

Alumina-Based Water-Dispersible Conducting Nanocomposites of Polypyrrole and Polypyrrole with Poly(*N*-vinylcarbazole)

Arjun Maity, Mukul Biswas

Department of Chemistry, Presidency College, Calcutta 700073, India

Received 31 July 2002; accepted 19 February 2003

ABSTRACT: Water-dispersible nanocomposites of polypyrrole with Al_2O_3 (PPY- Al_2O_3) and of poly(*N*-vinylcarbazole) with Al_2O_3 (PNVC- Al_2O_3) were prepared in an aqueous medium. Nanocomposites involving binary polymer systems—PNVC-(PPY- Al_2O_3) and PPY-(PNVC- Al_2O_3)—were prepared by precipitating PNVC or PPY onto a suspension of PPY- Al_2O_3 or PNVC- Al_2O_3 , respectively. The incorporation of the polymers in the composites was confirmed by Fourier transform infrared analyses. Scanning electron microscopy analyses revealed distinct morphological features of the composites. Transmission electron microscopy analyses of the PPY- Al_2O_3 , PNVC- Al_2O_3 , and PPY-(PNVC- Al_2O_3) composites confirmed the formation of spherical particles in the nanometer range. Thermogravimetric and differential thermal analyses revealed the stability order as: PNVC- Al_2O_3 > PNVC-(PPY- Al_2O_3) > PPY-

(PNVC- Al_2O_3) > PPY- Al_2O_3 . Direct current conductivity values of the PPY- Al_2O_3 , PNVC-(PPY- Al_2O_3), and PPY-(PNVC- Al_2O_3) composites were on the order of 2.8×10^{-4} , 1.7×10^{-5} , and 4.5×10^{-6} (S/cm), respectively. These nanocomposites dispersed in water, with stability decreasing in the order: PPY- Al_2O_3 (~40 h) > PNVC-(PPY- Al_2O_3) (30 h) > PPY-(PNVC- Al_2O_3) (20 h), and in the presence of polyvinylpyrrolidone a permanently stable suspension was obtained in all cases. The dispersibility appeared to be higher when the polymerization was conducted in a suspension containing a higher amount of Al_2O_3 . © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1058–1065, 2003

Key words: nanocomposite; nanodimensional alumina; polypyrrole; poly(*N*-vinylcarbazole); conductivity; water dispersibility

INTRODUCTION

Specialty polymers such as polypyrrole (PPY), polyaniline (PANI), and polythiophene (PTP) display outstanding conductivity and other bulk properties but suffer from processibility limitations because of their intractable nature. Considerable research attention globally has been directed to obtaining processible dispersion of these intractable specialty polymers. Armes et al.^{1–6} developed a large variety of PPY- or PANI-based water-dispersible nanocomposites using colloidal SiO_2 and other nanodimensional metal oxides. Biswas and SinhaRay reported on the preparation and evaluation of nanocomposites of PANI, PPY, and poly(*N*-vinylcarbazole) (PNVC) with montmorillonite clay^{7–11} and with nanodimensional metal oxides such as SiO_2 ,¹² MnO_2 ,¹³ and ZrO_2 .¹⁴

In the course of our ongoing research in this area, we recently have developed a simple method for preparing a nanocomposite of PNVC with nanodimensional alumina¹⁵ by depositing PNVC from its solution in tetrahydrofuran (THF) on a dispersion of Al_2O_3 in a water medium. We have since been able to extend these procedures to preparing water-dispersible nanocomposites of mixed polymer systems, such as polypyrrole-poly(*N*-vinylcarbazole) (PPY-PNVC). Thus, by adding pyrrole monomer to a suspension of poly(*N*-vinylcarbazole)- Al_2O_3 (PNVC- Al_2O_3) composite in water prepared as above¹⁵ in the presence of FeCl_3 , a PPY-(PNVC- Al_2O_3) composite could be readily prepared. Similarly, by adding preformed PNVC to a suspension of polypyrrole- Al_2O_3 (PPY- Al_2O_3) in water, a PNVC-(PPY- Al_2O_3) composite also could be prepared.

In this article we describe the details of these preparations and the evaluation of the essential bulk properties of these composites, emphasizing that our method involves simple experimental conditions and has a wide scope, as the procedure can be readily applied to any selective combination of polymers with a specialty polymer like PPY, PANI, or PTP as one of the components. The resulting composites from such

Correspondence to: M. Biswas (mbnb123@rediffmail.com).

Contract grant sponsor (to Mukul Biswas): Council of Scientific and Industrial Research, New Delhi, India; contract grant number: 80(0037)/EMR-II.

