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Research Paper

Synthesis and Characterization of Polyaniline Coated Carbon Fiber Composites

Chemistry

KEYWORDS : Carbon fibre, Polyaniline, Scanning Electron Microscope, Thermo Gravimetric Analysis.

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ABSTRACT

Conducting polymer composites are explored worldwide for their use in various applications such as solar cells, organic light emitting diode, electromagnetic interference shielding and corrosion protection. In this succession, herein, we synthesized a strategy for uniform coating of polyaniline on carbon fiber for their potential use in various fields. Β–Naphthalene sulphonic acid (β–NSA) was used as surfactant and dopant which offers the uniform coating on Carbon fiber. Polyaniline (PANI)–Carbon fiber composites have been prepared by chemical oxidative polymerization route whose conductivity lies in the range 10.73–23.5 S/cm. The TEM analysis of composites reveals the presence of thick and uniform coating of PANI over surface of carbon fiber. The SEM of PANI– carbon fiber also revealed the nonporous coating, which can be used for selective incorporation of other carbon forms. Morphology of PANI– carbon fiber shows the incorporation of carbon fiber in PANI matrix. Such planned conformally polymer coated carbon fiber could be a favourable candidate for next generation building block material in numerous applications.

A. INTRODUCTION

A lots of research has been done on the designing new polymeric composites for their exploitation in many applications like super capacitors & superconductors [1,2] optoelectronic devices[3], organic light emitting diode [4], electronic charge dissipation[5], electromagnetic interference shielding[6-8] and plastic solar cells[9]. Conducting polymers, which contained of conjugated electronic structures have attracted considerable attention in the field of material science due to their use in promising technological applications[10-14]. Uniform coating on the metal surface by polymeric materials have been widely used in industries for the protection of these materials against corrosion[15,16]. Generally, polymeric materials are light weight, cost effective, easy shaping, tuneable electrical conductivity can find applications in advance devices[17]. Polymer composites with various corbon forms such as carbon particles, graphene and its derivatives, graphite, carbon nanotube (CNTs [18,19]), carbon fiber [20] etc have been synthesized globally[12, 21, 22]. Therefore, the lightweight polymer composites are the center of research in material science and search of suitable lightweight materials with numerous functionality is the main focus among scientific groups[23-26]. intrinsically conducting polymers due their extended π-conjugated system have conductivity in semiconductor regime. Applications of ICPs and their composites (or blends) owing to the higher electrical conductivity of these polymers in doped states have been extensively studied by many researchers[27-29].

Among intrinsically conducting polymers, polyaniline (PANI) is accepted as one of the best polymer due to its environment stability and unique protonic conduction mechanism[30, 31]. Many research groups have reported the improved processability of PANI using different surfactant/dopant and mechanical properties by modifying the morphology (spherical/tubular) of the PANI. The protonation of PANI with organic sulphonic acids and macro molecules have been reported for the preparation of electrically conducting polymers with improved processability[32-34].

It is well established that Carbon fiber independently as well as in composite form are potentially used in hi-tech applications [18, 35, 36]. Because of their unique structural properties, high aspect ratio and good mechanical strength carbon nanotubes have been investigated for many potential applications [37-39]. Particularly, their fascinating electrical and mechanical properties offer a new arena for the development of advanced engineering materials [40, 41]. The small diameter, high aspect ratio, high conductivity, and mechanical strength of CNT, make them an excellent option for creating conductive composites for high-performance composites at low filing[19, 23]. The mechanical properties of CNT have\drawn intense interest in their potential for use as reinforcements in composite materials. As a result of these properties, CNT reinforcements are expected to produce significantly stronger and tougher composites than traditional reinforcing materials.

In this study, we attempt to design the uniform conformal coating of PANI on carbon fiber surface by chemical synthesis. The obtained results of composite are focused on the conductivity, surface morphology and gross structural/microstructural analysis of carbon fiber/PANI two phase systems. Moreover, the thermal stability of the composite system has been explored through thermogravimetric analysis. However, to the best of our knowledge, this type of conformal uniform polymer coating on carbon fiber has not been thoroughly explored yet.

