In-Situ Chemical Synthesis and Electrical Properties of PANI/TiO_2 Composites

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Abstract - *Present work reports on the development of PANI/TiO_2 composites with varying TiO_2 content by in-situ polymerization technique. The structure of the PANI-TiO_2 composites was confirmed by X-ray diffraction (XRD) technique. The DC conductivity of all the composites was investigated over the temperature range of room temperature to 200°C. The AC conductivity is frequency dependent and enhances with rise in frequency in all the composites. The dielectric constant was found to increase with the increase in TiO_2 concentration and was found to highest for composite with 45% TiO_2.*

Key Words: Polyaniline (PANI), PANI-TiO_2, X-ray diffraction, DC and AC conductivity & Dielectric constant.

1. INTRODUCTION

The conducting polymers have emerged as a new class of materials because of their unique electrical, optical and chemical properties. These properties may lead to a variety of practical applications such as information storage and optical signal processing, substitutes for batteries and materials for solar energy conversion. PANI is one of the mostly studied conducting polymer because of its ease of polymerization, environmental stability and electrical conductivity [1].

In fast few years the electronic industry is working towards development of polymer composites with high dielectric constants. In order to reduce the electromagnetic interference and to secure high speed signals these electronically conducting polymers are being considered. It is well known that polyaniline (PANI) is one of the most attractive polymers owing to its good electrical conductivity, high environmental stability and most important its low cost. In particular, the partially oxidized state of polyaniline known as emeraldine is most attractive due to its tunable states. However the main drawbacks of polyaniline are related to the processing in its doped form in organic solvents and poor mechanical properties [2].It can be synthesized by various routes like in-situ polymerization [3], dispersion [4], emulsion [5] and enzymatic polymerization [6]. The properties of polyaniline can be modified by the addition of various inorganic fillers. The inclusion of fillers can improve the properties like dielectric and electrical properties of the polyaniline material. The filler material like titanium dioxide (TiO_2) is well known for its outstanding combination of properties which includes biomedical, mechanical and chemical properties. TiO_2 due to its semiconducting properties has proved that it is outstanding photocatalyst owing to its very high photocatalytic activity. Due to its good photocatalytic activity under UV irradiation it is generally used in treatment of air and water pollutants. In addition to this latest application is its use in tribological applications due to its wear resistance and low friction properties [7, 8].

There have been many attempts to synthesize polyaniline/TiO_2 composites by various routes which include sol-gel spin coating [9], chemical oxidation [10] and in-situ polymerization. Mo et al [11] studied the dielectric properties of polyaniline/TiO_2 nanocomposites synthesized by in-situ polymerization technique with varying TiO_2 content. In their work Dey et al [12] studied the dielectric properties of PANI-TiO_2 composites prepared from TiO_2 colloidal sol. The inclusion of TiO_2 particles improved the dielectric constant of composites about 10 times that of pure PANI. The dielectric constant was found to be independent of frequency and decreased significantly with the increase in PANI content. Pawar et al [9] developed the titanium dioxide/polyaniline composites by sol-gel spin coating method in which the TiO_2 was synthesized by sol-gel technique and polyaniline by chemical oxidative polymerization. The electron microscopy studies of thin films of composites showed uniform dispersion of TiO_2 in PANI matrix. The room temperature resistivity of composites was found to be much lower than that of pure nanosized TiO_2 particles.

In this paper we report the synthesis of polyaniline and polyaniline/TiO_2 composites prepared by in-situ polymerization technique with varying TiO_2 content. The developed composites were characterized using X-ray diffraction. The AC conductivity, DC conductivity and dielectric constant of composites with varying TiO_2 concentration were also studied.

