# THERMAL AND ELECTROCHEMICAL PROPERTIES OF POLYVINYLIDENE FLOURIDE, FUMED ALUMINUM OXIDE, & SINGLE WALLED CARBON NANOTUBE NANOCOMPOSITES FOR SUPERCAPACITOR APPLICATIONS

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## ABSTRACT

The effect of dispersing single walled carbon nanotubes and fumed alumina in a polyvinylidene fluoride matrix was carried out to identify the thermal and electrical properties for flexible supercapacitor electrode applications. Addition of CNTs helped improve the polymer's conductive and charge storage capabilities. Characterization was carried out to understand the thermal characteristics of the nanocomposites using TGA and DSC which indicated a lowering in thermal stability upon addition of the nanofillers. Electrochemical tests were also conducted in the form of cyclic voltammetry and electrochemical impedance spectroscopy using 1M $H_2SO_4$ electrolyte, yielding specific gravimetric capacitance values close to 72.88 F/g. Results also identified the improvement in specific capacitance of the composite upon addition of very low (1wt%) of fumed alumina.

**Keywords:** Supercapacitors, polyvinylidene fluoride, fumed aluminum oxide, carbon nanotube, energy storage

## 1. INTRODUCTION

Flexible electronic storage devices are fast becoming the path forward in a world governed by energy drawing mobile devices which constantly are in need of replenishment. With battery technology being pushed to its limits, another candidate for energy storage arises in supercapacitors. Supercapacitors (SCs) have progressed over the recent past to being researched and developed to replace Li-ion batteries due to their incredibly high power-densities, charge cyclability, lifespan, and overall ease, as well as speed at which they can be charged over a wider range of temperatures. However, the limitations currently faced include low storage capacities and fast discharging rates. To address these shortcomings, a vast amount of research and funding have been channeled towards developing new materials and methods.

The effect of dispersing fumed alumina (high surface area aluminum oxide) as well as single walled carbon nanotubes with polyvinylidene fluoride was carried out in this study. The aim was to produce a conductive polymer composite for the purpose of charge storage capabilities for the development of supercapacitor electrode material. Improving/synthesizing SC material with high

surface to volume ratio, porosity, and electrical conductivity are key to overcoming the limitations currently faced. Graphene sheets are widely popular in most literature with this regard as it satisfies most of the required criteria [1].

The use of PVDF as a binder has been proven to be an effective polymer to suspend activated carbon with low internal resistance. As a result, for the purpose of this study, PVDF was used as the matrix for the SWCNTs, which are themselves highly conductive and possess charge holding capacity [2, 3].

# 2. EXPERIMENTATION

## 2.1 Materials

Polyvinylidene fluoride (PVDF) and single wall carbon nanotubes (SWCNTs) were provided by ATEN Industries LLC. Highly dispersed fumed aluminum oxide ($Al_2O_3$) under the product name AEROXIDE ® Alu C was provided by Evonik Industries. n,n-Dimethylformamide (DMF), ACS Reagent Grade was purchased from Right Price Chemicals and used as the solvent for dispersions carried out in this system.

## 2.2 Method

For the synthesis of the polymer composites, all solute masses were kept at 2g in total. Neat PVDF films with 0 wt% of nanofillers were initially created by dispersing the polymer powder in DMF via mechanical solution mixing in stepwise additions at room temperature. Varying wt% of fumed alumina and SWCNTs (1%, 5%, 10%, 50% respectively) were systematically varied alone with PVDF, as well as in combination with each other in the PVDF matrix. These combinations were carried out to study the effect of the nanofillers on the polymer. Each nanofiller (according to the respective wt%) was dispersed individually in DMF solvent under probe sonication and mechanical stirring at 5°C for around 45 min.

