Supporting Information

High Permittivity Polyaniline/Barium Titanate Nanocomposites with Excellent Electromagnetic Interference Shielding Response

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Supporting Information

DBSA can perform multiple functions of anionic surfactant, bulky dopant as well as template/structure directing agent and facilitating the encapsulation of TBT NPs within PANI matrix. Therefore, TBT-polyaniline (PANI) NCs were prepared by low temperature (-5ºC) in-situ emulsion polymerization (Fig. S1) of aniline monomer in the presence of aqueous emulsion of DBSA.

Fig. S1: Schematic representation of in-situ polymerization of aniline in the presence of DBSA (surfactant dopant) and BaTiO3 (dielectric filler) to form PANI-BaTiO3 nanocomposites (PBTs)

Shielding effectiveness (SE) measurements were performed using vector network analyzer (VNA, E8263BAgilent Technologies) on the rectangular pellets placed inside Ku-band (12.4-18.0 GHz frequency range) sample holder that was connected to coaxial-to-waveguide adopters as shown in Fig. S2.

Fig. S2: Picture of VNA showing different ports, coaxial connectors, coaxial-to-waveguide adaptors, short and sample holder
1. **In-situ polymerization**

The proper polymerization mechanism plays a crucial role in realization of uniform dispersion of inorganic NPs within ICP matrices. In-situ polymerization of aniline involves polymerization in the presence of filler (intended to be incorporated in PANI matrix) and protonic acid as dopant. The relatively high density of inorganic NPs (e.g. ~6-7 g/cm$^3$ for titanates) compared to water (1 g/cm$^3$), aniline (~0.9 g/cm$^3$) or many inorganic dopants like HCl (1.2 g/cm$^3$), HNO$_3$ (1.4 g/cm$^3$), H$_2$SO$_4$ (1.85 g/cm$^3$), as well as low viscosity of polymerization mixture, causes settling which may be partially prevented by mechanical agitation or stirring.

![Fig. S3: Schematic representation of different techniques for synthesis of PANI-BaTiO$_3$ composites showing superiority of in-situ emulsion polymerization (utilizing non-corrosive surfactant dopants e.g. DBSA) over ex-situ mixing (dry/wet grinding) or in-situ dispersion polymerization (utilizing corrosive mineral acids as dopants e.g. HCl/H$_2$SO$_4$)](image)

Such a settling tendency often results in poor dispersion of filler within conducting polymer matrix resulting in phase separation and formation of a microscopic heterogeneity. Further, due to their corrosive nature, strong mineral acids may rapidly react with fillers spoiling their properties or even converting them into their salts. This results in poor electromagnetic properties and irreproducible results. In this connection, a striking key can be offered by surfactant dopants like DBSA (Schematic illustration, Fig. 1C) which possesses enough viscosity and surface tension properties to counteract the agglomeration (due to their high surface energy and strong Van der Waal’s forces) and settling (due to high density) tendencies of the above nanofillers. Therefore, filler particles are already trapped and dispersed within polymer matrix (Fig. 1C) before any agglomeration or settling can occur. Further, the DBSA being an organic sulfonic acid is a soft and non-corrosive dopant so that filler properties remain more or less intact. This results in production of composites with homogenous and reproducible properties so that desired electromagnetic attributes and superior shielding performance can be realized.

2. **X-ray diffraction analysis**

The XRD peaks of BaTiO$_3$ were observed at 20 values of 22.21 (d=3.99 Å), 31.61 (d=2.83 Å), 38.96 (d=2.31 Å), 45.23 (d=2.01 Å), 50.98 (d=1.79 Å), 56.31 (d=1.63 Å) and 66.01 (d=1.41 Å) corresponding to reflections from (100), (101), (111), (200), (201), (211), and (202), planes of tetragonal BaTiO$_3$ (TBT) respectively and having lattice parameters of ‘a’ = ‘b’ = 3.9994 ± 0.0019 Å and ‘c’ = 4.0058 ± 0.0045 Å. In transagonal BaTiO$_3$ (TBT) respectively and having lattice parameters of ‘a’ = ‘b’ = 3.9994 ± 0.0019 Å and ‘c’ = 4.0058 ± 0.0045 Å. In contrast, the characteristic peaks of PANI were observed at 20 values of 20.04 (d=4.43 Å), 25.34 (d=3.51 Å) and 26.94 (d=3.31 Å) corresponding to (211), (240) and (022) reflections, respectively. The above peaks fit to a pseudo-orthorhombic structure with lattice parameters ‘a’ = 11.5895 ± 0.0097 Å, ‘b’ = 17.5163 ± 0.0076 Å and ‘c’ = 7.3334 ± 0.0009 Å. The (211) and (240) planes represents periodicity parallel and perpendicular to the chain axis and are characteristic of doped form of polyaniline (i.e. poly-emeraldine salt).
particular the relative intensity of peaks at 25° and 20° (i.e. $I_{25}/I_{20}$ ratio) can predict qualitative idea of the doping level. The main diffraction peaks of nanocomposite (PBT11) are located at 20 values of 20.52 (d=4.33Å), 22.20 (d=4.00Å), 24.97 (d=3.56Å), 25.95 (d=3.43Å), 26.94 (d=3.31Å), 28.87 (d=3.01Å), 31.60 (d=2.83Å), 38.95 (d=2.31Å), 42.82 (d=2.11Å), 45.29 (d=2.00Å), 50.97 (d=1.79Å), 56.29 (d=1.63Å) and 65.69 (d=1.42Å), which represents superimposed signatures of TBT as well as PANI indicates the presence of both these phases in the resultant nanocomposites. Furthermore, the estimated $I_{25}/I_{20}$ ratio (Table 1) was 1.32 for PANI (PBT10) and decreases to 1.26 in PBT12, indicating decrease in doping level with increase in weight fraction of TBT. In addition, the average size of the crystalline domains of BaTiO$_3$ particles were calculated from peak broadening using Scherrer equation and found to be ~21 and ~19 nm for pure TBT and PBT11, respectively.

