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In-situ polymerized polyaniline nanofibers based functional cotton and nylon fabrics as millimeter wave absorbers

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Abstract

Polyaniline nanofibers and its composite with graphite, have been synthesized by a simple chemical polymerization method. The polyaniline nanofibers graphite composite with thickness of 1 mm exhibit excellent electromagnetic interference (EMI) shielding of above 80 dB in the frequency range of 8.2-18 GHz. Thin EMI shielding fabrics of thickness 0.1 mm based on polyaniline nanofibers and its composite have been developed by in-situ polymerization route. These fabrics combine the properties of both polyaniline nanofibers as well as its composite and fabrics (cotton and nylon). The developed functional fabrics with 0.1 mm thickness exhibit EMI shielding effectiveness in the range of 11-15 dB in the 8.2-18 GHz frequency range. The optical and scanning electron microscopy studies indicate the uniform coating of polyaniline nanofibers over individual fibers and interweave regions. Thin and flexible shielding materials suitable for a broad range of millimeter wave shielding applications have been developed by simple and profitable method.

1 Introduction

The recent growth of electronics and widespread instrumentation in the world has caused electromagnetic interference (EMI) which is now becoming a vital concern in the millimeter wave frequency ranges. It is a kind of electromagnetic pollution which causes a disturbance, false operation of appliances and leakage of information. Exposure to electromagnetic waves (EM) can also affect the human health. EMI can cause adverse effect on all the contemporary electrical and electronic systems from day to day life to space exploration that can result in the loss of money, energy, time and even life. 1-3 Hence, there is an urgent requirement for suitable and efficient EMI shielding materials in the millimeter wave applications. Varying methods have been employed to develop lightweight and efficient EMI shielding materials to increase device lifetime and efficiency. Shielding of EMI is done by reflection or absorption or a combination of both mechanisms. The low-frequency EM radiations can be shielded by reflection mechanism while millimeter wave can be attenuated by absorption. Hence millimeter wave EM absorbers are one of the important currently researched areas due to its growing demand in various spheres of life. Moreover, thin and flexible shielding materials can provide the additional benefit of user friendly, inexpensive and can be used on all shaped surfaces. Conductive fabrics based shielding materials can serve these purposes. These materials can provide flexibility, excellent formability, mechanical properties, EM discharge, EMI protection, RF interference protection, light weight and thermal expansion matching. 4-6 Recently the primary applications of conducting fabrics include filters, EMI shielding materials, antibacterial and flame retardant materials. These fabrics can find application as shielding materials in aerospace/military, electronics, and medical equipment. They can mainly provide shielding, electromagnetic compatibility to radio frequency interference from ground sensitive electronic components and boards, protect cables, for display grounding and EMI shielding for sensors, laptop, to shield FM/AM radio,

wireless phone, cellular phone and computer which operates up to 1000 MHz frequency. Fabrics with low EMI shielding is required for ESD applications. ^{3,8,9} Traditional EMI shielding materials rely on metallic materials to effectively shield unwanted radiations. Gupta et al. reported hybrid woven fabrics having stainless steel/polyester composite yarn of thickness around 0.4 mm with EMI SE of 31 dB in the frequency range of 8-18 GHz.¹⁰ Metal coating is another approach to obtain good shielding materials. Shinagawa et al. tried electroless plating of Cu and Ni on paper and synthetic pulp. 11 The metal coated paper exhibits 40 dB SE between 10 MHz and 1 GHz. Kumar et al. reported EMI SE of 58.7 dB for carbon–copper (C–Cu) nanocomposites by coating nanocrystalline Cu on heat-treated polyaromatic hydrocarbons (HTPAHs) of 2 mm thickness in the Ku-band frequency range. 12 Perumalraj and Dasaradhan prepared fabric from nickel plated copper core conductive yarn with EMI SE of 25-45 in the frequency range of 200-1000 MHz.¹³ Carbon based shields are also widely used now a days due to their flexibility, corrosion resistance, lightweight, and formability. 14-19 Non/woven polyester and knitted cotton fabric coated with multiwalled carbon nanotubes, multiwalled carbon nanotubes + silver nano particles, multiwalled carbon nanotubes + nickel coated carbon fiber, nickel coated carbon fibers of 100-200 µm thickness show EMI SE in the range of 9-19 dB at 1 GHz.²⁰ Hence the current technology uses mainly metal/carbon shielding which can provide excellent EMI shielding effectiveness (EMI SE). In spite of better shielding performance, metal coated fabrics have many drawbacks such as reduced wear and scratch resistance, low mechanical properties, high rigidity, heavyweight, corrosion susceptibility, processing cost, shielding predominantly by reflection, etc. On the other hand, the use of carbon fillers also exhibits problems of cost, sloughing, health, and long-term environmental issues which limit their application as the shielding materials for many practical

applications. 21-23,4 Ideally, magnetic structures can exhibit effective absorption at high

frequency range due to the high magnetization. However, weak magnetocrystalline anisotropy and decrease of permeability due to the ferromagnetic resonance and eddy current losses induced by the EM wave at high frequencies especially in the gigahertz region limits its application for EM wave absorption. Hence proper modification of the magnetic fillers is needed to achieve good shielding performance. ²⁴⁻²⁶ Intrinsically conducting polymers with finite conductivity and non-transparency to microwaves can provide an attractive solution to solve this problem and deliver a new generation of EMI shielding for many millimeter wave applications. ²⁷⁻³² Notably, the conducting polymer polyaniline and its composites are gaining considerable attention because of its attractive electrical, thermal and mechanical properties as well as low density, tunable conductivity, non-corrosiveness, nominal cost, ease of synthesis, shielding by absorption rather than reflection, better electrostatic discharge (ESD) and environmental stability resulting in their use for the full range of techno-commercial applications. ^{28,33-36} Hence, polyaniline can have future critical scope in communication industry as a shielding material.³⁶ In spite of such exciting properties, their commercial utility is limited due to their poor mechanical properties due to its rigid characteristics by the chemical conformation of benzene rings. ^{28,37,38} Several efforts have been made to design such conducting polymer as flexible and extensive area EMI shield.³⁹⁻⁴¹ A simple approach to obtain thin and flexible shielding materials based on conducting polymers such as polyaniline is by developing conducting fabrics. Such materials combine mechanical property, stretchability and flexibility of the fabrics with the conductivity of the polymer and have been reported to find suitable to many applications in the electronics and communication industry. 3,22,28,31,42-46 Polyaniline based fabrics were reported for appropriate applications such as fibrous sensors, smart clothing, or for electromagnetic interference shielding as well as antistatic discharge applications such as packaging of microelectronic devices. 22,23,31,44,45 These fabrics can be used as EMI

