

Synthesis, Characterization and Studies of PANI-MMT Nanocomposites

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Abstract In this work synthesis & characterization of composite materials based on montmorillonite (MMT) clay and intrinsically conducting polyaniline (PANI) is studied. The MMT type of clay used is locally available in the region which was used after chemical activation. The main thrust of this work was to know the possibility of usage of locally available clay to synthesise novel nanocomposites. Synthesis of PANI and processing and treatment of this clay was carried out in the lab by the authors. PANI was successfully incorporated into MMT to form PANI-MMT nanocomposites. The resulting organic-inorganic hybrid material, PANI-MMT has been characterized by various physicochemical techniques. Formation of PANI inside the clay tactoid has been confirmed by X-ray diffraction studies. Infrared spectroscopy studies reveal the presence of physicochemical interaction, probably hydrogen bonding, between clay and polyaniline. One of the main technological applications of conducting polymers, particularly PANI, is in the area of corrosion protection of active metals. PANI-MMT nanocomposites synthesized using the present method is generally used to protect steel surface against corrosion.

Keywords Nanocomposites, PANI, Infrared Spectroscopy, Conducting Polymer, Corrosion

1. Introduction

Among the large amount of layered solids such as graphite, layered double hydroxides, transition metal dichalcogenides, metal phosphates and metal phosphonates, clay minerals especially the members of smectite group are the most suitable candidates for synthesis of polymer nanocomposites, because these possess a unique structure and reactivity together with high strength, stiffness and high aspect ratio of each platelet. In particular, montmorillonite $[M(OH)_2 \cdot nH_2O \cdot (AlMg_{x-2x})Si_4O_{10}(OH)_2 \cdot nH_2O]$ and hectorite $[M_x(Mg_{3-x}Li_x)Si_4O_{10}H_2O]$, are most widely used in this field. Montmorillonite is a hydrophilic mineral and belongs to the general family of 2:1 (so-called smectite) phyllosilicates composed of stacked layers of aluminum octahedron and silicon tetrahedrons. Substitution of aluminum with magnesium will create an overall negative charge which is compensated by exchangeable metal cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} [1]. Characteristics of clay minerals which make them important are their particle size and shape, cation exchangeability, adsorption properties and large surface area. The unique structure, low negative charge per

unit cell and weak van der Waals forces between adjacent layers can allow the interlayer space of clay minerals to expand upon the intercalation of organic cations, organic solvent or polymer. Clay minerals specially montmorillonite have widely been employed to synthesize polymer-clay nanocomposites due to their swelling behaviour, ubiquity and low cost.

With recent advancement in nanotechnology and its potential applications, organic-inorganic nanocomposites have received considerable attention due to the special nature of both components. Conducting polymers including PANI themselves could find their niche in electronics, pharmaceutical, biomedical industries etc. However, there are intrinsic problems with these materials that prevent them from wide commercial applications such as poor processability due to rigid chemical structure and porosity of their coating. Some of these limitations can be overcome by reinforcing the conducting polymers with nanosized filler such as clay particles[2]. The incorporation of clay in conducting polymers may provide characteristics which cannot be attained from pristine conducting polymer such as processability[3]. Among organic-inorganic nanocomposites, PANI-MMT nanocomposites are the most prevalent and interesting due to the special properties as well as wide uses of polyaniline[4], the nature, abundance, low cost of MMT and attractive features such as a large surface area and ion-exchange properties[5].

