

Dielectric Properties of Ultrasonicated Fly Ash and Polyaniline Composites

A. D. Dahegaonkar¹, S. B. Kondawar², D.V.Nandanwar³, V. A. Thabhane⁴

¹Department of Physics, N.S. Science and Arts College, Bhadrawati, Dist. Chandrapur

²Department of Physics, R. T. M. Nagpur University, Nagpur

³Department of Physics, Mohota Science College, Nagpur

⁴Department of Physics, Pune University, Pune

Abstract: *In situ* polymerization of polyaniline (PANI) was carried out in the presence of ultrasonicated fly ash (FA) to synthesize Polyaniline-fly ash composites (PANIFA) by chemical oxidation method. The PANIFA composites have been synthesized with various compositions (10, 20, 30, 40 and 50 wt %) of fly ash in polyaniline. Ultrasonication of as-received fly ash provided the energy for chemical reaction between fly ash contents and charged backbone of PANI, leading to significant interaction of PANI with fly ash. The surface morphology of these composites was studied with scanning electron micrograph (SEM). The polyaniline-fly ash composites were characterized by employing X-ray diffractometry (XRD) and UV-Vis Spectroscopy. A dielectric property of conducting polyaniline fly ash composites has been investigated as function of frequency. By incorporating fly ash into polyaniline, dielectric constant (ϵ') was found to be improved as compared to that of pure polyaniline. It was also noticed that dielectric constant of all composites found to be decreased with increasing frequency due to dielectric relaxation. The dielectric loss (ϵ'') of composites shows similar trends as that of dielectric constant. The results obtained for these composites are of greater scientific and technological interest for good quality of capacitor.

Keywords: Conducting polymers, Polyaniline, Fly ash, Composites, Dielectric properties.

1. Introduction

Polyaniline (PANI) continues to attract considerable attention because its electrical and optical properties can be changed by oxidation and protonation of the amine nitrogen atoms. PANI is known for its excellent thermal and environmental stability but poor processibility due to insolubility and brittleness that limits its commercial applications. PANI could be more processible in the composites form with another water soluble polymers such as PVA, poly (vinyl pyrrolidone), poly (acrylic acid) and poly (styrene sulfonic acid) (PSSA) which are used as stabilisers. A functionalised protonic acid can be added into the composites to chemically polymerise PANI. The PANI dispersion can then be casted to form composite film containing PANI nanoparticles [1]. To improve the conductivity further, conducting polymers have been irradiated with x-rays [2, 3], gamma radiation [4], and gamma and electron beams [5]. When ionising radiation interacts with polymer materials active species such as free radicals are produced, thereby initiating chemical reactions including cross linking, chain scission, and grafting. The ionic carriers induced by radiation scission can improve the conductivity of PANI.

The conducting polyaniline (PANI) is one of the promising conducting polymers due to its high conductivity, ease preparation, good environmental stability and large variety of applications [6] which make this polymer suitable for gas sensor, functional hybrid, as pH swchiting electrical conducting biopolymer hybrid for sensor applications, as an electrically active redox biomaterial for sensor applications, as a matrix for preparation of conducting polymer nanocomposites [7]. Therefore, there has been increasing

interest of the researchers for the preparation of nanocomposites based on PANI. The literature review on conducting polymer nanocomposites show that PANI has been successfully utilized for the preparation of nanocomposites [8, 9]. Various applications of conducting polymers have been proposed as transducers of biosensor [10], electrodes of rechargeable batteries, artificial nerves and muscles, gas sensors, solid electrolytic capacitor, diodes and transistors, anti-static electromagnetic shielding, and biomedical applications.

