

Water-Dispersible Conducting Nanocomposites of Binary Polymer Systems. I. Poly(*N*-vinylcarbazole)–Polyaniline–Al₂O₃ Nanocomposite System

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ABSTRACT: The chemical oxidative polymerization of a mixture of *N*-vinylcarbazole (NVC) and aniline (ANI), by FeCl₃ in aqueous medium, produced an insoluble polymer that contained polyaniline (PANI), along with some residual poly-*N*-vinylcarbazole (PNVC) not extractable with benzene. This insoluble PNVC–PANI composite could be obtained as a stable suspension in water when the above polymerization was conducted in the presence of nanodimensional Al₂O₃. Alternatively, PNVC–(PANI–Al₂O₃) composite could also be produced by precipitating a THF solution of preformed PNVC onto a PANI–Al₂O₃ suspension. Likewise PANI–(PNVC–Al₂O₃) could be obtained by polymerizing ANI onto an aqueous suspension of PNVC–Al₂O₃. The inclusion of either of these monomer units in the result-

ant polymer was confirmed by FTIR analysis. SEM analyses revealed formation of a lumpy aggregate, and TEM analyses confirmed particle sizes of the PNVC–PANI–Al₂O₃ composite to be in the 52–200 nm range. Thermogravimetric stability was in the order: PANI–Al₂O₃ < PNVC–PANI–Al₂O₃ < PNVC–Al₂O₃. The dc conductivity values (S/cm) followed the trend: PNVC–Al₂O₃ (10⁻⁷) < PNVC–PANI–Al₂O₃ (1.5 × 10⁻⁴) ≈ PANI–Al₂O₃ (1.1 × 10⁻⁴) < PNVC–PANI (1 × 10⁻³) at ambient temperature. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 803–811, 2004

Key words: poly(*N*-vinylcarbazole); polyaniline; nanocomposites; dispersions; conducting polymers

INTRODUCTION

Specialty polymers, such as polyaniline (PANI), polypyrrole (PPY), polythiophene (PTP), and polyfuran (PF) derived from chemical oxidative polymerization^{1–4} of the corresponding monomers, are usually intractable and suffer from processability limitations. Numerous attempts have been made to obtain processable dispersions of these specialty polymers in aqueous medium. By polymerizing water-soluble monomers, such as aniline (ANI) or pyrrole (PY), on nanosized SiO₂, SnO₂, MnO₂, and ZrO₂^{5–16} particulate, dispersions in aqueous medium in the presence of an oxidant (FeCl₃ and NH₄S₂O₈) were prepared. However, these procedures would not be applicable for water-insoluble monomer systems such as *N*-vinylcarbazole (NVC), thiophene (TP), and furan (F). In this context, preparation and characterization of nanocomposites of PNVC with SiO₂,¹⁷ Al₂O₃,¹⁸ MnO₂,¹⁴ ZrO₂,¹⁵ and of PTP with Al₂O₃¹⁹ were achieved in our laboratory.

During the course of these studies, the idea occurred to us that water-dispersible composites, constituting selective combinations of specialty polymers, might have wider scope and usefulness as processable materials with bulk property characteristics distinctive of both polymer components.

Literature on the preparation of water dispersible nanocomposites, involving binary polymer systems with nanodimensional metal oxides as particulate dispersants, appeared scanty. In recent publications, we described the preparation and evaluation of stable suspensions consisting of binary polymer systems such as PNVC–PPY and PNVC–PTP on nanosized Al₂O₃.^{20–22}

In this article we describe the preparation and some bulk properties of PNVC–PANI–Al₂O₃, PNVC–(PANI–Al₂O₃), and PANI–(PNVC–Al₂O₃) nanocomposites by (1) oxidative polymerization of a mixture of NVC and ANI in aqueous suspension in the presence of nanosized Al₂O₃ as particulate dispersants and (2) precipitation of preformed PNVC onto PANI–Al₂O₃ suspension and vice versa. The function of nanosized Al₂O₃ particles, used in this and other recently studied systems,^{18,19,20–22} was to serve as a particulate colloidal dispersant in the aqueous medium on which the polymeric moieties would be precipitated, thereby forming stable polymer–Al₂O₃ nanoparticle suspensions.