2. EXPERIMENTATION

2.1. SYNTHESIS OF PURE POLYANILINE (PANI)

Polyaniline was prepared by using extra pure and AR grade reagents aniline (99.9%), ammonium persulphate (99.9%), and hydrochloric acid (99.9%) using in-situ polymerization method. Ammonium persulphate (0.2 M) was added drop wise to a stirred solution to avoid warming of the aniline (0.1 M) solution dissolved in 1 M of an aqueous solution of hydrochloric acid (1 N, aniline hydrochloride) at a temperature around 5°C. Along with this addition, stirring was continued for 2 hours using a magnetic stirrer to affirm completion of the reaction. At the time of early pigmentation of mixing, the reactants depend on the attentiveness of protic acid and temperature. Throughout the polymerization reaction, HCl was used as a protic acid and the temperature was asserted at about 0^0 C (low) by using a freezing mixture. The end prepared product was a green-colored precipitate (emarldine salt). This precipitate was filtered by using Buckner funnel along with vacuum pump. Further, it is cleaned with acetone and demineralized water in order to remove the oligomers and excess ammonium persulphate and then with 1 N HCl solution to remove the Cl^- ions and unreacted aniline until clear filtrate. At last, the precipitate was dehydrated in burning air furnace for 24 hours at room temperature to attain a constant mass.

2.2. SYNTHESIS OF POLYANILINE/TiO_2 COMPOSITE

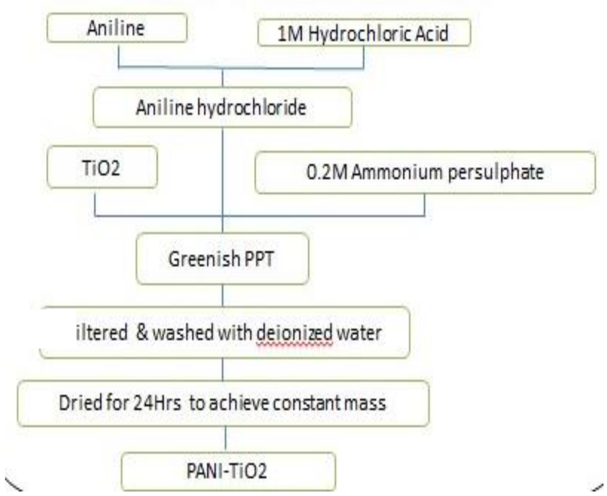

Figure-1: Flowchart designed for the synthesis of composite polyaniline

Synthesis of the PANI–TiO_2 composites was carried out by in-situ polymerization. Aniline (0.2 mole) was dissolved in 1 M HCl and stirred for 2 hours to form aniline hydrochloride. TiO_2 was added in the mass fraction to the above solution with vigorous stirring in order to keep the TiO_2 homogeneously suspended in the solution. To this mixture, 0.2 M of ammonium persulphate, which acts as an oxidant was slowly added drop-wise with continuous stirring at room temperature for 8 hours to completely polymerize the monomer aniline. The precipitate was filtered, washed with demonized water, and finally dried in an oven for 24 hours to achieve a constant mass. In this way, PANI–TiO_2 composites containing various mass fractions of TiO_2 (5%, 15%, 25%, 35% and 45%) in PANI were synthesized.

3. Characterization

The X-ray diffraction (XRD) patterns of the composites were taken using Philips XPERT diffractometer with Cu Kα radiation (λ = 1.54 A°). DC conductivity (Keithley 6514 electrometer) of the PANI and PANI- TiO_2 composites was measured by standard four probe method for temperature range of 20°C - 200°C varying at 20°C. The AC conductivity of the PANI and PANI- TiO_2 composites was studied in the frequency range of 0.2 to 10 MHz using LCR-Q meter (Wayne Kerr, 4300) analyzer.

4. RESULTS AND DISCUSSION

4.1. X-Ray Diffraction (XRD) Analysis

The X-ray diffraction shape of the pure polyaniline is depicted in the figure 2(a). The broad peak is observed at 2θ = 25.63^0, which clearly indicates complete amorphous nature which stimulates high mobility of the ions within the substance.