Fly ash is a waste product produced from coal fired thermal power stations during the combustion of coal. The Large number of coal fired power plants all over the world disposes large quantity of fly ash causing serious environmental problems. Less than half of the ash is used as a raw material for concrete manufacturing and construction; the remaining is directly dumped on land side as land fill or simply piled up. Due to environmental regulations, new ways of utilizing FA have to be explored in order to safeguard the environment and provide useful ways for its disposal. Hence, there is considerable interest in utilization of FA as raw material. For the first time, FA was used in the preparation of cordierite [11]. Because of the presence of SiO_2 and Al_2O_3 in high proportions, the FA was used to synthesize zeolites [12]. FA was treated hydrothermally and the performance of this material as cracking catalyst was investigated with heavy oil fraction as the cracking feed stock [13]. On the other hand, there were many experimental analyses on FA to undertake basic compositional, physical and chemical properties for technical studies and applications [14]. Raw fly ash consists of quartz and mullite as crystalline phases and some quantity of glassy phase [15]. Effort has been made to understand the electrical conductivity and dielectric behavior of fly ash and it was

observed that these materials possess very high relative dielectric constant of the order of 10^4 . Such a high dielectric constant is one of the important parameters in capacitor fabrication, and microwave absorption applications. Through this work we have made a successful effort in preparing polyaniline - fly ash composites, which gives newer ways of better utility of fly ash. Conducting polymer composites with some suitable compositions of one or more insulating materials lead to desirable properties. These materials are especially important owing to their bridging role between the world of conducting polymers and that of nanoparticles. For application of conducting polymers, knowing how these conducting polymer composites will affect the behavior in an electric field is a long-standing problem and is of great importance. But very little is known about the dielectric properties of conducting polymer associated with the conducting mechanism. Dielectric spectroscopy has been found to be a valuable experimental tool for understanding the phenomenon of charge transport in conducting polymers. Low frequency conductivity and dielectric relaxation measurements especially have proven to be valuable in giving additional information on the conducting mechanism that D.C. conductivity measurement alone does not provide. In this work a new potential use of FA has been proposed. The high dielectric constant FA has been used for the synthesis of PANIFA composites. In the present work, we report the study on morphology and dielectric properties of PANIFA composites, synthesized by chemical oxidation process. The study shows better utility of fly ash, in order to tailor dielectrically properties of PANIFA composites.

2. Experimental

The GR grade Aniline was purified by distillation under reduced pressure. A fine fresh clean and pure FA powder was collected from the Thermal Power Station, Chandrapur, India. FA contains elements like Cu, Pb, Cd, Ag, Mn, Ti, Na, Mo, S, P, Zn and Cl in different concentrations [16]. 0.4 M of distilled Aniline was added to the solution of 0.4 M of ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ and this reaction mixture was stirred continuously at room temperature to obtain polyaniline. To this reaction mixture, varied weight per cent of ultrasonicated fly ash powder (10, 20, 30, 40 and 50) was added to form polyaniline-fly ash composites. The obtained product was filtered and washed thoroughly with methanol (CH_3OH) and the sample was dried under vacuum for more than 24 h at room temperature. The obtained composites were pressed in the form of circular pellets of 1 cm diameter. The SEM images of polyaniline-fly ash composites were investigated using Field Emission Gun Scanning Electron Microscope. The X-ray diffraction patterns of the samples in this present case were recorded on Philips PW-1700 X-ray diffractometer using $\text{Cu-K}\alpha$ radiation of wavelength 1.544 Å with continuous scanning speed of $10^\circ \text{ min}^{-1}$ and accuracy of 0.01. The characterization of polyaniline and its composites by spectroscopic methods is important, as it gives information not only about various molecular-level interactions but also on the type of charge carriers.

3. Results and discussion

3.1. UV-Visible spectroscopy

The UV-Vis absorption spectra of PANI and PANIFA composite are shown in Fig. 1. Two absorption bands are observed in the wavelength region from 315 to 350 nm and a small band at 578 to 712 nm for the PANI. PANI always exhibits a $\pi-\pi^*$ transition, usually closer to 315 nm [17]. Partially oxidized PANI and its oligomers display an additional absorption at around 712 nm associated with the quinoid (oxidized) units [18]. These peaks are characteristic of the PANI emeraldine base and indicate that nanostructure PANI composites are stabilized in the emeraldine base redox state.

