Journal of ELECTRONIC MATERIALS, Vol. 49, No. 3, 2020
https://doi.org/10.1007/s11664-019-07631-7
© 2019 The Minerals, Metals & Materials Society

EMI Shielding Characteristics of Electrically Conductive Polymer Blends of PS/PANI in Microwave and IR Region

MUHAMMAD FAYZAN SHAKIR,[1] IQRA ABDUL RASHID,[1,2] ASRA TARIQ,[1,3] YASIR NAWAB,[1] AYESHA AFZAL,[1,4] MUHAMMAD NABEEL,[1] AHMAD NASEEM,[1] and USAMA HAMID[1]

1.—Polymer Engineering Department, National Textile University, Faisalabad, Pakistan. 2.—e-mail: iqra.rashid@ntu.edu.pk. 3.—e-mail: asra.tariq@ntu.edu.pk. 4.—e-mail: ayeshaafzal91@yahoo.com

Conductive polymeric blends (CPBs) of polystyrene and polyaniline (PS/PANI) were prepared by solution casting method in various compositions. Film thickness of CPBs was achieved ~ 250 micron. PS/PANI blend films were analyzed for electromagnetic interference (EMI) shielding characteristics in microwave and near-infrared (NIR) regions. PS/PANI blends showed remarkable features. Most mobile telecommunications use GHz frequency range and shielding effectiveness was observed in 9 GHz to 18 GHz. In 9 GHz to 18 GHz frequency range, 45 dB shielding effectiveness was measured. CPBs were also analyzed in the NIR region and showed transmittance of $<1\%$. Microwaves and NIR radiation are the most abundant in the environment and cause damage to human health. Both types of radiation causes serious damage to electronic devices as well.

Key words: Polyaniline, electrically conductive polymer blend, EMI shielding, IR blocking

INTRODUCTION

Electromagnetic interference (EMI) shielding acts as a barrier between the device and electromagnetic radiation. Electromagnetic interference diminishes the performance and life of the devices.[1] EMI shield is a coating on an electronic device which consists of conducting materials, for example, aluminum, copper and steel, however, nowadays polymeric coatings are in use.[2–5] A 50 dB shielding was reported using polyvinylidene fluoride/graphite composite using 70 wt.% of graphite flakes.[6] Reduced graphene oxide (rGO) anchored Ni-Co-Zn-Nd-ferrites. Polyaniline has been used and evaluated for 70 dB EMI shielding.[7] Polyaniline/graphene-based composite ink was prepared with 1 mm thickness that seemed to have attenuation of 70 dB whereas at lower thickness of 50 μm the shielding was observed at 17 dB.[8] Nylon and cotton-based fabric were prepared with incorporation of PANI nano-particles with thickness of 0.1 mm that gave 15 dB shielding effectiveness.[9] A four-component system based on PANI, carbon nanotube, graphene and epoxy were already prepared and evaluated that showed 45 dB of shielding effectiveness with shield thickness of 0.1 mm.[10] A three-component system of polyvinyl chloride/PANI/Graphene was with 15 wt.% PANI and 5 wt.% graphene were prepared and found out to have 52 dB shielding effectiveness.[4] Moreover, PANI is also being used in stretchable biosensors.[11] Conducting polymer materials are preferred over conventional metals, i.e., aluminum, copper and steel because of flexibility, lightweight, corrosion resistance and ease of processability. Moreover, conductive polymers were found easy to blend with other polymers with more flexibility and robust thermoplastics. Different blends of elastomeric polymers with conducting polymers were fabricated.

