PART-A ; Synthesis of Polyaniline (PANI) and PANI/c-SWCNT composites for EMI Coatings

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Abstract

Polyaniline (PANI) was synthesized by chemical oxidation process by using Ammonium per sulphate (APS) as oxidizer and HCl as dopant. The effects of change in stoichiometric ratio of monomer to oxidizer, addition time, reaction temperature and dopant concentration on the electrical conductivity of PANI were studied in detail. The synthesis procedure was optimized to yield the product with the best electrical conductivity. Maximum electrical conductivity of 5.6 S/cm was achieved for pure PANI synthesized by following the optimized procedure. Different PANI/c-SWCNT composites were prepared by optimized in-situ polymerization procedure by varying the c-SWCNT loading and characterized for FTIR, XRD, DSC, TGA, FESEM analysis and electrical conductivity. These studies revealed the fact that formation of PANI coating over c-SWCNT during in-situ synthesis was responsible for enhanced electrical conductivity. Maximum conductivity of 27.12 S/cm was realized for 20% c-SWCNT loaded PANI composite. To demonstrate the efficacy of in-situ method, 20% c-SWCNT loaded PANI composite was prepared by ex-situ method and electrical conductivity was evaluated. The results of these studies inferred that 20% c-SWCNT loaded PANI composite synthesized by in-situ method was the most effective filler for developing the polyurethane based coatings for EMI shielding applications. Development and characterization of PANI/c-SWCNT composite filled polyurethane based coatings for EMI shielding will be discussed separately as PART- B.

INTRODUCTION

Electromagnetic interference (EMI) is a phenomenon where an undesired electromagnetic induction generates signals in the nearby electronic circuits and thereby affects the performance of the electronic equipments. EMI is hazardous to health of human beings also. Hence to ensure the best performance of the equipments and safety of human beings, EMI shielding is essential [1-3]. A good shield for EMI should have either free electrons or electric/magnetic dipoles which interact with electric and magnetic components of Electro Magnetic Radiation and weaken its intensity. Metals are known to be good EMI shields. They can be used as sheets/mesh. However, they suffer from corrosion susceptibility and weight penalty [4-7]. Further, metal based coatings exhibit limited performance due to poor wear and scratch resistance. Conventional polymer matrices with carbon based inclusions by virtue of their light weight and corrosion resistance and electrical conductivity are best suited for EMI shielding [8, 9]. Many studies reported that carbon nanotubes (CNT) enhanced the electrical conductivity of the polymer matrices and thereby improved the EMI shielding effectiveness [10-12]. Recently use of intrinsically Conducting Polymers (ICPs) like Polyaniline (PANI) [7], Polypyrrole (PPy) [13, 14] and Poly-p-phenylene-benzobisthiazole (PBT) [15, 16] etc., as fillers to conventional polymers has been reported. However, the enhancement of conductivity depends on the intrinsic conductivity, loading concentration, degree of dispersion and extent of compatibility of the ICP with the host polymer. Generally as ICPs have limited conductivity, higher loadings are required to achieve the required level of electrical conductivity for shielding. Interestingly, when used as composite fillers in combination with other conducting materials like metals and CNT, these ICPs result in significant reduction in percolation threshold, increasing the conductivity thereby effective contribution to shielding performance [4]. Generally ICP/ CNTs composites are prepared either by direct mixing of the two components or in-situ polymerization of the ICP monomer in the presence of CNTs.

The present research work was aimed at two tasks Viz., Part A- synthesis of Poly aniline(PANI) /c-SWCNT composite and Part B-Development and characterization of PANI/c-SWCNT composite filled polyurethane based coatings using for EMI shielding .

This paper highlights the work carried out under PART –A i.e, the optimization of synthesis procedure for PANI and their c-SWCNT composites to be used as fillers for polyurethane based EMI coatings. Initially PANI was synthesized by chemical oxidation process by using

Ammonium per sulphate (APS) as oxidizer and HCl as dopant. The effects of change in stoichiometry of monomer oxidizer ratio, addition time, reaction temperature and dopant concentration on the electrical conductivity of PANI were studied in detail. The procedure was optimized to yield best electrical conductivity. Different PANI/c-SWCNT composites were prepared by optimized in-situ polymerization procedure by varying the c-SWCNT loading between 0-20 and their electrical conductivity was evaluated. PANI / c-SWCNT with 20% c-SWCNT loaded composite was prepared by ex situ method for comparative evaluation. Due to the formation of PANI coating over c-SWCNT during in-situ synthesis, the composites prepared by in-situ method exhibited higher electrical conductivity as compared to the composites prepared ex-situ method. The formation of PANI coating was confirmed by characterizing the in-situ prepared composites by FTIR, XRD, DSC, TGA and FESEM analysis. The results of these studies were discussed in the following sections.

