

**SYNTHESIS, CHARACTERIZATION AND CATALYTIC
APPLICATION OF CLAY-SULPHONATED PVA BASED
COMPOSITE MATERIALS**

A Dissertation
Submitted in partial fulfillment

FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMISTRY

Under The Academic Autonomy

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By

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DECLARATION

*The work embodied in this report is an original investigation carried out by the author, on the topic entitled, “**Synthesis, Characterization and Catalytic Application of Clay-Sulphonated PVA Based Composite Materials**” for partial fulfilment of degree in Master of Science (Chemistry), NIT Rourkela. To the best of my knowledge and belief, this work has not been submitted to any other University or Institution to confer any Degree or Diploma.*

APARAJITA NAYAK



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CERTIFICATE

This is to certify that the dissertation entitled, “***Synthesis, Characterization and Catalytic Application of Clay-Sulphonated PVA Based Composite Materials***”, being submitted by **Aparajita Nayak**, to the Department of Chemistry, National Institute of Technology, Rourkela, Odisha for partial fulfillment of the Master degree in Science (Chemistry) is a record of bonafide research work carried out by her under my guidance and supervision. I am satisfied that the dissertation has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.

Prof. B.G Mishra
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Aparajita Nayak

CHAPTER 1

INTRODUCTION

Clay-polymer nanocomposites and clay based nanohybrids have received considerable attention in recent years for their possible application as adsorbents, heterogeneous catalysts, structural materials and flame retardants [1-4]. Although, there are many investigations on the mechanical, chemical, thermal, optical, gas permeability and flame retardance properties of the polymer clay composites, there are very few reports on the application of these materials in heterogeneous catalysis and as possible materials for detoxification of aqueous sources. A polymer-clay nanocomposite is typically prepared by incorporating finely dispersed layered silicate materials in a polymer matrix. Broadly, there are two kinds of clay-polymer nanocomposites namely, intercalated and exfoliated polymer clay nanocomposites (Fig 1). Intercalated structures are formed when a single (or sometimes more) extended polymer chain is intercalated between the silicate layers [5]. The resultant material has a well ordered multilayer structure of alternating polymeric and inorganic layers, with a repeat distance between them. Intercalation causes an interlayer separation of 20–30 Å between the clay platelets. On the other hand, exfoliated or delaminated clay-polymer nanocomposites are obtained when the clay layers are well separated from one another and individually dispersed in the continuous polymer matrix. In this case, the clay sheets are typically separated by 80–100 Å. The exfoliated clay-polymer nanocomposites are of particular interest for catalysis and adsorption point of view because of the greater degree of interaction between the inorganic and polymeric matrix. Four major methods have been currently used for the preparation of the clay-polymer nanocomposites which are sol-gel method, Intercalation of prepolymer from solution, In situ intercalative polymerization and Melt intercalation [1]. In the sol-gel technique the clay minerals are synthesized within the polymer matrix, using an aqueous solution (or gel) containing the polymer and the silicate building blocks. As precursors for the clay, silica sol,

magnesium hydroxide sol and lithium fluoride are used. During the process, the polymer aids the nucleation and growth of the inorganic host crystals and gets trapped within the layers as they grow. Although theoretically this method has the potential of promoting the dispersion of the silicate layers in a one-step process it suffers from serious disadvantages. The condensation of the silicate units in to form two dimensional clay sheets requires high temperatures. It is likely that at this temperature the polymer may degrade leading to structural inhomogeneity and loss of active sites. Several polymer nanocomposites with poly(vinyl alcohol), polyaniline and polyacrylonitrile as the polymeric phase has been synthesized using this method [3,4,6].

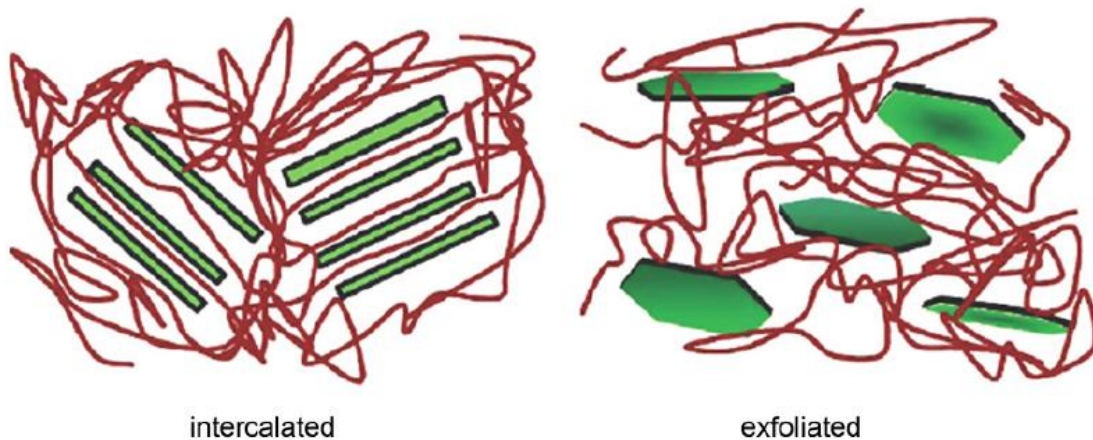


Fig.1.Schematic representation of the (a) intercalated and (b) exfoliated clay-polymer nanocomposites