(Received June 12, 2019; accepted September 7, 2019; published online September 18, 2019)

These blends include Polyurethane/Polyaniline (PU/PANI) system with shielding efficiency of 24 dB.[12] Acrylonitrile-Butadiene-Styrene/Polyaniline (ABS/PANI) blend showed shielding efficiency of 60 dB.[13] PANI/Graphene, PANI/PVC, PANI alone were also characterized for EMI shielding.[14–17] Three-phase system PVC/PANI/graphene was also evaluated and found out to be very effective.[18] EMI shielding materials are characterized by electrical conductivity, dielectric permittivity and magnetic permeability.[1] It is obvious from the study of insulative and conductive polymeric blends that both electrical conductivity and dielectric permittivity increases with the increasing concentration of conductive polymer. Special features of PS/PANI polymer blend can be utilized as EMI shielding material in the microwave and IR regions which will have the advantages of high protection against EM radiation, ease of fabrication, and it will also be cost-effective.

In this research work, electrically conductive polymer blends were fabricated using polystyrene as matrix and polyaniline as electrically conductive filler. The main purpose was to evaluate these flexible polymer blend films for EMI shielding applications in the microwave and IR regions. PS/PANI films were evaluated in the frequency range of 9–18 GHz for microwave attenuation. The 700 nm to 2500 nm wavelength range is used for IR blocking properties. Vector Network analyzer (VNA) coaxial cable method was used for microwave attenuation and IR spectroscopy for IR blocking properties.

MATERIALS

Aniline monomer was purchased from Sigma-Aldrich. Ammonium persulfate (APS) was purchased from DAU JUNG Korea. Formic Acid was purchased from Merck Schuchardt, Germany. Chloroform was from purchased from Fisher chemicals UK and commercial grade Polystyrene (PS) was donated by Chawla Enterprise (Pvt.) Limited Pakistan.

EXPERIMENT

Polymerization of Aniline

Chemical oxidative method was adopted for the polymerization of aniline.[19] APS (4.8 g) and Aniline (2 ml) solution was prepared in formic acid (50 ml) separately at 50°C in 100 ml beakers at continuous stirring. After the formation of homogeneous solutions, both beakers were placed in an ice bath to get the desired polymerization temperature of 0–5°C. As the temperature was achieved, APS solution was poured dropwise, 1–2 drops per second in aniline solution while keeping the temperature of the bottom solution constant at 0–5°C with continuous stirring. After a few minutes, the dark greenish color of PANI starts to appear. After that solution was left for complete polymerization by keeping temperature 0–5°C along with continuous stirring. PANI precipitates were then separated by evaporating formic acid at 90°C. PANI precipitates washed with ethanol and water and then dried in a vacuum oven at 80°C with 300 mbar pressure overnight. A flowchart of this method is shown below in Fig. 1 for a better understanding.

Fabrication of Polymer Blends

Solution casting method was used to prepare polymer blends of various components shown in Table I. PS and PANI were dissolved in chloroform as a separate mixture and sonicated for 2 h. Both solutions were then mixed together to get desired composition of each component and left for stirring afterward for 18 h. The samples were cast in glass petri dish, dried at room temperature for 4 h and then placed in a vacuum oven at 300 mbar pressure and 50°C overnight. The films obtained were about 200–250 μm thick. The polymer blend films were assessed with the well-established characterization technique like x-ray diffraction (XRD) for the confirmation of PANI. Vector Network Analyzer (VNA) for EMI shielding effectiveness measurements and UV/Vis/IR spectroscopy for measurement of IR blocking properties of electrically conductive polymer blends.

RESULTS AND DISCUSSIONS

X-ray Diffraction

PANI is semi-crystalline in nature and exhibits two unique peaks in XRD pattern. PANI was prepared by the chemical oxidative method and was evaluated by x-ray diffraction for the confirmation of successful fabrication of PANI. XRD pattern of PANI is shown in Fig. 2. It is clearly visible that two peaks appear at $2\theta = 19°$ and $2\theta = 25°$. The peaks around $2\theta = 19°$ and 25° are attributed to the periodicity parallel and perpendicular to the polymer chain, respectively. Similar results of PANI wwere also reported.[4,9–11,21] Atactic PS is amorphous in nature and did not show any prominent peak in XRD patterns. As 20 wt.% and 40 wt.% PANI is added in amorphous PS, characteristics peaks of PANI also appeared in both CPB-1 and CPB-2 at the exact same position and with same peak width, clearly indicating that PS and PANI are just mixed physically and have no chemical interaction between them.

