

Synthesis and Characterization of New Reducing Agent Based on Methylmethacrylate-Vinylpyridine Copolymer–Clay Nanocomposites

Nehal Salahuddin

Department of Chemistry, Faculty of Science, Tanta University, Tanta 31527, Egypt

Received 5 August 2006; accepted 21 November 2006

DOI 10.1002/app.25890

Published online 8 March 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Methylmethacrylate (MMA)-vinylpyridine (VP) copolymer-montmorillonite (MMT) nanocomposites were prepared, by direct interaction of sodium montmorillonite with various copolymers of MMA-VP, using different ratios of VP. The interaction occurred through ion exchange between sodium cations in MMT and pyridinium ions in the copolymers. The resulting composites were reacted with lithium aluminum hydride forming the supported reagents. The structure of the resulting composites, as determined by elemental analysis, Infrared spectroscopy, and X-ray diffraction, consisted of the insertions of MMA-VP macromolecules between lamellar layers. Because of cooperative formation of electrostatic bonding the copolymers were strongly fixed to

the inorganic surfaces. The absence of observable transition in the thermogram, using differential scanning calorimetry, confirmed the copolymer sandwiching between the inorganic layers. The thermal stability of nanocomposites was investigated by thermogravimetry analysis. The dispersion of the MMT particles in the polymer matrix was confirmed using scanning electron microscopy. The effectiveness of these materials has been examined in the reduction of potassium ferricyanide. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3317–3323, 2007

Key words: poly(methylmethacrylate); vinylpyridine; nanocomposites; clay; intercalating

INTRODUCTION

Chemical reagents covalently attached to polymeric carriers can be successfully used in organic synthesis.^{1–3} The reactions performed with such reagents displayed an increase of selectivity when compared with the analogous homogeneous reactions. They have implied milder, simpler, and more economical set-up and work up.⁴ However, they showed limited mechanical strength and thermal stability. The choice of solvent, which should swell the polymer and the capacity of the functionalized polymer are other limitations of this technique for industrial synthesis. Those difficulties, which are encountered in most petrochemical and other industrial process, have hindered their commercial applications.

Smectite clay constitute a naturally occurring class of inorganic catalysts. MMT was used for several important reactions,^{5–9} including polymerization, phase transfer catalysts, and oxidation reaction. Quaternary onium salts immobilized on clay have been used as triphase catalysts. Inherent disadvantages, such as low swelling capability in organic solvents, render these catalysts unsuitable for many reactions and preclude their use.

Significant improvements in the physical properties of polymers have been realized through the production of layered silicate polymer nanocomposites because of their unique phase morphology and improved interfacial properties. Formation of clay nanolayers in polymer matrix greatly improves the tensile and compressive properties of the matrix through the reinforcement provided by the silicate nanolayers. The effects of nanolayer reinforcement are also manifested in terms of improved chemical resistance, barrier properties, dimensional and thermal stability. Improved thermal stability of nanocomposites based on poly(dimethylsiloxane) and polyurethane was demonstrated by thermogravimetric analysis (TGA). The thermal stability at 50% weight loss was increased by 60°C.^{10,11} The most commonly used layered silicates are the smectite group of clay minerals such as MMT. The layered structure of MMT consists of two silica tetrahedral sheets and an aluminum octahedral sheet. Stacking of the layers by weak dipolar force leads to interlayer galleries. The galleries are normally occupied by cations such as Na⁺ or K⁺ and it is easy to form organophilic clay by the introduction of alkyl ammonium ions by cation exchange reaction.¹²

Polymer layered silicate nanocomposites have been synthesized using an incredibly wide range of polymeric resins, including polystyrene,¹³ polystyrenemaleicanhydride,¹⁴ polyoxyethylene methacrylate,¹⁵ polyamides,¹⁶ Polypropylene,¹⁷ polyethylene vinyl

Correspondence to: N. Salahuddin (snehal@dec1.tanta.eun.eg).

