Polymer-iron tungstate-reduced graphene oxide nanocomposites for microwave absorption

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Abstract. Three polymers were used in the preparation of three-component nanocomposites. Sulphonated poly(ether-ether-ketone) (SPEEK) was synthesized by sulphonation of powdered poly(ether-ether-ketone) (PEEK) using concentrated sulphuric acid. Polyvinyl alcohol (PVA) was used as purchased. Polyaniline (PANI) was synthesized using aniline, hydrochloric acid and ammonium persulphate. Three nanocomposite films based on SPEEK, PVA and PANI were synthesized through solution casting from N-Methyl-2-pyrrolidon (NMP) solutions with a magnetic filler, iron tungstate (FeWO₄) and a conductive filler, reduced graphene oxide (RGO) dispersed in them. The synthesized PANI was characterized by X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-vis), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) and the nanocomposites (RGO/PANI, FeWO₄/PANI, FeWO₄-RGO/PANI) were characterized by FTIR, TGA, DSC and SEM. The nanocomposite films based on SPEEK and PVA containing 2% RGO and 2% FeWO₄ showed the electromagnetic interference (EMI) reflection loss of only -0.5 dB for a 0.1 mm thick sample. The PANI based nanocomposite film containing 2% RGO and 2% FeWO₄ showed the maximum EMI reflection loss of -4.5 dB for a 0.1mm thick sample.

1. Introduction
The extensive advancements in the field of electronics have given rise to higher chances of electromagnetic interference (EMI), which can at times be disruptive to the normal functioning of an electronic equipment. This growth in the field of electronic equipment and communication devices has caused significant electromagnetic pollution. There are also safety concerns for humans and animals.[1] To avoid microwave electromagnetic interference, the devices and components are coated with materials which absorb, transmit or reflect the electromagnetic waves and this phenomenon is
called electromagnetic interference shielding.[2] EMI shielding strategies commonly use metals which tend to shield by reflecting the radiation owing to their high electrical conductivity.[3] Wei Chen and Xixi Zhu [4] prepared urchin like strontium ferrites to be used for microwave absorption. The urchin like structures enhanced the microwave absorbing capacity to exhibit a reflection loss less than -10 dB as compared to normal strontium ferrites which suffer from agglomeration. Yonglin Yaoa and Chuanfu Zhang [5] reported that their preparation of a paraffin composite using porous Fe-Ni powders showed that at 2.57 GHz, the reflection loss went below -10 dB when thickness was 2 mm and it was -52.58 dB at 6.82 GHz when thickness was 3 mm. Sukanta Das et al. [6] reported that for single layer graphene oxide/epoxy based absorber a reflection loss of -7.86 dB at 10.72 GHz was reported but when he substituted the graphene oxide component of the composite with FeCoB it showed a reflection loss of -13.3 dB at 11.67 GHz. The reflection loss further increased to -22.24 dB at 12.4 GHz when graphene oxide was coated with FeCoB/epoxy based single layer absorber.

However, metals have a disadvantage of being heavy, prone to corrosion and allowing very restricted tuning of their shielding effectiveness. Also, reflecting the electromagnetic radiation might not be acceptable for certain applications like stealth aircrafts. Polymers on the other hand, although primarily known to possess insulating properties are advantageous as they tend to absorb radiation, are lightweight, do not get corroded and are processible. Hongyu Wang et al. [7] used a polyimide resin as matrix and SiO₂ coated carbonyl iron as filler resulting in the preparation of an electromagnetic shielding material which had the added advantage of being a heat resistant material having a minimum reflection loss between -25 dB to -33 dB with the thickness of 1.5 mm to 2.1 mm. For this study, sulphonated poly(ether ether ketone) (SPEEK), polyvinyl alcohol (PVA) and polyaniline (PANI), were chosen as matrices for nanocomposites based on their different properties including mechanical stability, thermal stability, electrical conductivity, cost and chemical resistance. Each could be suitable for different applications. [8] Since the polymers show poor microwave absorption, reduced graphene oxide and iron tungstate were added as conductive and magnetic fillers respectively, to improve the overall shielding effectiveness of the nanocomposites.

2. Experimental

2.1. Materials

Injection moulded poly(ether-ether-ketone) was powdered, sulphuric acid (98.08%, Nice), N-Methyl-2-pyrrolidone (99.5%, SRL chemicals), polyvinyl alcohol (SRL chemicals) and ammonium persulphate (SDFCL fine-chem limited) were used. Aniline and hydrochloric acid was obtained from Finar. Aniline was double distilled before use.

