Effect of Nanosized Clay and TiO\textsubscript{2} on the Structure and Thermal Stability of Poly(aniline-co-o-toluidine)

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The present investigation is primarily focused on the study of effect of nanosized clay and TiO\textsubscript{2} on the structure and thermal properties of electrically conducting poly (aniline-co-o-toluidine)/nanocomposite system. These nanocomposites are synthesized by the \textit{in situ} oxidative polymerization method with peroxy disulphate as a lone chemical initiator, HCl as an external dopant and clay and TiO\textsubscript{2} as a host material. The nanocomposites are characterized by analytical tools like Fourier transform infrared, Keithley instrument, thermal gravimetric analysis, and high resolution transmission electron microscopy.

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1. Introduction

Recently, the chemists are very much interested in synthesis and analysis of organic-inorganic host-guest matrix because of their novel properties. Meanwhile the synthetic polymer chemists are keen interested in the synthesis and characterizations of polymer-layered nanomaterials composite with boosted physical and chemical properties. In that series poly (aniline) (PANI), an electronic conducting polymer plays a vital role in the latest human being’s luxurious life. For example, optical fiber based humidity sensor was made up by PANI copolymer \cite{1}. Aniline-anthranilic acid copolymer film is being used as a pH sensor \cite{2}. For such a super sensing activity, the structure of polymer is primarily important. Hence, many forces like nature of dopant, initiator, temperature and reaction time can alter the structure of polymer/copolymer. The structure of such a conducting polymer/copolymer can be nicely tuned with the aid of nanosized inorganic host materials. Recently, aniline copolymer intercalated meso structured MnO\textsubscript{2} composite was reported by Wang et al. \cite{3}. Basavaraja and co-workers \cite{4} studied the effect of Al\textsubscript{2}O\textsubscript{3} on the structure of aniline-NIPAAm copolymer. PANI intercalated Au nanocomposite was prepared for NH\textsubscript{3} gas sensing \cite{5}. Improved electro-rheological effect of PANI intercalated clay nanocomposite suspension was reported by Lim et al. \cite{6}. Alcohol sensors made up by V\textsubscript{2}O\textsubscript{5}-PANI nanocomposite with high toughness has been reported in the literature \cite{7}. PANI and its copolymers are made into nanocomposites with different inorganic host matrix \cite{8-10}. The availability, eco-friendly, inexpensive, easy surface modification process and catalytic activity of clay and TiO\textsubscript{2} urged us to use clay and TiO\textsubscript{2} as a nanomaterial in the present investigation.

Moreover, this method is economically cheaper than the chemical method with more accuracy. FTIR spectroscopy is a useful tool in various science and engineering fields, because of its high sensitivity or detectivity towards traces amount of sample, low noise to signal ratio and moreover this method is an easy and inexpensive one. FTIR spectroscopy is used in both qualitative \cite{11-15} quantitative analysis \cite{16-28}. For the first time, we are reporting here about the effect of clay and TiO\textsubscript{2} on the structure of aniline copolymer and the results are expressed.

2. Experimental

2.1. Materials

Aniline (ANI, M\textsubscript{1}), o-toluidine (OT, M\textsubscript{2}) were purchased from Merck, India and distilled under vacuum before use. Potassium peroxydisulphate (PDS), titanium oxide (TiO\textsubscript{2}) (Ottokemi, India) and hydrochloric acid (Rea Chem, India) were used as received. Hectorite type Clay with Li\textsuperscript{+} ion in the inner layer space was collected from our KCET campus and used after acid, base washing followed by washing with doubly distilled (DD) water. Thus, purified clay samples are dried and stored in a zipper bag. The clay details are indicated in our earlier publication \cite{29}.

2.2. Sample preparation method

Required quantity of ANI and OT solutions were taken in a polymer tube and de-aerated for 30 min. The copolymerization was initiated by the addition of calculated volumes of pre-aerated oxidizing agent such as PDS. The time of adding the oxidizing agent was taken as 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 h, air was blown into the polymer tube to freeze further reaction. The copolymerization was carried out at different reaction time and for different temperatures. Thus formed poly(ANI-co-OT) was filtered through already weighed G4 sintered crucible. The difference in weight gave the weight of copolymer formed. The same method was followed for the preparation of poly(ANI-co-OT) nanocomposites in the presence of different (weight% of clay and TiO$_2$).