In the intercalation method, the clay platelets are exfoliated into single layers using a polar solvent in which the polymer or the prepolymer is soluble. Prepolymers are particularly used when the polymer is insoluble in the solvent. After the clay platelets are completely separated in the solvent, the polymer solutions are added to the clay suspension which intercalates into the clay interlayer by diffusion to form the clay polymer nanocomposites. The solvent is subsequently removed by evaporation or precipitation method. Upon solvent removal the sheets reassemble, sandwiching the polymer to form a nanocomposite structure. The intercalation method has been used for synthesis

of polyethylene oxide, poly (vinyl acetate), Poly (vinyl ethylene) and poly(vinyl pyrrolidone) based clay-polymer nanocomposites [2,7,8].

In insitu intercalative polymerization process, the modified layered silicate is swollen by a liquid monomer or a monomer solution. The monomer migrates into the galleries of the layered silicate, so that the polymerization reaction can occur between the intercalated sheets. The reaction can be initiated either by heat or radiation or by the diffusion of a suitable initiator or catalyst fixed through cationic exchange inside the interlayer before the swelling step by the monomer. This method has been widely used to synthesize a broad range of thermoplastic and thermosetting polymers. Several types of thermoplastic polymers such as polyamides, polymethylmethacrylate, polystyrene, polybenzoxale, polyolefins, and polyethylene terephthalate (PET) have been used successfully for the synthesis of clay-polymer nanocomposites using the intercalative polymerization process [9-12].

The melt intercalation method consists of blending the layered silicate with the polymer matrix in the molten state. Under such conditions – if the layer surfaces are sufficiently compatible with the chosen polymer – the polymer can crawl into the interlayer space and form either an intercalated or exfoliated nanocomposites. This method has been mostly used to prepare thermoplastic based clay-polymer nanocomposites [1].

1.8 Objectives of the present study

The main objectives of the present study is to

1. To synthesize various clay-polymer nanocomposites using polyvinyl alcohol as polymer, chlorosulphonic acid as sulphonating agent for polymer and zirconia polyoxocations as pillaring agent for to increase the interlayer spacing of the clay materials.

2. To study the physicochemical characteristics of the synthesized clay polymer nanocomposites by various analytical techniques such as XRD, UV-Vis, FTIR, FESEM.
3. To study the catalytic application of the modified clay materials for the synthesis of hexahydropyrimidines and spiropyridines by multicomponent reaction of dicarbonyl compounds, various substituted anilines and formaldehyde under microwave irradiation

CHAPTER 2

MATERIALS AND METHODS

The Na-Montmorillonite, $(\text{Na}_{0.35}\text{K}_{0.01}\text{Ca}_{0.02}) (\text{Si}_{3.89}\text{Al}_{0.11})^{\text{tet}} (\text{Al}_{1.60}\text{Fe}_{0.08}\text{Mg}_{0.32})^{\text{oct}} \text{O}_{10}(\text{OH})_2.n\text{H}_2\text{O}$ (Kunipia-F, Kunimine industries, Japan) was used for the preparation of the pillared clay and clay – polymer composite catalysts. The cation exchange capacity of the clay is 120 mequiv $(100\text{g clay})^{-1}$. Polyvinyl alcohol (Mol wt: ~14000), chlorosulfonic acid, Zirconium oxychloride ($\text{ZrOCl}_2.8\text{H}_2\text{O}$) and CTAB were procured from Merck India Ltd., India. Double distilled water prepared in the laboratory was used in the synthesis procedure.

2.1 Preparation of the catalysts

2.1.1 Preparation of sulfonated polyvinyl alcohol (SPVA)

4.4 g of Polyvinyl alcohol (PVA) was dissolved in 15 mL of pyridine and refluxed for 2 h at 80°C. The polymeric solution was subsequently cooled in ice bath and stored in a freezer. 8 mL of chlorosulfonic acid was added dropwise for 30 min to another 15 mL of portion of pyridine which was previously kept in an ice bath. The resulting yellow solid was stored under cool condition in a freezer. During the sulfonation process, the yellow solid is dissolved in 15 mL of pyridine by warming at 60°C. The solution was then added dropwise to the polymeric solution under cold condition. The resulting solution was refluxed at 80°C for 4 h to obtain the sulfonated PVA. The sulfonated polymer was filtered, washed using acetone and purified by precipitation from hot water.

