

## 탄소나노튜브와 Poly(vinylidene fluoride)/Poly(vinyl acetate) 블렌드의 복합재료

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### Composites of Carbon Nanotubes with the Blend of Poly(vinylidene fluoride)/Poly(vinyl acetate)

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**Abstract:** Poly(vinylidene fluoride)/poly(vinyl acetate)/carbon nanotubes, PVDF/PVAc/CNT, composite films were prepared at various compositions via a solution casting method. The amorphous PVAc formed a miscible blend with PVDF and drastically improved dispersion of CNT in PVDF/CNT composites. Combination of ductile PVAc and rigid CNT had favorable effects on mechanical properties of PVDF. The elongation of PVDF increased from 8% to 300% with addition of 40 wt% PVAc and 0.5 wt% CNT and the modulus at 1.5 wt% CNT was almost 2.3 fold of that of the neat PVDF while retaining high ductility and tensile strength. XRD and FTIR results showed that CNT favored formation of  $\beta$ -crystalline phase in PVDF. Also DSC results showed that the addition of CNT resulted in higher melting temperatures,  $T_m$ , and higher crystallinity. Electrical conductivity of the composite films increased sharply by addition of only 1 wt% CNT that attributed to development of CNT network morphology in PVDF/PVAc matrix.

**Keywords:** carbon nanotube, poly(vinylidene fluoride), poly(vinyl acetate), nanocomposite.

## Introduction

Poly(vinylidene fluoride) (PVDF) has attracted much attention due to piezoelectric properties along with good chemical and ionizing radiation resistance and high mechanical strength. These properties of PVDF make it useful in a wide range of applications such as motion sensors, audio devices, batteries, high voltage and power sources, motors and reduction of vibrations.<sup>1-4</sup> PVDF is a semi crystalline polymer and could crystallize in various crystalline forms. Its normal crystalline form is called  $\alpha$  that in certain conditions could transform to  $\beta$  form which is of interest for piezoelectric properties.<sup>5</sup> In  $\beta$ -crystalline form fluorine and hydrogen atoms are on opposite sides of the polymer backbone forming a net non-zero dipole moment. The presence of dipoles makes PVDF a good piezoelectric polymer.<sup>2</sup> Several studies have been made on the effects of carbon nanotube (CNT) on crystalline structure of

PVDF in search for obtaining higher  $\beta$ -crystalline content.<sup>6-9</sup> A major challenge has been the difficulty in uniform dispersion of CNT within PVDF matrix. Some reports have shown that CNT containing carbonyl-group could homogeneously disperse in PVDF because of strong interactions between the fluorine atoms of PVDF and the carbonyl groups at the surface of CNT. Manna and Nandi<sup>10</sup> produced ester-functionalized CNTs that possessed grafted -C=O groups on the surface of CNTs and then incorporated the modified CNTs in PVDF via solution casting. They claimed that purely  $\beta$ -crystalline form was obtained at 1 wt% modified CNT while a mixture of  $\alpha$  and  $\beta$  forms developed at lower CNT content.

On the other hand it has been reported that  $\beta$ -crystals can form more easily from the melt in miscible blends of PVDF with amorphous polymers such as poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc).<sup>8,11-13</sup> Indeed, neat PVDF is crystallized mainly in  $\alpha$ -crystals from the melt and addition of a considerable amount of PMMA or PVAc to PVDF drastically reduces rate of  $\alpha$ -melt-crystallization and favors formation of  $\beta$ -crystalline form.

PVAc is a ductile polymer which forms miscible blend with

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PVDF due to a dipole-dipole interaction between  $-\text{CH}_2\text{-CF}_2$ - and  $-\text{C}=\text{O}$  groups.<sup>11,13,14</sup> Meanwhile CNT is well dispersed in PVAc and small amount of CNT remarkably reduces resistivity of PVAc.<sup>15,16</sup> Thus it is interesting to explore the combined effects of PVAc and CNT in solution-cast crystallization of PVDF. In this paper we investigate the role of PVAc in the state of CNT dispersion within PVDF and look at various aspects of the composites of CNT with PVDF/PVAc blends prepared by solution casting in terms of crystalline structure, mechanical and electrical properties.

