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AN ANALYTICAL STUDY OF TEMPERATURE- AND OXIDATION-INDUCED STRUCTURAL TRANSFORMATIONS IN PYRROLE–ANILINE COPOLYMERS

Chandresh Bari

R.D. and S.H. National College, Bandra (W), Mumbai

Anikt Mani

K.M. Agrawal College of Arts, Commerce and Science, Kalyan.

Abstract

The characteristics of copolymer of pyrrole and aniline – namely, poly (pyrrole-co-aniline) PPcA synthesized using insitu chemical oxidative polymerization method adding 1:1 molar ratio of the two monomers was studied. A proper ratio of co-polymer to different oxidants such as ferric chloride ($FeCl_3$) and ammonium persulphate ($N_2H_8S_2O_8$) at two different temperatures were used.

Structural and morphological properties were studied by XRD, FESEM & FTIR. The effect of change in temperature and oxidizing agent was seen on the size of the particle.

Keywords: Nanocomposite, copolymer, XRD, FTIR, FESEM, Scherrer's formula

Introduction

Nowadays a lot of research work is being done on conductive polymers, owing to their good electrical, electrochemical, electromagnetic shielding properties and optical properties. The conducting polymers are extensively used in light emitting diodes [1,2] anti-corrosion materials [3] batteries [4–6] photovoltaic cell, supercapacitors [7-9] and sensors [10]. Conductive polymers mainly include polystyrene acetylene, polystyrene, polyaniline (PANI), polypyrrole (PPy), poly phenylene acetylene and polythiophene, etc. PANI and PPy have been extensively investigated [1-10] and have proved to be the two most promising materials for potential applications because of its low cost, environmental stability and high electrical conductivity. However, the PANI/PPy system has only a limited application because of its partial miscibility or solubility in the common organic solvents. This restricts the use of these monomers for higher temperature applications.

The improvement of the physical and mechanical properties and processing properties of conducting polymers has always been the focus of research in this field. Copolymerization is an important modification method, because the properties of the copolymer are generally between the corresponding properties of the two homopolymers. Lot of research and developmental work has been carried out in synthesis and characterization of copolymer, but still there is much more scope to see the effect of variation of synthesis temperature, molar ratio of constitutes. This study of effect of various parameters can help to give more understanding and optimization of copolymer synthesis, therefore, the study of copolymerization modification of polyaniline and polypyrrole has become the main content of our study.

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In the present work, we report on the morphological evolution and structural properties of poly (pyrrole-co-aniline) PPcA prepared by chemical oxidative copolymerization process from monomer mixtures of aniline and pyrrole, using two different oxidants, namely, $FeCl_3$ and ammonium per sulfate (APS) at two different temperature conditions.

Synthesis & Characterization

Monomer Pyrrole (Py) 98%, Aniline (99%) was purchased from Sigma Aldrich. Anhydrous iron (III) chloride, also called ferric chloride ($FeCl_3$) 98%, and ammonium persulphate ($N_2H_8S_2O_8$) 98% were used as the oxidizing agent. All of them were also supplied by Sigma Aldrich. All materials were used as received. Freshly distilled water was used for the preparation of all aqueous solutions and the washing process.

Chemical Oxidative Polymerization of poly (pyrrole-co-aniline; PPcA) using $FeCl_3$ as oxidizing agent: 0.1 M Pyrrole solution to be prepared using distilled water and then mixed with oxidizing agent $FeCl_3$ in the ratio of 1:2.4 (monomer: oxidant), as proposed to be the optimum stoichiometry, slowly under constant stirring for 30 minutes. To this 0.1 M Aniline solution was added drop wise. Then the polymerization was conducted for 12 hours under constant slow stirring. This preparation was kept unagitated for 24 hours. The next day, the black colored powdered mass was recovered through centrifugation in the centrifuge tube. The residue was separated and washed three times, first with methanol (AR grade) and then with DI water and then was dried in an oven at 60°C for two hours. This process was done for two temperatures: 5°C and room temperature.