shielded cloth for concerned persons, radar shield in military, as well as heat generating fabrics for devices etc.²³ Such fabrics can be prepared either by coating conducting polymers or by in situ polymerization of various monomers.⁷ All the reported preparation of conducting fabrics based on polyaniline, involve many surfactants, solvents as well as tedious preparation process which make it less economically viable.^{22,23,31} Hence the need for cheap, thin and flexible EMI shields are the necessity of the present and future communication and electronics industry. The present work is an attempt to develop EMI shielding conducting cotton and nylon fabrics based on polyaniline nanofibers and its composite by simple in situ polymerization route. The synthesis method involves no surfactant and chemical solvents and yield polyaniline nanofibers of excellent conductivity and EMI shielding effectiveness.⁴⁷ Moreover the fibrillar morphology of the synthesized polyaniline provide an added advantage to the flexibility and stability of the developed fabrics. The polyaniline nanofibers composite was prepared by addition of graphite flakes (Gp) during the polymerization of polyaniline nanofibers.

2 Synthesis and characterization

2.1 Synthesis

2.1.1 Synthesis of polyaniline nanofibers and polyaniline nanofibers-graphite composite

The polyaniline nanofibers (P) were synthesized by the polymerization of aniline
hydrochloride monomer (Alfa Aesar, Ward Hill, MA, USA) by ammonium persulfate

(APS) (Aldrich, Chemical Company, Inc., Milwaukee, WI, USA) as the reducing agent.

The synthesis was achieved by the dropwise addition of APS dissolved in 1 M HCl into
the aniline hydrochloride solution in 1 M HCL at an oxidant monomer molar ratio of

1.15 at room temperature. The reaction mixture was kept stable for 36 hrs which
facilitate the growth of uniform polyaniline nanofibers. The resulting green precipitate
was filtered and washed with water and methanol to remove excess acids and byproducts

from polymerization. The obtained green powder was dried in vacuum oven at 60 $^{\circ}$ C for 24 hrs. 43

The graphite filler incorporated polyaniline nanofibers composite (GpP) was prepared in a way similar to that of pure polyaniline nanofibers by taking additional component graphite flakes (Gp). The graphite flakes were obtained from Carborundum Universal Ltd, Mumbai, India. The molar ratio of aniline hydrochloride to filler (Gp) in the preparation of GpP was 1:4 i.e., about 2.3 weight % (wt.%) of Gp in P.

2.1.2 Synthesis of polyaniline nanofibers and its graphite composite based cotton and nylon fabrics

The polyaniline based fabrics were prepared by in situ polymerization of aniline hydrochloride. The cotton or nylon fabrics were dipped in the aniline monomer solution for 24 hrs, and the polymerization was carried out by dropwise addition of APS followed by keeping the mixture reaction stable for 36 hrs similar to the synthesis of polyaniline nanofibers ⁴⁷ as schematically represented in Fig.1. Formation of the coating of polyaniline nanofibers on the surface of fabrics during polymerization was marked by the appearance of green color. The fabrics were removed from the solution, washed with methanol and dried in vacuum oven at 60 °C for 24 hrs.

2.2 Characterization

The phase formation was determined using X-ray diffraction (XRD) pattern using CuKα radiation (X'Pert PRO MPD X-ray diffractometer, PANalytical, Almelo, Netherlands) in the 2θ value range of 10-90°. The morphology of the synthesized polyaniline nanofibers and composite was studied using Transmission Electron Microscope (TEM) (FEI Tecnai-G2 30S-TWIN, FEI Company, Hillsboro, OR). The UV-vis absorption measurement of polyaniline nanofibers and its graphite composite was performed using Shimadzu 3600 UV-vis-NIR spectrophotometer. The photographic images were recorded with a digital camera (Sony, 10x optical zoom, 16M Pixel) and visual images

by optical microscopy (Leica, MRDX). The surface morphology of the fabrics based on synthesized polyaniline nanofibers was analyzed using Scanning Electron Microscope (SEM) (JEOL, JSM-5600LV, Tokyo, Japan). The EMI shielding measurements were performed by waveguide method connected to vector network analyzer (Agilent Technologies E5071C, ENA series, 300 kHz-20 GHz, CA) with samples of dimensions 22.86 × 10.80 mm for X-band (8.2-12.4 GHz) and 15.80 × 7.90 mm for Ku band (12.4-18 GHz) frequency range. The polyaniline nanofibers and its composite were pressed into a sample of thickness 1 mm for EMI shielding measurements.

