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Synthesis of Polyaniline- γ-Fe_2O_3 nano composites in Green Medium - Theoretical Justification of Electrical and Magnetic Properties

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Abstract

In this work polyaniline (PANI)-γ-Fe_2O_3 nano composites were synthesized via in-situ oxidative chemical polymerization technique in a green medium extracted from the fruit of plant Tamarindus indica. Various samples were prepared with 5, 10 and 15g of γ-Fe_2O_3 as filler in 0.4M aniline and were characterized by XRD, SEM and IR. Dielectric properties were determined in the frequency range of 100Hz to 20MHz and these values were compared with the theoretical values obtained from Maxwell-Wagner equation. Magnetic properties of the samples were analyzed by Vibrating Sample Magnetometer (VSM). A theoretical linear equation was applied to justify the saturation magnetization (Ms) values of the composites with different loading of γ-Fe_2O_3.

Keywords: Polyaniline, γ-Fe_2O_3, PANI-ferrite composite, Tamarindus indica

INTRODUCTION

Polyaniline and its composites with various ferrites find great importance in the modern industry due to their extensive applications in numerous fields[1]. Materials having both electrical and magnetic properties are required for the application of electrical and magnetic shielding, molecular electronics, nonlinear optics, sensor and microwave absorbent. Low production cost and wide applicability gave it a special attention of chemists and technologists. As the property of these materials depend on the method of synthesis, filler content, solvent used, temperature applied, nature and ratio of oxidant, various studies related to the factors affecting the properties of composites are inevitable. Researchers are also intended in the studies related to the tuning of dielectric properties, AC conductivity, electromagnetic absorbance and magnetic properties of the composite with filler content.

In recent years, researchers are more interested in the synthesis of nano particles using green medium such as plant extract due to its cost effectiveness and ease of conduction. It is also reported that nano particles synthesized via green methods have been found eco-friendly and safe[2]. Better homogeneity also has been reported for the particles synthesized in green medium[3].

The present work has been carried out to explore the possibility of tamarind fruit extract as a medium and dopant for the synthesis of PANI and PANI-ferrite composites. Tamarindus indica is a long living branched leguminous tree of family Fabaceae, which is a very common plant in Kerala. It produces a pod like fruit which contains a brown pulpy mass with seeds inside. A well grown tree may produce about 150 to 225kg of fruits annually with 30 to 55% of pulp. The sun-dried pulp can be stored for several years. Tamarind pulp is a promising source of tartaric acid. Extract of pulp with water is called tamarind syrup which is found to be acidic in nature[4]. It is reported that for better property, optimized pH for the synthesis PANI is around 2. The tamarind fruit extract prepared in distilled water has pH≈2 and therefore can be an effective medium for the synthesis of PANI and PANI -ferrite composites[5].

MATERIALS AND METHODS

Analytical grade ferric nitrate for the synthesis of γ-Fe_2O_3 was purchased from Qualigens chemicals. All the chemicals such as aniline, HCl and acetone used for the synthesis of polyaniline were purchased from Merck chemical company and ammonium peroxydisulphate (APS) from Spectrochem and all were of high purity. Aniline was used after double distillation. 30g tamarind pulp was squeezed with 250ml water and filtered to get tamarind extract having pH≈2.

γ-Fe_2O_3 particles were prepared by sol-gel method from ferric nitrate solution in minimum quantity of ethylene glycol. The solution was heated to 60℃ till a wet gel was obtained and was then heated to 100℃, resulted in fluffy gamma ferric oxide. It was then powdered and heated at 200℃ in a muffle furnace to get fine particles.

$2Fe(NO_3)_3.9H_2O$ + Ethylene glycol → Fe_2O_3 + volatilities

Conductive PANI coated ferrite particles were synthesized by in situ oxidative chemical polymerization of aniline in green medium tamarind extract in the presence of ferrite particles. Ferrite powder was added slowly to a mixture of 3.72g of aniline in 100ml tamarind extract, kept in an ice bath, with vigorous stirring in order to keep ferrite powder suspended in the solution. To this APS solution was added drop wise with aniline/persulphate ratio 1:1.25. Polymerization of aniline was allowed to takes place over fine graded ferrite

particles. After the complete addition of the oxidant, the solution was kept undisturbed overnight to complete the polymerization. The resulting precipitate was filtered, washed with distilled water and acetone and then dried in an air oven at 50°C for 24 hours. Obtained composite was grinded into a fine powder in smooth agate mortar in the presence of acetone medium. Pure PANI was synthesized by the same manner without the addition of ferrite.