Microstructure

Microstructure of PS and CPB-2 was analyzed using Scanning Electron Microscopy (SEM). SEM images of the front surface (where EM wave incident) and fractured surface (Cross-section) are shown in Figs. 3 and 4. Cross-section was obtained by avoiding chain elongation during cutting, therefore films were frozen to − 196°C by dipping them

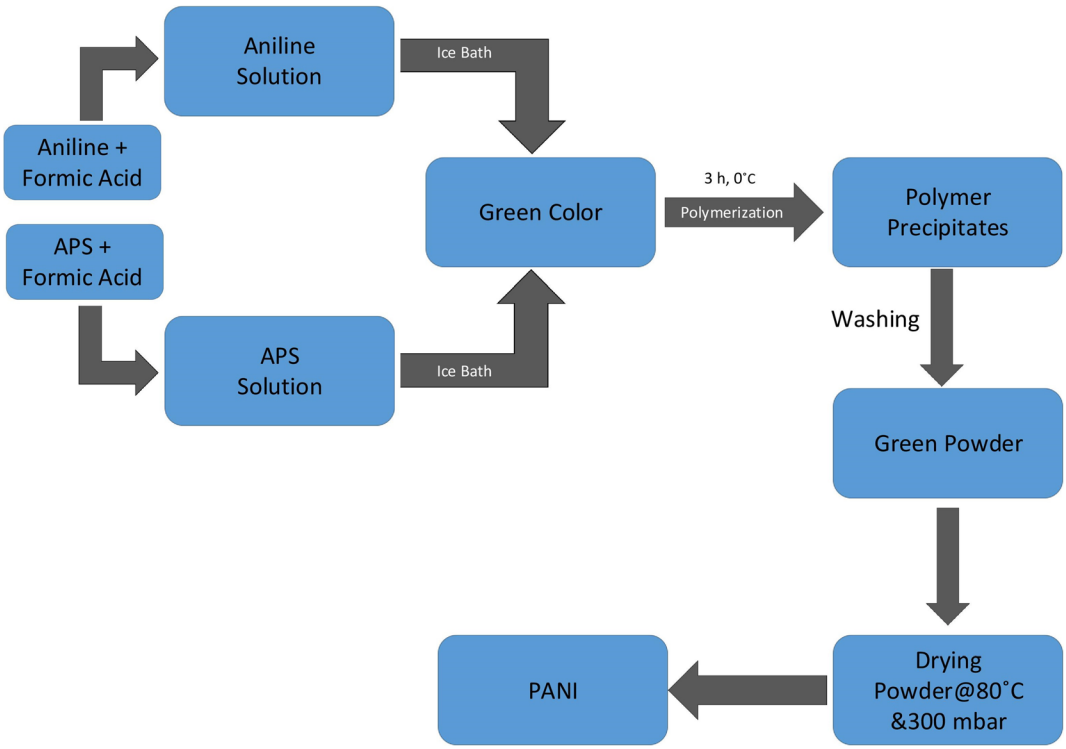

Fig. 1. Formic acid doped polyaniline synthesis flowchart.

Table I. Prepared samples information

No.	Sample name	Polystyrene%	Polyaniline%
1	PS	100	0
2	Conductive polymer blend-1 (CPB-1)	80	20
3	Conductive polymer blend-2 (CPB-2)	60	40

