

Water-Dispersible Nanocomposites of Polyaniline and Montmorillonite

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ABSTRACT: The polymerization of aniline (ANI) in aqueous medium in the presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and montmorillonite (MMT) resulted in the formation of a nanocomposite (PANI–MMT). The inclusion of PANI in the composite was confirmed by FTIR studies. The extent of PANI loading in the composite increased with ANI concentration at a fixed oxidant/MMT amount and with the oxidant amount at a fixed ANI and MMT weight, but decreased with an MMT amount at a fixed ANI and oxidant level. TGA revealed a higher stability for the PANI–MMT composite relative to PANI and confirmed a PANI loading of ca. 51% in the composite. The conductivity increased in all the cases. XRD analysis revealed no expansion of the d_{001} spacing at 9.8 Å, implying no intercalation of PANI within the MMT layers. Scanning electron micrography studies revealed interesting morphological features for the composites. Transmission electron micrography analysis revealed distinctive features and confirmed the formation of PANI–MMT composite particles of diameters in the 300- to 400-nm range. These composites could be obtained as stable colloids in the presence of poly (*N*-vinyl pyrrolidone) under selective conditions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2948–2956, 2000

Key words: nanocomposites; montmorillonite; polyaniline; conductivity; water dispersible

INTRODUCTION

In the past few years a substantial amount of literature has accumulated focussing on the preparation of stable aqueous colloidal dispersions of polyaniline (PANI) and polypyrrole (PPY). Armes et al.^{1,2} reported the preparation and characterization of PANI and PPY aqueous dispersions using colloidal silica without any polymeric stabilizers, where in the early stages of the polymerization, the precipitating conductive polymer deposited on the individual silica particles, which acted as a high surface area substrate.

A stable colloidal PANI dispersion was also obtained³ through the oxidative polymerization of ANI in the presence of polymeric stabilizers such as poly(vinyl methyl ether). Colloidal PPY dispersions were also reported by Simmons et al.⁴ and others⁵ using reactive polymeric stabilizers.

Montmorillonite clay-based polymer composites have also received wide attention. A variety of conventional vinyl polymers⁶ and polycondensates like epoxy resins and ϵ -caprolactone were used in composite preparations with layered MMT clays by *in situ* intercalative polymerization or by intercalation of polymer melts in layered silicates and by other procedures.⁷ Mehrotra and Giannelis⁸ prepared highly oriented multilayered films of PANI by intercalative polymerization of ANI in fluorohectorite—a synthetic mica type silicate.

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The paucity of information available prompted us to initiate research in the direction of preparation and evaluation of MMT-based water-dispersible nanocomposites of some potentially important heterocyclic polymers of *N*-vinylcarbazole (NVC), and pyrrole (PY). Recently, we reported⁹ that NVC could be directly polymerized by MMT, and in this process, a part of the resulting poly(*N*-vinylcarbazole) (PNVC) became intercalated in the MMT layer, producing a nanocomposite. However, the PNVC–MMT intercalate was not dispersible in aqueous/nonaqueous media, even in the presence of a polymeric dispersant. We further reported¹⁰ that PY polymerization could be very feebly initiated (ca. 5% in 3 h) by MMT alone. However, with FeCl₃ impregnated MMT, the polymerization of PY¹⁰ and NVC¹¹ occurred in high yield, resulting in the formation of PPY–MMT and PNVC–MMT nanocomposites. XRD analysis, however, revealed no intercalation of PPY¹⁰ and of PNVC¹¹ in the MMT lamellae.

In the above background, we have now explored the aniline–MMT polymerization/nanocomposite system and have developed a very simple methodology for the preparation of a water-dispersible stable colloid of the PANI–MMT composite, which would facilitate the practical application of this insoluble PANI-based composite system. The preparation, characterization, and property evaluation of PANI–MMT composites are highlighted in this article.

EXPERIMENTAL

Materials

Aniline (E. Merck, Germany) was freshly distilled under reduced pressure. Montmorillonite (Aldrich, Milwaukee, WI) was dried in vacuum at 100°C for 3 days prior to use in each experiment. All other reagents and chemicals were of A.R. grades.

