

Summary

In this chapter, a novel binary composite of ammonium phosphomolybdate (APM) with a conducting polymer *viz.* Polypyrrole (Ppy), has been synthesized by chemical oxidative polymerization method using ammonium per sulphate (APS) as the oxidant. The formation of APM-Ppy composite was confirmed by FTIR and PXRD. The morphology and composition of the composite was established using FESEM and EDAX. The thermal stability of the composite was investigated using TG analysis. The effect of various parameters such as molar ratio of reactants, stirring time and temperature on the formation of the composite was also studied. Further, the potential of the synthesized composite to be used as an indicator in acid-base titrations was also investigated.

VI.1 Introduction

Composite materials have gained significant attention due to their unique properties and potential for various applications. These materials are composed of two or more different components, which result in the final product having properties that are superior to those of the individual components. Keggin type phosphomolybdates belong to a class of polyoxometalate solids having the general formula $[\text{PMo}_{12}\text{O}_{40}]^{n-}$ and they possess several unique properties [1-3]. Recently, a few composites of Keggin-type phosphomolybdates (PMOs) have been synthesized, and they seem to have potential uses as sensors, catalysts, and in energy storage applications [4-7]. Such PMOs with its strong oxidizing potential and inherent acidity can also serve as ideal candidates for the formation of polyoxomolybdate-polymer composites with polymers like acrylonitrile, vinyl alcohol, etc. [8-10]. A review of such binary composites of phosphomolybdates with polymers published in the past decade has been summarized in Table VI.1.

Among the various Keggin based polyoxometalates, ammonium phosphomolybdate, $\{\text{NH}_4\}_3[\text{PMo}_{12}\text{O}_{40}].x\text{H}_2\text{O}$ is a redox active inorganic cluster solid exhibiting wide range of applications such as ion-exchanger, in drug delivery systems, DNA synthesis, dielectric material and memory device fabrication [11-15]. This versatile ammonium phosphomolybdate (APM) solid when embedded into the polymer matrix can often result in improved properties of the composites formed. For example, a composite of APM with polyacrylonitrile was found to be an effective ion-exchange membrane for selective removal of cobalt, strontium and cesium from radioactive laundry waste water as reported by Park *et.al.* [16]. Similarly, conducting polymers such as polypyrrole, polythiophene, polyaniline, etc. can serve as ideal platforms to embed the redox-active PMOs which in turn can produce novel composite materials with interesting properties [17].

Table VI.1 A review of phosphomolybdate-polymer composites reported in the last decade.

S. No.	Keggin type and polymer	Synthetic method	Property/ Application	Ref.
1.	APM - Polyacrylonitrile	Chemical polymerization method using surfactant	Removal of Cs ⁺ by ion exchange Removal of cobalt, strontium and cesium from nuclear-waste water	[8] [16]
2.	H ₃ PMo ₁₂ O ₄₀ - Poly vinyl alcohol	Layer by layer (LBL) assembly technique	Photochromic property	[10]
3.	H ₃ PMo ₁₂ O ₄₀ - Polyaniline	Chemical oxidative polymerization with APS	Electrocatalytic property	[18]
4.	H ₃ PMo ₁₂ O ₄₀ - polyacrylamide	Direct mixing of solutions in deionized water	Photochromic property	[19]
5.	H ₃ PMo ₁₂ O ₄₀ - Chitosan	Direct mixing of the reactants with a cross linking agent	Improved mechanical properties	[20]
6.	H ₃ PMo ₁₂ O ₄₀ - Chitosan	By sonication method in presence of surfactant	Antimicrobial activity	[21]
7.	H ₃ PMo ₁₂ O ₄₀ - Polymethylmethacrylate	Prepared by electrospinning	Photocatalytic property	[22]
8.	[PMo ₁₂ O ₄₀] ³⁻ - polyamidoamine	LBL assembly method	Electrocatalytic property	[23]
9.	[PMo ₁₂ O ₄₀] ³⁻ - polypyrrole	Co-electrodeposition using chrono-amperometric technique	Humidity sensing	[24]

Therefore, in this chapter, synthesis of composite of APM with a conducting polymer *viz.* Polypyrrole (Ppy) via chemical oxidative polymerization method using Ammonium persulphate (APS) has been carried out and characterized. Further, the role of reaction parameters on the formation of composite was explored by varying the concentration of the reactants, temperature and stirring time. In addition, the potential of APM-Ppy composite to act as an indicator in acid-base titrations was also studied.

VI.2 Experimental

VI.2.1 Synthesis of APM/Polymer composite

The synthesis of composite based on APM and Ppy was carried out as follows:

To a stirring solution of 20 mL ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.03 M, Merck, 99%) kept in a water bath, 10 mL of disodium hydrogen phosphate dihydrate, $\text{Na}_2\text{HPO}_4\cdot 2\text{H}_2\text{O}$ (0.2 N, Aldrich, 99%) in 8 mL conc. HNO_3 was added. 0.6 mL of pyrrole was dissolved in 10 mL of distilled water and was added in small aliquots along with 0.5g Ammonium persulphate (APS) simultaneously to the above stirring solution. The contents were stirred for 20 minutes and the resultant black powder was washed with water and filtered. The products thus obtained were dried in oven for 5 hours at 60°C.

