

When this complex attempts to stabilize, a redox reaction might occur between tellurium and tellurite ions due to surface instability of the tellurium nanoparticles, which triggers the polymerization of aniline. These nanoparticles not only facilitate the polymerization process but also stabilize the ES form of polyaniline by providing the necessary anionic support. Although the ES form of polyaniline exhibits good environmental stability, it is challenging to create a chemically stable solution. The composite is reasonably stable in dipolar aprotic solvent; however, in aqueous medium, the green color turns grayish, possibly due to weakening of the interaction between tellurium and the PANI functionality. It is possible that the presence of tellurium oxide as an impurity may generate anionic oxygen atoms that may stabilize the ES polyaniline due to the considerable difference in electronegativity. A change in the oxidation state of tellurium is believed to be the main cause of the oxidation of aniline and its subsequent polymerization. The nanocomposite was characterized by UV-Vis, IR, and XRD, *etc.* The powder was converted to pellets to measure its conductivity.

UV-visible absorbance in DMSO indicates a band for benzenoid ring-associated π - π^* transition at 354 nm. Excitation of the quinoid ring is identified with bands at 382 and 605 nm (Fig. 2). A low-intensity 605 nm band and an invisibly faint band at 836 nm is due to interaction with Te and TeO₂ and the reduction of quinoid moiety, indicating the conducting nature of the composite.³⁷ Such an impression has been described by various researchers when PANI interacts with inorganic elements.^{16,27–29,38} The product obtained is green, which indicates the form of polyaniline to be an ES form.

The FTIR spectra of polyaniline composites can provide valuable insights into their chemical composition and structural properties. The characteristic IR bands are observed, including the stretching (str.) vibration for N–H at about 3220 cm⁻¹, and other stretching vibrations at 1584, 1493, and 1334 cm⁻¹, respectively, for C=N, C=C, and C–N bonds. Additional bands for 1,4-disubstituted benzene ring are found at 1136 cm⁻¹, 998 cm⁻¹, and 513 cm⁻¹, which can be correlated



Fig. 2 UV-visible spectrum of PANI/Te in DMSO.

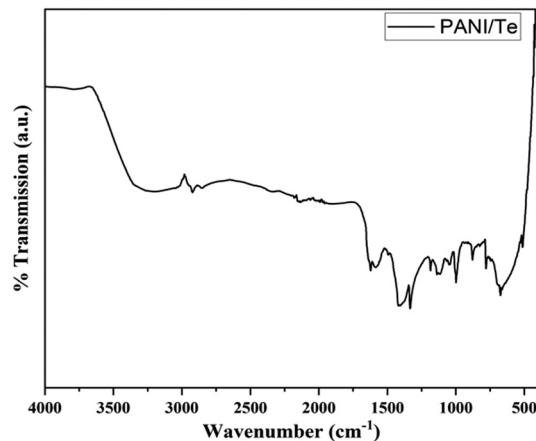


Fig. 3 FTIR spectrum of PANI/Te nanocomposite.

with in-plane bending and out-of-plane deformation vibration modes of aromatic C–H.^{27–29} (Fig. 3 and Table 1). The presence of benzenoid and quinoid rings leads to peaks at approximately 1500 cm⁻¹ and 1600 cm⁻¹, respectively. The presence of quinoid peaks confirms the ES form of polyaniline. The IR spectrum also contains peaks corresponding to the Te–O bond at 780 cm⁻¹ and 674 cm⁻¹, respectively.³⁸ All other FTIR bands can be attributed to stretching and bending of bonds in the polyaniline chain, as presented in Table 1.^{39,40} XRD analysis shows diffraction peaks for polyaniline, tellurium, and tellurium dioxide (Fig. 4). Although polyaniline is non-crystalline, it shows a semi-crystalline nature in some cases. It is reported that PANI (EB) has multiple peaks at $2\theta = 18.5, 19.4, 20.0, 22.2^\circ$ and even beyond.^{41a,b} In the present study, diffraction peaks for polyaniline are observed at 2θ values of 15.29, 16.22, 18.17, 19.84, and 21.08° in the XRD pattern of the PANI/Te nanocomposite. Major peaks of tellurium observed are 27.50, 38.23, 40.39, 43.31, and 49.61, with the respective planes (101), (102), (110), (111), and (021), along with some other minor peaks.^{27,29}

