FREQUENCY DEPENDANT DIELECTRIC PROPERTIES OF CONDUCTING POLY (O-ANISIDINE)-FLY ASH COMPOSITES

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A B S T R A C T

Fly ash is an industrial waste which creates environmental problems. There is a great challenge to use the waste of thermal power station in the form of fly ash as reinforcement for the conducting polymers to be good dielectric materials. The Dielectric properties of conducting poly (o-anisidine) fly ash composites have been investigated as a function of frequency with the help of impedance analyzer. There is an increasing interest of technical and scientific community to obtain new material with improved properties and processability of relatively low cost. In this paper we report the use of fly ash to prepare conducting polymer composite materials. In situ polymerization of o-anisidine was carried out in the presence of fly ash to synthesize conducting poly(o-anisidine) fly ash composites (POASFA) by chemical oxidation method in presence of Ammonium persulphate (APS) with various composition (10,20,30,40,50 wt%) of fly ash in conducting polymer. The surface morphology of these composites was studied by scanning electron microscopy (SEM), X-ray Diffractomentry(X-RD), and UV-Vis spectroscopy to investigate surface morphology and structure of the composites. By incorporating fly ash into conducting polymer dielectric constant of the composites was found to be improved as compared to that of conducting polymer. It was also noticed that dielectric constant of all the composites found to be decreased with increasing frequency due to dielectric relaxation. The dielectric loss of POASFA composites shows similar trend as that of dielectric constant. The sample of fly ash is of great scientific and technological interest because of its value of dielectric constant i.e. 10. The result obtained for these composites are of greater scientific and technological interest for good quality of capacitor.

Keywords: Conducting Polymer, Poly(O-anisidine), Fly ash, Composites, Dielectric Constant

1. Introduction

Polymers are typically utilized in electrical, optical and electronic optical and electronic devices as insulator [1]. The dielectric properties of heterogeneous polymer play an important role in device application such as high performance capacitor, electrical cable insulation, electric packing etc. polymers are usually poly conjugated structure, which are insulator in their pure state but when treated with oxidizing or reducing agents they can be converted into polymer salts having reasonable electrical conductivity. Conjugated polymers are plastic semiconductors [2]. They have wide applications in devices such as solar cell, rechargeable batteries, light emitting diode, micro-actuators, electrochromic display, field effect transistor, sensors [3].

Among the conducting polymers polyaniline and its derivatives have attracted much attention due to its ease of synthesis by chemical or electrochemical polymerization, ammonium persulphate is generally used as the oxidizing agent for the preparation. Although the chemical method offers mass production at a reasonable cost; the electrochemical method involves the direct formation of conducting polymer thin film with better control of thickness and morphology, which are suitable for application in electronic devices [4-9]. polyaniline and its derivatives are mainly used as coating to improve the corrosion resistance of oxidizing metals. These coating have also been considered for several applications such as the electronic industry; biosensor application [10-16]. polyaniline has shown variety of application such as rechargeable batteries, electro catalysis, electrochromic display; gas separation and biosensors. However the role of structural and mechanical behavior of polyaniline and its derivatives for their applications to biosensor has not yet been explored [17].

Fly ash is being considered as a waste material produced from thermal power plants is creating serve environmental pollution. It is creating serve environmental pollution; so much research is being conducted for more than two decades for its proper utilization as well as to control environmental pollution in the surrounding areas of power plants. Its utilization in industry or in market sector may being economic and ecological benefits and impact technological development [18-27]. A composite material is a combination of two or more materials (in certain proportions) whose performance characteristics exceed than that of its individual components. Now a day polymer composites are of interest; these can provide great strength and stiffness along with resistance to corrosion [28-29]. Hence development low cost composites materials using conducting polymer industrial waste materials from local resources is an an active field of research [30-31]. Presently much research attention is being given to use such materials for capacitor dielectric, insulation, encapsulation, ceramic chip, printed circuit boards etc. Fly ash based composites exhibit low dielectric constant and stabilized dielectric loss at high frequencies of applied field and hence are suitable for electronic application [32-34]

2. Experimental

2.1 Materials and method

The GR grade o-anisidine was purified by distillation under reduced pressure. A fine fresh clean and pure FA powder was collected from the Thermal Power Station, Chandrappur, India. FA contains elements like Cu, Pb, Cd, Ag, Mn, Ti, Na, Mo, S, P, Zn and Cl in different concentrations [35]. 0.4 M of distilled o-anisidine was added to the solution of 0.4 M of ammoniumpersulfate [$(NH_4)_2S_2O_8$] and this reaction mixture was stirred continuously at room temperature to obtain poly(o-anisidine). To this reaction mixture, varied weight per cent of fly ash powder (10 20, 30, 40 and 50) was added to form poly (o-anisidine)–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 poly (o-anisidine)–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 CuKα ☐radiation Continuous scan of 2 ^{0}/ minimum with accuracy of 0.01. The characterization of poly (o-anisidine) 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. The variation of impedance with frequency and temperature has been studied for all samples .The dielectric constant and dielectric loss are measured in frequency 100 Hz to 1 MHz Fly ash is a finely divided amorphous powder with the particle size ranging from 150 nm–120 µm. It is abrasive and refractory in nature. In the present study the fly ash employed is of cenosphere type, collected from Thermal Power Station Chandrapur, India

2.2 Dielectric measurement

The dielectric studies of POAS, FA, POASFA 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 - 1MHz are found out. Dielectric constant or relative permittivity is calculated by using the equation (1)

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \qquad \text{---- (1)}$$

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 x 10^{-12} F/m).

