Synthesis and Characterization of Polyaniline Coated Carbon Black Composites

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Abstract

Conducting polymer composites are examined universally for their use in various applications such as corrosion protection, electromagnetic interference shielding, and Solar cells and corrosion organic light emitting diode. In this coarse, here in, we made a strategy for homogeneous coating of polyaniline on carbon black for their potential use in different areas. Polyaniline coated carbon black shows larger surface area, high thermal stability, electrical conductivity and better corrosion resistance. Major application of Carbon black is as reinforcement in automobile tyres where it helps to conduct heat away from the treat and belt area of the tyre, reducing thermal damage and increasing its life. β–Naphthalenesulphonic acid (β–NSA) was used as surfactant and dopant which offers the homogeneous coating on carbon black. Polyaniline (PANI)–carbon black composites were prepared by chemical oxidative polymerization . The SEM of PANI– carbon black also revealed the nano porous nature of coating, which can be used for selective incorporation of other carbon forms. Morphology of PANI– carbon black displays the incorporation of carbon

black in PANI matrix. Such prepared conformally polymer coated carbon black could be a auspicious candidate for next generation building block material in several applications.

Keyword

Polyaniline, Carbon black, Scanning electron microscopy (SEM) , Thermogravimetric analysis (TGA)

1. Introduction

Many researches have been spent on the designing polymeric composites for their use in many applications like optoelectronic devices ,super capacitors & superconductors(1), organic light emitting diode(2), electromagnetic interference shielding(3,5) ,electronic charge dissipation(6) and plastic solar cell (7). Conducting polymers which embresed of conjugated electronic structures have aquired considerable attention in the field of material science for their use in promising technological applications (8-12). homogeneous coating on the metal surface by polymeric materials have been widely used in industries for the protection of these materials against corrosion(13,14) .The polymeric materials are light weight, cost effective, easy shaping, tuneable conductivity can find applications in prodigious devices(15). Polymer composites with different corbon forms such as carbon particles, graphene and its derivatives, graphite, carbon black (16,17), carbon fiber (18) etc have been used organic light emmiting diode(19,20,21).Therefore, the lightweight polymer composites are the main source of industrial use in material science and search of suitable lightweight materials with many functional groups is the main focus among industrial research(22). Intrinsically conducting polymers due their extended π-conjugated system have conductivity in semiconductor regime. Applications of Intrinsic conducting polymers and their composites (or blends) owing to the higher electrical conductivity of these polymers in doped states have been extensively studied by many researchers(23-25).

Among intrinsically conducting polymers, polyaniline (PANI) is used as one of the perfect polymer due to its environment stability and unique protonic conduction mechanism (26, 27). Many research groups have explaned the improved processability of PANI using different surfactants/dopants 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(28-30).

It is well established that carbon black independently as well as in composite form are probably used in decorated applications(31.32) . Because of their unique structural properties, high aspect ratio andgood mechanical strength carbon blacks have been analysed for many implied applications (33,34). Particularly, their fascinating electrical and mechanical properties offer a new arena for the development of advanced engineering materials(35,36). The small diameter, high aspect ratio, high conductivity, and mechanical strength of carbon black, make them an excellent option for creating conductive composites for high-performance composites at low filing(17,22).The mechanical properties of carbon black have\drawn intense interest in their potential for use as reinforcements in composite materials. As a result of these properties, carbon black reinforcements are expected to produce significantly stronger and tougher composites than traditional reinforcing materials.

In this study, we attempt to design the homogeneous conformal coating of PANI on carbon black surface by chemical synthesis. The obtained results of composite are focused on surface morphology. However, to the best of our knowledge, this type of conformal uniform polymer coating on carbon black has not been thoroughly explored yet.

2. Experiment

The conformally PANI coated carbon black 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 black were dispersed in β-NSA aqueous solution before polymerization. As a result, micelles containing carbon black particles form in the reaction, these micelles have core-shell structure as shown in Figure 2. 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 dropwise 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 black) 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 carbon black composite(29,30) and suggests that carbon black particles should be situated inside the polymer tubes. Schematic representation of incorporation of carbon black into PANI matrix is given in this scheme which suggests that carbon black embedded in PANI tubes leads to the formation of PANI composites which has better electrical and magnetic properties..

