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Structural, Mechanical and Electrical Characterization of Polypyrrole/ Poly(methyl methacrylate)/Fly ash Composite

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Abstract

The polypyrrole-poly(methyl methacrylate)-fly ash (PPy/PMMA/FA) composites were formed by in-citu polymerization of pyrrole in ammonium persulfate and PMMA latex medium in presence of fly ash. The structural characterization of the composite was carried out using XRD, SEM and FTIR techniques. A homogenous semicrystalline structure of the composite has been observed. The DC conductivity studies of the composite reveal that the conductivity increases with increasing FA component upto 35%. The microhardness of the composite is found to depend on the FA and PMMA components. Satisfactory conductivity of PPy+35%FA composite is exhibited when PMMA is mixed in the range of 5 to 10 %. The studies suggest that the addition of PMMA to PPy and FA composite can give rise to a conducting polymer composite with good mechanical stability.

Key words: XRD, SEM, FTIR, DC Conductivity, microhardness.

1 Introduction

The main advantages of conducting polymer based materials lie in their light weight and in the versatility with which their synthesis and manufacturing can be accomplished. Polypyrrole (PPy) has been extensively studied among these conductive materials, since it exhibits the advantages of ready synthesis, flexibility in the selection of dopant, and good mechanical as well as electrical properties[1-3]. Polypyrrole is a well-known conducting polymer, which is difficult to process since it is insoluble in many common organic solvents. A large number of technological applications of PPy such as fabrication of molecular electronic devices[4], electrodes for solid-state batteries[5], solid electrolytes for capacitors[6], electromagnetic interference shielding materials[7] and ion-sensors[8] have been proposed. Polypyrrole is an important member of the family of intrinsically conducting polymers which can be synthesized by electrochemical or chemical methods. It is reported to be a stable polymer that has excellent retention of its electrical, chemical, thermal, and mechanical properties[9-10].

Fly ash (FA) comes primarily from coal-fired electricity generating power plants. These power plants grind coal to powder fineness before it is burned. Fly ash which primarily is the mineral residue is produced by burning coal is captured from the power plant's exhaust gases and collected for use. It is an alkaline grey powder whose pH ranges from 9–9.9. Very large volume of fly ash is disposed by large number of coal fired power plants all over the world which causes serious environmental problems[11]. Fly ash is regarded by the public as a solid waste material, though it is increasingly being used for various beneficial purposes. Many attempts have been made to make use of FA for specified purposes. FA-jute-polymer composites have been studied[12] and its use has been proposed as a household, low cost building material and in automobile applications. Use of FA has been investigated by researchers to improve the electrical conductivity of conjugate polymers like PPy[13] and polyanilene (PANI)[14].

Several attempts have been made to improve the poor mechanical properties of conductive polymers by forming blends or composites with other polymers. A combination of conventional polymers or copolymers with conductive polymers allows the creation of new polymeric materials with interesting electrical properties. Moreover, blending with conductive polymers can also solve the problem of surface static charge of poly(methyl methacrylate). PMMA is often used as an alternative to glass, and is in competition with polycarbonate (PC) in this field. PMMA has a density of 1150-1190 kg/m^3. This is less than half the density of glass, and similar to that of other plastics. It is often preferred on account of its moderate properties, easy handling and processing, and low cost, but behaves in a brittle manner when loaded, especially under an impact force. The preparation of composites of poly(methyl methacrylate) and polypyrrole (PMMA/PPy) by a chemical oxidation of pyrrole in a PMMA latex medium resulting in a network like structure of polypyrrole embedded in the insulating polymer matrix has also been reported[15]. Polypyrrole/poly (methylmethacrylate) blend as selective sensor for acetone in lacquer has also been proposed by researchers[16]. It has been demonstrated that grafting between pyrrole and PMMA-co-PEMA-7 can be achieved via oxidative polymerization of pyrrole with $FeCl_3$ in nitromethane which produces insoluble films[17]. In the present work, we report the study of morphology and conducting properties of PMMA/PPy/FA composites, synthesized by chemical oxidation process. The synthesized materials were characterized using X-ray diffraction, FTIR spectra, scanning electron microscopy (SEM) and electrical conductivity. The microhardness of polymeric material in general and of the composites of conducting polymers[18] in particular has been of special interest amongst the material scientists. The brittleness and mechanical instability of PPy and PPY/FA composites pose major obstacles in their commercial use. It may be a matter of great importance if a conducting polymer composite can be developed with sufficient mechanical strength.