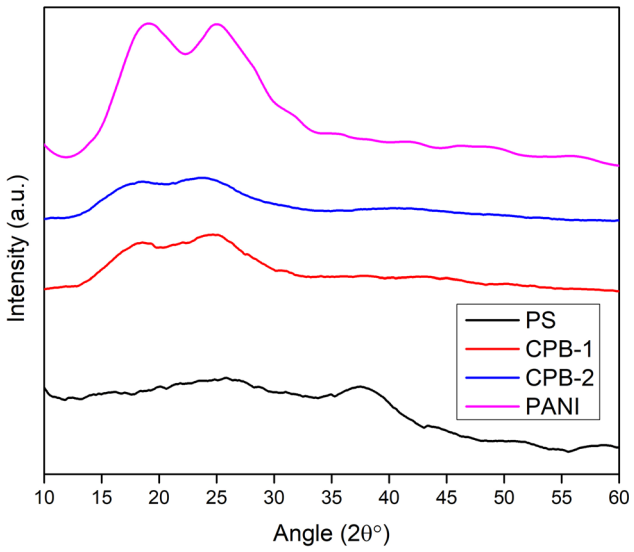

Fig. 2. X-ray diffraction of prepared samples.

into liquid nitrogen and then broken into two pieces exposing a cross-sectional surface. As atactic PS is completely amorphous in nature and so it did not show any prominent feature in both front and fractured surfaces. By adding 40 wt.% PANI in PS, very few PANI particles were seen on the front surface as compared to the fractured surface clearly indicating that almost 99% PANI particles are dispersed and formed interconnected network structure inside the PS matrix and the top surface is occupied by the insulative PS.

EMI Shielding

IR testing was carried out by IR Spectroscopy (Lambda 950, Perkin Elmer) in the NIR region (700 nm to 2500 nm). The reported accuracy of the instrument was 1%. Thin films were cut according to sample holder size (10 mm width and 30 mm length) of thickness 250 μm. Conventionally reflection of IR waves was achieved by layered structure of dielectric and electrically conductive materials.

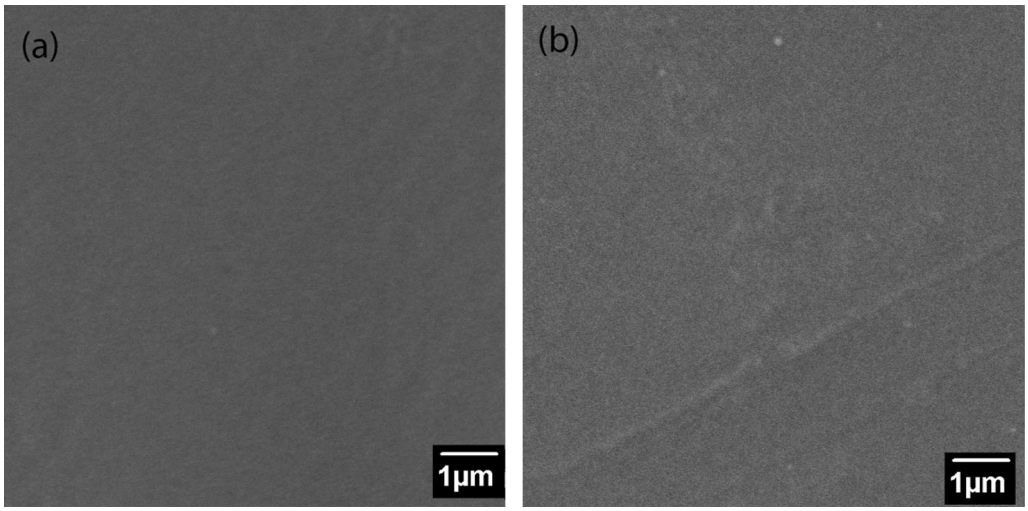

Fig. 3. SEM images of (a) PS front Surface (b) PS cross-sectional surface.