TABLE I
Percent Conversion and Loading Data for PPY-Al₂O₃ and PNVC-(PPY-Al₂O₃)
and PPY-(PNVC-Al₂O₃) Composite System

Entry no ^a	Weights (g) of				PPY in composite	% PPY loading per gram of composite	% PNVC loading per gram of composite
	Al ₂ O ₃	FeCl ₃	Preformed PNVC ^d	Composite			
1	0.1	0.50	—	0.19	0.09	47	—
2	0.1	1.50	—	0.28	0.18	64	—
3	0.1	3.00	—	0.30	0.20	67	—
4	0.1	1.50	—	0.23	0.13	56	—
5	0.1	1.50	—	0.15	0.05	34	—
6	0.2	1.50	—	0.36	0.16	44	—
7	0.3	1.50	—	0.47	0.17	36	—
8 ^b	0.3	1.50	0.2	0.68	0.18	27	29
9 ^c	0.3	1.50	0.2	0.56	0.06	10	36

^a For each set, weight of PY = 0.2 g; medium EtOH:H₂O (1:1) and EtOH (30 mL) for entries 4 and 5 and H₂O (30 mL) for the rest.

^b PNVC was added to a suspension of PPY-Al₂O₃ in water.

^c PY monomer was added to a suspension of PNVC-Al₂O₃-FeCl₃ in water.

^d Molecular weight of the fractionated PNVC (as determined by viscometry in benzene solution at 25°C) was 4100.

mixed polymer systems would be expected to exhibit the distinctive bulk properties of the individual polymer components.

EXPERIMENTAL

Materials

Pyrrole (Lancaster, Morecambe, England) was freshly distilled under reduced pressure. *N*-vinylcarbazole (BASF, Kurlschue, Germany) was recrystallized from predistilled *n*-hexane and stored in the dark. Nanodimensional Al₂O₃ powder was prepared and donated to us by the National Metallurgical Laboratory (Jamshedpur, India). Anhydrous FeCl₃ (Merck, Hohenbrunn, Germany) was used as such. All other reagents and chemicals were of analytic reagent grade and used after necessary purification by standard procedures.

Preparation of poly(*N*-vinylcarbazole)

In a typical polymerization system, 2 g of NVC monomer was dissolved in 50 mL of CHCl₃ to which 3 g of anhydrous FeCl₃ was added. The system was kept under stirring at ambient temperature for 3 h, and then the solution was poured in an excess of methanol. A dirty white precipitate was collected and dried under vacuum. The solid obtained was dissolved in an appropriate volume of CHCl₃ and filtered. Pure white PNVC was obtained by repeated precipitation in methanol. Finally, the separated mass was washed repeatedly with methanol to remove all adhering substances and dried at 70°C for 5 h under vacuum.

Preparation of PPY-Al₂O₃ composite

A known weight (0.1 g) of Al₂O₃ in fine powdery form was added slowly to 30 mL of water with continued stirring in a stoppered conical flask to produce a stable aqueous dispersion of Al₂O₃. To this dispersion 0.2 mL of freshly distilled pyrrole was syringed slowly, followed by the addition all at once of 0.5 g of anhydrous FeCl₃. After 3 h the total black mass was centrifuged at 10,500 rpm. It was washed thoroughly with distilled water until the FeCl₃ had been completely removed. Then the mass was again dispersed in distilled water and centrifuged. This process was repeated four times to remove all adhering substances. The separated black mass was washed repeatedly with methanol and finally dried at 70°C for 5 h under vacuum. After physicochemical characterization, this mass was confirmed to contain PPY along with Al₂O₃. The experiments were repeated with different amounts of Al₂O₃ and FeCl₃ (see Table I). To check the influence of solvent, polymerizations also were conducted in varying ratios of an H₂O-EtOH mixture (Table I).

Preparation of PNVC-(PPY-Al₂O₃) composite

Nanodimensional Al₂O₃ powder (0.3 g) was added with stirring to 30 mL of water in a stoppered conical flask to produce a stable aqueous dispersion of Al₂O₃. To it, 0.2 mL of pyrrole and 1.5 g of anhydrous FeCl₃ were added in succession. After 3 h a THF solution of 0.2 g of preformed PNVC (2 mL) was added dropwise to this reaction mixture. The reaction mixture was then continuously stirred at room temperature for 3 h. The total black mass of the flask was centrifuged at 10,500 rpm for 1 h. The separated mass was again

dispersed in distilled water and centrifuged. This process was repeated four times in order to completely remove all adhering substances. Finally, the separated mass was washed with methanol and dried at 70°C for 10 h under vacuum.

Preparation of PPY-(PNVC-Al₂O₃) composite

Al₂O₃ powder (0.3 g) was slowly stirred in 30 mL of water in a stoppered conical flask to produce a stable aqueous dispersion of Al₂O₃, to which 2 mL of a THF solution of 0.2 g of preformed PNVC was added. The reaction mixture was then continuously stirred at room temperature for 3 h. A definite volume (0.2 mL) of pyrrole was injected into the mixture, and 1.5 g of anhydrous FeCl₃ was added all at once to the system. The reaction mixture was continuously stirred for 3 h. The total black mass was centrifuged at 10,500 rpm for 1 h, and the separated mass was again dispersed in distilled water and centrifuged. This process was repeated four times in order to remove completely all adhering substances. Finally, the separated mass was washed with methanol and dried at 70°C for 10 h under vacuum.

All of both the PNVC-(PPY-Al₂O₃) and PPY-(PNVC-Al₂O₃) composites thus obtained were extracted with benzene through continuous refluxing for 3 h at 50°C. For both, the total contents were centrifuged, a process repeated at least four times until the extracts did not yield any precipitate with methanol of any surface-adsorbed PNVC. These residues were finally dried at 70°C for 10 h under vacuum. After various physicochemical characterizations, the composites were confirmed to contain PNVC along with Al₂O₃ and PPY.