The same process was repeated with APS as oxidizing agent at 5°C and room temperature.

It should be noted that a feed molar ratio of 1:1 (Py:An) was used since it was reported that by varying the ratios of aniline and pyrrole, copolymers with more PPy or PANI behave similar to those individual homopolymers of pyrrole or anilne, whilst the copolymers from equal molar ratios combined the characteristics of both homopolymers [11].

The X-ray diffraction patterns of powders were recorded on Rigaku SmartLab X-ray diffractometer using Cu Kα (λ = 1.54 A˚) radiation source. The diffractogram was in terms of 2θ in the range 10° to 80°. Field emission Scanning electron microscopy (FESEM) samples were prepared by using small amount of the synthesized materials. The morphology of powder samples was investigated by using Instrument Carl Zeiss Supra 55 which is a FESEM with a Schottky thermal field emission source and has an imaging resolution in the range of 2 nm. Infrared spectra were recorded using a Fourier transform infrared (FT-IR) spectrometer (Perkin Elmer Spectrum IR Version 10.7.2) by scanning wave numbers against intensity from 450 to 4000 cm^{-1} with a resolution of 4cm^{-1} and 32cm^{-1} scans using force gauze of 40N.

Before the synthesis of copolymer, polymerization of monomer were done we synthesized homo-polymers; Polypyrrole (PPy) and Polyaniline (PANI) using $FeCl_3$ and APS at 5° C and room temperature. The characteristics of the polymerized homopolymers were compared and correlated with the reported work. Further subsequent experimental results and discussion are done for the copolymers synthesized using different oxidizing agents at different temprature.