However, either *in situ* generated or due to surface oxidation, peaks for TeO₂ are also observed. Therefore, the composite material can be considered as a PANI/Te nanocomposite with some impurity of tellurium oxide, which is evident from the XRD pattern showing peaks at $2\theta = 30.02, 30.89, \text{ and } 44.29^\circ$, with respective Miller planes (111), (102) and (211) that correspond to α -TeO₂.^{42,43} By using the Scherrer formula, the average crystallite size for Te nanoparticles was estimated to be about 35 nm in the sample. Overall analysis confirms the formation of PANI/Te with impurities of TeO₂.⁴⁰

The SEM images are presented in Fig. 5(i), which show a mixed morphology mainly composed of spherical and rod-shaped components in the PANI/Te nanocomposite powder that appear to be platelets, and the particles are visible in and around; however, these may also be uniformly present in the film so as to boost their overall sturdy morphology. Images at various magnification levels (100 nm \times 50 000, 1 μm \times 5000, 1 μm \times 20 000, 100 nm \times 30 000) are presented. Obviously, PANI/Te possesses agglomerated spherical, rod, and stacked



Table 1 FTIR peak analysis of PANI/Te nanocomposite

Wavenumber (cm ⁻¹)	Vibrations (Stretching)
3220	N-H str.
2930	Aromatic C-H str.
1622, 1584	C=N (quinoid)
1493	C=C (benzenoid)
1419	C-N (benzenoid)
1334	Aromatic C-N (amine group)
1136	C-H bending (in plane)
779	<i>Para</i> -disubstituted aromatic rings indicating polymer formation
674	Te-O str.
513	C-H out of plane deformation

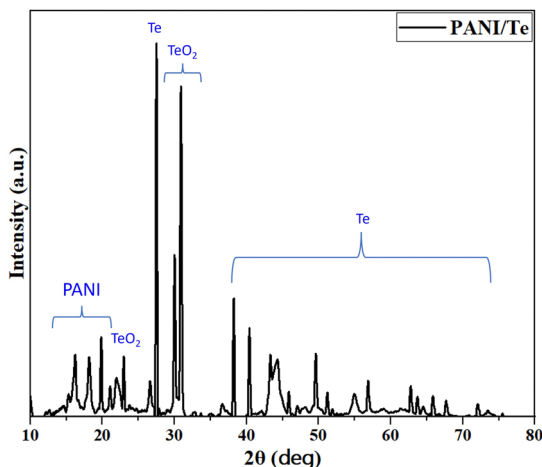


Fig. 4 XRD pattern of PANI/Te nanocomposite.

rod structures. The EDAX analysis clearly indicated the presence of respective components in the composite, as shown in Fig. S1 (ESI[†]). The presence of sulphur is also observed due to the fact that 2-mercaptoethanol was employed as the surface capping-cum-reducing agent. Fig. 5(ii) depicts the surface topology of a PANI/Te blended PVA film examined using atomic force microscopy (AFM). The heights of the partially spherical blobs are measured in nanometres, demonstrating the nano-domain topology of surfaces.

The shape of the film is known to be highly dependent on the mixing of the PANI/Te nanocomposite in the PVA solution. Structural heterogeneity is clearly visible in the image of the nanocomposite film, which is a characteristic property of most semicrystalline materials including amorphous constituents. Fig. 5 (ii) suggests different locations have distinct surface shapes due to blending of PANI/Te particles into the PVA polymer solution, possibly due to inhomogeneous size distribution. The heights of the hills and bumps are almost 100 nm, while the depths of the valleys within are nearly 50 nm. The AFM is nearly similar to those discussed in the literature.⁴⁴ It is reported that polyaniline is a hole-transporting material with conductivity in the semiconducting range with varying values of Te doping (10^{-9} – 10^{-3} S m⁻¹), up to 25% doping.¹⁶ In the present case, Te is assumed to be about 20–25% with respect to the *in situ* form of PANI, and therefore, the values obtained