2.3. Measurements

FTIR spectra of PANI samples were measured by the KBr pellet technique in the range of 4000–400/cm with Shimadzu 8400 S FTIR spectrophotometer instrument. The baseline correction was made carefully and the area of the peaks was determined using FTIR software. We know that PANI backbone is made up of benzenoid, quinonoid and semiquinonoid forms. The amount of formation of semiquinonoid form is negligible because it can be readily oxidized or reduced. Hence, we can write,

Structure of PANI = % amino form (benzenoid form) + % imino form (quinonoid form). \( (1) \)

Thermal gravimetric analysis (TGA) was performed under air purge at the heating rate of 10°C/min by using SDT 2960 simultaneous TGA and differential scanning calorimetry (DSC), TA instruments. Conductivity was determined by standard four probe method. High resolution transmission electron microscopy (HRTEM) was recorded by using TEM 3010 Transmission Electron Microscopy instrument, a product of JEOL.

3. Results and discussion

3.1. FTIR study

Figure 1 showed the FTIR spectra of 1 to 5 wt% of clay loaded poly(ANI-co-OT) systems. The important peaks are characterized below. Spectrum showed many peaks among which we are very much interested in peaks appearing at 799, 1482, and 1563 cm$^{-1}$ corresponding to the C–H out of plane bending vibration, benzenoid stretching, and quinonoid stretching, respectively. Peaks appearing at the lower wave number are corresponding to the metal oxide stretching of clay. Figure 2 showed the FTIR spectra of 1 to 5 wt% of TiO$_2$ loaded poly(ANI-co-OT) systems. Here also one can see the above-mentioned peaks, along with the 500 cm$^{-1}$ confirming the presence of TiO$_2$.

![Fig. 1. FTIR spectrum of poly(ANI-co-OT) loaded with clay at (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, (d) 4 wt%, (e) 5 wt%.](image1)

![Fig. 2. FTIR spectrum of poly(ANI-co-MT) loaded with TiO$_2$ at (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, (d) 4 wt%, (e) 5 wt%.](image2)

3.2. Effect of time on $R_p$ and FTIR-RI of PANI copolymers

Poly(ANI-co-OT)/clay nanocomposites were synthesized under different intervals of time. Variation in reaction time affected the $R_p$. While varying the reaction time from 3000 to 12000 s the other experimental conditions were kept constant. While increasing the time the $R_p$ value was found to be decreased. This is due to the bulk number in the denominator of $R_p$ equation. This is represented in Fig. 3a. Similarly, in the case of poly(ANI-co-OT)/TiO$_2$ the $R_p$ value was decreased with increase in time (Fig. 3b). In comparison, the PANI-TiO$_2$ containing copolymer system produced higher $R_p$ values than the copolymer clay system. Variation in reaction time affected the structure of copolymer, too. This is explained as follows: (1) Increase of reaction time leads to the possible interaction between monomer radical cations and free radicals with monomers. (2) Internal structural rearrangements.

3.3. Effect of [M] on $R_p$ and FTIR-RI of PANI copolymers

The [M$_1$/M$_2$] was varied between 0.40 and 1.60 while the other experimental conditions were kept constant. Here one can see that while increasing the [M], the $R_p$ is increased simultaneously. This is due to the following reasons. (1) Availability of monomer radical cations for the chain growing process [23]. (2) Auto acceleration
Fig. 3. Effect of time on $R_p$, (a) (ANI-co-OT)/clay, (b) poly(ANI-co-OT)/TiO$_2$. [ANI] = 0.125 M, [OT] = 0.125 M, [PDS] = 0.025 M; temperature = 45$^\circ$C, wt% of clay and TiO$_2$ = 3.

Fig. 4. Effect of $[M_1/M_2]$ on $R_p$, (a) poly(ANI-co-OT)/clay systems, (b) poly(ANI-co-OT)/TiO$_2$ system. [PDS] = 0.025 M; time = 2 h; temperature = 45$^\circ$C, wt% of nanomaterial = 3.

The plot indicated a straight line with the slope value of 0.95. This indicates that copolymerization of ANI with OT in the presence of clay proceeds through 1.0 order of reaction with respect to $[M_1/M_2]$. The $R_p$ can be written as follows: $R_p \propto [M_1/M_2]^{0.95}$. Similarly, in the case of poly(ANI-co-OT)/TiO$_2$, the $R_p$ value increased with the [M]. In order to find out the order of reaction, the slope value was determined from the graph drawn between log[M$_1$/M$_2$] and log $R_p$ as 0.98 (Fig. 4b). This confirmed the 1.0 order of reaction with respect to $[M_1/M_2]$. The $R_p$ can be written as follows: $R_p \propto [M_1/M_2]^{0.98}$. On comparison, the TiO$_2$ containing copolymer nanocomposite system produced higher $R_p$ values than the clay containing copolymer nanocomposite. The order of reaction indicated the uni-molecular termination reaction.

