

Flexible Conductive CNT/poly (vinyl chloride) Composite Thin Films with High Mechanical Strength and Thermal Stability

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Abstract: *The fabrication and characterization of ultrathin composite films of surfactant-wrapped CNT nanoflakes and poly (vinyl chloride) is described. Free-standing composite thin films were prepared by a simple solution blending, drop casting and annealing route. A significant enhancement in the mechanical properties of pure poly(vinyl chloride) films was obtained with a 2 wt.% loading of CNT, such as a 58% increase in Young's modulus and an almost 130% improvement of tensile strength. Thermal analysis of the composite films showed an increase in the glass transition temperature of the polymer, which confirms their enhanced thermal stability. The composite films had very low percolation threshold of 0.6 vol.% and showed a maximum electrical conductivity of 0.058 S/cm at 6.47 vol.% of the CNT loading.*

Keywords: Composite thin Films. CNT, CNT flakes, functionalized grapheme sheets, CNT/PVC

1. Introduction

Recently discovered planar 2D form of carbon known as CNT has become one of the most exciting materials today because of its unique properties [1]. Individual grapheme sheets show high values of thermal conductivity [2], Young's modulus [3], large surface area [4], ballistic transport on submicron scales and massless Dirac fermion charge carrier abilities [5,6]. These properties make CNT a promising material for using in many applications such as photovoltaic devices, sensors, transparent electrodes, super capacitors and conducting composites [4,7–12]. At present, carbon-based reinforcing materials employed in polymer composites are dominated by carbon nanotubes (CNT). But difficulty in dispersing CNT and high cost of production limits its widespread use. The present day challenge is to find an alternative for CNT and, CNT can be a suitable candidate because of its outstanding mechanical properties and ultra large interfacial surface area [3,4]. Incorporation of graphitic nanoflakes into elastomeric polymer matrix generates high performance composites with improved mechanical and functional properties [12–15]. Other interesting properties such as high dielectric permittivity and low percolation threshold have also been observed in CNT incorporated composites of poly (vinylidene fluoride) and polystyrene, respectively [16, 17]. Recently, CNT oxide (GO) has also been used as a filler in various polymer matrices, due to its hydrophilicity and ease of formation of stable colloidal suspensions [13,14]. Besides, functionalized grapheme sheets (FGS) are also employed as they provide better interactions with the host polymers compared to unmodified CNT or traditional expanded graphite (EG) [12]. Functional groups on the surface of CNT flakes can be modified to incorporate strong CNT – polymer interactions. In our current investigation, poly(vinyl chloride) (PVC) is chosen as the host polymer matrix, because of its wide range of applications, low cost, chemical stability, biocompatibility and sterilizability [18]. However, PVC has low thermal stability, which hinders some of its applications

[19]. The present day challenge is to introduce thermal stability along with high mechanical strength and electrical conductivity for PVC with the use of minimum amount of fillers.

Substantial amount of work has been carried out in the past few decades towards this goal [20–22]. Fillers such as clay [23, 24], wood flour [21], wood fibers [25], agricultural residues [26], cellulose whiskers [27] and calcium carbonate [28] were used to improve the thermal and mechanical stability of PVC. In order to improve the electrical conductivity, carbon black [29] and other conjugated polymers such as polyaniline (PANI) [30,31] and polypyrrole (PPy) [32] were incorporated in the PVC matrix. In recent times, CNT have also been identified as a suitable filler material for PVC [33]. Kevlar coated CNT used as additives to PVC resulted in composites with improved mechanical properties demonstrating up to 50 and 70% increase in tensile strength and Young's modulus, respectively at very low CNT loading [34]. Similarly, CNT grafted with styrene-maleic anhydride copolymers (SMA) was found to enhance the interaction with PVC matrix and both thermal and mechanical stabilities improved considerably [35]. But dispersion of CNT in organic solvents is a challenge, which is very critical for the preparation of polymer composites [13]. Moreover, no studies are available on the use of CNT as a filler material in PVC films. Herein, we have explored the use of surfactant stabilized soluble CNT nanoflakes [36] as reinforcing filler for PVC at a very low loading level. In order to have efficient reinforcement in polymer composites, it is important to have molecular level dispersion in the polymer matrix. In our case, both PVC and CNT sheets can be readily dispersed in N, N-dimethyl formamide (DMF) for solution blending, which will help to achieve molecular level dispersion.