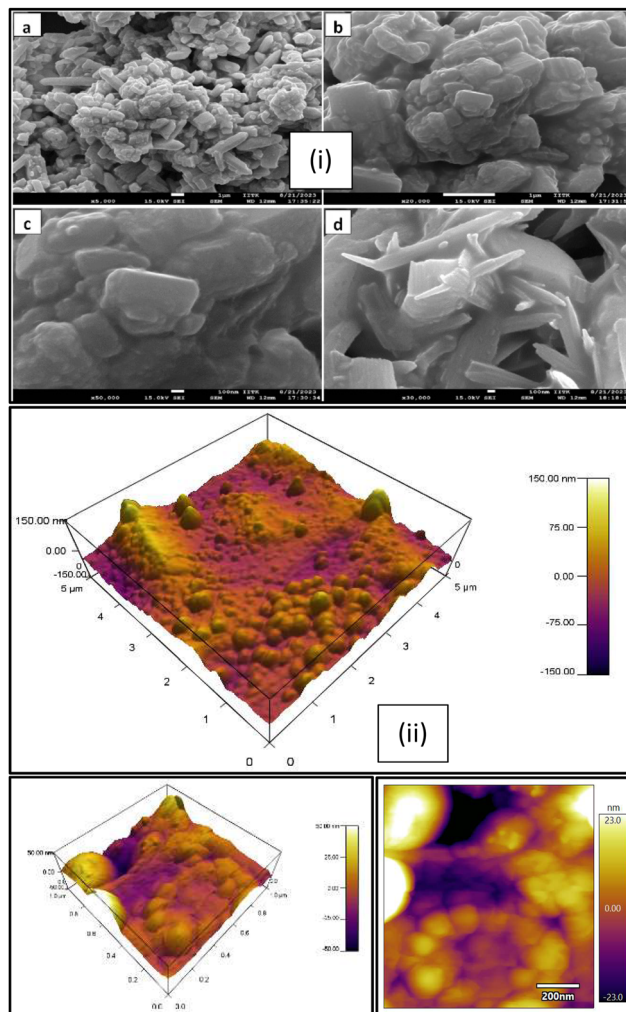


Fig. 5 (i) SEM images of the PANI/Te powder, (a, b) Scale-1 μm & (c, d) Scale-100 nm and (ii) AFM images of the PANI/Te-PVA film.

are comparable with literature. The calculated value for DC conductivity of the sample was found to be in the semiconducting range, *i.e.*, 2.1×10^{-5} S m⁻¹, which was measured using a two-probe method. The current was measured at a fixed voltage of 1.0 V, and a nearly constant value was obtained during the measurement. Conductivity can be calculated based on the dimensions of the pellet using the equation given below:



$$\sigma = t/RA,$$

where t = pellet thickness, R = the resistance and A = pellet surface area.

In the present case, thickness of the pellet was 1 mm and diameter was 12.5 mm. It is found that the PANI/Te nanocomposite was more conductive than undoped polyaniline, while the PANI/Te presented in this article has lower conductivity compared to 25% Te-doped polyaniline and Te nanowire alone.^{16,29} Movement of the polarons, *i.e.*, electron-phonon interaction in the polymer lattice, is responsible for its conducting nature. Hopping of charge carriers occurs between two polymer chains during conduction process.²⁹

Having observed reasonable conductivity of PANI/Te, it was appropriate to test the samples for EMI shielding behavior. PANI/Te polymer composite films were fabricated using a solution processing method. Microwave heating was employed to dissolve PVA in deionized water. Subsequently, PANI/Te composite was added to the PVA solution. In some cases, Ag NPs and Te powder were also added to evaluate their impact on the shielding property. A total of seven films of different compositions of PANI/Te were prepared (Table 2). The films were analysed by XRD and FTIR. The results of three samples, namely, PANI/Te-PVA (F2), PANI/Te/Ag-PVA (F4) and Te/PANI/Te/Ag-PVA (F7), are discussed herein briefly. PVA embedded films show significant changes in XRD pattern. It is expected that the peaks related to PANI and PVA may overlap, leading to shallow reflections in XRD (Fig. 6).