The effect of various parameters such as molar ratio of reactants, stirring time, temperature, etc. on the formation of the composite was also investigated.

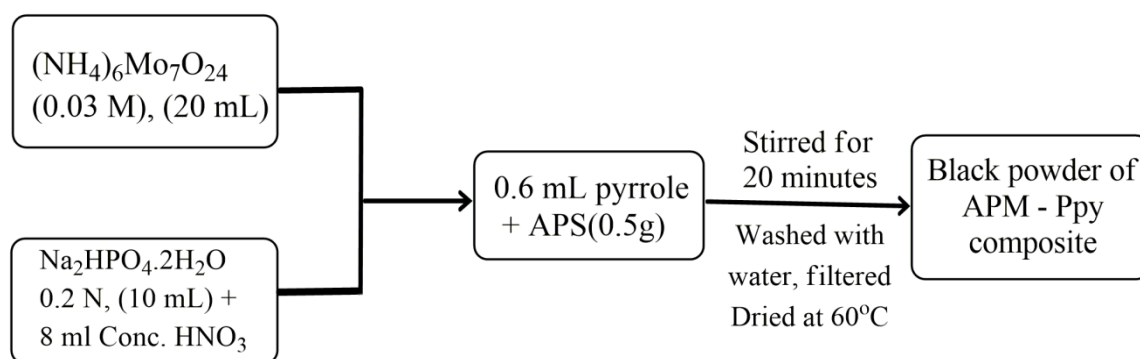
VI.2.2 Synthesis of APM

Synthesis of APM and Ppy were carried out independently in order to compare the FTIR and PXRD patterns of composite with that of APM and polymer, thereby it could also confirm the formation of the composite.

APM was synthesized as per the procedure reported in literature by Joseph *et. al.*[12]. A solution containing 11.05 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ with 15 mL of ammonia solution and 10 mL of distilled water was boiled and made upto 250 mL. 100 mL of the above solution was added to 40 mL of 0.067 M solution of $\text{Na}_2\text{HPO}_4\cdot 2\text{H}_2\text{O}$ and 20 mL of conc. HNO_3 and stirred for 10 minutes. The resultant solution was kept undisturbed for 18 hours. The canary yellow precipitate of APM thus obtained was washed with water, filtered and air dried.

VI.2.3 Synthesis of Polypyrrole

Ppy was synthesized via chemical oxidative polymerization of pyrrole using APS as the oxidant similar to the procedure reported in literature [25]. In a typical synthesis, 1.2 mL of pyrrole was dissolved in 20 mL of distilled water and kept in an ice bath. To the stirring solution, 0.5g APS dissolved in 10mL of distilled water was added and stirred for 4 hours. The black powder of Ppy formed was washed several times with ethanol and water, filtered and dried in oven for 6 hours at 100°C .



Scheme VI.1 Synthetic procedure for preparing APM-Ppy composite.

VI.3 Characterization

Synthesized APM-Ppy composite was characterized by techniques namely PXRD, FTIR and TGA as discussed under Section II.2.3 in Chapter II. The morphology and

composition of the composite was established using FESEM and EDAX as discussed under Section V.2.3 in Chapter V.

VI.4 APM-Ppy composite as acid-base indicator

Conducting polymers such as polyaniline are well-known for their electrical and optical properties that can be varied via protonation or deprotonation of the amine nitrogen atoms. Similarly, Polypyrrole also changes color in acidic and basic solutions due to protonation and deprotonation respectively. Therefore, APM-Ppy composite was tested for its behaviour in various acidic and basic solutions and investigated for its potential to be used as indicator in acid-base titrations.

VI.4.1 Solubility test

0.003g of Ppy and APM-Ppy was weighed separately in five beakers (i)-(v). 20mL of distilled water, HCl (0.1N), Oxalic acid (0.1N), Na₂CO₃ (0.1N) and NaOH (0.1N) solution was added respectively and stirred for 5 minutes. The contents were filtered and color in the beakers (i)-(v) was noted under visible light. Both Ppy and APM-Ppy showed yellow and reddish-brown color in acidic and basic solutions respectively. The change in color from yellow to reddish-brown upon increasing pH from acidic to neutral to basic was evaluated using UV-Vis spectroscopy as well. Therefore, it was tested as acid-base indicators for various titrations.

VI.4.2 Acid-base Indicator test

Preparation of Indicator Solution

Since Ppy and APM-Ppy composite showed color changes in acidic, basic and neutral conditions, its ability to act as acid-base indicators was tested. 0.003 g of Ppy and APM-

Ppy were dissolved separately in 10 mL of DMF. The indicator solutions were shaken well until the entire compound was dissolved completely.