acetate copolymers,¹⁸ polymethylmethacrylate,^{19,20} silicon rubber,²¹ polydiacetylene,²² acrylonitrile butadiene rubber,²³ polyurethanes,²⁴ poly(ethylene oxide),²⁵ polypyrrole,²⁶ polyaniline,²⁷ and epoxies.^{28,29} Three main techniques can be used to prepare polymer-clay nanocomposites: melt intercalation,¹⁷ polymer intercalation from solution^{14,23} and *in situ* intercalative polymerization.^{15,20} In the first two techniques, the performed polymer is mixed with the clay either in the molten state or in solution. In the third approach, clay is dispersed in the monomer which is then polymerized. In this study, layered silicate nanocomposites have been prepared by polymer intercalation from solution as previously reported for a variety of polymers including styrene maleic anhydride copolymer¹⁴ and amine terminated butadiene acrylonitrile.²³ Recently, polyvinylpyridinium-MMT intercalates was used as support for cobalt(II) phthalocyaninetetrasulfonate in the catalytic oxidation of 2-mercaptoethanol.³⁰ It showed good catalytic activity in auto oxidation. Recycling of the catalyst showed good stability up to three consecutive runs. This paper describes initial work on the preparation of a reducing agent attached to MMA-VP copolymer intercalated between the layered silicates to enhance the thermal properties of the polymeric reagent.

EXPERIMENTAL

Materials

The clay mineral used in this study was MMT from Southern Clay Products, under the trade name of mineral colloid BP. The clay was received in the form of fine particles. The cation exchange capacity (CEC) was 114.8 meq/100 g. The d_{001} spacing (interlayer or interlamellar), after drying in vacuum oven at 100 °C for 12 h, was 9.6 Å. MMA, VP, Dimethyl Formamide (DMF), Ethyl Iodide (EtI), benzoyl peroxide and LiAlH_4 were acquired from Aldrich (USA). DMF was dried over 4 Å Molecular sieve followed by distillation. VP was distilled under vacuum before using.

Instrumentation

Wide Angle X-ray Diffraction (WAXD) measurements were recorded, using a Phillips powder-Diffractometer equipped with a Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ Å), at a scanning rate of 0.005°/s and divergent slit 0.3°. The samples were dried in a vacuum oven at 80 °C for 12 h and then mounted on a sample holder with a large cavity. A smooth surface was obtained by pressing the powder with a glass plate. Bragg's Law ($n\lambda = 2d \sin\theta$) was used to compute the crystallographic spacing. IR measurement spectra were carried out on a Perkin-Elmer 1430 spectrophotometer using potassium bromide pressed disc technique in the

wavelength range of 4000–600 cm^{-1} . TGA data was obtained by using Perkin-Elmer thermal analyzer system at a temperature rising of 10 °C/min from 30 to 800 °C. Powders were compressed to discs with 0.65 cm diameter and 0.25 cm thickness. A JEOL JSM 5400 SEM was used to observe the particle size of MMT and the particle matrix adhesion in the composites on the fractured surface of the compressed samples. The specimens were coated with gold. DSC was recorded using Rigaku Thermo plus 2 DSC 8230 at a temperature rising of 10 °C/min from 30 to 200 °C under nitrogen. The absorption spectra were recorded using Shimadzu UV-2101 DC spectrophotometer.

Preparation of polymeric materials I_{a-f}

A mixture of 19.8 g (198 mmol) of MMA, 0.22 g (2.1 mmol) of VP, and 0.02 g of benzoyl peroxide as a radical initiator was refluxed at 80 °C for 10 h. The copolymer (I_a) was dissolved in acetone and precipitated in ether. The precipitated product was filtered off, washed with ether, and dried to give 18.1 g (90.4% yield, relative viscosity = 1.2 (0.1 g, 10 mL acetone, 30 °C)). Copolymers (I_{b-f}) with different ratios of VP and MMA were prepared as described for the preparation of I_a. The preparation data, the yield, and the relative viscosity are reported in Table I. Elemental analysis is listed in Table II.

Preparation of poly(methylmethacrylate)-vinylpyridine-MMT intercalates III_{a-f}

To a stirred solution of 1.8 g of I_a dissolved in 30 mL acetone, 0.5 mL (6 mmol) of ethyl iodide were added, followed by stirring for 24 h. The product II_a was added to 1 g of sodium MMT swelled in 30 mL of distilled water and the mixture was then stirred overnight. The precipitate III_a was filtered and washed with distilled water several times until no iodide ions were detected in the filtrate by testing with AgNO_3 . The resultant product was dried in vacuum oven at 60 °C to give 2.3 g (82.0% yields). The same procedure was followed for the other types of copolymers. In