Normally, the peaks for both are more or less in matching 2θ positions. It is reported that the peak at 2θ value of about 20° is attributed to the PVA (101) plane.⁴⁵ Samples F2, F4 and F7 differ with respect to the peaks for Ag. On comparison, it is found that the peak broadening has increased upon Ag doping. Peaks of Ag may have overlapped with tellurium in both F4 and F7 samples.^{28,29} The peaks in F4 had sharpened, with some shifts in diffraction angles indicating increased cluster diameter. Additionally, it is observed that peaks due to impurities of TeO_2 are suppressed in PVA composites. In film, F7 peak broadening is observed, confirming the nano-regime nature of the composite. Also in the films, some reflections are observed due to impurities of TeO_2 .⁴⁶ Some entities may not show XRD diffractions, as PVA quantity in the film is much higher than the elements and suppression of crystallinity is expected. Table S1 (ESI[†]) and Fig. 6 show the relevant XRD peaks for tellurium in the selected films F2, F4 and F7.

Table 2 Details of constituents of composite films

Sample name	PVA (gm)	PANI/Te (gm)	Te (gm)	Ag NPs (gm)
Te-PVA (F1)	2.0	—	0.25	—
PANI/Te-PVA(F2)	2.0	0.5	—	—
Te/Ag-PVA (F3)	2.0	—	0.25	0.02
PANI/Te/Ag -PVA (F4)	2.0	0.5	—	0.02
Te-PVA (F5)	2.0	—	0.5	—
Te/Ag-PVA (F6)	2.0	—	0.5	0.02
Te/PANI/Te/Ag-PVA (F7)	2.0	0.5	0.25	0.02

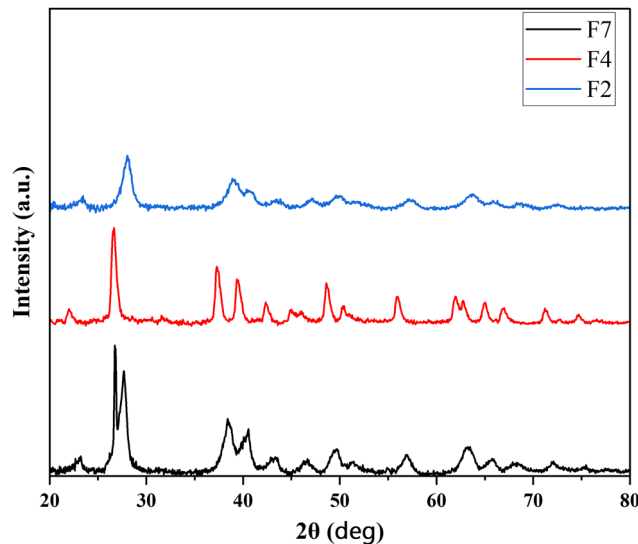


Fig. 6 XRD pattern of PANI/Te-PVA (F2), PANI/Te/Ag-PVA (F4) and Te/PANI/Te/Ag-PVA (F7) films.

FTIR analysis of the three representative composite films is presented in Fig. 7. Based on the literature on previously studied composite films,⁴⁵ it is noticed that the characteristic IR peaks corresponding to PVA in sample F2 are observed at 3235, 2924, 2353, 1451, 1368, 1015, 915 and 835 cm^{-1} . On comparison, it is found that the peak intensity at about 1400 cm^{-1} upon the addition of silver was enhanced in the sample. Other peaks were similar to PVA in all samples. In F7 film, the intensity of O-H at 3200 cm^{-1} , CH_2 near 2900 cm^{-1} , and C-C-O at 1400 cm^{-1} has increased as compared to F2 and F4. Also, the O-H stretching and CH_2 bending have slightly shifted to lower wavenumbers. It is observed that PVA functionality has been affected by the inorganic fillers. The N-H frequency for all samples relating to PANI are possibly

