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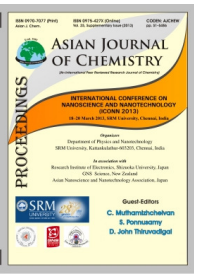

Optical and Morphological Studies on Novel Polyaniline-P_2O_5 Conductive Polymer Composites†

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Recently conducting polymer composites have attracted considerable interest due to their numerous applications. Present work reports the preparation of polyaniline polymeric material with P_2O_5 to form polyaniline-P_2O_5 composites by chemical oxidation method. FTIR analysis established the various modes of vibration due to diverse functional groups present in the composite and the presence of a strong interaction between P_2O_5 and polyaniline. The UV-VIS spectra confirmed the π-π^* and n-π^* transitions of the benzenoid and quinonoid structure of the composites. The linear optical nature was understood from the optical transmission spectrum. The XRD patterns exhibited a weak crystalline nature for the composites. Thermal stability of polyaniline-P_2O_5 was determined using TGA. The SEM images show the effect of P_2O_5 doping and on polyaniline morphology. EDAX was performed to confirm the presence of P_2O_5 and polyaniline. Surface topography of polyaniline-P_2O_5 composites were studied using AFM.

Key Words: Polymer composites, Polyaniline, Phosphorous pentaoxide, Thermal stability, SEM, Morphology.

INTRODUCTION

Conducting polymers with their distinctive electrical and optical properties have numerous potential applications such as sensors, rechargeable batteries, switchable membranes, optoelectronic devices, photo diodes and technological membranes[1,2]. Among the conducting polymers, polyaniline is unique due to its high conductivity, ease of synthesis, light weight, high stress, good environmental stability, low cost and along with low operational voltage making it a good candidate in the development of actuators[3-5]. Polyaniline can be synthesized by either oxidative chemical or electro chemical polymerization of monomer in liquid phase[6]. However, the major disadvantage of polyaniline is its insolubility in common organic solvents and its infusibility. One possible method for preparing soluble polyaniline is with the help of substituted groups[7,8].

Polyaniline can be prepared as a composite with the incorporation of various inorganic particles like Nb_2O_5[9], ZrO_2[10], Dy_2O_3[11], iron oxalate[12], polyvinyl alcohol[13], iron oxide[14] *etc.*, However, to the best of our knowledge, no work has been reported on the preparation of polyaniline composites using P_2O_5 by chemical oxidation method. Phosphorus pentaoxide, a strong dehydrating agent, removes a molecule of water from organic and inorganic compounds and thus acting as a powerful desiccant. The aim of the present work is to synthesize polyaniline/P_2O_5 composites with different mole percentages and characterize them using FTIR, UV-visible, XRD, SEM, EDAX, AFM and TGA.

EXPERIMENTAL

Aniline, ammonium persulfate, P_2O_5, DMF (all from Merck, India), sulphuric acid (Rankem, India), acetone, methanol and distilled water were used throughout the experiment. All the chemicals used were of analytical grade.

Synthesis of polyaniline: A low temperature (0-6°) chemical oxidation method was used to synthesize polyaniline. Initially aniline (0.8 M) was dissolved in 150 mL of distilled water to which 1.25 M of H_2SO_4 was added. Ammonium persulfate (0.8 M) used as an oxidant in the experiment was dissolved in 20 mL of distilled water separately. This solution was added slowly to the above reaction mixture with thorough and continuous stirring. The resultant dark green solution was filtered and washed sequentially with distilled water, acetone and methanol. The samples were then oven dried at 60 ºC for 24 h. The synthesized polyaniline was finally ground to a fine powder and used for further studies.

Synthesis of polyaniline/P_2O_5 Composites: The P_2O_5 powder (99.99 % pure, Merck) was used for the preparation of the polyaniline/P_2O_5 composites. To an already prepared

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solution of aniline (0.8 M) containing 1.25 M sulphuric acid, P_2O_5 in powder form was taken in the required quantity (8-12 g) and added slowly with continuous stirring. Ammonium persulfate (0.8 M) was then added drop wise to this reaction mixture in the form of an aqueous solution. The solution mixture was stirred for 0.5 h and allowed to stand for a further period of 3 h. The resultant product was filtered, washed with distilled water, acetone and methanol and dried in an oven at 60 ºC for 24 h. The resultant material was ground to a fine powder and used for further studies.