3 Results and Discussion

Cotton fabrics based on P and GpP composite are designated as PC and GpPC respectively while the corresponding nylon fabrics are respectively designated as PN and GpPN. The XRD pattern of polyaniline nanofibers (P) and polyaniline nanofibers graphite composite (GpP) is depicted in Fig. 2 (a) and (b) respectively. Fig. 2 (d-e) respectively depicts the XRD pattern of pure cotton fabrics (C), as well as, polyaniline nanofibers and polyaniline nanofibers graphite composite based cotton fabrics. The polyaniline nanofibers have peaks at 2θ values of around 11°, 15°, 20° and 25°. The presence of crystalline phase of polyaniline nanofibers indicates the metallic conductive state. 48 Peaks observed near 15° and 25° are crystalline peaks and that observed at 20° is the amorphous peak of polyaniline.⁴⁹ The XRD pattern of polyaniline nanofibers graphite composite (GpP) clearly reveals the presence of graphite in polyaniline nanofibers matrix. This also indicates that the interactions between polyaniline nanofibers and graphite are purely physical in nature. Diffraction peaks observed in the XRD pattern of pristine cotton fabrics are related to the crystalline structure of cellulose I.50-52 The peaks of polyaniline nanofibers are not clearly visible in the XRD pattern of polyaniline nanofibers and polyaniline nanofibers graphite composite based cotton

fabrics as it overlaps with the high-intensity peaks of cotton fabrics. The peaks can be seen while carefully examining the XRD patterns and are marked for better understanding. Peaks at $2\theta=26.5^{\circ}$ in the XRD pattern of polyaniline nanofibers graphite composite based cotton fabrics corresponds to the graphite phases from (002) reflection and indicate the good coating of polyaniline nanofibers graphite composite over cotton fabrics.⁵³ Successful growth of polyaniline nanofibers, and polyaniline nanofibers graphite composite can be seen from the XRD patterns shown in figure 2 (d-e). Similarly the XRD pattern of pure nylon fabrics (N), polyaniline nanofibers and polyaniline nanofibers graphite composite based nylon fabrics are presented in Fig.2 (f), (g) and (h) respectively. 54,55 Compared to the XRD pattern of pristine nylon fabrics, few new peaks corresponding to that of polyaniline nanofibers and polyaniline nanofibers graphite composite are observed in the XRD pattern and are marked. This clearly demonstrates the presence of polyaniline nanofibers and polyaniline nanofibers graphite composite on nylon fabrics. The growth of polyaniline nanofibers and polyaniline nanofibers graphite composite on the fabrics (both cotton and nylon) is evident from their XRD patterns and also from the green color of the coated fabrics shown in the photographic images (figure 4 (b and d)).

Fig. 3 (a), (b) and (c) respectively depicts the TEM images of graphite flakes, polyaniline nanofibers, and polyaniline nanofibers graphite composite. It is evident from the figure that the graphite is having flake-like morphology of few nanometer in thickness while polyaniline nanofibers exhibits fibrillar morphology of about 200 nm in diameter. The TEM image of polyaniline nanofibers graphite composite (Fig. 3 (c)) composite indicate that conducting polyaniline nanofibers composite is obtained by the uniform distribution of graphite fillers in the polyaniline matrix.

The solid state absorption spectra of polyaniline nanofibers, and polyaniline nanofibers graphite composite shown in Fig. 3 (d) has two bands attributed to the π – π * transition

within the benzenoid segment and $n-\pi^*$ transitions within the quinoid structure. This indicates the presence of localized polaronic states such that the synthesized polyaniline nanofibers are in emeraldine salt form.⁴⁷ A slight shift can be observed on the bands of UV-Vis spectra of polyaniline nanofibers graphite composite, which may be due to the formation of a charge transfer complex between the doped polyaniline nanofibers and graphite.⁵⁶ This eventually leads to good conductivity as well as high EMI shielding efficiency of the composite. Hence, the presence of graphite only has impacts on the conductivity and hence the EMI shielding property of the polyaniline nanofibers. The photographs of pristine and polyaniline nanofibers grown fabrics are shown in Fig. 4 (a-d). Pristine cotton (Fig. 4 (a)) and nylon (Fig. 4 (c)) fabrics are white in color and after the growth of polyaniline nanofibers, the color of both fabrics change to green as shown in Fig. 4 (b) and (d) respectively. This indicates that the coating of polyaniline nanofibers is extended over entire cotton and nylon fabrics. This is further confirmed by the optical and SEM images of coated and uncoated fabrics. The mesh openings of both pristine cotton and nylon fabrics are clearly seen in the optical images shown in Fig. 5 (a) and (c) as well as SEM images depicted in Fig. 6 (a) and (c) respectively. The mesh openings cannot be seen in the optical images of polyaniline nanofibers based cotton and nylon fabrics showed in Fig. 5 (b) and (d) respectively. This reveals that thin coatings of polyaniline nanofibers of few micrometer ranges are formed over the fabrics. Similar observations are also obtained from the SEM images of polyaniline nanofibers based cotton and nylon fabrics as shown in Fig. 6 (b) and (d) respectively. It is evident from the SEM images that the polyaniline nanofibers are uniformly formed over the fabrics producing uniform coatings. The fibrillar morphology of the polyaniline is also observed to be maintained even after coating. This is due to the consistent growth of polyaniline nanofibers over the fabrics as they were dipped in the monomer solution for about 24 hrs which results in the uniform coating of aniline monomer over the fabrics followed by

stable reaction time of 36 hrs. Reaction time less than 36 hrs does not provide uniform coatings as well as not much amount of polyaniline was coated on the fabrics. In addition to this, fibrillar morphology of the polyaniline is also not well obtained for low reaction time as reported in our earlier work ⁴⁷ and all these will result in low EMI shielding effectiveness. Moreover, higher reaction time provides larger polyaniline coating thickness which delaminates while washing as well as after drying the fabrics. Hence not much amount of polyaniline coating can be achieved and results in low EMI shielding effectiveness. The polyaniline nanofibers coated over the fabrics by 36 hrs of reaction time is uniform and obtained without any delamination as evident from the SEM images. Addition of reducing agent leads to the consistent and uniform growth of polyaniline nanofibers over the fabrics due to the combined effect of all reaction conditions. ⁴⁷ The presence of acid guide the self-assembled growth of nanofibers by helping the monomer to form micelles while the room temperature facilitates the reaction process and stable reaction condition prevents the secondary growth of polyaniline. The fabrics thus acts as substrates for the growth of polyaniline nanofibers which provide a conducting coating over individual fibers along with the formation of conducting layer covering the interfiber and interweave regions. This reduces the microwave transparent spaces resulting in the development of fabrics with efficient EMI shielding. Moreover, the thin coating of polyaniline nanofibers over the fabrics helps to maintain the mechanical properties of the fabrics. Similar uniform coatings are also obtained for polyaniline nanofibers graphite composite based fabrics due to same synthesis procedure.