Characterization and evaluation of composite properties

Fourier transform infrared (FTIR) spectra of the composites were taken with a JASCO-410 instrument. The surface morphologies of the composites were studied by taking scanning electron micrographs, using a JSM-2500 instrument. The solid samples were sputter-coated with a gold layer before taking the micrographs. The particle sizes of the composites were measured by a transmission electron microscope (Hitachi 600), with diluted suspensions (100 ppm) in isopropanol. PNVC-Al₂O₃ and PPY-Al₂O₃ suspensions were sonicated for 90 min, whereas the PNVC-(PPY-Al₂O₃) suspension was sonicated for 4 h. Then the diluted solutions were dried on carbon-coated Cu grids. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a Shimadzu DT-40 instrument. Direct current (dc) conductivity measurements were taken on pressed pellets with a

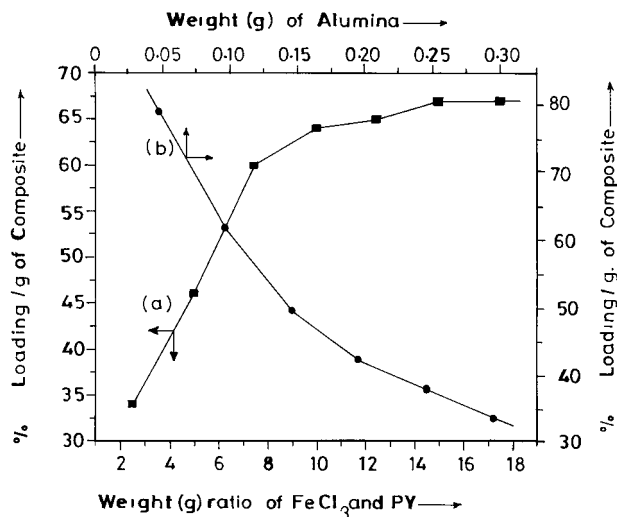


Figure 1 Variation of percent PPY loading per gram of composite with (a) weight ratio of [FeCl₃] and PY and (b) weight (g) of Al₂O₃.

silver coating, using the conventional four-probe technique.

RESULTS AND DISCUSSION

General features of composite formation

Table I shows some of the results for PPY-Al₂O₃, PPY-(PNVC-Al₂O₃), and PNVC-(PPY-Al₂O₃) composite formation under the conditions in the present experiments. In general, as shown in Figure 1(a), the percentage conversion vis-à-vis the loading of PPY per gram of composite was found to increase sharply with an increase in the FeCl₃:monomer feed ratio. Nearly 70% PPY conversion was realized at a FeCl₃:PY mole ratio of 6:1.

Figure 1(b) shows that the percent of PPY loading on the composite decreased with an increasing Al₂O₃ content in the initial feed at fixed PY and FeCl₃ concentrations. This trend was expected, as the weight percent of PPY formed was approximately the same, although the weight of Al₂O₃ increased, leading to a decrease in the percent of PPY loading, calculated per gram of composite.

A comparison of entries 2, 4, and 5 indicates that water was the best medium for high-yield PPY formation, although methanol could be used at the cost of somewhat decreased PPY yield but with increased dispersion stability of the PPY-Al₂O₃ composite.

Entries 8 and 9 represent an interesting set of results related to composite formation between PPY and PNVC with Al₂O₃ in an aqueous system. Interestingly, the residual PNVC (last column, entries 8 and 9) could not be removed from the PPY-(PNVC-Al₂O₃) and PNVC-(PPY-Al₂O₃) composite surfaces despite repeated extraction with benzene, which would dissolve

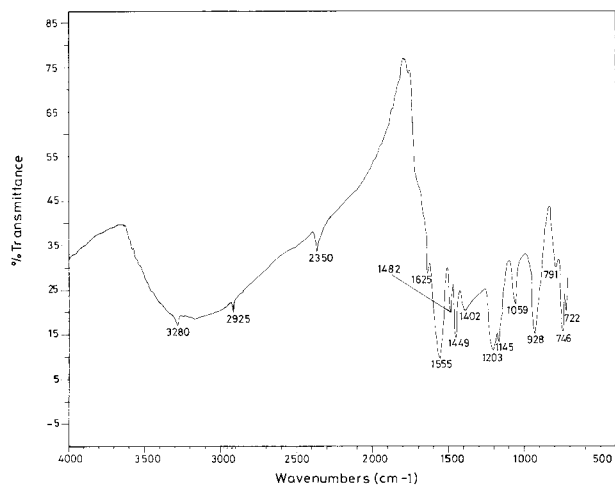


Figure 2 FTIR spectrum of PPY-(PNVC-Al₂O₃) composite.

any homopolymer of PNVC. This observation was in line with our earlier results¹⁵ and could be attributed to the stabilizing action of the acidic Al₂O₃ surface on the basic PNVC moieties precipitating out onto the dispersed Al₂O₃ particles. The precipitating PPY moieties would be deposited on any unoccupied dispersed Al₂O₃ particles, as they also would on the already-suspended PNVC-Al₂O₃ moieties in the medium. Entry 8 indicates that the percent of PPY loading per gram of composite was 26% against a value of 10% (entry 9), realized with the same recipe but with different orders of addition process. Evidently, the

addition of PNVC to PPY-Al₂O₃ dispersion resulted in a higher yield of the composite than that obtained with the addition of PY monomer to PNVC-Al₂O₃ and FeCl₃ suspension. The lower extent of PPY loading per gram of composite could be a result of the availability of smaller amounts of FeCl₃ with which to polymerize PY monomer because of its loss of acid-base interaction between the FeCl₃ and PNVC moieties.