2.2. Synthesis of SPEEK

Batch 1

PEEK (0.5 g) was added in a round bottom flask and 5 ml of sulphuric acid was added to it. The mixture was kept in an oil bath that was heated and stirred at a constant temperature of 50°C for 3.5 hours. The mixture was poured and quenched in the tray containing ice cold water (ice cold water used, because SPEEK dissolves in water at room temperature). A white rubbery cloth like SPEEK polymer was formed once the mixture was quenched. The SPEEK formed was washed continuously with ice cold water till pH neutral. After complete drying of the SPEEK formed, it was kept in a desiccator with calcium chloride used as desiccant.

No significant change in texture or colour of the product kept in the desiccator was observed even after 24 hours after product formation. But after 3 days of storage in the desiccator, the colour started to change to yellowish brown along with a texture change. This change is expected to have been because of the -SO3H (sulphonic acid group) present in the polymer chain.
Batch 2
Same procedure as for batch 1 was followed except that the reaction was carried out at room temperature for 72 hours 35 minutes.

Unlike last batch, the polymer formed in this batch was in gel form which was cloudy. A considerable amount of polymer was seen to dissolve even in ice cold water while quenching. From literature, we know that as degree of sulphonation increases, the solubility of the SPEEK increases. [9] So, as the reaction time for this batch was more, and moreover since it was found to be more soluble in water than the previous batch and as the product was in gel form, high degree of sulphonation of SPEEK is expected. 26 days after gel formation, the gel form of polymer formed was found to have become a transparent film.

2.2.1. Degree of Sulphonation
SPEEK (0.1 g) was soaked in 4mL of 0.1M NaCl solution for 24 hours and it was back-titrated with 0.1M NaOH solution using phenolphthalein as indicator.

\[
\text{Ion Exchange Capacity, } \text{IEC} = \frac{\text{Volume of NaOH} \times \text{molar concentration of NaOH}}{\text{weight of SPEEK}}
\]

\[
\text{Degree of Sulphonation, } (\text{DOS}) = \frac{M_p \times \text{IEC}}{(1000 - (M_{SO_3H} \times \text{IEC}))} \times 100
\]

where, \(M_p = 288 \text{ g/mol}\) and \(M_{SO_3H} = 81 \text{ g/mol}\) are molecular weights of PEEK monomer unit of polymer and suphonic group respectively. [10]

Batch 1:
\[
\text{IEC}= \frac{0.8 \text{ mL} \times 0.0966}{0.1 \text{ g}} = 0.77339 \text{ meq g}^{-1}
\]
\[
\text{DOS}= \frac{288 \times 0.77339}{1000 - (81 \times 0.77339)} \times 100 = 23.76\%
\]

Batch 2:
\[
\text{IEC}= \frac{2 \text{ mL} \times 0.0997}{0.1 \text{ g}} = 2.195 \text{ meq g}^{-1}
\]
\[
\text{DOS}= \frac{288 \times 2.195}{1000 - (81 \times 2.195)} \times 100 = 76.89\%
\]

2.3. Synthesis of PANI
Hydrochloric acid (30 mL) was taken in a standard flask and was made up to 250 mL by adding distilled water. Aniline (4.7 mL) was taken in a beaker and 50 mL of made up hydrochloric was added to it. The contents were sonicated for half an hour. Ammonium persulphate (11.409 g) was dissolved in a beaker containing 50 mL of distilled water. The prepared ammonium persulphate solution was transferred to a burette and added dropwise to the sonicated aniline and hydrochloric acid mixture which was stirred constantly while kept in a refrigerated bath at 0°C. After the ammonium persulphate solution was completely transferred into the beaker containing the sonicated aniline and hydrochloric acid mixture, the contents were stirred constantly and left undisturbed in the refrigerated bath at 0°C for 16 hours. After 16 hours, the mixture was taken out of the refrigerated bath and centrifuged once with just the contents, twice with distilled water and once with methanol to remove the unreacted
oligomers and obtain polyaniline. The polyaniline obtained was dried in a vacuum oven operated at 60°C. [11]

2.4. Solution casting of FeWO₄-RGO/SPEEK nanocomposite films
SPEEK obtained from batch 1 (0.2 g), iron tungstate (0.002 g), RGO (0.002 g) and each was added in three different test tubes and was dispersed by adding minimum amount of solvent NMP (0.6 mL NMP for SPEEK, 0.1 mL NMP for FeWO₄ and 0.3 mL NMP for RGO) and sonicating it in an ultrasonicator until each of the added components completely dispersed in NMP. Then, contents from each of the three test tubes were mixed together, casted drop-wise homogenously on a petri-dish and kept in a hot-air oven for 4 hours at 80°C. The same procedure was followed for solution casting using batch 2 SPEEK.