2.1.2 Preparation of sulfonated PVA-Clay composite material (Clay-SP)

2 gm of clay material was dispersed in 200 ml of deionized water to form clay slurry. The slurry was sonicated for 15 minutes for better dispersion of the clay platelets and then stirred at 60°C for 2 h. 2 gm of SPVA was dissolved in 50 mL of hot water. The polymeric solution was added dropwise to the clay slurry under constant stirring. The resulting suspension was stirred for 12 h

and then cooled near to ice temperature. The suspension was filtered, washed with cold water and dried at 120°C in a hot air oven to obtain the Clay-SP material.

2.1.3 Preparation of SPVA-Zr-Pillared clay composite material (ZrP-SP)

The 0.1 M Zr- pillaring solution was prepared by dissolving required amount of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ salt in 500mL of water. The pillaring solution was subjected to heat treatment at 70°C for 24 hours. 5 gm of clay was dispersed in 250 mL of water to form a clay suspension. To ensure well dispersion, the clay suspension was stirred at room temperature for 2 h followed by sonication for 15 minutes. The pillaring solution was added dropwise to the clay suspension at the rate of 50 mL per hour under continuous stirring at room temperature. The mixture was left for stirring under room temperature for 24 h which was subsequently filtered and washed six times with deionised water to remove the chloride ions. The obtained gel was air dried at 120°C followed by calcination at 450°C for two hours to obtain the Zr-Pillared clay (Zr-P). Similar procedure as discussed in the previous section was adopted for synthesis of ZrP-SP catalyst.

2.2 Characterization of the Clay-polymer nanocomposites

The clay-polymer nanocomposites synthesized in section 2.1 were characterized by X-Ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), UV-Visible spectroscopy (UV-Vis) and Fourier transformed Infrared Spectroscopy (FTIR).

X-ray diffraction:The X-ray diffraction patterns of the clay-polymer composite samples were recorded on a Ultima IV, Rigaku diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation. The XRD measurements were carried out in the 2θ range of 1-20° with a scan speed of 2 degrees per minute using Bragg-Brantano configuration.

Scanning Electron Microscopy:The FESEM analysis was carried out by using Nova NanoSEM/FEI microscope. Prior to FESEM analysis the powder sample is placed on carbon tape followed by carbon coating.

UV-Vis Spectroscopy: UV-Vis Spectra of clay-polymer composite materials were recorded using barium sulphate as reference compound on a Shimadzu spectrophotometer (UV-2450) in the range of 200-900 nm.

Infrared Spectroscopy: The IR spectra of different clay-polymer composite materials (as KBr pellets) were recorded using a Perkin-Elmer infrared spectrometer with a resolution of 4 cm^{-1} , in the range of 400 cm^{-1} to 4000 cm^{-1} . Nearly 3-4 mg of the sample was mixed thoroughly with 30 mg of oven dried KBr and made into pellets. The pellets were stored in vacuum desiccators and exposed to IR lamp for 1 minute prior to the IR measurement.

2.3 Catalytic studies for synthesis of hexahydropyrimidines

The catalytic activity of the clay-polymer composite materials was evaluated for the synthesis of hexahydropyrimidines by multi component condensation of 1,3-dicarbonyl compounds, substituted anilines and formaldehyde under solvent free condition using microwave as source of energy. Typically, a mixture of 1,3-dicarbonyl compounds (1 mmol), Aniline (1 mmol), aniline (2 mmol), formaldehyde (3 mmol) and 50 mg of different synthesized catalysts was exposed to microwave for the desired amount of time with an intermittent cooling interval of 2 minutes after every one minute exposure time. The reaction was monitored by TLC. After the completion of the reaction, 10 mL of ethanol was added to the the reaction mixture and the content was stirred for 30 minutes. The ethanolic suspension was subsequently filtered to separate the catalyst. The final product was recovered from the ethanol solution and recrystallized 1 to acquire the pure product. All the products obtained are known compounds and are characterized by comparing their physical and spectral characteristics with those reported in literature.

CHAPTER 3

RESULT AND DISCUSSION

3.1 XRD STUDY

The XRD patterns of the parent clay along with the calcined Zr-P material is presented in figure 3.1. The parent clay shows relatively broader and intense reflections at $2\theta = 6.8^\circ$ with basal spacing of 12.8 Å. This peak corresponds to the reflection from the (001) plane of the layered material. After the intercalation of the Zr-oxyhydroxy cluster into the clay layer the (001) peak has shifted to lower 2θ value indicating an expansion in the layer structure as a result of pillaring. The d_{001} value observed for the calcined Zr-P material is 19.0 Å.