The EMI shielding efficiency of these materials can be analyzed by measuring their EMI shielding effectiveness (EMI SE). It is determined by the combination of the amount of energy reflected (reflection shielding effectiveness (SE_R)) and absorbed (absorption shielding effectiveness (SE_A)) by the material during transmission of the electromagnetic

wave. Thus EMI SE is given as SE_R+SE_A , SE_R and SE_A and can be calculated from the scattering parameters according to the following equations:

 SE_R (dB) = -10 log (1- S_{11}^2) and SE_A (dB) = -10 log [(S_{21}^2)/(1- S_{11}^2)] where S_{11} and S_{12} are the magnitude of scattering parameters.^{57, 58}

The frequency dependence of the EMI SE of polyaniline nanofibers and its composite with a sample thickness of 1 mm in the X and Ku band frequency range (8.2-12.4 & 12.4-18 GHz) is given in Fig. 7. It is found that the shielding efficiency is greatly improved by the addition of graphite which may be due to the increased conductivity of the composite. The EMI SE increases from 71-77 dB to 83-89 dB with the addition of graphite to polyaniline nanofibers in the measured frequency range. The conductivity of pure polyaniline nanofibers is about 18.5 S/cm and increased to 24 S/cm by the addition of very small amount of graphite (2.3 wt.%) to the polyaniline nanofibers matrix. The graphite due to its good conducting nature and flake-like morphology act as a conducting link between polyaniline nanofibers which accelerates the charge transfer that in turn leads to increased conductivity and good EMI shielding property. 41 The EMI SE of polyaniline nanofibers and its composite is almost constant in this frequency range and exhibits a slightly growing trend with frequency. The behavior, as well as the value of EMI SE, depends on SE_R and SE_A. The SE_R and SE_A performance of polyaniline nanofibers and its composite in the frequency range of 8.2-18 GHz is also depicted in Fig. 7. The SE_R of these composites is found to decrease with frequency while that of SE_A shows an increasing trend with frequency. The addition of graphite filler leads to an increase in both SE_R and SE_A similar to EMI SE. The SE_R value of polyaniline nanofibers graphite composite is found to be in the range of 18-13 dB while that of polyaniline nanofibers is 14-10 dB in this frequency range. Similarly with graphite addition, the SE_A value increases from 57-67 dB to 65-76 dB in the measured frequency range. It is found that polyaniline nanofibers and its graphite composite exhibit attractive

EMI shielding response for small sample thickness value of 1 mm with a significant contribution from SE_A. The solid state absorption spectra of polyaniline nanofibers indicate the presence of localized polarons which will actually interact with the incident electromagnetic radiation leading to EMI shielding by absorption. 47 The presence of graphite improves the absorption dominated shielding of polyaniline nanofibers due to its conducting nature and flake-like morphology. 41 Hence the absorption dominated EMI shielding of polyaniline nanofibers and its graphite composite is due to the combined effect of conductivity of the composite, measurement frequency range of GHz, morphology of polyaniline nanofibers and graphite as well as the millimeter range thickness of the shielding material. 52,59-62 The excellent EMI shielding properties of polyaniline nanofibers and its graphite composite with can attenuate nearly 100 % of electromagnetic interference make them attractive for many practical applications. The shielding properties of pristine, polyaniline nanofibers and its composite based cotton and nylon fabrics are shown in Fig. 8. It is found that the EMI SE of both pristine nylon and cotton fabrics of thickness 0.1 mm is negligible and close to zero. Thin EMI shielding fabrics with EMI shielding in the range of 11-15 dB are obtained with the growth of pure and graphite filler added polyaniline nanofibers on these fabrics. Highest EMI shielding ability is shown by polyaniline nanofibers graphite composite based fabrics due to the relatively high EMI SE of the composite as shown in Fig. 7. An increase of hundred times in the EMI SE is observed with the formation of polyaniline nanofibers and its composites on cotton and nylon fabrics. The variation of SE_R as well as SE_A of these cotton and nylon fabrics with frequency are also shown in Fig. 8. These fabrics are also found to shield mainly by absorption similar to the polyaniline nanofibers and its composite. The SE_R of polyaniline nanofibers based fabrics (both nylon and cotton) in the measured frequency range is 3 dB, and that of SE_A is 8-9 dB. The value of above parameters for polyaniline nanofibers graphite composite based

fabrics is 4 and 10-11 dB respectively. Thus thin EMI shielding cotton and nylon fabrics of about 0.1 mm thickness which can attenuate the electromagnetic interference by about 97 % is achieved and is better compared to many of the reported polyaniline based fabrics in the same frequency range regarding EMI SE, thickness and synthesis procedure. ^{22,23,31} The EMI SE of these fabrics does not show appreciable variation with frequency. Moreover, the method of preparation of polyaniline nanofibers based fabrics is very simple as it can be achieved by in situ polymerization method without any structural directing agents or organic solvents at room temperature. This is an added advantage from the techno-commercial and industrial viewpoint. Thin, flexible natural and synthetic fabrics based on polyaniline nanofibers and its composite were prepared which can provide stable wide bandwidth for shielding applications, particularly for electrostatic discharge shielding applications.

