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ELECTRICALLY CONDUCTING POLYMER COMPOSITES OF POLYCARBONATE, POLYANILINE (PANI) AND MULTIWALLED CARBON NANOTUBES (MWCNTs)

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Abstract- Polyaniline (PANI) in its doped state with dodecyl benzene sulphonic acid (DBSA) blended with polycarbonate and Polycarbonate/Acrylonitrile Butadiene Styrene (PC/ABS) in Chloroform were compression molded and their electrical conductivity measured. Other commodity fillers like carbon black (CB), graphite (GRA) and Carbon fibers (CF) are used to study the conductivity variation in the composite. Effects of loading levels of conductive fillers on the electrical conductivity and morphology of the blends were investigated. The DC electrical conductivity of the composites were measured employing Keithley 6221/2812A instrument and the conductivity ranges from 0.3 to 6.02 S/cm with different proportions of PANI - DBSA, MWCNTs and other filler fraction in the composites. Electrical conductivity of these composites were PANI-DBSA-MWCNT > PANI-DBSA> PC-PANI-DBSA-CNT>PC-PANI-DBSA-MWCNT-CB/CF/Graphite in the conductive blend. Conductive filler of ~30 % loading showed an shielding electrical conductivity values much closer to unblended DBSA doped PANI (3 to 6 S/cm) which makes these conducting composites potential candidates as EMI shielding material for encapsulation of electronic circuits in high technological applications and transparent electrode materials in multijunction solar cells. This high electrical conductivity of the composites could be attributed to the electronic interactions between quinonoid ring of PANI and the MWCNTs and the connectivity created by the compatibilization effect of dodecyl benzene group with other fillers and the PC or PC/ABS matrix. To ensure the reproducibility of the doping procedure PANI is doped with DBSA in water and the electrical conductivity is measured. Literature value of 10.34 S/cm was reproduced.
Keywords: PC, PANI, MWCNTs, Electrical conductivity, composites

Introduction

The need to develop molecular scale electronic materials becomes inevitable due to the higher efficiency and miniaturization of electronic devices. The ultimate goal being the fabrication of electronic components from organic molecules [1,2]. Carbon based materials like polymers and nanotubes have immense potential to take part in variety of applications ranging from low cost circuits and display to power devices, microelectromechanical systems (MEMS) to super capacitors and sensors to solar cells [3-5]. Due to the exceptional electrical, mechanical and thermal properties of carbon nanotubes (CNTs), it is used in nanoelectronics and biomedical devices [6]. The preparation of nanotube/polymer composites is a promising approach for an effective incorporation of CNTs into electronic devices with all possible synergistic effects [7,8]. Based on the applications many polymers have been used as the matrix material in CNT/Polymer composite [9-12]. PANI/ MWCNT composites are reported by W.Feng et al in photovoltaic devices [13]. In view of its relatively facile processability, electrical conductivity and environmental stability[14,15], PANI acts as an important member among other intrinsically conducting polymers. Apparently, due to the associated electrical, electrochemical and optical properties, PANI is potentially attractive for applications such as a synthetic metal[16]. Apart from all the above mentioned properties, PANI possess reversible control of conductivity both by protonation and charge transfer doping[17,18]. Zengin et al[19] mixed MWCNTs with aniline via stirring followed by in situ polymerization to exhibit drastic increase in conductivity. Deng et al[20] used identical process to prepare PANI/MWCNT composite and studied conductivity.

The wide range of electrical, electrochemical and optical properties of polyaniline along with its excellent stability makes it a useful electronic material for various applications. Some of the potential devices based on polyaniline are organic light emitting diodes, low power rechargeable plastic batteries, gas sensors, super capacitors, photovoltaic cells, liquid crystal displays and Schottky devices[21-25]. Bulk polyaniline in its pure form is an insulator, but adding dopants like camphor sulphonic acid (CSA), dodecyl sulphonic acid and hydrochloric acid can enhance the electrical conductivity by many orders. The enhancement of the conductivity in