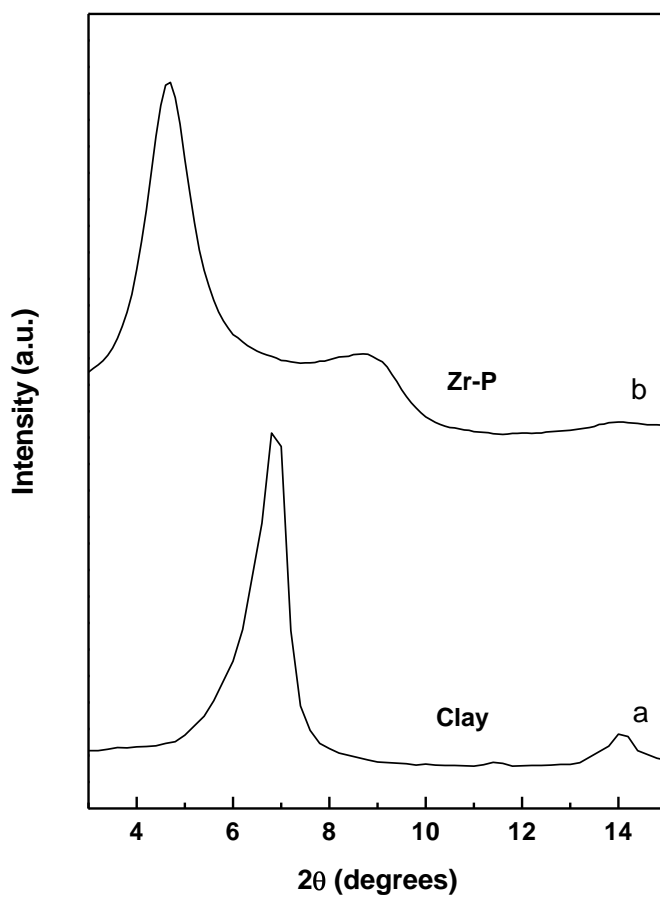


Figure 3.1 XRD patterns of (a) parent Clay and (b) Zr-pillared clay (Zr-P).

Zirconium ion is known to form stable tetrameric species in moderately concentrated and acidic solutions with structural formula $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ and size $0.89 \times 0.89 \times 0.58 \text{ nm}^3$. These tetrameric species are well characterized in solution and are considered to be the major oligomeric species present in the pillaring solution (Figure 3.2) [13]. The structure of the complex ion in solution is described as square planar with Zr^{4+} ions located at the corners of the square which are joined by two bridging OH^- ions along each edge [13]. The eight-fold coordination of Zr^{4+} ion is satisfied by the oxygen atoms of four surrounded water molecules. In the present study the basal spacing value of 19.0 \AA observed for the Zr-Pillared clay is in accordance with earlier reported value in literature.

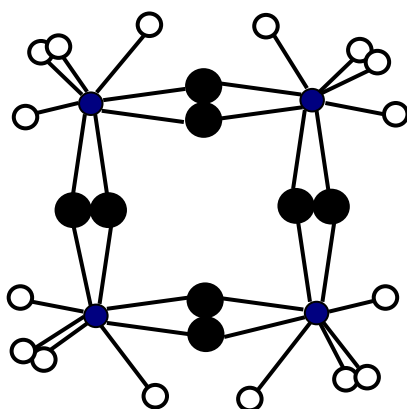


Figure 3.2 Structure of $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ cationic clusters

The XRD patterns of the clay-polymer nanocomposite materials are presented in figure 3.3. The corresponding basal spacing value calculated from the XRD profile is presented in Table 3.1. The Clay-SP material shows a well-defined intense peak at $2\theta = 6.9^\circ$ with a broad shoulder at 4.4° . The basal spacing value corresponding to these XRD peaks are 12.8 and 20.2 \AA respectively. This observation clearly suggested that a majority fraction of the polymer is not intercalated inside the clay interlayer when parent clay is used for the preparation of the composite oxide.

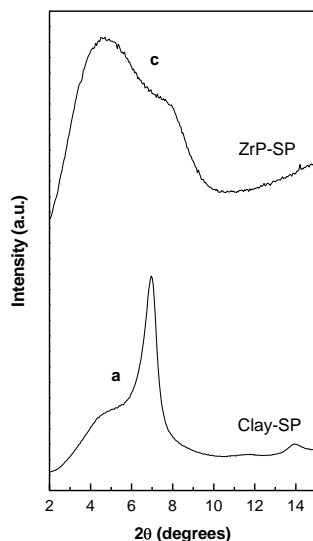


Figure 3.3 XRD patterns of (a) Clay-SP and (b) ZrP-SP.

The XRD patterns of the Zr-Pillared clay-sulfonated polyvinyl alcohol composite materials are presented in figure 3.3 b. The composite material is found to be structurally stable and shows well defined XRD peaks. The basal spacing value observed for this material is 19.2 Å which is identical to the Zr-pillared clay material. The expansion in the layer structure of the clay material and the structural rigidity achieved due to pillaring are important factors which promotes the diffusion and intercalation of the polymeric chains inside the clay interlayer. The enhanced interlayer space achieved due to pillaring can accommodate the SPVA chains forming composite materials which are thermally and structurally stable.