4 Conclusion

Flexible and lightweight EMI shields were developed by growing polyaniline nanofibers and its composite with graphite on cotton and nylon fabrics by in situ polymerization method. The polyaniline nanofibers graphite composite was prepared by the addition of graphite flakes during polymerization with aniline monomer filler ratio of 4:1. The incorporation of conducting filler results in the enhancement of shielding properties of polyaniline nanofibers and excellent EMI shielding in the range of 83-89 dB is obtained for polyaniline nanofibers graphite composite over wide frequency range of 8.2-18 GHz. The main shielding mechanism of polyaniline nanofibers and its composite is absorption. The developed fabrics which inherit the properties of polyaniline nanofibers as well as in situ incorporated conducting filler are thin (thickness in the range of 0.1 mm) and exhibit EMI shielding in the range of 15 dB for polyaniline nanofibers graphite composite based fabrics. Hence flexible, thin, broad band shielding materials which can prevent the electromagnetic interference by about 97 % and are suitable for a wide range of

shielding applications particularly electrostatic discharge is successfully achieved. This polyaniline nanofibers based fabrics are prepared by simple in situ polymerization route and can meet the growing demand for thin and flexible electromagnetic interference shielding materials.

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References

- D. A. Weston, Electromagnetic Compatibility: Principles and Applications, Marcel Dekker, New York, 2001.
- 2. X. C. Tong, Advanced Materials and Design for Electromagnetic Interference Shielding, CRC Press, United States, 2009.
- 3. K. Jagatheesan, A. Ramasamy, A. Das and A. Basu, Electromagnetic shielding behaviour of conductive filler composites and conductive fabrics A review, *Indian J. Fibre Text. Res.*, 2014, **39**, 329-342.
- 4. L. L. Wang, B. K. Tay and K. Y. See, Electromagnetic interference shielding effectiveness of carbon based materials prepared by screen printing, *Carbon*, 2009, **47**, 1905-1910.
- R. Neelakandan, V. R. Giridev, M. Murugesan and M. Madhusoothanan,
 Surface resistivity and shear characteristics of polyaniline coated polyester fabric,
 J. Ind. Text., 2009, 39, 175-186.
- 6. K. B. Cheng, T. H. Ueng and G. Dixon, Electrostatic discharge properties of stainless steel/polyester woven fabrics, *Text. Res. J.*, 2001, **71**, 732-738.
- 7. J. He, R. Li and F. Gu, Preparation of polyaniline/nylon conducting fabric by layer by layer assembly method, *J. Appl. Polym. Sci.*, 2013, **128**, 1673-1679.

- 8. P. Saini and V. Choudhary, Conducting polymer coated textile based multilayered shields for supression of microwave radiations in 8.2-12.4 GHz range, *J. Appl. Polym. Sci.*, 2013, **129**, 2832-2839.
- 9. H. Jin, Q. Chen, Z. Chen, Y. Hu, J. Zhang, Multi-LeapMotion sensor based demonstration for robotic refine tabletop object manipulation task, *CAAI*Transactions on Intelligence Technology, 2016, 1, 104-113.
- 10. K. K. Gupta, S. M. Abbas, A. C. Abhyankar, Ultra-lightweight hybrid woven fabric containing stainless steel/polyester composite yarn for total EMI shielding in frequency range 8–18 GHz, J. Electromagnet. Wave, 2015, 29, 1454-1472.
- 11. S. Shinagawa, Y. Kumagai and K. Urabe, Conductive papers containing metallized polyester fibers for electromagnetic interference shielding, *J. Porous* Mat., 1999, 6, 185-190.
- 12. A. Kumar, A. P. Singh, S. Kumari, P. K. Dutta, S. K. Dhawan and A. Dhar, Polyaromatic-hydrocarbon-based carbon copper composites for the suppression of electromagnetic pollution, *J. Mater. Chem. A*, 2014, 2, 16632-16639.
- 13. R. Perumalraj and B. S. Dasaradhan, Electroless nickel plated composite textile materials for electromagnet compatibility, *Indian J. Fibre Text. Res.*, 2011, **36**, 35-41.
- 14. T. K. Gupta, B. P. Singh, V. N. Singh, S. Teotia, A. P. Singh, I. Elizabeth, S. R. Dhakate, S. K. Dhawan and R. B. Mathur, MnO₂ decorated graphene nanoribbons with superior permittivity and excellent microwave shielding properties, *J. Mater. Chem. A*, 2014, 2, 4256-4263.
- 15. W. –L. Song, X. –T. Guan, L. –Z. Fan, W. –Q. Cao, C. –Y. Wang, Q. –L. Zhao and M.-S. Cao, Magnetic and conductive graphene papers toward thin layers of effective electromagnetic shielding, *J. Mater. Chem. A*, 2015, **3**, 2097-2107.

- 16. R. Qiang, Y. Du, H. Zhao, Y. Wang, C. Tian, Z. Li, X. Han and P. Xu, Metal organic framework-derived Fe/C nanocubes toward efficient microwave absorption, *J. Mater. Chem. A*, 2015, **3**, 13426-13434.
- 17. T. K. Gupta, B. P. Singh, S. R. Dhakate, V. N. Singh and R. B. Mathur, Improved nanoindentation and microwave shielding properties of modified MWCNT reinforced polyurethane composites, *J. Mater. Chem. A*, 2013, 1, 9138-9149.
- 18. R. Kumar, S. R. Dhakate, T. Gupta, P. Saini, B. P. Singh and R. B. Mathur, Effective improvement of the properties of light weight carbon foam by decoration with multi-wall carbon nanotubes, *J. Mater. Chem. A*, 2013, 1, 5727-5735.
- S. P. Pawar, D. A. Marathe, K. Pattabhi and S. Bose, Electromagnetic interference shielding through MWNT grafted Fe₃O₄ nanoparticles in PC/SAN blends, *J. Mater. Chem. A*, 2015, 3, 656-669.
- 20. R. R. Bonaldi, E. Siores and T. Shah, Characterization of electromagnetic shielding fabrics obtained from carbon nanotube composite coatings, *Synthetic Met.*, 2014, **187**, 1-8.
- 21. W. L. Song, S. C. Mao, M. L. Ming, B. Song, Y. W. Chan, L. Jia, Y. Jie and L. Z. Fan, Flexible graphene/polymer composite films in sandwich structures for effective electromagnetic interference shielding, *Carbon*, 2014, 66, 67-76.
- 22. N. M. Kumar and G. Thilagavathi, Surface resistivity and EMI shielding effectiveness of polyaniline coated polyester fabric, *Journal of Textile and Apparel, Technology and Management*, 2012, **7**, 1-6.
- 23. A. M. R. Abbasi and J. Militky, EMI shielding effectiveness of polypyrrole coated glass fabric, J. Chem. Chem. Eng., 2013, **7**, 256-259.