Various samples of PANI-ferrite composites were prepared in 0.4M aniline with 5, 10, and 15g of γ-ferric oxide (represented as F) and were denoted as P4F5, P4F10 and P4F15. Weight percentages of filler in these compositions are 57.3, 72.8 and 80.12 respectively.

The FTIR spectra was recorded on a Thermo Nicolate Avatar370 (Model) spectrophotometer in KBr medium in the region 4000-400 cm^{-1} having DTGS detector. The phase analysis of the samples was carried out using Rigaku D max-B model X-ray diffractometer using Cu Kα radiations. SEM analysis of the samples was done with the SEM make JEOL Model JSM-6390LV. Room temperature magnetic measurements of the ferrite and PANI composites were carried out by VSM: model Lakeshore VSM 7410. Dielectric permittivity was calculated by measuring the capacitance of the materials in various external frequency ranges from 100Hz to 20MHz.

RESULTS AND DISCUSSIONS

XRD

X-ray diffractograms of PANI, γ-ferric oxide and P4F5 (representative sample of the composite) are shown in the Figure 1.

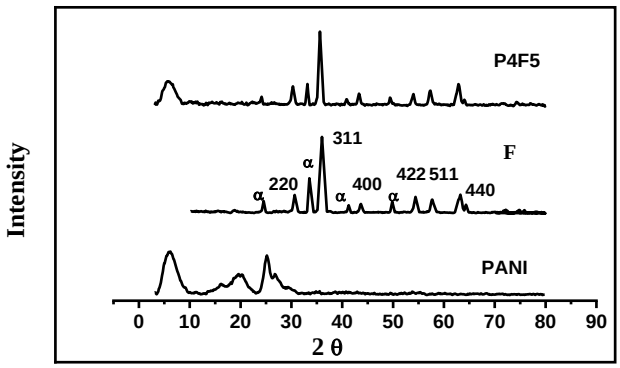

Figure 1. X- ray diffractogram of PANI, γ-Fe_2O_3 and PANI-γ-Fe_2O_3 composite

All the crystalline planes such as (220), (311), (400), (422) and (511) of γ-Fe_2O_3 (JCPDS data No. 39-1346) are observed in the XRD pattern of γ-Fe_2O_3. In the pattern peaks corresponding to α form of ferric oxide are also observed. Non-magnetic α form of ferrite may affect its magnetic properties. Presence of all the peaks of γ-Fe_2O_3 in the composite confirms the composite formation and retention of ferrite in the PANI matrix. Average particle size of composite calculated using Scherrer formula is 20.16nm.

IR studies

Figure 2 represents the FTIR spectrum of γ-Fe_2O_3 and PANI-γ-Fe_2O_3 composite. γ-Fe_2O_3 shows two absorption peaks at 541 and 645 cm^{-1} correspond to metal-oxygen stretching vibrations at tetrahedral and octahedral sites respectively. These are characteristic peaks observed in spinel ferrites[6]. The bands appear at 1485 and 1569 cm^{-1} corresponding to C=C stretching vibrations of N-B-N (benzenoid) and N=Q=N (qunanoid) structures respectively. Presence of these absorption bands confirms the formation of most conductive emeraldine form of PANI. Absorption band at 798 cm^{-1} is due to out of plane bending vibration of C-H bond of 1, 4-disubstituted benzene ring which confirms the conjugated π system present in PANI. A strong band appears at 1111cm^{-1} has been explained as an in-plane bending vibration of imino-1,4-phenylene. Presence of peaks due to PANI and ferrite in the FTIR spectrum of composite confirm the well dispersion of ferrite in the polymer matrix, without any structural change of the polymer.

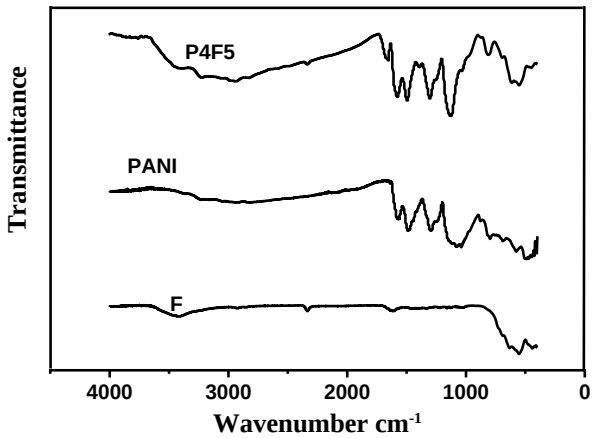

Figure 2. FTIR spectra of γ-Fe_2O_3, PANI and PANI-γ-Fe_2O_3 composite

SEM Analysis

Figure 3 represents the SEM micrograph of γ-Fe_2O_3 and it's composite with PANI. Enlarged SEM image clearly indicates significant difference in the morphology of the composite compared to pure ferrite. Agglomerated particles are observed in the SEM image of γ-Fe_2O_3. In composite better homogeneity and well dispersion of pani coated ferrite particles are observed.