Preparation of Composite

A measured volume of freshly distilled aniline was syringed slowly to a well-stirred solution of a known weight of (NH₄)₂S₂O₈ in 2 *M* HCl at 28°C. The gradual change of color from light gray to intense green was indicative of the formation of PANI. After 3 h the total mass was centrifuged, and the residue was washed with water. The mass was dried under vacuum at 90°C for 10 h to

yield a dark green fine powder. A control run was also conducted using the same amounts of ANI and the oxidant in 2 *M* HCl solution without any MMT, and allowing the reaction to proceed for 3 h with stirring.

The water-dispersible PANI–MMT composite was prepared as follows. A known weight of MMT was added to a stirred 2-*M* aqueous solution of poly(*N*-vinyl pyrrolidone) (PVP) in a stoppered conical flask to produce a stable aqueous dispersion of MMT. To this dispersion, a known volume of (NH₄)₂S₂O₈ solution of desired concentration was added, and a known volume of freshly distilled ANI was injected into the system. The reaction mixture was continuously stirred by a magnetic stirrer at room temperature for 16 h. The total contents of the flask were centrifuged at 18,500 rpm for 1 h. The separated black mass was repeatedly washed with water followed by methanol, and finally dried at 70°C for 5 h under vacuum. Notably, this composite powder could be redispersed in water as well as in alcohol or DMSO under sonication.

Characterization and Property Evaluation

FTIR spectra were taken on a Perkin-Elmer model 883 instrument. XRD analyses of MMT and PANI–MMT composite powders were performed on a Philips X-ray diffractometer, Cu LFF 40 kV 20 mA, with wavelengths of 1.54060 Å and 1.54438 Å. Surface morphologies of MMT and PANI–MMT were studied by taking scanning electron micrographs on an Hitachi S415A instrument. The particle size of the PANI–MMT composites were measured by a transmission electron microscope (Hitachi 600). For these measurements the dispersions in propanol were diluted to 100 ppm, and the dilute solutions were dried on carbon-coated copper grids. Thermogravimetric analyses (TG and DTA) were performed on a Shimadzu DT-40 instrument. DC conductivity measurements were conducted on pressed pellets with silver coating by the conventional four-probe technique.

RESULTS AND DISCUSSION

General Features of Composite Formation

Unlike *N*-vinylcarbazole–MMT polymerization,⁹ the addition of ANI monomer to MMT powder did not produce any polymer under a variety of con-

Table I Some Typical Data for ANI-MMT [(NH₄)₂S₂O₈] Polymerization/Composite Formation

Entry No	Weight of MMT (g)	Oxidant 10 ⁻³ (mol)	ANI 10 ⁻³ (mol)	Time of Polymerization (h)	% Yield of PANI	% PANI per gram of Composite	Conductivity (S/cm)
1	0.10	0.88	2.20	3	36.17	42.00	0.1 × 10 ⁻³
2	0.10	1.76	2.20	3	78.10	60.50	0.3 × 10 ⁻³
3	0.10	1.76	2.20	6	79.30	61.00	—
4	0.10	2.64	2.20	6	100.00	66.66	0.4 × 10 ⁻³
5	—	1.76	2.20	3	78.00	—	3.0 × 10 ⁻¹
6	0.20	1.76	2.20	3	81.10	44.62	0.7 × 10 ⁻³
7	0.30	1.76	2.20	3	76.00	33.41	1.0 × 10 ⁻³
8	0.40	1.76	2.20	3	72.10	25.26	5.0 × 10 ⁻³
9	0.40	4.40	2.20	3	100.00	32.85	1.1 × 10 ⁻³
10	0.40	4.40	4.40	3	100.00	48.93	5.0 × 10 ⁻³
11	0.40	4.40	6.60	3	93.20	58.50	9.0 × 10 ⁻³

ditions, and no color changes were observed. Relevantly, PY monomer was found by us¹⁰ to be very slowly polymerized in the presence of MMT (ca. 5% in 3 h). However, the addition of ANI to the S₂O₈²⁻-MMT-HCl system resulted in the formation of a dark green mass. Some typical polymerization/composite formation data are presented in Table I. The data (entry Nos. 1–4, Table I) suggest that the formation of PANI increased with increasing amount of the oxidant, which is the usual trend expected. Entries 2, 6, and 7, or 6, 7, and 8 of Table I further suggest a fall in PANI conversion corresponding to an increase in the MMT amount at a fixed oxidant and ANI amount. This is reasonable, because, in the presence of MMT as a heterogeneous surface, the ANI oxidation reaction might be somewhat discouraged. At a high MMT and oxidant amount (entries 9, 10, and 11, Table I) complete conversion to PANI occurred except that with a higher ANI amount in the initial feed (entry 11, Table I) the conversion to PANI tended to decrease somewhat due to oxidant depletion. The increase in the percentage loading of PANI per gram of the composite was interesting and significant from the view of monitoring the bulk properties of the composite such as conductivity.