these materials is either by the generation of extended states in doped molecules or by charged defects with electronic structures. Incorporation of dopants also modifies the structural properties of polyaniline. This modification plays an important role in enhancing the conductivity of the polymer. Sulphonic acid units may interact with amine/imine hydrogens, which enhances the electrical properties of polymers. In addition if these conducting PANI-DBSA is further dispersed with highly conducting MWCNTs (99% purity), the percolation path for the electrons to flow in the system increases tremendously. Apart from this mechanical strength of the composite also increases. If these highly electrically conducting PANI-DBSA-MWCNT composite is dispersed in an insulating polymer matrix in proportions higher than 30% by weight, their conductivity is still observed of the same order as PANI - DBSA, a tremendous increase in conductivity of the order of 10^{14} to 10^{16} S/cm is contributed by these conducting fillers to the insulating PC matrix (~10^{-14} to 10^{-16} S/cm).

In the present work we report the synthesis of PANI/MWCNT composites embedded in a polymer (thermoplastic) like PC or PC/ABS at various proportions of PANI, MWCNT, Carbon black, Carbon Fiber and graphite via solution method. The obtained composite is compression molded employing carver press and their DC conductivity is measured by Keithley 6221/2812A. The surface characteristics of the composite are studied by Scanning Electron Microscopy.

Experimental Section
Methodology for PANI - DBSA - MWCNT composite and PC - PANI - DBSA - MWCNT composite synthesis

5g of emeraldine base of polyaniline from PANIPOL is taken and added to 100ml of toluene. The above solution is sonicated for 30 minutes. To it 17.86ml of Dodecyl benzene sulphonic acid (70% wt in Isopropyl alcohol, Sigma Aldrich) is added. The above mixture is heated to 80^0 to 150^0C on a hot plate (REMI) with constant stirring employing REMI magnetic stirrer for 3 to 4hrs. A part of the resultant solution is cooled to room temperature and filtered using whatman filter paper. The filterate is then dried at 100^0C in a furnace to remove excess toluene present. Green coloured emeraldine salt of PANI - DBSA is obtained. It is compression molded to a thickness of approximately 0.5 cm and DC conductivity of the pellet is measured employing Keithley 6221/2812A. To another part of the above solution, 0.1g of MWCNT is added and sonicated for 30 minutes. Mixture of PANI - DBSA - MWCNT composite is obtained. Evaporate toluene and resultant powder is compression molded by Carver Press at 280^0C and 3tons pressure, thickness of the pellet being 5±1mm and DC conductivity is measured. The PANI - DBSA and PANI - DBSA - CNT composite synthesized by the above procedure is dried in a furnace at 100^0C for 2hrs and stored in a desicator. Two different compositions of PANI - DBSA - CNT composites are formed (i) 6.5:1 and (ii) 1:1 respectively.

Dissolve 4g of PC from Lexan, SABIAC (or PC/ABS, 50 - 50 blend of PC from Lexan and ABS from Tyrolac, Toray Industries) in 100ml Chloroform. Leave the solution at room temperature overnight to complete dissolution. Add 3g of PANI - DBSA synthesized according to Scheme 1 to the above solution and sonicate the mixture for 30 minutes. Heat the solution at temperature from 40 to 60^0C and add 1g of MWCNT (Nano amor, 95% purity) and sonicate for 2 to 3hrs. Evaporate the solvent and compression mold the composite into a pellet of thickness approximately 5±1 mm at 280^0C and the pressure applied is 3 tons. The PC-PANI-DBSA and PC-PANI-DBSA-CNT composite synthesized by the above procedure is dried in a furnace at 100^0C for 2hrs and stored in a desicator. To include other carbon fillers, the fraction of MWCNT in the composite is varied and appropriate concentration of Carbon Black/Carbon fiber/Graphite is added in weight percentage and the above procedure is repeated to measure the DC conductivity.

Results and Discussion

The formation of composites of PC-PANI-DBSA and PC-PANI-DBSA-CNT demonstrated in the current work is simple and novel. The process is highly economical and even the solvent used can be redistilled and reused. The charaterisation of the composites obtained employing SEM and conductivity measurements by Keithley 6221/2812A are discussed in the next sections.