3. Results & discussion

3.1 UV-Vis

Fig.1. Shows the UV –Vis absorption spectra of self –doped POAS with different weight percentage of fly ash in DMF .POAS showed two characteristics band at 290 nm in UV correspond to Π- Π* transition along the backbone of the POAS chain and 550 nm in visible corresponds to inter ring charge transfer ration of benzenoid to quinoidmoities [36].The characteristics bands in POAS have also been shifted to longer wavelengths due to incorporation of fly ash indicating the interaction between quinoid ring and fly ash observed in case of POAS[37].

3.2 SEM

SEM images of POAS FA and POASFA composites are shown in Fig. 4(a-f). It can be seen from SEM of POAS shows porous, non-uniform structure. POASFA composites shows the formation of dine base form of POAS significantly changes the aggregate state of polymeric molecular chain. The incorporation of metal oxides into the polymeric network induces uniform porosity and is expected to be advantage for gas and biosensing application. A very high magnification revels the homogeneous distribution of fly ash (cenospere) particle. It is seen from the micrograph that clusters and granular structure of POAS is maintained even after the addition of fly ash in POAS. Hence a network of fly ash and granular POAS has been formed in case of composites [38]. The presence of -OCH3 group in each benzene ring of the poly (o-anisidine) push apart the dopant and it make more disordered system as compared to that of polyaniline, as seen from its SEM which shows highly porous. It has been revealed that after binding of poly (o-anisidine) with fly ash the morphology has been changed. The change in the particle size was noticed due to incorporation of the different weight percentage of fly ash in poly (o-anisidine) matrix. The original fly ash is mainly constituted by compact or hollowed sphere but with a regular smooth texture. Also some quartz particles residue of un-burned coal or some vitreous unshaped fragments could be seen.

3.3 XRD

Fig.2. Shows the XRD of pure POAS and POAS composites it has been suggested that XRD study that POAS undergoes interfacial interaction with FA crystallites and losses its own morphology by its mixing with fly ash .POAS fly ash composites show peaks of fly ash as well as POAS indicating that fly ash crystallites have been uniformly mixed within the polymer chain. Carefully of X-ray diffraction of POASFA composite suggested that it exhibits semi-crystalline behavior. No structural change has been observed in fly ash dispersion in polymerization of reaction of POAS [39].

3.4 Frequency dependent dielectric properties

The dielectric constant (at 100 Hz frequency) is maximum for pure POAS sample and minimum for Fly ash. But when POAS and fly ash are combined together, dielectric constant drops down. The dielectric constant value and dielectric loss value initially decreases and attains a steady state with increase in frequency as shown in Fig. 4(a-d). This may be due to the fact (i) dielectric behavior is dependent on porosity, (ii) material properties and also (iii) interface bonding in case of composite materials. So, in this study the materials used have many diverse physico-mechanical properties. However, it is found that making a composite with these wastes, using a polymer binder is best suited for providing good mechanical strength without sacrificing its dielectric property.

The Polymers have a tendency of moisture absorption. Impregnation of poly (o-anisidine) and fly ash into it helps in the interface bonding and distribution of absorbed moisture in the material which may be one of the reasons for change in dielectric behavior. With increase in frequency, the dielectric constants of the composites decrease due to dielectric relaxation. From theoretical point of view, the dielectric relaxation involves oriental polarization which in turn depends on molecular arrangement of the material. It is known that, at high frequency, the rotational motion of polar molecule is not sufficiently rapid for attainment of equilibrium with applied electric field; hence, dielectric constant decreases, depending on the reinforcement content and types of reinforcement. Dielectric loss of our composite shows a stabilizing trend with increase in frequency, which appears to be beneficial in electronic industry and that to, can be processed by village artisans also.

4. Conclusion

With more than 100 million tonnes of fly ash produced in India, use of fly ash for the preparation of poly (o-anisidine)-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 poly (o-anisidine)-fly ash composites for electronic devices where the requirement of dielectric materials with good electrical conductivity. Conducting poly (o-anisidine) and poly (o-anisidine) / fly ash were synthesized successfully by using an in-situ chemical oxidation polymerization method. The interaction of FA with the polymer was confirmed from their XRD and SEM. The results of dielectric constant show strong dependence on the weight per cent of fly ash in poly (o-anisidine). The dielectric constant and loss was found to be decreased with weight percent of FA in composites. Further the dielectric constant of all the composites was found to be decreased with increasing frequency. As the composite is made using industrial waste materials from local resources, its cost is less as compared to other polymer composites available today. This can further open up a new frontier for industrialization in the rural sector.