The X-ray diffraction configurations of PANI/TiO_2 composites with different TiO_2 content are depicted in figure 2(b-f). All the patterns corresponding to composite with varying TiO_2 content from 5% to 45% displayed crystalline behaviour. The crystallinity of synthesized mixtures can be affirmed from distinct and sharp peaks. Many distinct peaks corresponding to TiO_2 particles were observed in all the patterns taken on different composites. These intense peaks seen at 2θ = 25.2°, 38.2°, 48° and 55.1° to (1 1 0), (1 0 1), (1 1 1), (2 1 1) planes which highlights the existence of TiO_2 in PANI which corresponds to anatase form of TiO_2 [13]. The inclusion of TiO_2 particles in the PANI will strongly affect its crystalline behaviour by restricting the crystallization or promote crystalline behaviour with the increase in the TiO_2 content. Overall when we observe the patterns they exhibit sharp and strong peaks for TiO_2 for all composites with varying TiO_2 content indicating crystallinity. Similar observations were reported by Deivanayaki et al [14] in their work on polyaniline-TiO_2 nanocomposite.

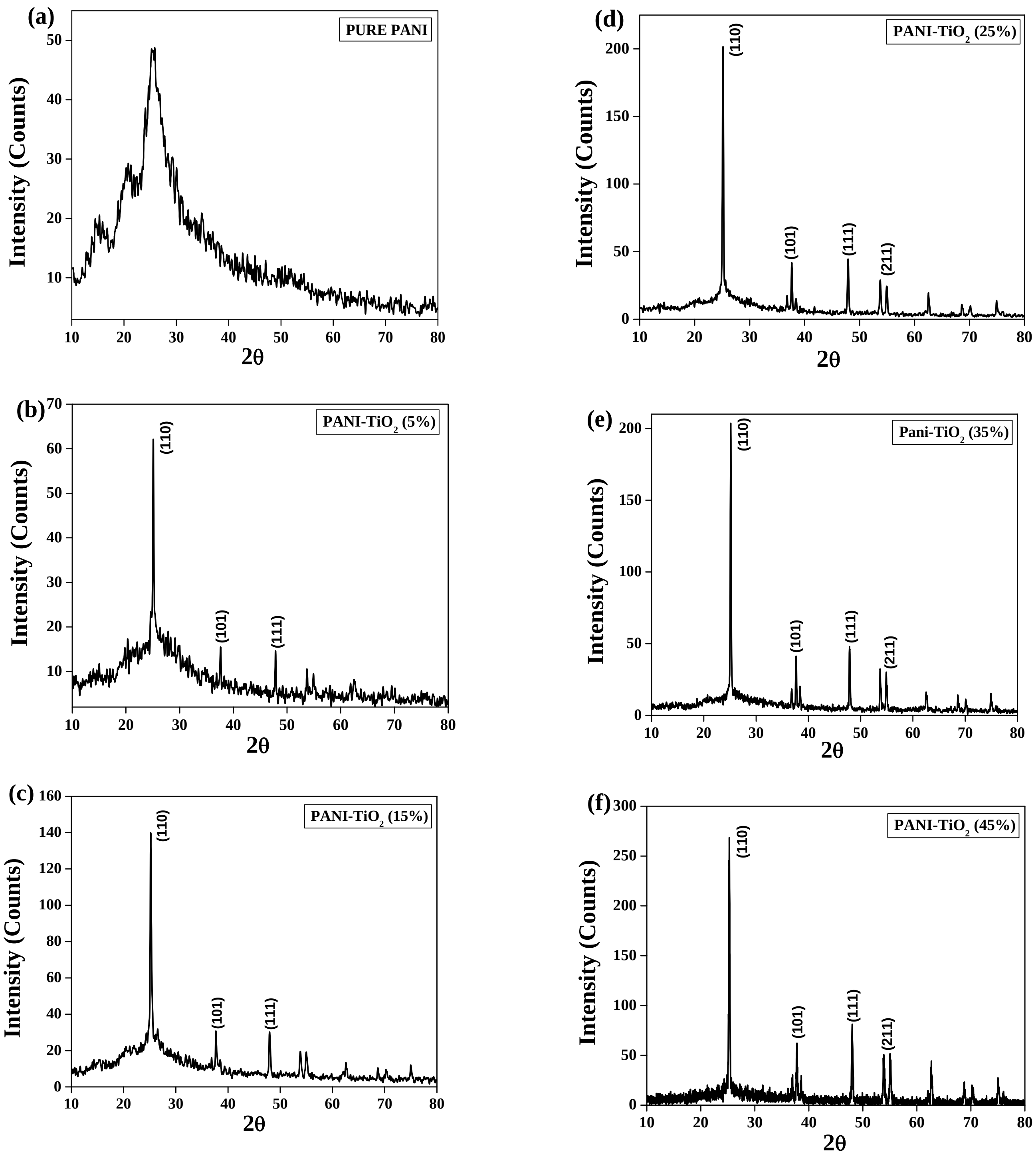

Figure-2: XRD configuration of (a) PANI, (b) PANI/ TiO_2 (5%), (c) PANI/ TiO_2 (15%), (d) PANI/ TiO_2 (25%), (e) PANI/TiO_2 (35%), (f) PANI/ TiO_2 (45%).

4.2. DC Conductivity Studies

The DC conductivity of PANI along with every single compound with changing TiO_2 content evaluated applying four probe method over a temperature from normal temperature to 200°C is shown in figure 3. The conductivity tends to decrease with the increase in temperature from room temperature to 120°C for all the composites. Above temperature of 120°C the conductivity for all composites tends to increase up to final temperature of 200°C. With the rise in temperature the efficiency of charge relocation between the TiO_2 particles and PANI also increase. So this is why we are observing high conductivity at higher temperatures. Further it is detected that the conductivity of complex with 45% TiO_2 content was highest when equated to other complexes