FTIR Absorption Characteristics

FTIR spectrum of PANI-MMT composite (Fig. 1) revealed bands at 1571 cm⁻¹, 1476 cm⁻¹ (N—H bending), 1302 cm⁻¹, 1243 cm⁻¹ (C—N stretching), and 3425 cm⁻¹ (>N—H stretching) ascribed to PANI principal peaks¹² and at 1049 cm⁻¹, 593 cm⁻¹, and 470 cm⁻¹, typical of major MMT peaks.¹³

XRD Analysis

XRD analysis of PANI-MMT composite revealed a peak at 9.8 Å conforming to d₀₀₁ spacing in unintercalated MMT,⁹ which ruled out any intercalation of PANI in the MMT lamellae. A similar feature was also observed by us in the XRD analysis of the PPY-MMT(FeCl₃) nanocomposite system¹¹ and also the PNVC-MMT(FeCl₃) nanocomposite system.¹³ The latter system did not reveal any d₀₀₁ spacing expansion, although after repeated benzene extraction, the composite retained the PNVC in the component. On the contrary, in the PNVC-MMT nanocomposite system prepared by direct interaction of *N*-vinylcarbazole with MMT,⁹ XRD confirmed the expansion of d₀₀₁ spacing to 14.6 Å, implying intercalation of polymer in the MMT lamellae. Generally, nanocomposites of layered silicates are either gallery⁸ intercalated or exfoliated/delaminated. In both cases, expansion and/or elimination of the MMT basal reflection is observed by XRD.⁸

In the presence of an oxidant, a common mechanism appeared to be operative in the MMT-based systems, leading to very fast polymerization.¹⁴ Eventually, the polymers precipitating out in the medium would coat the MMT particles as in the inorganic oxide-based systems involving these polymers^{15,16} rather than becoming intercalated.

Scanning Electron Micrography Characterization

Figure 2 represents SEM images of a PANI-MMT composite (a, b), a 1 : 1 mechanical mixture (1 : 1 w/w) of preformed PANI and MMT (c), and of PANI (d), respectively. The SEM of a highly di-