Table 3.1 Physicochemical characteristics and catalytic activity of the clay-polymer composite materials.

Sl No	Catalyst	Basal spacing (Å)	Acidity (mmol/g)	Microwave exposure Time (min)	Yield ^c
1	SP-Clay	12.8 (major) 20.1 (Minor)	0.32	08	42.3
3	SP-ZrP	19.2	0.72	06	76.8

3.2 UV-Vis study

The UV-Vis spectra of the parent clay, Zr-pillared clay along with the clay-polymer composite materials is presented in figure 3.4. The band observed at 247 nm (Fig. 3.4a) is characteristic for montmorillonite clay and attributed to the charge transfer transition for the structural iron present in the octahedral layer of the clay mineral ($\text{Fe}^{3+} \leftarrow \text{O}^{2-}$, OH^- or OH_2) [14]. Incorporation of the Zr-nanopillars into the clay interlayer results in a change in the absorption feature of the parent clay. For Zr-P material, an additional band was observed at 210 nm. This band can be assigned to the $\text{Zr}^{4+} \leftarrow \text{O}^{2-}$ charge transfer transition arising out of the zirconia nanopillars present in the clay interlayer [15]. In case of Zr-P material, it is likely that extremely small zirconium dioxide nanoclusters exist as pillars with octacoordination in the clay interlayer. After the incorporation of the polymeric species into the clay material, the clay-polymer composites shows absorption band at 257 nm.

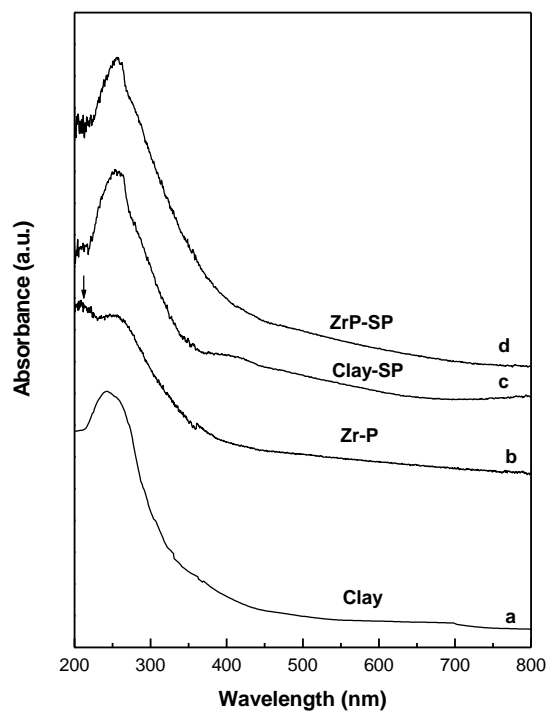


Figure 3.5 UV-Vis spectra of (a) parent clay, (b) Zr-P, (c) Clay-SP and (d) ZrP-SP materials.

3.3 FTIR study

The FTIR spectra of pure clay material along with the Clay-SP, CTAB-Clay-SP and ZrP-SP materials are presented in figure 3.6. All the clay materials shows two well defined intense bands at 3630 and 3425 cm^{-1} in the stretching region of the FTIR spectrum (panel I). These bands are assigned to the O-H stretching vibration from the structural hydroxyl group and the water molecules present in the interlayer space of the clay materials, respectively. In addition to the O-H stretching vibration, the clay-polymer composite materials show two less intense bands at 2850 and 2920 cm^{-1} . These peaks are ascribed to symmetric and asymmetric stretching vibrations of CH_2 group in the structural skeleton of the polymeric species.

