The Role of Nanotio2 on the Physical and Chemical Properties of Poly (Aniline)

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***Abstract*: Polymer nano composites made of poly (aniline) (PANI) with nano TiO_2 was prepared effectively by dispersing the inorganic nano layers of nano materials onto organic PANI matrix via in situ free radical polymerization with peroxodisulpahte (PDS) as individual initiator under different experimental conditions like variation in different wt% of nanomaterial. The functional group analysis was done by Fourier Transform Infrared Spectroscopy. Thermo gravimetric (TGA) analysis counseled the thermal stability of nano composites. Conductivity study was also done .The morphology of the polymer nano composite (PNC) has been studied by HRTEM.**

Keywords: ***Polymer nano composite; poly (aniline); TGA; conductivity.***

1. INTRODUCTION

The composite materials of conducting polymer and nano size materials integrate the thermal, mechanical, optical, electrical and magnetic properties. Such a conducting polymer nano composites are found applications in different fields like science, engineering, electronics and medicine. Hence, the polymer chemists turned their attention towards the synthesis and characterizations of conducting polymer nano composites. Poly (aniline) (PANI) is a first member in aromatic amine containing conducting polymer series. The backbone structure of PANI is built up by various forms like benzenoid, quinonoid and semi-quinonoid. Among them, benzenoid and quinonoid forms are the most stable forms and which can predict the structure and properties particularly, electrical property of PANI. The electrical property of PANI can be altered by the addition of 1D nano materials via adjusting the % of benzenoid and quinonoid forms of PANI and hence the electrical conductivity of PANI has increased to the metallic regime with improved thermal stability. Let us do review the literature available regarding PANI with 1D nano materials to form PANI/nano composites. Xiang et al. [1] reported the PANI/Fe_3O_4 nano composite by template method and they characterized the same by TEM, WAXD, and AFM images. Yilmaz and co-workers synthesized MWCNT filled/doped PANI and they studied about SEM, FTIR, XRD, conductivity measurements and TGA of the same [2]. Sol-gel method was adopted for the synthesis of PANI/Silica nano hybrid composites [3]. Chang and research team [4] published the results on PANI/Au/MWCNT nano composites for ammonia gas detection purpose. Recently, Ma et al. [5] synthesized and characterized the PANI/$HTiNbO_5$ nano composite. PANI/MoO_3 nano hybrid was synthesized and characterized through FTIR, XRD, TGA and NMR techniques [6]. In the year 2008, Neelgund et al. [7] reported the PANI/Silica nano composite with thermal and morphological characterizations. PANI/TiO_2 QCM sensor was synthesized and its thermal behavior was studied [8]. Recently, various methods are introduced to synthesis, characterization and properties of PANI/ nano composites [9-23]. Feng et al. [24] studied the photo conducting behavior of PANI/TiO_2 nano composite. In the present investigation, we took this job as a challenge and we successfully synthesized PANI/TiO_2 nanocomposites and characterized the same and analyze the comparative Physical-Chemical properties.

2. EXPERIMENTAL PROCEDURE

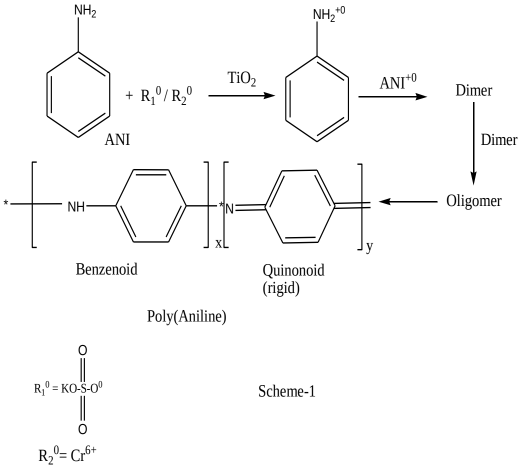
2.1 Materials

Aniline (ANI) monomer was purchased from Merck, India. In order to remove the impurities present in ANI, it was purified prior to polymerization reaction by distillation process. Hydrochloric acid (HCl, Reachem, India), Peroxy disulphate (PDS), TiO_2 (Ottokemi, India) and were used without subjecting them to further purification process.