Titrations

The following titrations were performed in the presence of 0.5 mL of the indicator solution at room temperature:

- (i) 20 mL 0.1 N of HCl versus 0.1N of NaOH
- (ii) 20 mL 0.1 N of Oxalic acid versus 0.1 N of NaOH
- (iii) 20 mL 0.1 N of HCl versus 0.1 N of Na₂CO₃
- (iv) 20 mL 0.1 N of Oxalic acid versus 0.1 N of Na₂CO₃

In all titrations, 20 mL of base was pipetted into a conical flask and 0.5 mL of indicator solution was added. The solution was titrated against acid till the color changed from reddish-brown to yellow. The titration was repeated to get concordant results. The titrations were also carried out using standard indicators namely phenolphthalein or methyl orange to validate the accuracy of the end point.

VI.5 Results and Discussion

APM-Ppy composite was synthesized via chemical oxidative polymerization method using APS as the oxidant. The formation of the composite was confirmed by comparing the FTIR and PXRD patterns of APM, Polypyrrole and APM-Ppy composite.

VI.5.1 APM-Ppy composite structure and characterization

Figure VI.1a shows the PXRD patterns of APM, Ppy and APM-Ppy composite. The X-ray diffraction pattern of Ppy displayed a broad peak at around $2\theta = 25^\circ$, which is the characteristic peak of amorphous Ppy [25]. PXRD pattern of APM showed well defined peaks corresponding to its crystalline nature and it matched well with JCPDS file no. 43-0315 indicating the formation of single-phasic cubic $\{\text{NH}_4\}_3[\text{PMO}_{12}\text{O}_{40}].x\text{H}_2\text{O}$ having

lattice constant $a = 11.67 \text{ \AA}$. The PXRD pattern of the APM-Ppy composite exhibits a semi-crystalline behavior with well-defined peaks of APM along with broad peaks of Ppy, thus confirming the formation of APM-Ppy composite.

The FTIR spectrum of APM-Ppy composite showed peaks characteristics of APM and Ppy (Figure VI.1b). The bands in the region $1100\text{-}500 \text{ cm}^{-1}$ were attributed to the characteristic peaks of Keggin type heteropoly anions [26]. The peaks at 1062 , 963 and 880 cm^{-1} were assigned to $\gamma_{as}(\text{P-Oa})$, $\gamma_{as}(\text{Mo-Od})$ and $\gamma_{as}(\text{Mo-Ob-Mo})$ respectively [12]. The peak at 3234 cm^{-1} was assigned to the presence of N-H stretching vibrations of Ppy. The characteristic peaks at 1518 cm^{-1} and 1423 cm^{-1} correspond to the C=C stretching, whereas peaks at 1656 cm^{-1} and 1355.4 cm^{-1} represented C=N and C-N vibrations respectively [27].

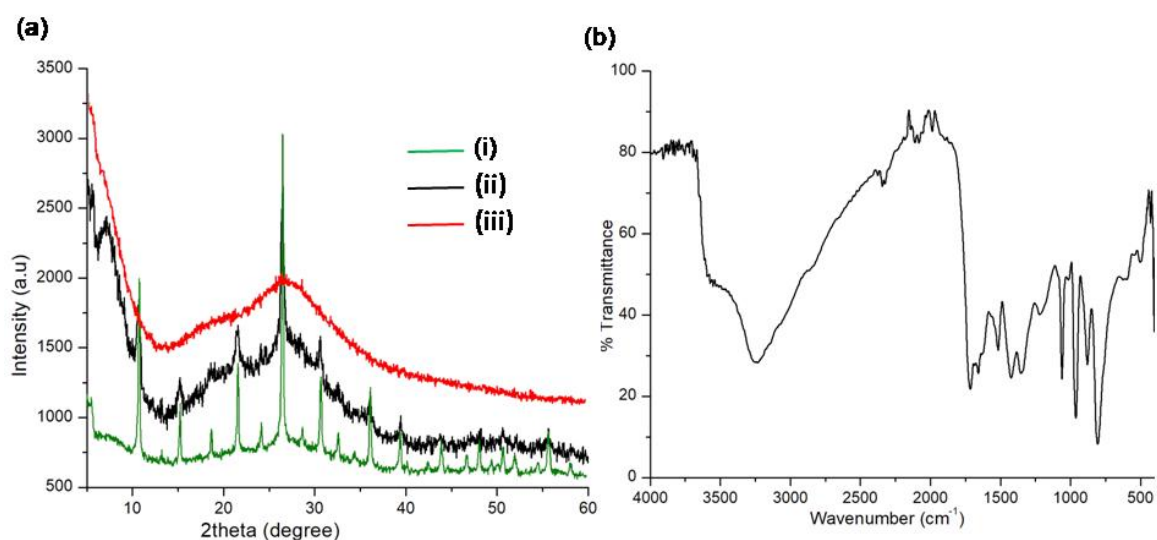


Figure VI.1 (a) PXRD of (i) APM (ii) APM-Ppy (iii) Polypyrrole and (b) FTIR of APM-Ppy composite.

FESEM image of the APM-Ppy composite indicated that the particles are having spherical morphology with particle size ranging from 50-140 nm (Figure VI.2a). EDAX spectrum showed the peaks of carbon, nitrogen, phosphorous, molybdenum and oxygen at 0.277(Ka1), 0.392(Ka1), 2.014(Ka1), 2.418(Lβ2) and 0.525(Ka1) respectively (Figure VI.2b). Scheme VI.2 shows the formation of APM-Ppy composite.