3.Illustration

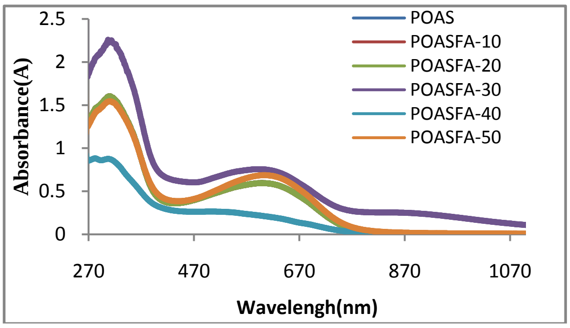

Fig. 1. UV-Vis spectra of POAS and POASFA composites.

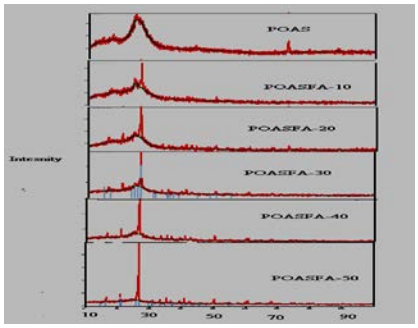

Fig.2. XRD spectra of of POAS and POASFA composites

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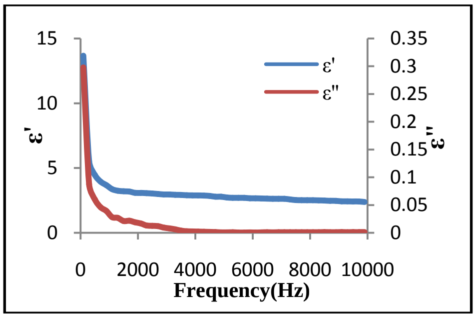

Fig. 3 (a) Dielectric constant and dielectric loss of FA

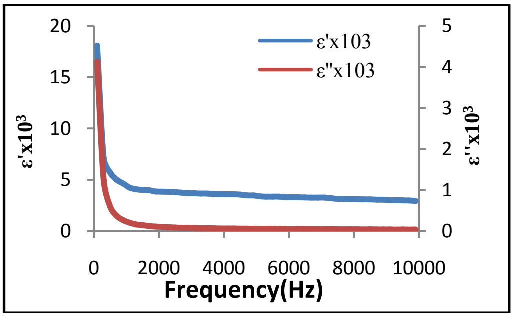

Fig.3 (b) Dielectric constant and dielectric loss of POAS

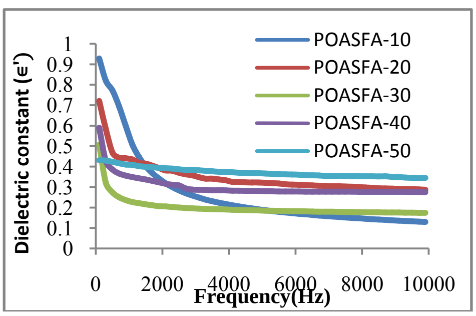

Fig. 3 (c) Dielectric constant of POASFA composites with frequency

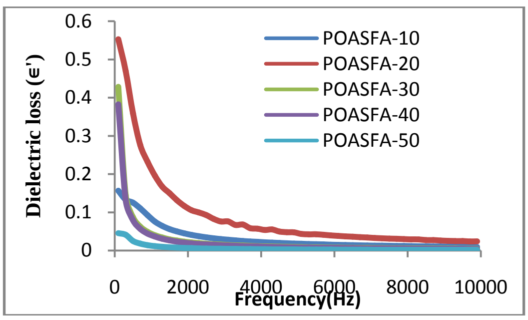

Fig.3 (d) Dielectric loss of POASFA composites with frequency.

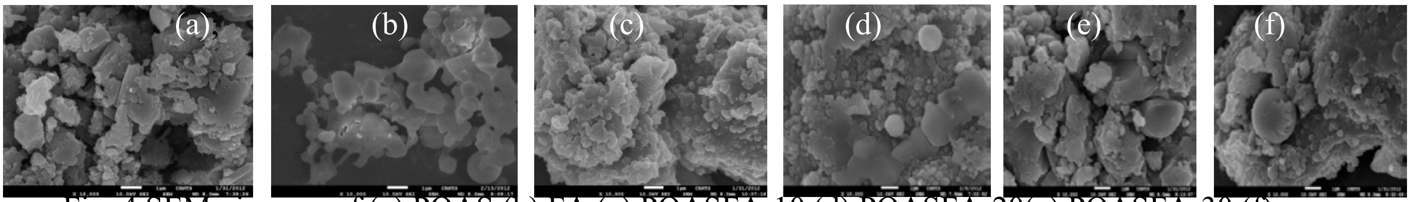

Fig. 4 SEM images of (a) POAS (b) FA (c) POASFA-10 (d) POASFA-20(e) POASFA-30 (f) POASFA-40

Equations:

$$\varepsilon_r = \frac{Cd}{\varepsilon_o} \quad (1)$$

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