2.2 Sample preparation

20 ml of 1M ANI (in 1M HCl) was taken in a polymer tube and de-aerated for 30 min. The polymerization was initiated by the addition of 20 ml of 0.10 M pre-aerated oxidizing agent such as PDS. The time of adding the oxidizing agent was the starting time of the reaction. The reaction mixture was found to turn green in color and visible appearance of the polymer formation was noticed. After 2 hours of polymerization reaction at 45°C, air was blown into the polymer tube to freeze further reaction [25].The formed PANI was filtered through already weighed G4 sintered crucible. The difference in weight gave the weight of the formed polymer. The same method

was adopted for the synthesis of PANI nano composites using 1% weight of TiO_2 with PDS as the initiator also. The reaction is mentioned in Scheme-1.



Scheme-1

2.3 Instrumentation

The polymer nano composites synthesized and analyzed above were subjected to various analytical characterizations like FTIR, TGA, HRTEM and conductivity measurements. FTIR spectra of PANI samples were recorded, using Shimadzu 8400S FTIR spectrophotometer instrument by KBr pelletisation method. The structure of PANI studied by PDS as a chemical initiator was confirmed by FTIR spectroscopy. TGA analysis was performed under air purge at the heating rate of 10º C/min by using SDT 2960, TA instrument. HRTEM was recorded for 5% weight of clay loaded PANI nano composite by using a TEM 3010, a product of JEOL. The Standard Four Probe instrument measured the d.c. conductivity value of samples.

3. RESULT AND DISCUSSION

3.1 FTIR spectroscopy

The structure of PANI/TiO_2 synthesized by PDS as an individual chemical initiator was analyzed by FTIR spectroscopy. A peak at 1563 cm^{-1} was due to the quinonoid structure of PANI. Another sharp peak at 1487 cm^{-1} was responsible for benzenoid structure of PANI. The peak at 822 cm^{-1} was the evidence of C-H out of plane bending vibration. Fig.1 shows the FTIR spectrum of PDS initiated ANI polymerization in the presence of TiO_2. One can observe the same peaks in the two spectra. Apart from these peaks, one more peak appeared around 500 cm^{-1} that confirmed the presence of metal-oxide stretching. This peak confirmed the PANI- TiO_2 nanocomposite formation.

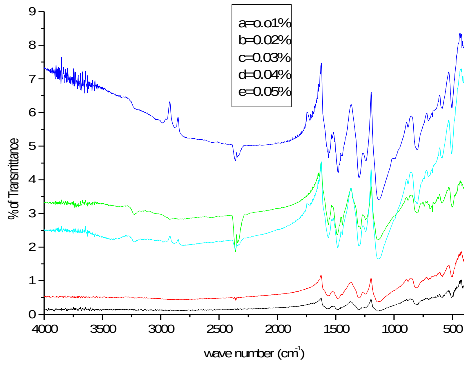


Fig.1 FTIR Spectra of PANI/TiO_2

3.2 Thermal Analysis (TGA)

The thermal stability of PANI nano composite synthesized by PDS as chemical initiator can be analyzed by TGA method. TGA of PANI loaded at different weight percentage of TiO_2 is shown in Fig.2. The thermogram shows a three step degradation process. This confirmed the thermal stability of PANI/TiO_2 nano composite. One interesting point noted after degradation above 700^0 C, PANI/TiO_2 nano composite system showed approximately 50% of the sample weight remained. As the above case, while increasing the weight percentage of TiO_2, the weight percentage residue that remained above 700^0 C was also increased. The added TiO_2 improved again the char forming nature (flame retardant nature) of PANI as that of clay. At higher weight percentage of TiO_2 PANI showed maximum thermal stability with highest weight percentage residue remained above 700^0 C. This is due to the compact structure, higher molecular weight of PANI, interaction of TiO_2 with PANI chains in the inner layer space of TiO_2 and PANI coated TiO_2.

