POLYANILINE NANOCOMPOSITES WITH DOPED FERRITES AS AN ELECTROMAGNETIC SHIELD

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ABSTRACT

Polyaniline (PANI) possesses good microwave absorption properties, with the maximum absorption rate of 15.8 dB, and greater than 10 dB within the frequency of 11.36-15.46 GHz. On mixing PANI in-situ with hybrid ferrites and doped ferrites, the resulting polyaniline nanocomposites (PANI NCs) behave as promising electromagnetic shield for a wide range of electromagnetic spectrum from 3GHz to 15.9GHz efficiently. In this review, literature on magnetic properties of Ni ferrite PANI NCs, NiGd ferrite PANI NCs, MnZn ferrite PANI and Sm dopant ferrite PANI NCs has been analyzed. In brief, the objective of this article is to emphasize on the preparation, processability and the application of the nano-hybrids of polyaniline as a shield for the absorption of electromagnetic radiations.

INTRODUCTION

To live in a technically progressed world with the synchronized protection of our environment is the prime concern of today’s world. The use of extensive electrical appliances generates electromagnetic radiations and these possess threat not only to the environment by creating e-pollution but also affect the lifespan of the instrument itself. Hence, in order to prevent these electromagnetic radiations, an efficient electro-magnetic absorber is required. PANI NCs with magnetic nanoparticles serve this purpose to a larger extent than alone PANI itself. PANI is a conductive polymer of the semi-flexible rod polymer family and PANI captured the intense attention of the scientific community due to its high electrical conductivity. With the emergence of nanotechnology and its vast application, polyaniline doped with magnetic particles have received a lot of acknowledgment. Nanocomposites (NCs) of polyaniline, polypyrrole, polythiophene and its derivative like poly-(3-hexyl thiophene) (P3HT), poly-(3,4-ethylenedioxythiophene) (PEDOT) etc. have remarkably improved electrical, thermal, optical and magnetic properties over their conventional counterparts (Rimbu et al. 2006). The advantage of using nanoparticles lies in the fact that these show considerable difference from their bulk counterparts in terms of their biological and physiochemical properties despite their similar chemical composition. These significant differences are attributed to their surface to volume ratio (Sharma et al. 2009). Polyaniline magnetic NCs consist of a polymer or copolymer having nanoparticles or nanofillers dispersed in the polymer matrix. These may be of different shape (e.g., platelets, fibers, spheroids), but at least one dimension must be in the range of 1–50 nm. Among conducting polymers, PANI has received greater attention due to its advantages over other conducting polymers like simplicity of its preparation from cheap materials, superior stability to air oxidation (environmental stability), light weight, controllable electrical conductivity by doping and de-doping (MacDiarmid et al. 1985) and ferromagnetic properties are some of them. When an electromagnetic wave falls on the surface of a material then from the principle of energy conservation, the electromagnetic wave can be reflected, transmitted or its intensity can be weakened gradually through the material. This behaviour depends on the intrinsic characteristics of the material namely the electric permittivity (ε) and magnetic permeability (µ) which in turn are related to the dielectric and magnetic properties of the material. Furthermore, the parameters like electric permittivity (ε) and magnetic permeability (µ) are directly linked to the absorbing characteristics of the material. When an electromagnetic wave interacts with a magnetic material consisting of dielectric and magnetic dipoles, there is the formation of electric dipoles which align in the direction of...
the applied field, and the dipole alignment is directly related to the absorption of electromagnetic energy (spectroscopy principle) (Folgueras et al. 2010). The real part of the permittivity is associated with the ability of the material to get polarized and to store energy, whereas the complex part deals with the dielectric loss or energy dissipation from the material (Lu et al. 2010). Thus, in order to act as an efficient electromagnetic absorber, the material should possess magnetic, dielectric and conductive properties. In case of in-situ formed PANI NCs, improved dielectric properties leads to higher value of loss tangent which further increases with increase in loading of magnetic nanoparticles. However, for a given thickness, total shielding is dominated by absorption and not by the reflection loss component as it becomes too high from the viewpoint of stealth technology. Inspite of good dielectric and magnetic properties of Intrinsic Conducting Polymers (ICPs), they remained poor to extend any significant contribution towards electromagnetic interference (EMI) regulation, which is attributed to their low conductivity. In principle, for highly conducting materials, only conductivity (σ) and magnetic permeability (μ) are important, such that the reflection loss (SE_r) is dependent upon their ratio (i.e. σ/μ) whereas the absorption loss (SE_a) is a function of their product (i.e. σμ) (Saini et al. 2012) In contrast, for moderately conducting materials (e.g. ICPs) permittivity (ε) also plays a significant role (besides σ and μ) in deciding absolute values of SE_r and SE_a (Joo et al.1994). As most ICPs are non-magnetic in nature (μr=μi=0), observed attenuations are mainly governed by σ and ε only. Therefore, it is expected that any improvement in magnetic properties will lead to definite improvement of absorption loss along with parallel reduction of reflection loss (Xiang et al., 2005).