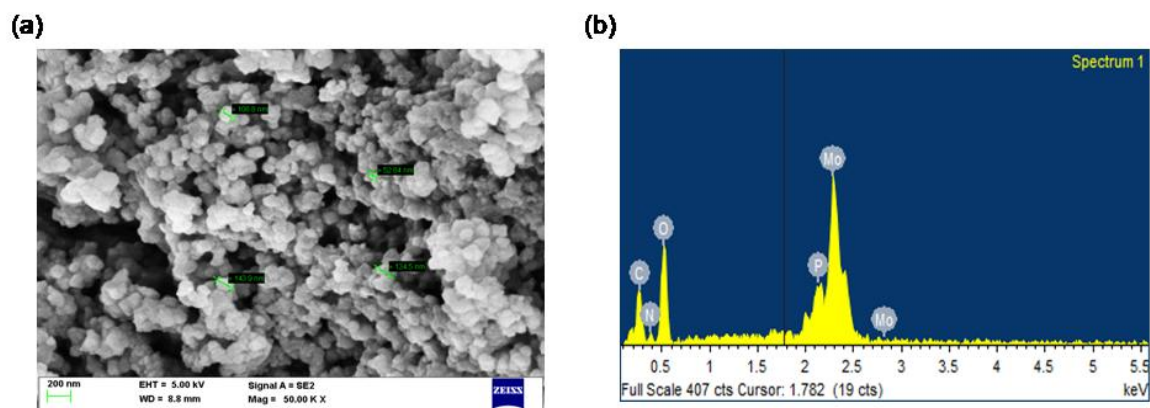
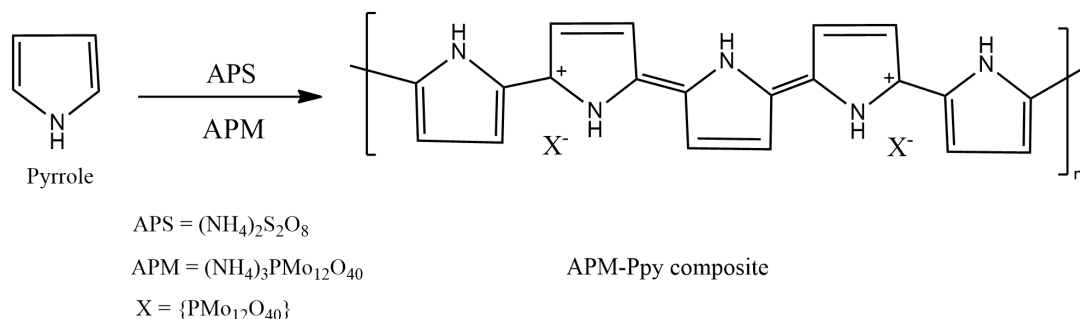


Figure VI.2 (a) FESEM image and (b) EDAX of APM-Ppy composite.



Scheme VI.2 Formation of APM-Ppy composite via oxidative polymerization.

VI.5.2 Thermal analysis

The thermal stability of the synthesized composite was studied using thermogravimetric analysis in the temperature range from RT to 800°C. Figure VI.3 shows the TG curve of APM-Ppy composite. The weight loss occurred in three steps corresponding to loss of

water molecules, Ppy moieties and finally formation of residual MoO_3 with simultaneous release of P_2O_5 .

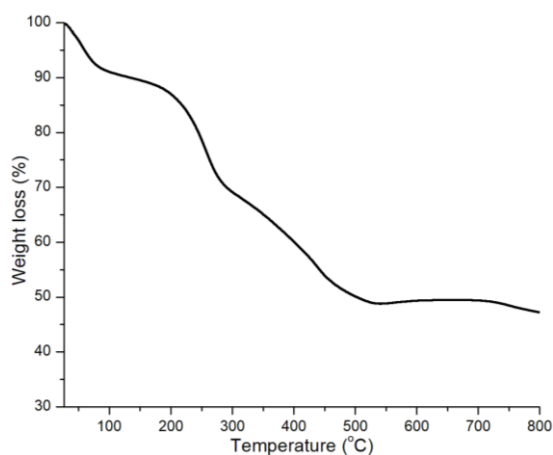


Figure VI.3 TG plot of APM-Ppy composite.

VI.5.3 Influence of reaction parameters on the formation of composite

The composition and morphology of composite materials are greatly influenced by reaction conditions such as molar ratio of the reactants, temperature, pH and stirring time. Therefore, the influence of reaction parameters viz. concentration of Ppy, stirring time and temperature on the formation of composite was studied.

VI.5.3.1 Effect of concentration of pyrrole

Different concentrations of pyrrole were used for preparing the APM-Ppy composite, keeping the concentrations of other reactants constant as per the procedure discussed under Section VI.2.1. It was observed that at lower concentrations of pyrrole (0.2 mL and 0.3 mL), phosphomolybdate solids were formed as indicated by the PXRD patterns in Figure VI.4. When the concentration was increased to (0.6 mL), APM-Ppy composite was formed. However, upon further increasing the concentration to 1.2 mL, pure Ppy was obtained which was confirmed from the PXRD pattern shown in Figure VI.4.