Characterization of PANI-DBSA and PANI-DBSA-CNT and composites by Scanning Electron Microscopy[26]

Figures 1 (A) and (B - D) represent the SEM image of PANI - DBSA and PANI - DBSA - CNT images respectively. The MWCNTs were found to be thoroughly mixed with PANI - DBSA. This high compatibility of PANI - DBSA with MWCNTs helps in the higher electrical conductivity of the composite (~ 10^1 S/cm). Figure 1 A indicate the flaky nature of the PANI - DBSA whereas Figures 1 (B - D) denote the high miscibility of PANI - DBSA with MWCNTs and hence no flakes of PANI - DBSA is seen separately. Figure 1 B implies that at 6.5:1 ratio of PANI - DBSA with MWCNTs also thorough mixing of both the conducting components. Although the percolation threshold is not reached, DC conductivity is seen even at very low fraction of MWCNTs in the composite.

Characterization of PC - PANI-DBSA and PC - PANI-DBSA-CNT and composites by Scanning Electron Microscopy

Figures 2A and 2(B - F) indicate the SEM images of PC - PANI - DBSA and PC - PANI - DBSA - CNT composites respectively. Figure 2 A shows that the PC - PANI - DBSA composite is flaky in nature and thorough mixing of PC and PANI - DBSA is present. This uniform blending of insulating thermoplastic, PC and the conductive component PANI - DBSA helps in the higher DC conductivity of the composite. Figure 2B implies the

cross section of the uniform blend of PC and PANI - DBSA in 60:40 weight percentages. Figures 2 (C - D) denotes the complete distribution and network formation of PANI - DBSA and MWCNTs in PC matrix, the weight ratio being 70:30 (PC:PANI - DBSA - CNT). Figures 2 (E and F) represent the uniform blend and distribution of PANI - DBSA and MWCNTs in PC matrix. The weight percentage being (PC:PANI - DBSA - CNT) 60:40 respectively. The presence of MWCNTs in the composite is found to increase the DC conductivity of the composite by an order of magnitude.

If the doping of PANI with DBSA is done in the presence of MWCNTs and PC, the conductivity of the resulting PC - PANI - DBSA - CNT composite is found to increase by two orders of magnitude. The excess DBSA present is then washed thoroughly with water to avoid decrease in conductivity.

Conductivity measurements
The conductivity of PC - PANI - DBSA and PC - PANI - DBSA - CNT - CB/CF/Gra composites are measured employing Keithley 6221/2812A instrument. The instrument measures resistance via two probe technique and the resistivity and conductivity are calculated based on the following equations

$$\rho = \frac{R * A}{t} \qquad (1)$$

and

$$\sigma = \frac{1}{\rho} \qquad (2)$$

where ρ is the resistivity in Ohms-cm; R being the resistance measured in Ohms; A being the area of the electrodes in cm^2 ; t is the thickness of the sample in cm and σ denotes the conductivity of the sample in S/cm.

Table 1 denotes the DC conductivity of the composites of PC, PANI - DBSA and MWCNTs at various proportions and in the presence and absence of excess DBSA. It can be seen from Table 1 that PANI when doped by DBSA in toluene medium comprise of DC conductivity 4.46 S/cm. Upon adding MWCNTs in the ratio 6.5:1 respectively, the DC conductivity decreases drastically. This anomalous behavior of PANI - DBSA - CNT composite in the weight ratio 6.5:1 can be attributed to the percolation mechanism change from particle percolation to combination of particles and high aspect ratio filler mechanism (ca. Fiber percolation mechanism) and no connectivity between PANI - DBSA and MWCNTs occur for the flow of electric current and hence the conductivity is lesser by an order of magnitude than the native PANI - DBSA.

In the case of equal proportions of PANI - DBSA and MWCNTs, the conductivity of the composite increases twice that of pure PANI - DBSA. This increase in conductivity can be justified by the fact that, as the concentration of MWCNTs increases in the composite, fiber percolation mechanism predominates and connectivity is well attained between the two conductive components. In fiber percolation mechanism, the orientation of the electron is towards fiber - axial direction and hence in PANI - DBSA - CNT composite, the electrons flow towards the orientation of the nanotubes in the composite and thereby increasing the conductivity to 9.23 S/cm.