B. EXPERIMENTAL

The conformally PANI coated carbon fiber have been prepared by in-situ emulsion polymerization using β-NSA as anionic surfactant molecule which also acts as a dopant. Due to its amphiphilic and surfactant nature, β-NSA molecule (with hydrophilic SO_3H head and hydrophobic tail) easily forms micelles in aqueous solution. First Carbon fiber were dispersed in β-NSA aqueous solution before polymerization. As a result, micelles containing carbon fiber particles form in the reaction, these micelles have core-shell structure as shown in Figure 1 b. 0.1 M aniline monomer was added to above emulsion and homogenized for another 1-h. During this, aniline reacts with β-NSA to form aniline/β-NSA micelles which act as a soft template. Afterward the homogenized mixture was transferred to reactor, pre-cooled to 0ºC. Polymerization was initiated by drop wise addition of ammonium peroxydisulfate and allowed continuous stirring at 0°C under. During this process the formed anilinium cations might be absorbed on the plane of these core-shell micelles. Furthermore, free aniline present in the solution might diffuse into the micelles to form aniline-filled micelles. Therefore, these micelles (with or without Carbon fiber) act as soft templates for the formation of the tube like structure. The attached -SO_3H groups impart additional dopant property to β-NSA. As the polymerization advances, the micelles containing particles would become bigger spheres and take the shape of tubes/rods by elongation. Therefore, subsequent oxidation of aniline results radical cations which combine with another unit to form neutral dimer. Further oxidation of Dimer leads to the formation of a trimer, tetramer and finally the formation of polymer composites. Figure 1 discussed self-assembly process resulting in tube like structure of PANI and PCs composite [33, 34] and suggests that carbon fiber particles should be situated inside the polymer tubes. Schematic representation of incorporation of carbon fiber into PANI matrix is given in this scheme which suggests that carbon fiber embedded in PANI tubes leads to the formation of PANI composites which has better electrical and magnetic properties.

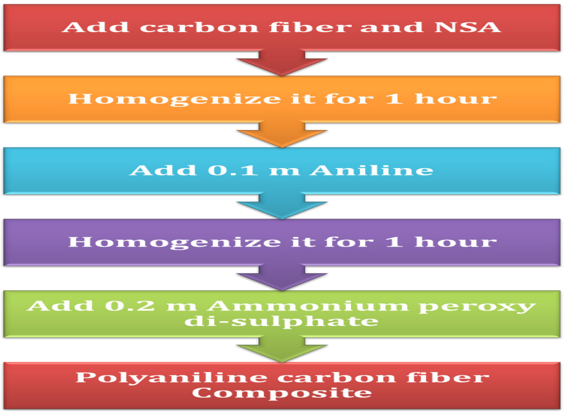

Figure 1. Flow chart of the synthesis procedure of PANI composite

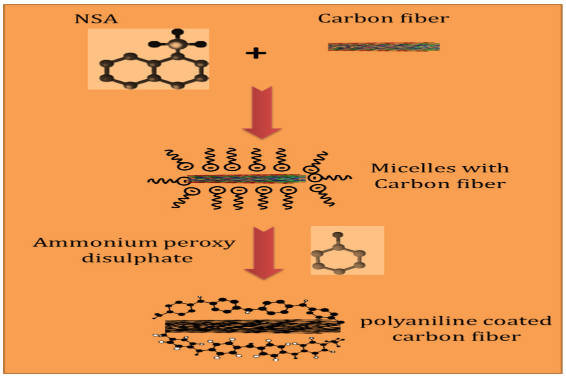

Figure 2. Schematic representation of the PANI/carbon fiber composite.