3.4. Effect of [PDS] on $R_p$ and FTIR-RI of PANI copolymers

The [PDS] was varied between $1 \times 10^{-2}$ and $3.5 \times 10^{-2}$ M while keeping other experimental conditions constant. While increasing the [PDS] the $R_p$ was increased abnormally. This is because of (1) production of more number of free radicals from PDS, (2) Auto acceleration effect due to formed copolymer surface. (3) Surface catalytic effect of nanomaterials. The order of reaction was determined by plotting log[PDS] vs. log $R_p$ (Fig. 5a). The plot indicated a linear increasing trend with a slope value of 0.48 in the case of poly(ANI-co-OT)/clay. The same type of plot (Fig. 5b) was made for poly(ANI-co-OT)/TiO$_2$ system and the slope value was determined as 0.43. These values confirmed the 0.50 order of reaction with respect to [PDS] for both the copolymers. It means that 0.50 mol of PDS is required to initiate one mole of monomer in the presence of clay. In comparison, the clay system exhibited higher $R_p$ values.

Fig. 5. Effect of [PDS] on $R_p$, (a) poly(ANI-co-OT)/clay system, (b) poly(ANI-co-OT)/TiO$_2$ system. [ANI] = 0.125 M, [OT] = 0.125 M; time = 2 h; temperature = 45$^\circ$C, wt% of nanomaterial = 3.

3.5. Effect of temperature on $R_p$ and FTIR-RI of PANI copolymers

ANI and OT were copolymerized in the presence of clay under different temperatures. The temperature was varied between 273 and 343 K. During the temperature variation, the other experimental conditions were constant. While increasing the temperature the $R_p$ value was increased. This is due to the following reasons. (1) Thermal initiation leads to formation of more and more monomer radical cations. (2) At higher temperature the dissociation rate of PDS was increased and hence production of more radicals. (3) Over oxidation or secondary oxidation led to the formation of oxidized quinonoid structure. (4) At higher temperature the clay moieties can swell more and more in the given reaction medium and the formation of monomer intercalated...
structure which can be readily oxidized to form monomer radical cations. The energy of activation ($E_a$) for the formation of copolymer structure can be determined by the famous Arrhenius equation. The plot was made between $1/T$ and $\log R_p$ (Fig. 6a) to determine the $E_a$.

From the slope value of the above-mentioned plots, the $E_a$ value was determined as 114.5 kJ/mol for ANI-OT-clay system. Similarly, in the copolymerization of ANI with TiO$_2$, the $E_a$ value was determined as 108.6 kJ/mol (Fig. 6b). In comparison, the later system yielded lower $E_a$ value and resulted with higher $R_p$ values.

### 3.6. Effect of wt% of clay and TiO$_2$ on $R_p$ and FTIR-RI of PANI copolymers

During the copolymerization of ANI with OT, the wt% of clay was varied from 1 to 5% by keeping the other experimental conditions as constant. While increasing the wt% of clay the $R_p$ value was found to be increased. This is due to the following reasons. (1) At lower wt% loading of nanosized clay, there is a chance for the exfoliation of clay stacks by the monomers and more and more active surface area will be available for the initiation purpose. (2) Surface catalytic effect of nanosized clay can initiate the monomers [29]. (3) At higher wt% loading of clay, intercalation of more and more monomers into the basal spacing of clay stacks and results with monomer radical cations. In order to find out the order of polymerization reaction, Fig. 7a was made between $\log$(wt% of clay) and $\log R_p$. The plot showed a straight line with a slope value of 0.48 which confirmed the 0.50 order of reaction with respect to wt% of clay. This inferred that 0.50 mol of clay is required to initiate one mole of monomer. In the case of poly(ANI-co-OT)/TiO$_2$ system, the slope value was calculated as 0.52 from the plot of $\log$(wt% of TiO$_2$) vs. $\log R_p$ (Fig. 7b). Here also 0.50 mol of TiO$_2$ is required to initiate one mole of monomer. In comparison, the later system produced higher $R_p$ values than the ANI-OT-clay system. This referred that $R_p$ depends on the amount of the monomer used but also the structure of the nanomaterials used. The increase in $R_p$ confirmed the role of nanomaterial as a catalyst through its surface effect. Currently, Anbarasan et al. [29] reported about the clay catalyzed synthesis of poly($\alpha$-naphthylamine), structurally similar to PANI, in which the $R_p$ showed the first order reaction with respect to wt% of clay.

