A Nanocomposite of Poly(*N*-vinylcarbazole) with Nanodimensional Alumina

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ABSTRACT: A nanocomposite of poly(*N*-vinylcarbazole) (PNVC) and Al_2O_3 was prepared by precipitation of a preformed PNVC in a tetrahydrofuran solution onto an aqueous suspension of nanodimensional Al_2O_3. Prolonged extraction of a PNVC–Al_2O_3 composite by benzene failed to extract the loaded PNVC from the Al_2O_3, as shown by Fourier transform infrared studies. Scanning electron microscopy analyses revealed distinct morphological features of the composite, and transmission electron microscopy analyses confirmed that the particle sizes were in the range of 120–240 nm. Thermogravimetric analyses demonstrated the enhanced stability of the nanocomposite relative to the base polymer. Direct current conductivity of the PNVC–Al_2O_3 composites was found to be about 0.14×10^{-6} S/cm.
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Key words: nanocomposite; Al_2O_3; poly(*N*-vinylcarbazole); transmission electron microscopy; conductivity; thermal stability

INTRODUCTION

Nanocomposites of polymers of water-soluble monomers such as pyrrole (PY) and aniline (ANI) with colloidal silica,[1] tin(IV) oxide,[2] montmorillonite clay (MMT),[3,4] MnO_2,[5] or ZrO_2[6,7] have been prepared by synthesizing the conducting polymers in an aqueous medium in the presence of the oxides as particulate dispersants with catalytic amounts of $FeCl_3$ or $(NH_4)_2S_2O_8$. Literature on the nanooxide-based composites of the polymers of water-insoluble monomers is rather scanty. Biswas and SinhaRay prepared composites of PNVC with nanosized MMT,[8,9] SiO_2,[10] MnO_2,[5] and ZrO_2[7] by polymerizing NVC monomer in the presence of MMT and the oxides with or without $FeCl_3$ and thereafter precipitating the polymer in alcohol.

In this article we will describe the preparation of a nanocomposite of poly(*N*-vinylcarbazole) (PNVC) with Al_2O_3 by a modified procedure in which a tetrahydrofuran (THF) solution of preformed PNVC was allowed to precipitate onto Al_2O_3 particles suspended in water. We also will compare some bulk properties of the PNVC–Al_2O_3 composite with those reported for SiO_2-,[10] MnO_2-,[5] and ZrO_2-based[7] composites of PNVC to identify the role, if any, of the metal ion component in the composite in enhancing the latter's properties. We believe this procedure will have a wide scope of applicability because any polymer soluble in a solvent, preferably nonaqueous, can be used for nanocomposite preparation with any water-dispersible metal oxide.

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EXPERIMENTAL

Materials

N-vinylcarbazole (BASF, Karlschue, Germany) was purified as has been described earlier.[5] Nanodimensional Al_2O_3 powder was prepared in the National Metallurgical Laboratory (Jamshedpur, India). All other chemicals and reagents were of AR grade and used after necessary purification by standard procedures.

Preparation of poly(*N*-vinylcarbazole)

A known weight of NVC monomer (2 g) was dissolved in a known volume of $CHCl_3$ to which a definite quantity of anhydrous $FeCl_3$ (3 g) was added. The system was kept under stirring at ambient temperature for 3 h, and then the solution was poured into an excess of methanol. The white PNVC thus obtained was fractionated several times in a benzene–methanol solvent system.

Preparation of PNVC–Al_2O_3 nanocomposite

A known weight of Al_2O_3 powder was slowly stirred in 45 mL of water in a stoppered conical flask to

TABLE I
Composite Formation in PNVC–Al_2O_3 System

Entry number[a]	Weight (g) in initial feed		Time (h) of interaction[c]	Weight (g) after refluxing with C_6H_6		Percent of PNVC loading per gram of composite
	PNVC[b]	Al_2O_3		Composite	PNVC	
1	0.025	0.1	3	0.022	0.006	27
2	0.025	0.1	6	0.087	0.013	15
3	0.025	0.1	18	0.088	0.015	17
4	0.025	0.2	3	0.041	0.010	24
5	0.025	0.3	3	0.061	0.011	18
6	0.025	0.4	3	0.070	0.012	17
7	0.016	0.3	3	0.058	0.005	8.6
8	0.035	0.3	3	0.057	0.011	19.5
9	0.045	0.3	3	0.060	0.013	22

[a] Each value is an average of three sets of experiments.
[b] Molecular weight of the fractionated PNVC (as determined by viscometry in benzene solution at 25°C) was about 4100.
[c] Interaction was allowed to take place at room temperature (25°C).

produce a stable aqueous dispersion of Al_2O_3 to which a known volume (5 mL) of a THF solution of PNVC was added. The reaction mixture was then continuously stirred at room temperature for different time intervals. The total contents of the flask were centrifuged at 10,500 rpm for 1 h. The separated mass was again dispersed in distilled water by sonication and then 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.

