

Thermal and Structural Property of Poly (Aniline) / Clay and TiO₂ Nano composites

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Abstract-- Polymer nano composites made of poly(aniline) (PANI) with layered clay and TiO₂ were prepared effectively by dispersing the inorganic nano layers of nano materials onto organic PANI matrix via in situ free radical polymerization with peroxodisulphate (PDS) and PDC as individual initiator under different experimental conditions like variation in time, monomer and concentration of initiator. The functional group analysis was done by Fourier Transform Infrared Spectroscopy. Thermogravimetric (TGA) analysis counseled the thermal stability of nano composites. The topographical image of the polymer nano composite materials was studied by high resolution transmission electron microscopy (HRTEM). Comparison was also done.

Keywords-- FTIR, Hectorite Clay, HRTEM, PANI- PolyAniline, TiO₂, TGA.

I. 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/Fe₃O₄ 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/HTiNbO₅ nano composite. PANI/MoO₃ nano hybrid was synthesized and characterized through FTIR, XRD, TGA and NMR techniques[6] Photoluminescence and electrochemistry of derivatives of PANI and TiO₂ nano composite was reported in the literature.[7] In the year 2008, Neelgund et al[8] reported the PANI/Silica nano composite

with thermal and morphological characterizations. PANI/TiO₂ QCM sensor was synthesized and its thermal behavior was studied[9]. Other authors also studied about PANI nano composites[10-28]. Clay is abundantly available on the earth with super power properties. Moreover, clay is economically cheaper material and eco-friendly. This is the reason for selecting clay as a 1D nano material for our study. One of the most recent nanomaterials that has been attracted a great attention due to its unique properties is titanium dioxide. Feng et al [29] studied the photo conducting behavior of PANI/TiO₂ nano composite. Other authors also studied about PANI-TiO₂ nano composite [30-32]. This paper describes the synthesis and characterization of organic / inorganic composite material from TiO₂ and Clay nano particles and PANI. This is the first time we select an easy synthesis technique and understand the unique physics of conducting polymer nanocomposites and the novel materials can be designed for new applications such as photo voltaic and opto electronic applications.

II. EXPERIMENTAL

A. 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,) potassium di chromate (K₂Cr₂O₇) TiO₂ (Ottokemi, India) and were used without subjecting them to further purification process. Clay, Hectorite type with Li⁺ ion in the inter layer space, was collected from KCET campus and subjected to acid, base treatment and water wash to obtain a neutral pH.

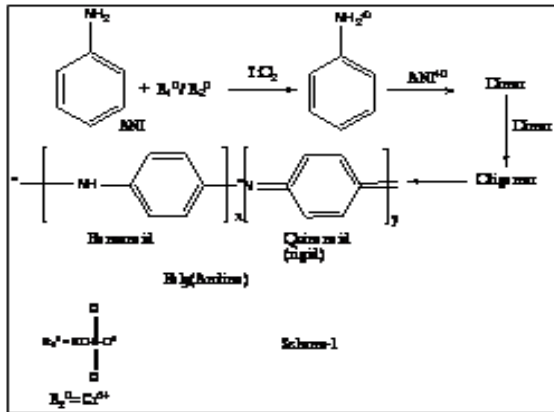
B. Synthesis of PANI/ TiO₂ and PANI/Clay nanocomposites

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 45⁰ C, air was blown into the polymer tube to freeze further reaction [33]. 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 nanocomposites using 1 % weight of clay/TiO₂ with PDS and PDC as the initiator. The reaction is mentioned in Scheme-1.

C. Characterizations

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 8400 S 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 10° 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.



III. RESULTS AND DISCUSSION

The added nano material simply acts as a filler or catalyst or dopant and interacts with the PANI chains. During the polymerization process intercalation of ANI into the basal spacing of Clay/ TiO₂ takes place and hence exfoliation or de-lamination of Clay /TiO₂ layer is possible. Among which intercalation of ANI into the basal spacing of Clay/TiO₂ without exfoliation or de-lamination is also possible. At lower % weight of nanomaterial, exfoliation or de-lamination is possible whereas at higher % weight of nanomaterial, due to agglomeration process, intercalation is the only possible reaction (i.e) insertion of PANI chains into the basal spacing of Clay/TiO₂. Formation of exfoliation or de-lamination or intercalation structure of Clay/TiO₂ can be further confirmed by HRTEM measurements in the forth coming sessions.