Characterization techniques: The chemical structure of the polyaniline and polyaniline/P_2O_5 powders were studied from the infrared spectra (Perkin Elmer FTIR spectrometer-Model RXI) in the range of 4000 cm^{-1} to 400 cm^{-1}. The KBr pellet technique was adopted to prepare the sample for recording the IR spectra. The UV-VIS spectra (Perkin Elmer - Model Lambda 35) of the samples, which were dispersed in DMF, were recorded from 190 nm-1100 nm.

X-ray diffraction analyses (Bruker AXS B8 advance) were carried out in the 2θ range from 10º-70º and the patterns were matched with the standard pattern provided in the JCPDS file. Morphological study and the elemental analysis of the samples of the polyaniline and polyaniline/P_2O_5 were observed using a scanning electron microscope (Model JSM-6390LV) operating at 20 KV at a magnification of 5000 X. The topographical analyses were done using AFM (Park AFM (XE-100) in the scan range of 10 × 10 µm. Thermo gravimetric analysis (SDTQ 600 V8.0 Build 95) of polyaniline and polyaniline/P_2O_5 was carried out at a heating rate of 10 ºC/min up to 1000 ºC in N_2 atmosphere.

RESULTS AND DISCUSSION

FTIR analysis of composites: FTIR spectra of polyaniline and polyaniline/P_2O_5 composites (Fig. 1) show the assigning of the main characteristics peaks of polyaniline as follows: the band at 3760 cm^{-1} is responsible for N-H stretching, the peak at 3433 cm^{-1} accounts for the O-H stretching of water molecules physisorbed the polyaniline backbone, the bands at 1638 cm^{-1} and 1404 cm^{-1} are attributed to C=C and C=N stretching modes of vibration for quinnooid and benzenoid rings of polyaniline and the peak at 1197 cm^{-1} is due to C-N stretching mode of benzenoid units (in-plane bending mode) and the quinonoid unit of polyaniline (N=Q=N). The assignment of peaks reveals that the synthesized product is polyaniline [10, 15-17].

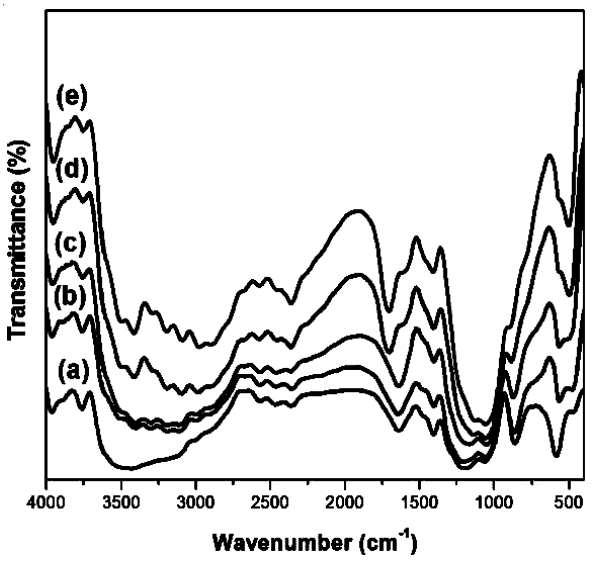


Fig. 1. FT-IR spectra of (a) Pure PANI (b) P_2O_5 (c) PANI/8P_2O_5 (d) PANI/10P_2O_5 (e) PANI/12P_2O_5

The band at 863 cm^{-1} is an evidence for C-H out of plane bending vibration. The peaks at 1234 cm^{-1} and 1022 cm^{-1} belong to the P=O stretching of P_2O_5[18]. A peak between1000-1090 cm^{-1} confirms the inclusion of P_2O_5 in polyaniline/P_2O_5 composites.

UV-visible spectra of composites: UV-visible absorption spectra (Fig. 2) for polyaniline and polyaniline/P_2O_5 composites show four absorption bands of polyaniline at 298, 355, 434 and 831 nm. The bands at 298, 355 and 434 nm are attributed to the π-π* and polaron-π* transitions of the benzoid ring and exciton absorption of quiniod rings respectively in polyaniline[19,20]. The polaron band around 831 nm characterizes protonation and it is identical to that of emeraldine salt form of polyaniline[21].

