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# Investigation of Structural, Electrical and Mechanical Behaviour of PPY/SWCNT/PVA Ternary Composites

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## Abstract

The nanocomposites of polypyrrole (PPy), single wall carbon nanotube (SWCNT) and polyvinyl alcohol (PVA) with different compositions were synthesized by the chemical oxidative polymerization and solution casting methods. The morphological and structural properties of the nanocomposites were investigated with the help of FTIR and SEM techniques. The Fourier transform infrared spectroscopy (FTIR) analysis showed that the addition of PPy/SWCNT nanocomposite into PVA created interaction within the composite structure. SEM images revealed that the incorporation of SWCNT significantly altered morphology of PPy and PVA. The PPy/SWCNT nanocomposites exhibit an enhanced electrical conductivity 0.746 $Scm^{-1}$ compared to $6.87 \times 10^{-3}$ $Scm^{-1}$ for pure PPy and $1.18 \times 10^{-15}$ $Scm^{-1}$ for neat PVA. However, the DC conductivity of PPy/SWCNT/PVA nanocomposite is found to drop a little giving a value of $2.44x10^{-4}$ $S/cm^{-1}$. PVA has been selected as the matrix for PPy/SWCNT nanocomposite in order to give mechanical stability to the PPy/SWCNT nanocomposites. The tensile strength study suggests that the incorporation of PVA makes it possible to cast the mechanically stable conducting film of the PPy/SWCNT/PVA ternary composite.

*Key words:* Polypyrrole; Single wall carbon nanotubes; Polyvinyl alcohol; conducting polymer; electrical conductivity; tensile strength.

## 1 Introduction

Conducting polymers are emerging as the suitable alternative to replace the metals in electronic industry because of their capability of withstanding high electric fields and low cost of fabrication. Conducting polymers exhibit significant level of electrical conductivity upon doping. They include polyacetylene, polyaniline, polypyrrole, polythiophene and polyphenylene etc., which have versatile promising applications in the field of energy storage[1], sensors[2], electronic and optical devices[3] and so on. Much research interests have been generated in the development of conducting polymers, which can be prepared either by chemical or electrochemical polymerization[4].

Non-processibility is one of the major problems with conducting polymers. Most of the conducting polymers are insoluble in common solvents and undergo degradation before reaching the melting point. Also they have poor mechanical strength and are environmentally unstable. Among all the conducting polymers, polypyrrole (PPy) has received much attention since the monomer pyrrole is easily oxidized, water soluble and commercially available. Although pyrrole is capable of producing conducting polymers with high electrical conductivity, environmental stability and good redox properties[5], still, it suffers from some drawbacks such as poor processibility and lacks essential mechanical properties. Efforts to overcome these drawbacks have led to numerous researches on the synthesis of polypyrrole by both electrochemical and chemical routes. Among them, a significant strategy to approach both high electrical conductivity and desirable mechanical properties is through preparing blends or composites of polypyrrole polymer with other insulating polymers having desirable mechanical properties[6,7]. Polymer matrices as host material such as polyvinyl chloride (PVC), poly (methyl methacrylate) (PMMA), and poly (vinyl alcohol) (PVA) have been used in order to increase the solubility as well as the mechanical strength of polypyrrole. Considering some advantages of poly(vinyl alcohol) (PVA) including its flexible molecular chains, high strength, good adhesion to electrodes and its ductile nature, some works on the synthesis and conductivity studies of PPy/PVA composites have been reported in the literature[8,9].

Carbon nanotubes (CNTs) are light, anisometric and conducting particles[10]. They are empty cylinders with diameters less than 100 nm and length on the micrometer scale and one of their features is their high surface to volume ratio. This combination of properties makes them ideal fillers to achieve light and conductive polymer composites which can be useful for electromagnetic shielding devices, antistatic plastics, packaging, *etc*. The conductivity of the composites is usually dominated by the inter-tube contacts which are more resistive than the CNTs. This is why it is expected that the conductivity of nanotube composites should strongly depend on the surface properties of CNTs and on the polymer confinement at the CNT interfaces. The introduction of CNTs into polymers can lead to improved mechanical properties, electrical and thermal conductivities.