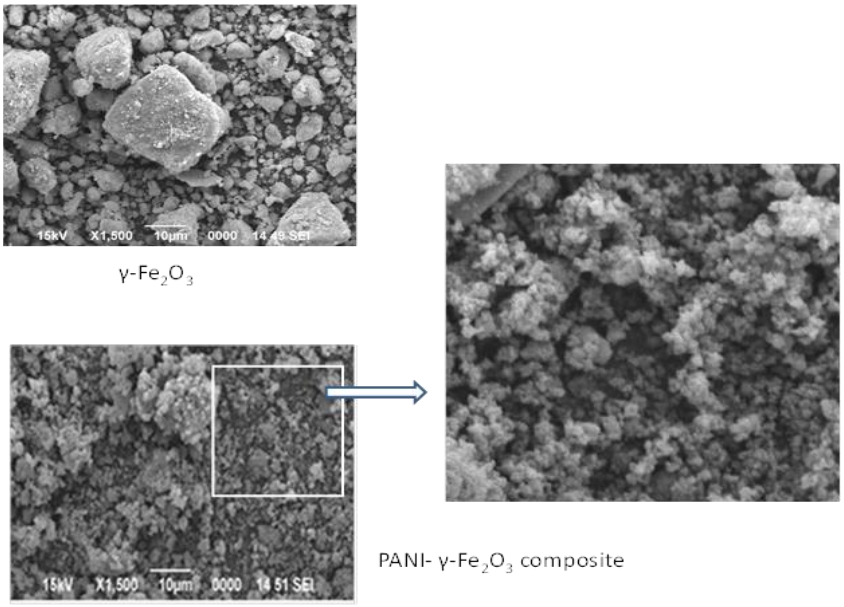

Figure 3. SEM micrographs of γ-Fe_2O_3 and PANI-γ-Fe_2O_3 composite

TG analysis

Figure 4 shows the thermogravimetric analysis for PANI and PANI-γ-Fe_2O_3 composite P4F15. PANI and composite show three stages of degradation due to loss of moisture, dopant evolution and decomposition of polymer chain. Thermal degradation of PANI is found to be started at a temperature about 340℃. Composite formation increases the stability and thermal degradation starts at a high temperature of about 350℃. This may be due to a well bonding between PANI and ferrite.

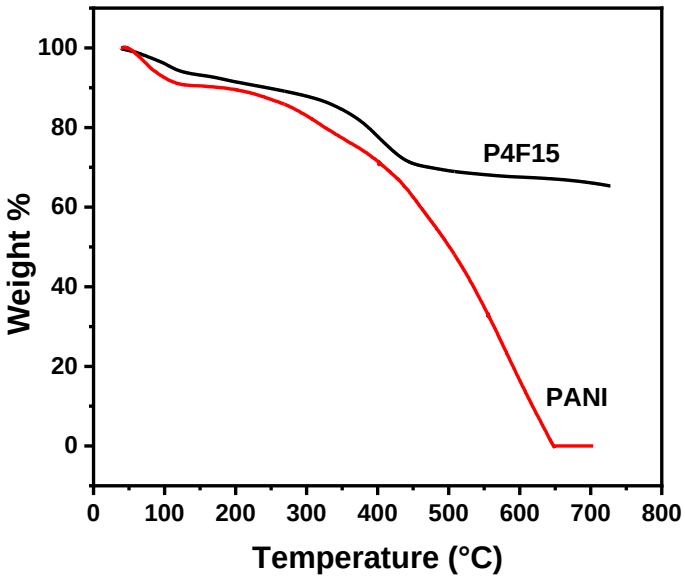

Figure 4. TGA curves of PANI and PANI-γ-Fe_2O_3 composite.

