Synthesis and Characterization of Lanthanum Oxide Doped Polyaniline (PANI/La_2O_3)

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Abstract

Pure polyaniline (PANI)and Lanthanum oxide (La_2O_3) modified polyaniline were synthesized by using *in-situ* polymerization method.Different concentration of doping agents was selected to study the effect of rare earth elements in polymer matrix for ionizing radiation attenuation. Synthesized samples were characterized by TGA to understand the thermal stability, SEM to understand the morphology, electrical parameters were understood with DC and AC conductivity, dielectric constant and dielectric loss were also studied. As concentration of doping agent increases conductivity decreases this leads to study the dielectric properties of the samples. Dielectric constant of the samples increased as frequency increases and dielectric loss in the materials is also very minimal. The prepared samples may find applications in the electronics field industry.

Keywords: Polyaniline, Lanthanum oxide, AC conductivity, Dielectric properties, SEM.

1. INTRODUCTION

Polymer research is a rapidly growing field, with scientists and engineers exploring unique possibilities for synthesizing various materials with diverse electrical, optical, and magnetic properties. This offers a huge potential for new materials that could have tremendous applications in the future.

Polymers, which are employed in an array of new technologies, are making a mark in the scientific world. These polymers can be used for energy storage [1], molecular recognition, EMI shielding, optoelectronic devices and sensors[2].

Organic conducting polymers have become indispensable in modern times as they possess unique chemical structures and electrical conduction properties. Polyaniline is becoming one of the most sought-after conducting polymers as it offers unique conduction mechanisms, simple synthesis techniques, environmental stability and easy processability from its non-conductive base form.

Polyaniline (PANI) has drawn a great deal of research interest due to its cost-effectiveness, exceptional stability and superior electrical conductivity.AlsoPANI is relatively simple to synthesize, which is an added bonus. Polyaniline has been gaining traction amongst researchers due to its affordability, superior redox properties and stability in the environment [3]. Polyaniline and its derivatives can be synthesized using either electrochemical or chemical methods [4]. Both routes have their own set of advantages and disadvantages, depending on the end goal. Two primary approaches for the mass production of polyaniline are chemical methods. These techniques are commonly used to generate large batches of this material quickly and economically. Traditional chemical treatments involve polymerizing aniline in water with oxidants and dopants. The resultant polyaniline appears in the form of irregular granules.

Polyaniline is formed when aniline undergoes oxidative polymerization. This type of super-molecular process generates structural units, like the five-membered rings [5]. PANI synthesis entails a two-step process. Firstly, monomers undergo a chain reaction with the production of single macromolecules. At the same time, growing chains are being put together to form intricate supramolecular structures. Subsequently, a polymer containing firmly-established supramolecular structures with distinct morphologies is created [6]. The antistatic coating of PANI being utilized for conducting polymer batteries and condensers is highly stable with a set of unique properties. This can also be used as a detector material in sensors to avoid corroding chemical reaction interference.

Lanthanum Oxide, also known as La_2O_3, is an inorganic compound made up of lanthanum and oxygen. It appears as a white, odorless solid that can't be dissolved in water but can be dissolved in dilute acids. Lanthanum oxide is a p-type semiconductor and has an energy band gap of 4.3 eV, making it suitable for sensing applications[7]. It is often used as a probe ion or signal transducer due to its recognizable sensitivity and accuracy compared to other materials. The Lanthanide elements make up the biggest group in the periodic table and they have common features due to similarities in their electronic structures. The absorption and emission spectra of the extra lanthanide ions, due to their increased charge, generally appear as a very narrow line. Consequently, the lanthanides in the complex have a semi "atomic" structure, resulting in the slim bands seen in lanthanide emission andabsorption spectra (La_2O_3) having some extremely one-of-a-kind features. Microwave assistants have many practical uses, ranging from enhancing features in optical filters to purifying water, or as dielectric materials. They are suitable for a wide range of applications. In recent years, the synthesis of new Nano-based complexes with uniform size, top-grade purity and homogeneity has gained immense interest from scientists. Currently, a variety of methods are available to create nanoparticles. These processes have a beneficial effect on the morphology of particles during the chemical conversion process or metabolic reaction leading to the final oxide [8].

2. Experimental

2.1. Materials and Instrumentation

High pure chemicals like Aniline, Ammonium Dichromate (ADC), Hydrochloric acid (HCl), Lanthanum oxide (La_2O_3) were used as starting precursors for the synthesis of pure polyaniline and lanthanum oxide doped polyaniline.