2 Experimental

Acros Organics (U.S.A.) make pyrrole monomer supplied by Ranbaxy, New Delhi, India was purified by distillation under reduced pressure. The fly ash in form of a fine, fresh and clean powder was collected from the Sanjay Gandhi Thermal Power Station, Birsinghpur, Madhya Pradesh, India. This fly ash was analyzed by Central Fuel Research Institute (CFRI), Dhanbad, Jharkhand. The following table shows the composition of this fly ash:

Table 1. Composition of Fly Ash (FA) used in the study

Material	Content (%)
SiO_2	63.94
Al_2O_3	26.95
Fe_2O_3	4.39
TiO_2	1.60
P_2O_5	0.51
SO_3	0.50
CaO	0.38
MgO	0.24
Na_2O	0.27
K_2O	1.20

The PPy/FA composite was obtained by adding 0.03 M of distilled pyrrole to the solution of 0.04 M of ammoniumpersulfate $[(NH_4)_2S_2O_8]$. This chemical mixture was stirred continuously at a constant temperature 5°C. Varied weight percent of fly ash powder (5, 10, 15, 20 and 25) was added to this reaction mixture, to form PPy/FA composites. The PMMA/PPy/FA composite was obtained by adding 0.03 M of distilled pyrrole to the solution of 0.04 M of ammoniumpersulfate $[(NH_4)_2S_2O_8]$ and PMMA latex medium. Methanol (CH_3OH) was used to wash the filtered material in order to procure fine composites of PPy/FA and PPy/PMMA/FA. This fine powder was dried in vacuum for 36 hours at room temperature in both cases. The obtained composites were pressed in the form of circular pellets of 1 cm diameter.

The blend specimens were indented at room temperature by Vickers diamond pyramidal indenter attached to Carl-Zeiss NU-2 microscope. The specimens were indented at the load of 80 g. The diameters of indentations were measured using a micrometer eyepiece. For each test the duration of indentation was 30 s. For each load at least five indentations were made at different points of the specimens and average hardness number was calculated. The Vickers hardness number, H_v, was calculated from the relation: $H_v = (1.854 \times L)/d^2$ kg/mm^2, where L is load and d the length of diagonal of indentation in mm. The SEM of prepared specimen were recorded on a scanning electron microscope JEOL JSM 5600 having the resolution of 3.5 nm and accelerating voltage of 0.5 to 30 KV. The X-ray diffraction of the sample was carried out using high resolution X-ray diffractometer having θ-θ goniometer with 0.0001 degree step size and 3 KW X-ray generator with Cu and Mo targets. Four Probe method setup supplied by Scientific Instruments, Roorkee was used for measuring DC conductivity of the composites.

3 Results and Discussion

3.1 Characterization

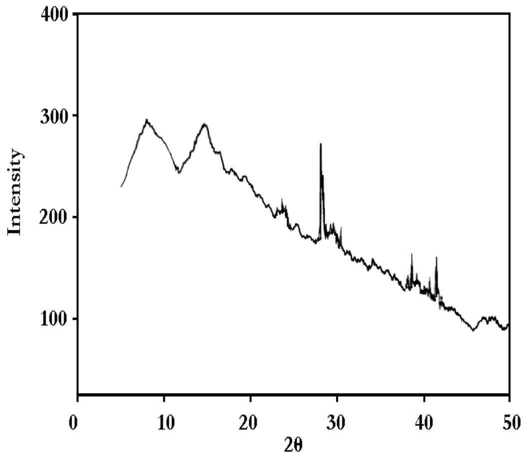

Figure 1. X-ray diffractogram of PPy/PMMA/FA composite

The X-ray diffraction pattern of (PPY/35 wt% FA)/10 wt% PMMA composite is depicted in figure 1. This composite sample was obtained by adding 10 wt% of PMMA to PPy matrix. The diffractogram exhibits the semi-crystalline behaviour of the composite. A homogenous distribution of PMMA in PPy/FA matrix can be inferred from the diffractogram.