2. Experimental

2.1 Materials and methods

Graphite powder, cetyltrimethyl ammonium bromide (CTAB) and PVC in powder form (Mw 120,000) were purchased from Sigma–Aldrich. Glacial acetic acid and DMF purchased from local suppliers were used as received. Milli-Q water was used for the washings.

2.2 Preparation of processable CNT nanoflakes

A few grams of graphite flakes were sonicated with 0.5 M CTAB solution in glacial acetic acid for several hours and the resultant solution was then heated at 100 °C for 48 h in N₂ atmosphere. Black powder obtained after centrifugation was washed with distilled water to remove the excess acid and CTAB. The resultant product formed stable dispersions in DMF [16].

2.3. Fabrication of CNT/PVC composite thin films

Liquid phase blending method was used to make all the composite thin films. PVC was dissolved in DMF. The graphene sheets dispersed in DMF were mixed with appropriate weight fractions of PVC solutions and sonicated for 2 h. The mixtures were then drop casted in glass cells and kept in an oven at 120 °C to evaporate the solvent slowly to get ultrathin CNT /PVC composite films. The films were peeled off from the cells and further annealed at 100 °C for 3 h to remove remaining traces of solvent.

2.4. Instrumentation

Atomic force microscopic (AFM) images were recorded using Agilent AFM with Pico plus molecular imaging system in the non-contact mode. Samples for AFM were prepared by spin coating a dilute suspension of CNT on freshly cleaved mica at a speed of 5000 rpm and then dried at room temperature. Field emission scanning electron microscopic (FESEM) images were recorded with JEOL JSM 6710 F field emission electron microscope. Thermal properties of the composites were studied by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was done using TA instrument 2960 with heating rate of 10 °C/min in N₂ atmosphere and DSC with TA instrument 2920 at heating rate 10 °C/min under N₂ at a flow rate of 90 mL/min. Powder X-ray pattern (XRD) was obtained with a D5005 Siemens X-ray diffractometer with Cu K α (1.5Å) radiation (40 kV, 40 mA). Raman spectra were recorded with Renishaw system 2000 with an excitation wavelength of 532 nm.

2.5. Mechanical characterization

A dynamic mechanical analyzer (DMA Q800, TA Instrument) was used for mechanical characterization of the composite thin films. Rectangular thin film strips of width 3mm was used for the tensile testing. The film strip was clamped on the tension clamp such that the specimen length was 10 mm. DMA controlled force mode was used with a preload force of 0.001 N. The temperature of the chamber was raised to 20 °C and was kept constant during force

ramping. The force was ramped at a rate of 0.01 N/min till the fracture occurred and the obtained mechanical properties were evaluated. For DMA, mult frequency-strain mode was utilized. A static load of 0.1 N was used and the amplitude of dynamic strain was kept constant at 0.1%. To find the influence of frequency, the specimen was held isothermally at 20 °C and deformed at the constant amplitude (strain 0.1%) over a range of frequencies and the mechanical properties were measured. To evaluate the thermal properties, the specimens were exposed to a series of increasing isothermal temperatures. At each temperature, the material was deformed at constant amplitude (strain 0.1%) over a frequency of 1 Hz and the subsequent mechanical properties were evaluated.

2.6. Electrical characterization

Film strip were accurately cut from the samples for conductivity measurements. Silver electrodes were fabricated at the end of these strips using a conductive silver pen (RS components). Tungsten probes with tip diameter 2.4 μm were used for the two probe conductivity studies. A source meter (Keithley 6430) was used for the current – voltage measurements, at room temperature. The volume fraction of CNT V_f was calculated according to the equation, $V_f = \frac{W_g q_p}{(W_g q_p + W_p q_g)}$, where W_g is the weight fraction of CNT and W_p the weight fraction of PVC [11]. Density of PVC (q_p) was taken as 1.37 gm/cc and the density of CNT (q_g) was taken as 2.2 gm/cc for calculations [11,13].