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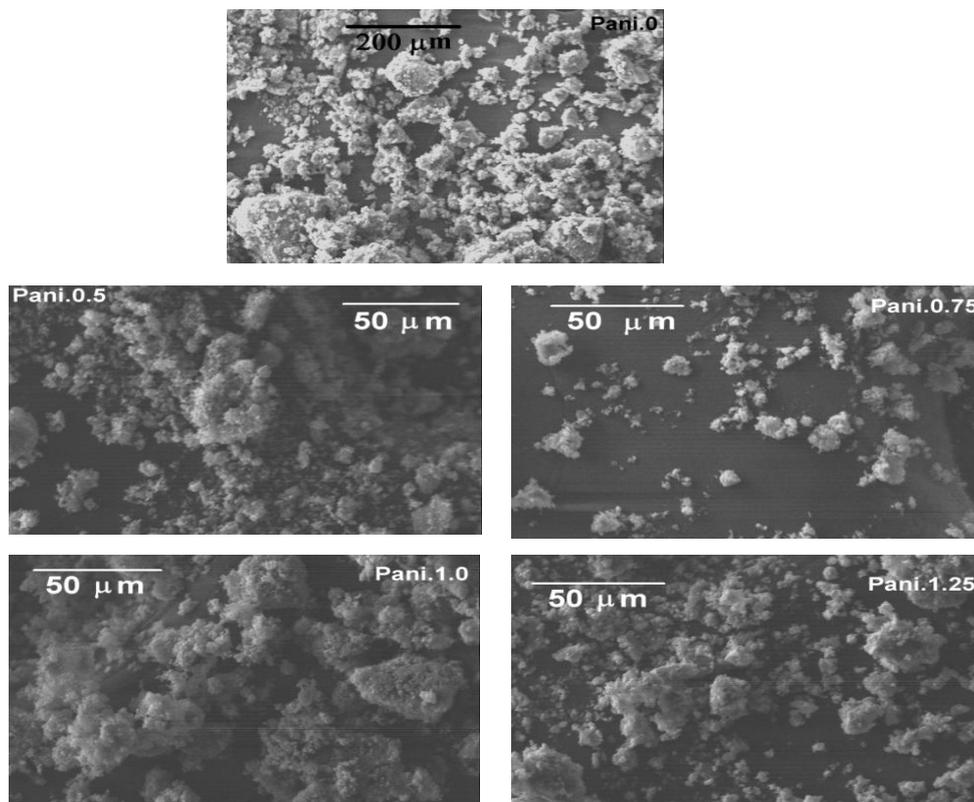