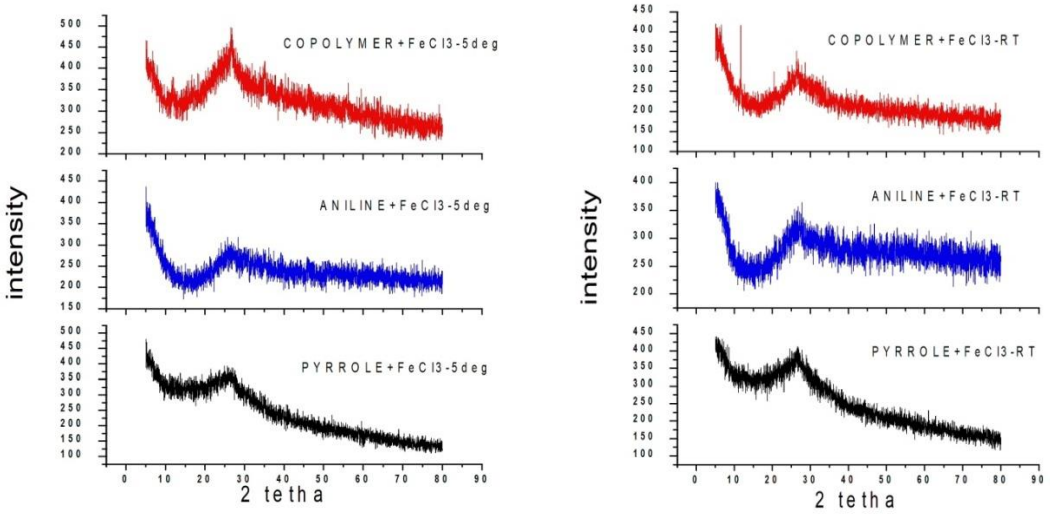
Results And Discussion

PPcA X-ray diffraction analysis

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X-ray diffraction (as shown in Fig. 1) was done for the comparative study of the structure of individual polymers PPY and PANI along with copolymer PPCA structures at 5° C (left hand side of Fig. 1) and room temperature (right hand side of Fig. 1) using FeCl3 (Fig. 1a) and APS (Fig. 1b) as oxidants. In case of both the oxidant broad peaks shows the amorphous short-range ordering in the copolymer indicating particle size in nano range. Comparing with individual polymer i.e PPY and PANI copolymer shows the same structure i.e broad peak at around 2θ = 26.7 in case of FeCl3 as an oxidizing agent for both the synthesis temperature i.e. 5°C & RT. In case of APS as oxidizing agent, one can clearly see the board peak centering around 2θ = 26.26 along with the number of overriding peaks at 17.92, 19.3, 23.7, 26.4, 30.4 prominent in case of PPy or PANI for both the synthesizing temperature i.e. 5°C & RT. Overriding peaks shows the crystallinity of APS which is also reported previously [13]. which majorly suppresses for copolymer but not completely diminished confirming again the nano structure with more crystalline nature compared to copolymer synthesized using FeCl3. Broad peak of copolymer synthesized using APS as oxidizing agent shifts towards the lower 2θ value along with the reduction in broadening as compared to the sample synthesized using FeCl3 oxidant. This can be attributed to the more crystallinity of the sample synthesize using APS as oxidant over FeCl3.



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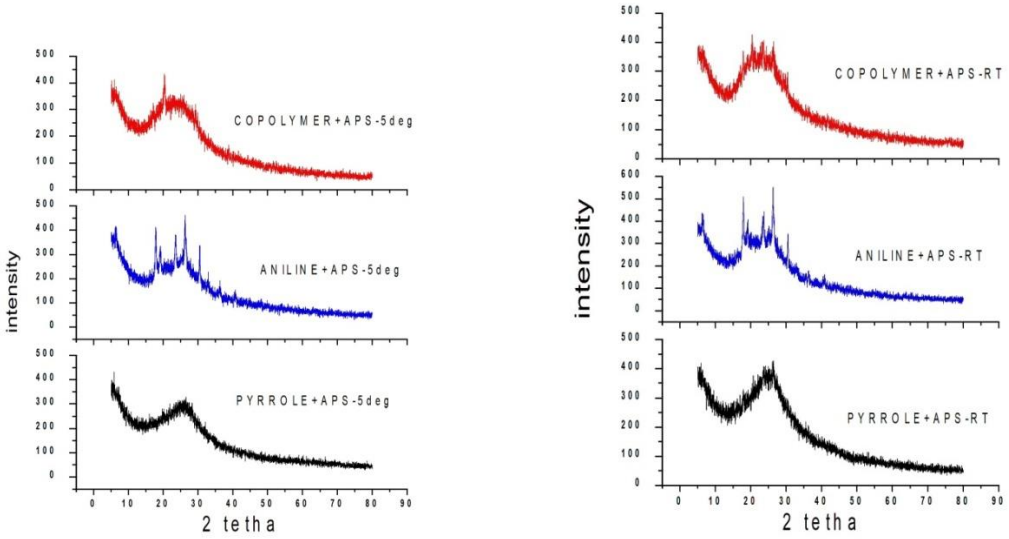
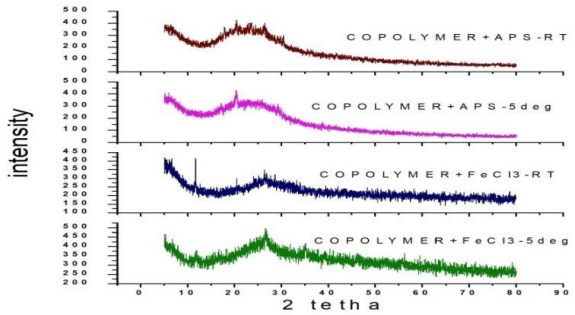


Figure – 1: X – Ray Diffraction Patterns for PPy, PANI & Copolymer (PPcA) at 5° C and Room Temperature using (a) FeCl3 (b)APS as oxidizing agent

The crystal size for PPcA is around 2 nm at room temperature while 15.5 nm at 5°C temperature (Fig. 2), for FeCl3 as oxidant, whereas for PPcA copolymer with APS as oxidizing agent the crystal size for both the temperatures found to be around 84 nm (shown in Table – 1) This increase in average particle size of the copolymer synthesized using APS over FeCl3 is due to more crystalline nature of sample. This crystallinity may be favorable for enhancing the conductivity of the sample. While with FeCl3 one can get the sample having less particle size advantageous in coating application.