2.2 Preparation of PANI-(La_2O_3) Nano composites

PANI-lanthanum oxide (La_2O_3)was prepared by in situ chemical oxidative polymerization method. Different proportions of La_2O_3(5% &15%) were added to 100mL of 0.25M of aniline in 1 N HCl in beaker stirred by magnetic stirrer for 2hours completion of the reaction and 100 ml of 0.25M ADC solution was added with continuous stirring. After the completion of the addition it was continuously stirred for 24hrs to polymerize. The precipitation was filtered and washed repeatedly with deionized water, acetone and 1N HCl to remove impurities.The sample was dried in hot air oven for 2hrs, the final product was in powder form[9].

3. Results and discussion

3.1. Thermal Analysis

Figure 1 reveals the thermal analysis of lanthanum oxide doped polyaniline with different concentrations; temperature is varied from RT to 800^{o}C. The percentage of weight loss can be measured and initial weight loss can be observed due to the moisture present in the sample. The sample was stable at the higher temperature after initial weight loss no further weight loss was observed [10]. Thermal properties of polyaniline may vary by doping of lanthanum oxide.

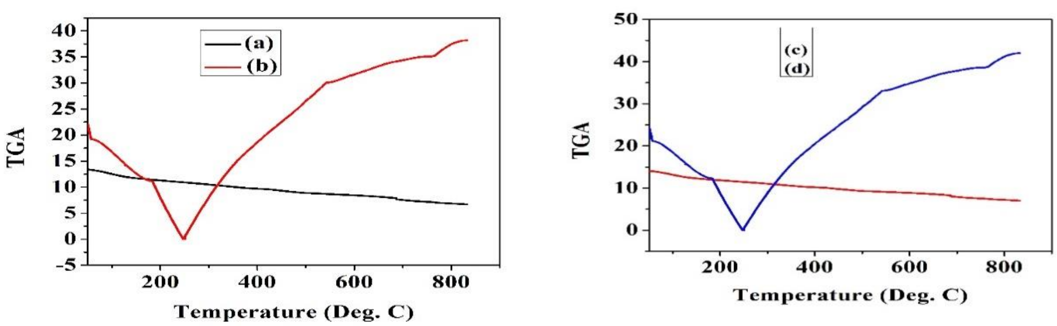

Figure 1:TGA and DSC stability PANI/La_2O_3 (5%) and PANI/La_2O_3 (15%)

3.2. Scanning Electron Microscopy

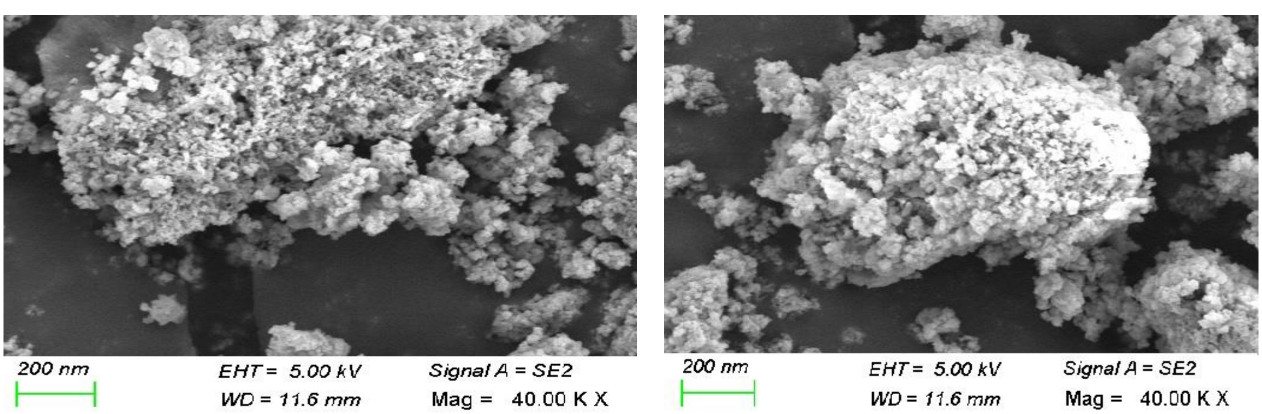

Figure 2: Morphology of SEM, PANI/La_2O_3 (5%) and PANI/La_2O_3 (15%).

The above morphological imagesare of lanthanum oxide (La_2O_3) doped pure PANI synthesized by in situ chemical polymerization method.Scanning electron microscopy (SEM) is a valuable tool for detecting properties like shapes and grain sizes in particles. SEM images of 200nm of both the samples of PANI/La_2O_3, the particles appear as small congregated globules of diverse sizes and the diameter of each particle is 26.2nm.