## Experimental

**Materials.** Poly(vinylidene fluoride) was Hylar 460 from Solvay Co. (density of  $1.76 \text{ g/cm}^3$ ). Multi-walled CNT or MWCNT (diameter of  $10\text{--}20 \text{ nm}$ , length of  $\sim 30 \mu\text{m}$  and purity of  $\sim 95 \text{ wt}\%$ ) was from Chinese Neutrino Co.. Poly(vinyl acetate) was obtained from Sigma-Aldrich with a weight-average molecular weight of  $140000 \text{ g/mol}$ . *N,N*-dimethyl formamide (DMF) solvent was from Merck.

**Sample Preparation.** PVDF/CNT composite films were prepared via solution casting method. PVDF was dissolved in DMF (4 wt%) under magnetic stirring for 2 h at  $70 \text{ }^\circ\text{C}$ . Pre-determined amount of neat CNT was dispersed in DMF (0.1% w/v) by applying ultra-sonication for 1 h. Then PVAc was added to the dispersed CNT in DMF and stirred for an hour and then sonicated for another hour until PVAc was thoroughly dissolved. Then the prepared PVDF solution was mixed with CNT/PVAc solution in desired proportions and stirred to obtain a good dispersion of CNT in PVDF/PVAc solution. Finally, PVDF/PVAc/CNT films were cast by evaporation of the solvent on flat dishes at  $70 \text{ }^\circ\text{C}$  for 24 h in an oven. Then the films were dried in a vacuum oven at  $70 \text{ }^\circ\text{C}$  for another 24 h. The concentration of CNT in the films of PVDF/PVAc/CNT composites were fixed at 0.5, 1, 1.5, 2 and 3 wt% and that of PVAc at 30 and 40 wt%. The composite with 40 wt% PVAc and 1.5 wt% CNT was denoted as PVDF/40PVAc/1.5CNT so that the weight percent of PVDF would be 58.5. A solution-cast sample of neat PVDF was also prepared.

**Characterization.** The state of dispersion of CNT nanotubes within PVDF/PVAc matrix was observed by a scanning electron microscope (SEM). The composite films were fractured in liquid nitrogen and the fractured surface was observed. X-ray diffraction (XRD) were carried out in the range of  $2\theta=5^\circ\text{--}40^\circ$  at a scanning rate of  $2^\circ/\text{min}$  using a STOE D-64295 instrument ( $\lambda=0.154 \text{ nm}$  and nickel-filtered  $\text{CuK}\alpha$  radiation).

Melting behavior of the neat PVDF and PVDF/PVAc/CNT composite films was investigated by a Perkin Elmer Pyris 1 differential scanning calorimeter (DSC). DSC thermograms were obtained under nitrogen gas atmosphere in the temperature range of  $50\text{--}200 \text{ }^\circ\text{C}$  at a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ . The percent of crystallinity,  $X_c$ , was calculated directly from measurement of melting enthalpy ( $\Delta H_m$ ) and using the following relation:

$$X_c = \frac{\Delta H_m}{\phi \Delta H_0} \times 100$$

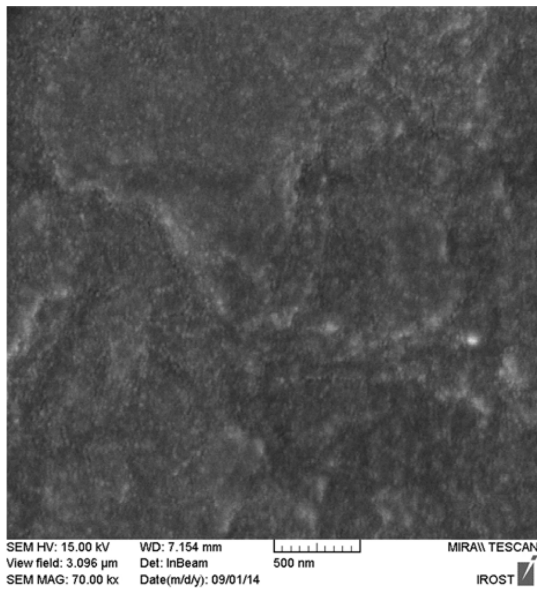
where  $\Delta H_0=104.6 \text{ J/g}$  is the enthalpy of fusion of 100% crystalline PVDF,<sup>7</sup>  $\phi$ , is the mass fraction of PVDF in the composite. Fourier transform infrared spectroscopy (FTIR) spectra were carried out on ABB BOMEM MB SERIES spectrometer. The tensile properties (tensile modulus, strength and elongation) of the composite films were measured at a tension speed of  $1 \text{ cm}/\text{min}$  using  $1 \text{ cm} \times 10 \text{ cm}$  rectangular films. The tensile modulus was measured at initial 2% elongation. Electrical resistance of the composites was measured by a 5 kV high electrical resistance tester using a Megger model BM 25 instrument. The reciprocal of the measured electrical resistivity (ohm.cm) renders electrical conductivity in siemens per cm.