Dielectric Studies

The dielectric permittivity (ε) of a dielectric material is, $\boldsymbol{\varepsilon = C\ t/\ \varepsilon_0 A}$, where, C = capacitance of the material used as the dielectric, C_0 = capacitance using vacuum as the dielectric, ε_0= Dielectric Permittivity of free space (8.854 x 10^{-12} F/m), A = sample cross sectional area, t = thickness of the sample.

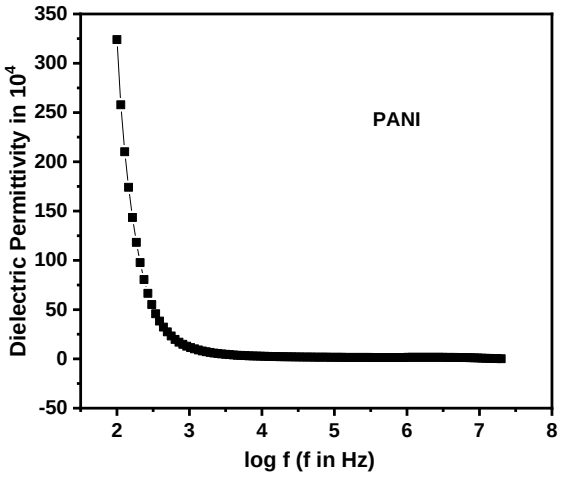

Figure.5. Variation of dielectric permittivity of PANI with frequency

Variation of dielectric permittivity of PANI with applied frequency is depicted in the Figure 5. It is found that PANI shows very high dielectric permittivity at low frequencies which decreases with the increase in frequency and reaches a constant value at very high frequencies. Very high value of dielectric permittivity confirms the dipolar structure of PANI matrix.

Dielectric behavior of a polymeric material under the influence of an external electric field depends on the polarization effect that occurs within the polymer matrix. At low frequencies the total polarization in polar materials is the sum of multi components ie. deformation polarization (electronic and ionic) and relaxation (orientation and interfacial) polarization. As the frequency is increased the dipole cannot able to oscillate rapidly and will lag behind the applied electric filed. So the dielectric permittivity of the polymeric materials decreases with the increase of the applied frequency and reaches a constant value at very high frequencies [7].

Variation of dielectric permittivity with frequency of γ-Fe_2O_3 is represented in the Figure 6.

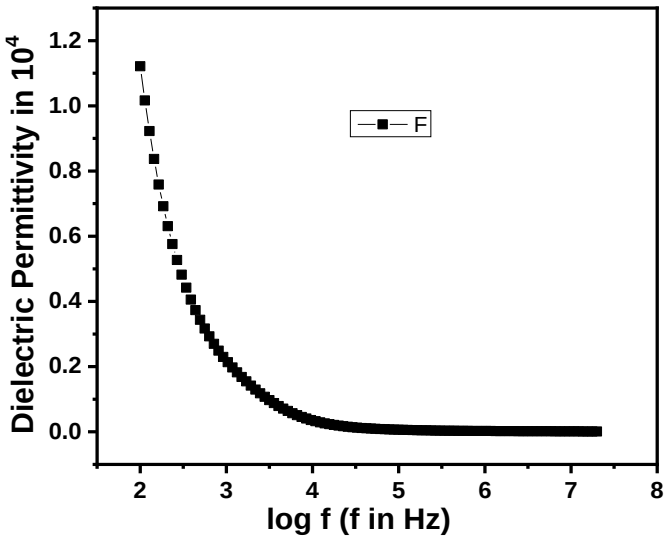

Figure 6. Variation of dielectric permittivity of γ-Fe_2O_3 with frequency

It can be seen that the dielectric permittivity decreases with increase in frequency and reaches a constant value at higher frequencies. This is the normal dielectric behavior of ferrite and can be explained by Maxwell-Wagner polarization model. According to this model the solids are assumed to be composed of well conducting grains separated by non-conducting grain boundaries. Due to the hoping of electrons between different oxidation states of the metals, electrons pile up at the grain boundaries. As a result interfacial polarization increases and gives high value of permittivity. At high frequency of the applied field the hopping frequency of electron lags

behind, hence the number electrons reaches the boundary decreases remarkably. As a result, interfacial polarization reaches a minimum and the dielectric permittivity attains a constant value [8].