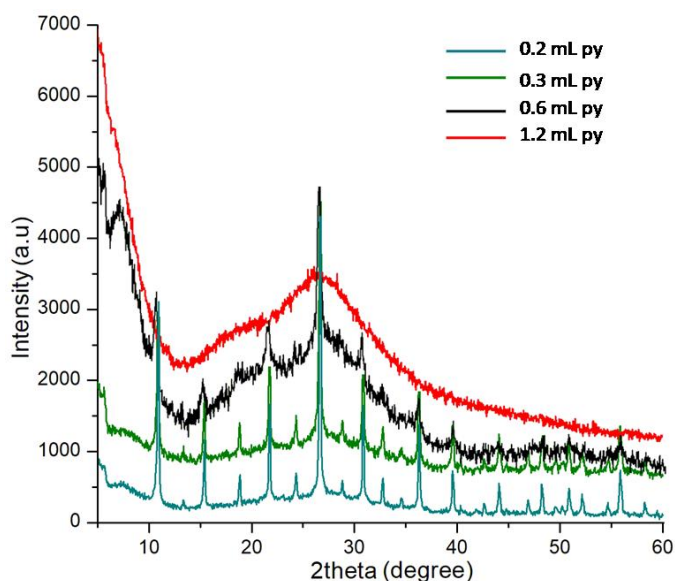


Figure VI.4 PXRD patterns of solids obtained at various concentrations of pyrrole.

VI.5.3.2 Effect of stirring time

The influence of stirring time on composite formation was also studied. At stirring times of 5 minutes and 10 minutes, APM was formed. The composite formation began on increasing the stirring time to 15 minutes and the optimum time required for forming APM-Ppy composite was found to be 20 minutes which was confirmed from the PXRD and FTIR spectra as shown in Figure VI.5

VI.5.3.3 Effect of temperature

Polymerization of pyrrole is usually carried out at lower temperatures as reported in literature [25]. Hence, during the synthesis of composite, the reactant mixture was kept in an ice bath for effective polymerization and formation of APM-Ppy composite. The synthesis was repeated at varying temperatures for studying the effect of temperature on the formation of composite. It was observed that composite formation easily took place at temperatures ranging from room temperature (RT) to as low as 3°C as indicated by Figure VI.6

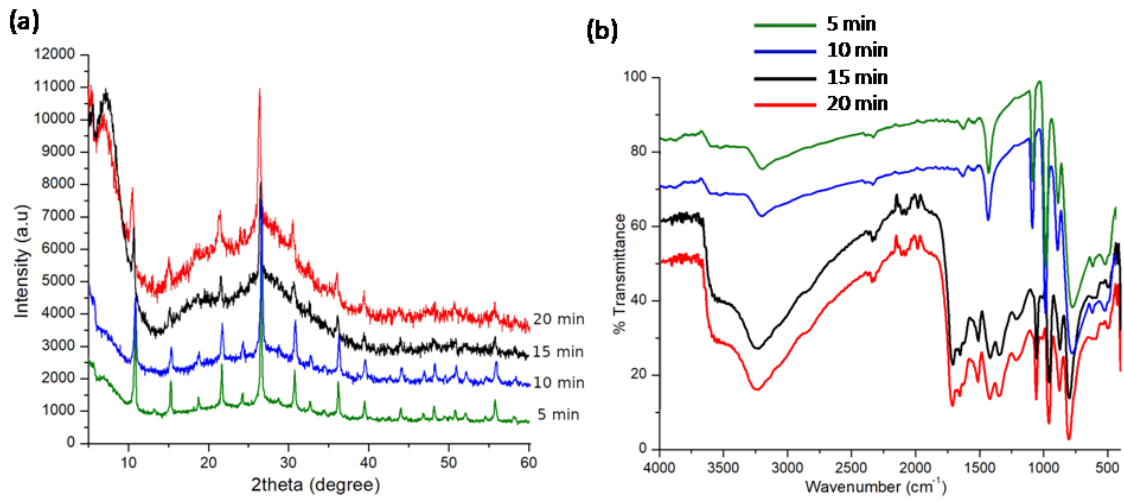


Figure VI.5 (a) XRD and (b) FTIR patterns of solids obtained at different stirring time.