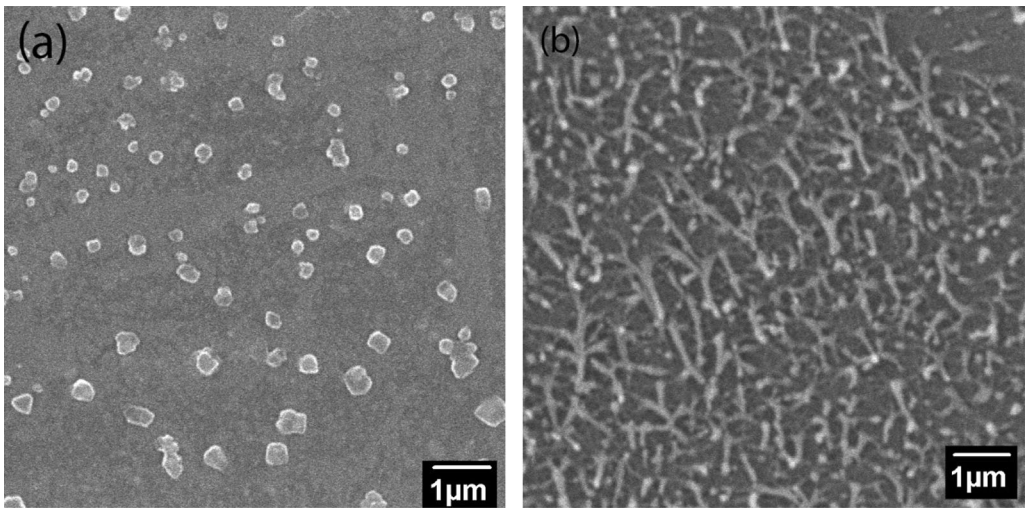

Fig. 4. SEM images of (a) CPB-2 front Surface (b) CPB-2 cross-sectional surface.

The use of polymeric blends opens up a wide range of applications due to its flexibility rather than rigid structure. Minimum of 40% transmission was achieved in the NIR region by using sandwich layered structure of dielectric material and copper.[20] While using CPB-2, less than one percent was achieved in the whole NIR region with the film thickness of 250 micron. According to EMI shielding theory, wheneveran electromagnetic (EM) wave falls on any surface, two phenomena happen, some part reflects back and some penetrate in the surface. Enhanced EMI shielding is observed both in IR and microwave regions. As pure PS is insulative in nature, therefore it did not exhibit any shielding properties both in IR and microwave regions. As 20 and 40 percent PANI were added in it, shielding was greatly enhanced as PANI is electrically conductive and dispersed in PS matrix in the form of nanoparticles creating a lot of interfaces, each provides a site to reflect EM waves and all this happens inside the thin shielding film and so is considered as absorbing as described in Fig. 5.

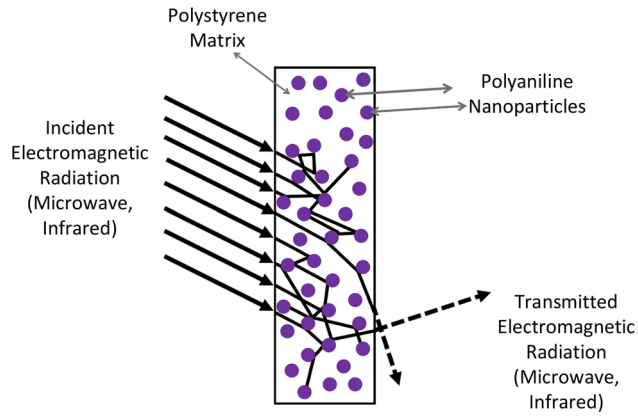

Fig. 5. Electromagnetic wave absorption schematic.