The counter phenomenon is noticed when the concentration of MWCNTs is kept constant while the PANI - DBSA - CNT is also blended with other particle mechanism conducting filler like Carbon black. The DC conductivity of PANI - DBSA - CNT - CB composite in the weight ratio 6.5:1:1 respectively is measured employing Keithley 6221/2812A. Although there is an increase in the conductivity of the composite, it is less than that of PANI - DBSA - CNT (1:1) composite. The DC conductivity value being 7.64S/cm. The decrease in conductivity in comparison with PANI - DBSA - CNT (1:1) is due to the change in the percolation mechanism as mentioned earlier, whereas the increase in conductivity when compared to PANI - DBSA could be attributed to the perfect miscibility of PANI - DBSA and CB, the particle mechanism predominates effectively than the mixed particle - fiber mechanism.

There is another scenario existing, when an insulting thermoplastic like PC or PC/ABS is blended with the PANI - DBSA - CNT matrix. The DC conductivity of PC - PANI - DBSA - CNT composite is found to decrease drastically by two orders of magnitude than its prerequisites. The conductivity values of PC - PANI - DBSA - CNT composite in 60:40 and 70:30 weight percentages are 0.0778 and 0.0282 S/cm respectively. Here PANI is doped with DBSA externally and mixed with MWCNTs and then blended with PC via solution casting method. The in situ preparation of the above composite by doping PANI with DBSA in the presence of PC and MWCNTs in the weight percentage of 60:40 improved the conductivity a lot. In the absence of excess DBSA in the composite the conductivity value is 2.18 S/cm whereas if excess DBSA is present, the conductivity being 0.16 S/cm. Although this value is better than the ex situ route, it is still less than 2.18 S/cm. The effect of other carbon fillers like Carbon fiber, Graphite on the conductivity of PANI - DBSA - CNT composite blended with PC and PC/ABS are also studied in the present work Graphite being a flaky material and carbon fiber being an high aspect ratio filler, the switch in conduction mechanism from particle to fiber to flaky seems to have a tremendous effect upon the electron flow in the composite. The synergistic effect due to high and low interaction among all the fillers and the polymer plays a major role in determining the conduction mechanism. Figures 3 and 4 indicate the DC conductivity values of the various compositions of PC, PC/ABS, PANI - DBSA, MWCNT and CB/CF/Gra. Table 2 shows the compositions of the above materials in weight percentage. The trend in the conductivity values seem to be identical in both the thermoplastic matrices.

It can be noticed from Table 2 and figures 3 and 4 that based on the conduction mechanism the conductivity varies in each composition done here. From samples 1

to 6 in Table 2, sample 1 with 40:30:30 composition of PC:PANI-DBSA:CNT possess the value nearer to the naïve PANI - DBSA - CNT composite. The presence of insulating matrix has reduced the conductivity half of the PANI - DBSA - CNT composite, whereas the complerte dispersion of MWCNTs and PANI - DBSA in the PC matrix has kept the conductivity values as 5.2 S/cm. If the composition of MWCNTs is changed from 30 to 15 weight % and 15 % weight of Carbon fiber is added to the above composite, the conductivity is found to decrease by an order of magnitude. This could be attributed to the negative synergistic effect of least interaction between MWCNTs and carbon fibers and the conductivity is 0.3 S/cm.

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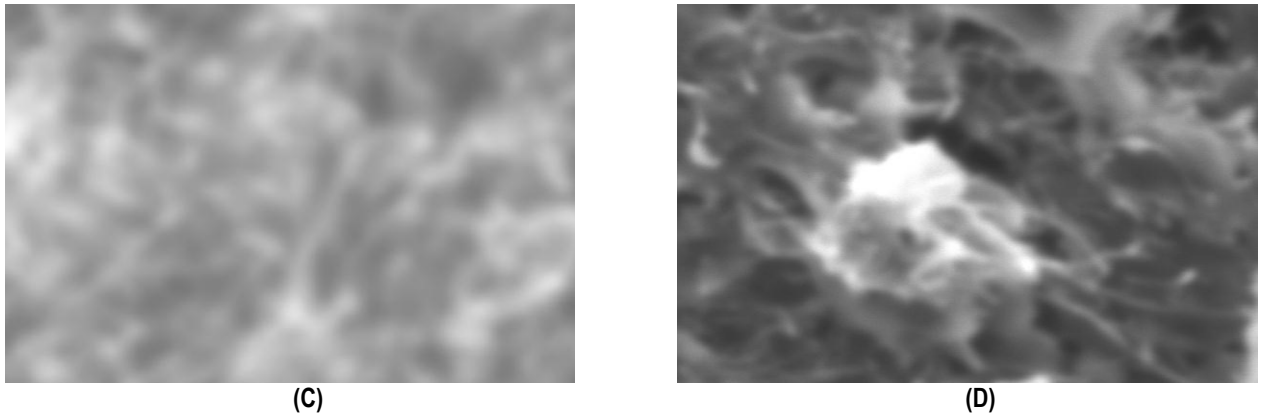
(A)