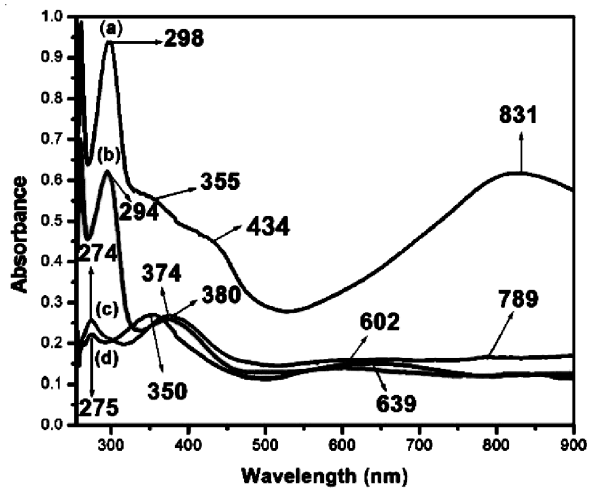


Fig. 2. UV-visible spectra of (a) PANI (b) PANI/8P_2O_5 (c) PANI/10P_2O_5 (d) PANI/12P_2O_5

In addition, in the polyaniline/P_2O_5 composites, a blue shift of the absorption band could be observed as the π-π* transition in the benzenoid ring is shifted to 374, 380 and 350 nm. The exciton absorption band of quiniod rings also shifts to 565-663 nm in the polyaniline/P_2O_5 composites due to the interaction of polyaniline with P_2O_5.

XRD analysis: Typical XRD patterns of polyaniline and polyaniline/P_2O_5 composites are shown in Fig. 3. The patterns of polyaniline exhibiting two peaks (2θ) at 19º and 21º can be ascribed to the presence of periodicity parallel and perpendicular to the polymer chain respectively[22-24]. In polyaniline/P_2O_5 composites, the peak at 25º exhibits a broader peak than polyaniline due to the interaction of P_2O_5 with polyaniline, thereby indicating the possibility that the crystalline behaviour of polyaniline gets affected slightly by the increasing content of P_2O_5. The average particle size (D), calculated using the scherrer formula ($D = K\lambda/\beta \cos\theta$) are shown in Table-1, wherein it is clearly seen that the average particle size decreases with the increasing content of P_2O_5.

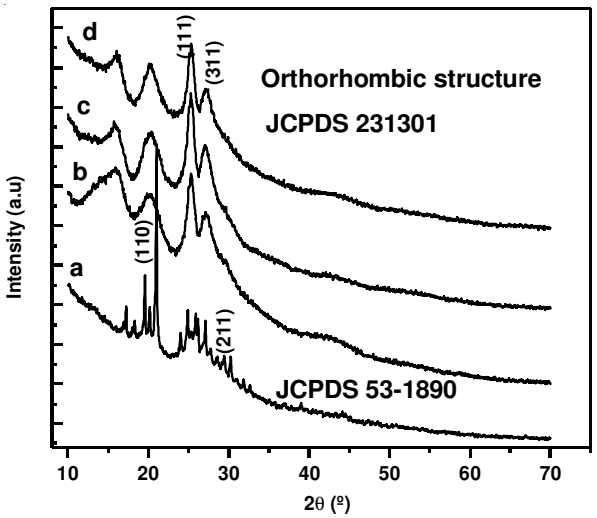
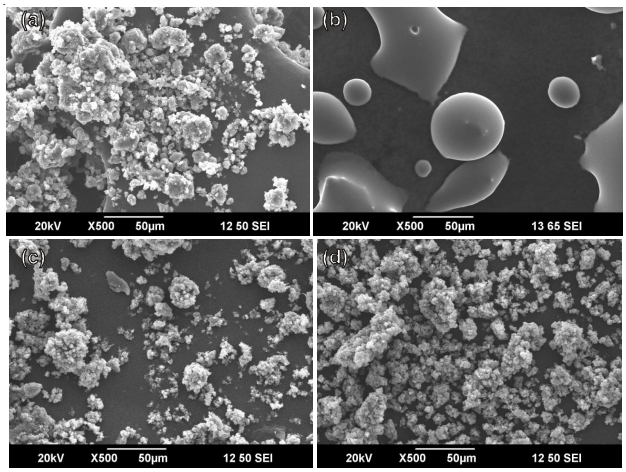