Figure 6a and b shows the SE_A and SE_R in frequency range of 9 GHz to 18 GHz. The reflective

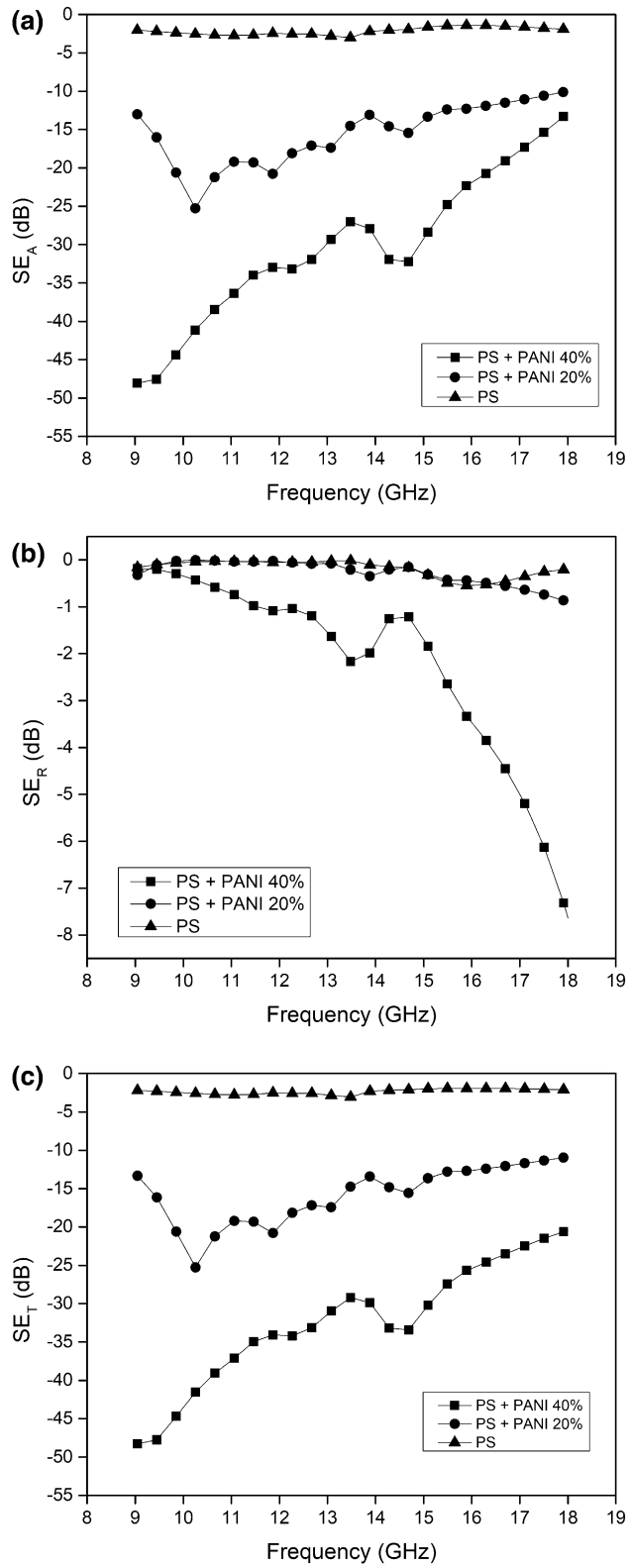

Fig. 6. (a) SE_A (b) SE_R (c) SE_T of PS, CPB-1 and CPB-2.

parameters S11, S12, S21, and S22 were obtained from vector network analyzer (VNA) using coaxial cable method. A disc-like sample was prepared according to test requirement with 7 mm outer diameter and 3 mm inner diameter with thickness of 250 μm and the following relations were used to calculate SE_R, SE_A, and SE_T.

$$SE_T = SE_R + SE_A.$$

Both SE_R and SE_A are expressed as:

$$SE_R = 10 \log \frac{1}{1 - |S_{11}|^2},$$

$$SE_A = 10 \log \frac{1 - |S_{11}|^2}{|S_{21}|^2},$$

$$SE = 50 + 10\mathrm{Log}\frac{\sigma}{f} + 1.7t\sqrt{\sigma f}.$$

EMI Shielding can also be calculated by the above equation where t, σ and f are thickness of film, electrical conductivity of film and frequency in MHz, respectively. All the films were prepared with a uniform thickness of 250 microns, that is why EMI shielding behavior in these samples was effected by PANI reinforcement only.