This paper reports the synthesis and electrical conductivity studies of the PPy/SWCNT and PPy/SWCNT/PVA nanocomposites. Efforts have also been made during this study to prepare the optimal ternary blends of PPy/SWCNT/PVA in order to produce mechanically stable polymeric films which exhibit good electrical conductivity as well.

## 2 Experimental

The PPy and PPy/SWCNT composites were synthesized by chemical oxidation method using $FeCl_3$ as oxidant. The monomer pyrrole supplied by Sisco Research Laboratories Pvt. Ltd., Mumbai, India was distilled prior to use in this study. SWCNT supplied by Nanoshel, Delware, USA was used as supplied. Polyvinyl alcohol (MW: 27000) was supplied by Fluka. Distilled water was used as the solvent. Various composites of PPy/SWCNT were produced using 0.1, 0.2, 0.3, 0.4 and 0.5 mg of SWCNT. PPy/SWCNT/PVA composite films were successfully fabricated by solution casting.

For the synthesis of polypyrrole/single wall carbon nanotube (PPy/SWCNT) nanocomposites in aqueous medium, the carbon nanotube dispersion in aqueous medium was first prepared by adding known weight of SWCNT into known volume of distilled water under constant stirring. $FeCl_3.6H_2O$ was added to the dispersion after 20 mins in such a way that it would attain the required concentration.

Pyrrole (known volume) was then added into the dispersion under constant stirring at $5^oC$. Total volume of the reaction mixture was kept 50 ml. Gradual change of colour from light black to deep greenish-black indicates the formation of polypyrrole. This reaction mixture was then kept at $5^oC$ for 3 hours. The resulting black mass was filtered and then it was thoroughly washed with distilled water until it was completely free from $FeCl_3$. This process was repeated several times to remove all adhering substances. Finally, the product was washed with methanol to remove last traces of unreacted pyrrole and then it was dried at 40°C for 24 h to yield a very fine black powder. KBr press pelletizer was used for making pellets of PPy and PPy/SWCNT composites by using stainless steel mold. A pressure of 10 ton/cm$^2$ pressures was applied under vacuum for 15 minutes for making pellets.

For preparing the PPy/SWCNT/PVA ternary blends, 1 g PVA was dissolved thoroughly in 50 ml distilled water under constant stirring for 1 hour at $90^oC$ temperature. This mixture was then allowed to cool down to room temperature ($24^oC$) while the stirring of mixture was continued to ensure a homogenous composition. The PPy/SWCNT composites having various concentrations of SWCNT (0.1, 0.2, 0.3, 0.4 and 0.5 mg) were dissolved one by one subsequently in the aqueous solutions of PVA to obtain various ternary composites of PPy/SWCNT/PVA. Every mixture of ternary composite was further stirred for 30 minutes to ensure homogeneity.

The mixture was then poured in a casting glass mould and left at room temperature for 120 hours. The film was finally ready at the expiry of this time which was peeled off the casting glass plate and cut into pieces for characterization.

The infrared spectra of samples were recorded in wave-number range from 500 – 4000 cm$^{-1}$ using a Shimadzu FT-IR Spectrophotometer. The scanning electron microscope (SEM, model S-4700, Hitachi) was used to get the micrographs of samples. DC conductivity was measured with the help of four point probe method. Hioki impedance analyzer IM 3570 was used for measuring the AC conductivity of the samples. The mechanical properties were investigated using a Universal Materials Testing Machine (AGS-500ND). In the tensile test, load was increased at a rate of 50 mN/min. The samples were cut into pieces of 5 mm width and 50 mm length.