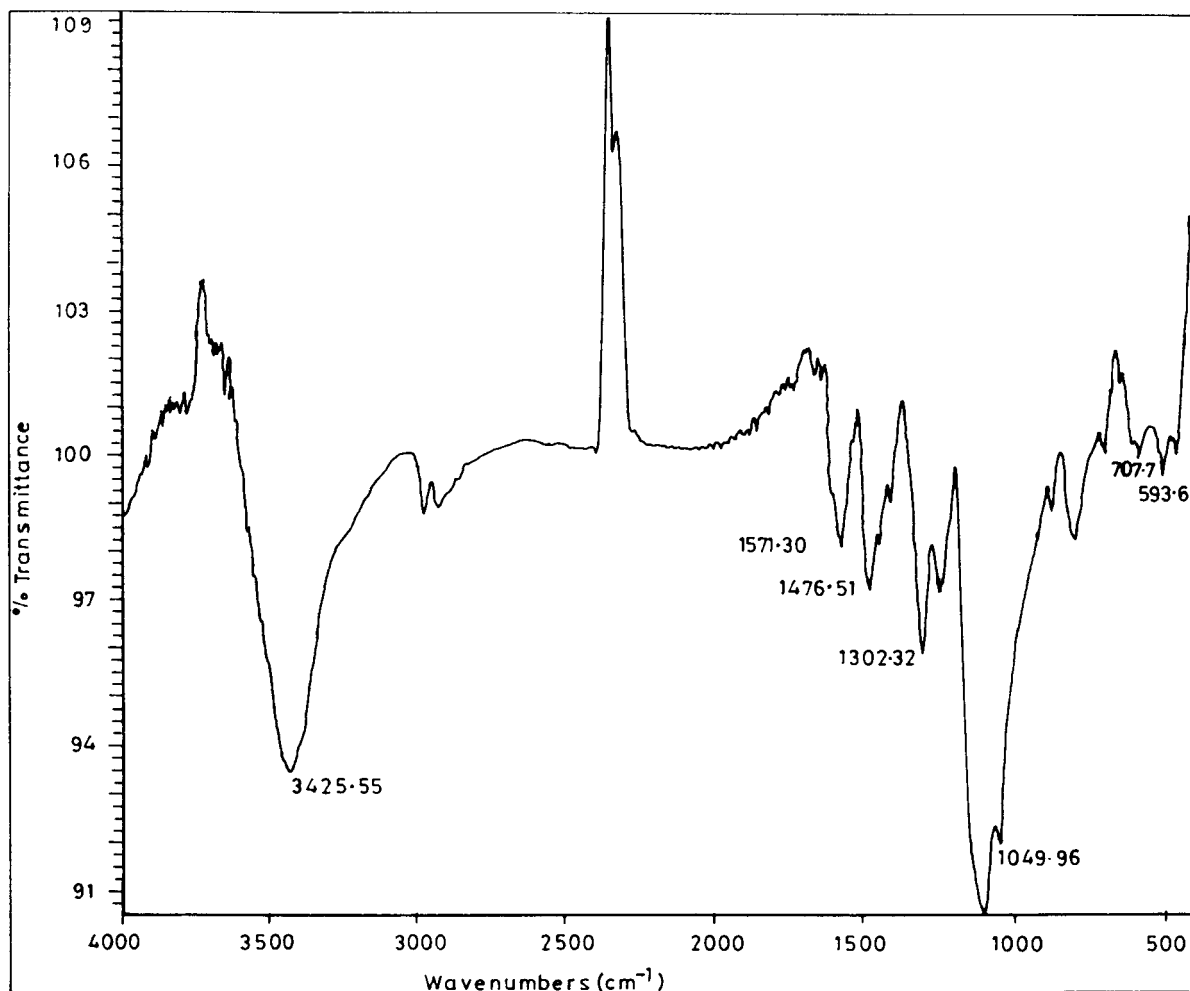


Figure 1 FTIR spectrum for the PANI-MMT composite.

luted (in the range of 100 ppm) colloid of the composite clearly indicated the formation of nearly spherical particles (b). The SEM photograph of an undiluted colloid (a) revealed the typical highly dense packing of the composite particles. The SEM for a 1 : 1 mechanical mixture of preformed PANI and MMT revealed a morphology distinct from that of the PANI (d) or of the composite (a or b).

Transmission Electron Micrography Analysis

Figure 3 represents the transmission electron micrographs of an undiluted PANI-MMT composite colloid (a), and the same for the highly diluted (in the range of 100 ppm) composite (b), a mechanical mixture (1 : 1 w/w) of preformed PANI and MMT (c), and of MMT (d), respectively. Figure 3(d) reveals that the MMT particles were elongated, and the presence of primary particles fused together

in short chains was noticeable. The formation of the PANI-MMT composite was clearly accompanied by a distinct change in the TEM image of MMT. Spherical globular PANI particles appeared to cluster around the stringy MMT particles. The TEM image for a mechanical mixture of PANI and MMT [Fig. 3(c)] clearly revealed the nonuniform coverage of MMT particles by the PANI moieties as distinct from the composite. The average diameters of the PANI-MMT composite particles were in the 300 to 480 nm range. Armes et al. contended in recent studies^{1,2,15,16} that the PANI- and PPY-silica-based nanocomposite particles were characterized by a typical raspberry morphology—where ultrafine silica particles were present not only on the surface but also distributed throughout the interior of the agglomerates. As the water-soluble monomers like ANI or PY started polymerizing in aqueous