- 24. Q. He, T. Yuan, X. Zhang, X. Yan, J. Guo, D. Ding, M. A. Khan, D. P. Young, A. Khasanov, Z. Luo, J. Liu, T. D. Shen, X. Liu, S. Wei, Z. Guo, Electromagnetic field absorbing polypropylene nanocomposites with tuned permittivity and permeability by nanoiron and carbon nanotubes, *J. Phys. Chem. C*, 2014, 118, 24784-24796.
- 25. J. Zhu, S. Wei, N. Haldolaarachchige, D. P. Young, Z. Guo, Electromagnetic field shielding polyurethane nanocomposites reinforced with core_shell Fe_silica nanoparticles, *J. Phys. Chem. C*, 2011, **115**, 15304-15310.
- 26. Z. Guo, S. Park, H. T. Hahn, S. Wei, M. Moldovan, A. B. Karki, D. P. Young, Magnetic and electromagnetic evaluation of magnetic nanoparticle filled polyurethane nanocomposites, *J. Appl. Phys.*, 2007, **101**, 09M511.
- 27. P. Chandrasekhar, *Conducting Polymers, Fundamentals and Applications: A Practical Approach*, Kluwer Academic, Netherlands, 1999.
- 28. P. Saini, V. Choudhary, N. Vijayan and R. K. Kotnala, Improved electromagnetic interference shielding response of poly(aniline)-coated fabrics containing dielectric and magnetic nanoparticles, *J. Phys. Chem. C*, 2012, **116**, 13403-13412.
- 29. T. A. Skotheim, R. L. Elsenbaumer and J. R. Reynolds, *Handbook of Conducting Polymers*, Marcel Dekker, New York, 1998.
- 30. J. Joo and A. J. Epstein, Electromagnetic radiation shielding by intrinsically conducting polymers, *Appl. Phys. Lett.*, 1994, **65**, 2278-2280.
- 31. P. Saini, V. Choudhary and S. K. Dhawan, Improved microwave absorption and electrostatic charge dissipation efficiencies of conducting polymer grafted fabrics prepared via in-situ polymerization, *Polym. Adv. Technol.*, 2012, **23**, 343-349.

- 32. F. Wu, A. Xie, M. Sun, Y. Wang and M. Wang, Reduced graphene oxide (RGO) modified spongelike polypyrrole (PPy) aerogel for excellent electromagnetic absorption, *J. Mater. Chem. A*, 2015, **3**, 14358-14369.
- 33. Sivaram, *Polymer Science Contemporary Themes*, Tata McGraw-Hill, India, 1991.
- M. Aldissi, *Intrinsically Conducting Polymers: An Emerging Technology*,
 Kluwer Academic, Netherlands, 1993.
- 35. T. A. Skotheim and J. R. Reynolds, *Handbook of Conducting Polymers third*edition: Conjugated Polymers—Processing and Applications, CRC Press, United
 States, 2007.
- 36. E. Hakansson, A. Amiet, S. Nahavandi and A. Kaynak, Electromagnetic interference shielding and radiation absorption in thin polypyrrole films *Eur. Polym. J.*, 2007, **43**, 205-213.
- 37. D. C. Trivedi, *Handbook of Organic Conductive Molecules and Polymers*, John Wiley & Sons Ltd, United Kingdom, 1997.
- 38. A. G. Macdiarmid, Synthetic metals: a novel role for organic polymers, *Synthetic Met.*, 2002, **125**, 11-22.
- 39. S. M. Abbas, A. K. Dixit, R. Chatterjee and T. C. Goel, Preparation of nanosize polyaniline and its utilization for microwave absorber *J. Nanosci. Nanotechnol.*, 2007, **7**, 2129-2133.
- 40. D. A. Makeiff and T. Huber, Microwave absorption by polyaniline–carbon nanotube composites, *Synth. Met.*, 2006, **156**, 497-505.
- 41. N. Joseph, J. Varghese and M. T. Sebastian, Facile formulation and excellent electromagnetic absorption of room temperature curable polyaniline nanofiber based inks *J. Mater. Chem. C*, 2016, **4**, 999-1008.

- 42. D. T. Seshadri and N. V. Bhat, Synthesis and properties of cotton fabrics modified with polypyrrole, *Sen'i Gakkaishi*, 2005, **61**, 103-108.
- 43. L. dall'Acqua, C. Tonin, R. Peila, F. Ferrero and M. Catellani, Performances and properties of intrinsic conductive cellulose -polypyrrole textiles, *Synthetic Met.*, 2004, **146**, 213-221.
- 44. B. Kim, V. Koncar and C. Dufour, Polyaniline-coated PET conductive yarns: study of electrical, mechanical and electro mechanical properties, *J. Appl. Polym. Sci.*, 2006, **101**, 1252-1256.
- 45. H. H. Kyung, W. O. Kyung and J. K. Tae, Polyaniline–Nylon 6 Composite Fabric for Ammonia gas sensor, *J. Appl. Polym. Sci.*, 2004, **92**, 37-42.
- 46. R. Li, G. Liu, F. Gu, W. Zheng, S. Yang and W. Jianqing, In situ polymerization of aniline on acrylamide grafted cotton, *J. Appl. Polym. Sci.*, 2011, **120**, 1126-1132.
- 47. N. Joseph, J. Varghese, M. T. Sebastian, Self-assembled polyaniline nanofibers with enhanced electromagnetic shielding properties, *RSC Adv.*, 2015, **5**, 20459-20466.
- 48. K. Lee, S. Cho, S. H. Park, A. J. Heeger, C. W. Lee and S. H. Lee, Metallic transport in polyaniline, *Nature*, 2006, **441**, 65-68.
- 49. H. R. Tantawy, D. E. Aston, J. R. Smith and J. L. Young, Comparison of electromagnetic shielding with polyaniline nanopowders produced in solvent-limited conditions, *ACS Appl. Mater. Interfaces*, 2013, **5**, 4648-4658.
- 50. L. Fang, X. Zhang, J. Ma, D. Sun, B. Zhang and J. Luan, Eco-friendly cationic modification of cotton fabrics for improving utilization of reactive dyes, *RSC* Adv., 2015, 5, 45654-45661.