## Results and Discussion

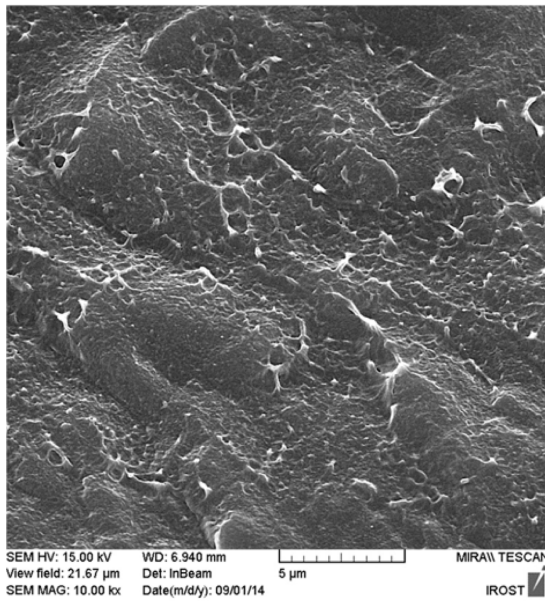
**Morphology.** SEM images of fractured surfaces of PVDF/40PVAc/CNT composites are shown in Figure 1. The carbon nanotubes are observed whiter than the matrix and exhibit somewhat network morphology (Figure 1(b)). It appears that carbon nanotubes are homogeneously dispersed within the PVDF matrix.

**Crystalline Structure Analysis by XRD and FTIR.** Figure 2 shows X-ray diffraction of PVDF and PVDF/40 PVAc/1.5CNT composite. The PVDF diffraction peaks located at  $2\theta=17.6^\circ$  (100),  $18.5^\circ$  (020),  $19.8^\circ$  (021),  $26.52^\circ$  (111), and  $39^\circ$  (002) correspond to the  $\alpha$ -crystalline phase and the peaks appeared at  $2\theta=20.3^\circ$  and  $36.6^\circ$  corresponding to the (110)/(200) and (101)/(020)  $\beta$ -crystalline phase.<sup>6,17</sup> As shown the XRD pattern of solvent-cast PVDF film indicates that the neat PVDF consists mainly of  $\alpha$ -crystals. However, the peaks at  $2\theta=20.3^\circ$  and  $36.6^\circ$  associated with  $\beta$ -crystalline form emerged more obvious in the composites while most of the diffraction peaks of the  $\alpha$ -crystalline phase appeared less intense.

From FTIR spectra it is also possible to analyze the crystalline phases of PVDF. The infrared spectra of neat PVDF,



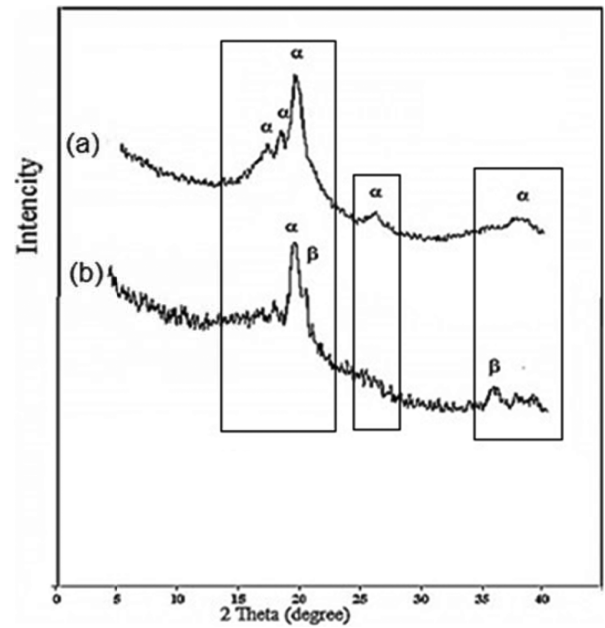
(a)



