagonal framework of MWNTs due to the disorder induced by $sp^3$ hybridization, whereas G band indicates a presence of ordered $sp^2$ hybridization. The band intensity ratio ($I_D/I_G$) between the D and G peaks can be used as a measure of a degree of functionalization of MWNTs [15]. From the Raman spectra, the intensity ratio of $I_D/I_G$ of pristine MWNTs and TFA-MWNTs were obtained

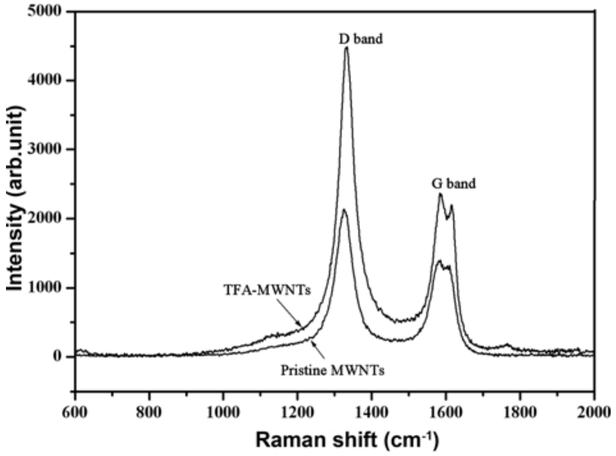

**Figure 2.** Raman spectra of pristine and functionalized MWNTs.

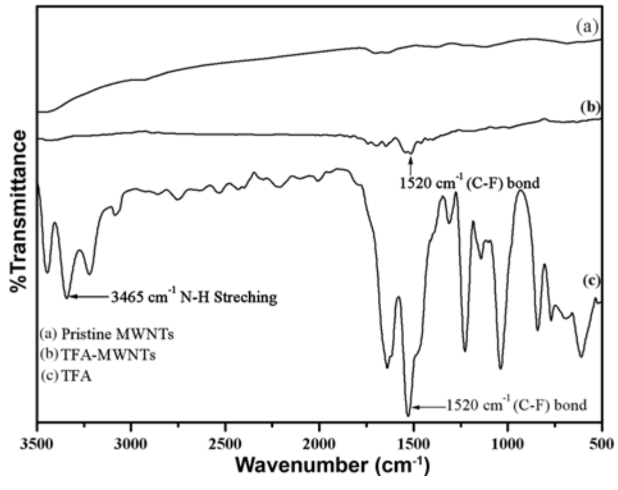

**Figure 3.** FT-IR spectra of TFA, pristine and functionalized MWNTs.

as 1.51 and 1.89, respectively. It is due to the covalent functionalization of MWNTs by TFA molecules.

The functionalized MWNTs were further characterized by FT-IR spectroscopy as shown in Figure 3. After functionalization of MWNTs with TFA, a new peak appeared around 1520 cm$^{-1}$ corresponding to C-F stretching [16]. It indicates the presence of 3,4,5-trifluorophenyl groups covalently bonded on MWNTs. In addition, IR spectra of TFA-MWNTs also showed absence of two peaks around 1300 cm$^{-1}$ and 3400 cm$^{-1}$ corresponding to C-N stretching and N-H stretching, respectively, confirming the complete reaction of TFA and MWNTs.

SEM and TEM images were obtained for the pristine and functionalized MWNTs as shown in Figure 4 and 5. TEM image of the pristine MWNTs indicates that surfaces of nanotubes are smooth and clean, whereas the functionalized MWNTs show some roughness due to the covalently bonded TFA chains on the MWNTs. Further from thermogravimetric curves shown in Figure 6, it can be seen that the TFA molecules are well functionalized on MWNTs by comparing the residue of pristine and functionalized MWNTs at 700 °C. The large difference in the residue between the pristine MWNTs and TFA-MWNTs at high temperature supports the amount of functionalized TFA molecules on MWNTs. Figure 7 shows the cross-sectional FE-SEM images of the nanocomposite films prepared by cutting the films in liquid nitrogen. It is seen that the TFA-MWNTs are uniformly dispersed in the polymer matrix. It may be due to some kind of interaction such as hydrogen bonding between TFA and polymer chains. However, it was difficult to confirm the IR peak from the measured IR spectra due to the very weak IR intensity of MWNTs.