EXPERIMENTAL

Materials used

Aniline, Ammonium persulphate (APS) and HCl were purchased from SDFCL chemicals, India. Aniline was vacuum distilled before use. Carboxylic Acid functionalized single walled carbon nanotubes (c-SWCNT) were purchased from nanoshel, USA with 90% purity. All other chemicals were used as received.

Synthesis of PANI and PANI/c-SWCNT composites (In-situ)

Aniline was taken in a round bottom flask with 1M of 100 ml HCl. Calculated amount of Ammonium per sulphate (APS) was dissolved in the 1M of 100 ml HCl and added to the aniline HCl mixture under stirring. The system was kept under vigorous stirring for 2hrs to complete the polymerization. The color change from colorless to dark green indicates the formation of PANI emeraldine salt. Then PANI was filtered and washed with 1M HCl and distilled water till filtrate turn into the colorless solution. The filtered PANI was dried in vacuum oven at 60° C for 24 hrs. This procedure was repeated by varying the stoichiometry of monomer oxidizer ratio, addition time, reaction temperature and dopant concentration in order to realize the PANI with best electrical conductivity. Table.1 presents the details of parameter variation followed during the synthesis and the electrical conductivities realized for PANI. The optimized PANI was labelled as PASC0. This optimized synthesis procedure was followed to prepare PANI/c-SWCNT composites with varying percentages (1, 5, 10 and

20) loading of c-SWCNT and labelled as PASC1, PASC5, PASC10 and PASC20 respectively.

Ex-situ

Ex-situ PANI/c-SWCNT composite was prepared by grinding the 20% Wt. c-SWCNTs in the mortar with Pure PANI (PASC0). This composite was labelled as EPASC20. This was prepared to compare the electrical conductivity values of in-situ and ex-situ synthesized PANI/c-SWCNT composites.

Table.1 Optimization of Polyaniline by changing the different parameters of Temperature, HCl concentration, Aniline APS ratio and Addition time

Procedure . No	Aniline/ APS molar ratio	Temperature °c	Concentration of HCl M	Addition Time	Electrical conductivity S/cm
1	1:1.125	0	1	Drop by drop for 2 hrs	1.5
2	1:1.125	-5	1	Drop by drop for 2 hrs	4.1
3	1:1.125	RT	1	Drop by drop for 2 hrs	5.7*
4	1:1.125	RT	2	Drop by drop for 2 hrs	5.08
5	2:1.125	RT	1	Drop by drop for 2 hrs	2
6	1:2.25	RT	1	Drop by drop for 2 hrs	1
7	1:1.125	RT	1	Instant addition	0.2

* Optimized conditions of PANI emeraldine salt.

Characterization

Electrical Conductivity was measured using Keithley 6221 Current source meter and 2187A nanovoltmeter. Polyaniline pellet was prepared by pressing the PANI powder at 7 ton

pressure using stain less steel dye. Vandur pou four probe method was used. Bruker Vector 22 was used for FTIR spectra in the wave-number range of 4000–400 cm^{-1} . The FTIR Specimens for analysis were prepared by grinding the powder sample with KBr powder (weight ratio 1 : 99) and then the pressing of the mixture into tablets. Differential Scanning Calorimetric (DSC) studies were performed on TA modal, USA from 40° C to 300° C at a scan rate of 10° C per minute heat flow. Thermal stabilities of these samples were characterized using TA (Universal V2.6D, USA) Thermogravimetric Analysis (TGA) in the inert atmosphere. The samples were scanned between 40 to 800° C Temperature at the heating rate of 20° C/min. Field Emission Scanning Electron Microscopy (FESEM-Carl Zeiss, Supra 40 VP) was used to examine the morphology of the samples. The XRD analysis was done with the help of Bruker D8 advanced diffractometer by using Cu K α X-rays of wave length 1.54Å in 2 θ range from 10 to 70.

