Dielectric Property and Conductivity Study of Polyaniline – CaF₂ Nanocomposites

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Abstract: Polyaniline – CaF_2 nanocomposite samples were synthesized by a combination of precipitation synthesis of CaF_2 nanocrystals and in – situ polymerization of aniline. Structural characteristics were investigated by XRD and FTIR spectroscopy. Optical properties were measured by UV – Visible spectroscopy. Conduction studies were done by using four – probe method. Dielectric measurements were done in the frequency range of 100 Hz – 1000 KHz at room temperature. XRD results show that the samples are crystalline in nature. It indicates the formation of cubic phase of CaF_2. The crystallite size of composite samples decrease with increase in the concentration of CaF_2 nanocrystals. FTIR spectroscopy shows the presence of different functional groups. UV – Visible spectrum of the samples show a strong absorption edge at 331 nm and 664 nm and a decrease in band gap with increase in precursor concentration. Electrical conductivity study shows decrease in the conductivity of the samples with an increase in the concentration of CaF_2. Dielectric measurements show that dielectric constant decreases with increase in the frequency. The highest value of dielectric constant at 100 Hz is 71415.18 and 25577.14 in the case of pure Polyaniline and Polyaniline – CaF_2 (20 wt %) respectively.

Keywords: Nanocomposite, Nanocrystal, Precipitation, Polymerization, Electrical conductivity, Dielectric constant, Band gap, Crystallite size.

1 Introduction

Conducting polymers offer the promise of achieving a new generation of nanocomposites which exhibit good optical and electrical properties. The features of conducting polymers such as reversibility, availability in film form and good environmental stability enhance their potential use for many practical applications. Among the family of conducting polymers, Polyaniline is one of the most promising polymer because of its unique electrical properties, easy polymerization, low cost of monomers, high environmental stability and its wide applications in microelectronic devices, light weight batteries, sensors, super capacitors, microwave absorption and corrosion inhibition [1,2].

Conducting polymer nanocomposites with inorganic nanoparticles have attracted significant interest because possible interactions between the inorganic nanoparticles and the polymer matrices may generate some unique physical properties upon the formation of various micro/nano composite [3].

CaF_2 is an alkali halide with a wide band gap of 12 eV exhibiting luminescence properties [4]. CaF_2 is a well-known host for luminescent ions due to its high transparency in a broad wavelength range, low refractive index and low phonon energy [5]. In this work, pure Polyaniline and its nanocomposites with CaF_2 were synthesized by in situ oxidative polymerization of aniline monomer with ammonium peroxydisulphate (APS). Appropriate addition of CaF_2 nanocrystals to the polymer matrix gives rise to new physical properties and novel behaviour of the original polymer matrix.

2 Experimental

2.1. Materials and Methods

AR grade of Calcium Chloride ($CaCl_2$), Ammonium Fluoride (NH_4F), Ethanol, Aniline, Ammonium Peroxydisulphate ((NH_4)$_2$$S_2$$O_8$), Hydrochloric acid (HCl) and Acetone were used for synthesis. CaF_2 was prepared by precipitation method.

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Polyaniline and its composite materials were prepared by chemical oxidative method. All aqueous solutions were prepared using distilled water.

The powder X-ray diffraction (XRD) patterns were recorded on a X'Pert Pro PANalytical powder diffractometer with Cu-Kα radiation source (λ = 1.54 Å) operated at 40 kV and 40 mA in the 2Θ range 20 - 80º at the scan speed of 0.05º per second. Fourier transform infrared spectra were recorded with a SHIMADZU FTIR – 8400S spectrometer over the wave number range of 4000 – 400 cm^{-1}. The spectra of CaF_2, pure Polyaniline and POLYANILINE – CaF_2 nanocomposites were taken using KBr disks. UV – Vis spectra were recorded on a SHIMADZU 2450 UV – Visible spectrophotometer in the range 200 – 800 nm. The electrical conductivity of POLYANILINE and POLYANILINE–CaF_2 nanocomposites were studied using a four probe set up in the temperature range of 30 – 300º C. Dielectric measurements were carried out using Hewlett Packard 4284 A (20 Hz – 1 MHz) Precision LCR meter.