for all the temperatures. The increase in TiO_2 content the conductivity is found to increase for all temperature values. The increase in conductivity with the rise in temperature particularly above 120°C in the current work displays the behaviour similar to that of semiconductors. Similar observations were reported by Su et al [15] in their work on polyaniline–titanium dioxide nanocomposites.

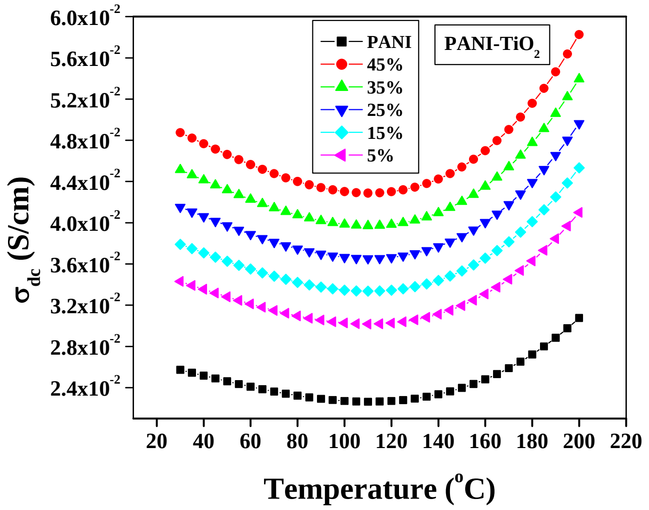

Figure-3: DC conductivity of PANI and PANI/TiO2 composites as a function of temperatures.

4.3. AC Conductivity Studies

Figure 4 depicts the fluctuation of AC conductivity with change in frequency for PANI and PANI/ TiO_2 (different wt%) composites. As shown in the figure, it is evident that the AC conductivity is frequency dependent and enhances with rise in frequency. This frequency related behavior can be clarified through Maxwell-Wagner double layer model [16]. The increase of AC conductivity through frequency is referable to the existence of numerous kinds of inhomogeneity present in the materials. All the combinations exhibit high AC conductivity than PANI. Imene et al [17] suggested that rise in conductivity of compound when equated with pure PANI is due to the information that, greater quantity of aniline have been inserted by solid–solid reaction inside the TiO_2 and hence, polymerized in the TiO_2 inner layer with a prolonged chain conformation which effects for the reducing of p defects and the polymer bridges and therefore the enhancement of the conductivity of the compounds. The inclusion of TiO_2 could promote the establishment of a more effective network for charge transportation in the base polyaniline matrix which leads to rise in conductivities [18-20].

The conductivity is analyzed from valuated real and imaginary divisions of the complex dielectric permittivity ($\varepsilon = \varepsilon' - i\varepsilon''$) using the following relation,

$$\sigma = \sigma' - i\sigma'' = 2i\pi f\varepsilon_o(\varepsilon - 1)$$

Where f is the measuring frequency, i= $\sqrt{-1}$ and ε_o is the permittivity of free space/vacuum.

