VIVECHAN International Journal of Research, Vol. 3, 2012

Polyacrylamide Intercalated OMMT Clay Nanocomposite: Synthesis and Characterization

Monika Srivastava* and Rajiv Prakash
School of Materials Science and Technology, Institute of Technology,
Banaras Hindu University, Varanasi 221 005, India.
*monikabhu.srivastava@gmail.com

Abstract

We report polyacrylamide (PAA) and organically modified montmorillonite (OMMT) clay nanocomposite using ex-situ incorporation of OMMT clay in the already prepared polymer matrix. A novel technique "Plasma Electrolysis" is used to prepare PAA by radical polymerization of acrylamide monomer. Modified clay is introduced in polyacrylamide with vigorous stirring and sonication to get intercalated and uniform nanocomposite. The as-prepared polyacrylamide–clay nanocomposite material is subsequently characterized for its structural property using wide-angle powder X-ray diffraction and scanning electron microscopic techniques. The effect of clay on thermal stability of composite is also studied by differential scanning calorimetry and thermogravimetric techniques. Nanocomposite obtained from simple synthesis route shows enormous potential for various technological applications.

Keywords- Plasma electrolysis, Polyacrylamide, Montmorillonite clay, Nanocomposite

Introduction

Montmorillonite (MMT) is a clay mineral consisting of stacked silicate sheets approximately 10 Å thick and approximately 2180 Å long (Yano and Okada, 1997). Because of its unique properties, extensive research interest developed for the preparation of various novel polymer–clay nanocomposite materials with advanced gas-barrier properties by Wang and Pinnavaia, 1998, thermal stability by Lan and Pinnavaia, 1994, mechanical strength by Tyan *et al.,* 1999 ; Yu *et al.,* 2003, fire retardance by Gilman *et al.,* 2000 and corrosion protection by Yeh *et al.,* 2001; 2002; 2003. Several research groups have devoted their contributions to the study of nanocomposites of polyacrylamide (PAA) and clay in a gel form (Gao *et al.,* 1999). So we prepare first time polyacrylamide – OMMT clay nanocomposite by ex-situ incorporation of organically modified MMT clay in the pre-prepared polyacrylamide through a novel unconventional electrochemical technique, called plasma electrolysis.

The electrochemical technique may be better over chemical routes because it replaces the use of chemical initiator based harsh synthetic procedures. Plasma electrolysis is also known as contact glow discharge electrolysis. It is an unconventional electrochemical technique, used for the synthesis purpose in which a luminous sheath of plasma is developed by DC glow discharges between an anode and the surrounding electrolyte. The phenomenon develops spontaneously at either of the anode or cathode during conventional normal electrolysis when the voltage applied is sufficiently high (greater than 400 V). The electrode, where the current density is larger, the electrolyte resistivity is higher, or the electrolyte surface tension is lower, is the preferred location of plasma electrolysis (Hickling and Conway, 1971; Sengupta and Singh, 1991; Gangal, Srivastava & Sengupta, 2009). A remarkable feature of this technique is its deviation from the yield expected according to the Faraday's law (Hickling and Conway, 1971; Sengupta and Palit, 1975; Sengupta and Palit, 1976; Sengupta and Singh, 1994; Sengupta, Singh and Srivastava, 1998). Gangal, Srivastava and Sengupta, 2010 showed that anodic plasma electrolysis is a potential tool for generating radicals like $H^\bullet$ and $OH^\bullet$ radicals mainly in vicinity of electrode at the plasma|electrolyte interface. Formation of these radicals in the electrolyte during anodic plasma electrolysis was proved by an ESR study using 5, 5-dimethyl pyrroline-1-oxide (DMPO) as the spin trap (Bullock, Gavin and Ingram, 1980; Hase and Harada, 2001). The potentiality of anodic plasma electrolysis as a tool for generating radicals has been thoroughly demonstrated by examples of its applications in the synthesis of hydrazine from ammonia by Liu, Zhou,Li,Li &Yu,2008, oxalic acid from formic acid by Sengupta, Singh and Srivastava,1995, polyacrylamide from acrylamide by Sengupta, Sandhir and Misra, 2001, glycine and α-alanine from ammonia and carboxylic acids by Sengupta and Srivastava, 2006, and of organic contaminants in waste waters(Gao *et al.,* 2003; Gai, 2007; Tomizawa and Tezuka, 2007; Liu and Jiang, 2008; Gong,Wang, Xie & Cai, 2008) and recently polymer nanocomposites by Gao *et al.,* 2008 & also by Srivastava and Prakash, 2011.