2.2. Synthesis of CaF_2 nanocrystals

Stoichiometric quantities of $CaCl_2$ and NH_4F were dissolved in 100 mL of distilled water in a 250 mL conical flask. The mixture was stirred for 3 h constantly to achieve homogeneity. During stirring, the transparent reaction mixture transforms into opaque white suspension gradually. After stirring, the solution was centrifuged for 20 min at 3000 rpm and a white residue was obtained. The residue was washed thoroughly with ethanol to remove the residual chloride and ammonium ions. The product was extracted on to a Petri dish and dried slowly in an oven maintained at 100 °C. The final product was in the form of white powder.

2.3. Synthesis of Polyaniline and Polyaniline – CaF_2 nanocomposites

For the synthesis of Polyaniline using chemical oxidative polymerization technique, 0.1 M aniline was dissolved in 1 M HCl to form aniline hydrochloride. Calcium Fluoride nanocrystals were added in the weight percent of 5, 10 and 20 to the above solution with vigorous stirring in order to keep the calcium fluoride suspended in the solution. Ammonium Peroxydisulphate (($NH_4)_2S_2O_8$) solution of 0.1 M was gradually added as an oxidant to the reaction mixture with continuous stirring for 3 hours at room temperature. Gradually the transparent mixture turns into black green color, which represents the formation of precipitates. The precipitates were recovered, vacuum filtered and washed with acetone as well as distilled water till the filtrate became colorless. Finally the resultant precipitates were dried in an oven for 24 hours.

3 Results

3.1. XRD Analysis

XRD analysis was used to examine the structure of Polyaniline and Polyaniline – CaF_2 nanocomposites and investigate the effect of different concentrations of CaF_2 nanocrystals on the structure of Polyaniline.

Figure 1 shows XRD pattern of pure CaF_2 nanocrystals prepared by precipitation method. Features of this pattern indicate the presence of a cubic phase for CaF_2 nanocrystals which is a typical structure for fluorides with fm3m spatial groups. Average lattice constant was 5.47222 Å calculated from 2θ values, which is in agreement with the recorded data of 5.4629 Å from JCPDS Card no. 75 – 0363. The sharp diffraction peaks confirm the high crystallinity of the synthesized CaF_2 nanocrystals. The average crystallite size was calculated from Debye – Scherer formula and found to be 53 nm.

Figure 2 shows the XRD pattern of Polyaniline and its composite. Broad diffraction peaks occur between 10˚ and 30˚ due to the parallel and perpendicular periodicity of the Polyaniline (polymer) chain. Two broad peaks of Polyaniline at 2Θ values of 19.78˚ and 25.27˚ were recorded with corresponding d – spacing of 4.4839 Å and 3.5212 Å respectively. XRD patterns show low crystallinity of the conducting polymers due to the repetition of benzenoid and quinoid rings in Polyaniline chains [6]. The crystallite size was found to be 34.1 nm. Two small peaks observed at 43.60˚ and 50.88˚ are corresponding to CaF_2 phases on comparison with CaF_2 JCPDS file. These peaks in the composite spectra confirm the presence of CaF_2 dispersed in Polyaniline composite. The crystallite size of the composite samples decreases with increasing the concentration of CaF_2.
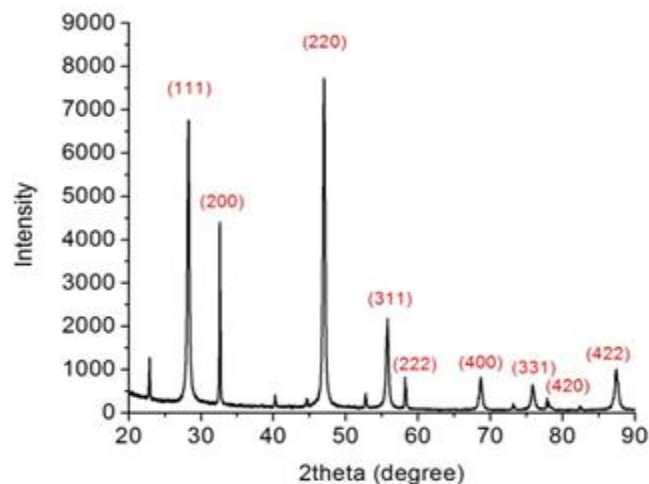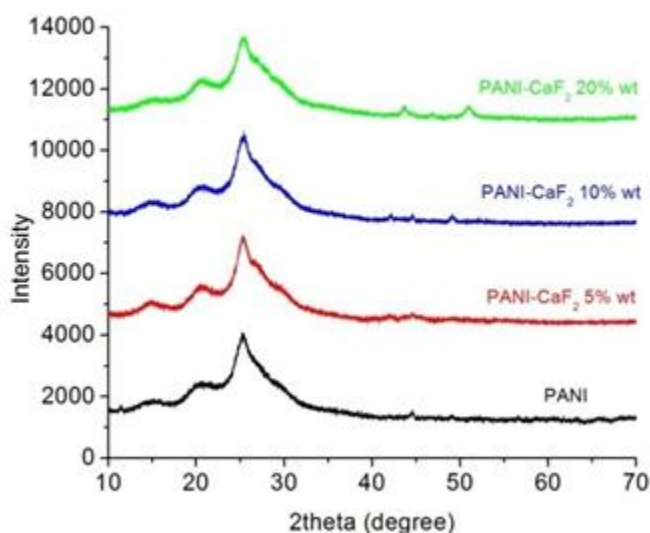
Figure 1: XRD patterns of CaF_2