In addition, the incorporation of high dielectric constant materials like BaTiO_3, ZnO, TiO_2 along with magnetic nanoparticles like ferrites etc. within PANI matrices are expected to further improve the microwave absorption response (Saini et al., 2012). Consequently, in recent years, lot of work has been carried out to formulate composites of polyaniline with dielectric or magnetic fillers, either using in-situ polymerization or ex-situ physical mixing processes. Such composites possess moderate polarization and magnetization along with good microwave conductivity so as to introduce absorbing properties into the material. They display dynamic dielectric and magnetic losses, upon impingement by incident electromagnetic waves (Abbas et al., 2007). The interaction between MFe_2O_4 (M= Ni^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+}, Co^{2+}) nanoparticles and PANI matrix may occur by the formation of the hydrogen bonding between the amine group of PANI and oxygen of MFe_2O_4 (Elsayed et al., 2011). However, when these spinel ferrite hybrids are doped with rare earth metals, then, due to occurrence of 4f-3d coupling, electromagnetic properties of ferrites can be improved because this coupling is responsible for magneto-crystalline anisotropy which is the anisotropy in ferrites. Therefore, rare earth ions are becoming promising additives for the improvement of electromagnetic properties and electromagnetic shielding effectiveness of ferrite (Sagar et al., 2014).

SYNTHESIS OF PANI AND ITS NCs

Higashimura & Kobayashi, 2004 have prepared PANI by the oxidative polymerization by using appropriate oxidizing agent. In general, Ammonium peroxydisulphate (NH_4S_2O_8) has been used (Scheme 1) or it can also be prepared by electro polymerization by applying appropriate amount of voltage. The mechanism of polymerization of PANI can be understood as:

\[
\text{[Polyaniline]_Cl} + 5n\text{(NH}_4\text{S}_2\text{O}_8) \rightarrow 273K, 24\text{Hour} \rightarrow \text{PANI-Cl} + 5n\text{(NH}_4\text{SO}_4} + \text{2nHCl} + \text{2nCl}_2
\]

\[R\text{ denotes polymer chain}\]

**Scheme 1.** Synthesis of PANI using anilinium hydrochloride and ammonium peroxydisulphate.

PANI exists in various well defined oxidation states as shown in Figure 1, from fully oxidized state namely pernigraniline having black color to fully reduced state known as leucoemeraldine having dark blue color via partially oxidized form namely emeraldine base having green color. (Ajayan et al. 1995) and (Toshima et al. 1995) Leucoemeraldine and permigraniline are both insulators but partially oxidized form i.e. emeraldine base after doping can be converted into emeraldine salt which is the conductive form of polyaniline. Doping of PANI increases its conductivity by generating mobile charge carriers in the form of polarons. In few earlier studies, protonic acid like HCl and H_2SO_4 have been used as classic dopants but due to the corrosive nature of these acids they can severely affect the properties of the filler inorganic nanoparticles in the matrix. Other alkysulfonic acids like toluene sulfonic acid, camphor sulfonic acid and surfactant based dopant like dodecylbenzene sulfonic acid (DBSA) are very much in trends for doping PANI (Bhadra et al. 2009). In order to achieve spin stabilization, large size dopant 2,6-quinonedisulfonic acid is employed. By making use of these moderate dopants in polyaniline, the electroactive properties and the processing of latter can be tailored (Makarova T. 2010). Consequently, in recent years, lot of work has been carried out to formulate composites of polyaniline with dielectric or magnetic fillers, either using in-situ polymerization or ex-situ physical mixing processes. Such composites possess moderate polarization and magnetization along with good microwave conductivity so as to introduce absorbing properties into the material. They display dynamic dielectric and magnetic losses, upon impingement by incident electromagnetic waves (Abbas et al., 2007). The interaction between MFe_2O_4 (M= Ni^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+}, Co^{2+}) nanoparticles and PANI matrix may occur by the formation of the hydrogen bonding between the amine group of PANI and oxygen of MFe_2O_4 (Elsayed et al., 2011). However, when these spinel ferrite hybrids are doped with rare earth metals, then, due to occurrence of 4f-3d coupling, electromagnetic properties of ferrites can be improved because this coupling is responsible for magneto-crystalline anisotropy which is the anisotropy in ferrites. Therefore, rare earth ions are becoming promising additives for the improvement of electromagnetic properties and electromagnetic shielding effectiveness of ferrite (Sagar et al., 2014).