## 3 Results and Discussion

### *3.1 Fourier Transform Infrared Spectroscopy:*

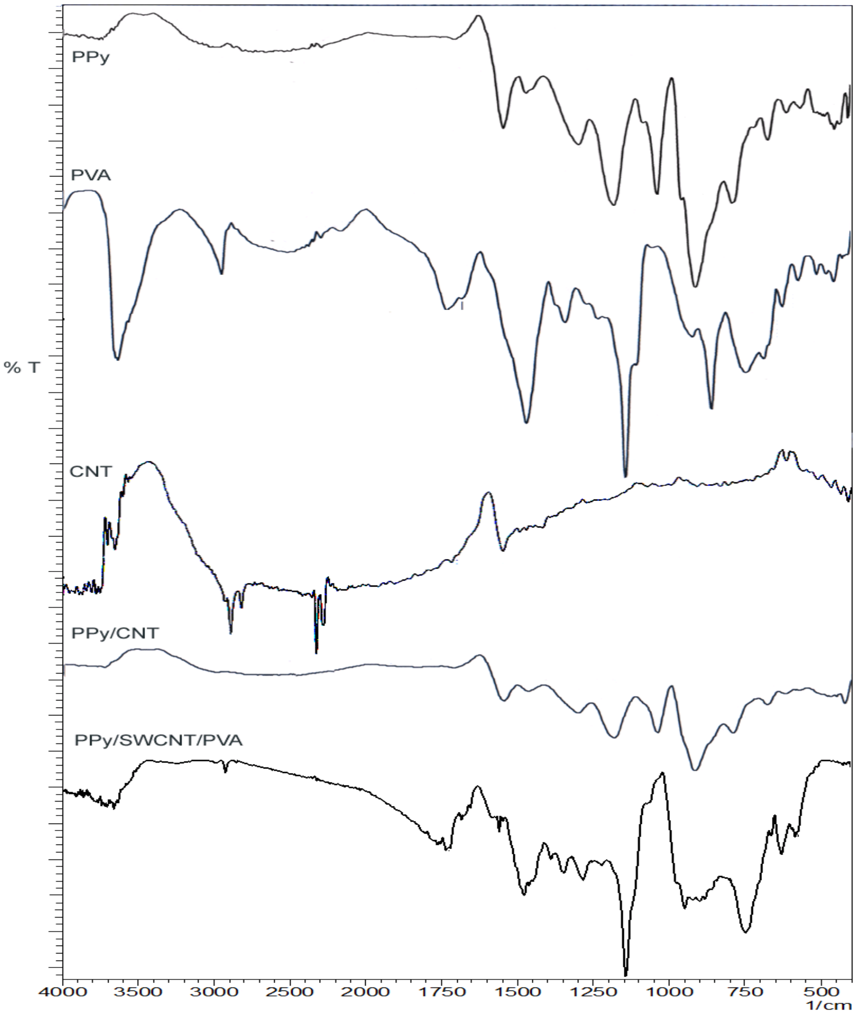

Fig. 1. The FTIR spectrograph of pure PPy, pure PVA, SWCNT and PPy/SWCNT, PPy/SWCNT/PVA composites

The FTIR spectrum of pure PPy, PVA and SWCNT as well as PPy/SWCNT and PPy/SWCNT/PVA composites are shown in figure 1. The band appearing in the region 3500-3700 $cm^{-1}$ of the ternary composite is due to N-H stretching frequency of an aromatic amine. Anions which typically form hydrogen bond with amine groups show variations in the intensity and shape of the NH band, thus indicating that the doping is higher in the sample. The peaks at 1560.46 and 1475.59 $cm^{-1}$ could be attributed to C–N and C–C asymmetric and symmetric ring-stretching, respectively. Additionally, the strong peaks near 1141.9 and 949 $cm^{-1}$ present the doping state of polypyrrole. The band at 2922.25 $cm^{-1}$ is due to $CH_2$ stretching. The shoulder observed at 1070 $cm^{-1}$ is due to symmetric and asymmetric C-O stretching vibrations of polyvinyl group, and the peak observed at 746.48 $cm^{-1}$ is due to the C-H bending.

### *3.2 Scanning Electron Microscopy :*

The scanning electron micrographs of various materials are shown in Figure 2. The PPy coating on SWCNT is very evident and this results into polymer coating of 150 nm in thickness. This is indicative of good interaction between SWCNT dopants and pyrrole monomer because SWCNT acted both as a dopant and also provided a large surface area for the polymerization process to take place. Surface morphology of PPy/SWCNT/PVA film shows relationship between adjacent particles and small group of particles. Figure exhibits better, porous, granular and globular surface morphology with very good uniformity and adhesiveness for synthesized film samples indicating their suitability for sensor applications.