Variation of dielectric permittivity of PANI-γ-Fe_2O_3 composites with frequency

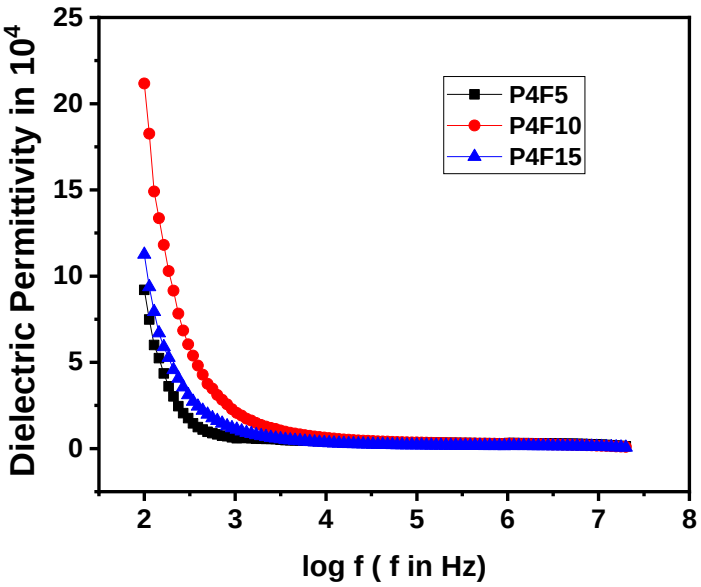

Figure 7. Variation of dielectric permittivity of PANI-γ-Fe_2O_3 composites with frequency

Effect of frequency on the dielectric permittivity of PANI-γ-Fe_2O_3 composites is shown in Figure 7. All the samples show very high dielectric permittivity values at lower frequencies which decrease with frequency and reach to a constant value at very high frequencies. The high dielectric permittivity values confirm the presence of polymer backbone in the composites. Figure 8 shows the loading dependence of dielectric property.

From the figure it is clear that, composite with 10g ferrite gives the highest value of ε and is found decreased for P4F15. This may due to the interference of excess ferrite content on the polarization of PANI in the composite especially at lower frequencies. At higher frequencies not much difference is observed in the dielectric permittivity values of various samples.

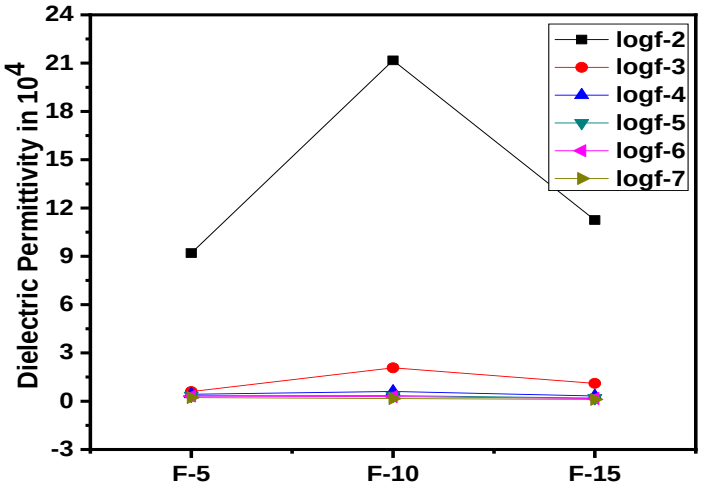

Figure 8. Loading dependence of dielectric permittivity of PANI - γ-Fe_2O_3 composites

Application of dielectric mixture equation for theoretical justification of dielectric properties of PANI-ferrite composites (PFCs)

Generally dielectric constant of a composite material comprises two different homogeneous dielectrics of the combining components[9]. Maxwell-Wagner mixing rule written in the form of Equation 1[10-11] can be applied to determine the effective dielectric permittivity of two component composite systems which is derived on the basis of various theoretical assumptions and experimental data[12].

$$\varepsilon_{eff} = \varepsilon_m \frac{\left[1 - 2V_f \frac{(\varepsilon_m - \varepsilon_f)}{(2\varepsilon_m + \varepsilon_f)}\right]}{\left[1 + V_f \frac{(\varepsilon_m - \varepsilon_f)}{(2\varepsilon_m + \varepsilon_f)}\right]} \qquad \textbf{(1)}$$

In this particular study equation 1 is applied with a modification that instead of volume fraction (V_f) weight fraction (W_f) of the components was used for calculation. The exact weight fraction of the polymer is not possible to obtain from the weight of aniline used for polymerization. Chance of formation of oligomers and presence of unreacted aniline should also be considered. These molecules will be washed out during the synthesis stage. So, a correction factor is included in the modified theoretical equation for PANI-ferrite composites. The modified equation is represented as 2.

$$\log(\varepsilon_{eff}) = \log\left(\varepsilon_m \frac{\left[1-2w_f \frac{(\varepsilon_m-\varepsilon_f)}{(2\varepsilon_m+\varepsilon_f)}\right]}{\left[1+w_f \frac{(\varepsilon_m-\varepsilon_f)}{(2\varepsilon_m+\varepsilon_f)}\right]} \right) + \log k \qquad \textbf{(2)}$$

where k is an empirical constant which varies with the percentage content of PANI and ferrite in PANI-ferrite composites.