Effect of temperature can be seen clearly for FeCl3 oxidant while the sample synthesized using APS as oxidant for both the temperature shows the same diffraction results.

It has been reported that for pyrrole and aniline, FeCl3 has been a better oxidizing agent compared to APS and hence the nanofibers oxidized by FeCl3 show smaller diameter, higher crystallinity and conductivity due to the lower oxidation/reduction potential of FeCl3, which indicates that FeCl3 is an ideal oxidant to prepare these polymers. [12]. The same is true with the copolymers prepared with the two oxidizing agents at 5° C and room temperature. The morphology of the copolymers hence has significant influence on the conductivity.



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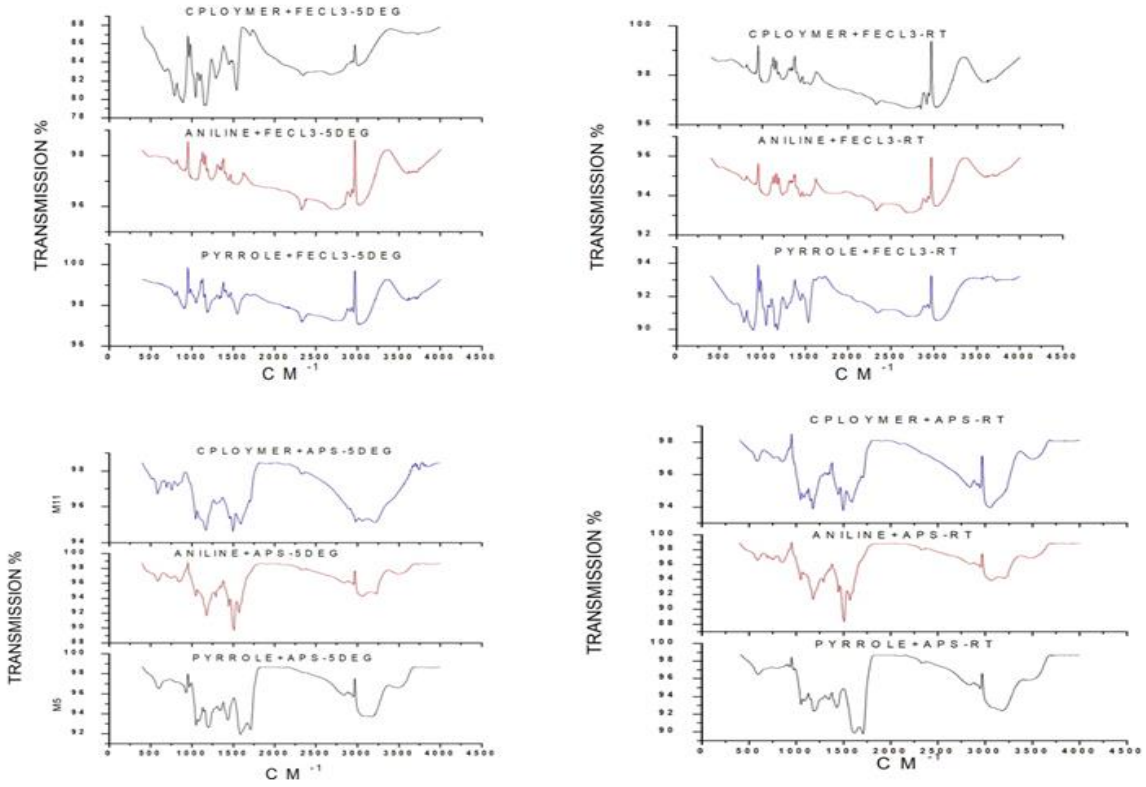
Figure – 2: X – ray Diffraction Patterns for Copolymer PPcA at 5° C and Room Temperature using FeCl3 & APS