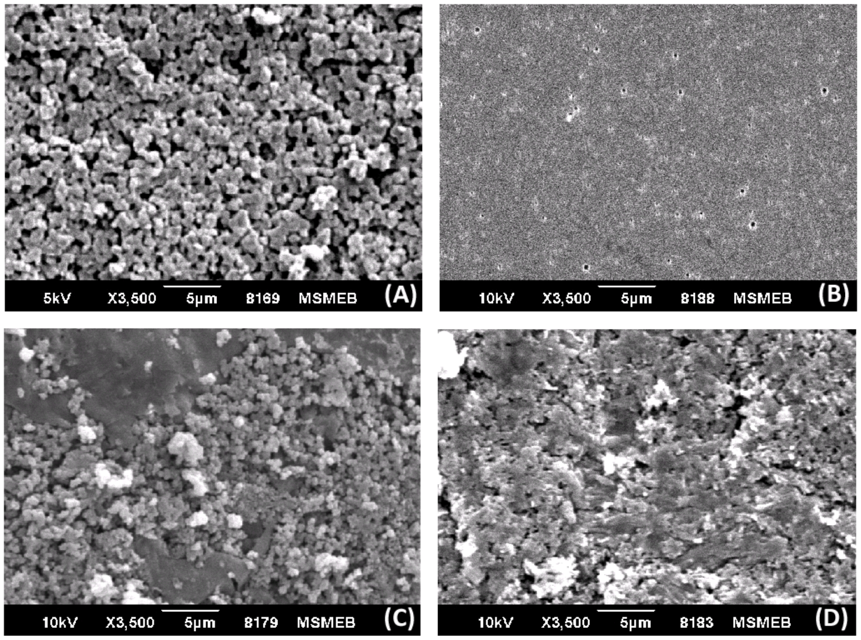

Fig. 2. The scanning electron micrographs of (A) Pure PPy (B) Pure PVA (C) PPy/SWCNT Composite (D) PPy/SWCNT/PVA composite

### *3.3 Electrical DC Conductivity :*

Fig. 3 (A) depicts conductivity of PPy/ SWCNT nanocomposites as a function of wt% of SWCNT in PPy. The conductivity is found to increase by increasing wt % of SWCNT in PPy. The maximum conductivity is observed to be 0.746 $Scm^{-1}$ for the PPy/ SWCNT composite having 0.5 wt% of SWCNT. This is a highly enhanced value of conductivity as compared to that of pure PPy, neat PVA, PPy/PVA and SWCNT/PVA samples. The DC conductivities of pure PPy and pure PVA measured with the help of four point probe method are found to be 0.068 $Scm^{-1}$ and $1.18\times10^{-15}$ $Scm^{-1}$, respectively. This suggests that nanotubes improve conductivity of the composite film by introducing a conductive network in polymer matrix. This may be due to the larger surface area of SWCNT that serves as a conducting bridge, connecting closely spaced but electrically isolated conducting domains of PPy and increasing the effective percolation[11]. This observation also suggests the possibility of modulating charge transport properties of the composite film by varying its composition. The combination of 99.5 wt % PPy and 0.5 wt % SWCNT is used for further studies. Addition of SWCNT beyond 0.5 wt % is avoided considering the economical and health related issues.