FTIR absorption characteristics of PPY-Al₂O₃, PNVC-Al₂O₃, PPY-(PNVC-Al₂O₃), and PNVC-(PPY-Al₂O₃) composites

Figure 2 shows the FTIR spectrum of the PPY-(PNVC-Al₂O₃) composite after refluxing with benzene for 3 h. Table II summarizes the FTIR absorption peaks for the PPY-Al₂O₃, PNVC-Al₂O₃, and PPY-(PNVC-Al₂O₃) composites, along with their probable assignments. FTIR absorption peaks for the binary polymer composites at 2925, 1625, 1449–1482, 1402, 1145–1203, 746, and 722 cm⁻¹ confirmed the presence of a PNVC moiety, whereas the peaks at 3280, 2350, 1555, 1059, and 791–928 cm⁻¹ confirmed the presence of a PPY moiety in the binary composite structure. Notably, the FTIR spectrum of the PNVC-(PPY-Al₂O₃) composite (not presented here) also was almost an exact match with the same for the PPY-(PNVC-Al₂O₃) composite.

Scanning electron micrographic characterization

Figure 3(a–d) shows scanning electron micrographs of the PPY-(PNVC-Al₂O₃), PNVC-(PPY-Al₂O₃), PNVC-

TABLE II
FTIR Absorption Characteristics

Composite	Observed peaks (cm ⁻¹)	Assignment of peaks
PPY-Al ₂ O ₃	3309	H-bonded N-H stretching
	2316	Aromatic ring vibration of pyrrole
	1530	2,5-substituted pyrrole
	1047	C-H vibration of 2,5-disubstituted pyrrole
	787–920	C-H deformation of 2,5-substituted pyrrole
	PPY-(PNVC-Al ₂ O ₃) (after repeated reflux with benzene)	3280
2925		Aromatic C-H stretching vibration
2350		Aromatic ring vibration of pyrrole
1625		C=C stretching vibration of vinylidene gr
1555		2,5-substituted pyrrole
1449–1482		ring vibration of NVC moiety
1402		>CH ₂ deformation of vinylidene gr
1145–1203		C-H in plane deformation of vinylidene gr
1059		C-H vibration of 2,5-disubstituted pyrrole
791–928		C-H deformation of 2,5-substituted pyrrole
746		>CH ₂ rocking vibration
PNVC-Al ₂ O ₃	722	ring deformation of substituted aromatic structure
	724	ring deformation of substituted aromatic structure
	746	>CH ₂ rocking vibration
	1150–1232	C-H in plane deformation of vinylidene gr
	1406	>CH ₂ deformation of vinylidene gr
	1449–1481	ring vibration of NVC moiety
	1627	C=C stretching vibration of vinylidene gr
2930	aromatic C-H stretching vibration	