Figure 8 shows the stress-strain curves of nanocomposites

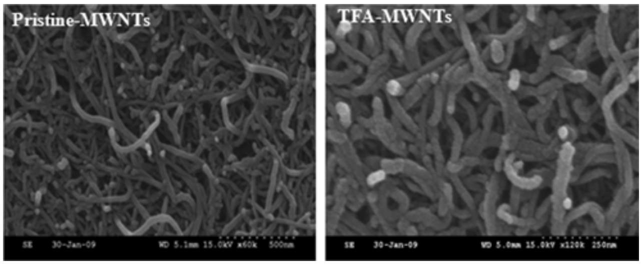

**Figure 4.** FE-SEM images of pristine and functionalized MWNTs.

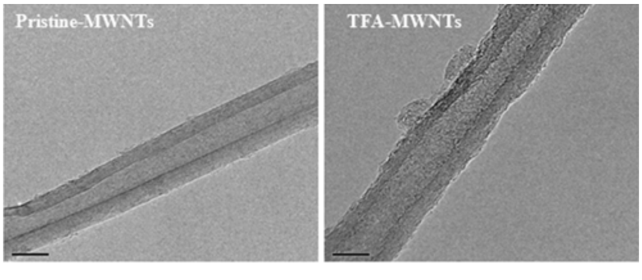

**Figure 5.** TEM images of pristine and functionalized MWNTs.

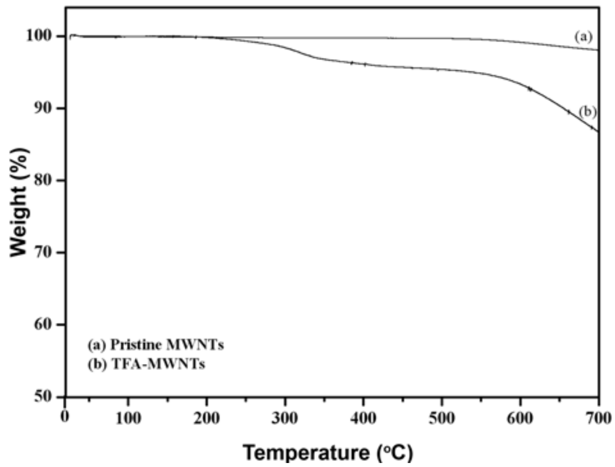

**Figure 6.** Thermogravimetric curves of pristine and functionalized MWNTs.

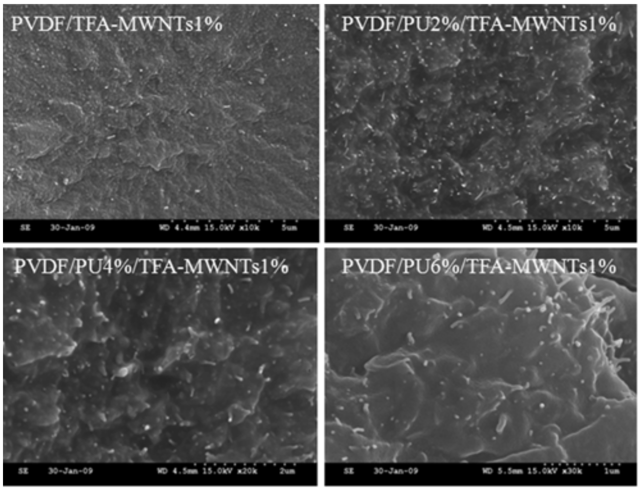

**Figure 7.** FE-SEM images of PVDF/TFA-MWNTs and PVDF/TFA/PU/TFA-MWNTs nanocomposites with different PU content.

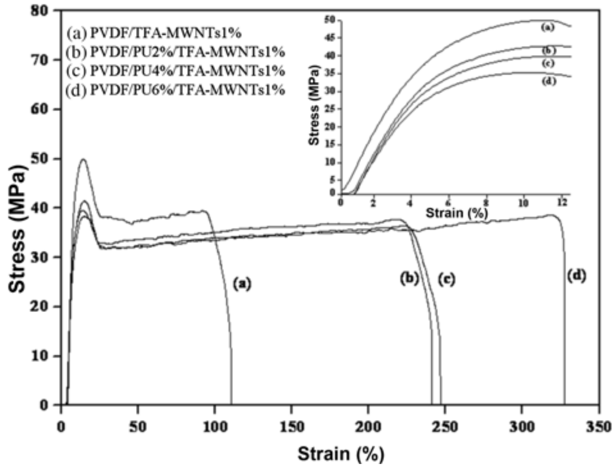

**Figure 8.** Strain-stress curves of PVDF/PU/TFA-MWNTs nanocomposites with different PU content.

**Table 2.** Mechanical properties of nanocomposites

| Sample | Breaking stress (MPa) | Elongation-at-break (%) | Modulus (MPa) | Yield stress (MPa) | Yield strain (%) |
|---|---|---|---|---|---|
| PVDF/TFA-MWNTs1% | 39.3 | 110 | 627 | 50.1 | 14.1 |
| PVDF/PU2%/TFA-MWNTs1% | 37.7 | 240 | 424 | 41.4 | 15.0 |
| PVDF/PU4%/TFA-MWNTs1% | 36.4 | 247 | 400 | 39.5 | 14.1 |
| PVDF/PU6%/TFA-MWNTs1% | 37.5 | 327 | 382 | 38.3 | 14.9 |