Figure 2. SEM images of Pani-clay at low and high magnifications

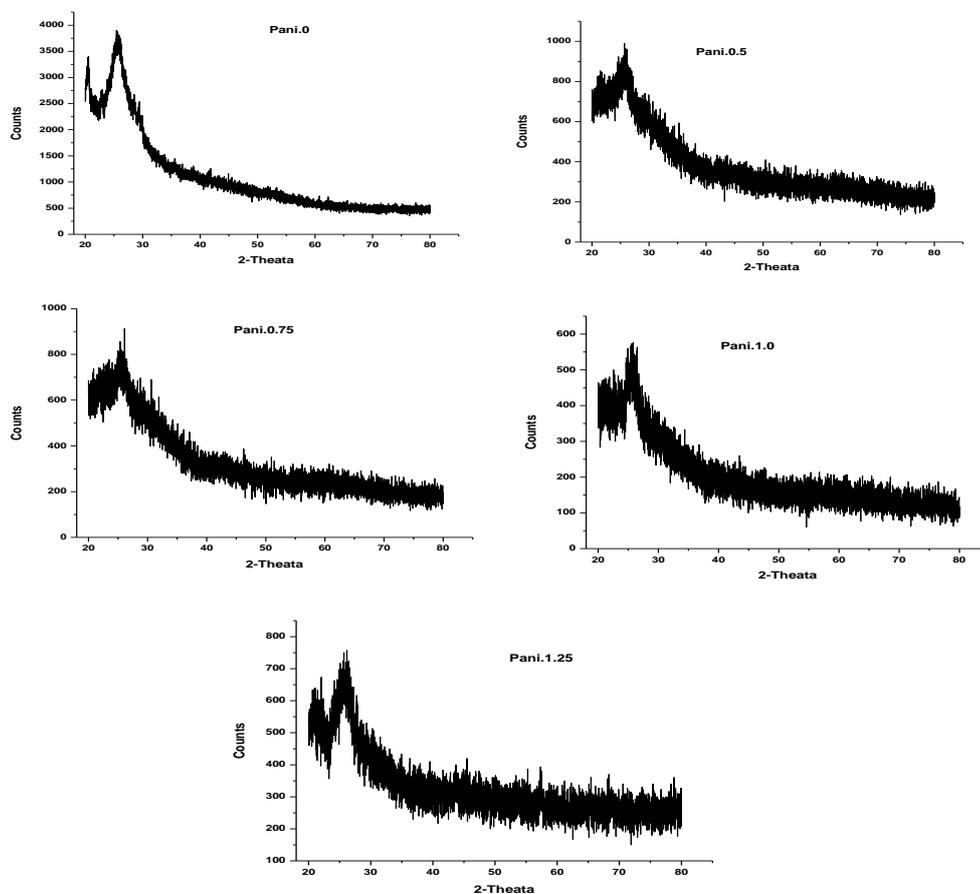


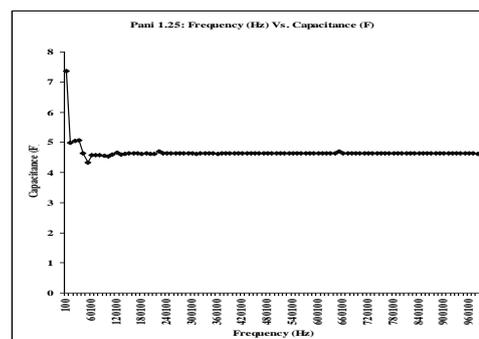
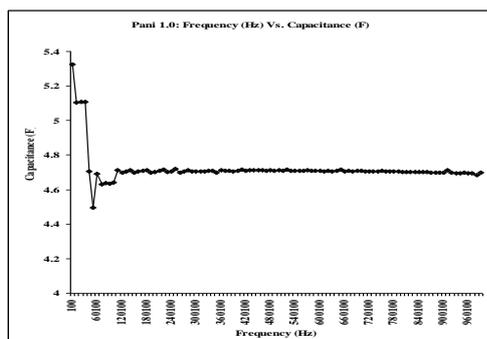
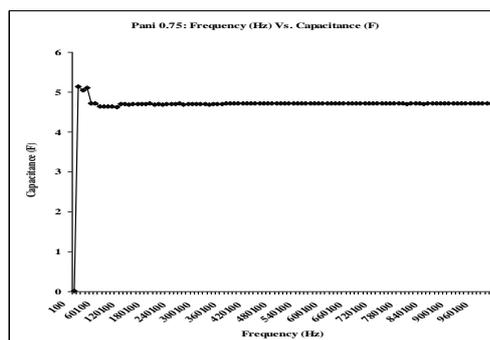
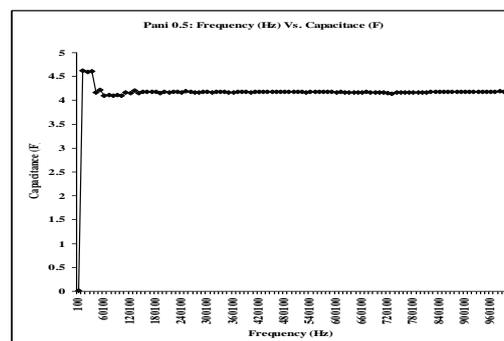
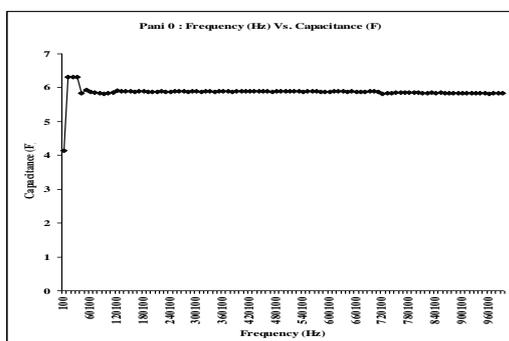
Figure 3. XRD spectra of PANI_MMT nanocomposites with different concentrations of clay