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TABLE I
Data on Polymerization and Composite Formation^a

Entry no.	Weight (g) of				Weight (g) of polymer/composite after refluxing with benzene	% of Polymer/composite formed ^b with respect to ANI
	ANI	NVC	Al ₂ O ₃	FeCl ₃		
1	0.2	—	—	1.5	0.13	65
2	0.2	—	—	3	0.17	85
3	0.2	0.5	—	1.5	0.18	90
4	0.2	0.5	—	3	0.22	110
5	0.4	0.5	—	3	0.39	97
6	0.2	0.7	—	3	0.24	120
7	0.2	—	0.3	3	0.41	55
8	0.2	—	0.5	3	0.60	50
9	0.2	0.5	0.3	3	0.56	130
10	0.2	0.5	0.5	3	0.66	110

^a Time of polymerization = 6 h; total volume of reaction mixture = 25 mL; temperature = 25°C.

^b Computed from the data of columns 2 and 6.

EXPERIMENTAL

Materials

Aniline (Aldrich, Milwaukee, WI) was purified by vacuum distillation and was stored in a dark cool place before use. *N*-Vinylcarbazole (BASF AG, Ludwigshafen, Germany) was recrystallized from *n*-hexane and stored in the dark before use. Anhydrous FeCl₃ (Merck, Darmstadt, Germany) was used as an oxidant. Nanodimensional Al₂O₃ powder was prepared and kindly donated to us by the National Metallurgical Laboratory, Jamshedpur, India. All other solvents were of analytical grade and were freshly distilled before use.

Preparation of poly(*N*-vinylcarbazole)

PNVC was prepared by our previously described procedure.^{18,20–22}

Homopolymerization of ANI by FeCl₃ in aqueous medium

A known volume (Table I) of ANI monomer was syringed into 25 mL water in a conical flask to which a known quantity (Table I) of FeCl₃ was added. Almost instantaneously, the solution turned green. The system was kept at room temperature under stirring for 6 h. The mass was filtered and washed abundantly, with 2N HCl, water, and methanol in turn until the washings were free of monomer and of any FeCl₃ solution color, followed by acetone to remove any oligomers of aniline.²³ The separated mass was dried at 70°C under vacuum.

Preparation of PANI–Al₂O₃ nanocomposite

A known weight (Table I) of Al₂O₃ powder was slowly stirred in 25 mL of 2M aqueous solution of HCl

to produce a stable dispersion. A known volume (Table I) of ANI was injected and, thereafter, a known quantity (Table I) of FeCl₃ was added. The gradual color of the reaction mixture changed from light blue to deep blue, green, and finally to deep green. The reaction mixture was continuously stirred at room temperature for 6 h. The total content of the flask was centrifuged and the separated green mass was again dispersed in distilled water by sonication and centrifuged. This process was repeated four times to completely remove all adhering substances. Finally, the green mass was washed with methanol, followed by acetone to remove any oligomers²³ of aniline, and dried at 70°C for 9h under vacuum. Notably, this composite powder could be redispersed in aqueous medium as well as in alcohol under sonication.

Preparation of binary polymer nanocomposites

Two procedures were adopted:

1. By aqueous suspension polymerization of a mixture of NVC and ANI monomers.

Preparation of PNVC–PANI composite by simultaneous polymerization

To an aqueous suspension of NVC in THF (Table I), a definite volume (Table I) of ANI was injected followed by the addition of anhydrous FeCl₃ (Table I). The mixture was continuously stirred for 6 h at ambient temperature and then the separated mass was poured into an excess of methanol and centrifuged. The centrifugate was repeatedly washed with 2N HCl and then with boiling methanol,²⁴ to remove any unreacted monomer and FeCl₃ color, followed by acetone to remove oligomers²³ of aniline. The separated mass was dried at 70°C under vacuum. The polymers thus separated were refluxed with benzene until the ben-

TABLE II
Data on Composite Formation Between PANI, PNVC, and Al₂O₃ by Precipitation Method

Composite	Weight (g) of			Percentage (%) of		
	PNVC	ANI	Al ₂ O ₃	Composite formed	PANI ^a loading/g of composite	PNVC ^a loading/g of composite
PNVC-(PANI-Al ₂ O ₃) ^b	0.1	0.2	0.3	88	28	16
	0.2	0.2	0.3	87	24	28
	0.3	0.2	0.3	83	22	33
	0.2	0.2	0.5	92	18	22
PANI-(PNVC-Al ₂ O ₃) ^c	0.1	0.2	0.3	85	23	18
	0.2	0.2	0.3	84	20	29
	0.3	0.2	0.3	87	17	39
	0.2	0.2	0.5	89	15	23

^a In composites after benzene extraction for 6 h.