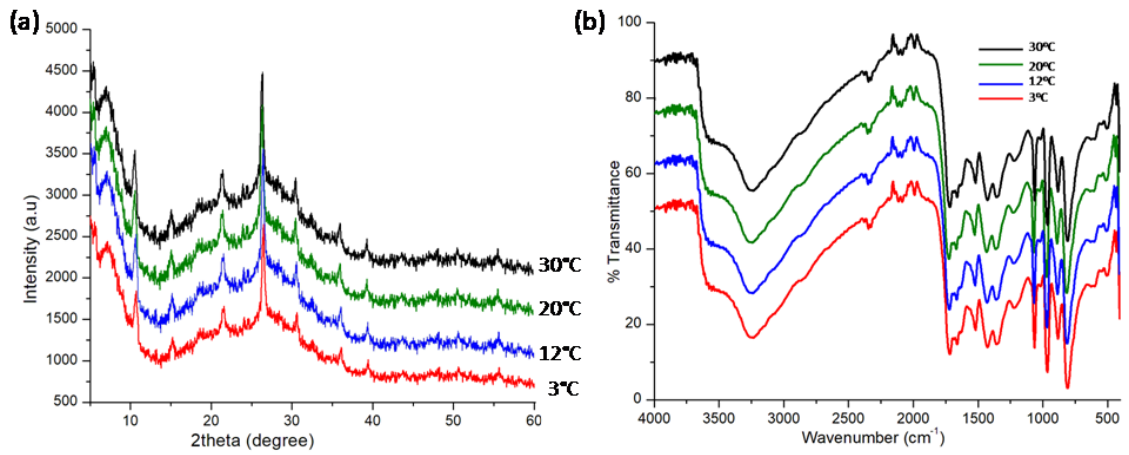


Figure VI.6 (a) XRD and (b) FTIR patterns of solids obtained at different temperatures.

VI.5.4 Solubility test and color

The solubility of Ppy and APM-Ppy composite was tested in various solutions such as distilled water, 0.1N HCl, 0.1N oxalic acid, 0.1N NaOH and 0.1N Na₂CO₃. It was observed that Ppy was insoluble in water and acidic solutions but soluble in NaOH and Na₂CO₃. It displayed yellow color in neutral and acidic solutions whereas the color changed to reddish-brown in basic solutions (Figure VI.7a). A similar color variation was also displayed by APM-Ppy composite (Figure VI.7b), but the solubility of the composite in the solutions was more when compared to the polymer.

Table VI.2 Table summarizing results obtained from solubility test and color displayed by Ppy and APM-Ppy in various acid-base solutions.

Ppy	Water	HCl	Oxalic acid	NaOH	Na₂CO₃
Solubility	Insoluble	Insoluble	Insoluble	Soluble	Soluble
Color	Yellow	Yellow	Yellow	Reddish-brown	Reddish-brown
APM-Ppy					
Solubility	Partially soluble	Partially soluble	Partially soluble	Soluble	Soluble
Color	Yellow	Yellow	Yellow	Reddish-brown	Reddish-brown

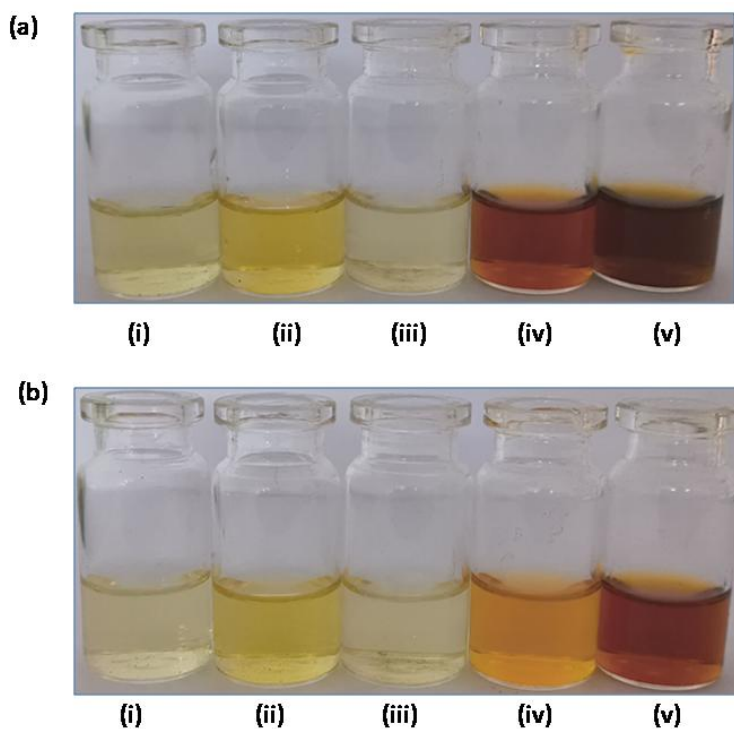


Figure VI.7 Color displayed by (a) Ppy and (b) APM-Ppy in (i) distilled water, (ii) HCl (0.1 N), (iii) Oxalic acid (0.1 N), (iv) Na₂CO₃ (0.1 N) and (v) NaOH (0.1 N).

VI.5.5 Acid-base Indicator test

Ppy and APM-Ppy composite had a stable color in acid, base and neutral solutions and showed reversible and sharp color changes when moving from acidic condition to the basic condition or vice versa. Hence, end point could be determined with high precision using both Ppy and APM-Ppy composite. The following tables include titration data of acid-base reactions that were used to evaluate the indicator property of Ppy and APM-Ppy. Figure VI.8 and VI.9 show the colors of solutions in acid and base conditions using Ppy and APM-Ppy indicator solutions respectively.