Keeping these aspects in mind, this paper is aimed to explore the simple procedure of forming uniform clay nanocomposite of polymers. Simple ex-situ mixing technique was adopted for the synthesis of uniform nanocomposite of OMMT clay with pre-prepared polyacrylamide formed by Plasma electrolysis.

Materials and method

Acrylamide (crystallized) and organically modified Montmorillonite clay (modified with 35-45wt. % dimethyl dialkyl (C 14-C18) amine) obtained from Aldrich-Sigma, Ca, USA. All other chemicals used were of A.R. grade.

Experimental set-up

For the polymer preparation (Srivastava and Prakash, 2011), electrolysis cell was a corning cylindrical cell (height 11cm, outer diameter 5cm of 3mm thickness) fitted with a platinum wire anode (length 10mm, diameter 0.45 mm) and a platinum foil cathode (1x1cm2, 0.1 mm thickness). Electrolyte used was 0.001 M K2SO4 containing 4% acrylamide monomer. The ambient temperature was 60±5 0C and the pressure was atmospheric. Anodic voltage of 660 V was applied to the anode at an average current of 55mA for 10 minutes. Power was supplied from DC regulated high voltage source. The entire study was carried out in double distilled water.

Preparation of Polyacrylamide

Electrolysis was carried out in the above described experimental set-up by Srivastava and Prakash, 2011. K2SO4 solution containing acrylamide (nearly after 3 minutes of electrolysis) became viscous after sometime, indicated the formation of polymer in the electrolysis cell. After passing sufficient coulomb, electrolysis was terminated after 10 minutes. Now the solution was left as such for a few hours till its temperature falls to room temperature.

Preparation of polyacrylamide-OMMT clay nanocomposite

Polyacrylamide-OMMT clay nanocomposite was formed by dispersing the 28 mg OMMT clay in the 20 ml of earlier prepared Polyacrylamide solution and stirred it overnight followed by sonication.

The prepared solution was poured in ice-cold methanol with constant rigorous stirring. The dirty white thread like precipitate obtained, thus allowed to settle and was filtered out using G-4 sintered crucible under vacuum filtration. The suction continued till the precipitate got dried. Polymer nanocomposite was cut into small pieces and dried under vacuum oven for 60 hours at 50°C continuously till it attained a constant weight.

Instrumentation

X-ray diffraction experiments were performed using a Bruker AXS D8 Advance wide-angle X-ray diffractometer (wavelength 0.154 nm) and a graphite monochromator. The generator was operated at 40 kV and 40 mA. Samples were scanned at diffraction angle 2θ from 2° to 60° at the scanning rate of 1°/min.

Fourier Transform Infrared (FTIR) spectroscopic analysis of the samples were conducted using Thermo (model 5700), Germany from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Thermal analyses were carried out using a Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analyser (TGA) (Mettler-Toledo), Switzerland at a heating rate of 20°C/min under nitrogen atmosphere. Scanning Electron Microscopy (SEM) studies were carried out using ZEISS (AG-Supra 40), Germany at operating voltage 5.0 kV.

Results and Discussion

Polyacrylamide polymer prepared by taking acrylamide as monomer through plasma electrolysis method was known and confirmed by determination of its molecular weight using viscosity measurement method (Moore and Hutchinson, 1963). We also found the same and the molecular weight variation was obtained of the order of 105gmol-1. Further Polyacrylamide-OMMT clay nanocomposites were formed and characterized by various techniques:

X-ray diffraction analysis

X-ray diffraction analysis was carried out for polyacrylamide as well as polyacrylamide-OMMT clay nanocomposite as shown in Figure 1. Polyacrylamide showed amorphous nature with broad hump and OMMT clay showed characteristic peak at 2 Theta=3.5° corresponding to the inter-gallery spacing of the clay. Both the characteristic exist in the Polymer-OMMT clay nanocomposites as shown in Figure-1 and more clearly in the inset for presence of clay in the polymer.