- 51. W. Duan, A. Xie, Y. Shen, X. Wang, F.Wang, Y. Zhang and J. Li, Fabrication of superhydrophobic cotton fabrics with UV protection based on CeO₂ particles, *Ind. Eng. Chem. Res.*, 2011, **50**, 4441-4445.
- 52. R. Aladpoosh, M. Montazer and N. Samadi, In situ green synthesis of silver nanoparticles on cotton fabric using Seidlitzia rosmarinus ashes, *Cellulose*, 2014, 21, 3755-3766.
- 53. H. Fuan, L. Sienting, L. C. Helen and F. Jintu, High dielectric permittivity and low percolation threshold in nanocomposites based on poly(vinylidene fluoride) and exfoliated graphite nanoplates, *Adv. Mater.*, 2009, **21**, 710-715.
- 54. Z. K. -Nia, M. Montazer and M. Latifi, Synthesis of nano copper/nylon composite using ascorbic acid and CTAB, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2013, **439**, 167-175.
- 55. M. Montazer, A. Mozaffari and F. Alimohammadi, Simultaneous dyeing and antibacterial finishing of nylon fabric using acid dyes and colloidal nanosilver, *Fibres Text. East. Eur.*, 2015, **23**, 100-106.
- 56. M. Abdullah Dar, R. K. Kotnala, V. Verma, J. Shah, W. A. Siddiqui and M. Alam, High Magneto-Crystalline Anisotropic Core-Shell Structured Mn_{0.5}Zn_{0.5}Fe₂O₄/polyaniline nanocomposites prepared by in situ emulsion polymerization, *J. Phys. Chem. C*, 2012, **116**, 5277-5287.
- 57. D. Annapurna and K. D. Sisir, Microwave Engineering, Tata McGraw Hill, India, 2009.
- 58. N. Joseph and M. T. Sebastian, Electromagnetic interference shielding nature of PVDF-carbonyl iron composites, *Mater. Lett.*, 2013, **90**, 64-67.
- 59. Z. Stempien, T. Rybicki, E. Rybicki, M. Kozanecki and M. I. Szynkowska, Insitu deposition of polyaniline and polypyrrole electroconductive layers on textile

- surfaces by the reactive ink-jet printing technique, *Synthetic Met.*, 2015, **202**, 49-62.
- 60. S. W. Guang, J. Z. Xiao, Z. W. Yun, H. Shuai, G. Lin and S. C. Mao, Polymer composites with enhanced wave absorption properties based on modified graphite and polyvinylidene fluoride, *J. Mater. Chem. A*, 2013, **1**, 7031-7036.
- 61. C. Zongping, X. Chuan, M. Chaoqun, R. Wencai and M. C. Hui, Lightweight and flexible graphene foam composites for high-performance electromagnetic interference shielding, *Adv. Mater.*, 2013, **25**, 1296-1300.
- 62. A. P. Singh, M. Mishra, P. Sambyal, B. K. Gupta, B. P. Singh, A. Chandrad and S. K. Dhawan, Encapsulation of γ-Fe₂O₃ decorated reduced graphene oxide in polyaniline core—shell tubes as an exceptional tracker for electromagnetic environmental pollution, *J. Mater. Chem. A*, 2014, **2**, 3581-3593.

Figures

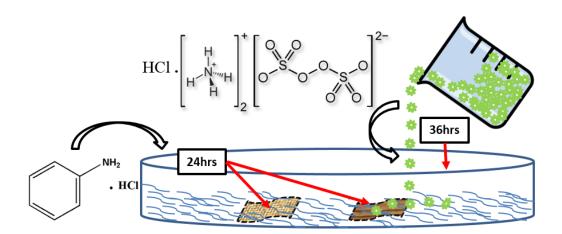


Figure 1 Schematic representation of the preparation of functional cotton and nylon fabrics based on polyaniline nanofibers and its composite.

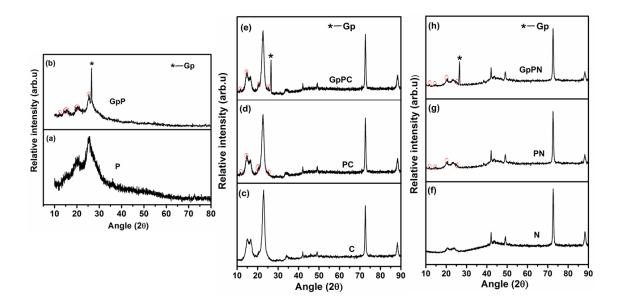


Figure 2 XRD pattern of (a) polyaniline nanofibers (P) (b) polyaniline nanofibers graphite composite (GpP) (c) pure cotton (C) (d) polyaniline nanofibers based cotton (PC) (e) polyaniline nanofibers graphite composite based cotton (GpPC) (f) pure nylon (N) (g) polyaniline nanofibers based nylon (PN) (h) polyaniline nanofibers graphite composite based nylon (GpPN) fabrics.