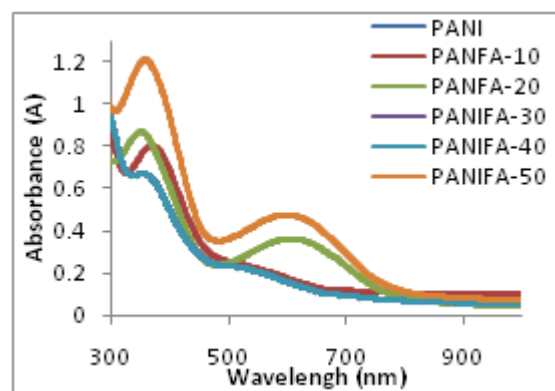


Figure 1: UV-Vis spectra of PANIFA Composites

The peak at 315 nm is attributed to $\pi-\pi^*$ transition of benzoid rings and the peak at 712 nm is attributed to the charge transfer excitation of the quinoid structure. PANIFA prepared without aging show clear similarity in their UV-Vis spectra particularly with the complete absence of the absorption maxima at 320 and 630 nm which is associated with the stabilization of the composite in the emeraldine form, comparatively PANIFA composite show clear similarity in their UV-Vis spectra particularly with the presence of the absorption maxima at 315 and 610 nm which is associated with the stabilization of the composite in the emeraldine form. Comparison of the PANI and PANIFA composite spectra shows that FA stabilizes the polyanilines in its emeraldine form [19].

3.2. Scanning Electron Microscopy

Fig. 2 shows the SEM micrograph of PANI, FA and PANIFA composites. SEM of PANI shows porous, non-uniform structure. SEM is showing the general features of the original fly ash. As it can be seen in the figure, the fly ash is mainly constituted by compact or hollowed spheres but with a regular smooth texture. Also, some quartz particles, residue of un-burnt coal or some vitreous unshaped fragments could be seen. A very high magnification reveals the homogeneous distribution of fly ash (cenosphere) particles. PANIFA composite shows the formation of dine base form of PANI significantly changes the aggregate state of polymeric molecular chain. It is seen from the micrograph that cluster and granular structure of polyaniline is maintained even after the addition of fly ash in polyaniline. Hence, a network of fly ash and granular polyaniline has been formed in case of composites.

3.3 X- ray diffraction

Fig. 3 shows the XRD of pure PANI and PANIFA composites. It has been suggested by XRD study that PANI undergoes interfacial interaction with FA crystallites and loses its own morphology by its mixing with fly ash. PANIFA composites show peaks of fly ash as well as polyaniline indicating that fly ash crystallites have been

uniformly mixed within the polymer chain.. Careful analysis of X-ray diffractogram of polyaniline–fly ash composite suggests that it exhibits semi-crystalline behavior. No structural change has been observed in fly ash due to its dispersion in polymerization of reaction of polyaniline [8].