Table II Clearly shows the bandwidth in which prepared conductive polymer blends shows less than − 10 dB and − 20 dB shielding effectiveness. CPB-1 and CPB-2 both have less than − 10 dB shielding effectiveness which means more than 90% of EM wave is blocked in whole 9 GHz to 18 GHz bandwidth. Where − 20 dB shows 99% shielding effectiveness. CPB-1 provide only 1 GHz frequency range where its shielding effectiveness goes below − 20 dB is from 9.5 GHz to 10.5 GHz whereas CPB-2 gives a 7 GHz frequency range from 9 GHz to 16 GHz where its shielding effectiveness falls below − 20 dB.

According to EMI shielding theory, the EM wave reflects back when it falls on an electrically conductive surface, PANI is dispersed inside the PS matrix and outer most surface has consisted of non-conductive PS. SE_R is almost zero indicating that a complete EM wave penetrated inside the shielding film. Once the EM wave penetrates the shield then the electrically conductive PS-PANI interfaces absorb EM wave through multiple reflection within 250 micron thin films as shown in Fig. 5. Figure 6c shows the complete EMI Shielding SE_T in the microwave region. Figure 7 shows that IR transmission is extremely low in the whole NIR region (700–2500 nm) that is $< 1\%$ for CPB-2 and the transmission is between 4% and 5% for CPB-1. CPB-2 is more effective than other shields mentioned in the literature because this gives a narrow region and can only be used in that specific region. The same is the case in the microwave region.[21,22] For CPBs, SE_T values are below − 10 dB in the whole frequency range of 9–18 GHz instead of having less than − 10 dB shielding effectiveness in

Table II. Bandwidth for less than − 10 dB and − 20 dB shielding effectiveness

	$SE_A < -10$ dB		$SE_A < -20$ dB	
Sample name	**Start frequency (GHz)**	**End frequency (GHz)**	**Start frequency (GHz)**	**End frequency (GHz)**
PS	–	–	–	–
CPB-1	9	18	9.5	10.5
CPB-2	9	18	9	16

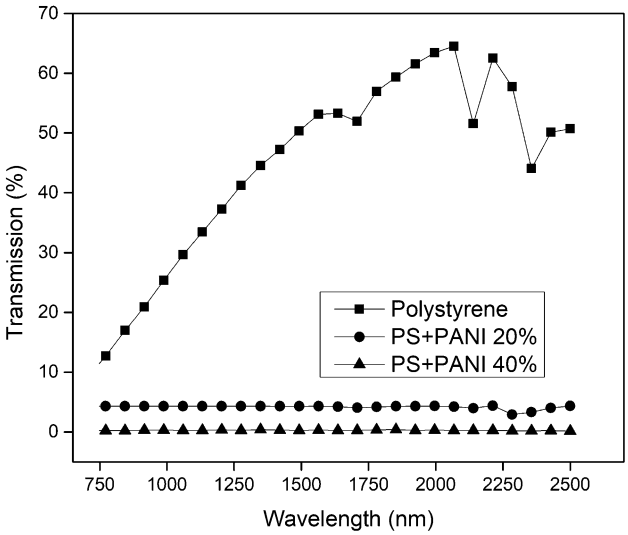

Fig. 7. IR Transmittance of PS and CPBs.

a small frequency range. A maximum of 49 dB value was achieved at 9 GHz for CPB-2 sample.

CONCLUSION

Formic acid doped polyaniline was successfully prepared by chemical oxidative technique. Polymer blend of polystyrene and polyaniline were prepared with the solution casting method. Thin films were obtained with the thickness of almost 250 μm. EMI shielding behavior in microwave and infrared regions were evaluated, and 48 dB in microwave region of 40% concentration of PANI in PS matrix was obtained. Less than 0.5% transmission was observed in whole NIR region (700 nm to 2500 nm). Conventionally, metal-based shield coatings were used that have the drawbacks of high weight, susceptible to corrosion, high production cost, etc. Nowadays CNTs and Graphene are the key areas of the ongoing research to produce highly effective shielding materials that also have limitations of high scale and high-quality production of CNTs and graphene and the use of sophisticated technology for the fabrication of thin films based on nano-level filler. The benefit of using conductive polymer blends for EMI shielding material is to have high shielding effectiveness with the use of a common polymer that is really easy to fabricate at large scale with high quality and also with the ease of processing of blends and converting into useable form.