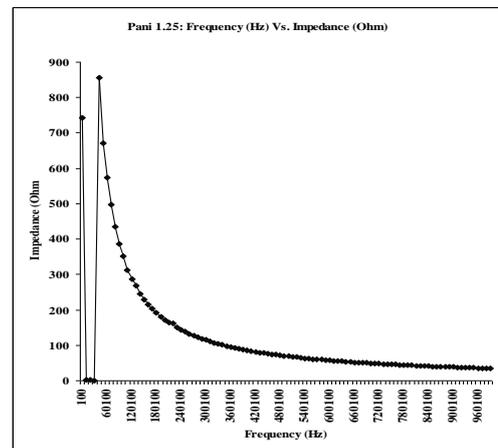
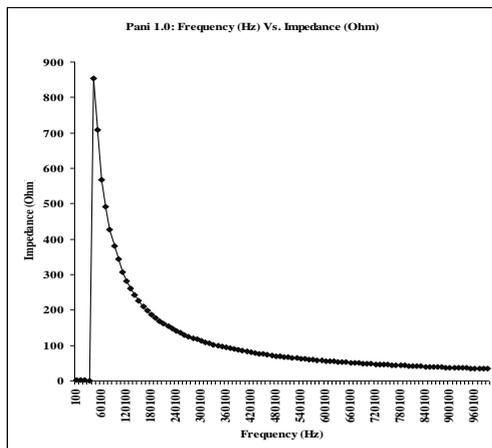
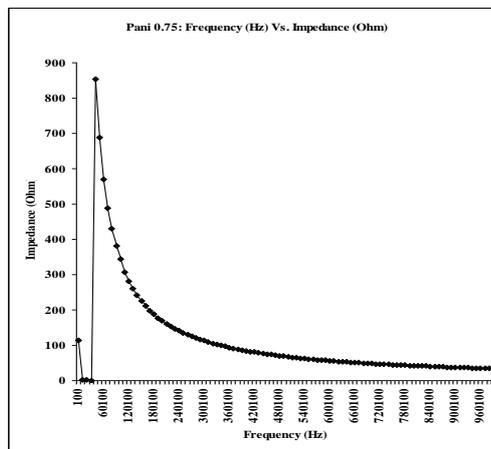
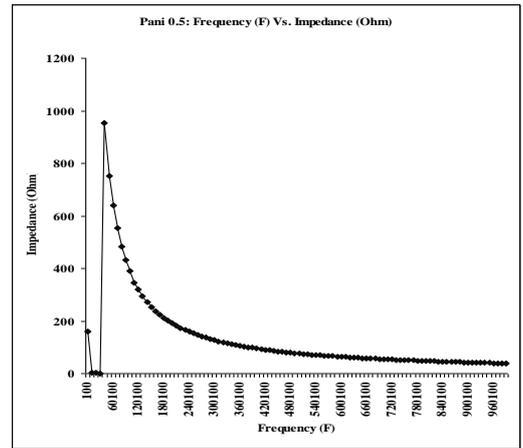
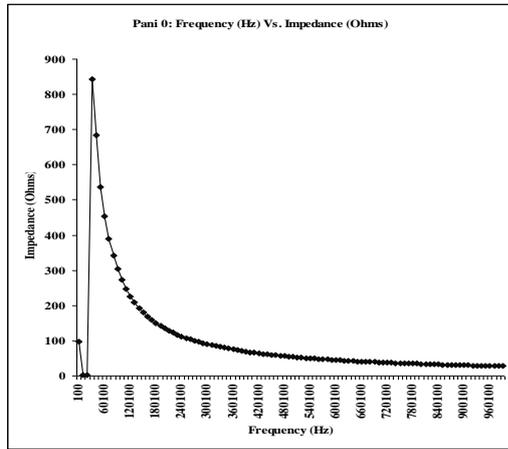
FTIR peaks cm^{-1}	Assigned Functional Groups
800-900	Out of plane C-H bond
1038	Si-O stretching (Clay)
1285-1300	C-N stretching of the secondary aromatic amine
1400-1480	Benzenoid rings.
1500-1567	Quinoid rings.

FTIR analysis: The spectrum showed peaks at 1290 cm^{-1} , 1441 cm^{-1} , which are the characteristic peaks of polyaniline. The relative intensity of the 1557 and 1481 cm^{-1} indicates the oxidation state of the material. For Pani, the peak area ratio was 1.0 the polymer is in the emeraldine salt. The peaks observed at $500-600 \text{ cm}^{-1}$, 1067 cm^{-1} are due to the presence of clay in the composite. The peak assignments are listed in the table[22- 25]. The spectrum showed characteristic peaks of polyaniline and clay at 1067 and 1430 cm^{-1} , the IR spectrum for the different composites is shown in the figure 1. It was difficult to detect the presence of polyaniline and clay in this system using IR spectrum. This could be due to the masking effect of polyaniline on the powder. As this was a filtered system, very fine particles were present in the system.

It is believed that the polyaniline matrix surrounded these particles, making it difficult to characterize them.

Figure 2 shows SEM micrographs images of Pani-clay composites with different amount of clay in the composites. Scanning electron micrograph (SEM) revealed some interesting morphological differences between the pure bentonite clay and Pani-clay composites. The surface of pure clay was flaky texture reflecting its layered structure[26] as shown in figure. Pani has a rod like network texture and Pani Clay composite has flower petals like appearance. It can be clearly seen in micrographs of all clay composites that the textures of both pani-clay are retained in the composites which are of different grain sizes. The micrographs of pani-clay 1.25% composites exhibit more ordered and dense structure (smaller sizes with high density of granules per unit area) comparing to pani-clay composite comparing to pani-clay 1.0% clay (bigger sizes with less density per unit area). It shows that the increase in clay percentage in the preparation solution will increase the compactness.