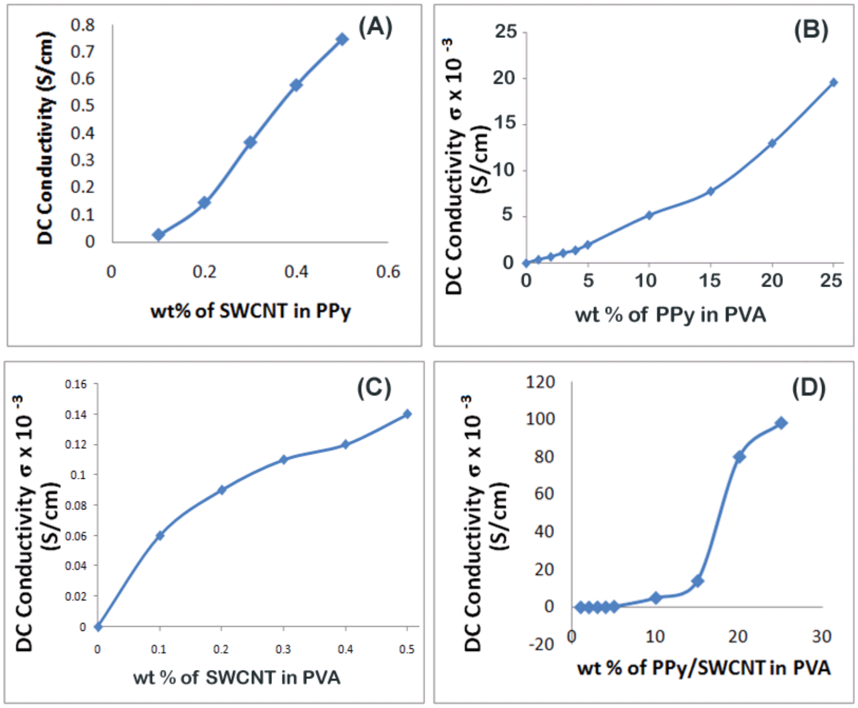

Fig. 3. (A)Variation of the DC Conductivity of PPy/SWCNT composite with respect to wt% of SWCNT in PPy (B) Variation of the DC Conductivity of PPy/SWCNT/PVA composite with respect to wt% of PPy/SWCNT in PVA

The variations of DC conductivities of PPy/PVA and SWCNT/PVA composites are shown in figures 3(B) and 3(C), respectively. The conductivities of these two composites are found increasing with increasing dopant (PPy in fig. 3(B) and SWCNT in fig. 3(C)) concentrations in PVA matrix but the order of conductivity is very much less as compared to that of PPy/SWCNT composite. On the other hand, these composites are exhibiting fairly higher order of conductivity when compared with that of pure PVA ($1.18 \times 10^{-15}$ $Scm^{-1}$). Fig. 3(D) shows the variation of DC conductivity of ternary PPy/SWCNT/PVA composite with respect to variation of PPy/SWCNT dopant in PVA matrix. The conductivity is found to increase with increasing dopant concentration giving a maximum value of $98 \times 10^{-3}$ $S/cm^{-1}$ for the 25 wt% of PPy/SWCNT dopant. This dopant is not added in higher wt % ratios as the homogeneous distribution of PPy/SWCNT is found to be missing in ternary composites having more than 25 wt % of PPy/SWCNT in PVA matrix. This non-homogeneous behavior is confirmed by the presence of lumps of PPy/SWCNT at various portions of the film of ternary composite. Though the conductivity of the ternary blend increases with increasing PPy/SWCNT content but the degree of conductivity is considerably dropped as compared to that of PPy/SWCNT composites. The conductivity of PPy/SWCNT/PVA composite can again be explained by considering the bridging action of nanotubes[12]. It has been reported that the microparticles are randomly oriented in pure PPy and the linkages among the polymer particles through grain boundaries are very poor, resulting in relatively lower conductivity[13].

The incorporation of single wall carbon nanotubes results in an improvement in the compactness of composite material. The change in compactness of composite becomes more significant by increasing wt% of SWCNT as a result of increasingly improved links between the grains. Coupling through the grain boundaries becomes stronger, which ultimately results in improvement in macroscopic conductivity. This effect in turn results in higher values of conductivity of PPy/SWCNT composites.