RESULTS AND DISCUSSION

Optimization of polyaniline synthesis

Initially, PANI was synthesized as per the standard procedure reported elsewhere in literature [17]. PANI synthesized according to the standard procedure exhibited electrical conductivity of 1.5 S/cm. Later experiments were carried out under different conditions by varying the reaction temperature, monomer to oxidizer, dopant concentration stoichiometry and addition time of oxidiser to monomer. The electrical conductivity of PANI samples synthesized by various experiments was measured and tabulated. From the table.1, it seen that, room temperature reaction yielded the PANI with the highest electrical conductivity of 5.7 S/cm. Higher concentration of the HCl dopant resulted in reduction of electrical conductivity of PANI 5.7 S/cm to 5.08 S/cm. This could be due to the disorder of extended conjugated structure of PANI caused by excess of protonic acid concentrations [18-21]. In the subsequent procedures, the monomer (Aniline) Vs oxidizer (APS) ratio was changed as listed in the table1. When the monomer molar ratio was high, due to inadequate concentration, APS could not oxidize aniline to complete the polymerization. As a consequence, decrease in electrical conductivity from 5.7 S/cm to 2 S/cm was observed. In another condition, when oxidizer molar ratio was high, further decrease in electrical conductivity (from 2 S/cm to 1 S/cm) was observed due to the complete oxidation of aniline as reported in the literature [22]. It is also observed that the instant addition of oxidizer to the monomer resulted in drastic

reduction in electrical conductivity (from 5.7 S/cm to 0.2 S/cm). From all these experiments, it was concluded that room temperature reaction of Aniline with approximately equal molar ratio of monomer and oxidizer (1:125), with a drop wise addition of oxidizer to monomer yielded the PANI emeraldine salt with highest conductivity. These optimum conditions were followed for preparing the various PANI/ c-SWCNT composites by in-situ synthesis. Scheme 1 represents the optimized procedure for PANI synthesis and scheme 2 represents the in-situ synthesis of PANI/ c-SWCNT composites. Since the carboxylic functionalized CNTs can enhance the adsorption of aniline onto SWCNT [23], c-SWCNTs was used to prepare various composites.

Scheme 1

Scheme 2

Electrical conductivity for PANI/c-SWCNT composites

The effect of percentage loading of c-SWCNT on the electrical conductivity of PANI/c-SWCNT composites was presented in Figure.1. From the figure, it was observed that the electrical conductivity decreased from 5.7 S/cm to 4.8 S/cm for five percent loading of c-SWCNT in PASC1 composite. This may be due to the improper dispersion, presence of impurities in c-SWCNT or the small quantity of c-SWCNT entanglement which will offer the electrical resistance [24]. Composite PASC5 showed drastic increase in the electrical conductivity due to the formation of percolation network. PASC10 showed the electrical conductivity 17.12 S/cm. Highest electrical conductivity of 27.21 S/cm was achieved for PASC20. Thus c-SWCNT embedded in the PANI matrix showed better conductivity as compared to pure PANI [25]. For comparative evaluation of in-situ and ex-situ methods, PANI composite with 20 percent loading of c-SWCNT (EPASC20) was prepared by ex-situ method. Electrical conductivity of 12 S/cm was realized for EPASC20. The greater enhancement of electrical conductivity in case of PASC20 was due to the effective site-

selective interactions between the quinoid ring of the PANI and the c-SWCNTs and thus forming a coating of PANI emeraldine salt over the c-SWCNT [26]. Also c-SWCNT serves as “conducting bridge” connecting the PANI conducting domain. This accelerates charge transfer processes between PANI and c-SWCNT and results in enhanced electronic properties which were further supported by FTIR, XRD and FESEM studies.