TABLE I
Synthesis and Relative Viscosity Data
of Polymeric Materials

Code	Monomers				Products		
	MMA		VP		Wt (g)	Yield (%)	η_{rel}
wt (g)	mmol	wt (g)	mmol				
I _a	19.8	198	0.22	2.1	18.1	90.4	1.20
I _b	21.8	218	0.47	4.5	21.4	96.2	1.21
I _c	19.0	190	1.06	10.2	12.7	63.3	1.38
I _d	18.0	180	2.00	19.2	20.0	100	1.19
I _e	16.0	160	4.10	39.42	16.6	82.6	1.24
I _f	16.5	165	7.50	72.1	16.4	98.75	1.15

TABLE II
Elemental Analysis Data of Polymeric Materials

Code	C%		N%		H%	
	Calculated	Found	Calculated	Found	Calculated	Found
I _c	61.05	60.88	0.698	0.73	7.93	8.64
I _d	62.09	61.72	1.39	1.43	7.86	8.81
I _e	64.16	64.24	2.77	2.41	7.72	8.64
I _f	66.21	67.83	4.14	3.99	7.59	8.38

case of copolymers I_{d-f}, a small amount of EtI equivalent to change 6% pyridinium group was added (Table III).

Preparation of poly(methylmethacrylate)-vinylpyridine-MMT supported reagents V_{d-f}

The remaining pyridine group in the intercalated products (III_{d-f}) was converted into onium salt by swelling in DMF, followed by addition of 4 mL EtI and stirring for 48 h. The products (IV_{d-f}) were precipitated in H₂O and washed with ethanol.

In 100 mL two neck round bottom flask, 5 g of IV_d was swelled in 30 mL DMF by stirring overnight at room temperature. 0.3 g (8 mmol) of LiAlH₄ was added portion wise to the stirred cooled suspension and the reaction mixture was stirred for 48 h at room temperature. The reaction container was cooled and 0.3 mL (16 mmol) of water was added with stirring followed by addition of 0.64 g (16 mmol) of sodium hydroxide (6.4 mL of 10% solution), then 0.9 mL (48 mmol) water according to the reported method.³¹ The product (V_d) was filtered and dried under vacuum to give 4.7 g. Other samples V_{e-f} were prepared using the same procedure (Table IV).

General procedure for reduction reaction

The reduction reactions were performed by stirring a slight excess of swelled polymer-MMT supported reagent in THF with a reactant for 48 h according to the following procedure.

To a stirred suspension of V_{d-f} reagent (25 mmol) in 20 mL THF, 10 mmol of potassium ferricyanide

was added. The reaction mixture was stirred for 48 h and filtered. The product was identified using UV radiation. The reduction of potassium ferricyanide (X) to potassium ferrocyanide is observed by the disappearance of the UV absorption at 417 cm⁻¹ (Fig. 7).

Calcinations measurements

A certain amount of the composites samples (III_{a-f}) were introduced into a porcelain crucible and dried in an electric oven overnight, then introduced into an ignition oven and the temperature was raised to 1000°C for 24 h. The crucibles were then left in a desiccators overnight to determine their weight. The copolymer loading of each sample is expressed as the weight loss by ignition per 100 g of the dry sample (Table III).

RESULTS AND DISCUSSIONS

Nanocomposite materials were prepared by the attachment of preformed polymers containing positively charged onium moieties as intercalating groups to the swelled clay. This modification technique is attractive due to the simplicity of the procedure and the high molecular weight of the intercalated polymer. However it is only depend upon the nature of the solvent mixtures used. In the present work, the intercalation of MMA-VP copolymer (I_{a-c}) containing 1–5% pyridinium group onto MMT interlayers was achieved by cation exchange process. The copolymers were prepared by the bulk radical copolymerization of the two monomers with different ratios of vinyl pyridine to study the effect of the change in the

TABLE III
Synthesis Data of Poly(methylmethacrylate)-vinylpyridine-MMT Intercalates

Code	Copolymer			Clay wt (g)	Product wt (g)	Calcinations	
	Type	Weight (g)	EtI (mL)			Clay (wt %)	Copolymer (wt %)
III _s	I _a	1.8	0.50	1.0	2.3	35.8	64.2
III _b	I _b	3.0	0.50	1.5	4.4	31.26	68.74
III _c	I _c	3.0	0.50	1.5	4.5	28.08	71.92
III _d	I _d	10	0.50	5.0	10.7	67.87	32.13
III _e	I _e	7.0	0.35	3.5	6.0	62.3	37.7
III _f	I _f	7.0	0.35	3.5	5.4	66.0	34.0