Once a uniform dispersion was visually obtained under the time frame, the contents were carefully poured into a premixed solution of PVDF/DMF in a beaker under slow stirring to blend the polymer and nanofillers together for around 8 hours until a viscous slurry was formed. Thin films of each slurry were coated using an MTI vacuum assisted film coater (coated at 0.5mm wet thickness) over a Teflon sheet and cured using the heater attachment set at around 45°C overnight until all visible solvent had completely dried out. The cured polymer composite films with thicknesses of around 0.03mm were simply peeled off the Teflon to be tested.

## 2.3 Characterization

The effect of the addition of fumed alumina and/or SWCNTs on the thermal characteristics of the polymer such as degradation and melting temperatures, enthalpy of melting, and degree of crystallinity were studied via thermogravimetric analysis and differential scanning calorimetry using TA Instruments' Q50 and Q20 respectively. TGA and DSC were carried out on each sample

with a ramping rate of 5°C/min starting from room temperature to 600°C and 450°C respectively under an inert nitrogen atmosphere. The melting peaks were observed for shifts and used to calculate the degree of crystallinity ($\chi_c$) using 100% crystalline PVDF heat of fusion ($\Delta H_o$) of 105J/g according to the formula [6]:

$$\chi_c = \frac{\Delta H_m}{99\% \times \Delta H_o} \times 100\% \quad [1]$$

Electrochemical testing for charge storage in terms of calculating capacitance was carried out by a series of cyclic voltammetry, ranging from scan rates of 5, 10, 25, 50, & 100mV/s in 1mol $H_2SO_4$ as the electrolyte from 0V to 1V. Electro chemical impedance was also measured for the samples from a frequency of 1MHz to 0.01Hz against an open circuit potential of 1V. These were all carried out on a Gamry Reference 3000 potentiostat using a Ag/AgCl reference electrode.

## 3. RESULTS & DISCUSSION

Thermogravimetric analysis of the samples indicated, that upon increasing the wt% addition of either fumed alumina or SWCNTs alone, the temperature at which the degradation of the polymer composite began was reduced.

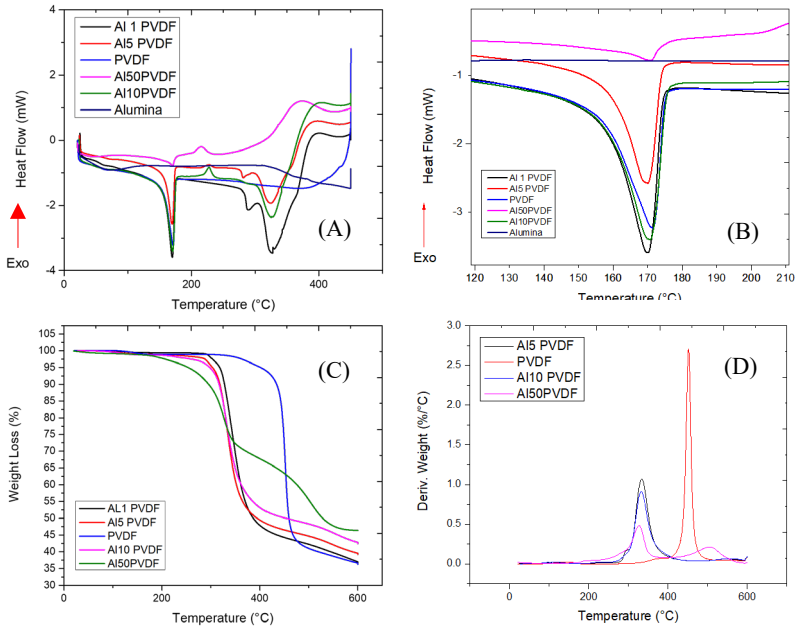


Figure 1. (A) DSC curve of PVDF with varying wt% of aluminum oxide carried out from room temperature to 450°C under nitrogen atmosphere. (B) Zoomed in portion of the DSC melting peaks. (C) TGA curve run from room temperature to 600°C under nitrogen atmosphere. (D) DTG curve.