(B)

(C)

(D)
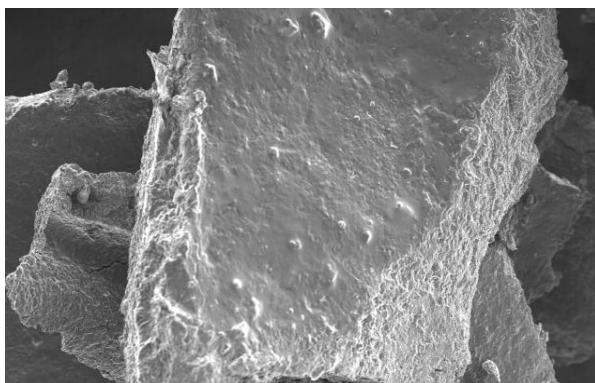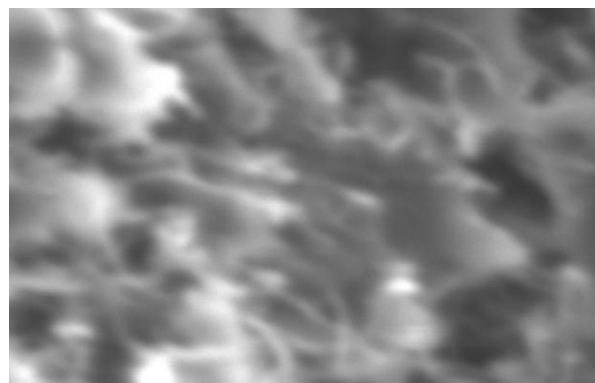
Fig. 1 (A-D) represents the SEM image of PANI-DBSA and PANI-DBSA-CNT composites, PANI - DBSA:MWCNT ratio beingB = (6.5:1); C,D = (1:1) respectively.
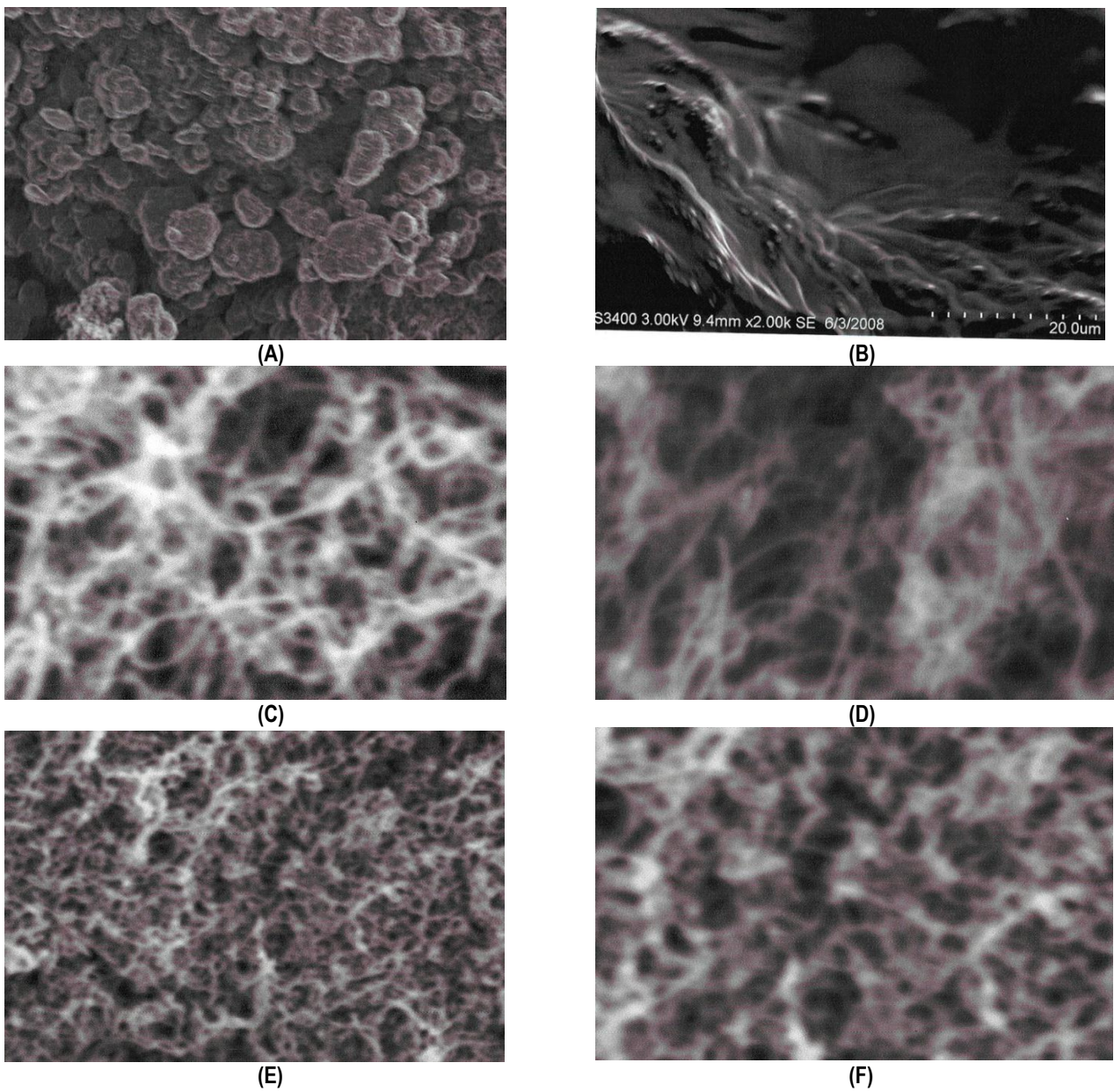