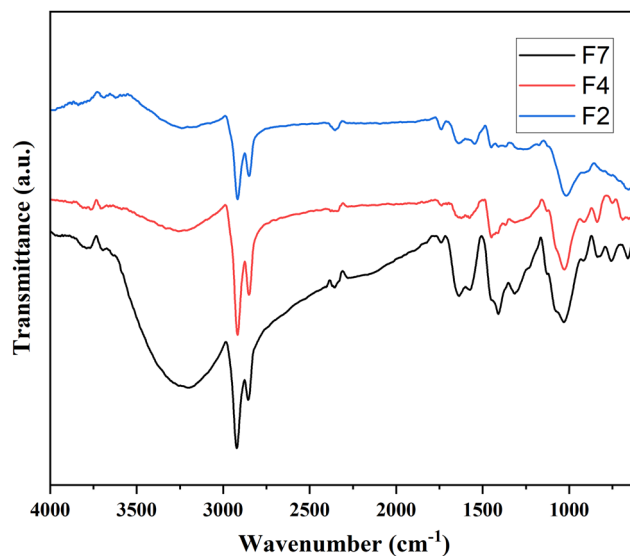


Fig. 7 FTIR spectra of F2, F4 and F7 films.



overlapped with the O–H functionality of PVA, as their values are very close to each other. Peaks at 1638 cm^{-1} for C=N due to quinoid stretching (for PANI) were also affected in all samples. However, the absorbed water may also result in peaks in this range, as has been reported by Jipa *et al.*⁴⁵ The peak values corresponding to PVA in all the three representative samples are shown in Table S2 (ESI†).

4. EMI shielding studies

EMI shielding is the material property that stops the transmission of EM waves. There are two primary ways of shielding any object from radiation, *i.e.*, reflection and absorption. A conductivity range of 10^{-3} to 1.0 S cm^{-1} is sufficient for blocking EM waves through reflection, due to ohmic (heating) loss because of electrons and holes (the charge carriers). Meanwhile, for absorption-mode EMI shielding, interaction of the electric and/or magnetic dipoles of the material with EM radiation is needed. It is well documented that a good shielding material should effectively attenuate more EM field.^{15,47,48} The EMI shielding properties of various polymer composite films are listed in Table 3. The EMI analysis was conducted using a two-port vector network analyzer (VNA) to measure complex scattering parameters known as *S*-parameters, namely, S_{11} (for incident wave) and S_{12} (for transmitted wave). These parameters can be suitably connected with the reflectance ($R = |S_{11}|^2$) and transmittance ($T = |S_{12}|^2$). The equation $A = (1 - R - T)$ was employed for calculation of the absorbance (A).^{15,33} Moreover, EM wave intensity related to reflection inside the shielding material was primarily determined by the quantity $(1 - R)$. This quantity can be utilized to normalize the absorbance (A), resulting in the effective absorbance denoted as $\{A_{\text{eff}} = [(1 - R - T)/(1 - R)]\}$. By employing this approach, the experimental reflection and absorption losses can be expressed as given below.^{47,48}

$$SE_R = 10 \log(1 - R) = 10 \log(1 - |S_{11}|^2) \quad (1)$$

$$SE_A = 10 \log(T/1 - R) = 10 \log(1 - |S_{12}|^2) \quad (2)$$

and

$$SE_A = 10 \log(1 - A_{\text{eff}}) \quad (3)$$

To calculate the total shielding effectiveness,

Table 3 EMI shielding property of the composite films

Sample name	SE_R dB (max)	SE_A dB (max)	SE_T (dB) (max)	% shielding
Te-PVA (F1)	-1.00	-3.19	-4.19	61.90
PANI/Te-PVA (F2)	-1.00	-3.00	-4.0	60.19
Te/Ag-PVA (F3)	-0.89	-2.00	-2.89	48.60
PANI/Te/Ag-PVA (F4)	-1.77	-7.00	-8.77	86.73
Te-PVA (F5)	-1.40	-2.70	-4.10	61.10
Te/Ag-PVA (F6)	-1.10	-2.10	-3.20	52.14
Te/PANI/Te/Ag-PVA (F7)	-2.80	-7.39	-10.19	90.43

$$SE_T = SE_R + SE_A = 10 \log(P_i/P_t) \quad (4)$$

and

$$SE_T = 10 \log(1 - T) \quad (5)$$

The % shielding formulation applied for the films is as follows:

$$(P_i/P_t) = 10^{(SE/10)},$$

where SE is total shielding effectiveness,

$$\%P_t = (P_i/P_t) \times 100$$

is percentage power transmitted, and

$$\% \text{ shielding} = 100 - \% P_t$$

is the percentage shielding.

