



Thermal Stability of PANI/MnO₂ Nanocomposite via Chemical Oxidation Technique

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Abstract- Polyaniline/MnO₂ nanocomposite has been prepared using chemical oxidation technique. The prepared products were characterized by FT-IR, and Transmission electron Microscopy and TGA thermogram. FTIR absorption band at 415 cm⁻¹ indicated the presence MnO₂ nanoparticles in the polymer matrix. TEM showed the MnO₂ particles are in nanorange with the average diameter of 20 nm. Thermo gravimetric analysis clearly indicated the increased in thermal stability of nanocomposite than the pure PANI.

Keywords- Polyaniline, , thermal stability, nanoparticle ,TGA,TEM

1. INTRODUCTION:

Conductive polymer with polyaromatic backbone including polypyrrole, polythiophene, polyaniline, etc. has received a great deal of attention in the last two decades [1]. Polyaniline (PANI) exists in a variety of forms that differ in chemical and physical properties [2–5]. PANI is one of the most promising conducting polymers due to its high conductivity, easy preparation, good environmental stability and large variety of applications [6]. Unlike other conjugated polymers, PANI has a simple and reversible acid/ base doping/dedoping chemistry, enabling control over properties such as solubility, thermal stability, electrical conductivity and optical activity [7]. Synthesis of PANI based nanocomposites has led to a number of potential applications in electronic and optical devices, catalysis and analytical sensors etc. Some examples of these PANI nanocomposites are PANI/TiO₂, PANI/PbS, PANI/Ag, PANI/CdS, PANI/Poly (vinyl chloride) etc. [8–12]. The preparation of PANI/inorganic nanocomposites has been the subject of considerable interest recently [13]. It has been found that the novel materials exhibit improved mechanical, electrical and thermal properties due to the synergistic effect of the organic and inorganic components. . MnO₂ is an interesting material from several points of view. It is one of the few oxides that show quantum confinement effects in an experimentally accessible size range [14]. Moreover, the wide range of morphological diversity in the nano-regime has made this material a promising candidate in the field of nanotechnology and opened up new possibilities for the fabrication of high performance devices based on these nanostructures [15–17].

Several research works have been published recently regarding the preparation of PANI/MnO₂ nanocomposites using an electrochemical method [9]. However, to the best of our knowledge, no works have been reported on preparing PANI/MnO₂ nanocomposites via chemical oxidation technique with (0.4N) H₂SO₄ and APS as oxidant. Under these circumstances, it is worthwhile to conduct an explorative\ investigation on preparing the nanocomposites by oxidation technique.





In this paper, we describe our initial work, which has been utilized for thermal and optical study of PANI/MnO₂ nanocomposite.

2. EXPERIMENTAL PART

MnO₂ (Aldrich) and aniline (Aldrich) were used after purification. Oxidant Ammonium per sulphate (Aldrich) was used without further purification.

2.1. Synthesis of Polyaniline via chemical oxidative polymerization:

Polymerization was carried out by the chemical oxidation of aniline in the presence of H₂SO₄ and APS (Ammonium per-sulphate) in 100ml distilled water both played the role as dopant and oxidant respectively. (0.4 mol) APS was dissolved in 100ml distilled water in a four-neck round bottom reaction flask and 0.4mol H₂SO₄ is also added under mechanical stirring for 2 hours. Aniline (0.4 mol) was stirred with 0.4mol of H₂SO₄ in 100ml distilled water. The solution of APS in H₂SO₄ was then added drop-wise in the solution of aniline with vigorous stirring on a magnetic stirrer for 3 hours to initiate the aniline polymerization. The reaction was later carried out at room temperature for 6-7 hours with stirring. A dark green colored PANI suspension was obtained with precipitation. The synthesized PANI was obtained as finely dispersed particles, which were recovered from the polymerization mixture by centrifugation and washed with deionized water repeatedly until the washing liquid was completely colourless. Finally, the mixture was filtered using filtered assembly. After keeping overnight, the dark gray colour precipitate was obtained. A precipitate of polyaniline was dried under at 60 – 80°C for more than 8 hours.

2.2. Synthesis of PANi-MnO₂ Nanocomposites:

The synthesis steps of PANI/MnO₂ nanocomposite are similar to the synthesis method of PANI. Different amount of MnO₂ was dispersed into the APS solution and stirred for 1 hour prior to the addition of aniline. Aniline (0.4 mol) stirred with 0.4mol H₂SO₄ in 100 ml of distilled water were added drop-wised using burette into the APS-MnO₂ solution and stirred vigorously to form homogeneous dispersion. For convenience, PANI Composites were prepared with different weight percentages of MnO₂ i.e. 5%, 10%, 15% & 20% Same synthesis conditions were maintained for all composites as that of pure PANi to compare the result.