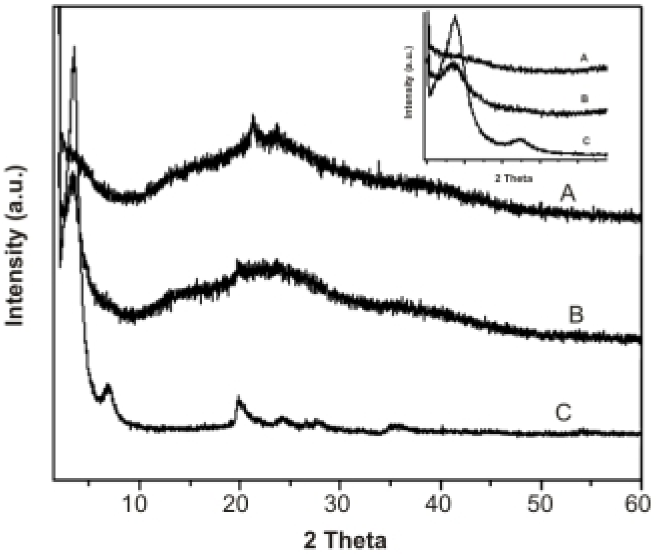

Figure 1: XRD of (A) PAM, (B) PAM-OMMT Clay nanocomposite and (C) pure OMMT clay. Inset: zoom for low angle peaks

Thermal Analysis

Thermal analysis of polyacrylamide and polyacrylamide-OMMT clay nanocomposite under N_2 atmosphere was carried out to study their degradation behavior. The glass transition temperature (T_g) of polyacrylamide and effect on nanocomposite formation was observed by Differential Scanning Calorimetry (DSC). Polyacrylamide showed T_g at 160°C in the second run of the DSC as shown in the Figure 2. A noteceable shift in the T_g (170°C) was observed after nanocomposite formation, which also supported the interaction of polymer chains with OMMT clay and uniform distribution of the OMMT clay in the polymer matrix. Thermal Gravimetric Analysis (TGA) study showed a three step weight loss process as shown in Figure 3. However, not any considerable increase in thermal degradation temperature of the nanocomposite was observed. Below 400°C polyacrylamide showed steep degradation, however, it followed nearly slow and gradual weight loss after this temperature.

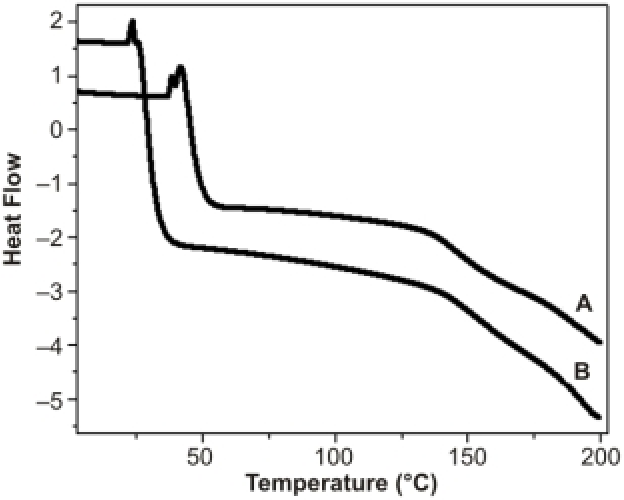

Figure 2: DSC of (A) PAM and (B) PAM-OMMT Clay nanocomposite

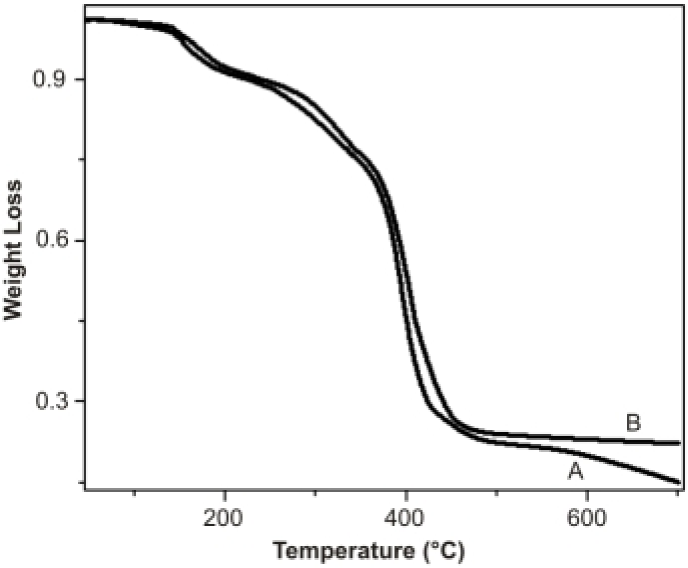

Figure 3: TGA of (A) PAM and (B) PAM-OMMT Clay nanocomposite

FTIR analysis

FTIR study did not show much difference before and after introduction of OMMT clay in the polyacrylamide matrix. However, from Figure 4 some broadening can be seen in case of polyacrylamide-OMMT clay nanocomposite at 3346 cm-1 showing NH_2 absorption band. There were also peaks for C=O stretching at 1740cm^{-1} and (NH) amide at 1625 cm^{-1}(Campet *et al.,* 1996). The characteristic FTIR spectra of the OMMT clay appear at 3429 cm-1, 1658 cm^{-1} and 1041 cm^{-1} because of O-H stretching, O-H bending and Si-O bending respectively (Erol, Unal and Sari,2010), which are also present in composites.