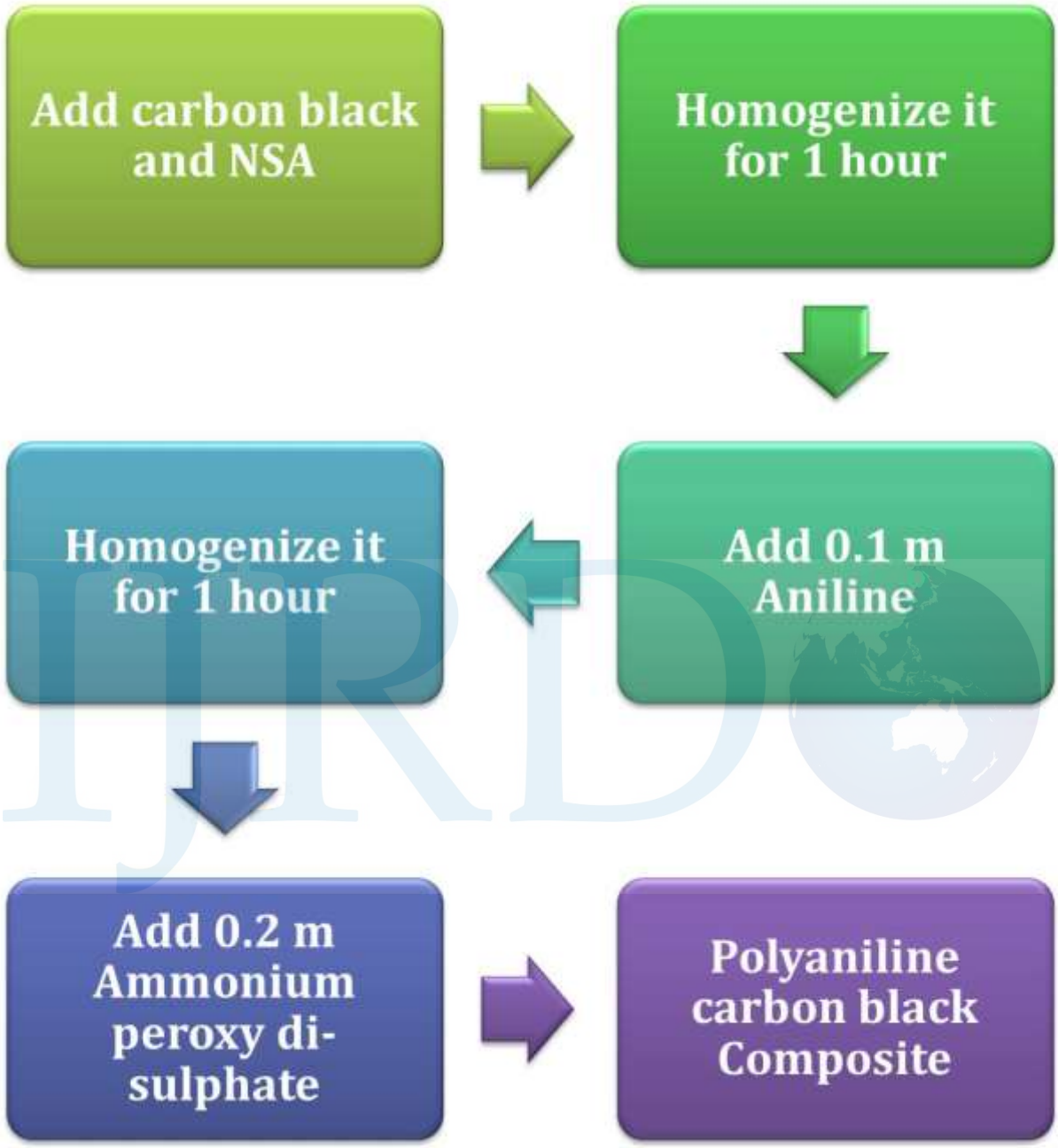

Figure 1. Flow chsart of the synthesis procedure of PANI composite

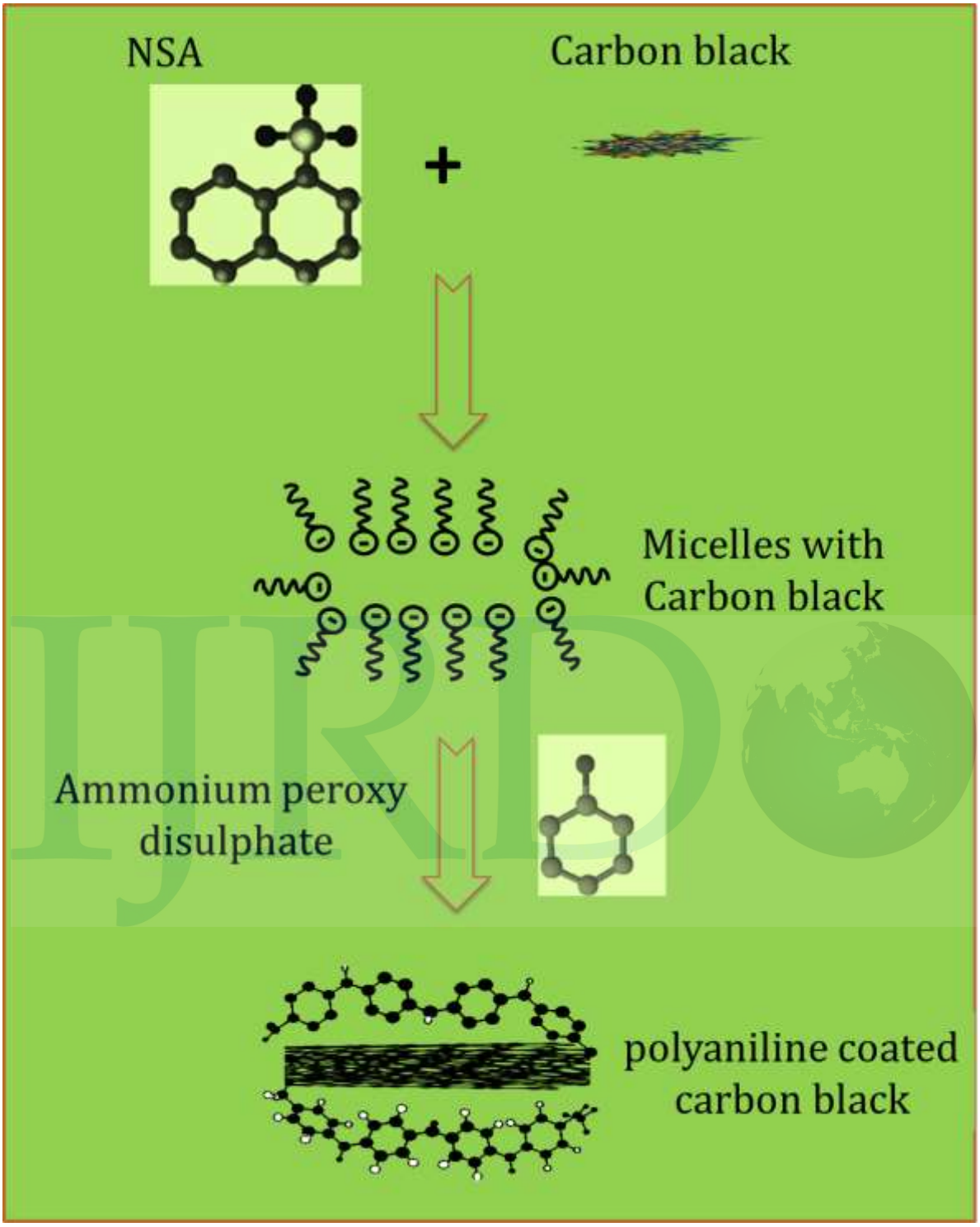

Figure 2. Schematic representation of the PANI/carbon black composite

3. Result and Discussion

3.1. Scanning electron microscopy (SEM)

Figure 3 showed the SEM images of PANI–carbon black composite. These micrographs showed that PANI–carbon black composite exited as highly tubular particles whereas as grown carbon black is entangled granules with diameter in the range of 90 nm and their lengths ranging in several microns. The small size of the carbon black having high specific surface area provides large number of sorption sites to aniline monomer which can polymerize to form coating over the carbon black. At very low concentration of carbon black, PANI coated tubes exist as tubular agglomerates . This may be attributed to the large proportion of bulk/solution polymerized PANI (existing in agglomerated form) as compared to aniline polymerized over carbon black surface. However, with the increase in carbon black content, there is systematic change in morphology from highly aggregated tubules towards uniformly coated granules. Therefore, at certain critical concentration of carbon black the polymerization takes place exclusively on surface of carbon black with minimal bulk polymerization and agglomeration effects. The SEM of PANI carbon black composite also revealed the nanoporous nature of coatings, which can be used for selective incorporation of other particles carbon black showed granular morphology .