The entire quantity of precipitated PNVC–Al_2O_3 composite thus isolated was extracted with benzene through continuous stirring for 30 min at 50°C. The total contents were centrifuged, and the process was repeated at least four times, until the extracts did not give any precipitate with methanol of any surface-adsorbed PNVC. This residue was finally dried at 70°C for 10 h under vacuum. This mass, after physicochemical characterization, was confirmed to contain PNVC along with Al_2O_3.

Characterization and property evaluation of PNVC–Al_2O_3 nanocomposite

The Fourier transform infrared (FTIR) spectrum of the PNVC–Al_2O_3 composite was taken on a JASCO-410 instrument. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses of the PNVC–Al_2O_3 composite were performed on Hitachi S415A and Hitachi 600 instruments, respectively. Thermogravimetric analyses of the Al_2O_3 and PNVC–Al_2O_3 composite were performed on a Shimadzu DT 40 instrument. Direct current (dc) conductivity measurements were conducted on silver-coated pressed pellets by the conventional four-probe technique.

RESULTS AND DISCUSSION

General features of composite formation

Table I presents some typical data on composite formation in the PNVC–Al_2O_3 system. The data show the interesting feature that while the PNVC was precipitating in the aqueous medium that contained the Al_2O_3 particles, a part of the PNVC formed a stable composite with the Al_2O_3. Even continued extraction with benzene failed to remove the polymer from the Al_2O_3 surface.

Entries 1, 4, 5, and 6 of Table I indicate that at a fixed amount of PNVC, the percentage of PNVC loading on the composite increased with an increasing amount of Al_2O_3 in the initial feed.

Entries 5, 7, 8, and 9 of Table I indicate that at a fixed amount of Al_2O_3, the percentage of PNVC loading on the composite increased with an increasing amount of PNVC in the initial feed.

Entries 1–3 of Table I show the variation in PNVC loading in a composite with an increasing time of interaction of the precipitating polymer with Al_2O_3 particles in the medium. Interestingly, the final weights of the composite recovered in the system and of the PNVC loaded in the composite increased progressively with an increasing time of interaction until finally attaining a limiting value. However, the percentage of PNVC loading per gram of composite was seen to fall. This was because the increase in the PNVC loading in the composite was not proportionate with the increase in the composite formation in the system.

The observed trend, strong bonding of PNVC onto the Al_2O_3 surface, is interesting and consistent with the observations of earlier work[5,7,10] on systems involving polypyrrole (PPY)–metal oxide,[1–3,5,6] PANI–metal oxide,[1,2,4,5,7] and PNVC–metal oxide.[5,7,10] De-

spite the researchers concerned with this field lacking a clear understanding of the mechanism for this stable adsorption process,[1,2,6,11] one tentative explanation offered for the PNVC–Al_2O_3 system, which appeared feasible to us, might involve an acid–base type of interaction between the basic PNVC moieties and the amphoteric Al_2O_3 particles, leading to stabilization of the PNVC moieties on the Al_2O_3 surface. Although the nano order particle size of the Al_2O_3 dispersion would facilitate such an interaction, the heterogeneous nature of the reaction involving PNVC and Al_2O_3 moieties would reduce the efficiency of the interaction, as evident from the low level of PNVC loading in the Al_2O_3 surface.

FTIR characteristics of the PNVC–Al_2O_3 composite

The presence of PNVC in the composite after repeated extraction with benzene was supported by the appearance of FTIR peaks common to PNVC and the PNVC–Al_2O_3 composite: 724 cm^{-1} (ring deformation of substituted aromatic structure), 745 cm^{-1} (> CH_2 rocking vibration), 1158 cm^{-1} (out-of-plane deformation of vinylidene gr), 1383 cm^{-1} (> CH_2 deformation of vinylidene gr), 1451–1484 cm^{-1} (ring vibration of NVC moiety), 1630 cm^{-1} (C═C stretching vibration of vinylidene gr), 3089 cm^{-1} (aromatic C—H stretching vibration).