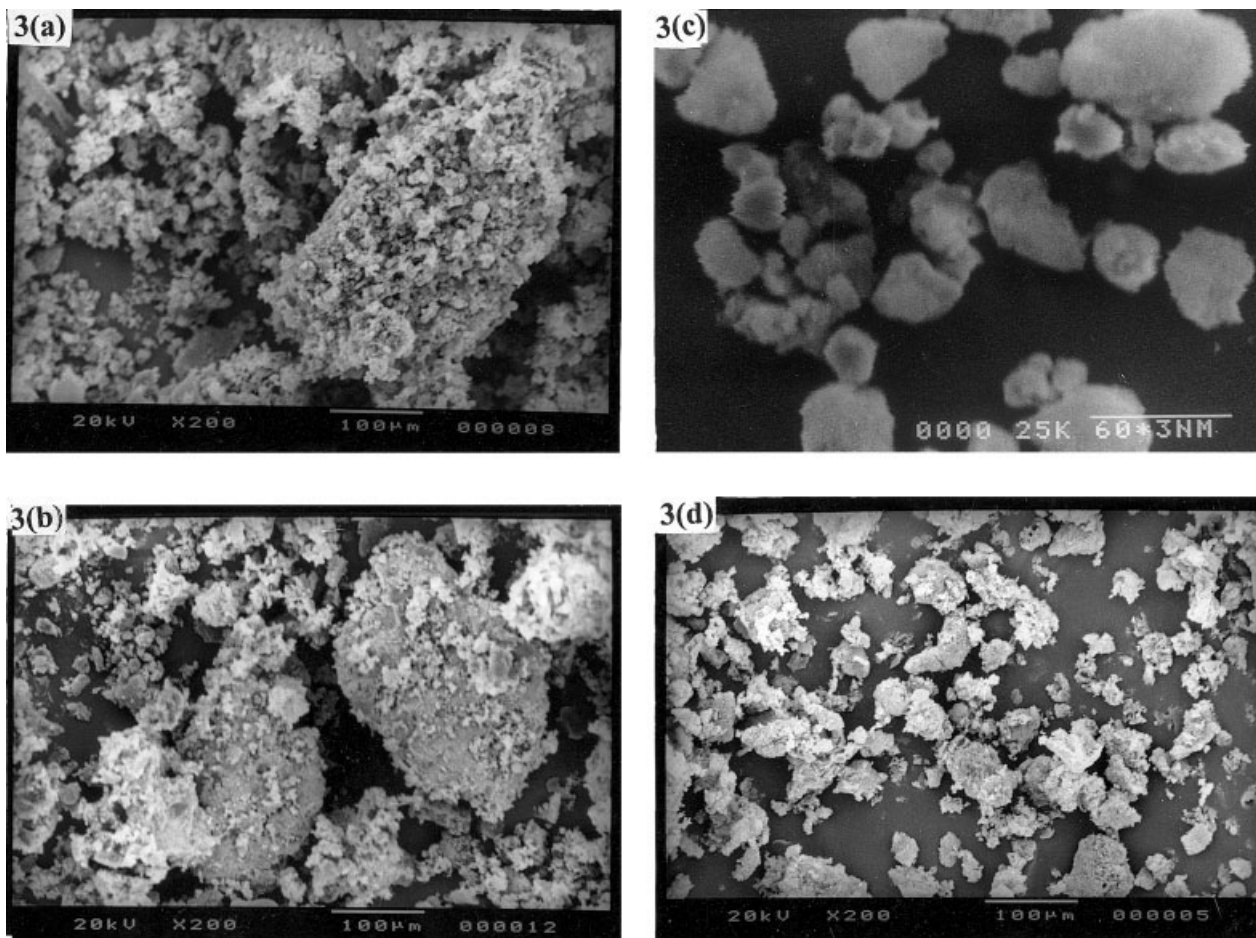


Figure 3 Scanning electron micrographs of: (a) PPY-(PNVC- Al_2O_3) nanocomposite, (b) PNVC-(PPY- Al_2O_3) nanocomposite, (c) PNVC- Al_2O_3 nanocomposite, and (d) PPY- Al_2O_3 nanocomposite.

Al_2O_3 , and PPY- Al_2O_3 composites, respectively. These micrographs were taken with the powdered composite particles without any dilution. In essence, the micrographs in Figure 3(a,b) show the presence of densely compacted aggregates of particles with the tendency to form large lumps comprising fine aggregates of particles. The largest lump in either micrograph corresponded to the sizes of 338 [Fig. 3(a)] and 265 μm [Fig. 3(b)]. This morphological pattern was reminiscent of the typical “raspberry” morphology noted by Armes et al.¹⁹ for the PPY- SiO_2 - and PANI- SiO_2 -based nanocomposites. The formation of such microaggregates through cementation of nanosized Al_2O_3 particles with the conducting polymers also would be significant for the development of conductivity in the nanocomposites.^{15,16} In contrast, scanning electron micrographs for PNVC- Al_2O_3 [Fig 3(c)] and PPY- Al_2O_3 [Fig 3(d)] revealed a preponderance of smaller-sized, less densely packed aggregates.

Transmission electron microscopic analysis

Transmission electron micrographs of PNVC- Al_2O_3 , PPY- Al_2O_3 , and PPY-(PNVC- Al_2O_3) composites are

shown in Figure 4(a-c), respectively. The appearance of dark globular particles corresponded to the formation of polymer-encapsulated Al_2O_3 suspensoids. The presence of lighter-shade particles in the background of the micrographs shown in Figure 4(a,b) resulted from uncoated Al_2O_3 suspensoids in the composite, implying that the polymer encapsulation was not uniform. The average particle sizes of these composites were in the nanometer range: 120–240 nm for PNVC- Al_2O_3 , 60–100 nm for PPY- Al_2O_3 . Transmission electron microscopy (TEM) analyses of the binary polymer composite PPY-(PNVC- Al_2O_3) showed lumpy aggregates after sonication for 1½ h, as was done in the previous cases. However, after continued sonication, a TEM micrograph was eventually obtained that showed the presence of somewhat smaller spherical particles, with sizes in the 20–40 nm range. Significantly, this micrograph [Fig. 4(c)] revealed the formation of dark globular particles with no perceptible lighter regions in the background, implying that the precipitating PPY moieties encapsulated not only the free Al_2O_3 sites but also the PNVC- Al_2O_3 sites in the composites and thereby leading to more efficient encapsulation. The micrograph of the nanodimensional Al_2O_3 suspension revealed the presence of stringy par-