3. Results and Discussion

3.1. Characterization of CNT and CNT/PVC thin films

CNT nanoflakes used in this method were prepared by CTAB assisted exfoliation of the graphite described elsewhere [22]. Fig. 1A displays the tapping mode AFM image of graphene nanoflakes, deposited onto the mica sheets from DMF suspension. AFM image indicated that the flakes were very small with dimensions of the order of <1 μm. From the height profile (Fig. 1B), the thickness was found to be of the order of 1.2 nm. Average thickness of the flakes was found to be 1.18 nm, corresponding to 1–3 CNT layers. CNT/PVC composite thin films were prepared by a simple solution blending, drop casting and annealing route as described in the experimental section. The thickness of the films prepared was in the range of 5–7 μm. The dispersion state of graphene in PVC matrix was investigated using FESEM. Since the graphene flakes are small, it is hard to locate them. Fig. 1C shows SEM image of CNT/PVC film with 2 wt.% loading of CNT. The image shows that most of the graphene nanoflakes are well dispersed in the PVC matrix, with a few restacks. It also demonstrates the random dispersion of CNT in the 3D polymer network. It should be noted that CNT flakes tend to organize inside the polymer matrix and are well dispersed in the PVC. Fig. 1D shows one of the fractured ends of the film after mechanical testing, which reveals the stacked CNT flakes. The thicknesses of the flakes are increased due to the complete covering of flakes by the polymer medium. XRD and Raman spectroscopy have also been employed to evaluate the structure of the composites. But analyses of our composite samples were difficult because of the low X-ray

diffraction intensity of PVC [23] and low amounts of added CNT. XRD of pure CNT showed a broad peak in the region of 20–30° (Fig. S1). However, after dispersing CNT nanoflakes into the PVC (trace b in Fig. S1) matrix, no significant changes were observed. The Raman spectra of the 2 wt.% CNT/PVC composite films were generally similar to that of the surfactant stabilized CNT flakes, indicating the distribution of CNT flakes in the polymer matrix [38,39]. Signature features of CNT (D, G and 2D bands) were clearly seen in the 2 wt.% CNT/PVC composite films (Fig. S2).

3.2. Mechanical characterization of the CNT/PVC thin films

It was expected that incorporation of CNT nanoflakes in PVC matrix would enhance the mechanical properties of PVC, because of the strong interfacial adhesion. The mechanical performance of CNT/PVC composite films was significantly increased compared with pure PVC film. Representative stress strain curves for various weight fractions of CNT/PVC composite films are plotted in Fig. 2A. The slope of the curves increases with increasing the concentration of CNT content. The presence of CNT flakes in the PVC matrix offers resistance to the segmental movement of the polymer chains upon application of the tensile stress which led to enhancement in modulus. The corresponding Young's modulus values are shown in Fig. 2B. The addition of CNT flakes significantly increased the Young's modulus. For the composite film with 2 wt.% of CNT loading, Young's modulus increased to 2 GPa, corresponding to an increase of 58% (relative to the pure PVC film).

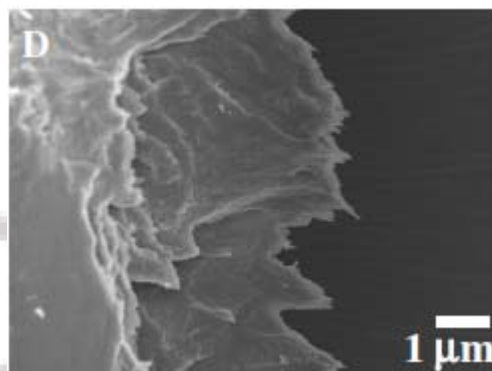
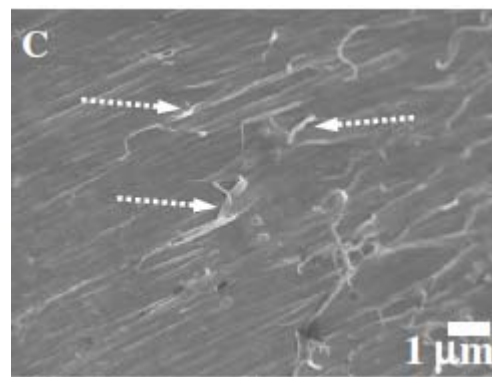


Figure 1 – (A) AFM image of the exfoliated CNT flakes, (B) height profile of one of the CNT flakes, (C) FESEM image of CNT/PVC composite thin film with concentration of CNT 2 wt.% and (D) FESEM image of the fractured end of the composite film after mechanical testing.