TABLE – 1: XRD & FESEM FOR COPOLYMER PPcA

Sr. No.	Oxidizing Agent	Temperature	Copolymer PPcA		
			XRD Peak	XRD: Crystal Size	FESEM: Particle Size
1	Fecl3	5° C	26.612	15.78 nm	125.82 nm
2		Room Temp	27.1572	1.33 nm	195.06 nm
3	APS	5° C	20.2996	84.33 nm	164.00 nm
4		Room Temp	20.5136	84.35 nm	179.16 nm

PPcA chemical structure: FTIR:

The FTIR spectroscopy was used to identify the structure of the copolymer PPcA. The FTIR spectra of copolymer at 5° C and room temperature using the two oxidizing agents FeCl3 and APS together with that of pure polypyrrole and polyaniline are shown in Figure 3.



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FIGURE – 3: FTIR of (a) PPy, PANI & Copolymer at 5°C using FeCl3; (b) PPy, PANI & Copolymer at room temp using FeCl3; (c) PPy, PANI & Copolymer at 5°C using APS; (d) PPy, PANI & Copolymer at room temp using APS

Figure 3 shows that the FTIR spectra of PPy powder at 5° C and room temperature with oxidizing agent FeCl3, the peaks at around 793 cm^{-1}, 820 cm^{-1}, 951 cm^{-1} attributed to C–H wagging. The characteristic peaks around 1530.4 cm^{-1} and 1498 cm^{-1} for both the oxidizing agents correspond to the C=C stretching, whereas peaks at 1666 cm^{-1} and 1309 cm^{-1} represent to respectively, C=N and C–N bonds [14]. The occurrence of small peaks at 3500 cm^{-1} is due to presence of N–H stretching vibrations. The peaks observed in the present work match well with the ones available in the literature [14] confirming the formation of Polypyrrole.

The FT-IR spectra of PANI samples for both the oxidizing agents at both the temperatures, shows approximately the same kind of peaks. The broad peaks range 3037 - 3370 cm^{-} due to N–H stretching. The absorption bands at 2971 and 2886 cm^{-1} are due to asymmetric C–H stretching and symmetric C–H stretching vibrations, respectively. The absorption peaks observed at 1641-1624 cm^{-1} were attributed to C=C stretching in aromatic nuclei. The band obtained at 1626–1500 cm^{-1} corresponds to C–H stretching in aromatic compounds. 1258, 1289 (C - N stretching), 1129 cm^{-1} (C–H in-plane vibrations). These peak positions match well with those reported in the literature [15].

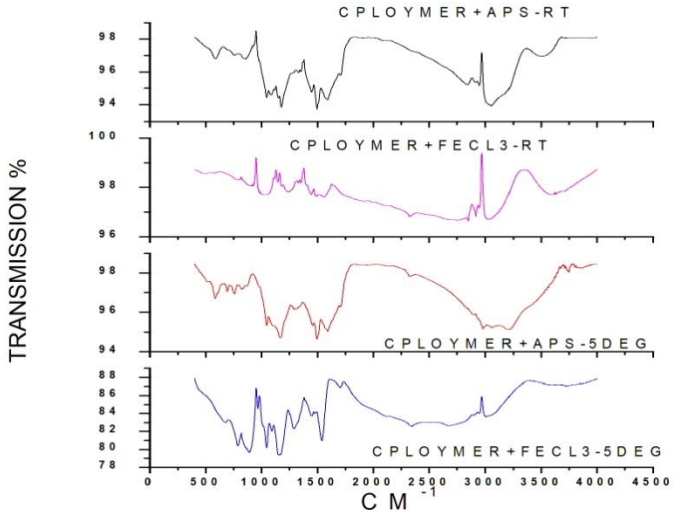


FIGURE – 4: FTIR of Copolymer PPcA **at 5°C and room temp using (a) FeCl3 (b) APS**