TABLE IV
Synthesis Data of Polymer-MMT Supported Reagents

Code	Polymer-MMT		LiAlH ₄		Product, wt (g)
	Type	wt (g)	wt (g)	mmol	
V _d	IV _d	5	0.3	8.0	4.70
V _e	IV _e	5	0.36	9.6	2.93
V _f	IV _v	5	0.55	14.4	3.16

composition of the polymer backbone on the intercalation. The conversion of VP into pyridinium ion using EtI is necessary for the attachment of the copolymer into MMT interlayer through an ionic bond. A schematic illustration of the nanocomposite synthesis is shown in Figure 1. In such composites, the interfacial effect between the silicate layers and polymers matrix is a key factor leading high stiffness, high modulus and heat resistance composites. However, usually very strong electrostatic interactions between silicate layers through intergallery cations make it extremely difficult to achieve complete exfoliation of the layers. The weight percentage of the polymer in the composite was determined by calcinations at 1000°C (Table III) and is expressed as the weight loss by ignition per 100 g of the dry sample.

The remained pyridinium group of the copolymers III_{d-f} containing high percentage of VP has been modified to produce onium salts (IV_{d-f}) which were reacted with lithium aluminum hydride forming the supported reagents (V_{d-f}). DMF was used to improve wetting of MMT interlayers and to stimulate inclusion of more polymer molecules between the wetted layers.

The IR spectra of the copolymers I_e, II_e, and their composites III_e, IV_e are shown in Figure 2. In I_e, the

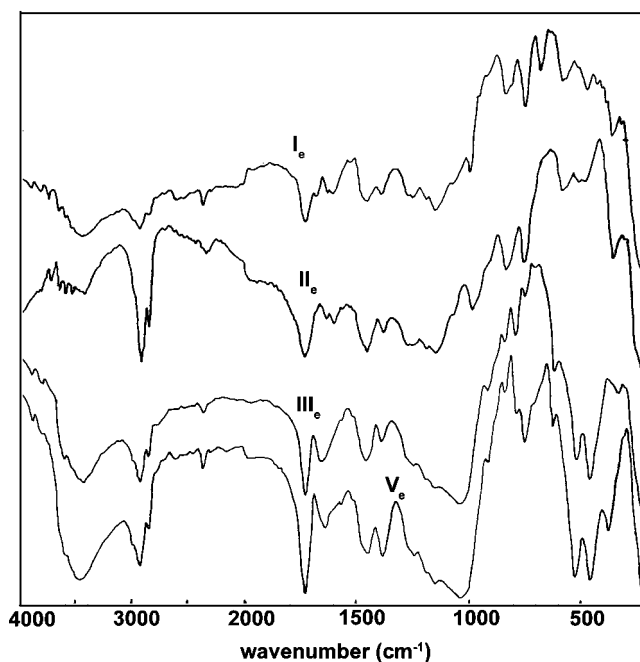


Figure 2 IR spectra of I_e, II_e, III_e, V_e in the region 4000–700 cm⁻¹.

positions of bands for distinctive functional group in copolymer confirm the chemical structure of MMA-VP copolymer. The bands at 1300–1100 cm⁻¹ and 1730 cm⁻¹ are characteristics to C–O stretching, C=O stretching. The band at 1603 cm⁻¹ characteristics to 4-substituted pyridine is also observed. This band is shifted in II_e to higher wavenumber involving N⁺I⁻ group.³² However the composite III_e reveals the presence of characteristic absorptions of both inorganic and organic components. Indeed, the peak at