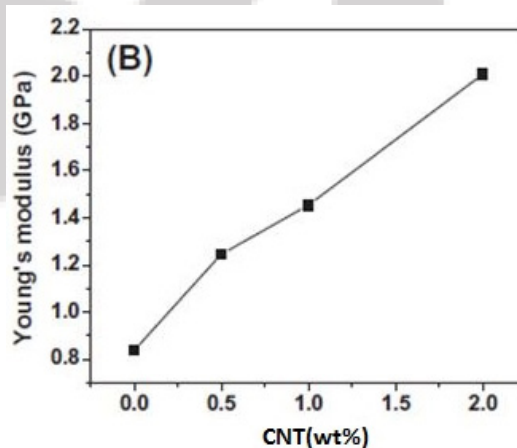
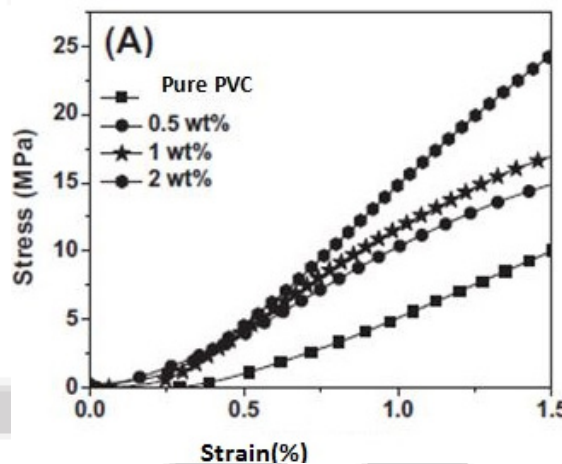
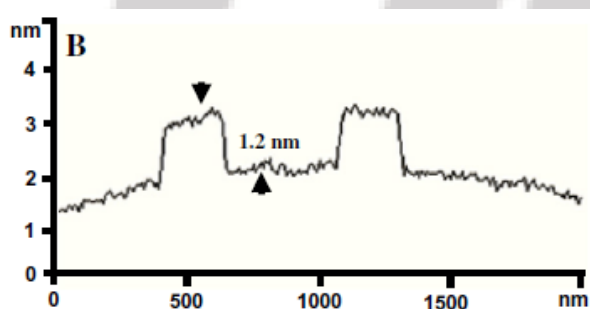
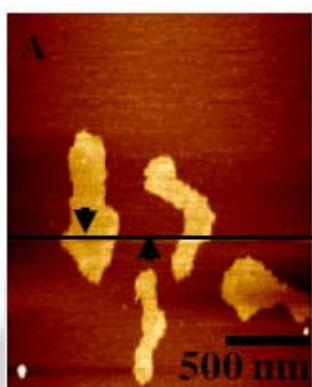


Figure 2: (A) Representative stress strain curves for various weight fractions of the CNT/PVC composite films

and (B) the calculated Young's modulus based on the slope of the elastic region.

The percentage elongation at breakage and the tensile strength of the CNT/PVC films are summarized in Fig. 3. It is obvious that the addition of CNT has a significant effect on the mechanical behavior of the pure PVC. The average value of percentage elongation decreased to 85% for 0.5 wt.% CNT loading from 124% for the pure PVC sample. However a further increase in the CNT loading significantly reduced the percentage elongation before the fracture (Fig. 3). This can be attributed to the interaction between CNT and the polymer matrix, which restricts the movement of polymer chains. On the other hand, tensile strength increases with increase in the CNT content. The average tensile strength for pure PVC thin film is 24 MPa. The strength gradually increased to 30 MPa for 1 wt.% and further to 55 MPa for 2 wt.% of CNT loading, which corresponds to an improvement of 130%. Further increase in the CNT content did not produce significant changes. When the CNT content was increased beyond 2 wt.%, the

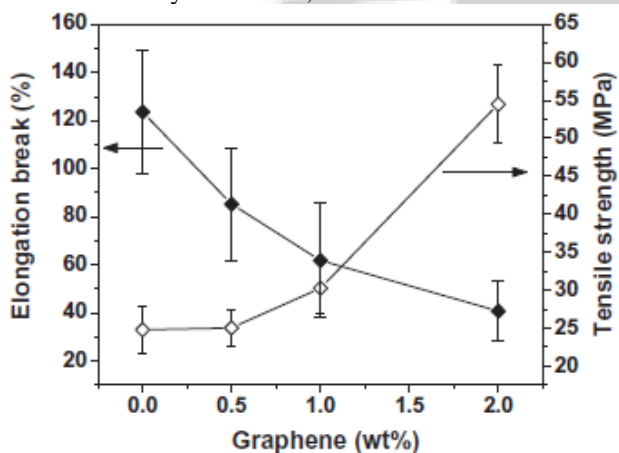


Figure 3: Mechanical properties of PVC thin films with different CNT loadings when stretched at the rate of 0.01 N/min at 20 °C.

