

## A Water Dispersible Nanocomposite of Polyacrylonitrile with Silica *via* Aqueous Polymerization of Acrylonitrile by $K_2CrO_4$ – $NaAsO_2$ Redox System

Arjun MAITY and Mukul BISWAS<sup>†</sup>

*Department of Chemistry, Presidency College, Calcutta-73, West Bengal, India*

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**ABSTRACT:** The aqueous polymerization of acrylonitrile initiated by the redox pair, potassium chromate-sodium arsenite produced polyacrylonitrile which was recovered as a coagulum in the medium. A simple procedure was developed for obtaining a stable suspension of polyacrylonitrile-SiO<sub>2</sub> nanocomposite by conducting the polymerization in presence of SiO<sub>2</sub> as a particulate dispersant. SEM analyses revealed distinct morphological features of the polyacrylonitrile-SiO<sub>2</sub> nanocomposite. TEM analyses indicated the particle sizes of the polyacrylonitrile-SiO<sub>2</sub> composite to be in the 28–100 nm range. TG analyses revealed the enhanced thermal stability of the polyacrylonitrile-SiO<sub>2</sub> nanocomposite relative to that of the base polymer polyacrylonitrile. The d.c. conductivities of the polyacrylonitrile-SiO<sub>2</sub> and polyacrylonitrile-SiO<sub>2</sub> (FeCl<sub>3</sub> doped) composites were in the order of 10<sup>-6</sup> S cm<sup>-1</sup> and 10<sup>-5</sup> S cm<sup>-1</sup> respectively.

**KEY WORDS** Homopolymerization / Polyacrylonitrile / Redox / Nanocomposite / Colloidal Silica / Water Dispersibility / Conductivity /

A vast literature exists on the preparation and evaluation of processible nanocomposites of intractable polymers like polyaniline (PANI),<sup>1</sup> polypyrrole (PPY),<sup>2</sup> polythiophene (PTP),<sup>3</sup> poly-*N*-vinylcarbazole (PNVC),<sup>4</sup> and binary combinations<sup>5</sup> thereof with montmorillonite (MMT)-clay,<sup>1–4</sup> nanometal oxides such as Al<sub>2</sub>O<sub>3</sub>,<sup>6–8</sup> ZrO<sub>2</sub>,<sup>9</sup> MnO<sub>2</sub>,<sup>10</sup> SiO<sub>2</sub>, and SnO<sub>2</sub><sup>11–19</sup> as particulate dispersants. The procedure generally adopted was to add pyrrole (PY) or aniline (ANI) to an aqueous dispersion of the nanodimensional metal oxides in presence of oxidants such as FeCl<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. For water-insoluble monomers like *N*-vinylcarbazole (NVC) or thiophene (TP), Biswas *et al.*<sup>20</sup> developed a suspension polymerization technique using combination of water and appropriate nonaqueous solvents (for the monomers) in presence of usual oxidants to produce the corresponding nanocomposites.

A significant recent development in this direction was the application of emulsion polymerization technique by Choi *et al.*<sup>21–24</sup> for the formation of nanocomposites of both speciality polymers (PANI, PPY) and the fundamental polymers (polystyrene, polyacrylonitrile, and copolymers thereof) with Na<sup>+</sup>-MMT clay. Inverted emulsion pathway was recently described by Choi *et al.*<sup>25</sup> for the preparation of intercalated PPY/Na<sup>+</sup>-MMT nanocomposite.

In the above background, we wish to report in this article a simple procedure of preparing a PAN-SiO<sub>2</sub> nanocomposite *via* aqueous polymerization of AN by Cr<sup>6+</sup>/AsO<sub>2</sub><sup>-</sup> redox pair in presence of nanodimensional silica as particulate dispersants. The scope of

this procedure is fairly wide since a variety of acrylic monomers and combinations thereof may be employed in presence of suitable particulate dispersants for the fabrication of the respective nanocomposites. We shall also describe some relevant bulk properties such as morphology, thermal stability, conductivity, and water dispersibility of the PAN-SiO<sub>2</sub> nanocomposite.

### EXPERIMENTAL

#### *Materials and Methods*

Acrylonitrile (Aldrich, USA) was freed from inhibitors by successive washings with dilute sodium carbonate solution, dilute sulfuric acid and finally with distilled water. It was kept over-night over calcium chloride and distilled in an all glass apparatus. The fraction boiling at 77–78 °C was collected and stored carefully. Potassium chromate (Riedel, Germany) and sodium arsenite (Riedel, Germany) were used as the oxidant and the reductant respectively. SM-30 Colloidal (30% weight suspension in water, density 1.22 g mL<sup>-1</sup>) SiO<sub>2</sub> (Aldrich, USA) was used as the particulate dispersant. All other solvents were of analytical grade and were freshly distilled before used.

#### *Polymerization of Acrylonitrile with K<sub>2</sub>CrO<sub>4</sub>-NaAsO<sub>2</sub> Redox System*

In a Pyrex flask, a definite amount (1.8–3.0 × 10<sup>-3</sup> mol) of K<sub>2</sub>CrO<sub>4</sub> was dissolved in 30 mL distilled water to which 0.02 mol of acrylonitrile was injected. The system was kept under stirring at ambient temperature under N<sub>2</sub> atmosphere for 10 min and there-

<sup>†</sup>To whom correspondence should be addressed (Tel: 0091-33- 2521-3556, Fax: 0091-33-234-6075, E-mail: mukul\_biswas@vsnl.net).

after, a definite amount ( $3.8 \times 10^{-4}$ – $2.3 \times 10^{-3}$  mol) of  $\text{NaAsO}_2$  was dissolved into this solution. The induction periods were within 3–5 min and the polymerization was allowed to continue for 2–6 h. Thereafter, the white polymer was centrifuged, washed in succession with distilled water, methanol, and acetone and finally dried in vacuum for 12 h. Conversions were estimated gravimetrically.