Figure 2: XRD patterns of Polyaniline and Polyaniline-CaF_2 nanocrystals

3.2. FTIR Spectroscopy

Polyaniline and Polyaniline – CaF_2 samples were studied by FTIR spectroscopy. The spectra show the presence of different functional groups and bonds. Figures 3 and 4 shows the FTIR spectra of CaF_2 nanocrystals and Polyaniline – CaF_2 nanocomposites respectively.

In the FTIR spectra of CaF_2 shown in figure 3, the peaks observed at 3038.82, 1760.99 and 1641.04 cm^{-1} are the characteristic peaks of H – O – H bonding of the H2O molecules which shows the presence of hydroxyl groups. The peak observed at 2829.32 cm^{-1} is due to KBr pellets used for recording of FTIR spectrum. Peaks at 1401.15 cm^{-1} and 3147.57 cm^{-1} correspond to N – O and O – H bonds respectively. Peaks observed at 670.91 and 652.53 cm^{-1} correspond to out of plane bend of hydroxyl group [10].

In figure 4, the characteristic absorption peak observed at 3740 cm^{-1} is attributed to vibration of – OH. The 2878 cm^{-1} peak is for the symmetric stretch vibration band of methylene and methyl group while the 1769 cm^{-1} peak corresponds to H – O – H bonding of the H_2O molecules which shows the presence of hydroxyl groups. The peak at 1586 cm^{-1} is attributed to C=N stretching vibrations of quinone ring. The 1486 cm^{-1} peak is for C=C stretching vibrations of benzene ring. The peak at 1306 cm^{-1} corresponds to C – N stretching of benzenoid ring. The 1126 cm^{-1} peak is for sulfate ions. The peaks at 811 cm^{-1}, 667 cm^{-1} and 505 cm^{-1} are attributed to the out of plane bending of C – H [11].
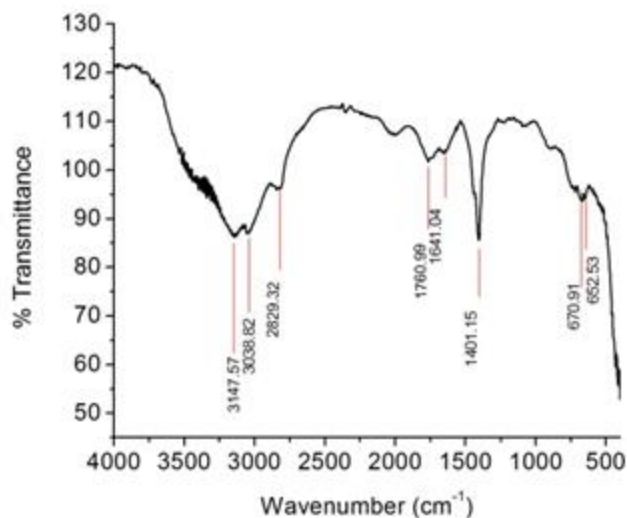
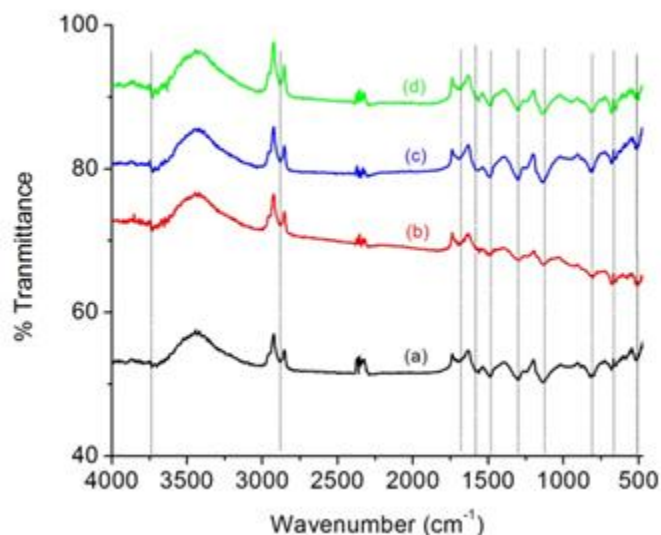**Figure 3:** FTIR spectra of CaF_2 nanocrystals.