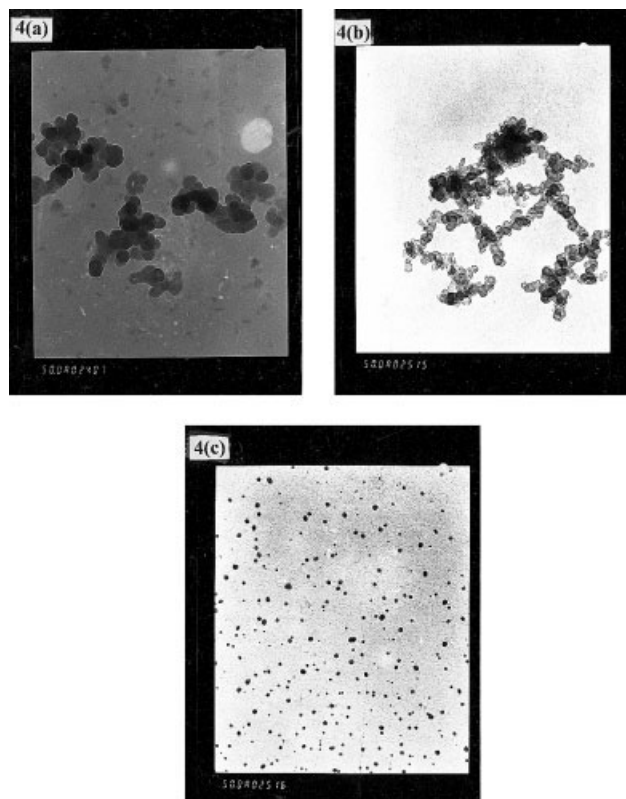


Figure 4 Transmission electron micrographs of: (a) PNVC- Al_2O_3 nanocomposite, (b) PPY- Al_2O_3 nanocomposite, and (c) PPY-(PNVC- Al_2O_3) nanocomposite.

ticles.^{15,16} The stringy morphology of the Al_2O_3 particles was thus modified to a spherical morphology on coating with PNVC [Fig. 4(a)], PPY [Fig. 4(b)], and PPY-PNVC polymer particles. A similar feature was also observed by Armes et al.¹⁷ for the PPY- SiO_2 nanocomposite system.

Thermal stability characteristics

Figure 5 shows the thermograms of the PNVC- Al_2O_3 , PNVC-(PPY- Al_2O_3), PPY-(PNVC- Al_2O_3), and PPY- Al_2O_3 composites. A comparison of the weight loss/temperature data for the various composites suggested the following trend in the overall thermogravimetric stability of the various composites: PNVC- Al_2O_3 > PNVC-(PPY- Al_2O_3) > PPY-(PNVC- Al_2O_3) > PPY- Al_2O_3 .

PNVC is well known⁸ for its remarkable thermal stability, which is further improved by composite formation with Al_2O_3 . Because PPY and PPY- Al_2O_3 were found to be less thermally stable than the PNVC-based systems under discussion, it was reasonable to expect that for the binary composites involving PPY and PNVC, the overall stability would be between PNVC and PPY, as is actually shown by the results. However, the high stability of PNVC-(PPY- Al_2O_3) relative to PPY-(PNVC- Al_2O_3) could be a result of greater individual polymer loading in the former composite (entries 8 and 9, Table I).

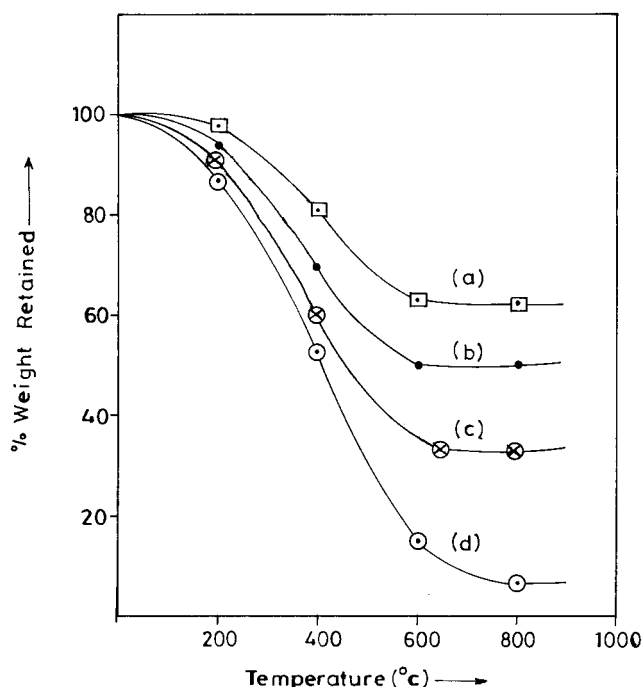


Figure 5 TGA scan of (a) PNVC- Al_2O_3 composite, (b) PNVC-(PPY- Al_2O_3) composite, (c) PPY-(PNVC- Al_2O_3) composite, and (d) (PPY- Al_2O_3) composite.

DTA scans for the various composites showed broad exothermic peaks at comparable temperatures: PNVC- Al_2O_3 , 430°C; PPY- Al_2O_3 , 440°C; PNVC-(PPY- Al_2O_3), 400°C; and PPY-(PNVC- Al_2O_3), 420°C. This trend implied that all these peaks, corresponded to the region of maximum weight loss in these composites, resulting from a common oxidative degradation process in the polymers in the composites.