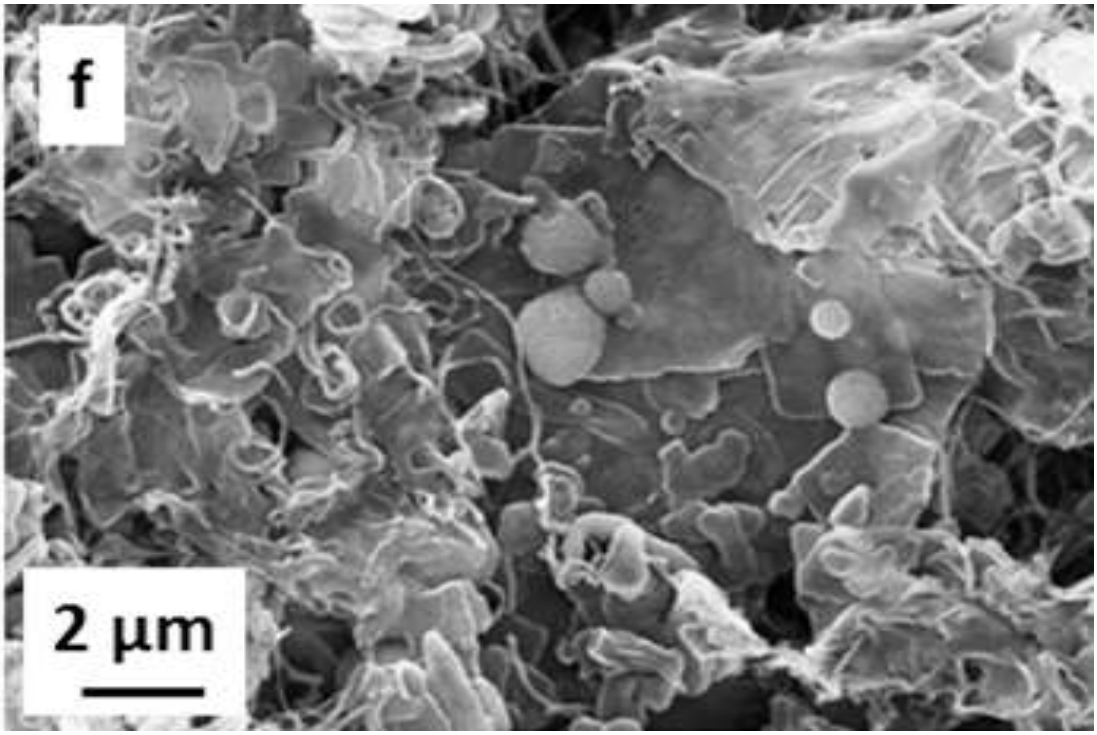

Figure 3 *SEM micrographs of PANI carbon black composites.*

3.2. UV-Visible studies

The UV absorption spectra of polyaniline and its composite with carbon black shows in figure. in case of polyaniline composite, two changes have been observed. First a red shift has been observed for the band from 615 to 655 nm which was ascribed to polaronic transition and absorption spectra show the red shift for the band 325 to 335 nm. This shifting may due to the interaction of carbon black 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.