^b See procedure 2(a) experimental section.

^c See procedure 2(b) experimental section.

zene solution yielded no precipitate in methanol resulting from PNVC homopolymer.

Preparation of PNVC-PANI-Al₂O₃ composite

The procedure described in (1) was repeated in the presence of Al₂O₃ suspension (Table I).

- By precipitation of preformed polymer, on a suspension of the other polymer in aqueous systems, two types of such composites were prepared: (a) PNVC-(PANI-Al₂O₃), in which preformed PNVC was precipitated onto an aqueous suspension of PANI-Al₂O₃ composite, and (b) PANI-(PNVC-Al₂O₃), in which ANI was polymerized in an aqueous medium containing PNVC-Al₂O₃ suspension.

(a) *PNVC-(PANI-Al₂O₃) composite.* Nanodimensional Al₂O₃ (0.3–0.5 g) was added with stirring to 30 mL of water in a stoppered conical flask to produce a stable aqueous dispersion of Al₂O₃. To this, 0.2 mL of ANI and 1.5 g of FeCl₃ were added in succession. After 3 h, 2 mL of THF solution of 0.1–0.3 g (Table II) of preformed PNVC was added dropwise to the reaction mixture. The reaction mixture was stirred continuously for 3 h at ambient temperature. The resulting light green mass 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 to remove completely all adhering substances. Finally, the separated mass was washed with acetone and boiling MeOH²⁰ and finally dried at 70°C for 10 h under vacuum.

(b) *PANI-(PNVC-Al₂O₃) composite.* Nanosized Al₂O₃ (0.3–0.5 g) was slowly stirred in 30 mL of water in a stoppered conical flask to produce an aqueous dispersion of Al₂O₃ to which 2 mL THF solution of 0.1–0.3 g (Table II) of preformed PNVC was added dropwise.

The reaction mixture was stirred continuously for 3 h at ambient temperature. Aniline (0.2 mL) was injected into the mixture and, thereafter, 1.5 g of FeCl₃ was added. The reaction mixture was continuously stirred for 3 h at room temperature. The total light green mass 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 to remove all adhering substances. Finally, the separated mass was washed with acetone and then with boiling methanol and dried at 70°C for 10 h.

Characterization and property evaluation

FTIR spectra of the polymers were taken on a Jasco-410 instrument (Essex, UK) in pressed KBr pellets. Scanning electron micrographic analyses were made on a Hitachi S415A (Tokyo, Japan) using dispersions of nanocomposites in isopropanol on a mica substrate. The particle sizes of composites were measured by a transmission electron microscope (Hitachi H 600), with diluted suspensions (1000 ppm) in isopropanol on a copper grid. Thermogravimetric analyses were performed on a Shimadzu DT-40 (Tokyo, Japan) instrument. The 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

Table I presents some polymerization data for ANI-FeCl₃, ANI-Al₂O₃-FeCl₃, ANI-NVC(THF)-FeCl₃, and ANI-NVC(THF)-Al₂O₃-FeCl₃ polymerization systems in aqueous medium. Entries 1 and 2 indicate that %PANI homopolymer formed varied from 65 to 90, depending on oxidant amount, as expected. Interestingly, entries 3–6 indicate that, in the presence of NVC

TABLE III
Observed FTIR Characteristic Bands (cm^{-1}) for PANI- Al_2O_3 , PNVC-PANI, PANI-(PNVC- Al_2O_3),
and PNVC- Al_2O_3 Along with Their Probable Assignments

Observed peaks (cm^{-1}) of				Assignment of peaks
PANI- Al_2O_3^a	PNVC-PANI	PANI-(PNVC- Al_2O_3)	PNVC- Al_2O_3^b	
	722	715	721	Ring deformation of substituted aromatic structure
	748	745	742	>CH_2 rocking vibration attributed to tail to tail addition
1243-1318	1149	1151-1240	1150-1232	C-H in plane deformation of aromatic ring
	1240	1329		$\text{C}\equiv\text{N}$ stretching vibration
	1317	1329	1329	C-H in plane deformation of vinylidene gr.
	1451	1451	1450	Ring deformation of NVC moiety
1484-1635	1487-1589	1484-1589		N-H bending vibration
	1625	1635	1627	$\text{C}=\text{C}$ stretching vibration of vinylidene gr.
	2926	2930	3060	Aromatic C-H asymmetric, stretching vibration
3425	3378	3369		>NH stretching vibration

^a From Socrates.³⁸

^b From Tetsuyoshi et al.³⁹

in the initial feed, the % polymer formed in the system was appreciably increased over the same realized in entries 1 and 2 under identical conditions. This trend could imply additional polymer loading in the former system through incorporation of some PNVC in the PANI-chain, which could not be removed by repeated benzene extraction, as stated earlier. A possible explanation of this feature will be presented in the mechanism section.