Fig.1 Electrical conductivity graph of PANI with increasing content of c-SWCNT

FTIR Analysis

Formation of coating of PANI over c-SWCNT through the interactions between the quinoid ring of the PANI and the c-SWCNTs was confirmed by FTIR analysis. Figure 2 shows the FTIR spectra of pure polyaniline (PASC0), c-SWCNTs and PANI/c-SWCNT composites with varying percentages of c-SWCNT. The peaks at 3434, 2923, 1563, 1488, 1294, 1232, 1118 and 798 cm^{-1} in pure PANI correspond to N-H stretching of secondary amine, NH^+ stretching of amine, quinoid ring stretching ($\text{N}=\text{Q}=\text{N}$), benzoide ring stretching ($\text{N}-\text{Q}-\text{N}$), C-N stretching, C-H stretching of quinoid ring and vibration frequency of benzene and quinoid ring C-H respectively. The strong peak at 1118 cm^{-1} is considered to be a measure of the delocalization of the electrons [27] hence accounts for the conductive nature of the PANI. The c-SWCNT spectrum showed the peaks at 3440, 1708, and 1631 cm^{-1} corresponding to carboxylic acid functional group of c-SWCNT. The peak at 1580 cm^{-1} is

corresponding to the FTIR-active phonon mode of the c-SWCNT. The peaks at 1457 and 1220 belong to C=C stretching of c-SWCNTs [28-29]. The spectrum of PANI/c-SWCNTs composites, the mid-FTIR range differed slightly from pure PANI with the new peak at 1631cm^{-1} which was due to the presence of carboxylic group of c-SWCNT. The intensity of strong band at 1118 cm^{-1} which was characteristic peak of PANI conductivity, increased with the increasing content of c-SWNTs. This infers the strong interaction between c-SWNTs and PANI which facilitated the more degree of electron delocalization and thus enhanced the conductivity of the polymer chains [30]. The results of IR confirmed the formation of PANI coating over c-SWCNT. This was in agreement with the electrical conductivity measurements.

Fig.2 FTIR spectra of PASC0, PASC1, PASC5, PASC10, PASC20 and PASC100

FESEM Analysis

To further confirm the PANI coating on c-SWCNT, the composite morphology was studied by FESEM. Fig (3a-3f) shows the FESEM images of PANI, c-SWCNT and PANI/c-SWCNT composites respectively. The SEM image fig (3a) clearly shows the irregular rod or chain like

structure of pure PANI. The SEM images of PASC1, PASC5, PASC10 and PASC20 are shown in fig 3b, 3c, 3d and 3e respectively. These SEMs clearly showed the c-SWCNT embedded PANI structure. In the case of PANI composites having higher c-SWCNT loadings, the orderly formation of polymer chain of PANI along the c-SWCNT was very clearly seen and the diameter of c-SWCNT seems to be increased several fold due to the coat of PANI on c-SWCNT which has resulted the drastic increase in electrical conductivity from 17.12 to 27.21 S/cm. These results were further supported by the XRD analysis.

Fig.3 FESEM images of a) PASC0, b) PASC1, c) PASC5, d) PASC10, e) PASC20 and f) PASC100

XRD analysis

PANI Chain growth through c-SWCNTs was further confirmed by XRD analysis. Figure 4 depicts the X-ray diffraction pattern (XRD) for PANI, c-SWCNTs and various PANI/c-SWCNT composites. The XRD diffractogram of pristine c-SWCNT showed the peaks at 2θ angles of 26.44° (strong), 43.56° (weak) and 53.5° (weak) corresponding to (003), (101) and (006) plane reflections. This pattern of c-SWCNT exactly matches with the JCPDS report no. 26-1079. The XRD diffractogram of PANI showed broad peaks at 2θ angles of 15.2° (weak), 21° (low intense), and 25.44° corresponding to (0 1 1), (0 2 0) and (2 0 0) plane reflections [31, 32]. These peaks in PANI might have arisen because of the regular repetition of the monomer unit aniline. In case of XRD patterns of the PANI–c-SWCNT there were no prominent changes seen for the peaks at 15.2° and 21° . But the peak at 25.44° got intensified, sharpened and shifted gradually to 26.18° indicating the formation of more ordered crystalline structure with the increase in CNT loading [6, 33].

Fig.4 XRD graphs of PASC0, PASC1, PASC5, PASC10, PASC20 and PASC100

To confirm the above fact, the lattice space and crystal size of PANI, c-SWCNT and PANI/c-SWCNT composites were estimated using the Bragg's and Scherrer formulae respectively.

$$n\lambda = 2d \sin \theta \quad \dots\dots\dots 1$$

Where n is an integer, λ is the wavelength of incident wave (1.5405 Å for Cu K α), d is the spacing between the planes in the atomic lattice and θ is the angle between the incident ray and the scattering planes.

$$D = 0.9\lambda / \beta \cos \theta \quad \dots\dots\dots 2$$

Where λ is wavelength, β is full width at half maximum (FWHM) of the diffraction peak, θ is the Bragg diffraction angle and D is the crystal size.