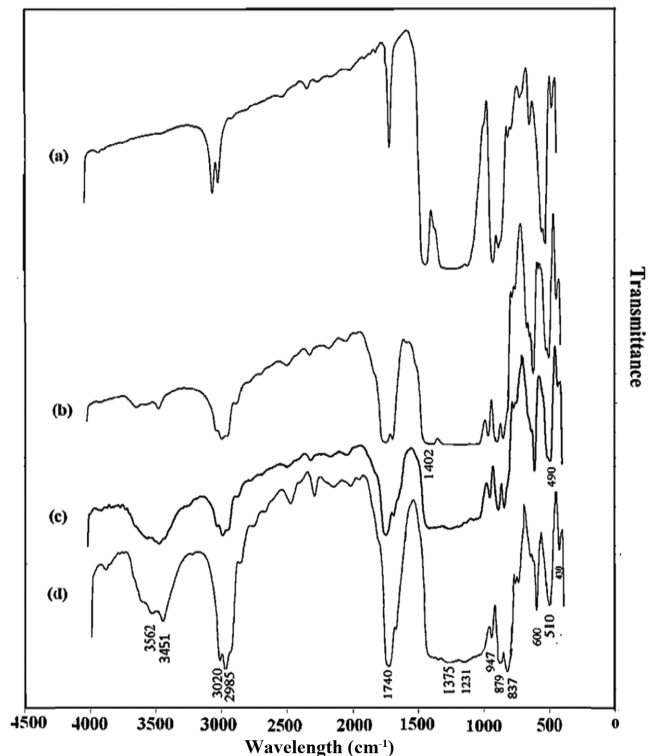
(b)

**Figure 1.** SEM images of PVDF/40PVAc/CNT composite at (a) 1 wt%; (b) 2 wt% CNT.

PVDF/40PVAc blend and the composites are shown in Figure 3. The neat PVDF shows both  $\alpha$  phase peaks (490 and  $1402\text{ cm}^{-1}$ ) and weak  $\beta$  characteristic peaks ( $600$  and  $837\text{ cm}^{-1}$ ).<sup>7</sup> It is readily seen that the peak at  $600\text{ cm}^{-1}$  of  $\beta$  phase increased in PVDF/PVAc blend and the composites while the peak at  $1402\text{ cm}^{-1}$  of  $\alpha$  phase decreased. The bands at  $947$  and  $1740\text{ cm}^{-1}$  are ascribed to C-CH<sub>3</sub> and C=O groups of PVAc respectively.

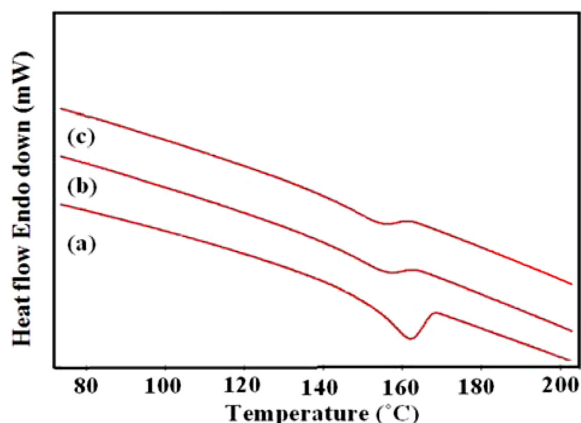


**Figure 2.** XRD of (a) PVDF; (b) PVDF/40 PVAc/1.5CNT.



**Figure 3.** FTIR spectra of (a) PVDF; (b) PVDF/40PVAc; (c) PVDF/40PVAc/1CNT; (d) PVDF/40 PVAc/1.5CNT.

**Thermal Analysis.** DSC curves of PVDF, PVDF/PVAc/CNT films are shown in Figure 4. The melting temperatures ( $T_m$ ) and crystallinity ( $X_c$ ) obtained from the DSC measure-