### 3.7. Thermogravimetric analysis

The TGA of 1 wt% clay loaded poly(ANI-co-OT)/clay (Fig. 8a) nanocomposite system showed a three-step degradation process. The first minor weight loss around 100°C is due to the removal of moisture and physisorbed water molecules. The second minor weight loss is associated with the removal of chemisorbed water molecules and dopant from copolymer chain. The third major weight loss around 400°C is due to the degradation of copolymer chain. Above 700°C, it showed the residue of copolymer as 44.6% for 1 wt% of clay loaded copolymer and 58 wt% for 5 wt% of clay loaded copolymer, respectively. This indicated the improved thermal stability of copolymer nanocomposites.
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Fig. 9. TGA of poly(ANI-co-OT) loaded with TiO$_2$ (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, (d) 4 wt%, (e) 5 wt%.

of TiO$_2$ loaded with the poly(ANI-co-OT)/TiO$_2$ showed the same type of degradation process. The wt% residue remaining above 700°C was increased with the increase of wt% of TiO$_2$. TGA of 1 wt% of TiO$_2$ nanocomposite systems showed a three-step degradation process (Fig. 9). Above 700°C the residue remaining is 42% for 1 wt% of TiO$_2$ and 60% for 5 wt% of TiO$_2$.

3.8. Conductivity measurements

Conductivity measurements informed that the co-monomer caused steric effect and hence reduction in conductivity value of a copolymer. The change in conductivity value is explained by altering the chemical structure of copolymer. Particularly, while increasing the wt% of nanomaterial, the conductivity value was increased slightly due to the host matrix nature of the nanomaterial. The electrical conductivity is increased due to the (1) higher % content of quinonoid form due to secondary oxidation, (2) increase of polymer chain length by surface catalytic effect due to the large surface area of nanomaterial, (3) doping nature of nanomaterials, (4) auto acceleration effect caused by polymeric surface, (5) charge mobility on the metal oxide surface [30].

The 1 and 5 wt% clay loaded copolymers exhibited the conductivity value of $5 \times 10^{-4}$ and $6.8 \times 10^{-4}$ S/cm, respectively, and that of TiO$_2$ loaded systems exhibited the conductivity value of $5.8 \times 10^{-4}$ S/cm and $7.5 \times 10^{-4}$ S/cm, respectively. Buvaneswari and co-workers [31] clearly explained the reasons for decrease in conductivity value of copolymer than the homopolymer.

3.9. HRTEM

Figure 10 represented the HRTEM of poly(ANI-co-OT)/clay nanocomposites. Figure 10a represented the layered structure of clay with the length of 5 to 10 nm with less than 0.1 nm breath. The same HRTEM image indicated the intercalation of copolymer chains into the basal spacing of clay. Figure 10b confirmed the agglomerated structure with the size of 20-25 nm. Figure 10c declared the bundle-like agglomerated structure due to the 5 wt% (heavy) loading of clay. Figure 10d revealed the linear agglomeration of clay particles with the size of 50-55 nm. The uniform dispersion of clay particles onto the matrix of copolymer was shown in Fig. 10e. The selected area electron diffraction pattern (SAED) (Fig. 10f) of copolymer nanocomposites showed some bright dots for (111), (200), (220) planes on a scattered manner. This indicates that the copolymer nanocomposites have a semicrystalline structure.

Fig. 10. HRTEM of poly(ANI-co-OT)-5 wt% clay polymer nanocomposite system.

Fig. 11. HRTEM of poly(ANI-co-OT)-5 wt% TiO$_2$ polymer nanocomposite system.

Figure 11 indicated the HRTEM topography of poly(ANI-co-OT)/TiO$_2$ nanocomposite system. Figure 11a confirmed the layered structure [21] of TiO$_2$ with the length of 15-20 nm and with the breath of 0.1 nm. The dark area in the image confirmed the intercalation of copolymer into the interlayer space of TiO$_2$. The added TiO$_2$ uniformly distributed on the copolymer matrix without any agglomeration (Fig. 11b). Here the nanosized TiO$_2$ appeared as a distorted spherical morphology. Figure 11c revealed the distribution of agglomerated TiO$_2$ nanoparticle on the copolymer matrix. The agglomeration is due to the heavy loading of TiO$_2$. The agglomerated particles are having the size of 0.1 µm. The SAED pattern (Fig. 11d) exposed the bright spots
for (110), (101) planes in a random manner. This confirmed the less crystalline nature of poly(ANI-co-OT)/TiO$_2$ nanocomposite system.

4. Conclusions

From the above kinetic study, the important points are presented here as conclusions. (1) The copolymer nanocomposites were synthesized by in situ oxidative polymerization method. (2) The structure of copolymer was altered by the clay and TiO$_2$ through its surface catalytic role. (3) The $R_p$ and the FTIR-RI values were changed due to the change in the chemical structure of copolymer by the surface catalytic effect of clay and TiO$_2$. (4) The thermal stability of the copolymer was increased with the increase of wt% loading of clay and TiO$_2$ due to the intercalation of copolymer into the basal spacing of nanomaterial or exfoliation or delamination of nanomaterial stacks and dispersed on the copolymer matrix. (5) The conductivity value of the copolymer nanocomposite was increased as the wt% of nanomaterial increased.

References