Entries 7-10 show data on PNVC-PANI composite formation in the presence of nanodisperse Al_2O_3 . These results also confirmed the characteristic increase in polymer loading relative to that observed in PANI homopolymer loading in the composite.

Table II presents some quantitative data on the formation of the composites of PANI with PNVC and nanodimensional Al_2O_3 by the precipitation method. Data presented in the last two columns of Table II indicate that a residual amount of PNVC was always associated with the binary composites, which could not be removed after repeated reflux in benzene. Such stabilization of PNVC could be attributed to an acid-base interaction between the basic PNVC and the amphoteric Al_2O_3 particles. We reported a similar feature in the cases of PNVC- Al_2O_3 ,¹⁸ PPY-(PNVC- Al_2O_3), and PNVC-(PPY- Al_2O_3) composite systems.²⁰ In support of this contention the PNVC-(PANI- Al_2O_3) nanocomposite prepared above was leached with concentrated HCl and, thereafter, the polymer was washed with water and subsequently dried. Upon refluxing with benzene this polymer showed no trace of any residual PNVC.

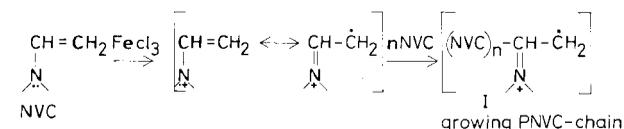
FTIR absorption characteristics

The manifestation of peaks (Table III) characteristic of PNVC and of PANI in the PNVC-PANI and PANI-(PNVC- Al_2O_3) spectra confirmed the incorporation of either of these polymer moieties in composites. However, unlike PNVC homopolymer, any PANI homopolymer likely to be formed in the system would also coexist with the PNVC-PANI composite.

Mechanism of homopolymerization of NVC and ANI and of PNVC-PANI composite formation

The polymerization of NVC by FeCl_3 has been the subject of much controversy²⁵ and discussed by several workers including Wang,^{26,27} Bawn et al.,²⁸ and Gaylord.²⁹ In light of this information, the possible

Scheme - a:



Scheme - b:

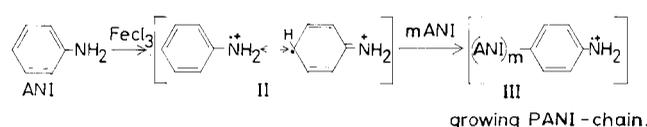


Figure 1 Polymerization pathway for NVC- FeCl_3 system [Scheme (a)] and ANI- FeCl_3 system [Scheme (b)].