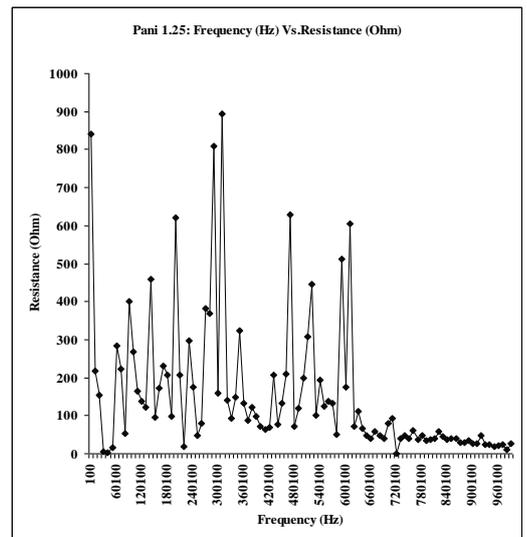
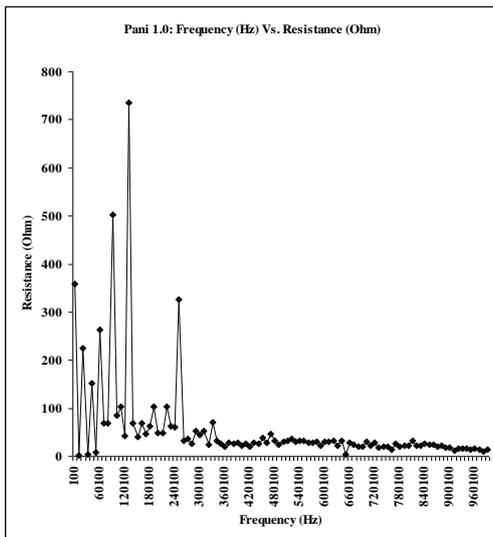
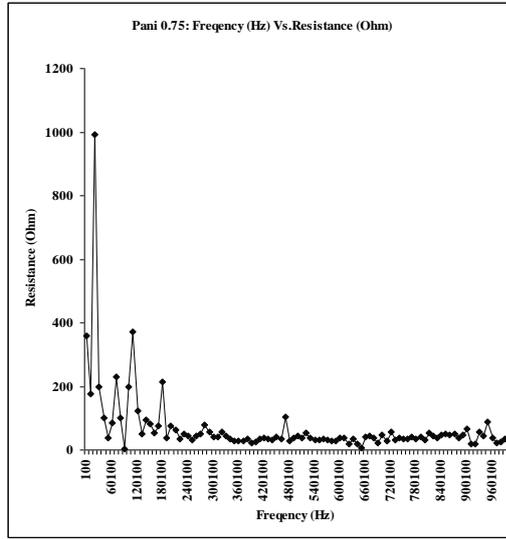