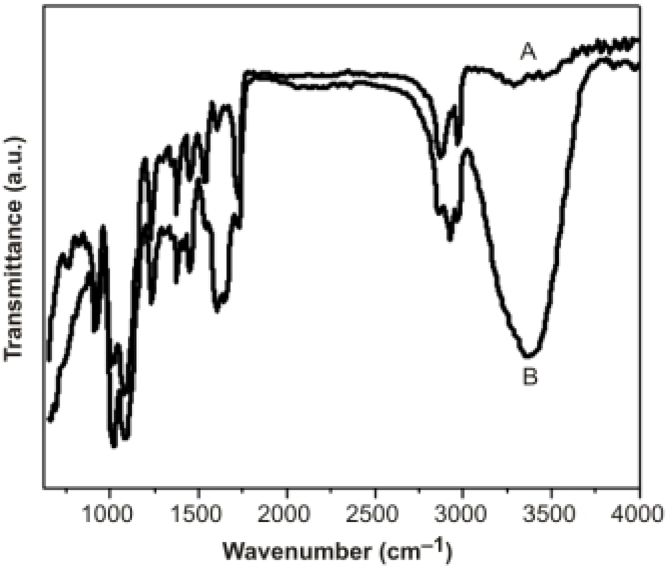

Figure 4: FTIR of (A) PAM and (B) PAM-OMMT Clay nanocomposite

Morphological analysis

Morphology of the pure polyacrylamide and its nanocomposite was studied using SEM and compared at same magnification (80,000) as shown in the Figure 5. Clear change in morphology was observed for polyacrylamide and polyacrylamide-OMMT clay nanocomposite. Flax like structure can be seen in polyacrylamide-OMMT clay nanocomposite. Probably these morphology were observed due to templet effect of the nano-fillers and solidification of polymer assisted by the templets.

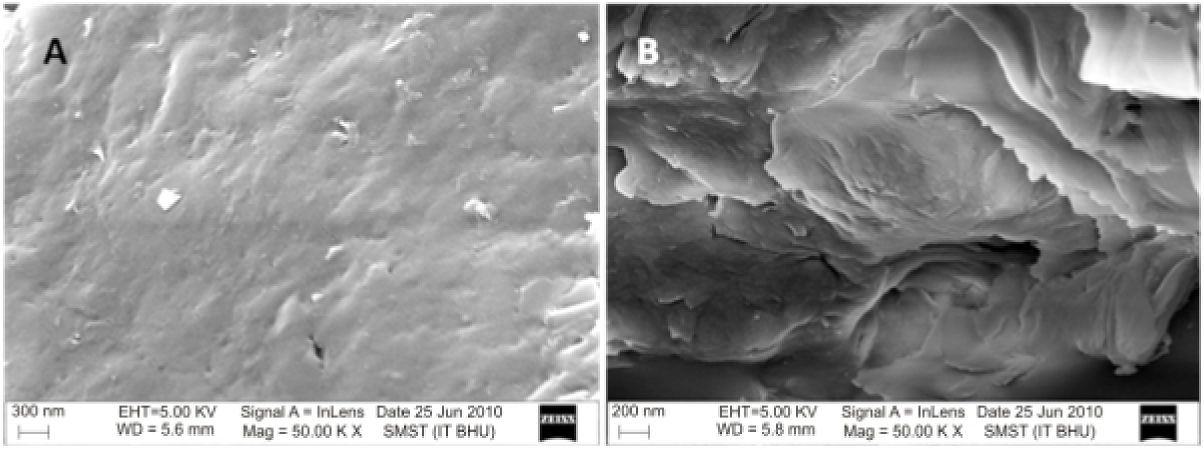

Figure 5: SEM of (A) PAM and (B) PAM-OMMT Clay nanocomposite at 50,000 magnifications

Conclusion

Polyacrylamide polymer is synthesized by plasma electrolysis technique which is non-conventional electrochemical technique. Further this polymer is used for the formation of nanocomposite by simple ex-situ incorporation of OMMT clay. The polymer-OMMT clay nanocomposite is characterized by X-ray diffraction, FTIR, DSC, TGA and SEM techniques. This simple method is not only produced homogeneous interactive composite but also showed potential for various nanocomposites formation.