with different blend ratio of PVDF/PU/MWNTs. The PVDF nanocomposite of 1 wt% TFA-MWNTs content exhibits an elongation-at-break of 110 % with a yield point at 14 % elongation. However, an addition of PU of 2 to 6 wt% to the PVDF resulted in increasing their elongation-at-break dominantly without losing their tensile strength largely (Table 2). In case of nanocomposite including 6 wt% PU, the large elongation-at-break of 327 % was obtained, which must be interesting. It means that an addition of only a little PU to the PVDF/MWNTs nanocomposites can enhance the elongation-at-breaking of the samples highly. Moreover the modulus of nanocomposites deceases largely with the PU content, indicating the enhanced flexibility as the actuator materials. For example, the modulus of nanocomposite with 6 % PU exhibits decreases a half of the nanocomposite without PU. The yield stress was also a little suppressed with increasing the PU content. The enhanced elongation-at-break of nanocomposites with the incorporation of a little PU chains is regarded to be due to a contribution of PU chains as a lubricating agent [17]. It may be important for application of PVDF/PU/TFA-MWNTs nanocomposites as the dielectric elastomer actuator materials because the highly stretchable and soft properties are required for the dielectric elastomer actuators [18].

The dielectric constants of the nanocomposites were measured as a function of frequency for PVDF/MWNTs and PVDF/PU/MWNTs samples as shown in Figures 9 and 10.

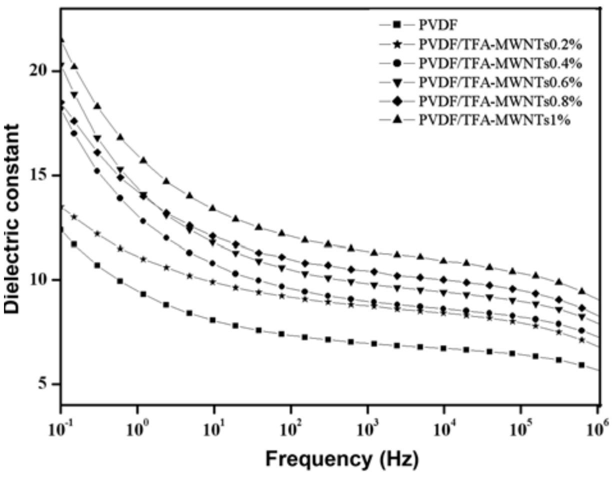

**Figure 9.** Dielectric constant of the PVDF/TFA-MWNTs nanocomposites with different TFA-MWNTs as a function of frequency.

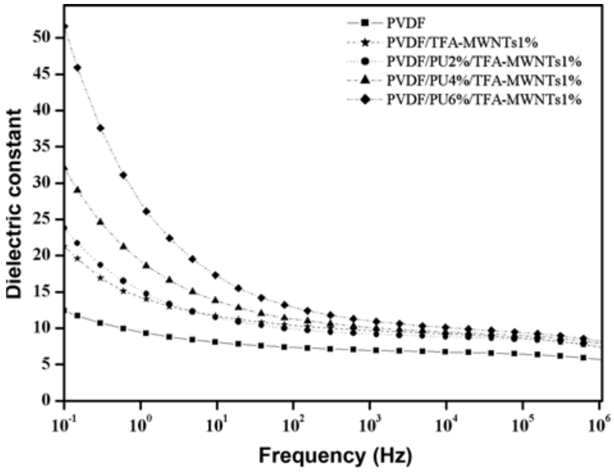

**Figure 10.** Dielectric constant of nanocomposites with different PU content as a function of frequency.

Figure 9 exhibits that the dielectric constant of PVDF samples increases with an increase of TFA-MWNTs content. It is due to the increase of TFA-MWNTs content having high dielectric TFA molecules. It is also seen from Figure 10 that the dielectric constant of the PVDF/MWNTs nanocomposites increases with increasing the PU content, and decreased with increasing the frequency from $10^{-1}$ to $10^{6}$ Hz. Since the dielectric constants of pure PVDF and PU are 8-13 and 0.6-1.2, respectively [19,20], it is very interesting that an incorporation of a small PU to PVDF/MWNTs increases their dielectric constants from 23 to 51 at $10^{-1}$ Hz. It is due to the presence of PU chains as a lubricant agent which can make the polar chain rotation of polymers easier. So it is sure that the incorporation of PU and TFA-MWNTs is very effective for enhancing the mechanical and dielectric properties of samples. It suggests that the polymer blend nanocomposites can be an alternative method for preparation of dielectric elastomer actuator materials.

## Conclusion

After MWNTs functionalization with TFA molecules, PVDF/PU/TFA-MWNTs nanocomposites were prepared and their mechanical and dielectric properties were investigated. The functionalization of MWNTs by fluorinated molecules of TFA increased the dielectric properties and dispersion of

MWNTs in the PVDF matrix. The mechanical properties of PVDF/MWNTs nanocomposites such as elongation-at-breaking were improved dominantly with an addition of only a few PU content. As a result, the incorporation of PU and TFA-MWNTs was very effective for enhancing the mechanical and dielectric properties of PVDF samples. It suggests that the polymer blend nanocomposites can be an alternative method for preparation of dielectric elastomer actuator materials.

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