Solution casting using batch 1 SPEEK yielded an almost transparent thin nanocomposite film which was of dark-brown colour, whereas when batch 2 SPEEK was used, it yielded an almost transparent thin nanocomposite film which was of yellowish-brown colour. Both the nanocomposite films showed very little or almost negligible conductivity when it was tested under two probes. Preliminary studies using X-band reflectivity test were carried out on the nanocomposite films to assess their microwave absorption. Both the nanocomposite films of 0.1mm thickness showed a reflection loss of only -0.5 dB when it was tested using a 10 GHz microwave source.

2.5. Solution casting of FeWO₄-RGO/PVA nanocomposite films
PVA (0.5 g), iron tungstate (0.005 g) and reduced graphene oxide (0.005 g) each were added in three different test tubes and solution casting was performed using the same procedure as in 2.4.

An almost transparent thin nanocomposite film was formed which was brown in colour. When the material was tested under two probes it showed a resistivity of 125.8 MΩ.m across 7.5 cm length and 30.2 MΩ.m across 2 cm length (i.e. 7.9491 X 10⁻⁹ S/m and 3.3113 X 10⁻⁸ S/m conductivity respectively). Preliminary studies using X-band reflectivity test were carried out on the nanocomposite film to assess their microwave absorption. The nanocomposite film of 0.1mm thickness showed a reflection loss of only -0.5 dB when it was tested using a 10 GHz microwave source.

2.6. Solution casting of FeWO₄-RGO/PANI nanocomposite films
PANI (0.5 g), iron tungstate (0.005 g), reduced graphene oxide (0.005 g) each was added in three different test tubes and solution casting was performed using the same procedure as in 2.4 except that the contents from each of the three test tubes were then mixed together, casted drop-wise homogenously on a glass plates and kept in a hot-air oven for 2 hours at 60°C. [12]

An almost dried nanocomposite film was formed which was dark greenish-black in colour. Preliminary studies using X-band reflectivity test were carried out on the semi-dried nanocomposite film to assess their microwave absorption. The almost-dried nanocomposite film of 0.1mm thickness showed a reflection loss of -4.5 dB when it was tested using a 10 GHz microwave source.

3. Results and discussions
Owing to poor conductivity and reflection loss of FeWO₄-RGO/SPEEK and FeWO₄-RGO/PVA nanocomposite films, material characterization was performed only for polyaniline-based nanocomposites because of its comparatively better reflection loss.

3.1 SEM analysis
The SEM images of PANI reveal its granular external morphology, although further magnification shows a cloudy image from which it can be inferred that the surface is uneven and not well defined. Figure 1 shows SEM images of PANI, FeWO₄, FeWO₄/PANI, RGO/PANI and FeWO₄-RGO/PANI. A grainy morphology with close packing is seen in the images of FeWO₄ and fine nanoparticles ranging less than 30nm are found. The surface appears to have become well defined; a connected granular morphology with voids is visible after the addition of FeWO₄ to PANI. When RGO is added to PANI,
the surface appears to be cloudy, agglomerated and there are some voids observed which were initially absent in the surface of PANI. The images of FeWO₄-RGO/PANI show less voids in surface in comparison with RGO/PANI and there are also clusters of tiny rice like structures on the surface with a decent connectivity in its morphology. The grainy morphology of FeWO₄ is expected to have imparted the connected granular morphology to the matrix.