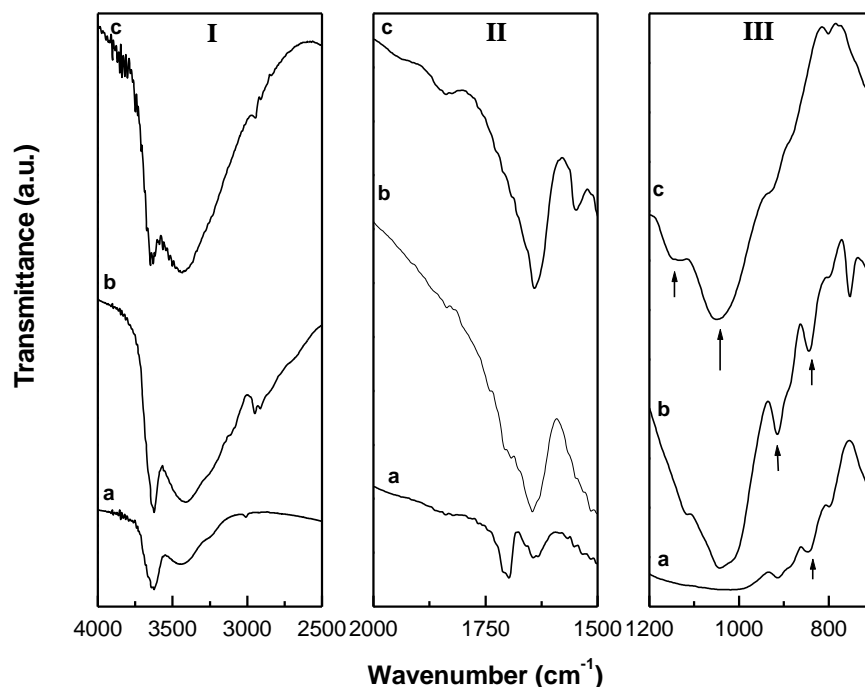


Figure 3.6 FTIR spectra of (a) Clay, (b) Clay-SP, (c) ZrP-SP.

The IR band observed at 1630 cm^{-1} in Fig. 4.3 (panel II) is due to the bending vibration mode of OH groups. Montmorillonite clay is known to possess two types of hydroxyl groups. One of them

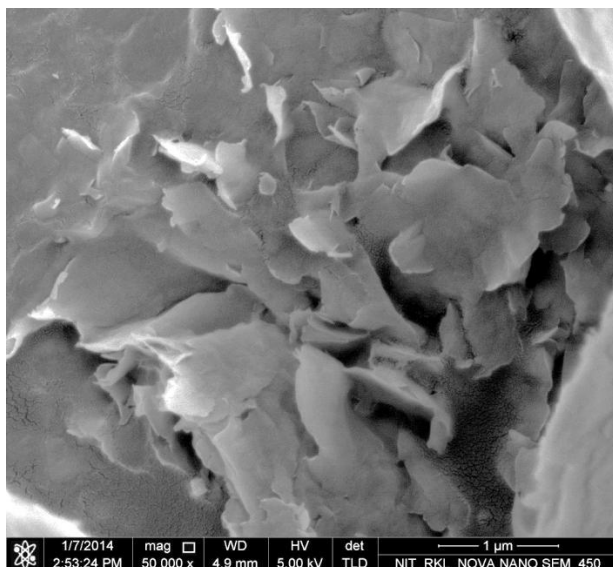
is more labile with IR absorption pattern similar to that of liquid water and has been ascribed to the water molecules present in the outer coordination spheres of the interlayer cations [16]. The other type is more firmly held and associated with the water molecules directly coordinated to the exchangeable cations. The later type also contributes significantly to the absorption band at 1630 cm^{-1} and also responsible for the acidity of the material [17]. The intense band observed at 1630 cm^{-1} for the ZrP-SP materials suggests the possibility of increase in acidity due to pillaring with Zr-polycation as well as dispersion of the SPVA polymer in the Zr-P matrix.

Montmorillonite clay shows a series of discrete peaks between 700 and 950 cm^{-1} and is related to the structural OH-bending mode of the octahedral sheet [18]. In case of parent clay, three IR bands were observed at 912 , 840 and 795 cm^{-1} corresponding to the bending vibration modes of the Al-Al-OH, Al-Mg-OH and Mg-Mg-OH groups, respectively, in the octahedral layer of the montmorillonite. These bands were found to be preserved in the clay-polymer composite materials indicating the structural integrity of the clay in the pillared clay-SPVA composite. In addition to the characteristics clay vibrations, two additional bands are observed at 1155 and 1030 cm^{-1} for the clay-polymer composites. These bands are ascribed to the S=O and O-S-O vibrations of the sulfonate ($-\text{SO}_3\text{H}$) group present in the polymer skeleton. The FTIR study clearly indicates the presence of sulfonated polymeric species in the clay interlayer and the clay material retains its structural integrity in the composite material.

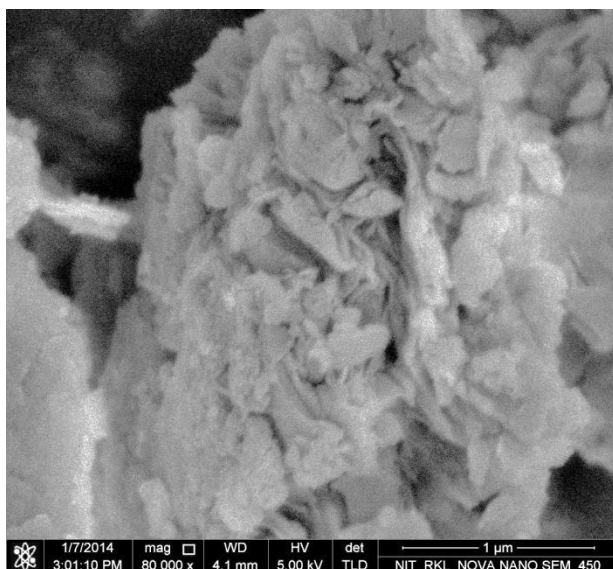
3.4 FESEM study

The FESEM image of the Clay-SP and ZrP-SP materials are presented in figure 3.7. Considerable exfoliation of the clay sheets are observed in the SEM image if the Clay-SP material. The individual clay platelets are visible in the scanning electron micrograph and they are separated from one another (Fig. 3.7 a). The presence of the SPVA polymeric chains disturbs the staking arrangement of the clay platelets which results in exfoliation. The ZrP-SP on the other hand, shows

folded particle morphology. The platelets are folded due to enhanced face to edge and edge to edge interactions. The structural rigidity achieved due to pillaring promotes these interactions which resulted in particle morphology (Fig. 3.7 b).