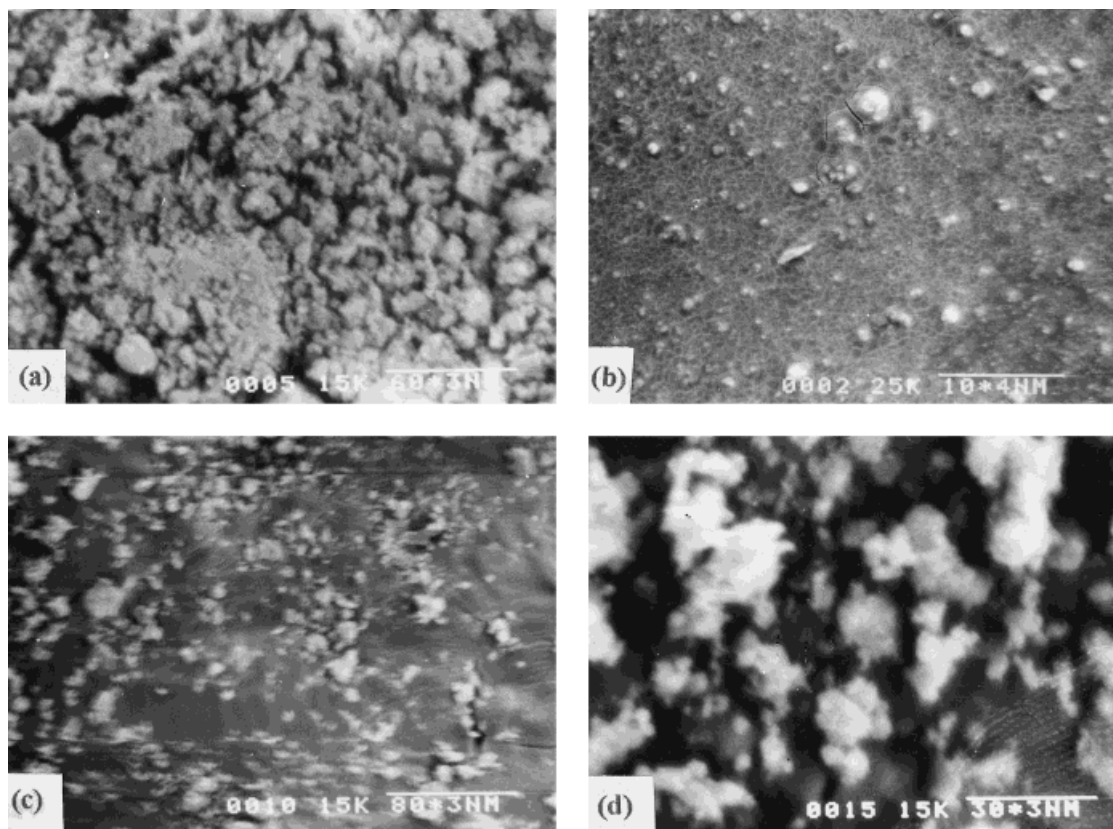


Figure 2 Scanning Electron Micrographs for (a) undiluted PANI–MMT composite dispersion, (b) diluted PANI–MMT composite dispersion (in the range of 100 ppm), (c) a 1 : 1 mechanical mixture of preformed PANI and MMT, and (d) PANI.

medium, the insoluble polymers “glued”^{1,15,16} the silica particles to the microaggregates of the polymer, silica particles. The precise reason for the composite formation process is, however, somewhat obscure. The water solubility of PANI and PY is low, and it may be that the water solubility of the corresponding oxidised intermediates may be of relevance in the composite formation process, which could depend on the affinity of the formed polymer nuclei for the electrically negative surface of silica and MMT.¹⁷ In the PANI–MMT nanocomposite system, a similar situation might possibly prevail, although the manifestation of a typical raspberry morphology could not be clearly distinguished in our TEM images.

Thermal Stability Characteristics

Figures 4(a) and (b) represent typical weight loss versus temperature data for the PANI–MMT composite and PANI, respectively. Table II compares the thermal stabilities of the PANI–MMT composite, PANI, and MMT,⁹ respectively. Al-

though PANI decomposition was complete at a temperature of 571°C onwards, the composite underwent 64% weight loss at 950°C. Our previous result on the thermal stability analysis of MMT indicated a 13% weight loss at 999°C due to probable loss of the volatile impurities. Hence, the PANI loading in the composite was $(64-13)\% = 51\%$. This figure compared reasonably with the gravimetric result of a PANI loading of 49% (entry 10, Table I) in the composite used for the thermal stability analysis.