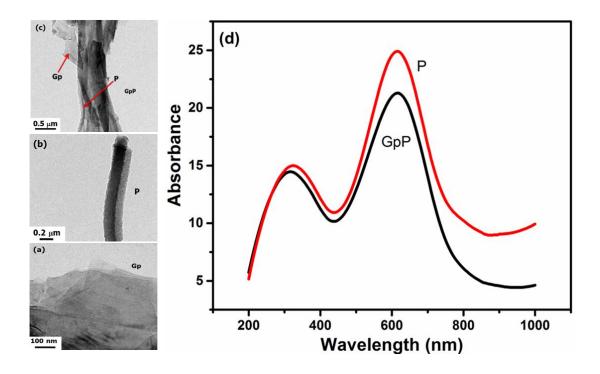


Figure 3 (a) TEM of (a) graphite (b) polyaniline nanofibers (P) (c) polyaniline nanofibers graphite composite (GpP) and (d) Solid state UV-vis spectra of polyaniline nanofibers and its graphite composite.

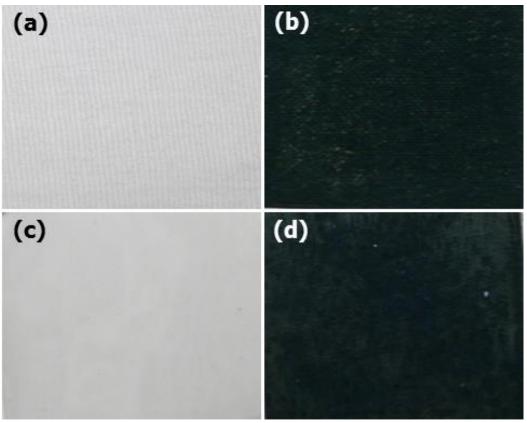


Figure 4 Photographic images of (a) pure and (b) polyaniline nanofibers based cotton, (c) pure and (d) polyaniline nanofibers based nylon fabrics

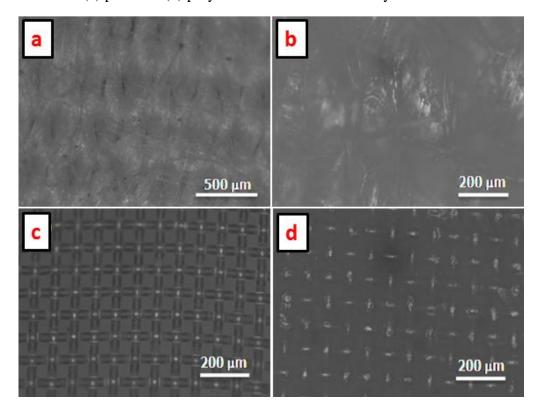


Figure 5 Optical images of (a) pure and (b) polyaniline nanofibers based cotton, (c) pure and (d) polyaniline nanofibers based nylon fabrics.

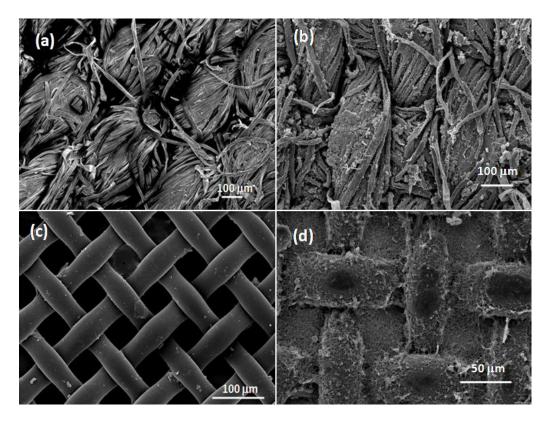


Figure 6 SEM images of (a) pure and (b) polyaniline nanofibers based cotton, (c) pure and (d) polyaniline nanofibers based nylon fabrics.

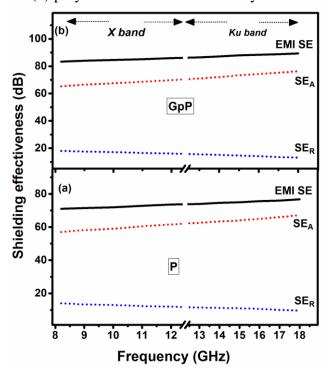


Figure 7 Variation of EMI SE, SE_A and SE_R of (a) polyaniline nanofibers (P) and (b) polyaniline nanofibers graphite composite (GpP) of thickness 1mm in the 8.2-18 GHz frequency range.

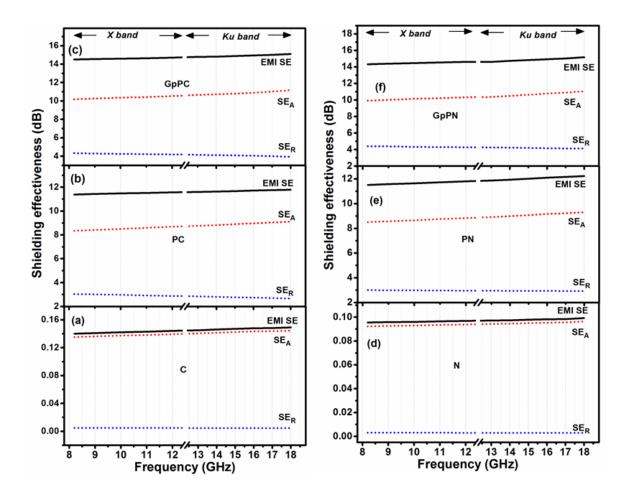


Figure 8 Variation of EMI SE, SE_A and SE_R of (a) pure (C), (b) polyaniline nanofibers based (PC), (c) polyaniline nanofibers graphite composite based (GpPC) cotton fabrics, (d) pure (N), (e) polyaniline nanofibers based (PN), (f) polyaniline nanofibers graphite composite based (GpPN) nylon fabrics of thickness 0.1 mm in the 8.2-18 GHz frequency range.

In-situ polymerized polyaniline nanofibers based functional cotton and nylon fabrics as millimeter wave absorbers

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Keyword: polymer synthesis, In situ polymerization, morphology, EMI shielding, X-ray diffraction

Schematic representation depicts the synthesis, microstructure and EMI shielding properties of functional cotton and nylon fabrics based on polyaniline nanofibers.