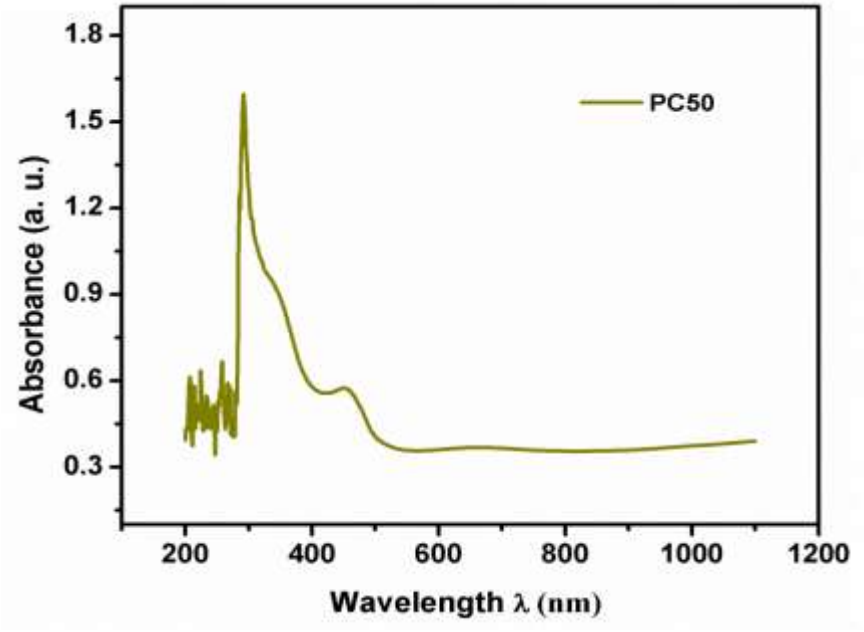

Figure 4 Visible spectra PANI & carbon black composites

3.3. Thermogravimetric analysis(TGA)

Figure 5 shows the thermo-gravimetric curves (TG) of carbon black and PANI composites. The materials were heated from 35 to 905°C under a constant heating rate of 10°C/min and in the inert atmosphere of nitrogen gas (60 ml/min). The carbon black has excellent thermal stability up to 900°C and weight loss was only 2.5 %. The TGA curve of PANI and carbon black composites indicated first weight loss at 115°C may be attributed to the loss of water and other volatiles species. The weight loss in the second step at about 285°C involves the loss of phosphateions as well as onset of degradation of polyaniline backbone. The increasing carbon black content slightly affects the decomposition temperature (DT) which increases from 285°C (PANI) to 295°C (composites). 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 black incorporated in polymer was found to 21 %. The results indicate that actually incorporated carbon black fraction is less than the ratio of aniline: carbon black 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.

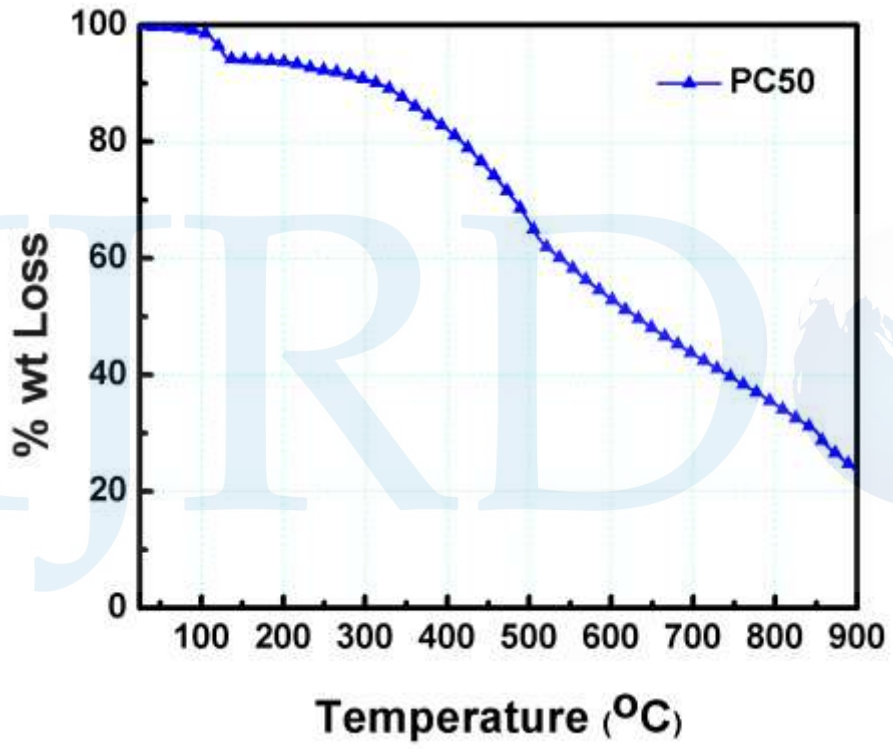

Figure 5 Thermal gravimetric analysis ofcarbon black and PANI composite

4. Conclusion

Extremely conducting PANI–carbon black composites were synthesized by in situ polymerization. The SEM pictures show uniform coating of PANI over surface of individual carbon black. Based on observed morphological features, it was suggested that the probable formation mechanism of these composites. This suggests significant interactions between the

carbon black and PANI. At very low concentration of carbon black, PANI coated tubes exist as globular agglomerates and as concentration of carbon black increases it changes in to tubular form .