The FTIR spectra of copolymer PPcA in figure 2 shows the characterization of evolution of the absorption bands located around 1449 to 1460 cm^{-1}. The peaks present in between 1045 cm^{-1} to 1236 cm^{-1} represent the vibrations occurring due to the stretching of C-N bonds present in the aniline as well as pyrrole ring structure. The peak shift observed around the spectra at 951–796 cm^{-1}. Furthermore, the peak's broadening and shift was observed around 796–629 cm^{-1}. It is observed that the peaks shifted to a lower wave-numbers for the copolymer (poly (aniline-co-pyrrole)) demonstrating the presence of aniline and pyrrole units. The spectrum of PPcA

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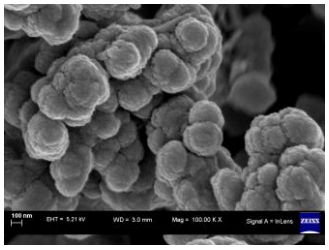
copolymer has a strong peak around 3358 - 3370 cm^{-1} due to the stretching vibrations of N-H bonds present in the corresponding homopolymer [16]

PPcA FESEM - Morphological and structural analysis:

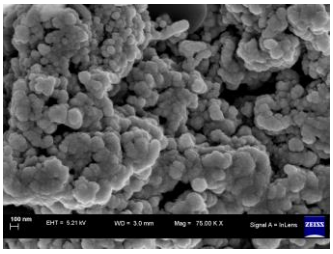
FESEM images shows that at lower temperature the agglomeration is more whereas at RT its less for both the oxidizing agents. FESEM images exhibit chain like agglomerated polymer.

As we have seen the enhanced crystalline structure in case of APS as oxidizing agent can also be seen clearly here from FESEM study. FESEM of constituent polymer i.e. PPy and PANI shows that in case of FeCl3 the individual spherical structures of agglomerate are in the size of approximate tens of nanometer while in case of APS these are in the range of nearly 100 nm consistent with XRD results. In case of APS the copolymer didn't show many changes in morphology or size as compared to individual polymer which is not the case for the FeCl3 as oxidizing agent. For FeCl3 fusion of can be seen clearly.

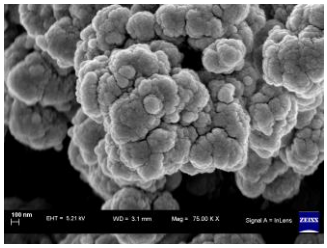
FESEM morphology of the homopolymers of PANI and PPy and copolymers of PANI–PPy (PPcA) at different temperatures and different oxidizing agents are shown in Fig. 5, respectively. The micrograph in Fig. 5 shows cauliflower like structure for PPy and either a 'rod-like' or a fibrillar structure for PANI. SEM analysis confirm that due to the copolymerization process the poly(aniline-co-pyrrole) PPcA FESEM image showed spherical structures with granular morphology/flaky structures formed by agglomerated particles, completely different form that of its counterpart PANI (fibrillar morphology) [17, 18] and PPy. The agglomerates of the copolymer vary between 120 and 170 nm in diameter size (shown in Table – 1) while the constituents spherical structures are in few nanometer range only which is consistent with XRD particle size analysis.