![SEM images of (a) PANI (b) FeWO₄ (c) FeWO₄/PANI (d) RGO/PANI (e) FeWO₄-RGO/PANI](image-url)

**Figure 1:** SEM images of (a) PANI (b) FeWO₄ (c) FeWO₄/PANI (d) RGO/PANI (e) FeWO₄-RGO/PANI
3.2 X-ray diffraction analysis

Figure 2 shows X-ray diffraction of FeWO$_4$ and PANI with diffraction peaks of FeWO$_4$ at $2\theta = 30.21^\circ$, 35.52$^\circ$, 43.11$^\circ$, 57.26$^\circ$ and 62.77$^\circ$, PANI at $2\theta = 20.01^\circ$ and 26.42$^\circ$ respectively. The FeWO$_4$ XRD pattern shows well-defined peaks which has been JCPDS indexed to assert that the tested compound is iron tungstate. The PANI XRD pattern shows sharp and well-defined peaks, which indicate the semi-crystalline nature of polyaniline. The plains of benzenoid and quinoid rings of PANI chain are responsible for crystalline structure. The sharp peaks have been JCPDS indexed to assert that this tested compound is polyaniline. [13]

![Figure 2: XRD pattern of FeWO$_4$ and PANI](image)

3.3 UV-visible spectroscopy

Figure 3 shows the ultraviolet and visible spectra for the synthesized PANI. Distilled water was used as solvent during the analysis. The above figure shows the UV-visible pattern of PANI. The spectrum has a peak at 437 nm and 830 nm. This peak represents the presence of benzenoid group and lone pair of electrons of nitrogen. This in turn leads to $\pi-\pi^*$ interactions of the molecule and this shows that it is a conducting polymer and also asserts that the synthesized chemical is PANI. [14]

![Figure 3: UV-visible spectrum of PANI](image)

3.4 Fourier transform infrared spectroscopy

Figure 4 shows the FTIR spectrum of PANI, FeWO$_4$, FeWO$_4$/PANI, RGO/PANI and FeWO$_4$-RGO/PANI. PANI showed its major characteristic peaks at 3417, 3145, 1648, 1400, 1112 and 597 cm$^{-1}$ which are similar to the ones reported in the literature. [15] In addition to these bands, there is a peak at 1648 cm$^{-1}$ which corresponds to -NH$_2$ link in the polymeric chain. This peak infers the presence of
some monomer units still present in the polymer chain. The FTIR spectrum of RGO was recorded to confirm its reduction to RGO. The peaks near 1600 cm\(^{-1}\) were due to various skeletal vibrations of C=C aromatic unoxidized graphitic domains. The peak around 1100-1200 cm\(^{-1}\) were due to C-C, C-OH stretching vibrations. The FTIR spectrum of RGO showed some sharp peaks corresponding to oxygen functionalities which confirm the inefficient reduction of GO into RGO.\(^{[16]}\) The peaks around 3400 cm\(^{-1}\) were due to N-H asymmetric stretching and sharp peak at 1400 cm\(^{-1}\) corresponds to N-H deformation. It is also observed that there are no significant peaks around 1600 cm\(^{-1}\) in RGO/PANI, FeWO\(_4\)/PANI or FeWO\(_4\)-RGO/PANI curves except for the peak at 1648 cm\(^{-1}\) which corresponds to -NH\(_2\) link in the polymeric chain. This could mean that the inefficient reduction of graphene oxide resulted in it being incompatible with the polymer matrix.

![Figure 4: FTIR spectrum for PANI, RGO, RGO/PANI, FeWO\(_4\)/PANI and FeWO\(_4\)-RGO/SPEEK](image)

3.5 Thermogravimetric analysis

Figure 5 shows the TGA curves of PANI, RGO/PANI, FeWO\(_4\)/PANI, PANI and FeWO\(_4\)-RGO/PANI and there are three major weight losses observed in each of them. In figure 5(a), the first weight loss occurred between 30-160°C with a weight loss percentage of 26.53% which may be attributed to loss of any moisture content present in the PANI sample. The second major weight loss occurred between 160-400°C with a weight loss percentage of 37.69% which may be ascribed to loss of any impurities present in the sample. The third major weight loss occurred between 400-800°C with a weight loss percentage of 28.02 which may be accredited to polymer degradation.\(^{[17]}\) In figure 5(b), the first major weight loss occurred between 30°C-160°C with a weight loss percentage of 16.21% which may be attributed to loss of any trapped moisture in the sample. The second major weight loss occurred between 160-400°C with a weight loss percentage of 38.29% which is thought to be caused by the elimination of remaining functional groups of RGO. The third major weight loss occurred between 400-800°C with a weight loss percentage of 16.36% which is accredited to polymer degradation. In figure 5(c), the first major weight loss took place between 20-200°C with a weight loss percentage of 16.29% which is attributed to moisture loss. The second major weight loss occurred between the temperatures 200-400°C with a weight loss percentage of 23.71%. This weight loss is ascribed to loss of any impurities present since iron tungstate is stable till around 1000°C. The third major weight loss occurred between 400-800°C with a weight loss percentage of 13.99% and is attributed to polymer degradation. IN figure 5(d), the first major weight loss occurred between 20-200°C with a weight loss percentage of 17.76%. This is attributed to loss of any moisture content present in the sample. The second weight loss occurred between 200-400°C presenting a weight loss percentage of 35.12% ascribed to the loss of any impurities as well as the elimination of remaining functional groups of RGO. The third major weight
loss occurred between 400-800°C with a weight loss percentage of 13.29%. This weight loss is accredited to polymer degradation.