Conductivity characteristics

Table III summarizes the conductivity data of the prepared composites along with some literature data on conductivity of several related composite systems.

TABLE III
Conductivity Data of Various Inorganic Oxide-Based Nanocomposites of PPY and PNVC

Composites	Conductivity (S/cm)	Reference
1. PPY- Al_2O_3 ^a	2.8×10^{-4}	This study
2. PNVC-(PPY- Al_2O_3) ^a	1.7×10^{-5}	This study
3. PPY-(PNVC- Al_2O_3) ^a	4.48×10^{-6}	This study
4. PNVC- Al_2O_3	0.14×10^{-6}	15
5. PPY- MnO_2	0.92×10^{-2}	13
6. PPY- SiO_2	2×10^{-5}	19
7. PPY-MMT	8.3×10^{-5}	11
8. PPY- SnO_2	2-0.6	20
9. PPY- ZrO_2	1-15	21

^a Samples were doped with anhydrous FeCl_3 for 9 days.

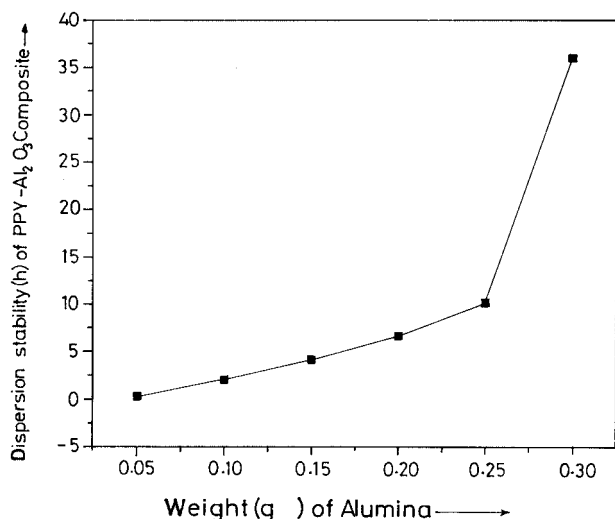


Figure 6 Variation of dispersion stability (h) of PPY-Al₂O₃ composite with weight (g) of Al₂O₃.

Entries 1 and 2 indicate that the conductivity of the PNVC-(PPY-Al₂O₃) composite was lower than that of the PPY-Al₂O₃ base polymer. Evidently, this was because of the coating of the PPY-Al₂O₃ composite particles by less conductive PNVC moieties. It is of interest that the PNVC-Al₂O₃ composite's conductivity was significantly higher than was the same for PNVC (10^{-10} - 10^{-12} S/cm).¹³

A comparison of entries 2 and 3 indicates that the conductivity of the PNVC-coated PPY-Al₂O₃ composite was fourfold higher than that of the PPY-coated PNVC-Al₂O₃ composite. Finally, entries 3 and 4 indicate that the PPY-coated PNVC-Al₂O₃ had a dc conductivity value 32-fold higher than that of the PNVC-Al₂O₃ composite.

In general, Al₂O₃-based composites had lower conductivity values than the MnO₂, SnO₂, and ZrO₂ composites. Accordingly, binary composites based on ZrO₂ perhaps should be more promising.

Water dispersibility of Al₂O₃-based nanocomposites

The stability of the PPY-Al₂O₃ composite in a water medium was found to increase with an increasing weight of Al₂O₃ in the initial feed, as shown in Figure 6. This trend was consistent with the stabilizing action of nanosized Al₂O₃ particles on the precipitating PPY moieties in the aqueous medium. It is reasonable to expect that the larger the concentration of Al₂O₃ particles in the medium, the higher would be the stability of the polymer-Al₂O₃ composites.

The results summarized in Table IV lead to the following conclusions:

1. In the presence of PNVC, the dispersion stability of the PPY-Al₂O₃ composites decreased (compare entries 1 and 2).

2. In the presence of PPY, the dispersion stability of the PNVC-Al₂O₃ composite increased significantly (compare entries 3 and 4).
3. In the presence of polyvinylpyrrolidone (PVP), an externally added polymeric stabilizer, the PPY-Al₂O₃ (entry 5), PNVC-(PPY-Al₂O₃) (entry 6), and PPY-(PNVC-Al₂O₃) (entry 7) composites produced permanently stable dispersions in an aqueous medium.

A general comparison of the dispersion stability characteristics already reported for some PNVC-based composites with SiO₂,¹² MnO₂,¹³ and ZrO₂,¹⁴ and with an Al₂O₃¹⁵-based system leads to no simple generalization except that in the presence of PVP—an externally added polymeric stabilizer—the PNVC-based suspensions exhibited almost permanent dispersion stability.