RESULT AND DISCUSSION

Surface morphology & microstructural analysis

Figure-3 shows the SEM micrograph of carbon fiber. The scanning electron micrographs of particles, PANI and carbon fiber composites are shown in Figure 3 shows the SEM images of carbon fiber, PANI and PANI–carbon fiber composite. These micrographs show that PANI–carbon fiber composite (Figure 4 a, b) exits as highly agglomerated globular particles whereas as grown carbon fiber is entangled tubules (Figure 3) with diameter in the range of 96 nm and their lengths ranging in several microns. The small size of the carbon fiber having high specific surface area provides large number of sorption sites to aniline monomer which can polymerize to form coating over the carbon fiber. At very low concentration of Carbon fiber, PANI coated tubes exist as globular agglomerates (Figure 4b). This may be attributed to the large proportion of bulk/solution polymerized PANI (existing in agglomerated form) as compared to aniline polymerized over carbon fibre surface. However, with the increase in carbon fibre content, there is systematic change in morphology from highly aggregated globules (Figure 4b) towards uniformly coated tubules. Therefore, at certain critical concentration of carbon fiber the polymerization takes place exclusively on surface of carbon fiber with minimal bulk polymerization and agglomeration effects. The SEM of PANi carbon fiber composite also revealed the nanoporous nature of coatings, which can be used for selective incorporation of other particles carbon fiber showed tubular morphology and PANI also showed tubular morphology. Morphology of PC indicates the incorporation of carbon fiber in PANI matrix. SEM image of composite revealed that the entrapment of carbon fiber in the tubular space of PANI matrix during insitu polymerisation of polyaniline.

Figure -3 Optical photograph of carbon fiber.

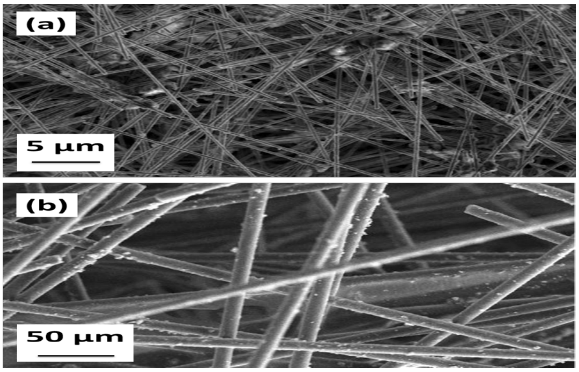

Figure -4 SEM micrographs of (a) carbon fiber and (b) PANI carbon fiber composites.

XRD Analysis

Figure 5 show the XRD patterns of carbon fiber, PANI and PANI–carbon fiber composites. The pure carbon fiber shows a sharp peak centered on 2value of 26β which corresponds to the (002) planes of carbon fiber. The peaks around 43β are due to the (110) and (100) graphitic planes plus small amount of catalyst particle encapsulated inside the walls of the Carbon fiber. The characteristic peaks of the doped PANI are observed around 2values of 15, 20, 25, 30 β corresponding to (0 1 1), (0 2 0), (2 0 0) and (0 2 2) reflections of emeraldine salt form. The composites show the characteristic peaks of both PANI and carbon fiber without any additional bands indicating absence of covalent interactions between the phases[6]. As the carbon fiber content increases, the relative intensity of characteristic bands of PANI decreases whereas bands of carbon fiber become more prominent. The slight shifting in the peak positions may be ascribed to charge transfer interactions between PANI and Carbon fiber leading to variations in chain packing and configurations

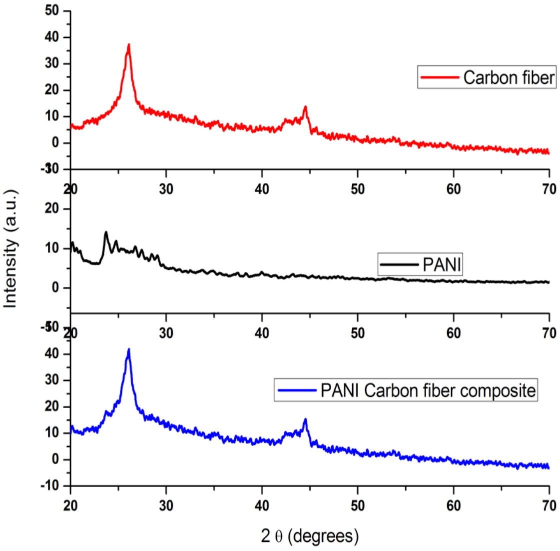

Figure 5. XRD pattern of pure carbon fiber, XRD pattern of PANI carbon fiber composite containing 10 wt% of carbon fiber in PANI matrix.