References

Bullock, A.T., Gavin, D.L., Ingram, M.D. 1980. Electron spin resonance detection of spin-trapped radicals formed during the glow-discharge electrolysis of aqueous solutions. *Journal of the Chemical Society, Faraday Transactions* 1, 76, 648-653.

Campet, G., Rabardel, L., Portier, J., Dweik, H. S., Subramanian, M. A. 1996. Synthesis and properties of polyacrylamide-bismuth halogenated hybrids. *Active and Passive Electronic Components*, 19(2), 99-104.

Erol, O., Unal, H. I., Sari B. 2010. Synthesis, electrorheology, and creep behaviors of in situ intercalated polyindole/organo-montmorillonite conducting nanocomposite. *Polymer Composites*, 31(3), 471-481.

Gai, K. 2007. Plasma-induced degradation of diphenylamine in aqueous solution. *Journal of Hazardous Material*,146(1-2), 249-254.

Gangal, U., Srivastava, M., Sengupta, S. K. 2010. Scavenging Effects of Aliphatic Alcohols and Acetone on $H^\bullet$ Radicals in Anodic Contact Glow Discharge Electrolysis: Determination of the Primary Yield of $H^\bullet$ Radicals. *Plasma chemistry and Plasma Process*, 30(2), 299-309.

Gangal, U., Srivastava, M., Sengupta, S. K. 2009. Mechanism of the Breakdown of Normal Electrolysis and the Transition to Contact Glow Discharge Electrolysis. *Journal of the Electrochemical Society*, 156(10),131-136.

Gao, J., Wang, A., Li, Y., Fu, Y., Wu, J., Wang, Y., Wang, Y. 2008. Synthesis and characterization of superabsorbent composite by using glow discharge electrolysis plasma. *Reactive and Functional Polymers*, 68(9), 1377-1383.

Gao, J., Wang, X., Hu, Z., Deng, H., Hou, J., Lu, X., Kang, J . 2003. Plasma degradation of dyes in water with contact glow discharge electrolysis. *Water Research*, 37(2), 267-272.

Gao, D., Heimann, R. B., Williams, M. C., Wardhaugh, L. T., Muhammad, M. 1999. Rheological properties of poly (acrylamide)-bentonite composite hydrogels. *Journal of Material Science*, 34, 1543-1552.

Gilman, J. W., Jackson, C. L., Morgan, A. B., Hayyis, R., Jr., Manias, E., Giannelis, E. P., Wuthenow, M., Hilton, D., Phillips, S. H. 2000. Flammability Properties of Polymer-Layered-Silicate Nanocomposites. Polypropylene and Polystyrene Nanocomposites. *Chemistry of Materials*, 12(7), 1866-1873.

Gong, J., Wang, J., Xie, W., Cai, W. 2008. Enhanced degradation of aqueous methyl orange by contact glow discharge electrolysis using Fe^{2+} as catalyst. *Journal of Applied Electrochemistry*, 38(12),1749-1755.

Hase H., Harada K. 2001. ESR Detection of OH and H Radicals Generated By Contact Glow Discharge In Aqueous Solutions. *Viva Origino* 29(2),61-62.

Hickling, A., Bockris, J., Conway, B.E. 1971. *Modern aspects of electrochemistry*, Butterworths, London, Vol. 6, pp 329.

Lan, T., Kaviratna, P. D., Pinnavaia, T. J. 1994. On the Nature of Polyimide-Clay Hybrid Composites. *Chemistry of Materials*, 6,573-575.

Liu, C., Zhou, Y., Li, S.,. Li, L., Yu, M. 2008. Preparation and characterization of polyaniline/MMT conductive composites. *Polymers for Advance Technology*, 19(12), 1693-1697.

Liu, Y., Jiang, X. 2008. Plasma-induced Degradation of Chlorobenzene in Aqueous Solution. *Plasma Chemistry and Plasma Processing*, 28(1),15-24.

Moore, W. R., Hutchinson, R. J. 1963. Viscosity - Molecular Weight Relationship for Polyvinyl Chloride. *Nature*, 200,1095-1096.