Characterizations:

Fourier Transform Infra Red (FTIR) spectroscopy (Model: Perkin Elmer 100) of PANi: MnO₂ nanocomposite was studied in the frequency range of 400–4000 cm⁻¹. TGA thermograms of all samples were recorded on Perkin-Elmer Diamond TGA/DTA in argon atmosphere at a heating rate of 10°C/ min. TGA profile were taken over the temperature range of 30-800°C. TEM micrographs of synthesized PANI & MnO₂ were taken on Transmission Electron Microscope PHILIPS model- CM200 with resolution 2.4Å.



3. RESULT AND DISCUSSION:

3.1. FT-IR SPECTRA:

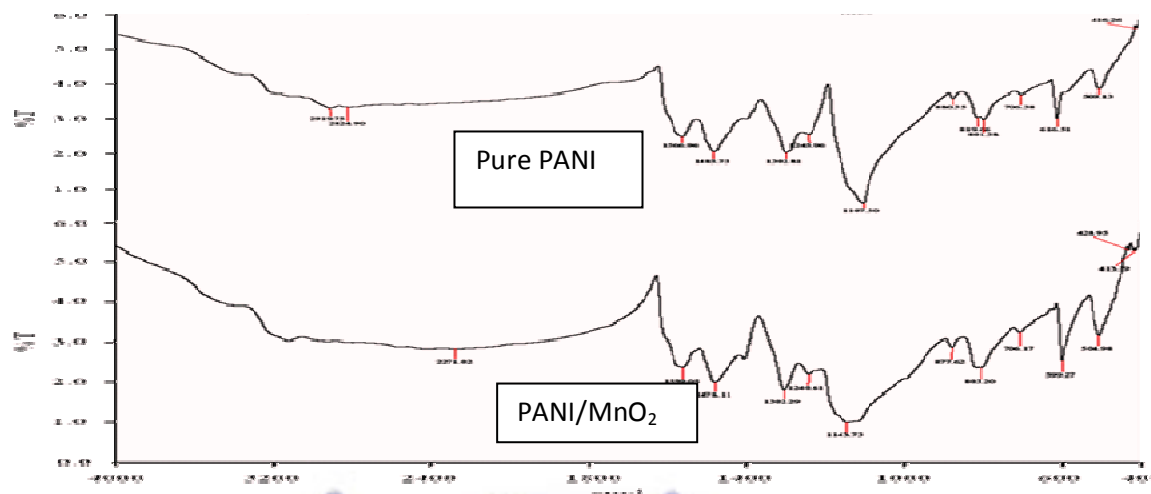
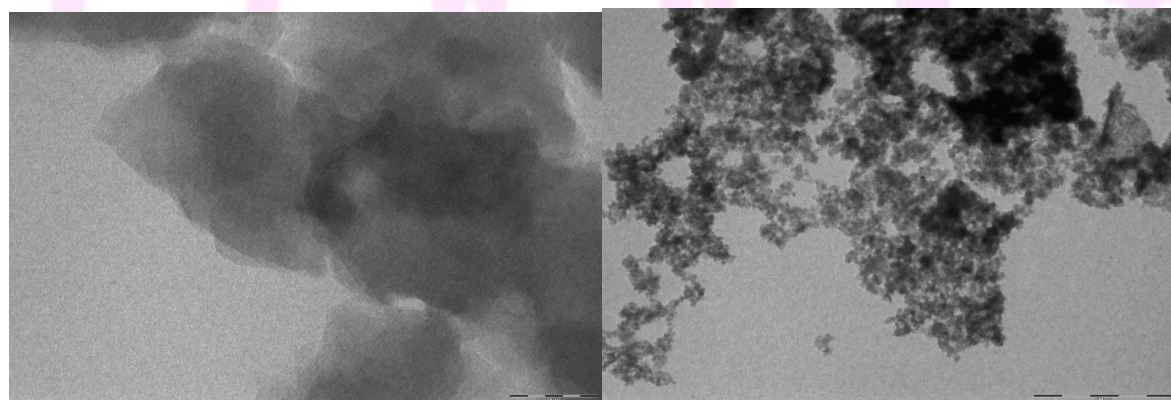


Fig 1. Shows the FT-IR spectra pure PANI, & PANI/MnO₂ nanocomposite. PANI samples show specific stretching vibrations for the different structural forms of PANI. The specific groups of PANI and their IR vibration frequencies from the literature are given below:

1. Absorption band near 2900 cm⁻¹ is assigned to aliphatic C-H stretching of the Polymer
2. Quinonoid ring - 1587 cm⁻¹, Benzenoid ring - 1510 cm⁻¹
3. C-N stretching - ~1380 cm⁻¹
4. Combination modes of benzenoid and quinonoid unit - 1150 cm⁻¹
5. SO₃ stretching frequency of the various dopant acids - 1100 cm⁻¹
6. Weak absorption band for MnO₂ 415 cm⁻¹

All the spectra show the characteristics band of PANI. Thus, the IR study clearly indicates that MnO₂ are definitely incorporated into the polymer matrix.