Thermogravimetric Analysis

Figure 4 shows the thermo-gravimetric curves (TG) of pure carbon fiber, PANI and their composites. The materials were heated from 25 to 900˚C under a constant heating rate of 10˚C/min and in the inert atmosphere of nitrogen gas (60 ml/min). The carbon fiber has excellent thermal stability up to 900˚C and weight loss was only 1.5 %. The TGA curve of PCs indicated, first weight loss at 110˚C may be attributed to the loss of water and other volatiles species. The weight loss in the second step at about 280˚C involves the loss of phosphateions as well as onset of degradation of polyaniline backbone. The increasing carbon fiber content slightly affects the decomposition temperature (DT) which increases from 280˚C (PANI) to 295˚C (PC). The third weight loss step between 300 to 800˚C can be ascribed to the complete degradation of dopant as well as polymeric backbone. The composites show little weight loss between the 800-900˚C and the residue remaining in this region gives an approximate estimate of filler content. Therefore, the final weight of carbon fiber incorporated in polymer was found to 21 %. The results indicate that actually incorporated carbon fiber fraction is less than the ratio of aniline: carbon fiber taken in the initial reaction mass. The TGA data clarify that these composites are thermally stability up to 295˚C, which envisages them as a good candidate for melt blending with conventional thermoplastics like polyethylene, polypropylene, polystyrene etc.

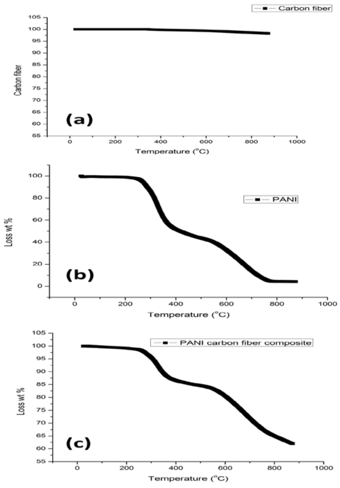

Figure 6. Thermal gravimetric analysis of carbon fiber, PANI and its composite carbon fiber respectively.

UV-Visible Studies

Figure 5. show the UV absorption spectra of polyaniline and its composite with carbon fiber. The polyaniline shows band around 326 nm is related to the π–> π*transition, whereas bands around 431 nm (polaron-π*) and 619 nm (π-polaron) are the characteristics of polarons. But in case of polyaniline composite, two changes have been observed. First a red shift has been observed for the band from 619 to 654 nm which was ascribed to polaronic transition and absorption spectra show the red shift for the band 326 to 336 nm. This shifting may due to the interaction of carbon fiber particles with PANI matrix, which may make the energy of antibonding orbital to decrease, leading to the energy of the π-π* and (π-polaron) transition of the benzenoid and quinoid ring to decrease, and consequently the absorption peaks of composite exhibit a red shift

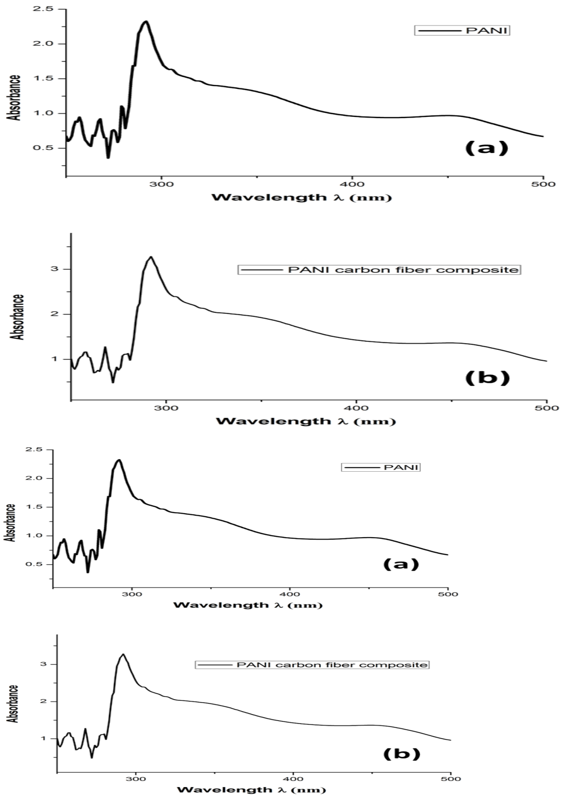

Figure 7. UV–Visible spectra PANI and its carbon fiber composite respectively.