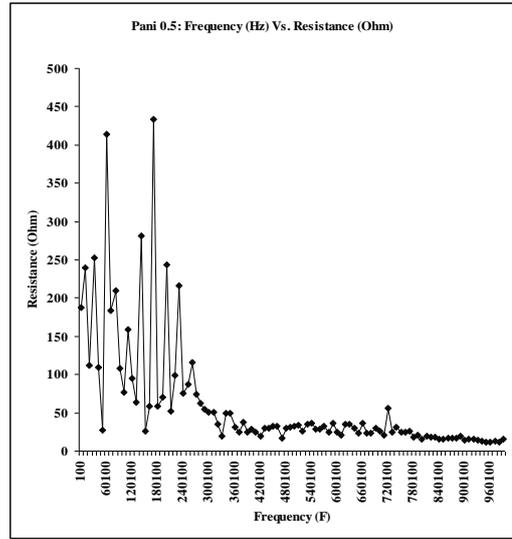
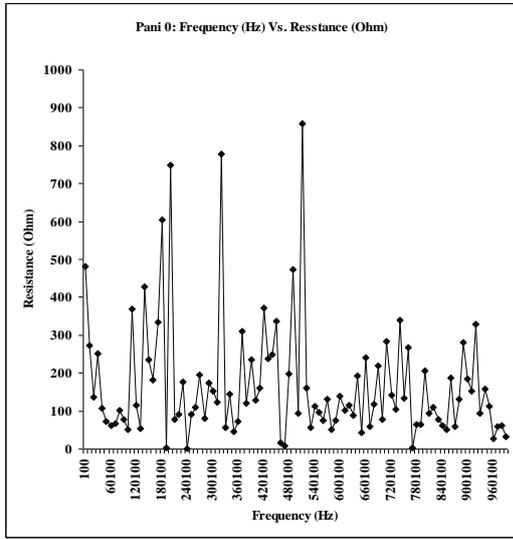
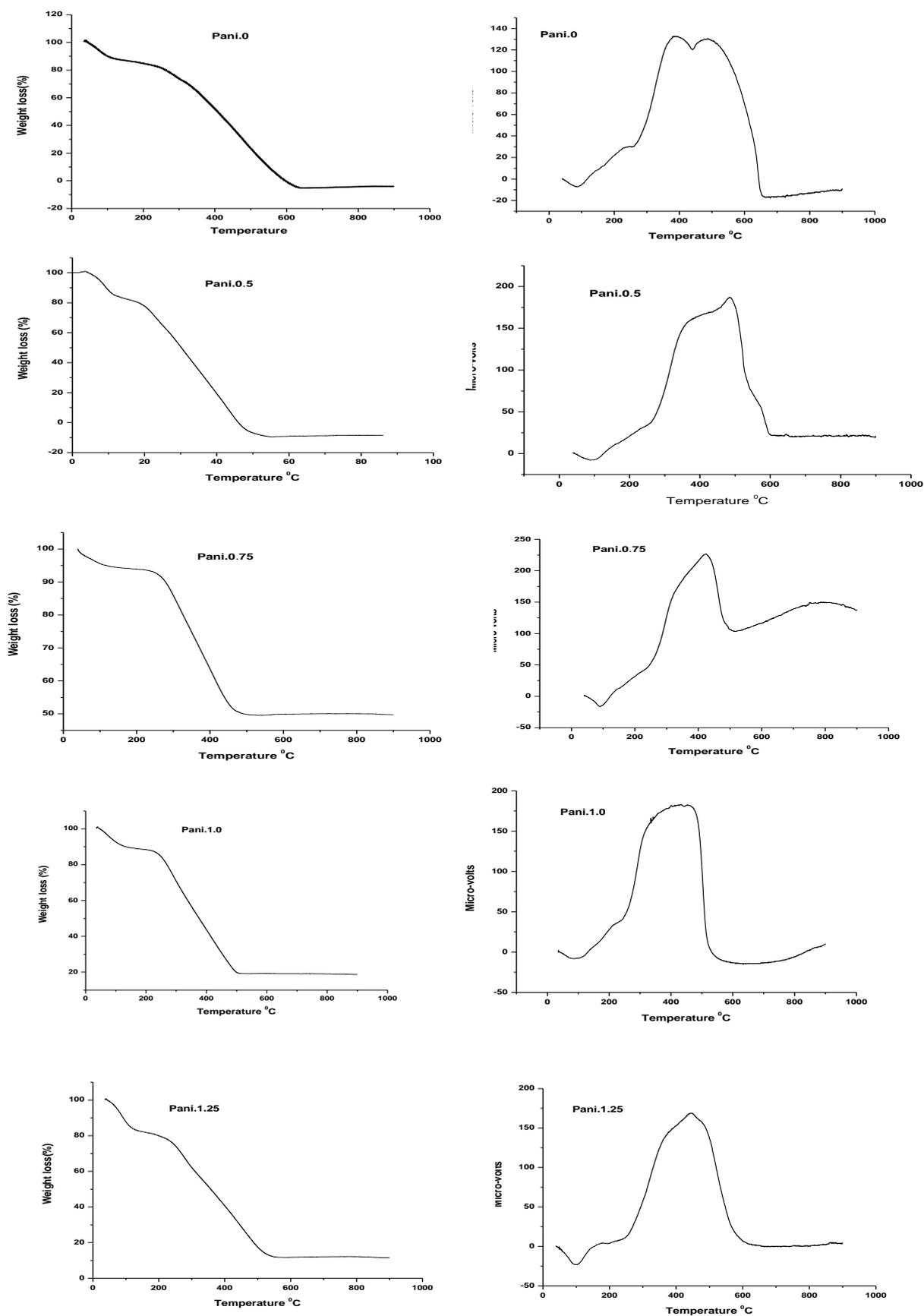