In the present study, the behavior of the composites was investigated in the X-band (8–12 GHz). The values of S_{11} and S_{12} were obtained from the EMI shielding test using the shielding effectiveness values, which are estimated and presented in Table 3 (Fig. 8, 9 and 10). The PANI/Te-PVA nanocomposite shows reasonably encouraging shielding effectiveness by virtue of contribution from the conducting nanofillers. Appropriately, it is observed that by adding Ag NPs to the composite, nearly 2.5 times increase in shielding effectiveness can be realized. Such a result can be considered promising EMI shielding for radar, terrestrial and space applications.¹⁴ In the case of PVA/Te films without PANI, *i.e.*, F1, F3, F5 and F6, very small effect on SE is observed in the presence of Ag NPs. According to Fig. 8, the maximum shielding efficiency for these films is observed at ~ 8.5 GHz. However, in PVA films of PANI/Te, *i.e.*, F2, F4 and F7, the effect of Ag NPs is remarkable. Film F4 shows the maximum estimated increase in SE_T of -4.77 dB when compared with film F2. This enhancement comes from SE_R and SE_A ,

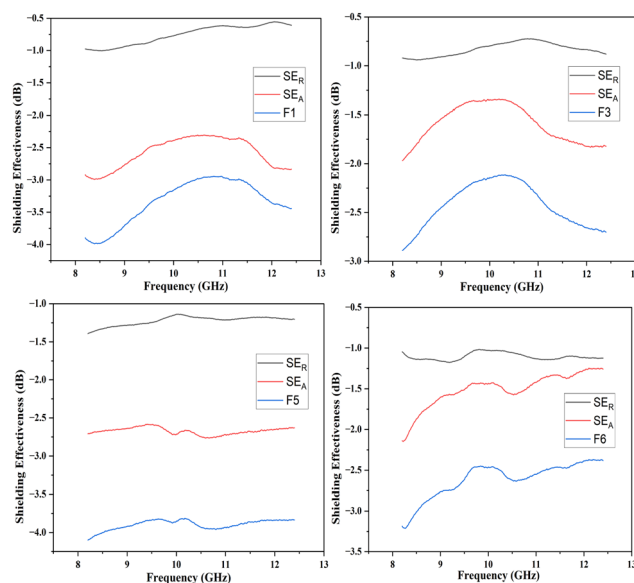


Fig. 8 Shielding effectiveness (SE) of the nanocomposite films without PANI.



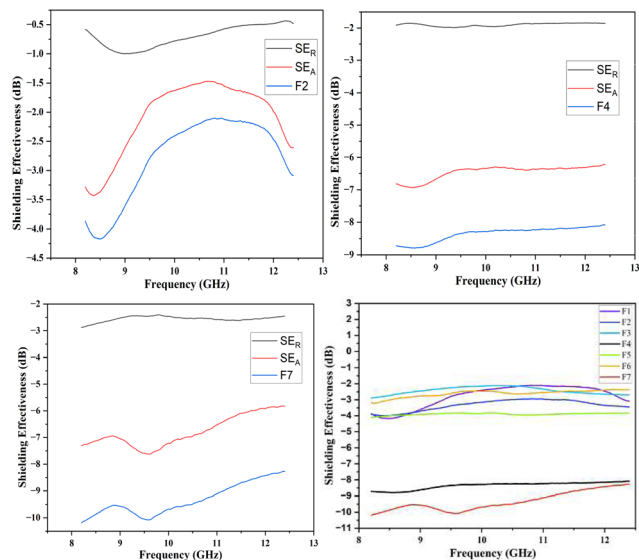


Fig. 9 Shielding effectiveness (SE) of F2, F4, F7 and of all films.