5. Reference

[1] Chen, D., Feng, H. and Li, J. (2012). Graphene oxide: preparation, functionalization, and electrochemical applications. *Chemical Reviews*, **112**,(11),6027-6053.

[2] Francis, G.C. and Jacobs, S. J. (2001). Organic light emitting diodes. U.S. Patent, **6**,274,979, issued August 14,.

[3] Liang, J., Wang, Y., Huang, Y., Ma, Y., Liu, Z., Cai, J., Zhang, C., Gao, H. and Chen, Y. (2009). Electromagnetic interference shielding of graphene/epoxy composites. *Carbon*, **47**, (3), 922-925.

[4] Yang, Y., Gupta, M. C., Dudley, K. L. and Lawrence, R.W. (2005). Novel carbon nanotube−polystyrene foam composites for electromagnetic interference shielding. *Nano Letters,* **5**,(11), 2131-2134.

[5] Chung, D. D. L. (2001). Electromagnetic interference shielding effectiveness of carbon materials. *Carbon,* **39**, (2), 279-285).

[6] Lepert, A. Y. and Rayna, F. D. (2002). Static charge dissipation pads for sensors. U.S. Patent, **6**,346,739, issued February 12,.

[7] Huang, J., Li, G. and Yang, Y. (2008). A semi-transparent plastic solar cell fabricated by a lamination process. *Advanced Materials,* **20**,(3), 415-419.

[8]Cha, C., Su, R. S., Annabi, N., Dokmeci, R. M. and Khademhosseini, A. (2013). Carbon-based nanomaterials: multifunctional materials for biomedical engineering. *ACS Nano,* **7**,(4), 2891-2897.

[9] Rivnay, J., Owens, R. M. and Malliaras, G. G. (2013). The rise of organic bioelectronics. *Chemistry of Materials,* **26**,(1), 679-685.

[10] Gao , Z., Wanlu, Y., Wang, J., Wang, B., Li, Z., Liu, Q., Zhang, M. and Liu, L. (2012). A new partially reduced graphene oxide nanosheet/polyaniline nanowafer hybrid as supercapacitor electrode material. *Energy & Fuels,* **27**,(1), 568-575.

[11] Liu, J., Lam, J.W.Y., Cathy, K.W.J., CY, J. N., Shi ,J., Su, H., Fai, K. and Yeung, A. (2010). Thiol− yne click polymerization: regio-and stereoselective synthesis of sulfur-rich acetylenic polymers with controllable chain conformations and tunable optical properties. *Macromolecules,* **44**, (1), 68-79.

[12] Lei, S., Tomoyo, M., Seki, S. and Dincă, M. (2013). Mn2 (2, 5-disulfhydrylbenzene-1, 4-dicarboxylate): A microporous metal–organic framework with infinite (− Mn–S−)∞ chains and high intrinsic charge mobility. *Journal of the American Chemical Society* ,**135**, (22), 8185-8188.

[13] Wang, D. and Bierwagen, G. P. (2009). Sol–gel coatings on metals for corrosion protection. *Progress in Organic Coatings* ,**64**,(4) ,327-338.

[14] Kasemann, R. and Helmut, K. S. (1994). Coatings for mechanical and chemical protection based on organic-inorganic sol-gel nanocomposites..

[15] Kotal, M., Jaehwan, K., Oh, J. and Oh, IK. (2016). Recent progress in multifunctional graphene aerogels. *Frontiers in Materials*,**3**, 29.

[16] Stoller, M. D., Sungjin, P., Yanwu, Z., Jinho, A. and Rodney, S. R. (2008). Graphene-based ultracapacitors. *Nano Letters*,**8**,(10), 3498-3502.

[17] Pandolfo, A. G. and Hollenkamp, A. F. (2006). Carbon properties and their role in supercapacitors. *Journal of Power Sources,* **157**,(1), 11-27.

[18] Kumar, S., Doshi, H., Srinivasarao, M., Jung, P.O. and Schiraldi, D. A. (2002). Fibers from polypropylene/nano carbon fiber composites. *Polymer,***43**,(5), 1701-1703.