Bevaviour of the conducting PPy/SWCNT in PVA can be considered similar to that of metallic filler in a polymeric medium. The variation of logarithmic conductivity with respect to the weight percentage of PPy/SWCNT in PVA matrix is shown in Fig. 4 (A). The percolation theory[14] offers following expression to describe the dependence of the electrical conductivity on filler volume content in the $x > x_c$ region:

$$\sigma(x) = k(x-x_c)^t \qquad (1)$$

where k is a constant, $x_c$ is percolation threshold and t is a critical exponent whose value generally falls in the range of 1.6–1.9[14-15]. However, often, this formal equation does not correspond to experimental results for conductive composites having fillers. This is due to the fact that this equation does not take account of specific system structure peculiarities (particle shape, polymer– filler interaction, existence of contact phenomena on the particle–particle boundary, influence of preparation conditions on the volume distribution of conductive particles)[14,16].

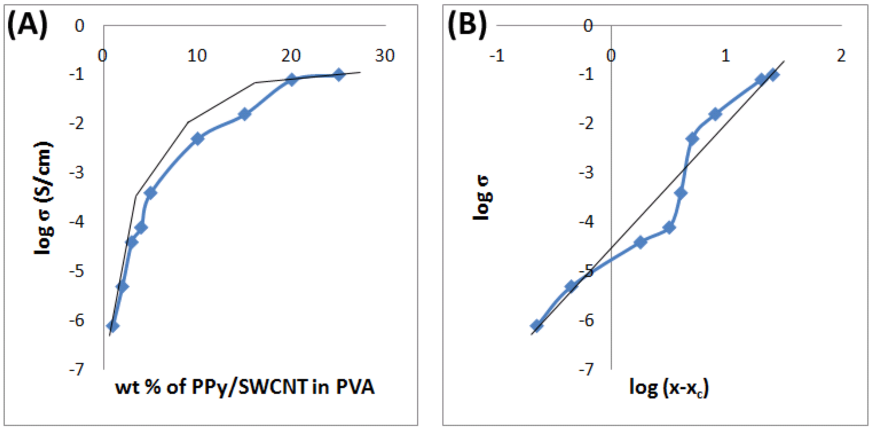

Fig. 4. (A) Logarithmic variation of DC conductivity of PPy/SWCNT/PVA composites with respect to the varying weight percentage of PPy/SWCNT in PVA matrix (B) Plot of log σ versus log (x-$x_c$) for calculating $x_c$ and t

The best fitted values for $x_c$ and t come out to be 3.18x10$^{-4}$ and 2.62±0.2, respectively from figures 4(A) and 4 (B). It is seen that the value of t is greater than the standard value for three dimensional percolating systems. Similar behaviour of t is also found in other conducting blends PANI–PVA[17]. Various models have been proposed by researchers[15-16, 18-19] to explain the enhanced value of t. They suggest that the increment in t is due to different mechanisms like contribution of tunnelling conductivity or complex structure of conductive cluster skeleton with the presence of necks, nodes and blobs. The conductive filler concentration has also been reported[20] to vary the value of t. This suggests that PPy/SWCNT composite is acting almost like metallic filler in PVA matrix.

### *3.4 Electrical AC Conductivity :*

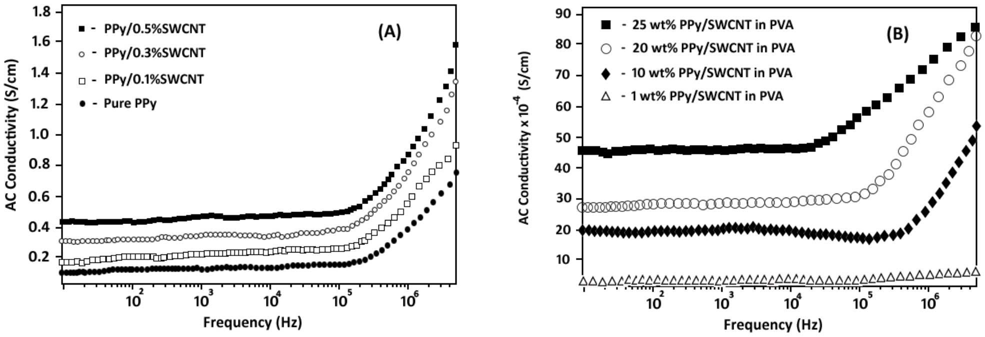

Fig 5 (A). Variation of the AC Conductivity of PPy/SWCNT composite with respect to frequency (B) Variation of the AC Conductivity of PPy/SWCNT/PVA composite with respect to frequency