Figure 4. Electrical parameters versus frequency

**Figure 5.** TGA/DSC traces of pani-clay composites

It should also be noted here that most of the pani-clay composites chains are intercalated into the interlayer spacings of clay based on the XRD data shown in figure 3. As a result, this SEM data strongly support the fact that the pani chains (i.e. free pani-clay domains) play an important role in the electrical conductivity of the composites. It is evident that the improvement in the conductivity of the pani-clay composite could be attributed to more ordered and dense structure enhancing inter-chain electron hopping [26].

Insertion of the clay into the pani was also examined by XRD, which confirmed that the pani chain was aligned with the clay. Figure 3 shows X-ray diffraction pattern for Pure Pani, Pani.0.5, Pani.0.75, Pani.1.0 and Pani.1.25. All the spectra show amorphous structure due to the absence of sharp peaks. The broad maxima in the 2θ were obtained in the range of 250 for all the samples (including Pure Pani), which suggests the structure of pure pani to be amorphous. [27].

Electrical Parameters:

Figure 4 shows the various electrical parameters versus frequency were plotted and the results were correlated with pure polymer (pani) and polymer clay composites for various compositions. These results show noticeable change in electrical properties of the composites as compared with the pure polymer [28].

Thermal analysis:

Thermal stability of polyaniline/clay composites of different composition have been analyzed and compared with that of pure pani. Figure 5 shows the thermal traces of Pani-clay nanocomposites and pure pani. The initial weight loss of 5-10% (up to 180°C) is due to the loss of physically adsorbed water. From the TGA result it is observed that weight loss of Pani-clay composite is less compared to pure pani. This is clear indication of thermal stability of pani-clay composites [29-30]. It is observed that the shift in the DSC thermogram and peak area of polymer-clay composites is less compared to pure Pani [31]. From the present result it can be predicted that the thermal stability of pani-clay composites is enhanced due to the attractive coulomb interaction between the positive group of Pani Layer and negatively charged surface of the clay layer.

4. Conclusions

Polymer-clay based composites of pani were successfully obtained by polymerizing polyaniline in the presence of ammonium persulphate-impregnated clay by chemical oxidative method. From these XRD patterns and the SEM photographs it is observed. That there is possible intercalation of PANI in clay. This justified the objective that this clay can be used for synthesizing PANI clay composite. The intercalation of Pani- Bentonite. The shift in IR peaks of the Pani-clay samples suggest interaction between the Pani-clay composites. The morphological study from the SEM analysis shows the compact morphology with the increase in clay. From the TGA/DSC results, we observe the thermal stability

of the nanocomposites of Pani-clay is relatively enhanced through the intercalation. Frequency versus various electrical parameters graph show, enhanced shifts in values of electrical parameters, reflecting possible changes in property values with relative percentage of clay.

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REFERENCES

- [1] Q. H. Zeng, D. Z. Wang, A. B. Yu, and G.Q. Lu, "Synthesis of polymer-montmorillonite nanocomposites by in situ intercalative polymerization" *Nanotechnology*, vol. 13, pp. 549-553, Aug.2002.
- [2] B. Feng, Y. Su, J. Song, and K. Kong, "Electropolymerization of polyaniline/montmorillonite nanocomposite" *J. Mater. Sci. Lett.*, vol. 20, pp. 293-294, 2001.
- [3] Y. Zhu, Synthesis, characterization and corrosion performance of polyaniline montmorillonite clay nanocomposites, PhD thesis, 2003.
- [4] D.B.Mahesh, S.Basavaraja, D.S. Balaji, V.Shivkumar, L.Arunkumar, and A.Venkataraman, "Preparation and characterization of Pani and Pani-Ag nanocomposites via interfacial polymerization", *Polymer Composites Vol. 30, Issue 11*, pp. 1668-1677, November 2009.
- [5] S. Yoshimoto, F. Ohashi, Y. Ohnihi, and T. Nonami, "Synthesis of Polyaniline - montmorillonite nanocomposites by the mechanochemical intercalation method", *Synth. Met*, vol. 145, pp. 265-270 September, 2004.
- [6] S. Yoshimoto, F. Ohashi, and T. Kameyama, "Simple Preparation of Sulfate Anion-Doped Polyaniline-Clay Nanocomposites by an Environmentally Friendly Mechanochemical Synthesis Route", *Macromolecular Rapid Communications. Volume 25, Issue 19*, pages 1687-1691, October, 2004.
- [7] N. Hasegawa, H. Okamoto, M. Kawasumi, M. Kato, A. Tsukigase, and A. "Usuki. Polyolefin-clay hybrids based on modified polyolefins and organoclay". *Macromol. Mater. Engng.*, Vol. 280/281, pp. 76-79, 2000.
- [8] M. Alexandre, and P. Dubois, "Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials", *Mater. Sci. Eng.*, vol.28, pp.1-63, March 2000.
- [9] D. Garcia-Lopez, O. Picazo, J.C. Merino, and J.M. Pastor, "Polypropylene - clay nanocomposites: effect of compatibilizing agents on clay dispersion", *European Polymer Journal*, vol.39 pp. 945-950, 2002.
- [10] T. Agag, and T. Takeichi, "Polybenzoxazine-Montmorillonite Hybrid Nanocomposites Synthesis and Characterization",

Polymer, vol. 41(19), pp. 7083-7090, 2000.