(a)

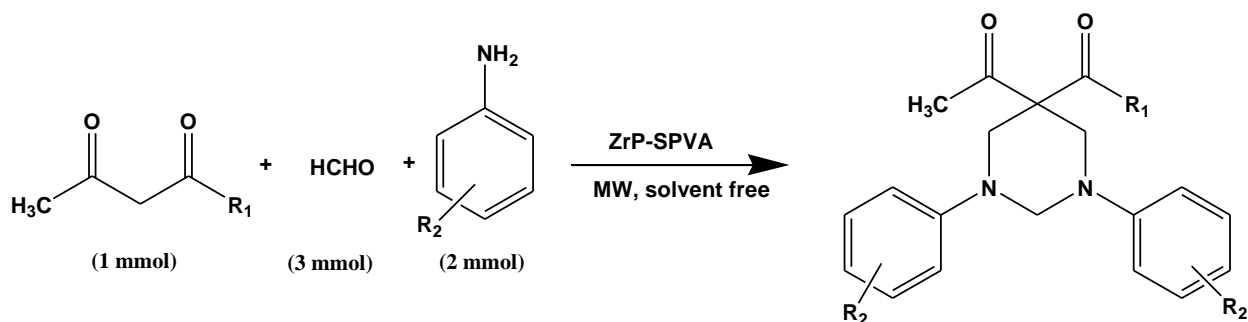


(b)

Figure 3.7 Field Emission Scanning Electron Micrograph of (a) Clay-SP and (b) ZrP-SP.

3.5 Catalytic studies for synthesis of hexahydropyrimidines

In the present investigation, we have successfully used the clay-polymer composites for the synthesis of a variety of substituted hexahydropyrimidines. Hexahydropyrimidines forms the basic skeletal framework of various pharmaceutical products as well as other biologically important molecules. The substituted hexahydropyrimidines (hhp) display antitumour properties. Spermidine-nitroimidazole drugs used for lung carcinoma are obtained from the substituted hexahydropyrimidines [19]. The hhp moieties are also helpful as R-adrenergic blockers and are found in drugs used for inhibiting segregation of platelets [20]. Considering the vast importance of hexahydropyrimidines and their analogues in pharmaceutical products, we have designed a simpler protocol for synthesis of these biologically active molecules using the clay-SPVA polymer as ecofriendly catalyst under mild conditions. In this investigation, structurally diverse hexahydropyrimidines are synthesized by multicomponent one pot condensation of formaldehyde, substituted anilines and β -dicarbonyl compounds (Scheme 3.1). Initially, the condensation of formaldehyde, aniline and ethylacetoacetate was taken as a model reaction and various clay-polymer composites were tested for their catalytic activity under solvent free conditions using microwave as energy source. Table 3.1 gives the catalytic activity of various clay-polymer composite materials for the model reactions.



Scheme 1. Multicomponent one pot synthesis of hexahydropyrimidines catalysed by Clay-polymer composite materials

Among all the clay-polymer composite materials the ZrP-SP gives highest yield of the product in a short reaction time. This material also shows more number of acidic sites compared to the other clay-polymer composites determined by non-aqueous titration method. Hence the SP-ZrP material was selected for further study. In order to optimize the protocol, the catalyst amount and the microwave power was varied, the results of which is presented in Figure 3.8.