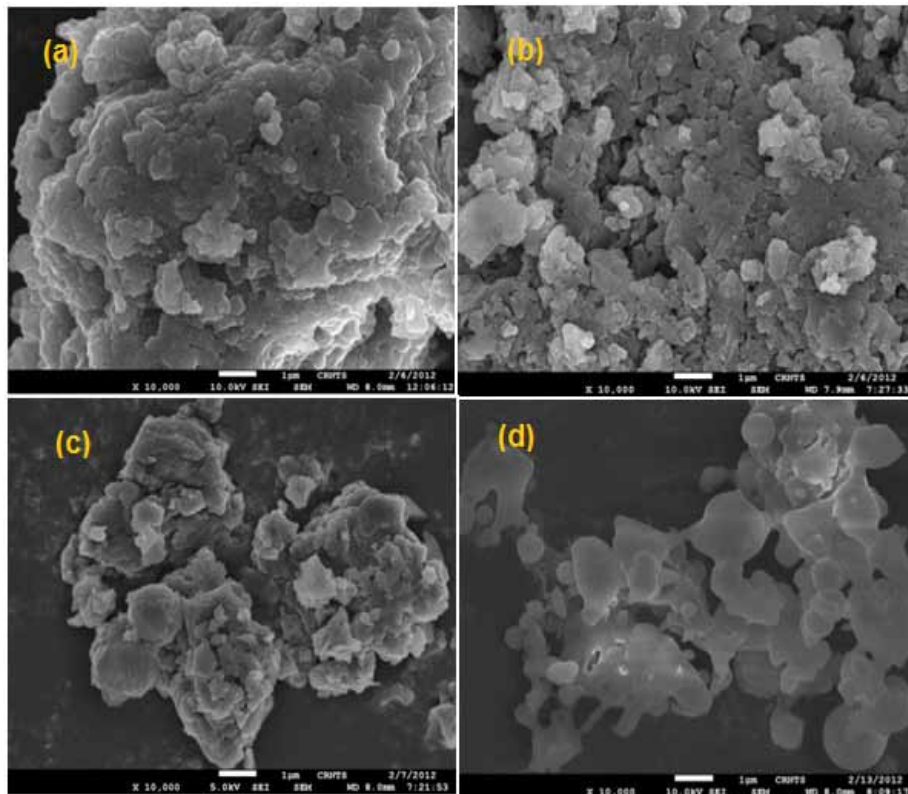


Figure 2: Scanning electron micrograph of (a) PANI, (b) PANIFA-10, (c) PANIFA-40, (d) FA

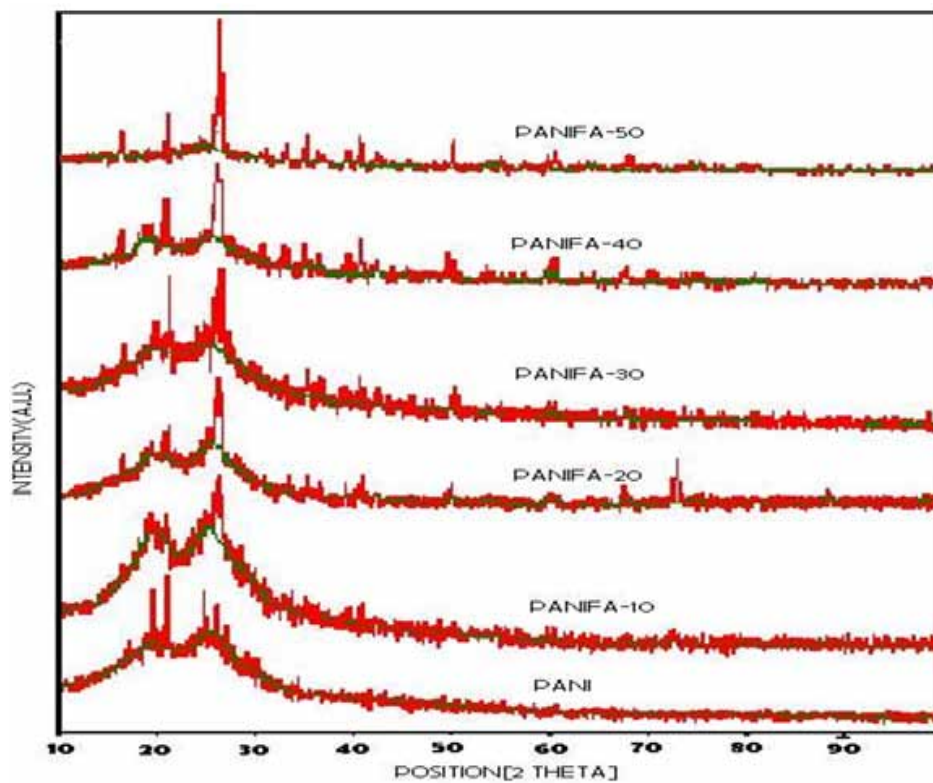


Figure 3: X-ray diffraction pattern of PANI, PANIFA Composites

3.4 Dielectric measurement

The dielectric studies of PANI, FA and PANIFA carried out by using impedance analyzer (Model: TF-600). The 1 cm in diameter disc shaped sample is used to find out the dielectric constant. The capacitance and dielectric loss in the frequency range 100 Hz- 10 KHz are found out. Dielectric constant or relative permittivity is calculated by using the formula:

$$\epsilon_r = \frac{Cd}{\epsilon_0 A}$$

Where, d is the thickness of the sample, C the capacitance and A the area of cross section of the sample ϵ_r is the relative permittivity of the material which is a dimensionless quantity. ϵ_0 is the dielectric permittivity of vacuum (8.854×10^{-12} F/m). Fig. 4 shows variation of dielectric constant and dielectric loss as a function of frequency for pure FA and PANI. It is observed that at low frequencies dielectric constant was found to decrease with increasing frequency. This could be due to fact that ions are unable to oppose the effect of the field and tightly pinned to the polymer chain. It is also observed that dielectric constant is decreased rapidly at lower frequency are showed almost frequency

independent behavior at higher frequency. Fig. 5 shows variation of dielectric constant and dielectric loss as a function of frequency for PANIFA composites (different wt %). It is observed that dielectric constant and dielectric loss in case of polyaniline and its composite decreases as a function of frequency [20]. The higher value of ϵ' at low frequency could also be accounted for the tendency of induced dipoles in polymer matrix to orient themselves in the direction of applied field. The value of ϵ' found to be higher at low frequency region, which makes the composites suitable for utilization as a charge storing devices at low frequency region. The dielectric constant is found to be low frequency dependent while invariable toward high frequency this could be attributed to orientation of the dipole and conduction of the charge carrier at higher frequency [21]. The variation of dielectric loss is found to be frequency dependent. At lower frequency the value of ϵ'' is high and decreases rapidly and becomes almost constant in high frequency region. The high dielectric loss is due to the large leakage current in the composites in the low frequency region. Both polyaniline and its composites exhibit small value of dielectric loss at higher frequency [22]. Hence, it is suitable for capacitor fabrication.

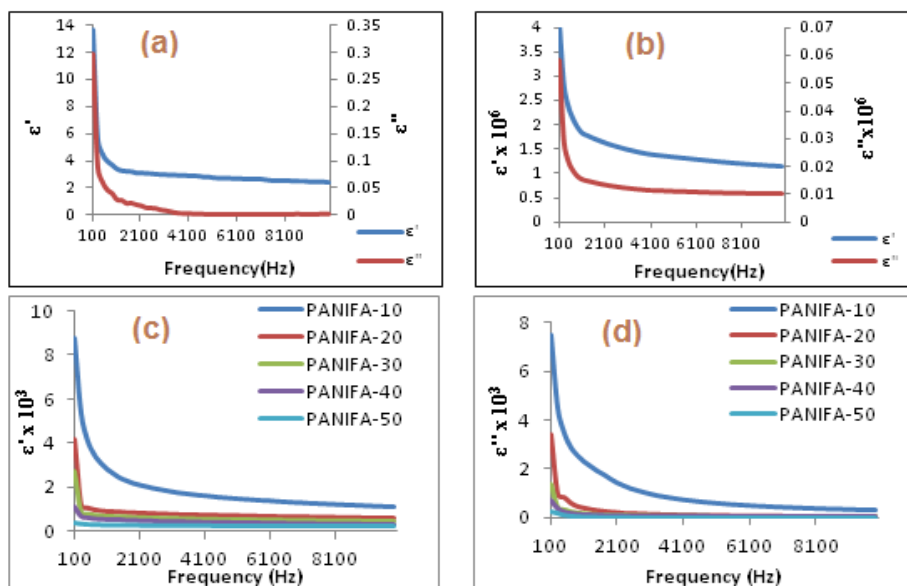


Figure 4: Variation of Dielectric Constant (ϵ') and Dielectric Loss (ϵ'') of (a) FA, (b) PANI and (c-d) PANIFA composites with frequency

4. Conclusions

With more than 100 million tones of fly ash produced in India, use of fly ash for the preparation of polyaniline- fly ash composites will in no way help in its bulk utilization. Still the authors have made an effort towards the better utility of fly ash by synthesizing polyaniline –fly ash composites. The detailed characterization of these composites was successfully carried out through XRD, SEM and UV-vis. Dielectric property is an important property of material. The results of dielectric constant show a strong dependence on the weight percent of fly ash in polyaniline which can be best suitable for capacitor fabrication.

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