Titration I: 20 mL 0.1 N of HCl versus 0.1 N of NaOH

Indicator used	Volume of NaOH (mL)	Color in acid	Color in base
Phenolphthalein	19.4	Colorless	Pink
PPy	19.2	Yellow	Reddish-brown
APM-Ppy	19.1	Yellow	Reddish-brown

Titration II: 20 mL 0.1 N of Oxalic acid versus 0.1 N of NaOH

Indicator used	Volume of NaOH (mL)	Color in acid	Color in base
Phenolphthalein	19.8	Colorless	Pink
PPy	19.7	Yellow	Reddish-brown
APM-Ppy	19.7	Yellow	Reddish-brown

Titration III: 20 mL 0.1 N of HCl versus 0.1 N of Na₂CO₃

Indicator used	Volume of Na ₂ CO ₃ (mL)	Color in acid	Color in base
Methyl orange	18.4	red	Yellow
PPy	18.2	Yellow	Reddish-brown
APM-PPy	18.1	Yellow	Reddish-brown

Titration IV: 20 mL 0.1 N of Oxalic acid versus 0.1 N of Na₂CO₃

Indicator used	Volume of Na ₂ CO ₃ (mL)	Color in acid	Color in base
PPy	20.5	Yellow	Reddish-brown
APM-PPy	20.4	Yellow	Reddish-brown

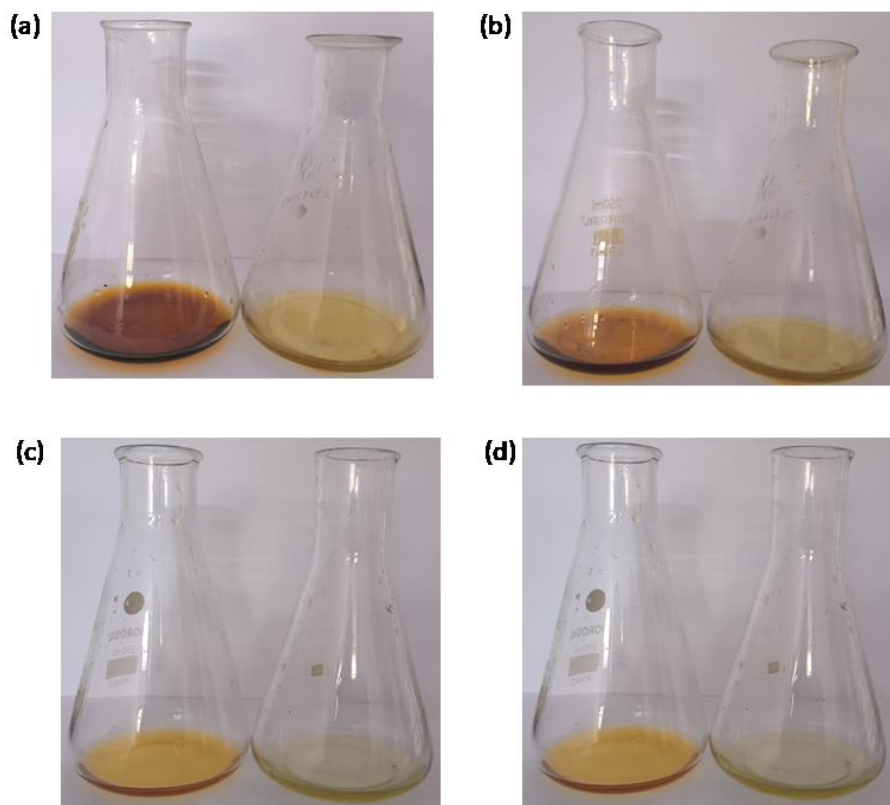


Figure VI.8 Colors of solution before and after end point in using Ppy indicator solution in (a) HCl versus NaOH (b) Oxalic acid versus NaOH (c) HCl versus Na₂CO₃ (d) Oxalic acid versus Na₂CO₃ titration.