Sengupta, S. K., Srivastava, M. 2006. Chemical effects of anodic Contact Glow Discharge electrolysis:Formation of amino acid. *Journal Indian Chemical Society*, 83(8),787-791.

Sengupta, S. K., Palit, S. R. 1976. Studies in Galvanoluminiscence:Part lll.Production and chemical Effects of Anode Glow. *Journal Indian Chemical Society*, 53, 472.

Sengupta, S. K., Sandhir, U., Misra, N. 2001. A study on acrylamide polymerization by anodic contact glow-discharge electrolysis: A novel tool. *Journal of Polymer Science Part A: Polymer Chemistry*, 39(10), 1584-1588.

Sengupta, S. K., Singh, O. P. 1994. Contact glow discharge electrolysis: a study of its chemical yields in aqueous inert-type electrolytes. *Journal of Electroanalytical Chemistry*, 369(1-2),113-120.

Sengupta, S. K., Singh, R.,Srivastava, A. K. 1995. Glow-discharge electrolysis in aqueous solutions. *Indian Journal of Chemistry*,34A,459-461.

Sengupta, S.K., Singh, O.P. 1991. Contact glow discharge electrolysis: A study of its onset and location. *Journal of Electroanalytical Chemistry*, 301,189-197.

Sengupta, S.K., Singh, R., Srivastava, A. K. 1998. A study on the origin of nonfaradaic behavior of anodic contact glow discharge electrolysis, The relationship between power dissipated in glow discharges and nonfaradaic yields. *Journal of the Electrochemical Society*,145, 2209.

Sengupta, S. K., Palit, S. R. 1975. Studies in Galvanoluminiscence:Part ll.Chemical Effects of cathode Glow. *Journal of Indian Chemical Society*, 52,91.

Srivastava, M., Prakash, R. 2011. Synthesis of Polyacrylamide-MMT clay nanocomposite using non-conventional Electrochemical Technique. *Journal of Nanoscience and Nanotechnology* (In Press).

Tomizawa, S., Tezuka, M. 2007. Kinetics and mechanism of the organic degradation in aqueous solution irradiated with gaseous plasma. *Plasma Chemistry and Plasma Processing*, 27(4), 486-495.

Tyan, H.L., Liu, Y.C., Wei, K.H. 1999. Thermally and Mechanically Enhanced Clay/Polyimide Nanocomposite via Reactive Organoclay. *Chemistry of Materials*, 11(7),1942-1947.

Wang, Z., Pinnavaia, T. J. 1998. Nanolayer reinforcement of elastomeric polyurethane. *Chemistry of Materials*, 10(12), 3769-3771.

Yano, K., Usuki, A., Okada, A. 1997. Synthesis and properties of polyimide-clay hybrid films. *Journal of Applied Polymer Science Part A: Polymer Chemistry*, 35(11), 2289-2294.

Yeh, J. M., Liou, S.J., Lin, C.Y., Cheng, C.Y., Chang, Y.W., Lee, K.R. 2002. Anticorrosively Enhanced PMMA−Clay Nanocomposite Materials with Quaternary Alkylphosphonium Salt as an Intercalating

Agent. *Chemistry of Materials*,14(1),154-161.

Yeh, J.M., Chen, C.L., Chen, Y.C., Ma, C.Y., Lee, K.R., Wei, Y., Li, S. 2002. Enhancement of corrosion protection effect of poly (o-ethoxyaniline) via the formation of poly (o-ethoxyaniline)–clay nanocomposite materials. *Polymer*, 43, 2729-2736.

Yeh, J.M., Chin, C.P., Chang, S. 2003. Enhanced corrosion protection coatings prepared from soluble electronically conductive polypyrrole-clay nanocomposite materials. *Journal of Applied Polymer Science*, 88(14), 3264-3272.

Yeh, J.M., Liou, S.J., Lai, C.Y., Wu, P.C., Tsai, T.Y. 2001. Enhancement of Corrosion Protection Effect in Polyaniline via the Formation of Polyaniline−Clay Nanocomposite Materials. *Chemistry of Materials*, 13(3),1131-1136.

Yeh, J.M., Chin, C.P. 2003. Structure and properties of poly(o-methoxyaniline)-clay nanocomposite materials. *Journal of Applied Polymer Science*, 88(4),1072-1080.

Yu, Y.H., Lin, C.Y., Yeh, J.M., Lin, W.H. 2003. Preparation and properties of poly (vinyl alcohol)–clay nanocomposite materials. *Polymer*, 44(12), 3553-3560.