**Fig. 1.** Different oxidized forms of pani
2001). The insolubility of PANI is also a major concern which is resolved by various alkyl sulfonic dopants by the presence of counter alkyl chain in these alkylsulfonic dopants. Also the ions of the acids used to dope PANI have effect on its structure and redox characteristics which can be determined by voltammetric studies and spectroscopic techniques. The voltammetric and spectroscopic behavior of the PANI doped with different anions indicate that both the protons and the anions of dopant acids influence the structure and redox properties of the polymer (Hatchett et al. 1999). As shown in Figure 2, PANI NCs with ferrites can be prepared by conventional reported method according to which in-situ addition of ferrite nanoparticles during (Wang et al. 2008) oxidative polymerization of aniline (monomer) in presence of suitable oxidizing agent such as ammonium peroxy disulphate (APS) is carried out. The reported methods of preparing ferrite nanoparticles include Sol-gel method (Sharma et al. 2008), Co-precipitation method (Arulmurugan et al., 2005) and Ball milling method (Chakka et al. 2006).

**STRUCTURE OF FERRITES**

Ferrites generally have the chemical composition of MFe$_2$O$_4$ and have spinel structure (where M can be Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$, Mn$^{3+}$, Co$^{3+}$). Some of the ferrites such as Fe$_3$O$_4$ have inverse spinel structure with one Fe$^{3+}$ and two Fe$^{2+}$ atoms whereby all tetrahedral sites are occupied by Fe$^{3+}$ and octahedral sites are occupied by both Fe$^{2+}$ and Fe$^{3+}$, resulting in a net magnetic moment of 4 Bohr Magneton (Özgür et al., 2009). Spinel ferrites exhibit good magnetic, optical and electronic properties. Among these properties magnetic property is of principal interest for the purpose of this review (Mathew et al., 2007) and (Abbas et al. 2005). These properties are governed by the type of the metal ion and their method of synthesis. In this review, we will focus on Fe$_3$O$_4$ and hybrids of different ferrites as a filling component for preparing electromagnetic wave absorber material.

**MICROWAVE ABSORPTION PARAMETERS**

When an electromagnetic wave arrives on the surface of PANI NCs then, the wave can undergo three processes simultaneously namely absorption, reflection and transmission. According to the Electromagnetic wave theory, Electromagnetic Shielding Efficiency can be defined as:

\[
SE(dB) = SE_{ab}(dB) + SE_{rl}(dB) + SE_{ef}(dB)
\]

where \(SE_{ab}(dB)\) is the absorption loss, \(SE_{rl}(dB)\) the reflection loss and \(SE_{ef}(dB)\) the transmission loss. \(M\) is a term which takes into account the loss caused by multiple reflections inside the shield [24]. The thickness (t) of the shield (t=3.10-3.0m) was chosen superior to the skin depth (δ). The skin depth (δ) is defined as the depth of penetration at which the incident electromagnetic radiation is reduced to 33% of its original strength and can be expressed in terms of real permeability (\(\mu'\)), \(\sigma_T\) and \(\omega\) as \(\delta = \left[\frac{2}{\sigma_T\omega\mu'}\right]^{1/2}\). In these conditions, the loss due to the multiple reflections is neglected. The electromagnetic interference shielding efficiency can be expressed as summation of the initial reflection loss (\(R_{i}\)) and absorption loss (\(A_{ab}\)). Electromagnetic Interference Shielding Efficiency (EMI SE) value expressed in dB is also defined as the ratio of the incident to transmitted power of the electromagnetic wave.