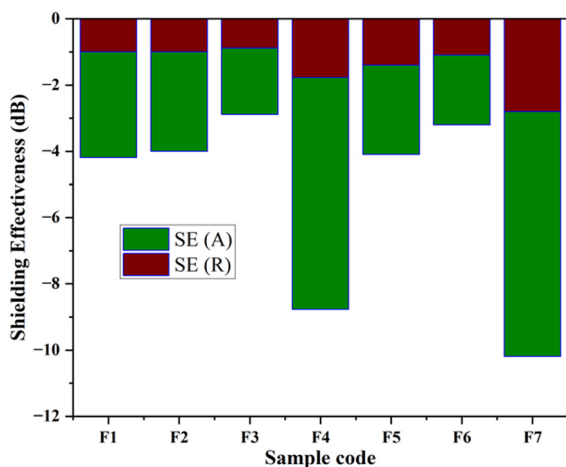


Fig. 10 Bar chart of shielding effectiveness (SE) of all the films.

by -0.77 dB and 4.00 dB, respectively. Therefore, it is confirmed that an increase in the dipolar nature of the PANI/Te nanocomposite film can be attained with additional Ag nanofiller. Thus, the value in film F4 has increased to -8.77 dB (86.73% shielding) as against -4.00 dB (60.19% shielding) in film F2. The effect of additional tellurium in the composite has also been investigated for film F4 by doubling the tellurium content in the PANI/Te/Ag powder, and the resultant film was named F7. This film has shown a further increase in SE_T of -1.42 dB (3.7%) as compared to F4. It is realized that the contributions from SE_R and SE_A are -2.80 dB and -7.39 dB, respectively, and the total shielding effectiveness value is -10.19 dB (90.43% shielding). Also, there has been an increase in SE at 9.5 GHz frequency in F7, which shows a value of approx. -10 dB. It can be said that the conducting nature of Ag nanofiller causes an increase in the absorption mode of shielding, which could be due to the enhanced dipolar properties of

the nanocomposite material. Overall, it is observed that the EMI efficiency has improved from -4.0 dB for F2 to -8.77 for F4, which further improved to -10.19 dB in the case of F7, highlighting the impact of inorganic fillers in the nanocomposites.^{14,47,48} It should be noted that the EMI shielding efficiency of pure PANI is reported in the range of -0.5 dB,⁴⁹ and that of PVA film is reported to be -0.34 dB.⁵⁰ The mechanism of EMI shielding is similar to what has been proposed by several searchers, where the contribution from reflectance as well as absorbance has been correlated with shielding efficiency.^{51,52}

5. Conclusion

Overall, the present article is unique in presenting a novel approach to the synthesis of polyaniline/tellurium nanocomposite. The UV-visible absorption spectrum of the PANI/Te powder in DMSO showed bands at 354 nm for the associated benzenoid rings and at 382 and 605 nm for the quinoid ring. This is probably the first study on EMI shielding using the PANI/Te nanocomposite. The composite was characterized by XRD and FTIR to establish its correctness and the functionality of polyaniline. It was observed that the composite may acquire TeO_2 impurities *in situ* due to incomplete reduction of sodium telluride, which is supported by XRD showing peaks for Te at $2\theta = 30.02, 30.89,$ and 44.29 for $\alpha-TeO_2$.

In the EMI shielding application, metal nanoparticles enhanced the shielding effectiveness of the PANI/Te nanocomposite by increasing the conductivity of the material. There have been positive impacts from different constituents on the PANI/Te nanocomposite, e.g., Ag NPs and tellurium, while the presence of Ag in the PANI/Te nanocomposite increased the SE due mainly to absorption efficiency. EMI efficiency improved from -4.0 dB for F2 to -8.77 for F4, which further improved to -10.19 dB in the case of F7 due to the presence of silver nanoparticles. The polyaniline, being conducting in nature, may be useful for effective EMI shielding in various electronics and photonic devices.

Author contributions

Experiments were designed by Prof. Pawan K. Khanna. Experiments were conducted by Alok Kumar Yadav and Naem. Characterization was carried out by Alok and Naem, while the results were analysed by all three. Manuscript draft was prepared by Alok and finalized by the corresponding author.

Conflicts of interest

There are no conflicts to declare.

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