Fig. 3. XRD spectra of (a) PANI (b) PANI/8P_2O_5 (c) PANI/10P_2O_5 (d) PANI/12P_2O_5

TABLE-1
CALCULATED VALUES OF GRAIN SIZE 'D' FOR PANI AND PANI/ P_2O_5 COMPOSITES

Polymer/ Polymer composite	Position 2θ (º)	FWHM (º)	d-spacing (Å)		Particle Size D (in nm)
			Calculated	JCPDS	
PANI	29.4451	0.2244	3.367	3.03357	38
PANI/ 8P_2O_5	25.3611	0.6731	3.508	3.5113	12.63
PANI/ 10P_2O_5	25.3346	0.6731	3.897	3.5156	12.58
PANI/ 12P_2O_5	25.3414	0.7478	3.895	3.51466	11.32

SEM and EDAX analysis: The morphologies of polyaniline, P_2O_5 and polyaniline/P_2O_5 composites were compared at different magnifications (500 and 5000 X). From the Fig. (4a) a granular texture could be observed for polyaniline containing clusters of globules[9,15,25]. The spherical nature of P_2O_5 particles can be seen from Fig. 4b. With increasing amounts of P_2O_5 (8 g, 10 g, 12 g) there is a visible increase in the grain size suggesting to intermixing of P_2O_5 particles with polyaniline (Fig. 4c-e). polyaniline/P_2O_5 composites show a transformation from granular (polyaniline) to spherical morphology. The SEM images also help us to draw the conclusion that the doping of P_2O_5 strong affects the morphology of



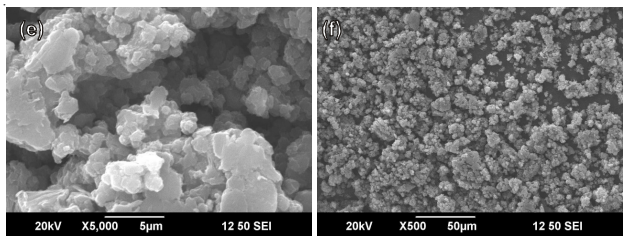


Fig. 4. SEM Micrographs a) PANI, b) P_2O_5, c) PANI/8P_2O_5, d) PANI/10P_2O_5, e) PANI/12P_2O_5

polyaniline. The EDAX analysis of the composite sample (Fig. 5) shows the presence of the constituents of both P_2O_5 and polyaniline.

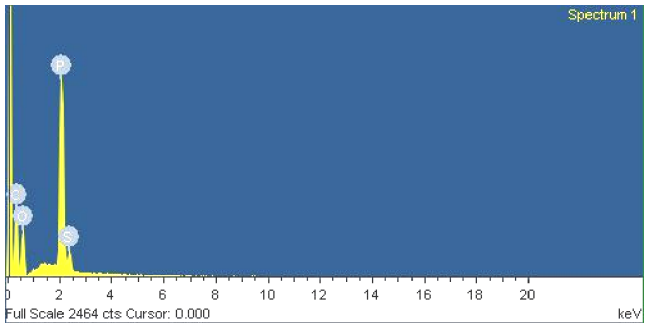


Fig. 5. EDAX spectrum of PANI/12P_2O_5

Atomic force microscopy analysis: Fig. 6a-6d show the three dimensional (3D) AFM images of polyaniline and polyaniline/P_2O_5 composites taken in a scan range of 10 × 10 µm. The topographical view of polyaniline shows deep valleys in between polymer chains. Well defined grains of approximately 200 nm sizes and with irregular tips projected to the surface are observed in the 3D images of polyaniline[26,27]. The deep valleys in the polymer chain disappear due to the increasing amount of P_2O_5 particles being accommodated in the polymer chain. The uniform grain sizes of approximately 100 nm are projected on the surface as seen in the 3D images of polyaniline/P_2O_5 composites.