Figure 2 depicts the FTIR spectra of the PMMA/PPy/FA composite. The carbonyl peak appears at 1737 cm^{-1} which closely resembles to a characteristic of pure PMMA. The composite exhibits absorption peaks at 1692, 1546, 1305, 1172, 1036, 918, 801, 684 and 554 cm^{-1}. These peaks suggest the presence of various metal oxides in the composite[19].

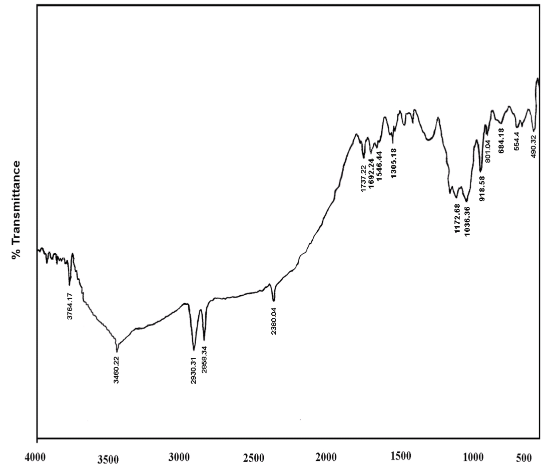

Figure 2. FTIR spectra of (PPy/35 wt% FA)/10 wt %PMMA composite

The SEM micrograph of PMMA/PPy/35 wt% FA is depicted in figure 3. A high magnification confirms the homogeneous distribution of fly ash particles in PPy matrix. The PPy and FA are finely interspersed in the presence of PMMA which reveals the binding nature of PMMA. A stable network is suggested by the SEM micrograph which suggests that the studies composite can be used in industry with much improved mechanical properties.

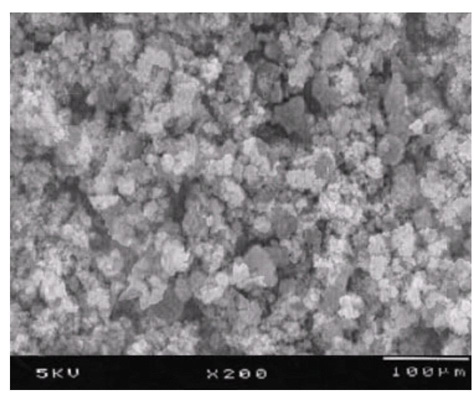

Figure 3. Scanning electron micrograph of (PPy/35 wt% FA)/10 wt %PMMA composite

Fig. 4 exhibits the dc conductivity of polypyrrole:fly ash composites at room temperature (32 ^oC). The microparticles of pure PPy are very light weighted and hence randomly oriented. The linkage among the particles of PPy through the grain boundaries is very weak resulting in relatively lower conductivity[20]. The variation of D.C. conductivity with the varying weight percentage of fly ash in PPy is depicted in Fig. 1.

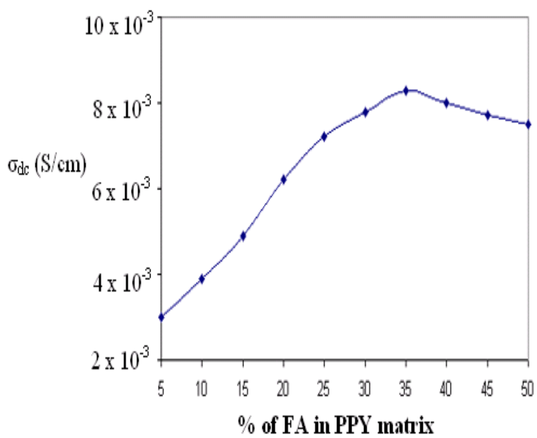

Figure 4. DC conductivity of PPY/FA composite with varying weight percentage of FA

The DC conductivity of the PPy/FA composite increases with increasing content of FA upto 35 wt% and it starts decreasing thereafter. The composite exhibits highest conductivity for the 65 wt%PPy+35 wt% FA combination. This high value of conductivity can be explained on the basis of access charge carriers formed due to presence of metallic contents in fly ash. At this composition the polarization due to hopping conduction dominates. The larger particle size or the clustering of fly ash particles provide hindrance in the hopping of charge carriers inside the composite matrix thereby reducing the dc conductivity beyond 35 wt%[14,21].