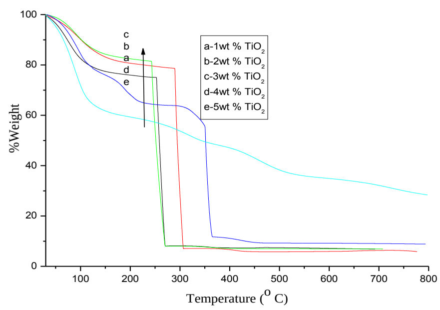


Fig.2. TGA of PANI/TiO_2 nano composites

3.3 HRTEM Analysis

The Fig.3 (a) indicated that TiO_2 had a layered structure with the diameter of < 7 nm and part of them was exfoliated by PANI backbone. The PANI-TiO_2 nano composite also showed the layered structure even after in-situ polymerization reaction. This informed us that the intercalation of PANI chains into the basal spacing of TiO_2 without exfoliation or de-lamination of layered structure of TiO_2. Remaining photographs (Fig.3b, c&d) indicated the dispersion of TiO_2 nano particles on PANI backbone with or without agglomeration (due to higher % weight of TiO_2 loading). The SAED report indicates that the polymer nano composite was having a semi crystalline structure. This confirmed the dispersion of nano sized TiO_2 particles of length approximately of 25 nm uniformly on the PANI backbone. The total crystallinity of polymer nano composite was also increased.

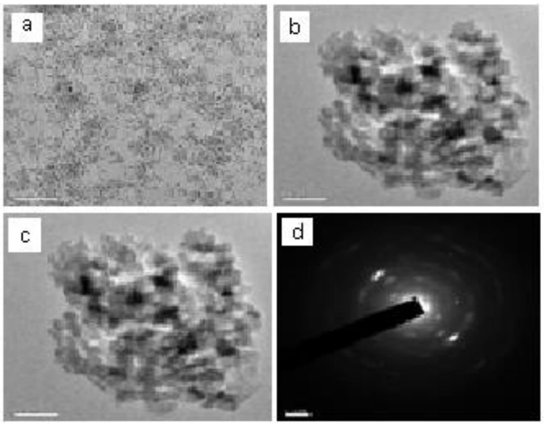


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Fig.3. HRTEM of PANI/TiO_2

3.4 Conductivity measurement

The d.c. conductivity values of pure PANI and PANI/TiO_2 system were calculated. The electrical conductivity of pure PANI is $2.2x10^{-4}$ S/cm. As the weight percentage of nanomaterial increases, the electrical conductivity values were also increased it was found to be $4.2x10^{-4}$ S/cm. This proved that the added nano material not only increased the thermal stability but also increased the conductivity, by acting as a dopant or host material. This is in accordance with our earlier publication [26].

TABLE.1 Electrical conductivity of PANI/TiO_2

SI.no	Sample	d.c Conductivity 10^{-4} S/cm
1	PANI+TiO_2 (0 wt %)	2.2
2	PANI+TiO_2 (1 wt %)	3.3
3	PANI+TiO_2 (2 wt %)	3.6
4	PANI+TiO_2 (3 wt %)	3.8
5	PANI+TiO_2 (4 wt %)	4.0
6	PANI+TiO_2 (5 wt %)	4.2

4. CONCLUSIONS

The following important points are summarized here as conclusions. PANI/TiO_2 nanocomposites are synthesized successfully by in-situ polymerization method. The initial degradation as well as the PANI backbone degradation temperature was increased for the PANI/TiO_2 nano composite system and concluded that PANI/TiO_2 system has better thermal stability. HRTEM confirmed the dispersion of TiO_2 on the PANI matrix and TiO_2 had a layered structure with the diameter of < 7 nm. The d.c. conductivity values of nano composite systems were increased with the increase of (weight percentage of nanomaterial) which confirmed the catalytic effect as well as oxidizing/ dopant nature of nanomaterial with PANI chains.

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