Figure 4: FTIR spectra of Polyaniline and Polyaniline-CaF_2 nanocomposites

3.3. UV – Visible Analysis

UV – Visible spectroscopy was carried out to investigate optical properties of the synthesized samples. Figures 5, 6 and 7 show the UV – Visible spectrum for CaF_2 nanocrystals, Polyaniline and Polyaniline – CaF_2 nanocomposites respectively.

The absorption spectra show that characteristic absorption peaks are present in the UV region. Figure 5 shows a prominent absorption band with a peak at 264 nm and a weak one at 205 nm.

As shown in the figure 6, the two absorption peaks at 331 nm and 641 nm are attributed to the transition of electron from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) which is related to $\pi \rightarrow \pi^*$ electron transition of the benzenoid ring and $n \rightarrow \pi^*$ transition of benzenoid to quinoid respectively [7]. The shapes of UV – Vis spectra of composite are similar to those of Polyaniline. A small shift in the bands is observed as shown in the figure 7. There is a decrease in intensity of the peak around 331 – 334 nm due to the interaction between CaF_2 NCs and Polyaniline molecules.

The energy band gap Eg was obtained from the optical absorption spectra by extrapolating the straight line plot of $(\alpha h\nu)^2$ versus $(h\nu)$ to the energy axis by the method proposed by Wood and Tauc [8]. Figures 8, 9 and 10 show the Tauc's plot of CaF_2 nanocrystals, Polyaniline and Polyaniline – CaF_2 composite respectively.
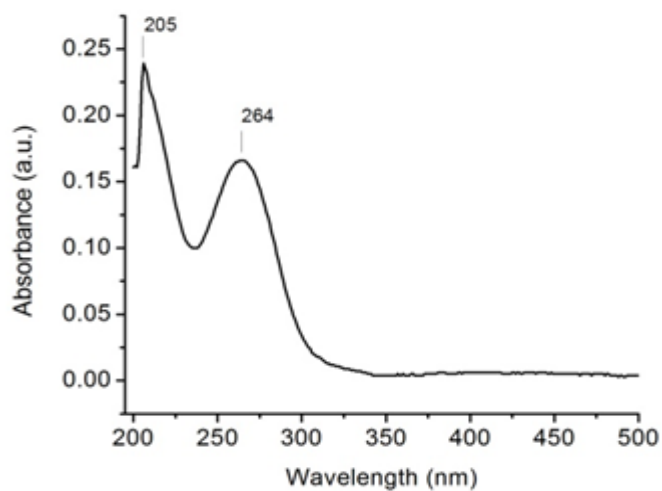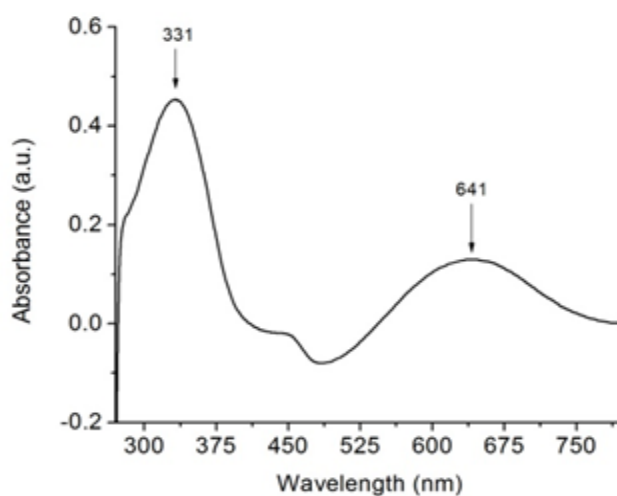
Figure 5: UV – Vis spectra of CaF_2 nanocrystals
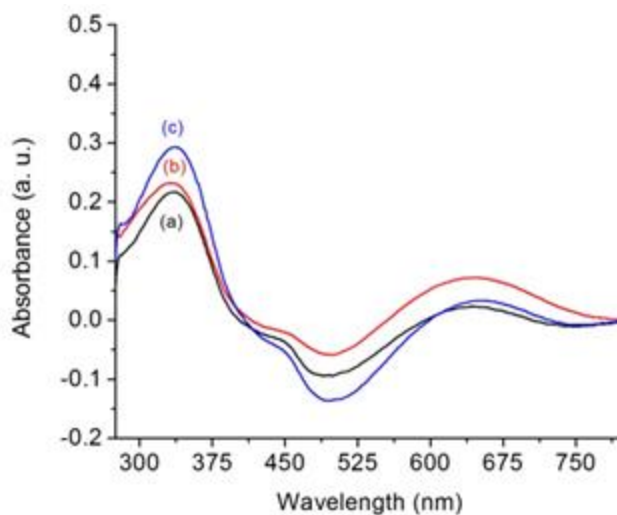