The theoretical fitting curves of dielectric permittivity values obtained from Maxwell-Wagner equations **1** and **2** with the experimental values of the samples P4F5, P4F10 and P4F15 are depicted in the Figures 9-11. From the Figure 9**,** it is clear that P4F5 shows a small deviation in the observed value from the calculated value. The experimental value of P4F5 is found lower than that of the theoretical value. An appreciable difference is observed especially in the low frequency. At lower frequencies the major contribution of dielectric permittivity is from the orientation polarization of PANI. The variation in ε may be due to the difference in actual weight fraction and expected weight fraction of PANI in the composite. The curve corresponding to equation **2** with a correction factor of k=0.6 shows a good promise with the experimental values especially at higher frequencies.

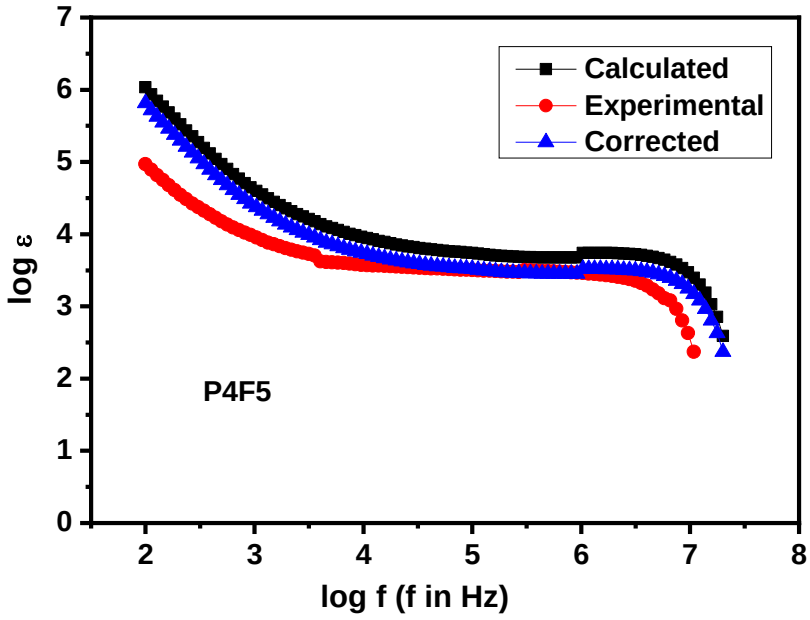

Figure 9. Maxwell-Wagner and experimental log ε versus log f for P4F5 composite

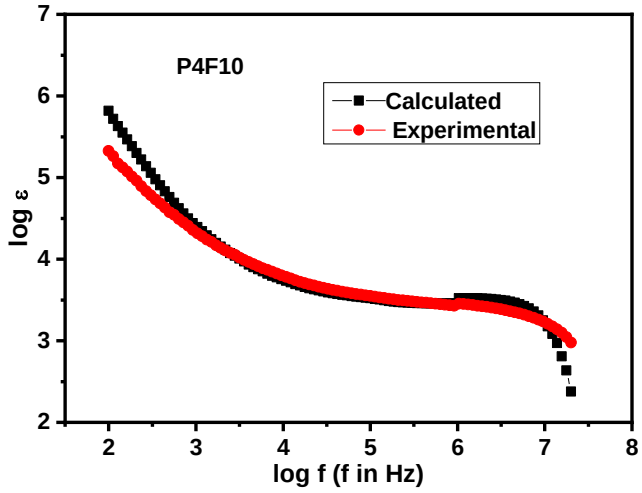

Figure 10. Maxwell-Wagner and experimental log ε versus log f for P4F10 composite