- [11] M.H. Al-Saleh, and U. Sundararaj, "Processing –microstructure-property relationship in conductive polymer nanocomposites", *Polymer*, vol. 51, 2740-2747, 2010.
- [12] S.H. Hong, B.H. Kim, J. Joo, J.W. Kim, and H.J. Choi, "Polypyrrole–montmorillonite nanocomposites synthesized by emulsion polymerization", *Curr. Appl. Phys.* vol.1, pp.447-450, Dec.2001.
- [13] M. Omastova, M. mrave'a' kova, J. Piontek, and I. Choda'k. In proceeding of the conference Nanocomposites, San Francisco, USA, 2003.
- [14] H. Enomoto, and M.M. Lerner, "Synthesis of polymer/1T-TaS₂ layered nanocomposites", *Mater. Res. Bull.*, vol.37, pp. 1499-1507, July 2002.
- [15] M.H. Yeh, W.S. Hwang and Y.C. Chang "Preparation and Mechanical Properties of Polychloroprene–Montmorillonite Composites", *Jpn. J. Appl. Phys.* Vol.44 pp. 6847-6854, Sept.2005.
- [16] P.Kiliaris, and C.D. Papaspyrides, "Polymer/layered silicate (clay) nanocomposites: An overview of flame retardancy", *Prog. Polym. Sci.*, vol. 35, 902-958, 2010.
- [17] Q.H. Zeng, A.B. Yu, G. Q. Lu (Max), and D.R. Paul, "Clay-Based Polymer Nanocomposites: Research and Commercial Development", *Journal of Nanoscience and Nanotechnology*, Vol. 5, No. 10, pp. 1574-1592, October 2005.
- [18] S.S. Ray, and M. Okamoto, "Polymer/layered silicate nanocomposites: a review from preparation to processing" *Prog. Polym. Sci.* vol.28, pp. 1539–164, Aug. 2003.
- [19] S. Letayef, P. Aranda, and E. Ruiz-Hitzky. "Influence of iron in the formation of conductive polypyrrole-clay nanocomposites", *Appl. Clay Sci.*, vol.28, pp. 183-198, 2005.
- [20] G.M. do Nascimento, V.R.L. Constantino, R. Landers, and M.L.A. Temperini, "Aniline Polymerization into Montmorillonite Clay: A Spectroscopic Investigation of the Intercalated Conducting Polymer", *Macromolecules*, vol.37, pp. 9373-9385, Nov. 2004.
- [21] D. Lee, K. Char, S.W. Lee, and Y.W. Park, "Structural changes of polyaniline/montmorillonite nanocomposites and their effects on physical properties", *J. Mater. Chem.*, vol. 13, pp. 2942-2947, 2003.
- [22] N. Ballav, and M. Biswas, "A conducting nano composite via intercalative polymerisation of thiophene in montmorillonite clay", *Synth. Met.*, Vol.142, 309-315, April 2004.
- [23] Bedre, M.D.; Salimath, B.; Sawle, B.; Lagashetty, A.; Venkataraman, A. *Polymer Compos* 30, 2009, 1668.
- [24] Swaruparani, H.; Basavaraja, S.; Basavaraja, C.; Huh, D. S.; Venkataraman, A. *J App Polym Sci* doi 10.1002/app.31745.
- [25] R.L. Frost, and A.M. Vassallo, "The dehydroxylation of the kaolinite clay minerals using infrared emission spectroscopy", *Clays and Clay Minerals*, Vol. 44, No. 5, pp.635-651, 1996.
- [26] M. Darder, M. Colilla, and E. Ruiz-Hitzky, "Biopolymer–Clay Nanocomposites Based on Chitosan Intercalated in Montmorillonite", *Chem. Mater.*, vol.15 (20), pp 3774–3780, Sept.2003.
- [27] A. Kassim, M. Sagadavan, F. Adzmi, H.N. and M. Mahmud Ekramul, "Conducting polymer/clay composites: Preparation and characterization", *Materials Science (Medziagotyra)*, vol. 10/3, pp. 255-258, 2004.
- [28] Abdul Shakoor, Tasneem Zahra Rizvi and Ahmad Nawaz, "Raman spectroscopy and AC conductivity of polyaniline montmorillonite (PANI-MMT) nanocomposites", *J. Mat. Sci. Mater. Electronics*, vol. 22 No. 8, 1076-1080, 2011.
- [29] S.S. Ray, and M. Bousima, "Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world", *Prog. Mater. Sci.* Vol. 50, pp. 962-1079, 2005.
- [30] O. Becker, R.J. Varley, and G.P. Simon, "Thermal stability and water uptake of high performance epoxy layered silicate nanocomposites". *Euro. Polym. J.*, Vol. 40, pp.187-195, 2004.
- [31] S.S. Deng and L. Guang, "Preparation and Characterization of Polyaniline/Montmorillonite Composite by Situ Emulsion Polymerization", *J. Advan. Mater. Research*, vol. 476-478, pp. 809-813, 2012.