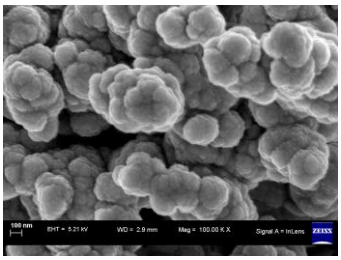
PPy + FeCl3 @ 5° C



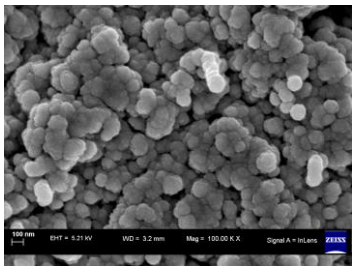
PANI + FeCl3 @ 5° C



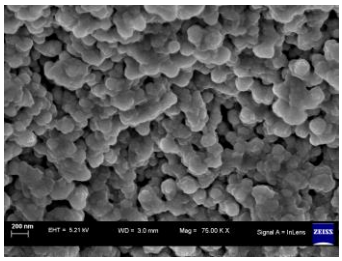
Copolymer - PPcA + FeCl3 @ 5° C



PPy + FeCl3 @ RT



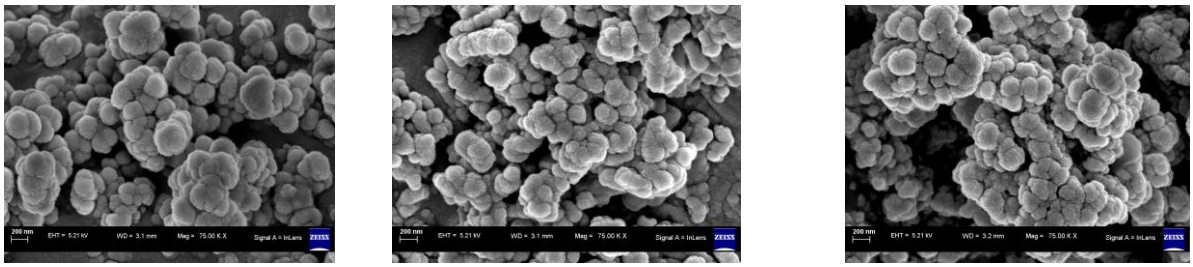
PANI + FeCl3 @ RT



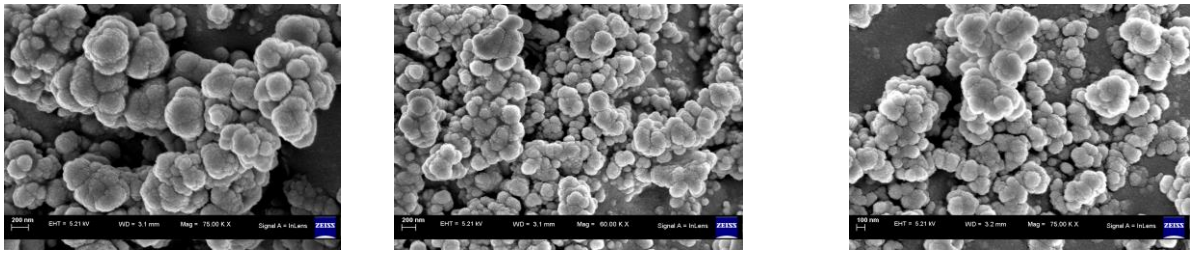
Copolymer - PPcA + FeCl3 @ RT

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PPy + APS @ 5° C | PANI + APS @ 5° C | Copolymer – PPcA + APS @ 5° C



PPy + APS @ RT | PANI + APS @ RT | Copolymer – PPcA + APS @ RT

Figure 5: FESEM Images for PPy, PANI and PPcA **copolymer at 5° C and room temperature using (a) FeCl3, (b) APS**

Conclusions

The PPcA synthesized using APS may be favorable for enhancing the conductivity of the sample as the average particle size of copolymer PPcA is more compared to the PPcA synthesized using FeCl3. PPcA sample synthesized with FeCl3 can be advantageous in coating application as it will have less particle size. FTIR showed the peaks shifted to a lower wave-numbers for the copolymer PPcA demonstrating the presence of aniline and pyrrole units. PPcA FESEM image showed spherical structures with granular morphology/flaky structures formed by agglomerated particles, completely different from that of its homopolymers PANI and PPy.

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8. Physicochemical and morphological properties of poly(aniline-co-pyrrole) Sipho E. Mavundla • Gerald F. Malgas • David E. Motaung • Emmanuel I. Iwuoha

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