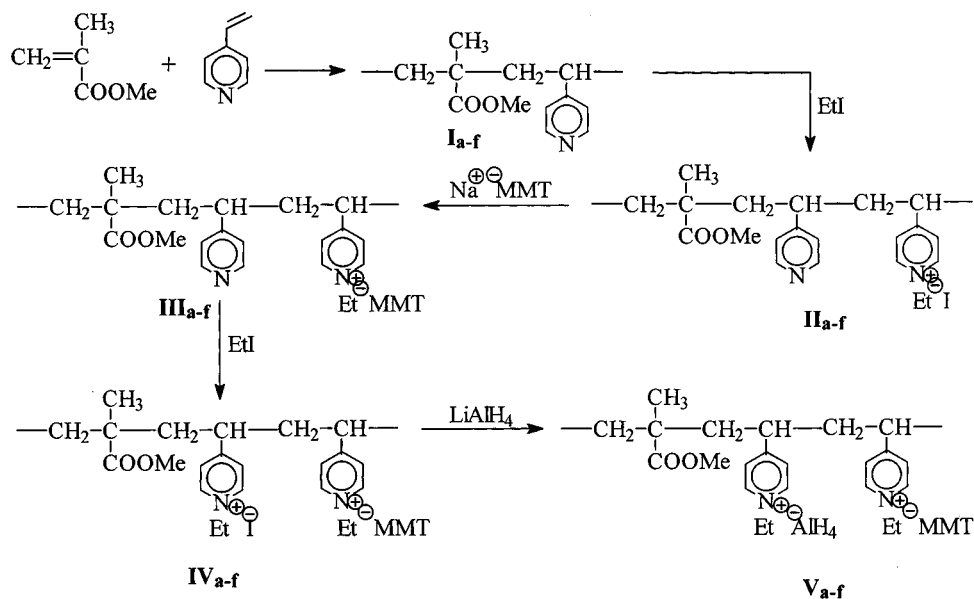
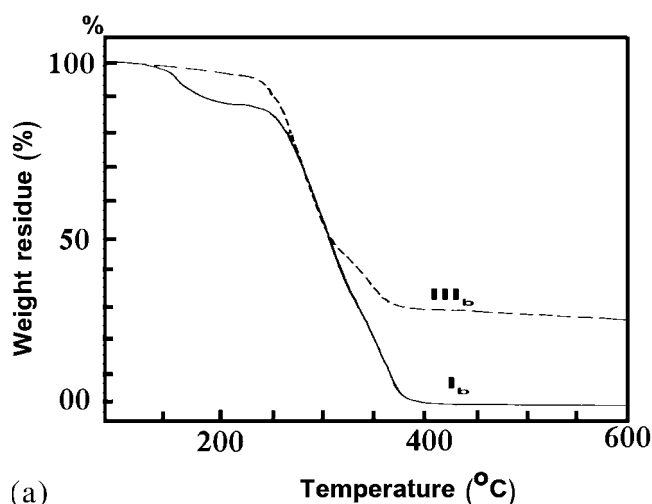
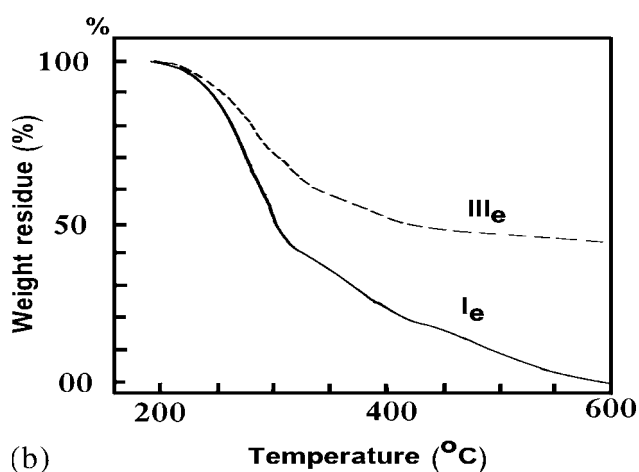


Figure 1 Schematic illustration of the nanocomposite synthesis.



(a)



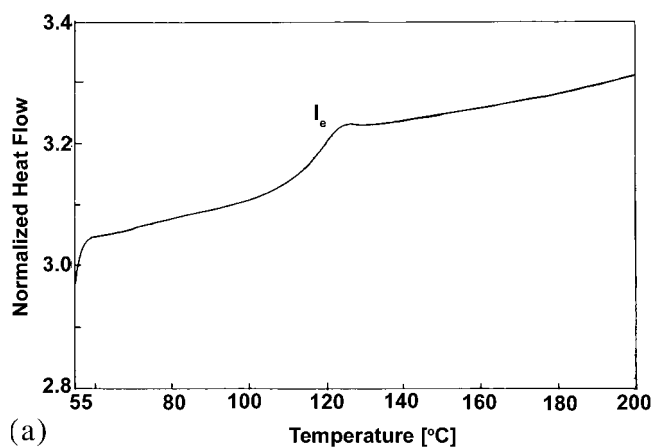
(b)

Figure 3 TGA thermogram of weight loss as a function of temperature for (a) MMA-VP copolymer (I_b) and MMA-VP copolymer-MMT composite (III_b); (b) MMA-VP copolymer (I_e) and MMA-VP copolymer-MMT composite (III_e).