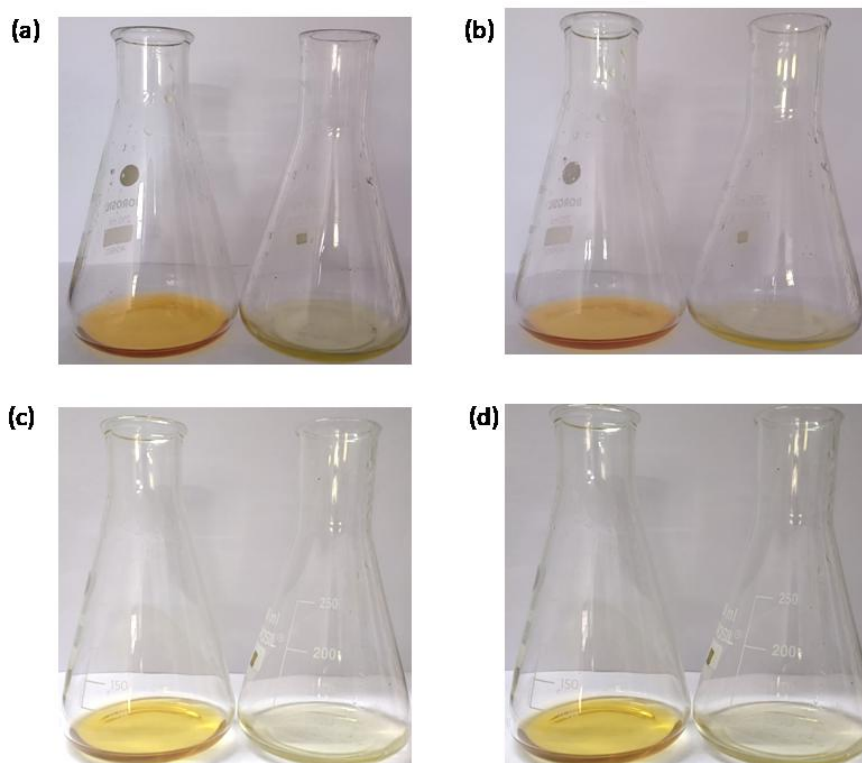


Figure VI.9 Colors of solution before and after end point in using APM-Ppy indicator solution in (a) HCl versus NaOH (b) Oxalic acid versus NaOH (c) HCl versus Na₂CO₃ (d) Oxalic acid versus Na₂CO₃ titration.



Base solution $\xrightarrow{\text{acid}}$ End point $\xrightarrow{\text{base}}$ Reversible colour change

Figure VI.10 Reversible color change of solution indicating the utility of APM-Ppy indicator solution for double burette titration as well.

The change in color from yellow to reddish-brown upon increasing pH from acidic to neutral to basic was evaluated using UV-Vis spectroscopy as well for APM-Ppy composite. A shift in λ_{\max} was observed upon change in pH as shown in Figure VI.11. The absorption peak of APM-Ppy composite showed a red shift in basic solutions due to the deprotonation of the pyrrole units. At lower pH solutions pyrrole moieties become protonated which causes a blue shift in the UV-visible spectra.

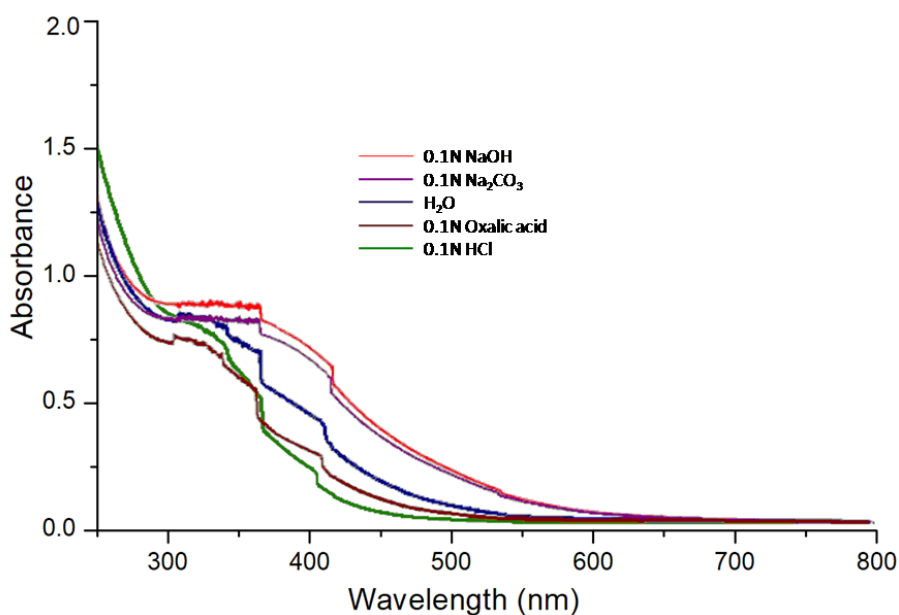


Figure VI.11 UV-visible spectra of APM-Ppy composite in acidic, neutral and basic solutions.

Table VI.3 λ_{\max} values with varying pH.

Solution	pH	APM-Ppy, λ_{\max} (nm)
Distilled water	7.0	412
0.1 N of HCl	1.5	409
0.1 N of Oxalic acid	3.1	410
0.1 N of NaOH	10.2	418
0.1 N of Na ₂ CO ₃	8.3	417

From the above results it can be observed that the APM-Ppy composite retains the acid-base properties of Polypyrrole. Moreover, the composite is soluble in all solvents when compared to Polypyrrole and APM. This makes it an excellent medium as an indicator in acid-base titrations and also as a pH sensor.

VI.6 Conclusions

A novel composite of APM-Ppy was synthesized by chemical oxidative polymerization method using APS and characterized using FTIR, PXRD, FESEM and EDAX. The thermal stability of the composite was studied by thermogravimetric analysis. The influence of reaction parameters such as concentration of pyrrole, stirring time and temperature on composite formation was investigated. It was found that composite could be easily synthesized at temperatures ranging from RT to as low as 3°C, with 0.6mL pyrrole and 20 minutes stirring time. APM-Ppy composite was also found to be an excellent acid-base indicator in various titrations and can be used as a pH sensor.

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