**Figure 4.** DSC curves of (a) pure PVDF; (b) PVDF/30PVAc/1CNT; (c) PVDF/40PVAc/1CNT.

**Table 1. DSC Results of Pure PVDF and PVDF/PVAc/CNT Composites**

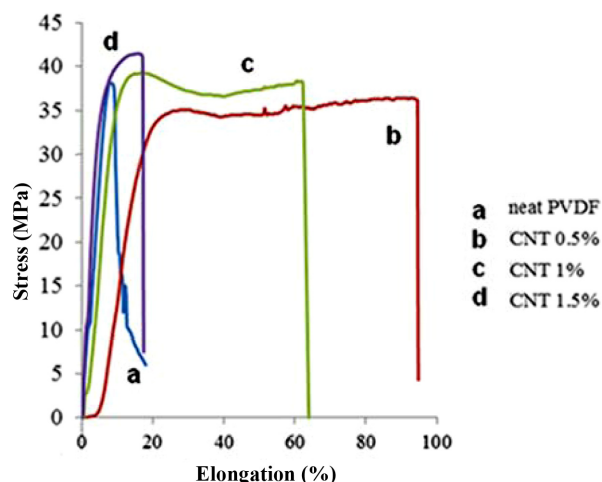
	$T_m$ (°C)	$X_c$ (%)
PVDF	158	28.5
PVDF/30PVAc/1CNT	156	21.6
PVDF/40PVAc/1CNT	153.6	16.5
PVDF/40PVAc/0.5CNT	151	16.0
PVDF/40PVAc/2CNT	157.4	21.4
PVDF/40PVAc/3CNT	160	23.2

ments are tabulated in Table 1.

It was found that  $T_m$  of the neat PVDF at 158 °C decreased down to 156 °C and 153.6 °C with addition of 30 wt% and 40 wt% PVAc respectively. Also crystallinity of PVDF decreased accordingly indicating good miscibility between semi-crystalline PVDF and amorphous PVAc. On the other hand  $T_m$  and crystallinity of PVDF/40PVAc increased significantly with addition of CNT arising from strong interaction between acetate groups in PVAc and hydroxyl group on the surface of CNT. Thus miscibility of PVDF and PVAc on one hand and strong interaction between PVAc and CNT on the other hand led to intimate dispersion of CNT within PVDF. The shift in the melting temperature of PVDF/40PVAc/0.5 CNT at 151.1 °C to higher temperatures upon further addition of CNT suggested increase in  $\beta$  crystalline phase of PVDF which was

**Table 2. Stress-Strain Data of PVDF/30PVAc/CNT Composites**

	Neat PVDF	0.5 wt% CNT	1 wt% CNT	1.5 wt% CNT
Tensile modulus (MPa)	500	370	490	1140
Elongation at break (%)	8	93	60	15
Yield stress (MPa)	38	35	39	41



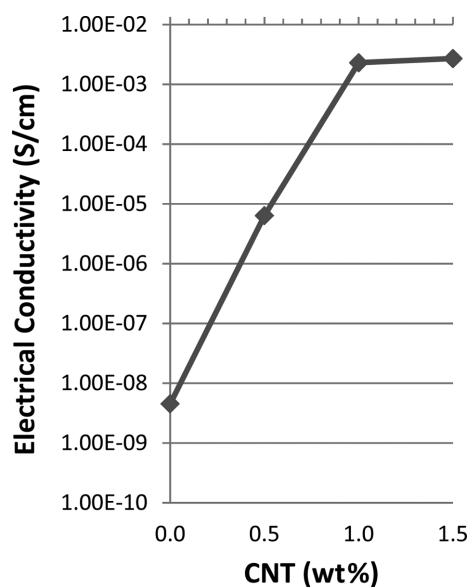
**Figure 5.** Stress strain curves of PVDF/30PVAc/CNT composites.

**Table 3. Comparison of the Mechanical Properties of PVDF/30PVAc/0.5CNT and PVDF/40PVAc/0.5CNT Composites**

	30% PVAc	40% PVAc
Young modulus (MPa)	370	320
Elongation at break (%)	93	308
Yield stress (MPa)	35	34.8

in agreement with XRD results. It should be noted that the  $\beta$  crystalline phase of PVDF has all-trans conformations and can pack more compactly in the crystal lattice giving a higher melting temperature than the  $\alpha$  phase with trans-gauche chain conformation. Also the increase in crystallinity of PVDF with increasing CNT content suggested that CNT could serve as a nucleation agent for crystallization of PVDF.<sup>18</sup>

**Mechanical Properties.** The stress-strain curves of PVDF/30PVAc/CNT composites at various contents of CNT are presented in Figure 5 and the measured values of modulus, tensile strength and elongation are depicted in Table 2. Also the effect of PVAc content on the mechanical properties of the composites at a fixed CNT concentration of 0.5 wt% is depicted in Table 3. There was a large gain in ductility along with only small loss in modulus and essentially no change in yield stress as PVAc content increased from 30 to 40 wt%, a further evidence for miscibility of PVDF and PVAc.