3.2. TEM MICROGRAPH:



a. Pure PANI

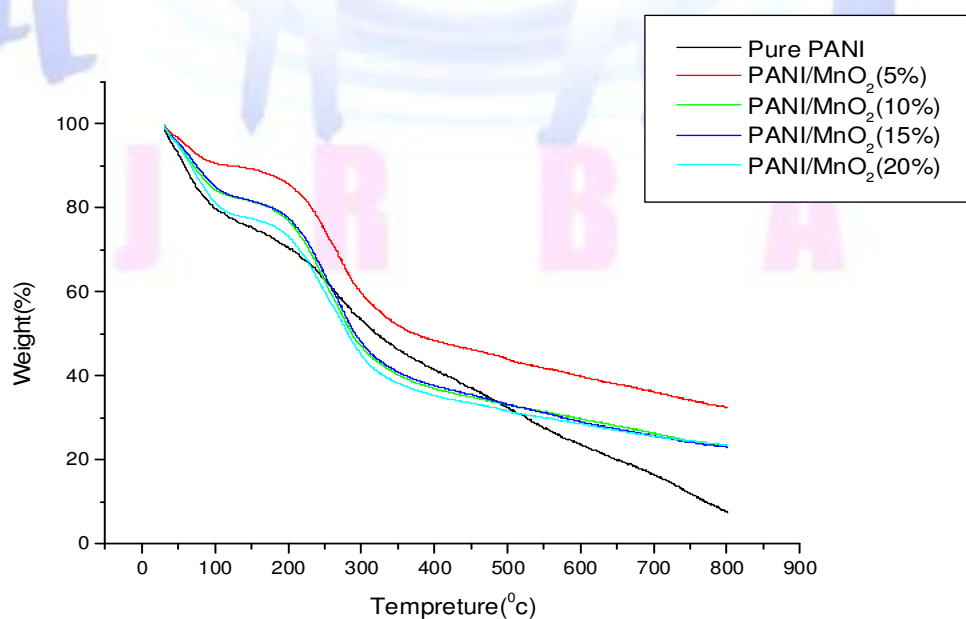
b. PANI/MnO₂

Fig.2. TEM micrograph of Pure PANI and PANI/MnO₂ nanocomposite.



From the fig 2. it is clear that PANI/ MnO₂ nanocomposite are in the nanorange with diameter 20nm. The particle size of PANI/MnO₂ is in 55nm scale and that of pure PANI is 100nm scale.

3.3. TGA THERMOGRAPH: The TGA measurements of PANI/MnO₂ nanocomposites show that MnO₂ nanoparticles may improve the thermal stability of these nanocomposites. The TGA was performed under nitrogen atmosphere to minimize undesired mass increase due to the oxidation reactions in the ferrite, and PANI be thermally decomposed almost completely. Fig. 3. Shows the TGA curves of PANI/ MnO₂ nanocomposites compared with free PANI. TGA curve of free PANI show that around 93 % in weight was lost when the sample was heated from room-temperature up to 800 C°. The decomposition temperatures obtained from thermograms of pure PANI exhibits two stage weight-loss behaviour. The first step at 38 to 150 C° which is due to expulsion of water molecules, the evaporation of residual solvents such as methanol, acid and small molecules from polymer structure. The weight loses during this stage is about 11.67%. The second step at 263 -800 C° shows decomposition or thermal degradation of the polymer, and has the great weight loss of about 93%. The decomposition temperatures obtained from thermograms of PANI/ MnO₂ nanocomposites exhibit two stage weight-loss behaviour. The first step is due to expulsion of water molecules, the evaporation of residual solvents such as methanol from polymer matrix, while the second step is a decomposition step. The two stage weight loss of these nanocomposites is listed in Table 6 together with the pure PANI. The weight loss of all samples which heated from room temperature up to 800C° is also presented. The weight loss at all stage is much less for nanocomposites compared to that of pure PANI. The result of PANI/ MnO₂ nanocomposite is in agreement with that recorded in literature .The difference between PANI/ MnO₂ nanocomposites in weight loss Table 6 may be due to the difference in their chemical and geometrical nature.





4. CONCLUSIONS:

Polyaniline-coated cadmium supplied nanocomposites have been synthesized via chemical oxidation technique. The concentration of the MnO₂ in nanocomposites was low as a very weak vibration absorption peak of Mn–O bonding at 414 cm⁻¹ is observed in the FTIR spectrum. The average size of the nanocomposites is estimated to be 55 nm as observed in the TEM micrograph. The thermal stability for the nanocomposites has been improved as major mass losses occurred at higher decomposition temperature as compared to the pure polymer in the TGA profile.

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