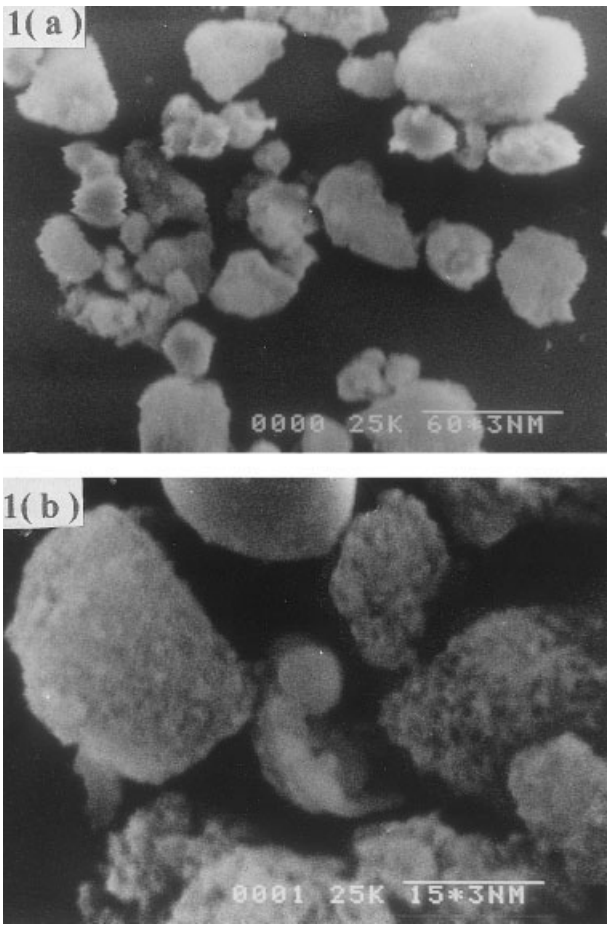

Figure 1 SEM of PNVC–Al_2O_3 composite at two magnifications [(a) and (b)].

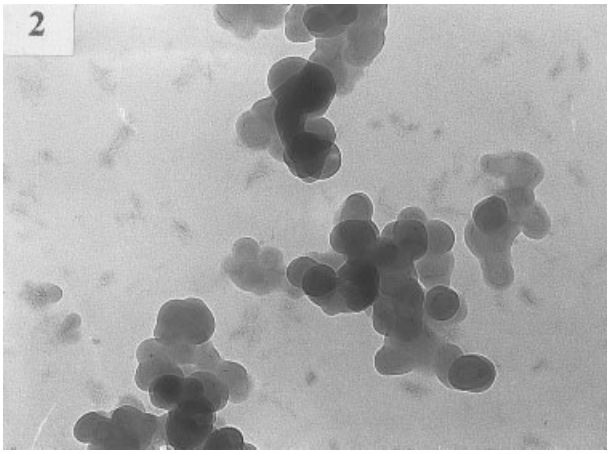

Figure 2 TEM image of PNVC–Al_2O_3 composite.

Scanning electron microscopic analysis

Two SEM photographs of the PNVC–Al_2O_3 nanocomposite at two different magnifications, shown in Figure 1(a,b), reveal the formation of agglomerates of particles of nonuniform sizes and shapes. In a recent study Stjeskal et al. contended[11] that the PANI- and PPY–SiO_2-based composite particles were characterized by a typical "raspberry" morphology, in which ultrafine silica particles were present not only on the surface but also were distributed throughout the interior of the agglomerates. In Figure 1(b) a morphology pattern of the PNVC–Al_2O_3 agglomerate can be seen that is rather similar to those for the aforementioned systems.[1,11] In this background the SEM characteristics for the PNVC–Al_2O_3 system apparently indicate that the ultrasmall Al_2O_3 particles provided a high surface area of colloidal substrate for the precipitating PNVC and that the resulting composite particles were formed of microaggregates of polymer particles glued together by the fine Al_2O_3 particles.

Transmission electron microscopic analysis

TEM analysis of the Al_2O_3 powder dispersion showed a preponderance of stringy particles (diameter ~ 10 nm)[12] that were transformed into discrete spherical particles (diameter ~ 120–240 nm) during composite formation with PNVC (Fig. 2). This further indicates that superimposition of globular polymer particles (dark regions in the photograph) occurred nonuni-

TABLE II
Direct Current Conductivity Values of Some PNVC-based Composites

Material	Particle size (nm)	Dopant	Conductivity (S/cm)	Reference
1. Unmodified PNVC	—	—	10^{-12}–10^{-16}	Ref. 5
Modified PNVC				
2. PNVC–Al_2O_3	120–240	$FeCl_3$	0.14×10^{-6}	This study
3. PNVC–MnO_2	200–250	$FeCl_3$	4×10^{-5}	Ref. 5
4. PNVC–ZrO_2	300–500	$FeCl_3$	1.2×10^{-5}	Ref. 7
5. PNVC–MMT	30–40	$FeCl_3$	$3–5 \times 10^{-5}$	Ref. 9
6. PNVC–SiO_2	20–30	$FeCl_3$	1×10^{-5}	Ref. 10

formly and the tendency toward cluster formation was clearly evident.