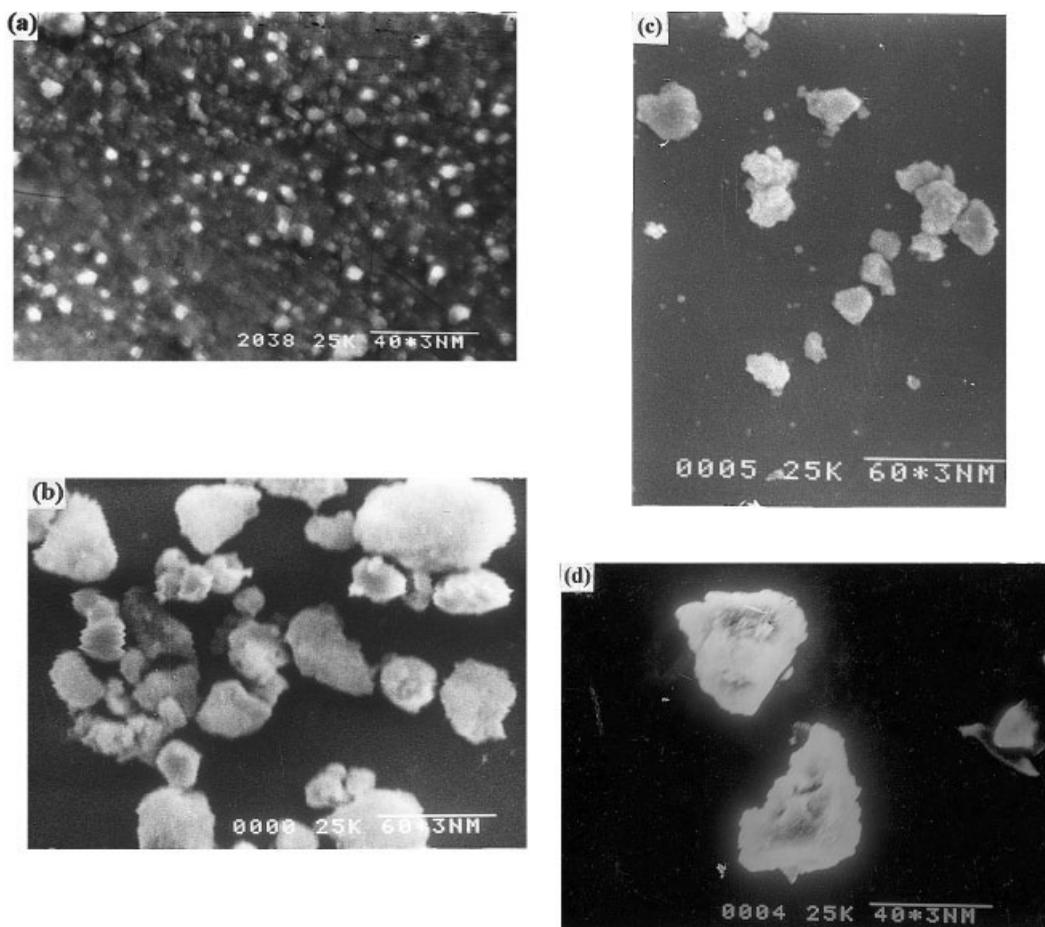


Figure 2 Scanning electron micrographs of (a) PANI- Al_2O_3 composite, (b) PNVC- Al_2O_3 composite, (c) PNVC-PANI- Al_2O_3 composite, (d) PNVC-(PANI- Al_2O_3) composite.

pathway for NVC homopolymerization by FeCl_3 is shown in Scheme (a) (Fig. 1).

Scheme (b) (Fig. 1) shows the conventional pathway for ANI homopolymerization by oxidants [FeCl_3 , CuCl_2 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$], as suggested by Toshima and Hara.³⁰ The formation of the radical cation (II) is essential for subsequent propagation (III).

When a mixture of NVC and ANI was interacted with FeCl_3 , as in the present case, the polymerization would be expected to yield a mixture of PNVC and PANI, the former being completely extractable with benzene. Contrary to this expectation, our system produced PANI with some residual PNVC, which could not be removed even after prolonged extraction (1 week) with benzene.

In a separate experiment, preformed PNVC dissolved in THF was added slowly to a solution of ANI in water in the presence of FeCl_3 . A green mass, attributed to PANI homopolymer formation, was recovered that was filtered and repeatedly washed with THF to remove any PNVC. The FTIR scan for this mass did not reveal any characteristic peaks of PNVC.

In another set of experiments, a mixture of NVC and ANI in CHCl_3 was treated with a catalytic amount of *o*-chloranil (*o*-CA) (well-known charge transfer initiator for NVC). A slightly colored polymer was obtained after 3 h, which was completely extractable in benzene and confirmed to be PNVC by FTIR analyses. This result confirmed that *o*-CA polymerized NVC selectively but not ANI.

The foregoing observations indicate that the formation of PNVC-PANI composite associated with nonextractable PNVC was possible only when both of the monomers were polymerized simultaneously in the presence of FeCl_3 . The observed insolubility of PNVC in the PNVC-PANI- Al_2O_3 composite could result if it could somehow become attached to the insoluble PANI moiety simultaneously formed during the reaction. In light of the well-established²⁵⁻³⁰ oxidative polymerization mechanism for NVC and ANI polymer [Schemes (a) and (b), respectively, in Fig. 1] one possible pathway in the present polymerization could involve interaction of propagating PNVC^{•+} cation radicals(I) with PANI^{•+} cation radicals(III) by free-radical coupling.