![TGA curves](image)

**Figure 5:** TGA curves for (a) PANI (b) RGO/PANI (c) FeWO₄/PANI (d) FeWO₄-RGO/PANI

### 3.6 Differential scanning calorimetry

Figure 6 shows the DSC curves of PANI, RGO/PANI, FeWO₄/PANI, PANI and FeWO₄-RGO/PANI which was recorded from 30°C to 307°C at 10°C/min heat flow. The adsorbed water was first removed from the samples from 30°C up to 150°C under nitrogen gas atmosphere, which was done by using the DSC technique in order to verify the water content removal. The change in baseline might be due to structural changes in the polymer morphology due to the thermal treatment. For PANI, the thermograph shows two peaks at 64.18°C and 224.92°C. These peaks might be attributed to the glass transition and degradation temperature of the synthesized polymer. The final valley point around 271.21°C is expected to attribute the melting point of the polymer. Similarly, for remaining curves the first and the second peaks correspond to the glass transition and degradation temperatures respectively and the final valley point attributes to melting point.

![DSC curves](image)

**Figure 6:** DSC curves for PANI, RGO/PANI, FeWO₄/PANI and FeWO₄-RGO/PANI
3.7 Microwave reflection loss test

Table 1: Output power and reflection loss of iron tungstate-reduced graphene oxide-based nanocomposites

| Sample                  | Glass | FeWO₄-RGO/SPEEK (23.76% DOS) | FeWO₄-RGO/SPEEK (76.89% DOS) | FeWO₄-RGO/PVA | FeWO₄-RGO/PANI |
|-------------------------|-------|------------------------------|------------------------------|---------------|---------------|
| Output power (dB)       | -6.5  | -7                           | -7                           | -7            | -11           |
| Reflection loss (dB)    | -     | -0.5                         | -0.5                         | -0.5          | -4.5          |

4. Conclusions

It was observed that neither FeWO₄-rGO/SPEEK nanocomposite films nor FeWO₄-rGO/PVA nanocomposite films met acceptable levels of conductivity and showed only a reflection loss -0.5 dB which is very less for microwave shielding. Therefore, we synthesized a nanocomposite film consisting of a conducting polymer PANI and were able to achieve a comparatively better reflection loss of -4.5 dB for same sample thickness of 0.1mm. Although the UV-visible spectroscopy asserts that the synthesized polymer is PANI, the FTIR spectroscopy adds further information with the presence of a peak at 1648 cm⁻¹ which corresponds to -NH₂ link in the polymeric chain. It can be inferred from the peak about the presence of some monomer units in the polymer chain. With the presence of monomer in the polymeric chain, it is safe to assert that complete polymerization has not occurred and which in turn can imply about the less molecular weight build-up of the polymer, thereby accrediting to the less film forming tendency of the synthesized PANI. This less molecular weight build-up of the polymer can further be corroborated by the TGA curves which show continuous weight loss, which is not likely a phenomenon in case of polymers which are expected to be stable up to its degradation temperature. Also, the FTIR spectroscopy tells about the inefficient reduction of GO into RGO because of the sharp peaks corresponding to oxygen functionalities. This could mean that the inefficient reduction of graphene oxide resulted in it being incompatible with the polymer matrix therefore not enabling to form a connected morphology which is supposed to play a role in increasing the conductivity of the entire matrix and thus attributing to very less microwave shielding.

Further studies can be done in improving the molecular weight of the polymer PANI (maybe by changing the dopant from hydrochloric acid to para toluene sulffonic acid, as hydrochloric acid forms covalent bonds with PANI and makes it inhomogeneous), preparing a fully reduced graphene oxide for filler applications which can enable the formation of a connected morphology within the nanocomposite which can subsequently account for good electrical conductivity and thus good microwave absorbing capacity. The proportions of the fillers can also be optimized to suit different applications which are likely to yield further improvements in the reflection loss of the composites.

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