Figure 6: UV – Vis spectra of Polyaniline.

Figure 7: UV – Vis spectra of Polyaniline – CaF_2 composites (a) 5%wt CaF_2, (b) 10%wt CaF_2 (c) 20%wt CaF_2
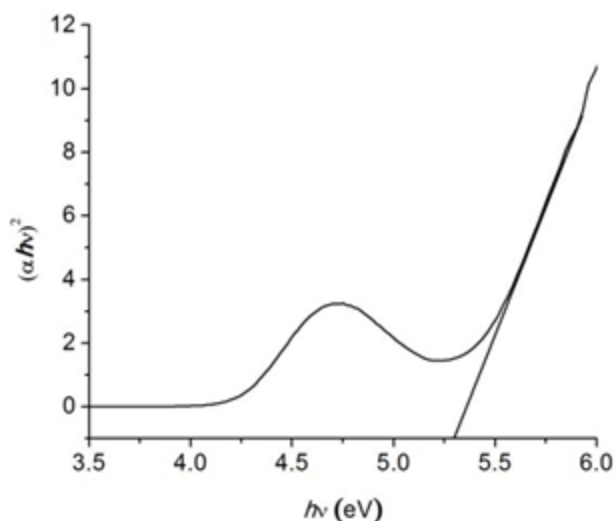
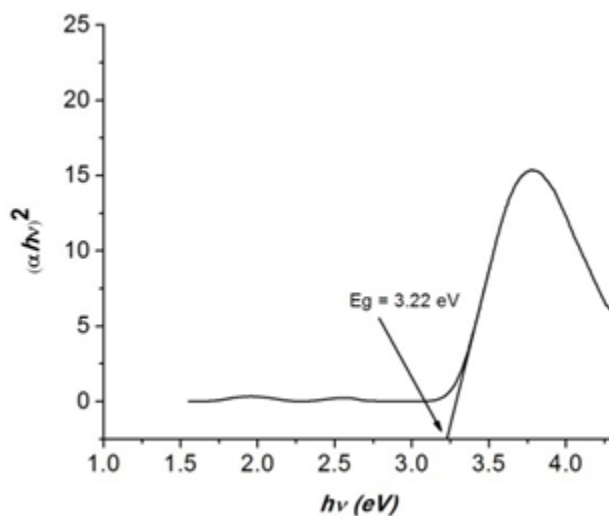**Figure 8:** Energy band gap of CaF$_2$ nanocrystals

Figure 9: Energy band gap of Polyaniline.