This depreciation in thermal stability was also observed in the combinatorial wt% addition of both SWCNTs and fumed alumina, thus indicating the lowering of the thermal stability of the system upon addition of these nanofillers.

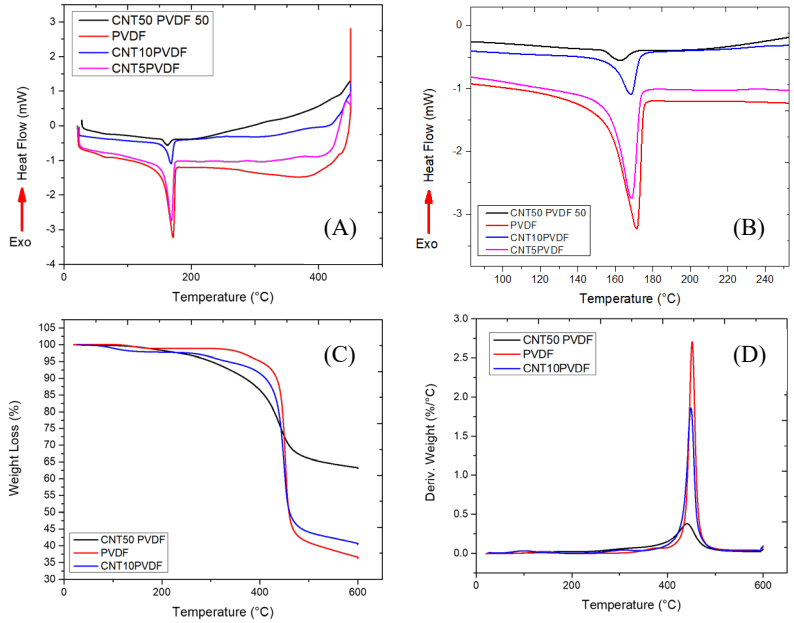


Figure 2. (A) DSC curve of PVDF with varying wt% of single wall carbon nanotubes carried out from room temperature to 450°C under nitrogen atmosphere. (B) Zoomed in portion of the DSC melting peaks. (C) TGA curve run from room temperature to 600°C under nitrogen atmosphere. (D) DTG curve

The TGA graphs in figure1C indicate that neat PVDF begins to degrade close to 450°C. The derivative weight loss curve in figure 2D shows an interesting trend with the addition of only SWCNTs in PVDF, shifting the neat PVDF peak at 452°C to as much as 440°C at 50 wt% loading. However, this shift (figure 1D) is much more prominent in the fumed alumina PVDF nanocomposite, reducing from 452°C to 327°C at 50 wt% loading.

As can be seen from the results in table 1, the addition of fumed alumina doesn't have a considerable decrease in the melting point temperature of the PVDF system. Nevertheless, its melting point temperature is inversely proportional upon the addition of alumina. The enthalpy of melting is also seen to decrease upon added loading of alumina into the system, with the lowest enthalpy of melting observed at highest loading.

Addition of SWCNTs also decrease the melting temperature of the neat PVDF system, but more considerably - close to a decrease of almost 9°C with a 50 wt% loading. This also resulted in the drop of enthalpy of melting by about 86.0%.

An interesting exothermic peak is observed in alumina based PVDF nanocomposites in figure 1A and figure 3A after the melting peaks between 200°C to 240°C. The shift in the peaks of combined alumina SWCNT PVDF nanocomposites are also observed, but less shifted towards lower temperatures than variants of the polymer with only alumina nanofiller present. The DTG curves in figure 1D indicate the most apparent weight losses occurring at relatively lower temperatures in the composites containing only alumina (around 340°C) as compared to those containing only SWCNT (around 450°C). The higher the content of alumina the lower the DTG peak height and temperature at which it was present.