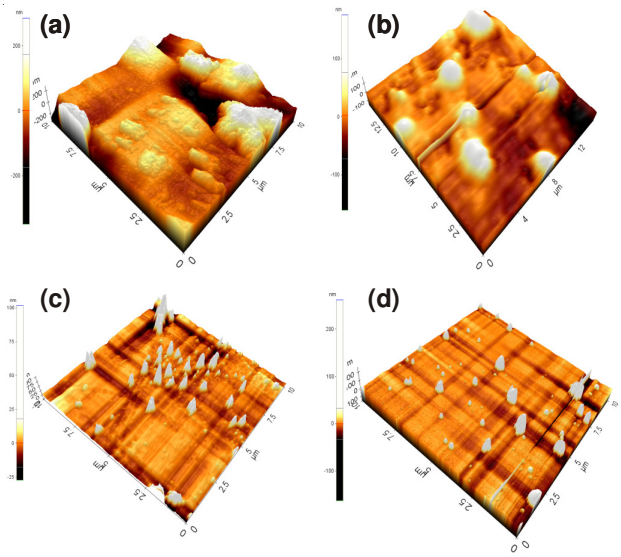
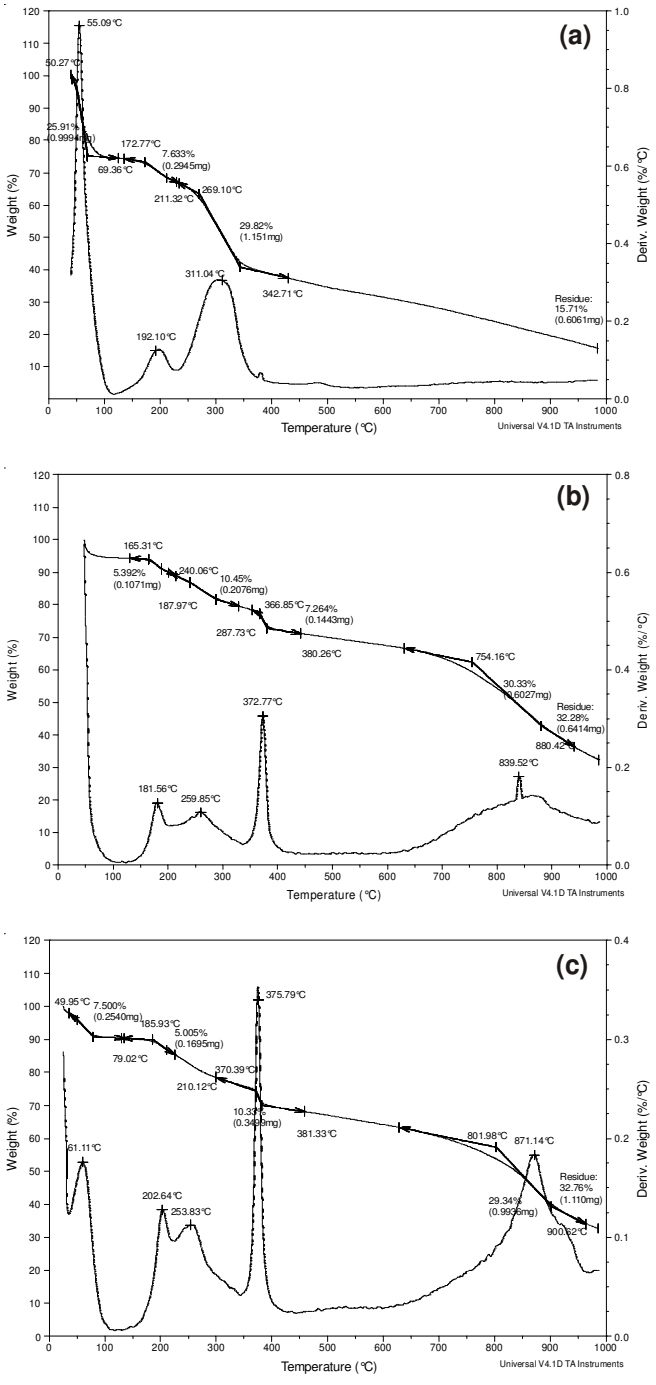