Biswas and SinhaRay observed¹³ that nanodimensional MnO₂ produced the most stable PNVC suspension in water compared to ZrO₂,¹⁴ SiO₂,¹² and MMT⁷-based composites of PNVC. The last two oxide-based systems required PVP to obtain a stable disper-

TABLE IV
Dispersion Stability of Various Al₂O₃-Based Composites in Aqueous/Methanol Medium

Conditions applied for obtaining aqueous dispersion	Observation
1) Al ₂ O ₃ was added to water and stirred for 2 h; PY and FeCl ₃ were added serially and stirred magnetically for 3 h.	Dispersion stable up to 36 h and redispersible
2) THF solution (2 mL) of preformed PNVC was added to PPY-Al ₂ O ₃ aqueous suspension and then stirred magnetically for 3 h.	Dispersion stable up to 29 h
3) Al ₂ O ₃ was added to water and stirred for 2 h; then THF solution of preformed PNVC was added dropwise and stirred magnetically for 3 h.	Dispersion stable up to 30 min
4) PY monomer was injected to PNVC-Al ₂ O ₃ -FeCl ₃ aqueous suspension and then stirred magnetically for 3 h.	Dispersion stable up to 20 h
5) Al ₂ O ₃ was added to an aqueous solution of PVP and stirred for 2 h; PY and FeCl ₃ were added serially and stirred magnetically for 3 h.	Permanently stable dispersion that was redispersible
6) THF solution (2 mL) of preformed PNVC was added to PPY-Al ₂ O ₃ aqueous suspension in the presence of PVP and then stirred magnetically for 3 h.	Permanently stable dispersion and redispersible
7) PY monomer was injected into PNVC-Al ₂ O ₃ -FeCl ₃ aqueous suspension in the presence of PVP and then stirred magnetically for 3 h.	Permanently stable dispersion and redispersible

sion. It is significant that nanodimensional Al_2O_3 produced a PNVC composite that retained its stability for almost 40 h (Fig. 6).

Unfortunately, these data fail to suggest any definite trend for the role of oxides in conferring stability on a PNVC suspension in water. In fact, as pointed out by Armes et al.,¹ several factors, including preadsorption characteristics of the reacting species on the oxide surface, high surface area, and surface charge on the oxide surface, might be relevant factors controlling the overall stability of the polymer-metal oxide suspensions. However, no definite conclusion on the polymer suspension stability vis-à-vis the nature of the metal oxide dispersant can be drawn from the information available now.

CONCLUSIONS

This article has presented a simple method for preparing water-dispersible nanocomposites of mixed specialty polymers based on PNVC and PPY by depositing PNVC on a PPY- Al_2O_3 dispersion and PPY on a PNVC- Al_2O_3 dispersion in water. These materials possess high thermal stability and exhibit conductivity characteristics somewhat different from the individual polymers involved in the composite formation.

We are grateful to the head of the Department of Chemistry and to the principal, Presidency College, Calcutta, India, for

facilities; to Dr. H. S. Maiti, Central Glass and Ceramic Research Institute (CG&CRI), Calcutta, India, for useful discussions and help with the conductivity measurements; and to Mr. P. Ray, Saha Institute of Nuclear Physics (SINP), Calcutta, India, for TEM analyses.

References

1. Stejskal, J.; Kratochvil, P.; Armes, S. P.; Lascelles, S.F.; Riede, A.; Helmstedt, M.; Frokes, J.; Krivka, I. *Macromolecules* 1996, 29, 6814.
2. Armes, S. P.; Gottesfeld, S.; Berry, J. G.; Garzon, F.; Agnew, S. F. *Polymer* 1992, 32, 2325.
3. Maeda, S.; Armes, S. P. *Synth Met* 1995, 73, 155.
4. Maeda, S.; Gill, M.; Armes, S. P. *Chem Mater* 1995, 11, 1959.
5. Tadros, P.; Armes, S. P.; Luk, S. K. *J Mater Chem* 1992, 2, 125.
6. Maeda, S.; Armes, S. P. *J Mater Chem* 1994, 4, 935.
7. Biswas, M.; SinhaRay, S. *Polymer* 1998, 39, 6423.
8. Biswas, M.; SinhaRay, S. *Adv Polmer Sci* 2001, 155, 167.
9. SinhaRay, S.; Biswas, M. *J Appl Polym Sci* 1999, 73, 2971.
10. SinhaRay, S.; Biswas, M. *J Appl Polym Sci* 2000, 77, 2948.
11. SinhaRay, S.; Biswas, M. *Met Res Bull* 1999, 34, 1187.
12. SinhaRay, S.; Biswas, M. *Met Res Bull* 1998, 33, 533.
13. Biswas, M.; SinhaRay, S.; Liu, Y. *Synth Met* 1999, 105, 99.
14. SinhaRay, S.; Biswas, M. *Synth Met* 2000, 108, 231.
15. Maity, A.; Biswas, M. *J Appl Polym Sci* 2002, 88, 2233.
16. Ballav, N.; Biswas, M. *Polym Int* 2003, 52, 179.
17. Rebecca, F.; Jagdeep, J.; Shuichi, M.; Armes, S. P. *J Colloid Interface Sci* 1995, 173, 135.
18. Maeda, S.; Armes, S. P. *Chem Met* 1995, 7, 171.
19. Maeda, S.; Gill, M.; Armes, S. P. *Langmuir* 1995, 11, 1899.
20. Bhattacharyya, A.; Ganguly, K. M.; De, A.; Sakar, S. *Mat Res Bull* 1996, 31, 527.