The refractive index of the synthesized samples was calculated using the following relation between Refractive index (η) and Energy band gap (Eg) [9].

$$\eta = K \, (Eg)^C$$

Where, K = 3.3668 and C = − 0.32234 are constant.

Table 1: Energy band gap and refractive index of CaF$_2$, Polyaniline and Polyaniline – CaF$_2$ composite

Material	Energy band gap (eV)	Refractive index (η)
CaF$_2$	5.29	1.96
Pure Polyaniline	3.22	2.30
Polyaniline – CaF$_2$ (5 %wt)	3.16	2.32
Polyaniline – CaF$_2$ (10 %wt)	3.13	2.33
Polyaniline – CaF$_2$ (20 %wt)	3.10	2.33

Table 1 shows the calculated energy band gap and refractive index of CaF$_2$, Polyaniline and Polyaniline – CaF$_2$ composite. There is a slight decrease in the band gap of the nanocomposites samples with increase in the concentration of CaF$_2$.
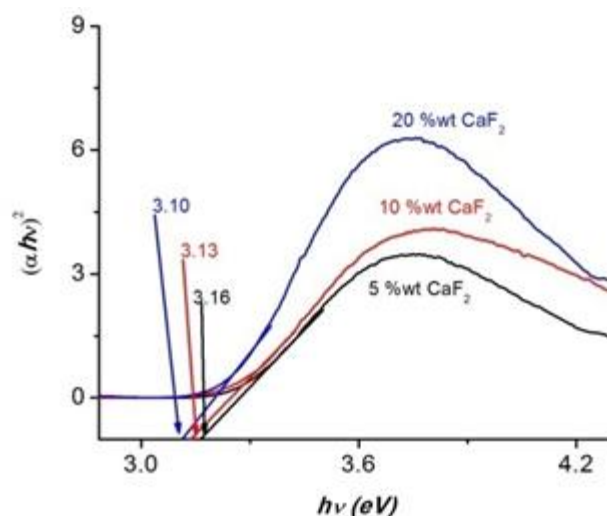
Figure 10: Energy band gap of Polyaniline – CaF$_2$ composite for 5%wt CaF$_2$, 10%wt CaF$_2$ and 20%wt CaF$_2$

3.4 Electrical Conductivity

Electrical conductivities of Polyaniline and Polyaniline – CaF$_2$ nanocomposites are given in the table 2. Generally, the electric conductivity of Polyaniline ranges between 10^{-10} and 10^3 Siemens/cm based on the acid dopant and fillers [12].

Table 2: Electrical conductivity of Polyaniline and Polyaniline – CaF$_2$ composite at room temperature.

Composition	Electrical conductivity (S cm^{-1})
Pure Polyaniline	0.0144
Polyaniline – CaF$_2$ (5 %wt)	0.0139
Polyaniline – CaF$_2$ (10 %wt)	0.0103
Polyaniline – CaF$_2$ (20 %wt)	0.0068

Results given in the table 2 show that electrical conductivity of the nanocomposites decrease with increase in the content of CaF$_2$. This is attributed to adsorption of –NH of Polyaniline on the surface of CaF$_2$ nanocrystals and bond formation in the structure. In Polyaniline, polarons and bipolarons are produced due to doping of protonic acid. The conductivity of the polymer depends on the nature of dopant and the concentration of inorganic materials, which have an important role in conductivity of the composite [13]. The electric conductivity of Polyaniline was found to be 0.0144 S/cm, which reduces to 0.0139, 0.0103 and 0.0068 S/cm with addition of 5 %, 10 % and 20 % CaF$_2$ respectively.

3.5. Dielectric Measurement

Figures 11 and 12 show the variation of Dielectric constant (ε) as a function of frequency for the samples at room temperature (RT) in the frequency range of 100 Hz to 1000 KHz.

The maximum value of dielectric constant is for pure aniline followed by the composite samples. With increase in the concentration of CaF$_2$, the dielectric constant further decreases. Higher values of dielectric constant are obtained in the low frequency range. Debye type relaxation mechanism may be responsible for higher value of dielectric constant at low frequency [14].

Table 3: Highest Dielectric constant of the material with frequency.