Fig. 6. AFM images of a) 3D PANI, b) 3D PANI/8P_2O_5, c) 3D PANI/10P_2O_5, d) 3D PANI/12P_2O_5

TABLE-2
THERMOGRAM RESULTS FOR PANI AND PANI/ P_2O_5 COMPOSITES

Polymer/polymer composite	Range (°C)			Final decomposition (in °C)	Residue (in %)	Final total wt. loss (in %)
	1st wt. loss (due to loss of moisture)	2nd wt. loss (due to loss of dopant ion)	3rd wt. loss (due to P_2O_5 addition)			
PANI	50-69	172-211	--	> 342	15.7	84.3
PANI/8P_2O_5	45-165	240-287	366-380	> 754	32.0	68.0
PANI/10P_2O_5	49-79	185-210	370-381	> 801	32.7	67.3
PANI/12P_2O_5	43-76	200-276	376-390	> 810	20.9	79.0

Thermogravimetric analysis: Thermogravimetric analyses of polyaniline and polyaniline/P_2O_5 composites were done in the temperature range of 0-1000 ºC and are shown in Fig. 7a-7d. The thermogram of polyaniline exhibits a three-step weight loss process. In the first step, a weight loss in the range of 50-69 ºC is attributed to the expulsion of water molecules from the polymer chain. The second weight loss occurring between 172-211 ºC is associated with the loss of dopant ion from the polymer matrix. The third weight loss beyond 342 ºC is due to the complete degradation and decomposition of the polymer after elimination of the dopant ion[16,28,29].



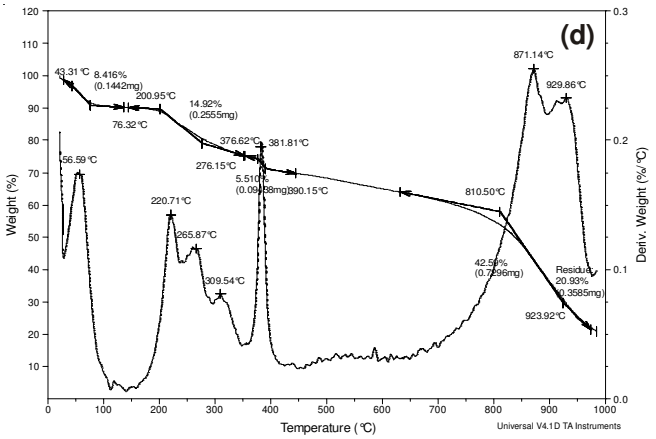


Fig. 7. TGA spectrum a) PANI b) PANI/8P_2O_5 c) PANI/10 P_2O_5 d) PANI/ 12 P_2O_5

The TGA curves of polyaniline/P_2O_5 composites have a four step weight loss, with the first three steps similar to that of pure polyaniline (Table-2). The additional fourth step weight loss in polyaniline/P_2O_5 composites around 366-390 ºC may be due to the decomposition of P_2O_5 in the composites. From Table-2, it is clear that, as the quantity of P_2O_5 is increased, the bonding becomes stronger and hence a reduction in the final weight loss is observed in the polymer composites and hence it could be implied that the samples become more stable with respect to temperature.

Conclusion

The polyaniline/P_2O_5 composites are synthesized by a low temperature chemical oxidation method. Structural changes, transitions, crystallinity, morphology, grain size and stability of polyaniline/P_2O_5 composites are found to be affected by the concentration of P_2O_5. A strong interaction between polyaniline and P_2O_5 could be inferred from the FT-IR and UV-visible spectroscopic results. The XRD analysis reveals that crystallinity of polyaniline is affected mildly with increasing P_2O_5 content. The changes in the morphology of polyaniline due to the addition of P_2O_5 could be observed from the SEM images. The EDAX spectrum clearly shows and confirms the presence of elemental polyaniline and P_2O_5. AFM analysis shows the topographical view of polyaniline with deep valleys between the polymer chains, while in polyaniline/P_2O_5 composites the deep valleys between the polymer chains are

found to disappear with increasing concentrations of P_2O_5. The thermal stability of the composite materials shows reduced decomposition compared to pure polyaniline.

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