3. **Energy dispersive X-ray (EDX) elemental analysis**

Fig. S4 shows the energy dispersive X-ray (EDX) elemental analysis of the samples recorded using EDX analyzer attached to HRTEM. The EDX spectra shows number of peaks corresponding to elements present in the material. Cu-peaks are from copper support grid used for TEM analysis. The relative intensity of peaks due to N, S and Ba (or Ti) can be used as markers for tracing (presence/concentration) of polymer matrix (PANI), dopant (DBSA) and filler (BaTiO$_3$) respectively. Since the N and S peaks are characteristic of polyaniline and dopant respectively; therefore, S/N ratio can be taken as qualitative measure of achieved doping level.

![Energy dispersive X-ray (EDX) elemental analysis](image)

**Fig. S4**: Energy dispersive X-ray (EDX) elemental analysis of the samples (a) PBT10 and (b) PBT11, recorded using an EDX analyzer attached with HRTEM
The recorded S/N ratio was found to exhibit an increase from 0.71 (for PBT10) to 0.90 (for PBT12) with the increase in BT/aniline weight ratio (see Table 1), which suggests enhancement of doping level. However, the above S/N ratio trend is contrary to the observed decrease in conductivity with increasing BT content. In actual practice, both free (not used for doping) and bound (used for doping) DBSA contributes towards observed S/N ratio. Therefore, we propose that increase in S/N ratio was due to the attachment of free DBSA molecules (not involved in doping) with the BT particles and incorporation of them within PANI matrix. As the BT content increases, the more free DBSA molecules get entrapped within PANI matrix; therefore, accounting for enhanced S/N ratio.

4. SEM investigations

Fig. S5 shows the SEM micrographs of pure polyaniline (PBT10) and its nanocomposites with different weight ratio of BaTiO$_3$ (BT) viz. PBT21, PBT11 and PBT12 in pressed pellet form.

![SEM micrographs](image)

Fig. S5: SEM micrographs of (a) PBT10, (b) PBT21, (c) PBT11 and (d) PBT12

It has been observed that the pressed samples contain number of surface micro-cracks. As the concentration of BT increases, the number of such micro-cracks increases. This may contribute towards reduced inter-grain contact and hence reduced conductivity. Further, the enhancement in amount of incorporated BT can be seen as systematic change in the contrast of the pictures. As the BT content increases, bright colored spotty areas increases indicating increase in level of BT incorporation. Furthermore, for any given sample, the same contrast throughout the image indicates uniform dispersion of BT particles within PANI matrix and demonstrates the good dispersive power of surfactant-dopant DBSA.

5. Energy dispersive X-ray spectroscopy (EDS) elemental analysis

Fig. S6 shows the energy dispersive X-ray (EDX) elemental analysis of the samples. It has been observed that incorporation of BaTiO$_3$ leads to systematic variation in the relative intensity of peaks due to N, S and Ba (or Ti) that can be used as markers for tracing (presence/concentration) of polymer matrix (PANI), dopant (DBSA) and filler (BaTiO$_3$), respectively.
In fact, S/N and B/N ratios can be used as qualitative measures of doping level and filler content, respectively. The enhancement in the observed B/N ratio from 0.03 (for PBT21) to 0.14 (for PBT12) revealed that emulsion polymerization leads to proper entrapment of BT particles within PANI matrix. Furthermore, the S/N ratio was also found to exhibit an increase from 0.89 (for PBT10) to 1.31 (for PBT12) with the increase in BT/aniline weight ratio, which suggests enhancement of doping level. However, the above S/N ratio trend is contrary to the observed decrease in conductivity with increasing BT content. These results are in good agreement with HRTEM-EDX results any differences can be attributed to the method of sample preparation, sensitivity levels and kind of information (surface composition for SEM-EDS and bulk composition for HRTEM-EDX) furnished by two techniques. Therefore, we conclude that, like HRTEM-EDX results, increase in S/N ratio was due to the incorporation of additional DBSA molecules (not involved in doping) along with the BT nanoparticles.