A comparison of DTA scans in the thermograms revealed the manifestation of smaller exothermic peaks at 209, 362°C, and a sharp peak at 532.9°C for PANI, whereby 70% of PANI degradation was completed. Characteristically, in the DTA curve for the PANI–MMT composite, a broad hump at 407.8°C appeared corresponding to a loss of 30% of the composite. No minor PANI peaks could be detected in this range. Thus, these data readily confirmed the enhanced thermogravimetric stability for the PANI–MMT composite relative to PANI.

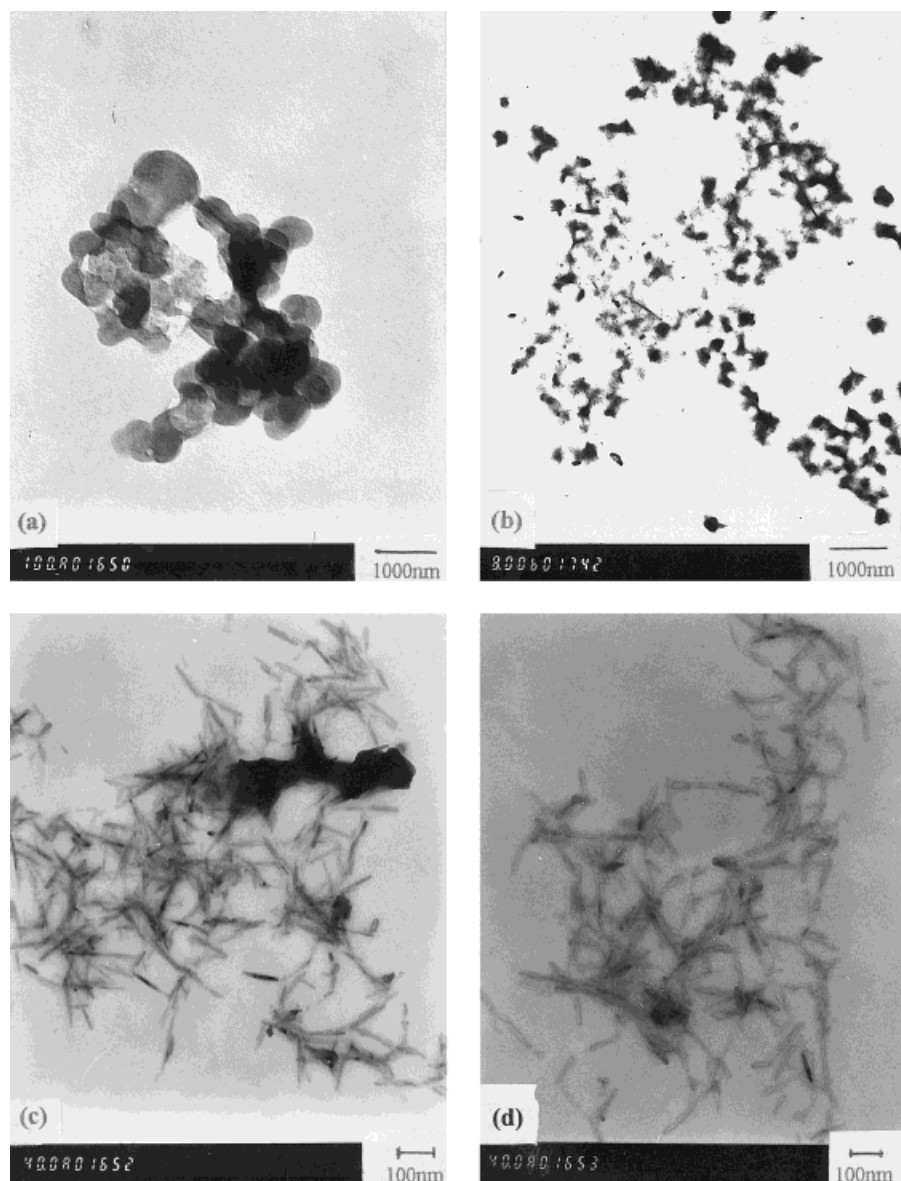


Figure 3 Transmission Electron Micrographs for (a) undiluted PANI–MMT composite dispersion, (b) diluted PANI–MMT composite dispersion (in the range of 100 ppm), (c) a 1 : 1 mechanical mixture of preformed PANI–MMT, and (d) MMT.