Mathematically,

\[
SE = 10 \log \left( \frac{P_1}{P_2} \right) = 20 \log \left( \frac{E_1}{E_2} \right) \text{ (decibels, dB)}
\]

Where \(P_1, E_1, P_2,\) and \(E_2\) is the incident power, incident electric field, transmitted power and transmitted electric field respectively.

By measuring the reflectance (\(R_{i}\)) and the transmittance (\(T_r\)) of the material, the absorbance (\(A_{ab}\)) can be calculated using the following equation.

\[
A_{ab} = 1 - T_r - R_c
\]

Where, \(R_c\) and \(T_r\) are the squares of the ratio of reflected (\(E_3\)) and transmitted (\(E_2\)) electric fields to the incident electric field (\(E_1\)), respectively, as following.
The scattering factors (S factors) can be measured by Agilent 8722ES vector network analyzer to evaluate absorbance. From the theory of electromagnetic radiation, dependence of reflection and absorption losses can be related to the total conductivity ($\sigma$), real permeability ($\mu$), skin depth ($\delta$) and thickness ($t$) of the shield material as:

$$SE_{\text{Ab}}(\text{dB}) = -20 \log_{10} e^{-\frac{\delta}{\delta}} \left[\frac{\epsilon}{\epsilon}\right]$$

where, $f$ is the frequency of microwave, $c$ is the velocity of light and $t$ is the sample thickness. In general, the materials with higher $\mu'$ and $\epsilon'$ are considered as loss materials indicating strong absorption. It is known that the spinel ferrite is an important microwave absorbing material because of the higher values of $\mu'$ and $\epsilon'$. Consequently, the reflection loss of the PANI NCs is higher than that of the PANI alone (Lee et al. 1999)

**MAGNETIC PROPERTIES OF PANI NCs**

For a material to act as an electromagnetic wave absorber, it must show large magneto-crystalline anisotropy, high initial permeability and high saturation magnetization (Feng et al. 2006). Transition metals and rare earth metals ferrites in PANI NCs serve this purpose very well. Some of them have been discussed here.

**Fe FERRITE PANI NCs**

The value of magnetic saturation ($M_s$) of Fe$_3$O$_4$ nanoparticles has been reported as 44.57 emu/g (Tjong et al., 2010) and it was observed that with decrease of Fe$_3$O$_4$ content, both the values of magnetic saturation ($M_s$) and coercivity ($H_c$) for the PANI/NANO-Fe$_3$O$_4$ composites also decreases. The magnetic properties exhibited by PANI NCs can also be explained through several anisotropy mechanisms such as magnetocrystalline anisotropy, surface anisotropy and interparticle interaction (Zhang et al. 2010). The coating of ferrite nanoparticles with PANI has been reported to manipulate the contribution of the surface anisotropy and interparticle interaction to the net anisotropy (K) without affecting the magnetocrystalline anisotropy (Vestal et al. 2003). Surface anisotropy ($K_s$) originates from low coordination symmetry for spin orbit coupling at the surface of NPs and contributes to K as:

$$K = K_s + (6/d)K_a$$

where $K_a$ is the magnetocrystalline anisotropy and d is the particle diameter. It has been observed that value of $K_a$ decreases with coating. In addition to it, the magnetic properties of the magnetic materials also depends on the substituted metal cations in ferrites. As a result these magnetic properties can also be varied with different substituted metal cations (Ni$^{2+}$, Cu$^{2+}$, Mn$^{2+}$, Zn$^{2+}$ etc.). This is due to the change of the net magnetic moment of crystal unit of ferrite nanoparticles (Hashim et al., 2013). So it gives an easy way to tune the magnetic properties of ferrite particles by using different metal salts during reaction process.