Electrical conductivity

The room temperature current–voltage (I–V) characteristics were measured and resistance values were obtained from the slope of these plots. The electrical conductivities of the pellets can be calculated by considering the sample dimensions as:

$$R=\rho L/A \qquad (1)$$

where "L" is the length of the pellet, "R" is resistance and "A" is crosssectional area of the pellets normal to direction of current flow.

The conductivity (Figure 6) was found to exhibit continuous increase with the increase in the carbon fiber content. The high conductivities of these composites are due to micrometer long Carbon fiber as core and PANI coating as shell (see Fig. 8 SEM images).Measurement of electrical conductivity of terphenyl and quaterphenyl films revealed that organic crystallites play interface trapping levels effectively interacting with phonon subsystems[53]. These states may be principal for the achievement of conductivities varying in the large range of parameters. Introduction of carbon fiber to PANI enhances the electrical properties by facilitating the charge transfer processes between the two components[54]. Due to their highly conducting nature as well as high aspect ratio, fiber can act as interconnecting bridge between the various conducting grains of the polyaniline, which are coated over individual Carbon fiber. This increases the coherence or coupling between the chains and leads to enhancement of interchain transport. Further, the PANI–NSA coating is likely to facilitate the intertube charge transport by reducing the interfacial contact and tunneling resistances. This may be explained on the basis of cushioning effect of softer polyaniline coating over tubes which deforms easily during the pellet formation improving the surface contacts of coated tubes. This synergistic effect of two complementing phases (i.e. PANI and carbon fiber) leads to improvement in conductivity, which is even better than bulk conductivity of either phase alone, i.e. control carbon fiber or pure PANI. The lower conductivity of bulk carbon fiber pellet may be due to the fact that pressed pellets of uncoated Carbon fiber contain highly entangled tubes which even after pelletization represents poorly packed system. The uniform coating of PANI reduces the disorder/voids in composites and improves intertubular charge transport leading to enhanced electrical properties.

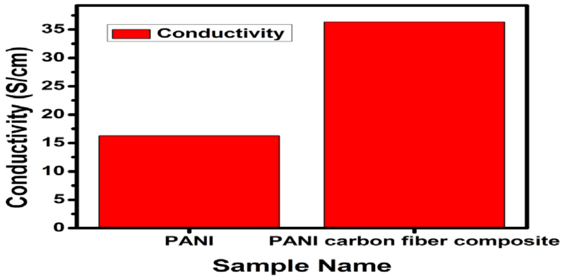

Figure 8. Behaviour of room temperature electrical conductivity of PANI–carbon fiber composites.

CONCLUSIONS

Extremely conducting PANI–carbon fiber composites were synthesized by in situ polymerization. The SEM pictures show uniform coating of PANI over surface of individual Carbon fiber. Based on observed morphological features, we have suggested the probable formation mechanism of these composites. The XRD show systematic shifting in the positions of characteristic bands and peaks of PANI. This suggests significant interactions between the carbon fiber and PANI. At very low concentration of Carbon fiber, PANI coated tubes exist as globular agglomerates. However, at certain critical concentration of carbon fiber the polymerization takes place exclusively on surface of carbon fiber. The high electrical conductivity of (even better than bulk conductivity of control carbon fiber pellet 35 S cm^{-1}) has been ascribed to the synergistic effect of two complementing phases (PANI and carbon fiber). The TGA studies indicate that increasing amount of Carbon fiber does not have any effect on the thermal decomposition temperature. These PANI coated Carbon fiber with large aspect ratio are also proposed as hybrid conductive fillers in various thermoplastic matrices.

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