[19] Reineke, S., Lindner, F., Schwartz, F., Seidler, N., Walzer, K., Lüssem, B. and Leo, K. (2009). White organic light-emitting diodes with fluorescent tube efficiency. *MRS Online Proceedings Library Archive,* 1212.

[20] Lai, C.M., Yung, H. Y. and Huang, Y. H. (2006). Pixel structure of active matrix organic light-emitting diode and method for fabricating the same. U.S. Patent Application, **11**, 308,015, Filed March, 3,.

[21] Kulkarni, A .P., Christopher, J. T., Babel, A. and Samson, A. J. (2004). Electron transport materials for organic light-emitting diodes. *Chemistry of Materials,* **16**, (23), 4556-4573.

[22] Mohanty, A. K., Misra, M. and Hinrichsen, G. (2000). Biofibers, biodegradable polymers and biocomposites: an overview. *Macromolecular Materials and Engineering*, **276**,(1),1-24.

[23] Yangyong, W. and Xinli, J.(2005). Intrinsically conducting polymers for electromagnetic interference shielding. *Polymers for Advanced Technologies,* **16**,(4), 344-351.

[24] Kanatzidls, M.G.(1990). Conductive polymers. *C&EN Special Report* , **36**.

[25] Kang, E. T., Neoh, K. G. and Tan, K. L.. (1998). Polyaniline: a polymer with many interesting intrinsic redox states. *Progress in Polymer Science*,**23**, (2),277-324.

[26] Bhadra, S., Khastgir, D., Singha, N.K. and Joong, H. L. (2009). Progress in preparation, processing and applications of polyaniline. *Progress in Polymer Science,* **34**,(8), 783-810.

[27] Li, D., Jiaxing, H. and Kaner, R. B. (2008). Polyaniline nanofibers: a unique polymer nanostructure for versatile applications. *Accounts of Chemical Research,* **42**,(1),135-145 .

[28] Kim, B.J., Oh, S.G., Han, M.G. and Im, S.S. (2000). Preparation of polyaniline nanoparticles in micellar solutions as polymerization medium. *Langmuir,* **16**,(14), 5841-5845.

[29] Huang, J., Virji, S., Weiller, B. H. and Kaner, R. B. (2003). Polyaniline nanofibers: facile synthesis and chemical sensors. *Journal of the American Chemical Society,* **125**,(2), 314-315.

[30] Paul, R. K. and Pillai, C. K. S. (2000). Melt/solution processable conducting polyaniline with novel sulfonic acid dopants and its thermoplastic blends. *Synthetic Metals,* **114**,(1), 27-35.

[31] Feng, X. M., Li, R. M., Ma, R. W., .Chen, R. F., Shi, N. E., Fan, Q. L. and Huang, W. (2011). One-step electrochemical synthesis of graphene/polyaniline composite film and its applications. *Advanced Functional Materials,* **21**, (15), 2989-2996.

[32] Kaliski, A. F. (1992). Process for making structural aggregate pigments. U.S. Patent, **5**,116,418, issued May 26,.

[33] Barick, A. K. and Tripathy, D. K.(2011). Preparation, characterization and properties of acid functionalized multi-walled carbon nanotube reinforced thermoplastic polyurethane nanocomposites. *Materials Science and Engineering, B,* **176**,(18), 1435-1447.

[34] Olek, M., Ostrander, J., .Jurgal, S, Möhwald, H., Kotov, N., Kempa, K. and Giersig, M.(2004). Layer-by-layer assembled composites from multiwall carbon nanotubes with different morphologies. *Nano Letters,* **4**,(10),1889-1895.

[35] Li, N., Huang, Y., Du, F., He, X., Lin, X., Gao, H., Ma, Y., Li, F., Chen, Y. and.Eklund P. C. (2006). Electromagnetic interference (EMI) shielding of single-walled carbon nanotube epoxy composites. *Nano Letters,* **6**, (6), 1141-1145.

[36] Singh, A. P., Mishra, M., Hashim, D. P., Narayanan, T. N., Hahm, M. G., Kumar, P., and Dwivedi, J. (2015). Probing the engineered sandwich network of vertically aligned carbon nanotube–reduced graphene oxide composites for high performance electromagnetic interference shielding applications. *Carbon,* **85** 79-88.