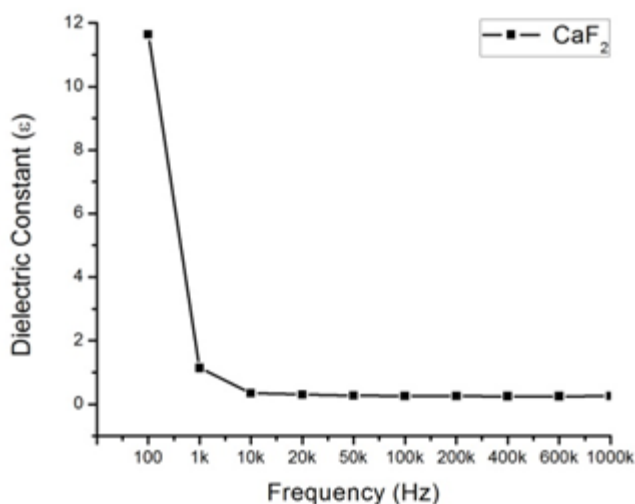| Material	Highest Dielectric Constant at 100 Hz
CaF$_2$	11.63
Pure Polyaniline	71415.18
Polyaniline – CaF$_2$ (5 %wt)	1404.08
Polyaniline – CaF$_2$ (10 %wt)	575.31
Polyaniline – CaF$_2$ (20 %wt)	25577.14

Figure 11: Variation of Dielectric constant (ε) as a function of frequency for CaF_2 nanocrystals at RT.
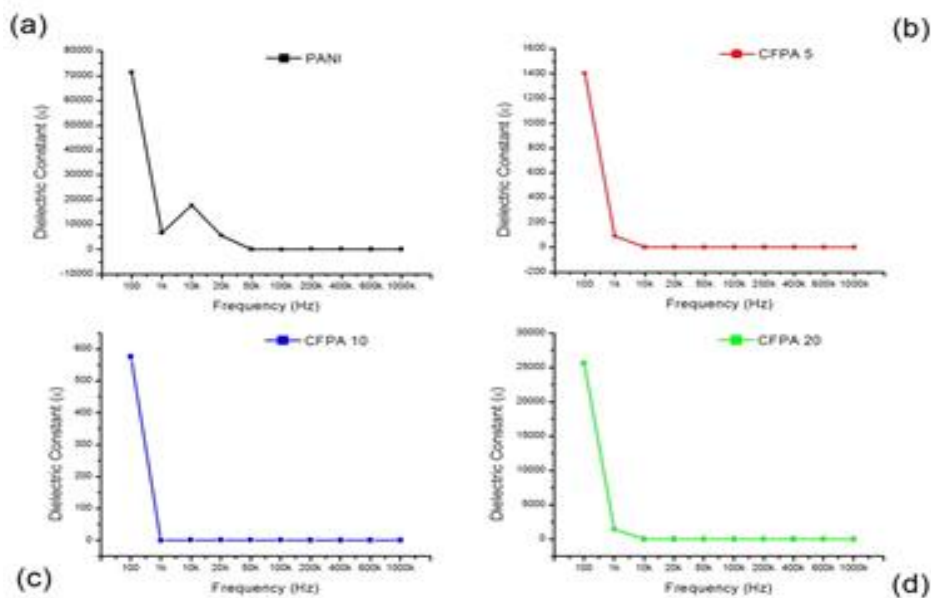

Figure 12: Variation of (ε) as a function of frequency of (a) Polyaniline and (b) 5 wt%, (C) 10 wt% (d) 20 wt% Polyaniline – CaF_2 composite at room temperature.

Table 3 shows the dielectric constant for CaF_2, Polyaniline and Polyaniline – CaF_2 composite. These are the highest values of dielectric constant, which were obtained at 100 Hz.

4 Conclusion

Polyaniline – CaF_2 nanocomposites were prepared successfully by in-situ chemical oxidative polymerization method. Polyaniline – CaF_2 nanocomposites show polaronic bands as observed from UV – Visible spectra. This also reveals the well incorporation of the nano sized CaF_2 in the Polyaniline matrix. The electric conductivity was found to be decreases with increasing in the concentration of CaF_2. Dielectric constants of synthesized nanocomposites samples decreases with the increase in the concentration of CaF_2.

Acknowledgements

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