Conductivity Characteristics

The observed conductivities of the PANI–MMT nanocomposites, prepared at fixed MMT and oxidant amounts in the initial feed, increased steadily with increasing amount of ANI in the charge (entries 9–11, Table I). This was apparently due to a parallel increase in the extent of conducting PANI loading per gram of the composite. The conductivities of the PANI–MMT composites increased with the amount of oxidant in the initial charge (entries 1, 2, and 4, Table I). Both

the overall PANI yield, as well as the PANI loading per gram of the composite, increased with the amount of the oxidant. Hence, the observed conductivity trend was reasonable. The conductivities of the PANI–MMT composites also increased with an increase of MMT amount in the initial feed (entries 2, 6, 7, and 8, Table I), while both the total conversion to PANI as well as the amount of PANI loading per gram of the composite decreased. Because the inherent conductivity of MMT would be low, the above trend was puzzling,

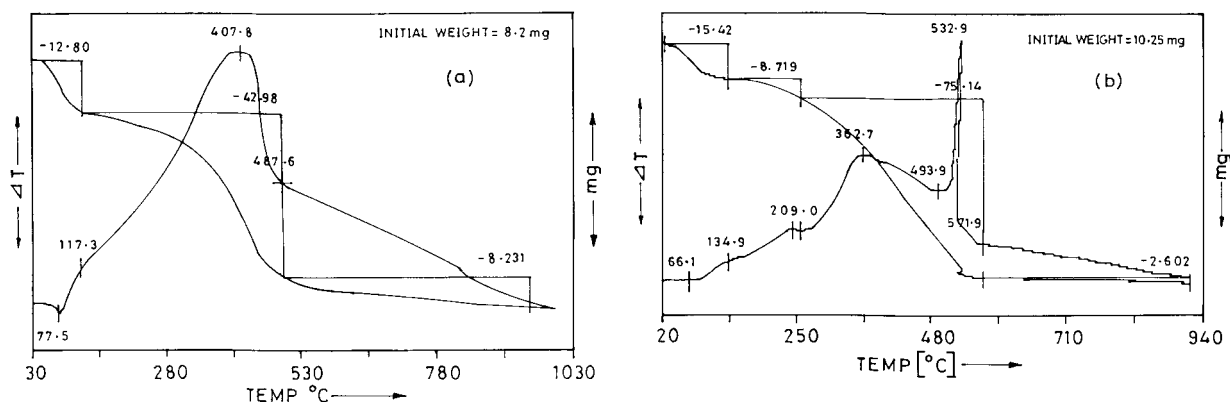


Figure 4 Weight loss vs. temperature data for (a) the PANI–MMT composite, and (b) PANI.

and the conductivities should have been expected to fall rather than increase, a trend parallel to PANI loading as in the other two instances referred above. Armes et al. pointed out that the electrical properties of the PANI oxide-based composites were virtually the same as that of loaded PANI in PANI–poly(vinyl alcohol) or PANI–poly(*N*-vinyl pyrrolidone) composites.³ Accordingly, the presence of the insulating silica or any other materials like MMT would not affect the nature of conduction.

With this background we tentatively propose the following explanation for the observed trend. It is well known¹⁴ that the electrical conductivity of PANI can be widely varied by acidic protonation. With an increase in the MMT amount, the conversion to PANI decreased. Because the proton concentration in the media was kept fixed (2 *M*), in entries 2, 6, 7, and 8, the extent of protonation of PANI would be expected to increase with decreasing PANI content in the system. Protonation in PANI would lead to the formation of radical cations by an internal redox reaction, causing reorganization of electronic structure to produce semiquinone radical cations, and accordingly the conductivity would be enhanced.

Entry 5 (Table I) shows a much higher conductivity for the PANI prepared under the same con-

dition without any MMT. The lower conductivity values ($\sim 10^{-3}$ S/cm) consistently observed for the PANI–MMT composites may result from the presence of low conducting MMT in the materials.