### 6. Electron paramagnetic resonance (EPR) analysis

The EPR spectra of conducting polymers can be analyzed using Gaussian/Lorentzian distribution function. A typical EPR spectrum in derivative signal form is shown in Fig. S7. The recorded spectra contains vital information about various parameters such as $\Delta H_{pp}$, $g$-value, asymmetry parameter, spin concentration and $T_2$, which are further related to material structure/properties. The $g$-value (2.0023 for free electron) and asymmetry parameter (i.e. $A/B$ ratio) gives information about the metallic character of composites and degree of freedom of charge carriers. The peak-to-peak width ($\Delta H_{pp}$) and normalized area under peak carries information about spin-environment interaction (relaxation) and spin concentration respectively.
The doping of polyaniline produces localized defects within the band leading to generation of charge carriers. In case of polyaniline, polaron (q=+e, s=1/2) and bipolaron (q=+2e, s=0) are thought to charge carriers, where symbols ‘q’ and ‘s’ denote carrier’s charge and spin, respectively. The spin-less nature of bipolarons (dications) makes them undetectable during EPR measurement. However, polarons (radical cations) with associated unpaired electron can easily be identified as paramagnetic centers. Therefore, with bipolarons being EPR forbidden, the contribution to spin concentration comes exclusively from the spin bearing polarons. These polarons can move along (intra-chain) and across (inter-chain) the chains imparting electrical conductivity to material. The A/B ratio is a measure of asymmetry of the spectra and its high value can be attributed to the predominance of mobile spins and diffuse motion of spin during delocalization leading to inter-chain coupling. The line width (ΔH_{pp}) is closely related to rates of various relaxation processes viz. spin-lattice (T1) or spin-spin (T2) relaxation processes. The spin-spin relaxation process is characterized by a time constant (i.e. T2), which is a function of static magnetic field. It depends on the rate of absorption and dissipation of microwave energy and can be expressed as:

\[
\frac{1}{T_2 (sec^{-1})} = \frac{4\pi g \beta \sqrt{3} \Delta H_{pp}}{h}
\]  \hspace{1cm} (1)

where ‘β’ and ‘h’ are Bohr Magneton (= 9.274 x 10^{-21} erg G^{-1}) and Plank’s constant (6.626 x 10^{-29} erg sec) respectively.

X-ray photoelectron spectroscopy (XPS) analysis

Fig. S8 shows the structure of different units that can be present along the doped polyaniline chains. These segments are associated with different energy states of nitrogen atom; therefore, can be identified as separate subcomponent peaks in the deconvoluted N1s core level XPS spectra. The first peak (I) with lowest binding energy (~398 eV) can be assigned to quinoid imine (-N=) segment whereas the second component (II) at ~399 eV can be assigned to benzenoid amine units (-NH-).
Fig. S8: Structure of various possible units present along the doped polyaniline chains

The next two peaks can be observed around ~401 and 402-403 eV and can be attributed to bipolaronic (III) and polaronic forms (IV) respectively. However, some authors have proposed the origin of 402-403 eV peak as sp\(^3\) bonded protonated amine (V) units. Nevertheless, the normalized areas of the last two peaks (i.e. N\(^+/\)N ratio) which are separated by ~1.3 and ~2.9 eV from the amine component, represents the actual doping level.

8. Electrical conductivity

Fig. S9 shows that electrical conductivity of PANI and its BaTiO\(_3\) based nanocomposites increases exponentially with temperature reflecting their semiconducting behavior. At any given temperature, the conductivity of nanocomposites decreases with increase in BaTiO\(_3\) content. This can be attributed to the hindrance to conduction path and consequent charge carrier scattering, offered by poorly conducting BT particles.

Fig. S9: Temperature dependence of electrical conductivity (\(\sigma_{dc}\)) of pressed pellets of polyaniline (PBT10) and its BaTiO\(_3\) based nanocomposites viz. PBT21, PBT11 and PBT12
In addition, as inferred from XRD/EPD (qualitatively) and XPS (quantitatively), the presence of BT nanoparticles also leads to decrement of the achieved doping level. Furthermore, SEM images reflected that incorporated BT leads to number of micro-cracks in the pressed pellets which increases with BT content. These cracks may contribute towards reduced inter-grain contact and hence reduced inter-particle resistance. All, the above factors contribute towards reduction of electrical conductivity.