A. Fourier Transform Infrared Spectroscopy

The structure of PANI synthesized by PDS and PDC 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 and Fig.2 show the FTIR spectrum of PDS initiated ANI polymerization in the presence of clay and TiO₂ respectively. 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 confirmed the PANI-Clay and PANI-TiO₂ nano composite formation.

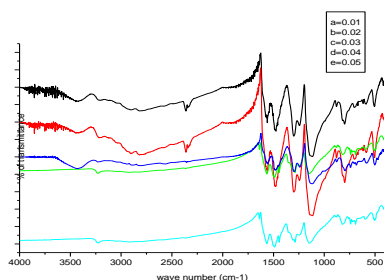


Figure 1: FTIR spectrum for Nanomaterial variation of PANI/Clay

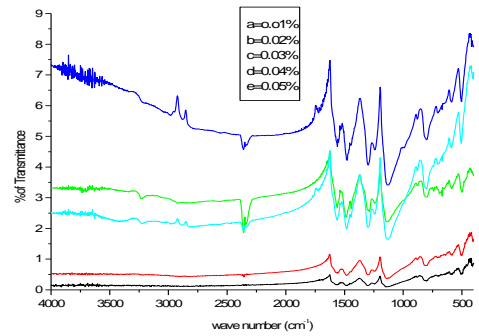


Figure 2: FTIR spectrum for Nanomaterial variation of PANI/TiO₂.

B. Thermo gravimetric Analysis

The thermal stability of PANI/Clay nano composite synthesized by PDC as chemical initiator can be analyzed by TGA method. TGA of PANI loaded at different (% weight of clay) was shown in Fig. 3. The thermogram showed a three step degradation process. The first minor weight loss step was due to the removal of physisorbed water molecules and moisture. The second minor weight loss step was due to the removal of dopant from PANI backbone and the slight degradation of benzenoid structure of PANI. The third weight loss step was due to the degradation of PANI. After degradation and above 700° C, the PANI/Clay nanocomposite system showed approximately 5% weight of the sample remained. This confirmed the thermal stability of PANI/Clay nanocomposite. While increasing the (% weight of Clay), the % weight residue remains above 700° C is also increased. The added clay improved the char forming nature of PANI. Sung et al [36] reported that Poly(o-ethoxy aniline)/Clay nanocomposite system and showed higher thermal stability than the pristine poly(o-ethoxy aniline). Our results are in accordance with the literature [37,38].

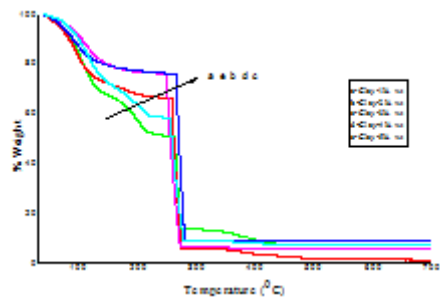


Figure 3: TGA of PANI with different Wt % of Clay

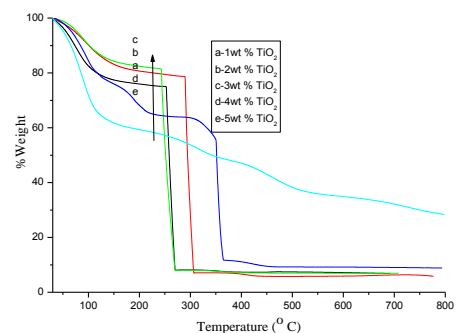


Figure 4: TGA of PANI with different Wt % of TiO₂ nanomaterial

TGA of PANI loaded at different % weight of TiO₂ is shown in Fig. 4. The thermogram again shows a three step degradation process. This confirmed the thermal stability of PANI/TiO₂ nano composite. One interesting point noted after degradation above 700⁰ C, PANI/TiO₂ nano composite system showed approximately 50% of the sample weight remained. So we report that among the two nanocomposites PANI /TiO₂ is more thermally stable than the PANI /Clay. As the above case, while increasing the % weight of TiO₂, the % weight residue that remained above 700⁰ C was also increased. The added TiO₂ improved again the char forming nature (flame retardant nature) of PANI as that of clay. At higher % weight of TiO₂ PANI showed maximum thermal stability with highest % weight residue remained above 700⁰ C. This is due to the compact structure, higher molecular weight of PANI, interaction of TiO₂ with PANI chains in the inter layer space of TiO₂ and PANI coated TiO₂