3.3. DC Conductivity

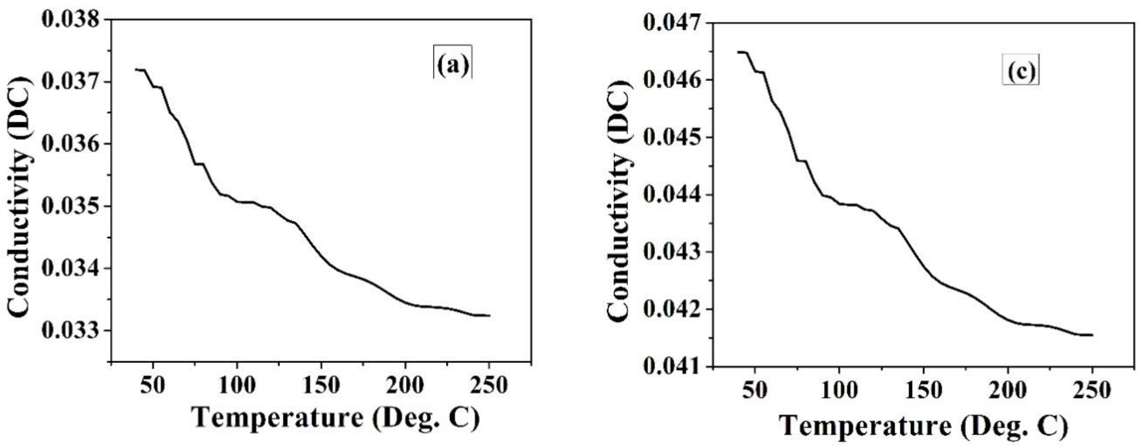

Figure 3: DC conductivity for PANI/La_2O_3 (5%) and PANI/La_2O_3 (15%)

From the above figure 3, it is absorbed that the DC conductivity decreases with increasing temperature and also understood the effect of La_2O_3on PANI. Maximum conductivity is 0.0372 S cm^{-1} was observed at RT. Both doping concentrations were shown same behavior thought the temperature range.

3.4. AC Conductivity

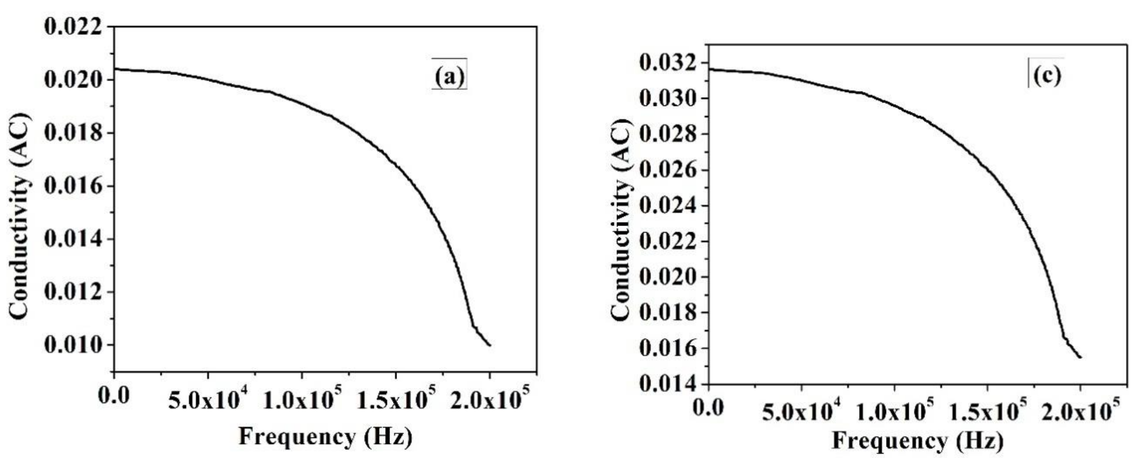

Figure 4: AC conductivity for PANI/La_2O_3 (5%) and PANI/La_2O_3 (15%)

Frequency depended AC conductivity of the sample were shown in the figure 4. Lanthanum oxide doped polyaniline is showing decrease in the conductivity with increasing frequency (in the range of 100 Hz to 2.0x10^5 Hz). This type of behavior may be due to hopping of the electrons in the synthesized samples. This decrease in the conductivity indicates good dielectric behavior of the samples. AC conductivity of the sampleswas recorded with high range as 0.021 S cm $^{-1}$ and low as 0.010 S cm $^{-1}$.