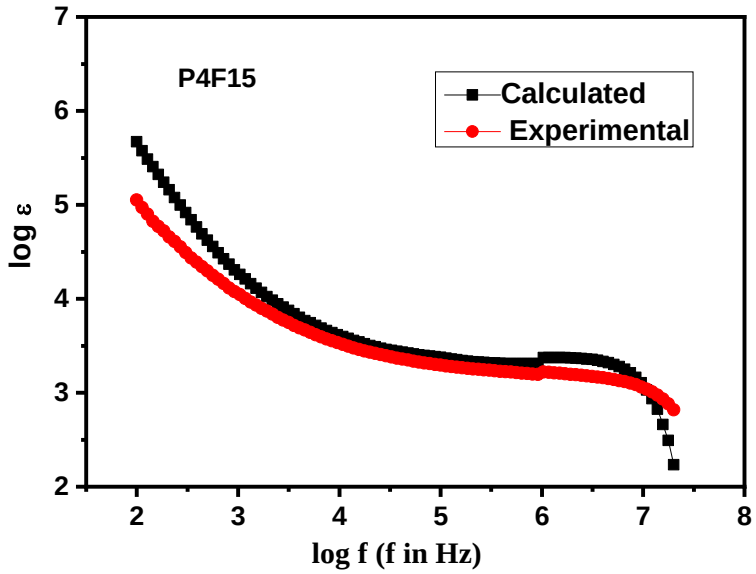

Figure 11. Maxwell-Wagner and experimental log ε versus log f for P4F15 composites

From the Figures 10 and 11, it is clear that P4F10 and P4F15 have good confinement between the calculated and experimental values of dielectric permittivity without any correction factor. At higher frequencies the curves are almost merged in to one. It confirms the very well composite formation in the respective compositions.

Magnetic properties of PANI

Polymers are generally non-magnetic and may exhibit very low magnetic behavior. From the VSM analysis, magnetic properties of PANI such as saturation magnetization Ms, magnetic remanance Mr and coercivity Hc are found to be 0.06, 0.01 and 231.19 respectively. Very low value of Ms exhibited by PANI may be due to the unpaired electrons present in the doped PANI.

Magnetic properties of γ-Fe_2O_3 and PANI- γ-Fe_2O_3 composites

Figure 12 represents the magnetization versus field curve of γ-Fe_2O_3. Saturation magnetization of the sample is found to be 45.5emu/g, magnetic remanence is 3.52emu/g and coercivity is 71Oe. The reported values of Ms and Hc of the bulk sample of γ-Fe_2O_3 are 75emu/g and 300Oe respectively. The decrease in magnetic property compared to the bulk values may due to the decrease in the particle size to the nano regime. In the nano regime surface to volume ratio is very high and therefore surface spins to total spins increases. This will result surface anisotropy and causes deviation from the bulk properties. Presence of non-magnetic alpha phase of ferric oxide is also found in the XRD. This also cause reduction in magnetic properties.

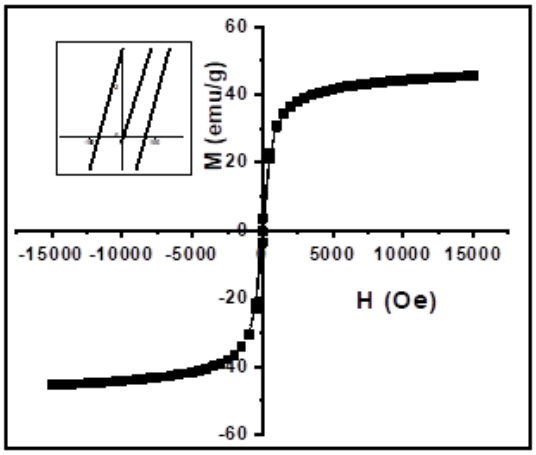

Figure 12. Magnetization versus field curve of γ-Fe_2O_3

Figure 13 represents the magnetization versus field curves of P4F5, P4F10 and P4F15 composites and the parameters Ms, Mr and Hc are tabulated in the Table 1. It is found that saturation magnetization increased with increase in ferrite content from 5 to 15g and maximum value is for P4F15. Thus it is clear that magnetic property can be tuned by varying the amount of filler in the matrix.