(A)

(B)

(C)

(D)

(E)

(F)

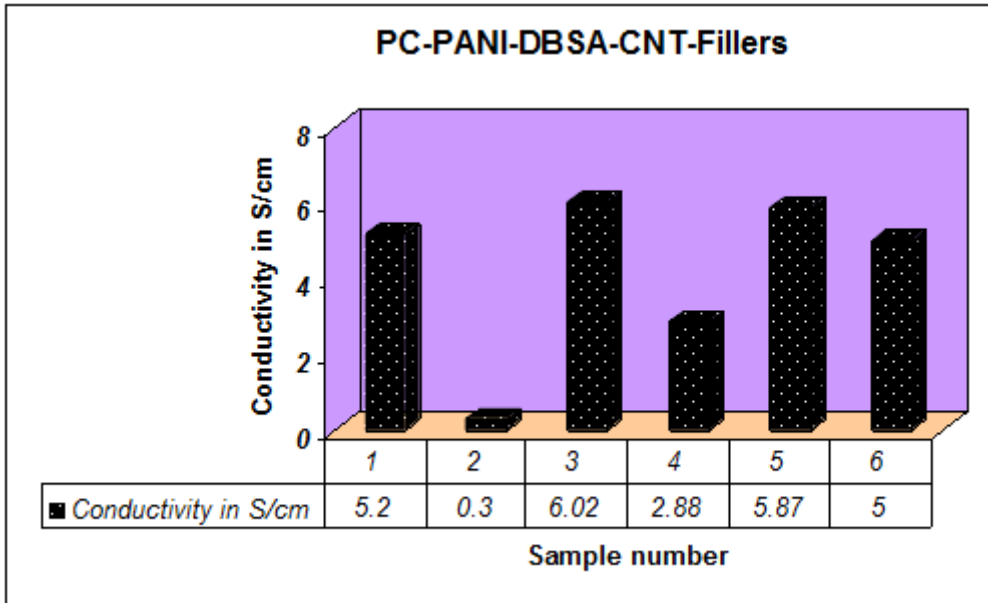**Fig. 2 (A-F)-** SEM images of PC - PANI - DBSA and PC - PANI **- DBSA – CNT**