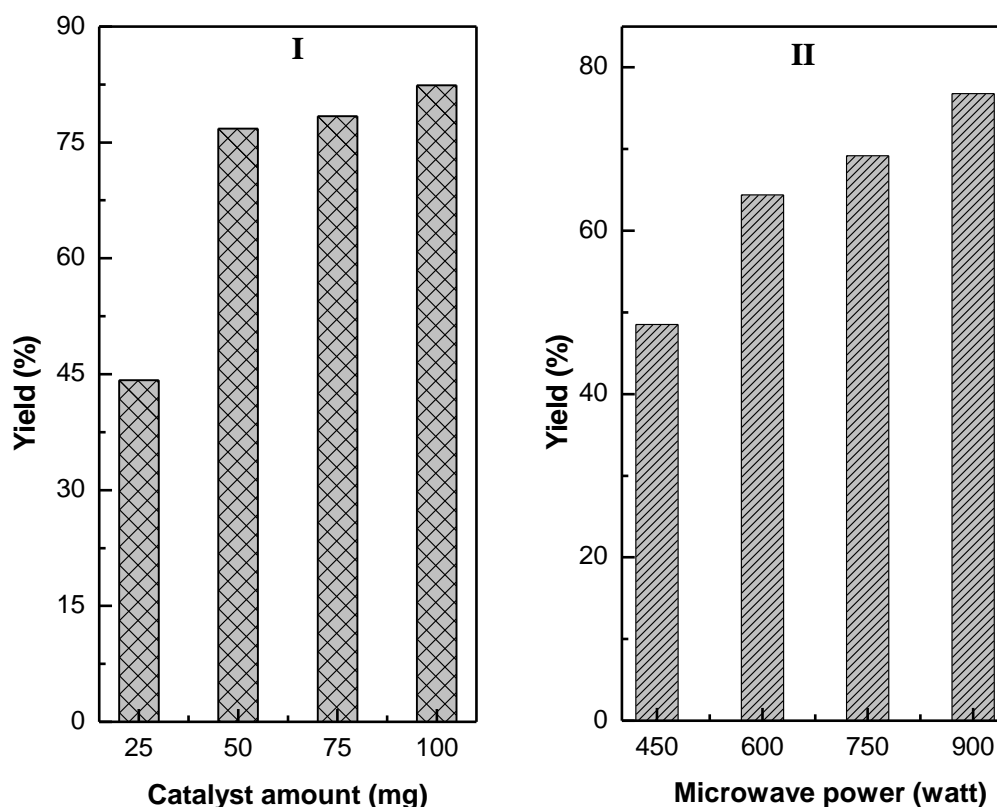


Figure 3.8 Effect of catalyst amount and microwave power on the activity of ZrP-SP catalyst.

It is observed that for reaction involving one mmol of β -dicarbonyl compounds the yield of the product increases rapidly upto 50 mg of the catalyst. Further increase in the catalyst amount does not have a marked impact in yield. Hence 50 mg of the catalyst was chosen for reaction involving one mmol of β -dicarbonyl compounds. The microwave power was varied between 450-900 w. With increase in microwave power the yield of the product was found to improve. Hence 900 W

microwave power was chosen for further study. After optimizing the reaction conditions, we explore the scope and limitation of the catalytic protocol by using various substituted aniline and β -dicarbonyl compounds in the optimized protocol (Table 3.2). It was observed that all the substituted anilines reacted efficiently in the optimized protocol to give the corresponding hexahydropyrimidines in high yield and purity.

Table 3.2 Catalytic activity of ZrP-Sp catalyst for synthesis of structurally diverse hexahydropyrimidines

Sl No	R ₁	R ₂	MW exposure time (min)	Yield (%)
1	OC ₂ H ₅	H	6	76.8
2	O C ₂ H ₅	4-Cl	8	75.2
3	O C ₂ H ₅	4-OCH ₃	6	85.2
4	OCH ₃	H	6	79.5
5	OCH ₃	4-Cl	6	80.0
6	O CH ₃	4-OCH ₃	9	86.3
7	Ph	H	8	71.5
8	Ph	4-Cl	8	67.4
9	Ph	4-OCH ₃	8	74.6

The presence of electron withdrawing group in the aniline was found to improve the yield of the product. Among the β -dicarbonyl compounds the benzoyl acetone was least reactive and best activity was observed for methyl acetoacetate. In conclusion a variety of hexahydropyrimidines are synthesized using the ZrP-SP catalyst.

CHAPTER 4

CONCLUSION

In this work we have reported the synthesis, characterization and catalytic application of Zr pillared clay-sulfonated polyvinyl alcohol composite materials for synthesis of hexahydropyrimidines. The clay-polymer composites were prepared by dispersion of the sulfonated PVA polymer in the clay matrix. Pure clay was ineffective for the dispersion of the polymeric material. The Zr-pillared clay was found to be quite efficient for the dispersion of the SPVA polymer. The structural integrity and the retention of the crystalline character of the clay material in the ZrP-SP composite material were evident from the XRD study. The UV-Vis study indicated the presence of small zirconia nanoclusters inside the clay interlayer as pillars. FTIR study indicated the structural integrity of the clay material in the composite. The characteristic vibrational feature of the clay sheet as well as the sulfonated polymer was confirmed from the FTIR study. The exfoliation of the clay sheets and the desegregation of the clay platelets were noted from the FESEM study. The ZrP-SP material was used as catalyst for the synthesis of structurally diverse hexahydropyrimidines by multicomponent one pot condensation of substituted aniline, β -dicarbonyl compounds and formaldehyde under solvent free condition and microwave irradiation. The catalytic study suggested that the SP-ZrP material is highly active for the reaction yielding a variety of hexahydropyrimidines. In this work, a novel attempt has been made to prepare clay-polymer composite having polymer with acidic functionality.

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