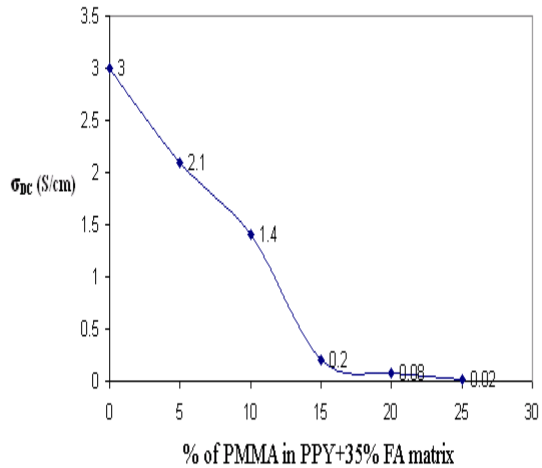

Figure 5. DC conductivity of PPy/PMMA/ FA composite with varying weight percentage of PMMA

Figure 5 depicts the variation of dc conductivity of the PMMA/(PPy/35 wt% FA) with the changing weight percentage of PMMA. The ever decreasing trend of the composite is observed with increasing content of PMMA. The composition PPy+35 wt% of FA was chosen for this study as this composite exhibits highest DC conductivity. The large size of PMMA molecules block the hopping mechanism of charge carriers and this eventually causes for reduced conductivity.

The PPY/ PMMA/FA composite is highly disordered, containing a mixture of crystalline and amorphous regions. The transport of charge carriers along and between the polymer chains and also the complex boundaries established by the multiple numbers of phases gives rise to the overall conductivity of the composite. The movement of charge carriers between localized sites or between soliton, polaron or bipolaron states can be understood as the major contributors for the conductivity of these composites. The inhomogeneous doping produced by metallic oxides of fly ash dispersed in insulating PMMA matrix gives rise to the conduction by movement of charge carriers between highly conducting domains. Charge transfer between these conducting domains also occurs by thermally activated hopping or tunneling.

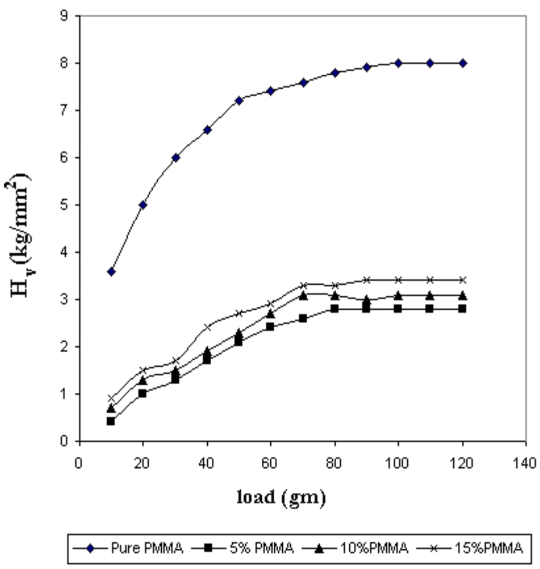

Figure 6. Vicker's microhardness of (PPy/ 35 wt% FA)/ PMMA composite with varying weight percentage of PMMA

Figure 6 depicts the microhardness of pure PMMA and PPy/PMMA/35 wt% FA composite as a function of varying weight % of PMMA. It can be observed that the studied composite shows considerably reduced micro-hardness as compared to that of pure PMMA. The microhardness of this composite increases with increasing wt % of PMMA. But at the same time figure 5 shows a decreasing dc conductivity of the composite with increasing PMMA content. The compromise between the dc conductivity and microhardnes recommends the combinations of 5 to 10 wt% of PMMA with PPy+35 wt% FA composite. The PPy/ PMMA/FA composite having 10 wt% of PMMA exhibits microhardness almost 25 % as of pure PMMA.

Conclusions

The characterization techniques reveal that PPy/PMMA/FA composite can be formed as a stable matrix. The mixing of FA increases the conductivity of PPy. A composite having 35 wt% of FA in PPy matrix may be considered as one of the most promising conducting polymer composite. The commercialization of PPy/FA composite can be ensured by enhancing its mechanical strength with the inclusion of PMMA which acts as a binder for the studied composite. The PPy/PMMA/ FA composite exhibits improvised microhardness and it can be developed as a commercial conducting polymeric material.

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