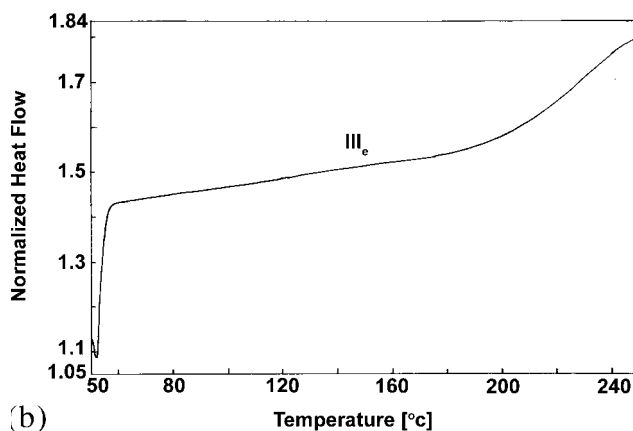
1040 cm^{-1} can be associated with Si—O stretching vibrations and those between 600 and 400 cm^{-1} with stretching of Al—O and bending of Si—O. The band at 1603 cm^{-1} characteristic to 4-substituted pyridine is shifted to higher wavenumber, suggesting that fixation occurs by electrostatic bonds. On the other hand the ester groups does not change. This attributed to limited interactions with the inorganic surface material and the macromolecule is fixed through the pyridinium group by ionic bonding.

Figure 3(a,b) shows a TGA thermogram of weight residue (%) as a function of temperature for copolymers I_b , I_e , and their composites III_b , III_e , respectively. The thermal stability of these nanocomposites is higher than that of MMA-VP copolymers. The TGA data showing the temperature at which 10 and 50% degradation occurs confirm the stability. The temperature at which 10% degradation occurs is 200°C , 232°C for I_b , I_e copolymers and 267°C , 250°C for III_b ,

III_e composites respectively. The temperature at which 50% degradation occurs is 317 , 320°C for I_b , I_e copolymers and 334 , 400°C for III_b , III_e composites, respectively. The increase in the degradation temperature is considered as a measure of thermal stability. A similar behavior was observed in PMMA-MMT nanocomposites prepared by *in situ* polymerization.³³ The initial step in degradation (I_b , I_e) has been attributed to the presence of weak links in the polymer chain.³⁴ This behavior is not observed in the presence of clay (III_b , III_e). This improvement in the decomposition temperature in the new materials was attributed to the presence of a constrained region in the nanocomposites. The first indication of enhanced thermal stability in nanocomposites appears in the reports of Blumustien et al.^{35,36} who studied the thermal stability of PMMA intercalated into clay. He proposed that the enhanced thermal stability was due to both the difference of chemical structure and restricted thermal motion of polymer chain in the silicate interlayers. The difference in enhancement between III_b and III_e was attributed to the high percentage of clay.³⁷



(a)



(b)

Figure 4 DSC thermogram of (a) MMA-VP copolymer (I_e); (b) MMA-VP copolymer-MMT composite (III_e).