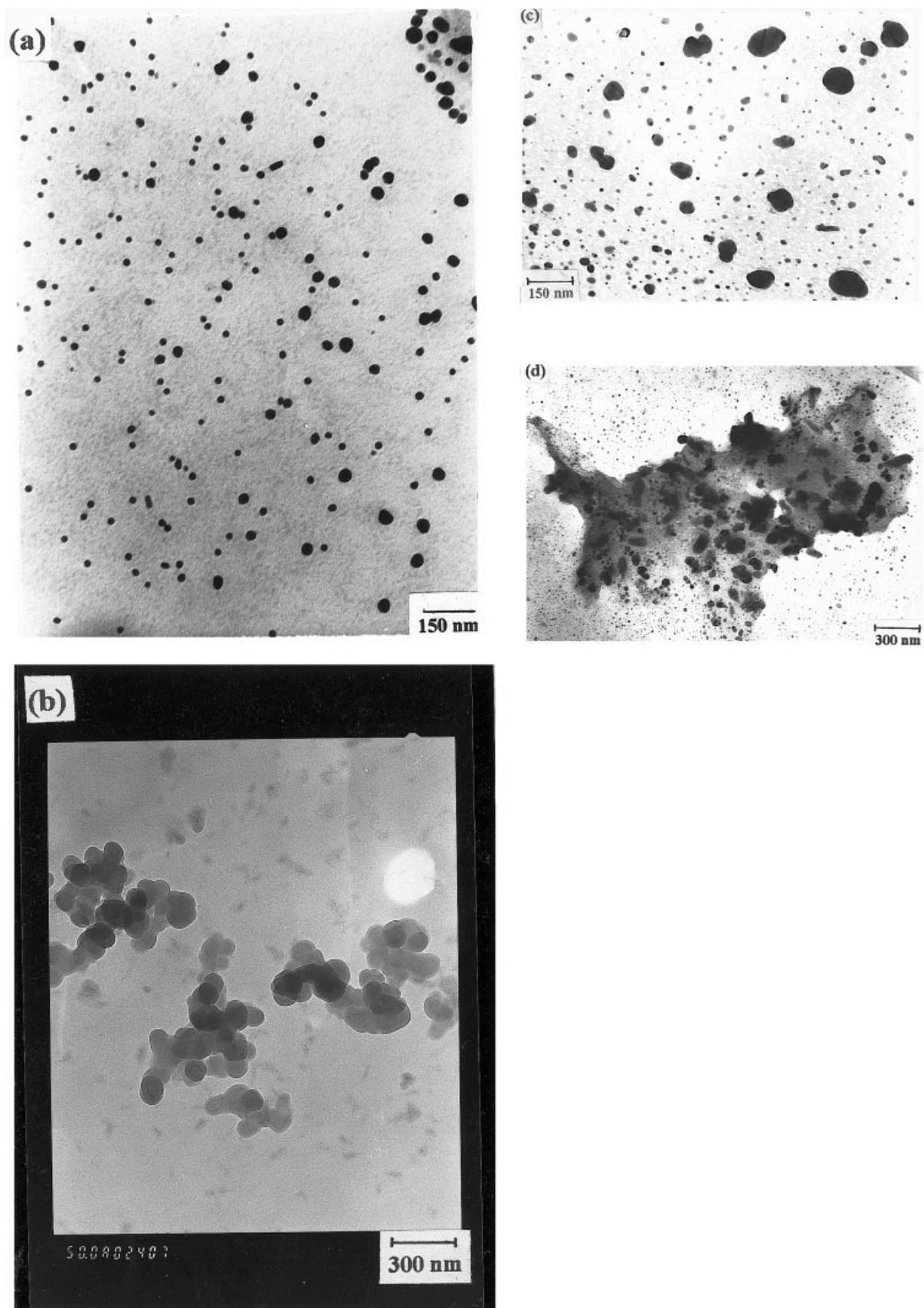


Figure 3 Transmission electron micrographs of (a) PANI-Al₂O₃ composite, (b) PNVC-Al₂O₃ composite, (c) PNVC-PANI-Al₂O₃ composite, (d) PNVC-(PANI-Al₂O₃) composite.

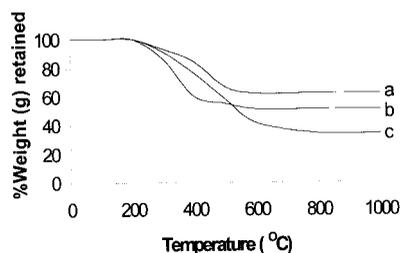


Figure 4 TGA thermograms of (a) PNVC–Al₂O₃ composite, (b) PNVC–PANI–Al₂O₃ composite, (c) PANI–Al₂O₃ composite.