C. HRTEM

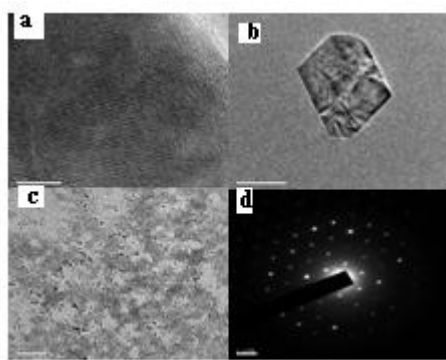


Figure 5: HRTEM of PANI/Clay

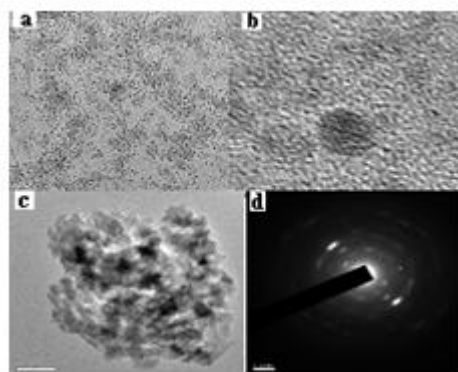


Figure 6: HRTEM of PANI/TiO₂

Figure 5 and 6 indicated the HRTEM photograph of PANI loaded with 5% weight of clay and TiO₂. The photograph (Fig.5a) indicated that clay particles had a layered structure with the length of 25 nm and part of them was exfoliated by PANI backbone (Figs. 5c and d). Remaining photographs indicated the dispersion of clay nano particles on PANI backbone with agglomeration (Figs.6b and c). The SAED (Fig. 5d) indicated that the polymer nano composite had a semi-crystalline structure. This confirmed the dispersion of nano sized clay particles (of length 25 nm approximately) on PANI backbone. Also, the crystallinity of polymer nano composite was increased. The exfoliation as well as the agglomeration structure of conducting polymer / metal oxides nano composites were discussed by our research team [37,38]. The present system also followed the same concepts. The Fig. 6a indicated that TiO₂ had a layered structure with the diameter of

< 7 nm and part of them was exfoliated by PANI backbone. The PANI-TiO₂ 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 TiO₂ without exfoliation or de-lamination of layered structure of TiO₂. Remaining photographs (Fig 6b&c) indicated the dispersion of TiO₂ nano particles on PANI backbone with or without agglomeration (due to higher % weight of TiO₂ loading). The SAED report indicates that the polymer nano composite was having a semi crystalline structure. This confirmed the dispersion of nano sized TiO₂ particles of length approximately of 25 nm uniformly on the PANI backbone. The total crystallinity of polymer nano composite was also increased.

D. Conductivity

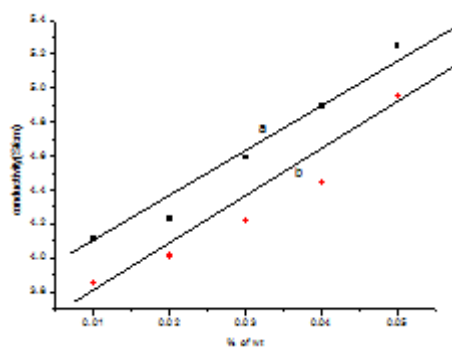


Figure 7: Conductivity variation with % of wt of nanomaterial

a) PANI /TiO₂ b) PANI/Clay

The d.c. conductivity values of PANI/Clay and PANI/TiO₂ system were calculated using four probe method and it was found to be 3.8x10⁻⁴ S/cm for clay and 4.2x10⁻⁴ S/cm. The variation of conductivity with wt % was shown in Fig 7a and b. As the % weight of nanomaterial increases, the electrical conductivity values were also increased in both the cases. 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 [38]. The d.c conductivity was slightly higher for the PANI/TiO₂ nano composite

CONCLUSION

From the above study the following important points are summarized here as conclusions. PANI/Hectorite clay and PANI/TiO₂ nanocomposites were synthesized successfully by in-situ polymerization method. The initial degradation as well as the PANI backbone degradation temperature was increased for both the PANI/Clay and PANI/TiO₂ nano composite system and concluded that PANI/TiO₂ system showed better thermal stability than that of PANI/clay nanocomposite. HRTEM confirmed the dispersion of clay platelets of 25 nm on the PANI matrix and TiO₂ 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 of nanomaterial) which confirmed the catalytic effect as well as oxidizing/ dopant nature of nanomaterial with PANI chains.

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