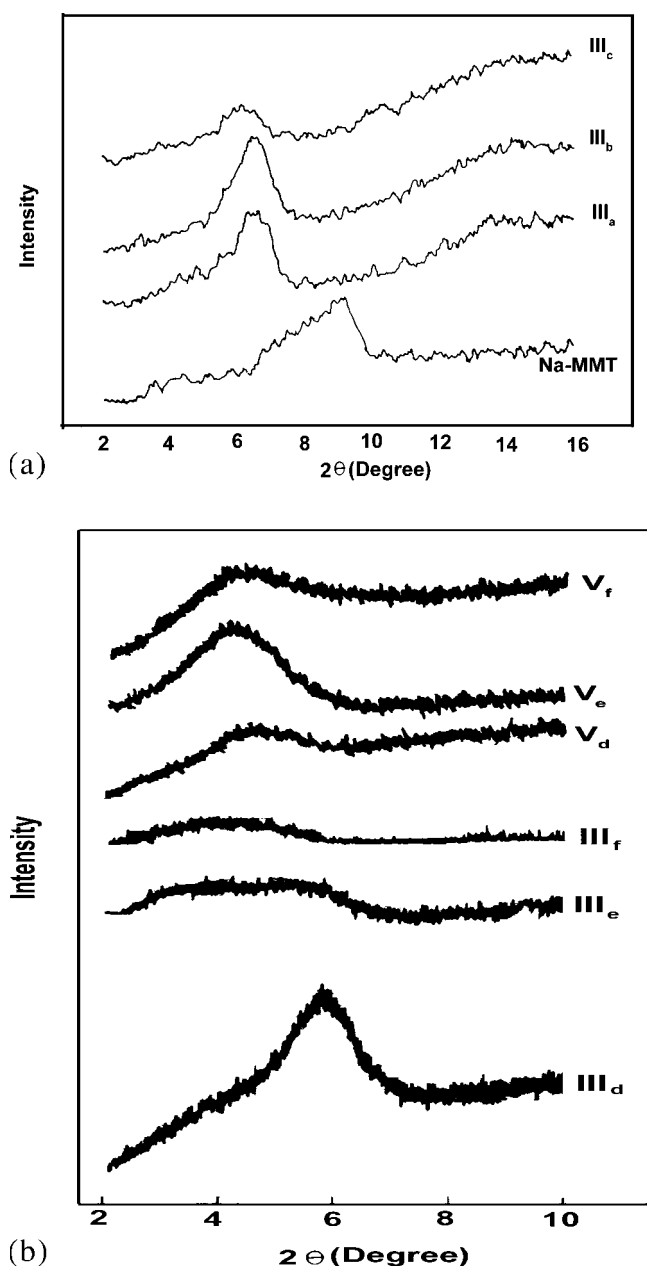


Figure 5 X-ray diffraction pattern of (a) Na-MMT, MMA-VP copolymer-MMT composites (III_{a-c}); (b) MMA-VP copolymer-MMT composites (III_{d-f}) and MMA-VP copolymer-MMT supported reagents (V_{d-f}).

DSC traces of MMA-VP copolymer (I_e) and composite (III_e) are shown in Figure 4(a,b). The pure copolymer exhibits an endotherm at approximately 116.4°C, corresponding to the T_g of MMA-VP copolymer. Nevertheless, the intercalated copolymer (III_e) does not show any traces of clear transitions. This is tentatively ascribed to the confinement of the intercalated polymer chains within the silicate galleries that prevents the segmental motions of the polymer chains.

X-ray diffraction data of the composites containing different percentage of Vinyl Pyridinium group in the

copolymer indicates that Na-MMT allows the copolymer to migrate between the layers. It is noted that the MMT galleries are expanded from 9.6 Å basal spacing for anhydrous Na-MMT. This implies that silicate layers were intercalated by copolymers. The diffraction pattern displayed in Figure 5(a) shows a regular lattice spacing of 13.59, 13.81, 14.73 Å for III_a, III_b, III_c with an expansion of 4.29, 4.51, and 5.43 Å, respectively. Subtracting the thickness of the silicate layer 9.3 Å from the observed d_{001} spacing produces the thickness of the polymer within the interlamellar span. The increasing in d -spacing from 13.59 to 14.73 Å can be explained by the fact that as the percentage of VP in the copolymer increased, the macromolecules became more fixed between the layers through an ion exchange process. It is worth noting that in III_c there was a broad diffraction. The broadness with the small intensity of the peak suggested that the stacking of silicate layers became disordered. From the width of the diffraction curve, the thickness of a particular set reflecting planes, t , for composites was calculated according to Scherrer's formula³⁸ $t = 0.9 \lambda / \beta \cos \Theta_{\beta}$, where $\lambda = 1.5418$ Å, β = width of diffraction curve in radians. It was measured by taking half the difference between two extreme angles at which the intensity is zero. The thickness of the reflecting plane decreases as the width of diffraction curve increases. The thickness varied from 39 to 53.4 Å for III_{a-c}. The larger layer distance in III_c demonstrates the advantage of using this ratio in preparation III_{d-f} composites. Figure 5(b) presents X-ray diffraction patterns corresponding to (III_{d-f}) composites and (V_{d-f}) reducing agent materials. In III_d, a diffraction peak at $2\theta = 5.6^\circ$, corresponding to basal spacing of the clay platelets of 15.78 Å was observed. Large d spacing may be related to the large size of pyridine ring. This peak was disappeared in V_d and a broad peak was shown