The calculated crystal size and lattice space for PANI, c-SWCNT and PANI/c-SWCNT composites were tabulated in table 2.

Table 2 Crystal size and lattice space respective to their 2 theta of PANI, c-SWCNT and PANI/c-SWCNT composites

Designation	2 θ	FWHM	Lattice Spacing (d) Å°	Crystallite Size (D) Å°
PASC0	25.44	0.8460	3.4968	1.6796
PASC1	25.62	0.7424	3.4732	1.9147
PASC5	25.8	0.5933	3.4483	2.3965
PASC10	25.96	0.5205	3.4283	2.7327
PASC20	26.18	0.3697	3.3996	3.8495
PASC100	26.42	0.2929	3.3698	4.8602

From the table 2, it was observed that FWHM was decreasing with increase in c-SWCNT loading which means the most ordered state of PANI backbone (the smaller the value of half-width to height, higher the order). The crystal size was also increased with increasing content of c-SWCNT. This was a clear evidence of PANI coating formation on c-SWCNT. Higher size of the crystal grain dramatically enhances the conductivity [34]. This was in agreement with our electrical conductivity measurements.

TGA analysis

The thermal stability of the PANI/c-SWCNT composites was evaluated by TGA .Figure 5 shows the TGA results of pure PANI, c-SWCNT and PANI/c-SWCNT composites. From the figure it was seen that the thermogram of PANI exhibited a three-step decomposition. The first step was due to release of water molecules at temperatures less than 100 °C, the second step was due to the loss of dopant anion in the temperature range 180–280°C and the third step was due to the decomposition of PANI in the temperature range 405–750°C [32]. For pure PANI at 800° C weight loss of 54.95% was observed. In case of c-SWCNT the decomposition took place in the temperature range 500° - 600°C [35, 36] and at 800° C weight loss of 13.16% was seen. Weight loss ranging from 39.59-48.96 percent was realized for PANI/ c-SWCNT composites at 800° C. These degradation patterns of the composites indicated the enhanced thermal stability which was due to the ordered structure with increasing content of c-SWCNT in the composites. The thermal stability was further confirmed by DSC studies.

Fig.5 TGA graphs of PASC0, PASC1, PASC20 and PASC100

DSC Analysis

The glass transition temperature T_g is measure of thermal stabiltly of the composites. T_g for various PANI/c-SWCNT composites was measured by Differential Scannig calorimetry (DSC). Figure 6 shows the DSC thermograms of PANI, PANI/c-SWCNT composites and pristine c-SWCNT. The thermogram of pure PANI showed exotherm peak at 91.36°C corresponding to its glass transition temperature (T_g) [37]. The PASC1, PASC5, PASC10 and PASC20 composites showed T_g at 93.86, 94.53, 95.34 and 99.06 °C respectively. The T_g improvement with increasing content of c-SWCNTs clearly infers the formation of orderly structure which was responsible for the enhanced thermal stability.

Fig.6 DSC graphs of PASC0, PASC1, PASC5, PASC10, PASC20 and PASC100

CONCLUSIONS

The synthesis procedure for PANI was optimized to yield PANI with best electrical conductivity. With the optimized procedure, highest electrical conductivity of 5.7 S/cm was realized for PANI. Different PANI/c-SWCNT composites were prepared by optimized in-situ polymerization procedure by varying the c-SWCNT loading. Maximum conductivity of 27.12 S/cm was achieved for 20% c-SWCNT loaded PANI composite. The composite prepared

with the same percentage of c-SWCNT loading by ex situ method exhibited the electrical conductivity of 12 S/cm. The greater enhancement of electrical conductivity in case of in-situ method was ascribed to PANI coating over c-SWCNT which was confirmed by FTIR, FESEM and XRD analysis. Further, DSC and TGA data substantiated the improved thermal stability in case of PANI/c-SWCNT composites. Among the various composites developed PASC20 with highest electrical conductivity, ordered crystalline structure and thermal stability was found to be the choicest of filler materials studied for developing poly urethane based coating for EMI applications.

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