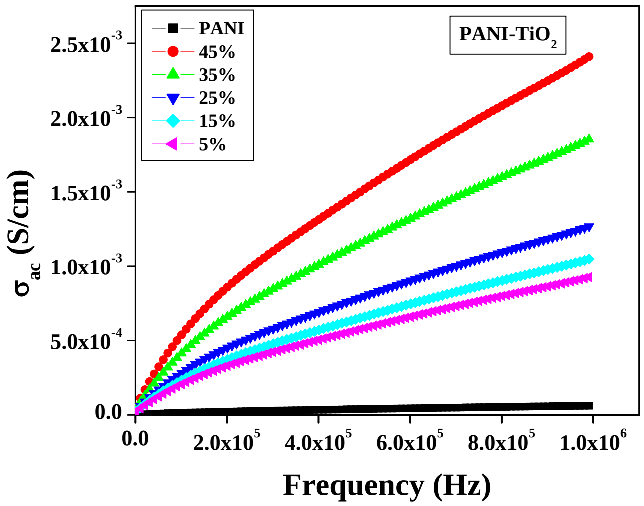

Figure-4: AC conductivity of PANI and PANI/TiO2 composites at different frequency.

4.4. Dielectric Constant

Dependence of dielectric constant with varying frequency ranging from 1MHz–6MHz at room temperature for PANI and PANI- TiO_2 compounds is designed in figure 5. It was observed that dielectric constant is high at low frequency and reduces suddenly as frequency rises and almost becomes constants at high frequencies showing the usual diffusion. This can be attributed to Debye-like relaxation mechanism. The structure reveals firm interfacial polarization at low frequency [21, 22].

The growing dielectric constant with falling frequency is owed to the conductivity which is directly connected to the increase in movement of localized charge carriers since dipole can react quickly to field and dipole polarization at its maximum value and hence highest dielectric constant. This might be referable to space charge polarization. At high frequencies, electric dipoles are not capable to go along with the alternating supplied electric field i.e, electric field cannot stimulate the dipole moment, so dielectric constant value attains minimum [23].

Very high measures of dielectric constant at the lesser frequencies when compared to that of higher frequencies might be rightful to the existence of all types of polarization such as atomic, electrode, dipolar, interfacial, ionic and electronic polarizations. So, these results are in effective understanding with the literature [24, 25].

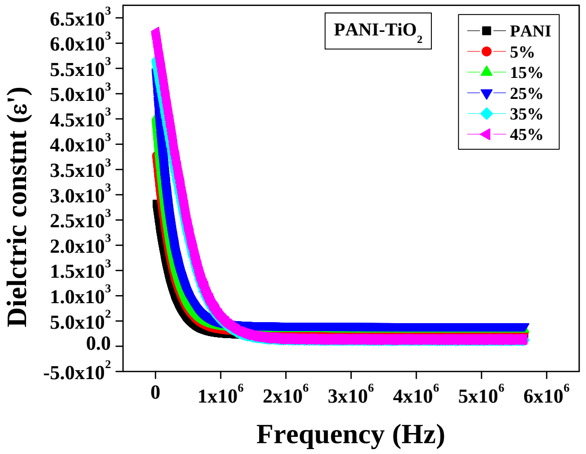

Figure-5: Dielectric Constant of PANI and PANI/TiO_2 composites as a function of frequency.

CONCLUSION

In this present work PANI/TiO_2 composites with varying TiO_2 content have been successfully synthesized by in-situ polymerization technique. The composites showed higher conductivity values above temperature of 120°C due to improvement in charge transfer efficiency at higher temperatures. Out of all, the composite with highest TiO_2 content of 45% was found to possess highest DC conductivity at higher temperatures. Increase in AC conductivity observed with the increase in frequency for PANI and PANI- TiO_2 composite. The increased Dielectric constant with increase in TiO_2 content is attributed to the formation of a better charge transport network in the relatively insulating polyaniline matrix.

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