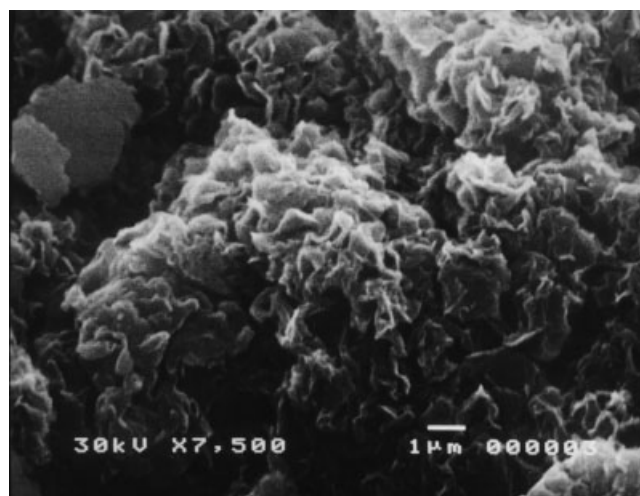


Figure 6 Scanning electron micrograph of MMA-VP copolymer-MMT composite (III_e).

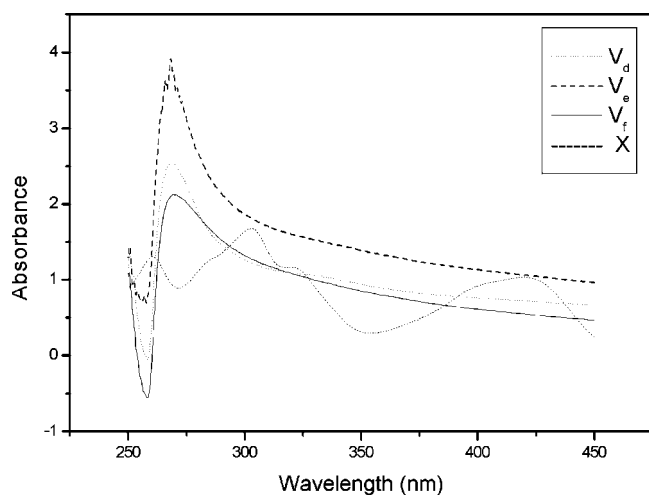


Figure 7 UV spectra of potassium ferricyanide (x) and the product of reduction using supported reagents V_{d-f} .

at lower 2θ (4.6°) suggesting the presence of MMT disordered layers. This is due to the swelling of the composites in DMF that allow more polymers to intercalate during the reaction. A different situation was observed in III_e and III_f . The results showed that the peak of the clay at $2\theta = 4^\circ$ corresponding to a basal spacing of 22.09 \AA does not shift to lower angle in V_e and V_f .

Searching for mineral agglomerates at the highest possible magnification (Fig. 6) using SEM reveals the absence of large aggregates. This indicates that the mineral domains are submicron in size and their size are too small to be seen at this magnification level.

The effectiveness of the resulting materials was examined in reduction reaction of potassium ferricyanide and was confirmed by the disappearance of the UV band at 417 cm^{-1} (Fig. 7).

CONCLUSIONS

A method to prepare nanocomposites of poly(methylmethacrylate-vinylpyridine)-MMT is disclosed. It entails two steps: copolymerization of methylmethacrylate and vinyl pyridine and formation of pyridinium ion, which is then chemically intercalated to MMT through an ion exchange process. The resulting nanocomposites were reacted with lithium aluminum hydride forming the supported reagents. The copolymer intercalation produces an interlamellar expansion, which suggests copolymer packing between the layers of MMT. SEM images proved that agglomerate of MMT has been disappeared. The intercalated nanocomposites showed a noticeable enhancement of the thermal stability, compared with (MMA-VP) copolymer. This enhancement is attributed to the presence of ionic bond between the copolymer and clay. The

supported reagents were used in the reduction of potassium ferricyanide.

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