Conductivity characteristics

Table II presents the dc conductivity values of the PNVC–Al_2O_3 nanocomposite along with the corresponding data for unmodified PNVC and some PNVC–metal oxide–based materials. The dc conductivity of the PNVC–Al_2O_3 nanocomposite was on the order of 0.14×10^{-6} S/cm, a remarkably improved value compared with that for the PNVC homopolymer[5] and lower than those reported for the SiO_2-,[10] MnO_2-,[5] ZrO2-,[7] and montmorillonite clay–based composites of PNVC systems prepared by earlier procedures of Biswas and SinhaRay. These results imply that the particle size of the composite did not influence the manifestation of improved conductivity and that the metal ion centers including transitional and nontransitional elements did not significantly influence the conductivity values of the PNVC-based composites. On the other hand, enhancement of conductivity up to a limiting value (10^{-5} S/cm), observed in all the PNVC–oxide composites, appears to have resulted from a common cause: improved linking between the PNVC moieties because of the cementing of the PNVC grains together with the metal oxide particles, manifested in a raspberry-pattern morphology, as proposed by Armes et al.[1]

Thermogravimetric stability

A representative thermogravimetric analysis (TGA) scan is shown in Figure 3 for the PNVC–Al_2O_3 composite, which suffered a 3% weight loss at 300°C and a 39% weight loss at temperatures up to 600°C, whereas the PNVC homopolymer[8] showed an 8% weight loss at 400°C, a 75% weight loss at 555°C, and complete weight loss at 799°C. Thus, the thermal stability of the composite was improved relative to the base polymer. On a comparative basis, the PNVC–SiO_2[10] nanocomposite showed 32% decomposition at 799°C, and the PNVC–MMT[8] nanocomposite showed a 20% weight loss at 999°C. This general enhancement of the thermal stability of the polymer metal oxide composite was possibly a result of the manifestation of a compact polymer metal oxide morphology during gluing of the polymer by the oxide particles. However, all the oxides used during composite formation with PNVC, except for MMT,[8,9] showed more or less similar improvement in stability. The observed trend is also consistent with the previously stated finding that repeated benzene extraction of PNVC–Al_2O_3 composite was unable to remove the loaded PNVC from the Al_2O_3 particles, implying strong adherence between them.

Dispersibility of PNVC–Al_2O_3 nanocomposite in aqueous and nonaqueous media

The suspension of the PNVC–Al_2O_3 composite in aqueous and nonaqueous media was stable for 30 min. Notably, the pH of the Al_2O_3 suspension in water (3.83) was not altered after PNVC loading (3.77). In the presence of PVP as a polymeric stabilizer, the suspension showed some enhanced stability for up to 3 h. A comparison of these features with those of PNVC–SiO_2,[10] PNVC–MnO_2,[5] and PNVC–ZrO_2[7] nanocompos-

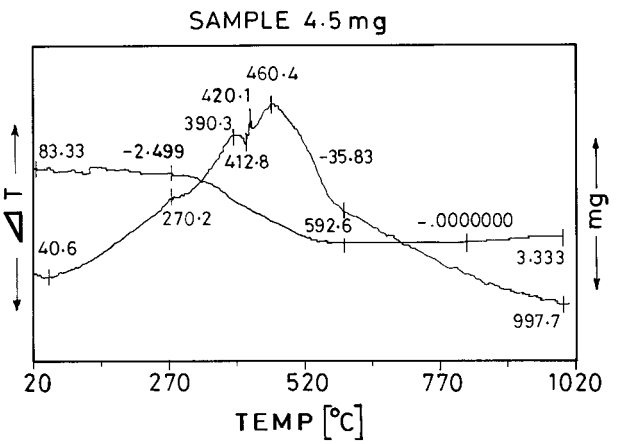

Figure 3 TGA and DTA scan for PNVC–Al_2O_3 nanocomposite.

ite systems revealed that the PNVC–SiO_2[10] nanocomposite produced a stable dispersion in the presence of PVP, whereas without PVP the suspension was stable up to 20 h. For the PNVC–ZrO_2[7] nanocomposite, sonication was necessary for 3–4 h to produce a stable colloid, whereas in the PNVC–MnO_2 system[5] no sonication was required to produce a stable suspension. Thus, these results indicate that nanodimensional Al_2O_3 was inferior to SiO_2, MnO_2, and ZrO_2 in being able to produce a stable water-dispersible composite with PNVC. At present, the reason for this trend is not clear.

CONCLUSION

The novel feature of the results of this study was that precipitation of preformed PNVC (in THF solution) on nanosized Al_2O_3 particles suspended in an aqueous medium led to the formation of a stable PNVC–Al_2O_3 composite from which residual PNVC could not be removed by repeated solvent extraction. The PNVC–Al_2O_3 composite showed high conductivity and thermogravimetric stability relative to the base polymer.

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