The frequency dependence of AC conductivity of PPy/SWCNT and PPy/SWCNT/PVA composites is depicted in Figures 5(A) and 5(B), respectively. The AC conductivity of PPy/SWCNT specimens is, in general found to increase with increasing SWCNT content. This outcome is similar to that obtained in case of DC conductivity analysis reported in this study. Further, the conductivity behaviour of all the composites is almost similar in frequency range 1 to $10^5$ Hz. There is no significant variation in conductivity of all the samples with respect to frequency in this range. However the conductivity is found to increase remarkably beyond $10^5$ Hz. This increase in the AC conductivity can be explained on the basis of formation of excess charge carriers in form of polarons and bipolarons[21]. Almost similar trend is observed in conductivity of PPy/SWCNT/PVA ternary samples.

The total frequency dependent conductivity $\sigma(\omega)$ at a given temperature and frequency can be expressed[22] as:

$$\sigma(\omega) = \sigma_{ac}(\omega) + \sigma_{dc} \tag{2}$$

where $\sigma_{dc}$ is the dc electrical conductivity and the $\sigma_{ac}(\omega)$ ac conductivity.

This equation suggests that the total conductivity of the polymeric material at a given frequency is made up of two components, $\sigma_{ac}(\omega)$ and $\sigma_{dc}$ which is simply the limit of $\sigma_{ac}(\omega)$ when $\omega$ tends to 0. It can be observed from Figure 5 that conductivity is independent of frequency at lower frequency, but may be dependent on temperature.

### *3.5 Tensile Strength :*

Figure 6 depicts the variation of the tensile strength of various composites with respect to the weight percentage of SWCNT in the PPy/SWCNT/PVA composite. It can be observed that the tensile strength increases with increasing SWCNT content in the composite. This is quite obvious as carbon nanotubes are known for their high mechanical strength. It is worth mentioning here that casting of the film of PPy/SWCNT composite is very dificult because of poor processability and brittle nature of PPy. The tensile strength of pure PVA is found to be 17.34 MPa in this study. There is remarkabe decrement in the tensile strength of PVA due to the incorporation of PPy/SWCNT. It can be due to the brittle nature of PPy. It is observed that the casting of a conducting film is possible by incorporation of PVA with PPy/SWCNT. This observation suggests that the PPy/SWCNT/PVA ternary composite can be used in certain applications where values of elecrical conductivity and mechanical strength are negotiable.

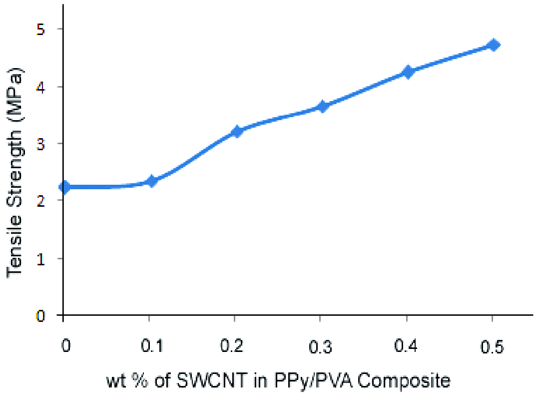

Fig. 6. Variation of tensile strength of PPy/SWCNT/PVA composite with respect to wt% of SWCNT

## 4 Conclusion

The dependence of DC and AC conductivities of PPy on SWCNT is confirmed through this study. The conductivities of pure PPy and PPy/PVA composite increase with addition of SWCNT. Further, the addition of PPy/SWCNT composite in PVA increases the conductivity of PPy/SWCNT/PVA ternary composite. The bridging action of carbon nanotubes can be considered as a cause for this increment of conductivity in PPy/SWCNT as well as PPy/SWCNT/PVA composites. It can also be concluded that PPy/SWCNT acts like a metallic filler in PVA matrix. A film of PPy/SWCNT/PVA ternary blend with considerable conductivity and better mechanical properties can be cast which can be developed as a promising material for various applications.

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