Scanning electron micrographic characterization

In the present systems, the formation of polymer-based nanocomposite particles originated from the encapsulation of the nanodimensional Al₂O₃ particle suspensoids in the aqueous medium by the precipitating polymeric moieties. The morphology pattern of such polymer-laden suspensoids can be examined by SEM analysis as used by other workers in the field.^{11,14,15,18–21} The scanning electron micrograph for the PANI–Al₂O₃ composite [Fig. 2(a)] revealed formation of spherical particles (16–30 nm). In contrast, PNVC–Al₂O₃ composite [Fig. 2(b)] showed formation of a lumpy aggregate with irregular size (41–260 nm) and shape distribution. The average sizes of the lumps were larger than those in the PANI–Al₂O₃ system. The morphological patterns exhibited by the binary composites were different from those shown by the corresponding homopolymer composites. In general, the aggregate sizes of the PNVC–PANI–Al₂O₃ composite [Fig. 2(c)] (20–120 nm), prepared by simultaneous polymerization, were smaller than those of the respective composites [Fig. 2(d)] (71–162 nm) obtained by the alternative (precipitation) method.

Transmission electron micrographic analyses

TEM analysis of the Al₂O₃ powder dispersion revealed the presence of stringy particles.¹⁹ In contrast,

the TEM pattern of the PANI–Al₂O₃ composite [Fig. 3(a)] exhibited formation of globular particles (17–33 nm), whereas that of PNVC–Al₂O₃ composite [Fig. 3(b)] showed formation of spherical particles with average sizes in the 120–240 nm range. TEM patterns for PNVC–PANI–Al₂O₃ nanocomposite, obtained by the simultaneous polymerization technique [Fig. 3(c)], and by the precipitation technique [Fig. 3(d)] revealed some interesting differences. In the former system, a globular morphology with particles in the 52–200 nm range could be distinguished. In the latter system somewhat inhomogeneous encapsulation could be noticed with a tendency to form agglomerates of polymer particles varying in size distribution (70–260 nm). Notably, in Figure 3(c) the existence of much smaller particles in the 10–40 nm range could also be distinguished. Such a pattern was likely to arise from the coexistence of Al₂O₃ particles encapsulated by the PNVC–PANI composite and by PANI homopolymer, respectively.

Thermogravimetric stability characteristics

The overall thermal stability of PNVC–PANI–Al₂O₃, prepared by the simultaneous polymerization technique, was almost similar to that for PNVC–(PANI–Al₂O₃) and PANI–(PNVC–Al₂O₃) composites prepared by the precipitation process. Figure 4 shows that the overall thermogravimetric stability varied in the following order: PANI–Al₂O₃ < PNVC–PANI–Al₂O₃ < PNVC–Al₂O₃. The highest stability of the PNVC–Al₂O₃¹⁷ composite was consistent with the reported³¹ stability of PNVC homopolymer, which would be further enhanced after composite formation.^{13,14,16,17} Incorporation of the less-stable PANI moiety in the PNVC–PANI network would evidently cause a decrease in the stability of the PNVC–PANI–Al₂O₃ composite and thus the observed trend was reasonable.

The DTA of PANI showed³² one exothermic peak at 344°C and that of PNVC also exhibited³³ one sharp

TABLE IV
Conductivity Data of Various PANI-Based Composites

Entry no.	Materials	Conductivity (S/cm)	Reference
1	PANI–Al ₂ O ₃	1.1 × 10 ⁻⁴	This study
2 ^a	PNVC–PANI	1.0 × 10 ⁻³	This study
3 ^a	PNVC–PANI–Al ₂ O ₃ (simultaneous polymerization)	1.5 × 10 ⁻⁴	This study
4 ^a	PNVC–(PANI–Al ₂ O ₃) (precipitation method)	3.0 × 10 ⁻⁴	This study
5 ^a	PANI–(PNVC–Al ₂ O ₃) (precipitation method)	2.0 × 10 ⁻⁴	This study
6 ^a	PNVC–Al ₂ O ₃	1.0 × 10 ⁻⁷	18
7	PANI–SiO ₂	10 ⁻² –10 ⁻³	6
8	PANI–MMT	10 ⁻² –10 ⁻³	35
9	PANI–Fe ₃ O ₄	10 ⁻²	36
10	PANI–MnO ₂	10 ⁻²	14
11	PANI–ZrO ₂	10 ⁻²	15
12	PANI–V ₂ O ₅	10 ⁻¹	r37

^a Samples were doped with anhydrous FeCl₃ for 9 days.