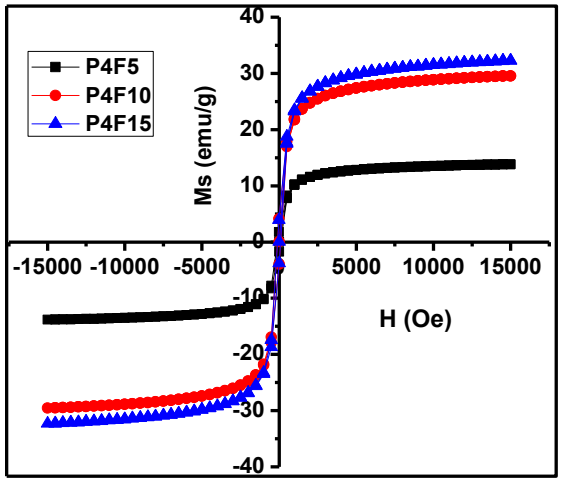

Figure 13. Magnetization versus field curve of PANI- γ-Fe_2O_3 composites

Table 1. Magnetic properties of PANI- γ-Fe_2O_3 composites

Sample	Ms (emu/g)	Mr (emu/g)	Hc (Oe)
P4F5	13.82	1.76	95
P4F10	29.56	4.04	96
P4F15	32.29	3.86	91

Comparison of theoretically expected Ms with the experimental Ms of PANI- γ-Fe_2O_3 composites

Magnetic properties of the composite depend on the amount of magnetic ferrite filler in that composite. Equation 3 can be used to calculate the expected Ms values of the composites with the variation of composition.

$$Ms = W_1M_1 + W_2M_2 \quad \text{.....} \quad \mathbf{3}$$

where Ms is the saturation magnetization of the composite, W_1 and W_2 are the weight fractions and M_1 and M_2 are the saturation magnetizations of the ferrite and polymer respectively. Since the polymer used for the composite preparation is non-magnetic, the modified equation 4, can be used to evaluate the Ms of the composites.

$$Ms = W_1M_1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{4}$$

Calculated Ms obtained as per the equation 4 and the experimental values of the PANI- γ-Fe_2O_3 composites are plotted in the Figure 14. Experimental values are very low as compared to the calculated values. This decrease may due to the effect of non-magnetic PANI, coated over ferrite particles, in the presence of magnetization field. Considering the negative effect of PANI during the magnetization of ferrite in the composite, equation 4 can be modified as equation 5 by including a correction factor 'k'.

$$Ms = W_1M_1\text{-}k \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{5}$$

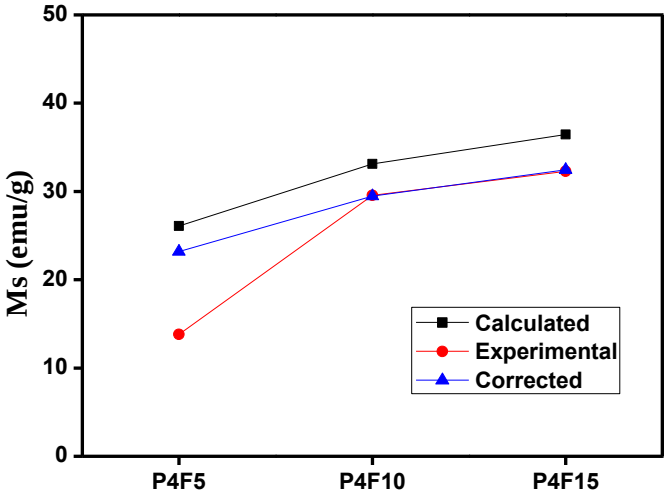

Figure 14. Experimental, calculated and corrected Ms values of PANI-γ-Fe_2O_3 composites

It is found that k factor of 11% of the theoretical value makes fitting of the experimental curve to the theoretical curve in the case of P4F10 and P4F15 as given in figure 14. Thus we can say that about 89% of magnetic property of the filler could be retained in the PANI-gamma ferric oxide composites of P4F10 and P4F15 even in non-magnetic PANI matrix. For the sample P4F5, appreciable variation is observed in the Ms value and may due to the formation of bare PANI or oligomer as the PANI-ferrite weight ratio is the highest in this composite. This will change the actual weight fractions of the components in the composite.

Conclusions

Organic-inorganic polymer composites show promise for the production of various materials and can replace metals and semiconductors. In this work a natural resource Tamarind fruit extract is used in place of

conventional solvents HCl, H_2SO_4 etc, for the synthesis of polyaniline- γ-Fe_2O_3 composites. Samples were in the nano dimension and showed better thermal stability, dielectric and magnetic properties. It is also found that dielectric permittivity depends on the filler and monomer content and ultimately it depends on the effective composite formation. For 0.4M aniline better property is observed for composite with 10g ferrite. Thus, it can conclude that tamarind extract is an effective green medium for the synthesis of polyaniline nano composite having desired electric and magnetic properties.

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