Fig. 3- The conductivity values of various proportions of PANI - DBSA, MWCNTs, CB, CF and Graphite blended in PC matrix.
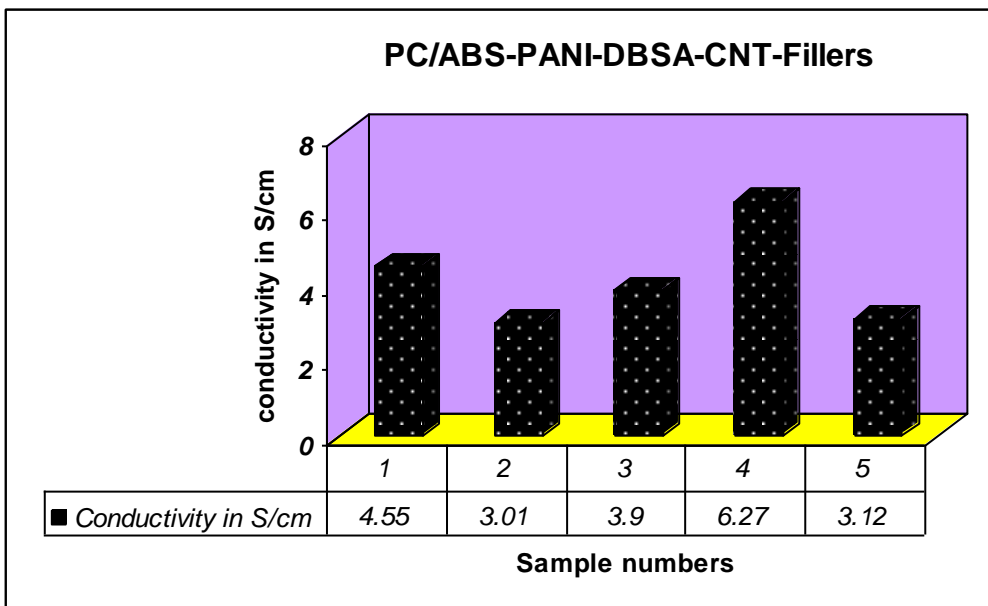

Fig. 4- The conductivity values of various proportions of PANI - DBSA, MWCNTs, CB, CF and Graphite blended in PC/ABS matrix.

Table 1- Represnts the DC conductivity values of different samples of PANI - DBSA, PC - PANI - DBSA and PANI - DBSA - CNT and PC - PANI - DBSA - CNT composites in the presence and absence of excess DBSA

S.No	SAMPLE	THICKNESS (cm)	RESISTANCE (OHMS)	RESISTIVITY (OHM-cm)	CONDUCTIVITY (S/cm)
1	PANI-DBSA	0.7509	0.859	0.224	4.46
2	PANI-DBSA-CNT(6.5:1)	0.8767	16	3.59	0.278
3	PANI-DBSA-CNT(1:1)	0.9583	0.49	0.108	9.23
4	PANI-DBSA-CNT-CB (6.5:1:1)	0.7345	3990	1.31	7.64
5	PC-PANI-DBSA-CNT (60:40)	0.6091	0.529	12.8	0.0778
6	PC-PANI-DBSA-CNT(60:40) EXCESS DBSA	1.122	35.6	6.23	0.16
7	PC-PANI-DBSA-CNT(IN-SITU,60:40)	0.5009	1.17	0.459	2.18
8	PC-PANI-DBSA-CNT (70:30)	0.234	41.6	34.9	0.0282

Table 2- Conductivity values of PC - PANI - DBSA - CNT in the presence of CB, CF, Graphite

Samples	PC	PANI-DBSA	CNT	GRA	CF	CB	Conductivity (S/cm)
1	40	30	30	0	0	0	5.2
2	40	30	15	0	15	0	0.3
3	40	30	10	0	20	0	6.02
4	40	30	10	0	0	20	2.88
5	40	20	10	0	0	30	5.87
6	40	20	10	30	0	0	5
	PC/ABS	PANI -DBSA	CNT	GRA	CF	CB	
7	40	30	30	0	0	0	4.55
8	40	30	10	0	20	0	3.01
9	40	30	10	20	0	0	3.9
10	40	20	10	0	0	30	6.27
11	40	20	10	30	0	0	3.12