9. EMI shielding and microwave absorption

Shielding is defined as the reduction in strength of the incident electromagnetic (EM) waves on passing through intended shield material. The efficiency of shield or shielding effectiveness (SE) is generally expressed as:

$$\text{SE}_T (\text{dB}) = 10 \log_{10}(P_I/P_T) = 20 \log_{10}(E_I/E_T)$$

where $P_I$ (or $E_I$) and $P_T$ (or $E_T$) represents power level (or electric field strength) of incident and transmitted EM radiation respectively. The total shielding effectiveness ($\text{SE}_T$) can be described as the sum of loss contributions due to reflection ($\text{SE}_R$), absorption ($\text{SE}_A$), and multiple reflections ($\text{SE}_M$) i.e. $\text{SE}_T = \text{SE}_R + \text{SE}_A + \text{SE}_M$. The reflectance ($R$) and transmittance ($T$) can be correlated with scattering parameters (or $S$-parameters) of two port VNA i.e. $T = |E_T/E_I|^2 = |S_{12}|^2$, $R = |E_R/E_I|^2 = |S_{11}|^2 = |S_{21}|^2$ and $A = (1-R-T)$. The reflection term ($\text{SE}_R$) is given by expression:

$$\text{SE}_M = 20 \log_{10} \left( 1 - e^{-21/\delta} \right) = 20 \log_{10} \left( 1 - 10^{-\text{SE}_A/10} \right)$$

Therefore, it is clear from equation (3) that when attenuation due to absorption ($\text{SE}_A$) is greater than -10 dB, $\text{SE}_M$ is negligible and can be safely ignored. Further, the absorbance ($A$) has to be normalized with quantity ($1-R$) to define the term effective absorbance [$A_{\text{eff}} = A/(1-R)$]. Therefore, $\text{SE}_R$ and $\text{SE}_A$ can be expressed purely in terms of $R$ and $T$ as:

$$\text{SE}_R = 10 \log_{10} (1-R) \quad \text{and} \quad \text{SE}_A = 10 \log_{10} (1-A_{\text{eff}}) = 10 \log_{10} [T/(1-R)]$$

Further, depending on the distance ($r$) between radiation source and detector and wavenumber ($k$), EM wave propagation mode can be classified as near filed ($kr<<1$) or far field ($kr>>1$). In far-filed regime, which is the case in our measurement range (i.e. in P-band), the EM wave front propagates with constant characteristic impedance (i.e. $E/H$ ratio) of 377$\Omega$ and can be seen as plane wave radiation.

Now, according to plane wave theory, for an electrically thick ($t>\delta$) good conductor ($\sigma T/\omega\varepsilon>0$), theoretical $\text{SE}_R$ and $\text{SE}_A$ can be mathematically expressed as:

$$\text{SE}_R (\text{dB}) = -10 \log_{10} \left( \frac{\sigma T}{16\omega\varepsilon\mu'} \right)$$

$$\text{SE}_A (\text{dB}) = -20 \frac{t}{\delta} \log_{10} e = -8.68 \left( \frac{t}{\delta} \right)$$

where parameters $\sigma_T$ (i.e. $\sigma_{ac} + \sigma_{dc}$) $\omega$, $\mu'$, $\delta$ and $t$ represents total conductivity (i.e. ac and dc components) angular frequency, real permeability, skin depth and shield thickness respectively. The $\sigma_T$ and $\delta$ can be further related to imaginary permittivity ($\varepsilon''$) and real permeability ($\mu''$) as $\sigma_T = \omega\varepsilon''\mu''$ and $\delta = \left( \frac{2}{\sigma_T \omega \mu''} \right)^{1/2}$ which gives absorption loss as:

$$\text{SE}_A (\text{dB}) = -8.68t \left( \frac{\sigma_T \omega \mu''}{2} \right)^{1/2}$$

The above simplified expressions can be used to explain the frequency and conductivity dependence of $\text{SE}_R$ and $\text{SE}_A$ as:
\[ \text{SE}_R \text{ (dB)} \propto -\log_{10}(\omega) \] (i.e. negative logarithmic frequency dependence)

\[ \text{SE}_A \text{ (dB)} \propto (\omega)^{1/2} \] (i.e. square root frequency dependence)

\[ \text{SE}_R \text{ (dB)} \propto \log_{10}(\sigma_T) \] (i.e. logarithmic conductivity dependence)

\[ \text{SE}_A \text{ (dB)} \propto (\sigma_T)^{1/2} \] (i.e. square root conductivity)