3.5. Dielectric analysis

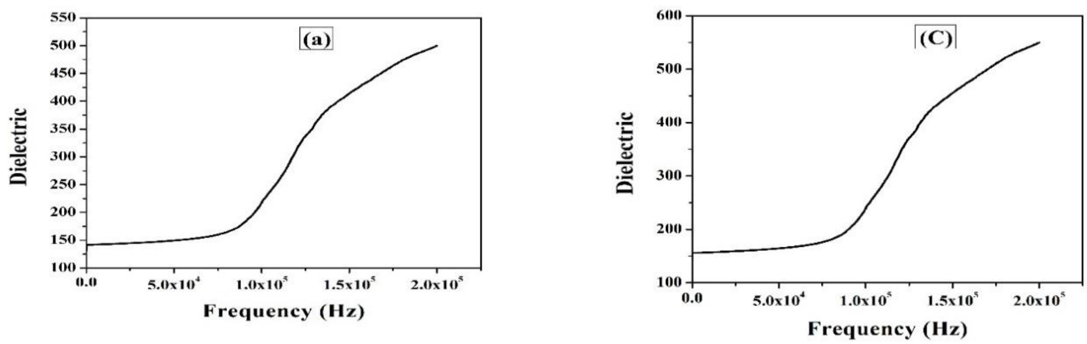

Figure 5: Dielectric constant of PANI/La_2O_3 (5%) and PANI/La_2O_3 (15%)

Dielectric constant was measured as a function of frequency and is illustrated in figure 4. At the beginning the dielectric constant was seems to be constant but as frequency increases there is increase in the dielectric constant and was due to the space charges taking enough time to move longerdistance in the sample at applied frequency. Conducting nature of polyaniline was reported in many literatureswith oxidizing agent ammonium per sulfate, but the oxidizing agent ammonium dichromate may change the polyaniline from conducting to dielectric, was observed in the synthesized sample. As the concentration of doping agent increases there is increase in dielectric constant.

3.6. Dielectric loss

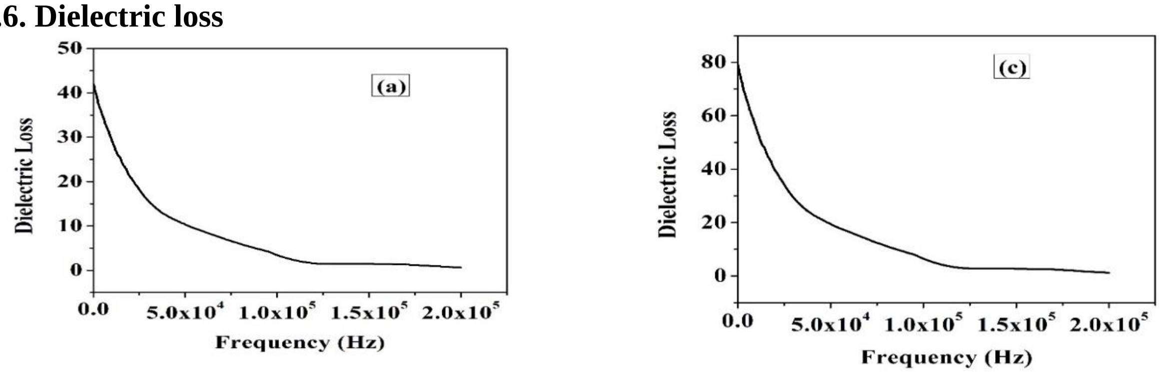

Figure 6: DC conductivity for PANI/La_2O_3 (5%) and PANI/La_2O_3 (15%)

Figure 6 shows the dielectric loss of the material,the energy losses may occur in dielectrics were due to dipole relaxation and dc conductivity. As frequency increases it was observed that there is a decrease in dielectric loss throughout the measurement. Low losses of a dielectric material at higher is useful indicator of the low energy loss, heatand these factor makes lanthanum oxide doped polyaniline as one of the promising materials for high frequency device applications.

4. Conclusions

Present work was attempted to synthesize lanthanum oxide doped polyaniline for electronics applications. Conductivity is also measured as a function of temperature and frequency but in both measurements decreases in conductivity was observed and this decrease in conductivity encouraged us to measure dielectric property of the sample. Use of ammonium dichromate may change the behavior of polyaniline from conducting to dielectric and doping agent strengthened the above property of the synthesized sample. Low dielectric loss at high frequency of La_2O_3 doped PANI will become the promising material for high frequency electronics applications.

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