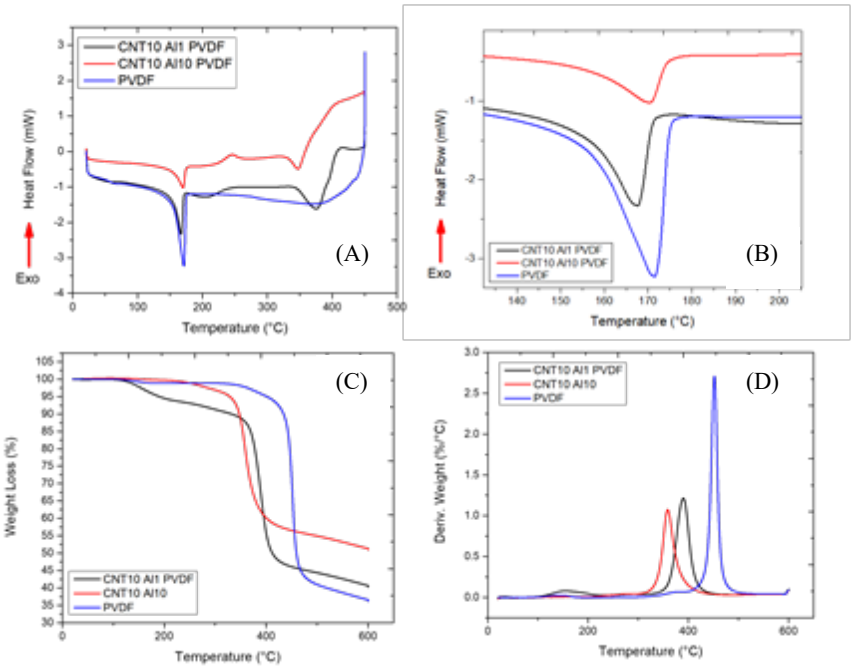


Figure 3. (A) DSC curve of PVDF with varying wt% of single wall carbon nanotubes and fumed alumina carried out from room temperature to 450°C under nitrogen atmosphere. (B) Zoomed in portion of the DSC melting peaks. (C) TGA curve run from room temperature to 600°C under nitrogen atmosphere. (D) DTG curve.

Using equation [1] the degrees of crystallization are displayed in Table 1.0.

Table 1. Enthalpy of melting $\Delta H_m$ and degree of crystallinity $\chi_C$ of nanocomposite samples.

| **Composite** | **Tm (°C)** | **$\Delta H_0$ (heat of fusion of 100% crystalline PVDF) (J/g)** | **$\Delta H_m$ (J/g)** | **$\chi_C$ (%)** |
|---|---|---|---|---|
| Neat PVDF | 171.6 | 105 | 53.2 | 51.3 |
| 5 wt% SWCNT | 168.9 | 105 | 56.4 | 54.3 |
| 10 wt% SWCNT | 168.6 | 105 | 54.7 | 52.7 |

| | | | | |
|---|---|---|---|---|
| 50 wt% SWCNT | 162.7 | 105 | 7.4 | 7.1 |
| 1 wt% $Al_2O_3$ | 170.2 | 105 | 57.0 | 54.9 |
| 5 wt% $Al_2O_3$ | 170.0 | 105 | 38.0 | 36.6 |
| 10 wt% $Al_2O_3$ | 170.8 | 105 | 52.1 | 50.1 |
| 50 wt% $Al_2O_3$ | 171.0 | 105 | 21.5 | 20.7 |
| 1 wt% SWCNT, 1 wt% $Al_2O_3$ | 172.6 | 105 | 64.6 | 62.2 |
| 5 wt% SWCNT, 1 wt% $Al_2O_3$ | 169.7 | 105 | 47.2 | 45.4 |
| 1 wt% SWCNT, 5 wt% $Al_2O_3$ | 169.5 | 105 | 54.2 | 52.2 |
| 10 wt% SWCNT, 1 wt% $Al_2O_3$ | 167.7 | 105 | 40.7 | 39.2 |
| 1 wt% SWCNT, 10 wt% $Al_2O_3$ | 170.3 | 105 | 50.4 | 48.5 |
| 5 wt% SWCNT, 5 wt% $Al_2O_3$ | 168.3 | 105 | 45.5 | 43.8 |
| 10 wt% SWCNT, 10 wt% $Al_2O_3$ | 170.4 | 105 | 37.4 | 36.0 |