**NI FERRITES PANI NCs**

Nickel ferrite (NiFe$_2$O$_4$) is an inverse ferromagnetic spinel with Ni$^{2+}$ ions occupying the octahedral sub-lattices and Fe$^{3+}$ ions occupying the tetrahedral sites and octahedral sub-lattices. The synthesis of PANI–NiFe$_2$O$_4$ nanocomposites with different contents of NiFe$_2$O$_4$ via in-situ chemical oxidation polymerization has been reported (Hu et al. 2006) where the nanoparticles of nickel ferrite were synthesized by sol–gel method (Kannan et al., 2014). Few other properties of PANI–NiFe$_2$O$_4$ nanocomposites (Kondawar et al., 2014) are tabulated below in Table 1. From table 1, the values of saturation magnetization of nanocomposites increased drastically from 0.97 emu/g to 2.083 emu/g as the content of mass % of PANI changed from 95% to 85% indicating the application of such nanocomposites as a good electro-ferromagnetic material in electromagnetic devices. The coercivity value for nanocomposites greatly increased from 101.944 Oe to 115.134 Oe, showing increase in magnetization which indicates very well interaction between nanocrystalline NiFe$_2$O$_4$ and PANI. Also the low value of reflection loss at 85% composition of PANI suggests Ni ferrites PANI NCs to act as a promising electromagnetic wave shield (Pervaiz et al., 2013).

<table>
<thead>
<tr>
<th>PANI (Mass %)</th>
<th>Conductivity (Scm$^{-1}$)</th>
<th>$M_s$ (emu/g)</th>
<th>Reflection Loss (dB)</th>
<th>Coercivity (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95%</td>
<td>1.089</td>
<td>0.97</td>
<td>-23.4dB</td>
<td>101.944</td>
</tr>
<tr>
<td>85%</td>
<td>0.267</td>
<td>2.083</td>
<td>115.34</td>
<td></td>
</tr>
</tbody>
</table>

The synthesis of nanosized Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ferrite PANI NCs has been carried out by various experimentalists. One method to obtain these composites is reverse microemulsion reaction process. Core–shell NCs composed of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocrystals which are obtained in the micellar solution of dodecyl benzene sulfonic acid (DBSA) acting both as a surfactant and a dopant and conjugated polymer polyamine were successfully synthesized from this simple and inexpensive process, accompanied by in-situ chemical oxidative polymerization of aniline (Kazantsavaa et al., 2006). These Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ferrite PANI NCs show both electrical and magnetic properties. It is seen that MnZn–PANI (30% PANI) has coercivity value of 6.5 Oe, saturation magnetization of 67 emu/g and electrical conductivity of 1.089 Scm$^{-1}$.
The studies demonstrate that the saturation magnetization decreases as the ferrite fraction increases but the coercivity value remains almost same for all the samples which implies that PANI is not enough to affect the interaction among particles. On comparing saturation magnetization values (Table 2) it is clear that on doping with rare earth ion, saturated magnetic field value in Gd-doped ferrites PANI NCs increases with increase in mass percent of PANI (Aphesteguia et al. 2007). The magnetic moment of rare earth ion is caused by the delocalized electrons present in the 4f subshell at lower temperature (<40k) but as the temperature increases alignment of magnetic moment dipole gets destroyed, even at room temperature also, therefore Gd acts as a non magnetic ion in ferrites and causes net decrease in magnetic moment of PANI NCs. (Jing et al., 2007).

### Table 2. Variation of magnetic saturation of gd-doped ferrites pani NCs as a function of pani’s content (in mass percentage)

<table>
<thead>
<tr>
<th>PANI(mass %)</th>
<th>10.7%</th>
<th>24.5%</th>
<th>32.3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_s(emu/g)</td>
<td>5.1</td>
<td>8.8</td>
<td>13.7</td>
</tr>
</tbody>
</table>

**Conclusion**

The use of electromagnetic radiations in almost every sphere of life has made the environment including humans highly exposed to them. PANI nanocomposites, because of their good electromagnetic absorption property come to the rescue in this case. Moreover, various experimental studies have shown that hybridized and doped ferrites modify the electromagnetic properties of PANI NCs towards the beneficial side. On doping the ferrite NCs with rare earth ions, the magnetic saturation ($M_s$) increases and coercivity ($H_c$) of PANI NCs decreases, hence improving the electromagnetic shielding effect.

### REFERENCES


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