tensile strength increase slightly from 55 to 56 MPa (with 5 wt.% loading). Besides, the change in value of elongation at break is also not very prominent (40% for 2 wt.% and 38% for 5 wt.% grapheme loading). It could be due to the restacking of CNT nanoflakes after a critical filler loading level. This offers no significant improvement in mechanical properties. This kind of behavior could be due to the restacking of CNT sheets after certain level of loading. Beyond this critical loading limit, tensile strength will not be significantly affected [13-18].

3.3. Electrical properties

The electrical properties of the exfoliated CNT have been investigated by preparing ultra thin composite films using a highly insulating PVC matrix. The electrical conductivity, σ of CNT/PVC composite thin films plotted as a function of volume percentage of CNT is shown in Fig. 4. The conductivity of pristine PVC thin film is less than 10^{-16} S/cm [18-22]. At a CNT content of about 0.025, 0.05 and 0.075 vol.%, the composite films did not show any measurable

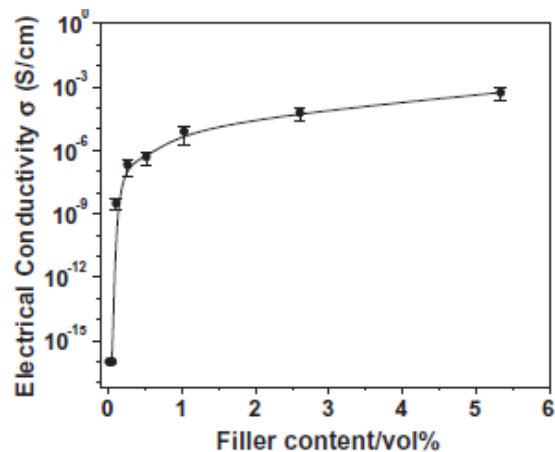


Figure 4: Graph showing the influence of exfoliated grapheme on the electrical conductivity of PVC.

values of conductivity. However at about 0.1 vol.%, a sharp increase in the conductivity was observed. A further increase in the volume fraction of CNT gave rise to a sharp increase in the conductivity (Fig. 4). At 0.12 vol.%, the conductivity was $3.19 \cdot 10^{-9}$ S/cm, whereas at 0.3 vol.% the conductivity increased to $2.14 \cdot 10^{-7}$ S/cm. Subsequent increase in concentration to 0.6 and 1.3 vol.% led to an increase of conductivity to $4.92 \cdot 10^{-7}$ S/cm and $7.81 \cdot 10^{-6}$ S/cm, respectively. A further increase in concentration levels up to 6 vol.% give only moderate rise in conductivity. From the graph, it can be clearly seen that there is a rapid increase in the conductivity at 0.6 vol.% of the filler content, which is the percolation threshold for the composite films. Thus, it is concluded that the conductivity increases drastically up to 0.6 vol.% of CNT, above which the rate of increase was minimum. The maximum conductivity observed was 0.058 S/cm, at 6.47 vol.% of the filler content which is 10 times higher than that of the single walled CNT/PVC composites [22-27].

4. Conclusions

Ultra thin composite films of CNT and PVC are fabricated and the mechanical, thermal and electrical properties are investigated. The composite thin films were prepared by a solution blending route in which the PVC was appropriately blended with CNT nanoflakes prepared by CTAB assisted exfoliation. Mechanical characterization of the thin films demonstrated increase in Young's modulus and ultimate tensile strength with very low CNT loading. Dynamic mechanical analysis showed fivefold increase in the storage modulus compared to pristine PVC films. Thermal stability was found to be improved to a greater extent with an increase in the glass transition temperature. The films were found to possess high electrical conductivity with a low percolation threshold of 0.6 vol.%. Composites using CNT is promising but the availability of processable CNT sheets in large quantities is crucial for its applications in composites.

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