Water Dispersibility of the PANI–MMT Nanocomposites

Table III summarizes the conditions applied for producing stable aqueous dispersions of PANI–MMT nanocomposites. The corresponding information for PPY–MMT¹⁰ and PNVC–MMT-based systems^{9,11} have also been included for comparison. The use of a polymeric dispersant like PVP was essential for the production of stable dispersions of PANI–MMT nanocomposites. This was also corroborated in our recent results on the water dispersibility of MMT-based composites of PPY.¹⁰ Possibly, a polymeric dispersant would be indispensable for stabilizing aqueous MMT dispersions. We failed to detect any change in the d_{001} spacing of MMT after sonication in presence of the polymeric dispersant. So intercalation of PVP in the MMT, and eventually trapping of PANI to yield a stable dispersion, was possibly not important.

Previous studies on the synthesis of PANI dispersions reported a lack of success with poly(vinyl

Table II Weight Loss vs. Temperature Data for PANI, PANI–MMT Composites and MMT

Materials	% Weight Loss [Temperature (°C)]		
PANI	15.42 (134.90)	24.13 (259)	complete (571.90)
PANI–MMT composite	12.88 (117.80)	42.98 (487.6)	64.09 (950)
MMT	8.30 (190.90)	12.20 (682)	13.20 (999.70)

Table III Dispersibility of the PANI–MMT Nanocomposite in Aqueous Medium

Serial No.	Conditions Applied for Obtaining Aqueous Dispersion	Observation
1. a	PANI–MMT composite was added to water and sonicated for 5 h	Dispersion stable up to 3 days.
b	PANI–MMT composite was added to an aqueous solution of PVP and sonicated for 5 h	Stable colloid but not redispersible
c	MMT was added to an aqueous solution of PVP and stirred for 2 h, the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution and ANI were added serially and stirred magnetically for 20 h	Permanently stable colloid and redispersible
2. a	PPY–MMT composite was added to water and sonicated for 5 h ¹⁰	Dispersion stable up to 40 h
b	PPY–MMT composite was added to an aqueous solution of PVP and sonicated for 5 h ¹⁰	Stable colloid but not redispersible
c	MMT was added to an aqueous solution of PVP and stirred for 2 h; the FeCl_3 solution and PY were added serially and stirred magnetically for 16 h ¹⁰	Permanently stable colloid and redispersible
3. a	PNVC–MMT composite was added to water and sonicated for 5 h ⁹	Unstable dispersion
b	MMT was added to PVP solution in alcohol and stirred for 2 h. A benzene solution of PNVC was added and the system was stirred magnetically for 22 h ¹¹	No composite formation

alcohol) (PVA) and other polymeric dispersants,^{3,18} the probable reason being the poor adsorption of these stabilizers on the PANI surface. On the contrary, Gospodinova et al.¹⁹ and others^{20–22} claimed successful dispersions using PVA due to efficient grafting of PVA on to the PANI particles. To overcome the problem of low adsorption of conventional stabilizers, Tadros et al.²⁰ used tailor-made stabilizers—which could undergo graft copolymerization with ANI and thus get anchored on PANI particles to assist stable dispersion.

Our results further show that PVP was an effective stabilizer if used with MMT prior to addition of the polymerizing monomers (ANI and PY) and the oxidants. Apparently, this procedure would help surface adsorption of the precipitating polymers by the available polymeric stabilizer particles.

The observed failure of the PNVC–MMT system to yield a stable dispersion in the presence of PVP in contrast to PANI/PPY-based systems is indeed interesting. We do not as yet have any convincing explanation for this difference, but we feel water compatibility of the base monomers (ANI or PY water soluble but NVC insoluble) might be an important factor. In addition, since PNVC is bulkier than PPY or PANI, steric factors may limit the stabilization of the PNVC moieties by PVP relative to that for PPY or PANI.

CONCLUSION

A nanodimensional composite of polyaniline and montmorillonite can be obtained by the oxidative polymerization of aniline in aqueous medium in presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and MMT. The composite can be obtained as a stable dispersion in water in the presence of a polymeric stabilizer poly(*N*-vinyl pyrrolidone) under selective conditions. The bulk conductivities of these dispersions can be increased by increasing the loading of PANI on the composite by varying amounts of ANI or oxidant in the initial feed.

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