Table 1 shows an overall decrease in degree of crystallinity upon addition of the fillers, except for a marked increase in the sample that contains 1 wt% CNT, 1 wt% $Al_2O_3$ ($\chi_C$ =62.2%). The lowest degree of crystallinity is observed at 50 wt% CNT. This lowering of the polymer composite's thermal stability can be related to a study done by Ma, J., Haque, R. I., & Larsen [6] who proposed that the addition of the nano fillers also bring with it contaminants of metal catalyst by-products, as well as the presence of defects in the SWCNT which may account for this decrease in thermal stability as compared to neat PVDF. Furthermore, according to the same study, the impact of nano fibers was mentioned to have improved the degree of crystallization, where in this case the presence of very low wt% of fumed alumina or SWCNT, either together or separately have contributed to do so.

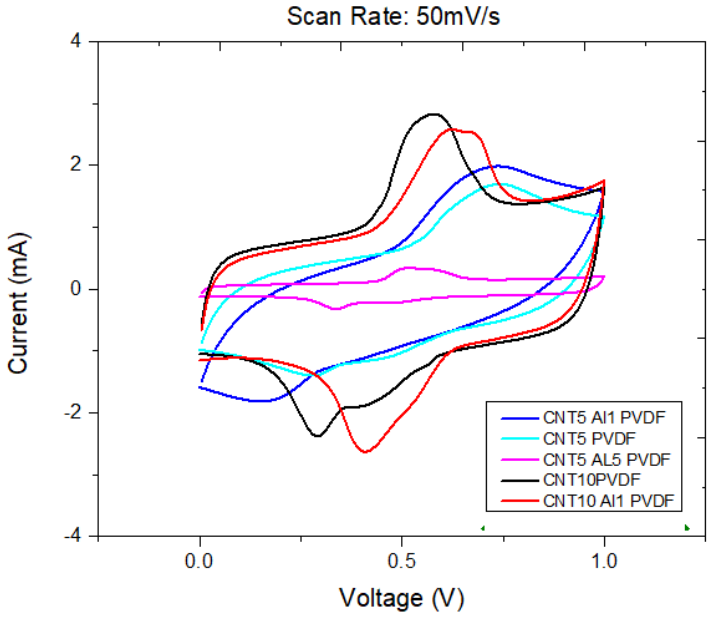


Figure 4. Cyclic voltammogram of nanocomposite samples carried out at 50mV/s scan rate in 1M $H_2SO_4$ at room temperature using a Ag/AgCl reference electrode.

The improvement of the capacitance as shown in the voltammogram in figure 4 is due to the highly conductive nature of carbon nanotubes and the porosity of the structure formed [3]. Higher loading of SWCNTs increases the conductive nature of the polymer, resulting in a higher capacitance value.