TABLE V
Dispersion Stability of Al₂O₃-Based Composites in Aqueous Medium

Conditions applied for obtaining aqueous dispersion	Observations
PANI: PANI homopolymer was sonicated in water for 1 h.	Immediate precipitation of polymer occurred. No coloration of the supernatant solution was noted.
PANI-Al ₂ O ₃ : Al ₂ O ₃ was added to water and stirred for 1 h; ANI and FeCl ₃ were added serially and the system was stirred magnetically for 6 h.	A green colored permanently stable dispersion was formed that was redispersible in water (i.e., the dispersion could be dried and then the solid could be redispersed in water to produce a stable colloid).
PNVC-Al ₂ O ₃ : Al ₂ O ₃ was added to water and stirred for 1 h, after which THF solution of preformed PNVC was added dropwise and the system was stirred magnetically for 6 h.	The suspension of the PNVC-Al ₂ O ₃ was stable up to 30 min
PNVC-PANI-Al ₂ O ₃ : NVC was dissolved in minimum volume of THF, water, and then Al ₂ O ₃ was added. To this milky white suspension, ANI and thereafter FeCl ₃ were added and the system was stirred magnetically for 6 h.	Stable aqueous dispersion with the development of light green coloration was formed.
PANI-(PNVC-Al ₂ O ₃): ANI monomer was injected to PNVC-Al ₂ O ₃ -FeCl ₃ aqueous suspension, which was stirred magnetically for 6 h.	A permanently stable dispersion (light green) was formed that was redispersible
PNVC-(PANI-Al ₂ O ₃): THF solution of preformed PNVC was added to PANI-Al ₂ O ₃ aqueous suspension, which was stirred for 6 h.	A permanently stable dispersion (light green) was formed that was redispersible

exothermic peak at 500°C, attributed to oxidative degradation. The DTA of the PNVC-PANI-Al₂O₃ composite, however, revealed two exothermic peaks at 357 and 470°C (sharp). These features imply that both PANI and PNVC moieties were present in the PNVC-PANI-Al₂O₃ composite.

Conductivity characteristics

Entries 1–5 in Table IV show that the PNVC-PANI composite has reasonably high conductivity values (1×10^{-3} S/cm) despite the presence of the nonconducting PNVC moiety (10^{-12} – 10^{-16} S/cm).³⁴ Upon composite formation with Al₂O₃, by both processes, the conductivity showed a decrease by one order: a frequently observed trend²⁰ that might be attributable to incorporation of less conducting Al₂O₃ moieties in the composite. Consistently, PANI-Al₂O₃ showed lower conductivity than that of PANI.³⁰ In general, composites of PANI with several oxides (Table IV) reportedly exhibited conductivities in comparable ranges.^{35–37}

Dispersibility of composites in aqueous medium

Results of Table IV indicate that, without Al₂O₃ as the particulate dispersant, PANI could not produce a stable dispersion in water. PNVC homopolymer dispersion in water was also unstable even in the presence of Al₂O₃, as reported in our earlier studies.¹⁸ Significantly, the binary composites obtained by either method were observed to be stable without any extraneous polymeric stabilizer. Numerous literature re-

ports^{4–15} establish that PANI and PPY could be readily rendered dispersible in aqueous systems in the presence of nanodimensional oxide dispersants. By virtue of this property these polymers should be able to render other polymer components attached to them dispersible in aqueous medium. The method should be of wide scope because in principle a wide variety of the second polymeric components could be used.

CONCLUSIONS

Water-dispersible nanocomposites of poly-*N*-vinylcarbazole with polyaniline, with conductivities in the order of 10^{-4} S/cm, could be prepared by polymerizing a mixture of *N*-vinylcarbazole (in THF solution) and ANI in aqueous suspension in the presence of FeCl₃ and nanodimensional Al₂O₃, and also by precipitating a preformed polymer component onto an aqueous suspension of the other polymeric component and vice versa. This procedure could be extended to a variety of combinations of water-soluble and water-insoluble monomers through suspension polymerization using appropriate catalysts.

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