REFERENCES

1. S.P. Pawar, S. Biswas, G.P. Kar, and S. Bose, *Polym. (United Kingdom)* 84, 398 (2015).
2. R. Jan, A. Habib, M.A. Akram, I. Ahmad, A. Shah, M. Sadiq, and A. Hussain, *Mater. Res. Express* 4, 35605 (2017).
3. X. Wang, *J. Electromagn. Anal. Appl.* 03, 160 (2011).
4. M. Fayzan, A. Nawaz, R. Khan, S. Javed, A. Tariq, M. Azeem, A. Riaz, A. Shafqat, H.M. Cheema, M. Aftab, I. Ahmad, and R. Jan, *Results Phys.* 14, 102365 (2019).
5. V. Panwar, B. Kang, J.O. Park, S. Park, and R.M. Mehra, *Eur. Polym. J.* 45, 1777 (2009).
6. N. Joseph, J. Varghese, and M.T. Sebastian, *Compos. Part B Eng.* 123, 271 (2017).
7. M. Hamedi, J. Wigenius, F. Tai, P. Björk, and D. Aili, 2058 (2010).
8. N. Joseph, J. Varghese, and M.T. Sebastian, *J. Mater. Chem. C* 4, 999 (2016).
9. N. Joseph, J. Varghese, and M.T. Sebastian, *Polym. J.* 49, 391 (2017).
10. Y. Huangfu, K. Ruan, H. Qiu, Y. Lu, C. Liang, J. Kong, and J. Gu, *Compos. Part A Appl. Sci. Manuf.* 121, 265 (2019).
11. I. A. Rashid, M. S. Irfan, Y. Q. Gill, R. Nazar, F. Saeed, A. Afzal, H. Ehsan, A. A. Qaiser, and A. Shakoor, Polym. Bull. (2019).
12. K. Lakshmi, H. John, K.T. Mathew, R. Joseph, and K.E. George, *Acta Mater.* 57, 371 (2009).
13. S. Koul, R. Chandra, and S. Dhawan, *Polymer (Guildf).* 41, 9305 (2000).
14. C. Tian, Y. Du, P. Xu, R. Qiang, Y. Wang, D. Ding, J. Xue, J. Ma, H. Zhao, and X. Han, *A.C.S. Appl. Mater. Interfaces* 7, 20090 (2015).
15. S. Ameen, V. Ali, M. Zulfequar, M. Mazharul Haq, and M. Husain, *Phys. B Condens. Matter* 403, 2861 (2008).
16. T. Mäkelä, S. Pienimaa, T. Taka, S. Jussila, and H. Isotalo, *Synth. Met.* 85, 1335 (1997).
17. H. Baniasadi, A. Ramazani, S. Mashayekhan, and F. Ghaderinezhad, *Synth. Met.* 196, 199 (2014).
18. H. M. F. Shakir, A. Tariq, A. Afzal, and I. Abdul, *J. Mater. Sci. Mater. Electron.* (2019).
19. E.C. Gomes and M.A.S. Oliveira, *Am. J. Polym. Sci.* 2, 5 (2012).
20. K. Gao, A. Raza, H. Shen, A. A. Haidry, and S. A. Muhammad, Mater. Res. Express (2019).
21. F. Wang, X. Wang, J. Zhu, H. Yang, X. Kong, and X. Liu, *Sci. Rep.* 6, 1 (2016).
22. R. Kumar, S. Kumari, and S.R. Dhakate, *Appl. Nanosci.* 5, 553 (2015).

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.