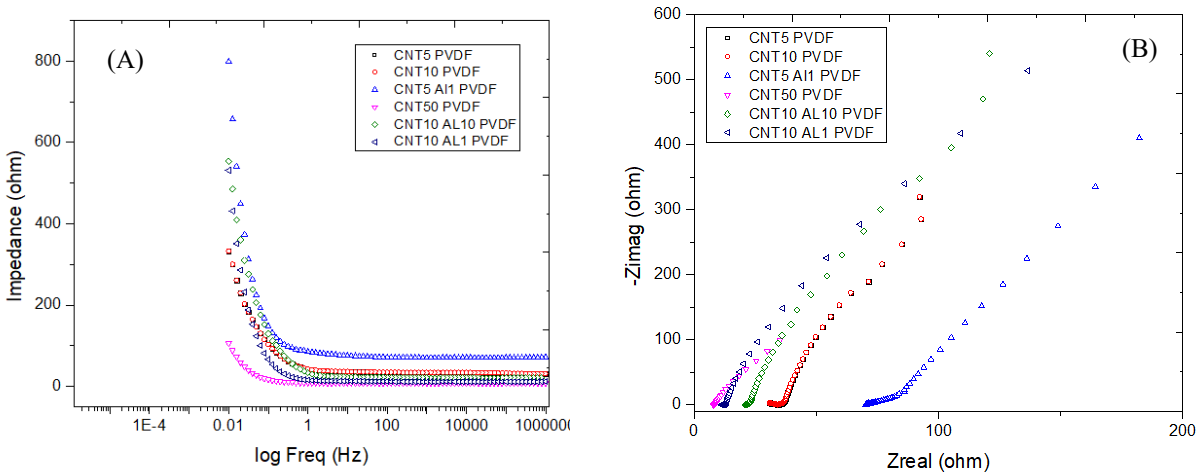


Figure 5. Electrochemical impedance spectroscopy showing (A) Bode plot and (B) Nyquist plot.

The results of gravimetric capacitance calculated using CV for a scan rate of 50mV/s are shown tabulated in Table 2 below.

Table 2. Gravimetric capacitance measured using cyclic voltammetry.

| **Composite** | **Specific Gravimetric Capacitance (F/g)** |
|---|---|
| 5 wt% SWCNT | 6.43 |
| 10 wt% SWCNT | 9.24 |
| 50 wt% SWCNT | 72.88 |
| 5 wt% SWCNT, 1 wt% $Al_2O_3$ | 8.8 |
| 5 wt% SWCNT, 5 wt% $Al_2O_3$ | 1.69 |
| 10 wt% SWCNT, 1 wt% $Al_2O_3$ | 12.04 |
| 10 wt% SWCNT, 10 wt% $Al_2O_3$ | 3.72 |

The CV curve in figure 4 shows a very visible increase in charge storage as the SWCNT loading is increased. The addition of alumina in the composite decreases the gravimetric capacitance but only at higher weight percentages. As observed, a 1 wt% addition of alumina in a SWCNT/PVDF composite improves the charge storage capability per gram compared with a PVDF composite having the same wt% of SWCNT alone.

The EIS curves of the Nyquist plot (figure 5B) show that increasing wt% of the SWCNTs results in a reduction of the resistance of the polymer with the electrolyte interface. The plot also gives a good demonstration of the pore resistance that impacts the diffusion resistance within the bulk of the material by running it at frequency ranges of 0.01Hz to 1MHz. At higher alumina loading it can be observed that a higher resistance is introduced, shifting the plot to the right. [5]

## 4. CONCLUSIONS

The addition of SWCNT into the PVDF polymer matrix was observed to improve the electrical conductivity of the composite systematically with increasing wt%. The gravimetric capacitance was improved significantly (upto 12 times) from a 6.4F/g at 5 wt% to 72.9F/g at 50 wt% loading of SWCNT. The fumed alumina was not observed to improve the charge storage capabilities of the polymer composite but did show a slight increase in the gravimetric capacitance for only a very small loading percentage (5wt% SWCNT 1%$Al_2O_3$ ) as compared to the polymer composite with the same loading of SWCNT (5 wt% CNT) – an improvement in gravimetric capacitance by 2.37F/g.

Addition of both the nano fillers did not improve the thermal stability of PVDF but reduced the onset of degradation temperature, with fumed alumina reducing it more than SWCNT of the same weight loading. In terms of a flexible and chemically resistant composite supercapacitor electrode material, this study shows that fumed alumina, SWCNT, PVDF can be used for charge storage applications. Effective results of these composite electrodes indicate them to be composed of a higher loading percentage of SWCNT and with very low percentage of alumina.

## 5. REFERENCES


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