**Figure 6.** Electrical conductivity of PVDF/30PVAc/CNT composites.

While addition of 30 wt% PVAc resulted in ductility of PVDF and rendered large elongations at break, CNT acted as an effective reinforcement and increased the modulus and tensile strength. For the composite with 0.5 wt% CNT, PVAc played a dominant role in ductility and elongation increased drastically with only small loss in tensile strength and the modulus. The effect of CNT became more prominent at higher contents so that tensile strength and modulus increased with moderate loss in elongation. The increase in modulus at 1.5 wt% CNT was particularly large along with higher ductility and strength over those of neat PVDF.

**Electrical Conductivity.** Electrical conductivity of PVDF/30PVAc/CNT composites as a function of CNT content is plotted in Figure 6. A percolation behaviour was observed with the percolation threshold of around 1 wt%. Beyond this limit, conductivity increases slowly with the increase of the CNT content. The conductivity of PVDF/30PVAc films increased sharply from  $4.5 \times 10^{-9}$  to  $6.37 \times 10^{-6}$  S/cm by addition of only 0.5 wt% CNT reaching a value of  $2.3 \times 10^{-3}$  S/cm at 1 wt% CNT. Further addition of CNT up to 1.5 wt% had essentially little effect. The sharp increase in electrical conductivity at 1 wt% CNT is closely corresponds with CNT network morphology as shown in Figure 1. Kim *et al.*<sup>17</sup> recently reported PVDF/CNT composites without any surface modification of CNT and achieved extremely low electrical conductivity of about  $10^{-9}$  S/cm at 1 wt% CNT. Other researchers<sup>10</sup> also have shown formation of network morphology in PVDF/function-

alized-CNT composite at 1 wt% CNT. They oxidized the surface of CNT with strong acids in order to create C=O groups on CNT surface followed by laborious treatments in anticipation of strong interactions between C=O groups created on the surface of CNT and CF<sub>2</sub> groups of PVDF. Choi *et al.*<sup>15</sup> reported an increased electrical conductivity of about  $3 \times 10^{-8}$  S/cm for PVAc/CNT composite at 0.5 wt% CNT compared to  $5 \times 10^{-14}$  S/m for neat PVAc arising from uniform dispersion of CNT within PVAc shown with TEM images. Thus PVAc is not a conducting material and has no contribution to conductivity of PVDF. However CNT has strong affinity with PVAc and could readily disperse within PVAc matrix. Therefore the enhanced conductivity of PVDF/30PVAc/CNT arises from better dispersion of CNT in PVDF matrix through presence of PVAc.

## Conclusions

Poly(vinylidene fluoride)/poly(vinyl acetate)/carbon nanotubes composite films were made by solution casting method. It was demonstrated that PVAc assisted good dispersion of CNT in PVDF. While addition of CNT to PVDF increased the degree of crystallinity and also melting point of PVDF, PVAc had inverse effect on  $T_m$ . The increase in  $T_m$  by addition of CNT arises mainly by formation of  $\beta$  crystalline phase at the expense of  $\alpha$  form. Again CNT and PVAc had opposing effect on mechanical properties. Higher modulus and tensile strength achieved at low concentrations of CNT with relatively low elongation at break. On the other hand PVAc increased drastically the elongation at break with somewhat decrease in modulus and strength. As a result the combination of CNT and PVAc in PVDF matrix produced favorable mechanical properties. The elongation at break increases from 7.98% to 308% with addition of 40 wt% PVAc and 0.5 wt% CNT. High electrical conductivity obtained with addition of CNT so that at a concentration of only 1 wt% CNT the conductivity increased by 6 orders of magnitude. Therefore this investigation offers a conducting and high performance composite.

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