#### Preparation of PAN-SiO<sub>2</sub> Nanocomposite

0.1–0.5 g of silica was added to 30 mL of distilled water taken in a 50 mL Pyrex flask under sonication in which a definite amount ( $1.8$ – $3.0 \times 10^{-3}$  mol) of  $\text{K}_2\text{CrO}_4$  was dissolved and 0.02 mol of acrylonitrile monomer was injected. The system was kept under stirring at ambient temperature under  $\text{N}_2$  atmosphere for 10 min. Thereafter, a definite amount ( $3.8 \times 10^{-4}$ – $2.3 \times 10^{-3}$  mol) of  $\text{NaAsO}_2$  was added to it. The system was allowed to polymerize for a definite time period. The white suspension was centrifuged and the separated mass was washed in succession with distilled water, methanol and acetone and finally dried in vacuum for 12 h.

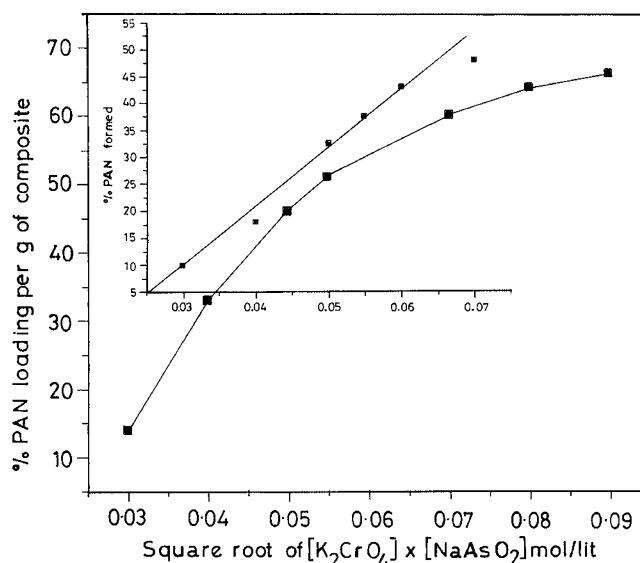
#### Characterization and Property Evaluation of PAN and PAN-SiO<sub>2</sub> Nanocomposite

Intrinsic viscosity of PAN homopolymer was determined with in Ostwald viscometer in dimethylformamide (DMF) solution at 25 °C and molecular weight was calculated using the Ueberreiter-Springer equation,  $[\eta] = 16.6 \times 10^{-5} \times M^{0.81}$ .<sup>26,27</sup> The Fourier transform infrared (FT-IR) spectra of PAN and PAN-SiO<sub>2</sub> composite were taken on a JASCO-410 instrument (Essex, UK) in pressed KBr pellets. Dispersion of PAN-SiO<sub>2</sub> nanocomposite in 2-Propanol was microsprayed on a mica substrate. The sample was sputter coated with gold layer and a Hitachi S-415A (Tokyo, Japan) scanning electron micrograph was used to take the micrograph. The particle sizes of the PAN-SiO<sub>2</sub> composites were measured by a Hitachi H-600 transmission electron microscope (Tokyo, Japan), with diluted suspension (1000 ppm) in 2-Propanol on the copper grid. Thermogravimetric analyses were performed on a Shimadzu DT-40 (Kyoto, Japan) instrument.

## RESULTS AND DISCUSSION

#### General Features of PAN-SiO<sub>2</sub> Nanocomposite Formation

The aqueous polymerization of AN could not be induced by  $\text{Cr}^{6+}$  or  $\text{AsO}_2^-$  alone under ambient and higher temperature conditions. Polymerization occurred only when both the constituents were present in



**Figure 1.** Dependence of % PAN loading per g of composite and of % PAN homopolymerization (inset) on the  $\sqrt{[\text{K}_2\text{CrO}_4][\text{NaAsO}_2]}$  mol L<sup>-1</sup>;  $[\text{AN}] = 0.75$  mol L<sup>-1</sup>.

the reaction mixture.

With the recipe used in the present study the polymerizations were pretty fast and after an induction period varying from 3–5 min, the appearance of a milky white suspension of polymer PAN could be noted. At the end of the polymerization time the suspension coagulated in the medium which was centrifuged and the % conversion was determined gravimetrically. PAN homopolymer thus collected was characterized by FT-IR spectroscopy. The molecular weight of the polymer as determined viscometrically was  $7.9 \times 10^4$  g mol<sup>-1</sup>.

In presence of nanodimensional SiO<sub>2</sub> dispersed in the water medium the polymerization of AN occurred with comparable speed as in the homopolymerization system. In this case a PAN suspension was obtained which was centrifuged at 15000 rpm to estimate the solid content. PAN content in this PAN-SiO<sub>2</sub> composite thus obtained was determined by subtracting the weight of SiO<sub>2</sub> in the initial feed from the total weight of PAN-SiO<sub>2</sub> composite. The FT-IR scan for PAN-SiO<sub>2</sub> composite revealed the manifestation of peaks (cm<sup>-1</sup>) at 2939 (C–H stretching), 2250 (C≡N stretching) and 1454 (C–H bending) which matched with the reported FT-IR spectra for PAN.<sup>28–30</sup>

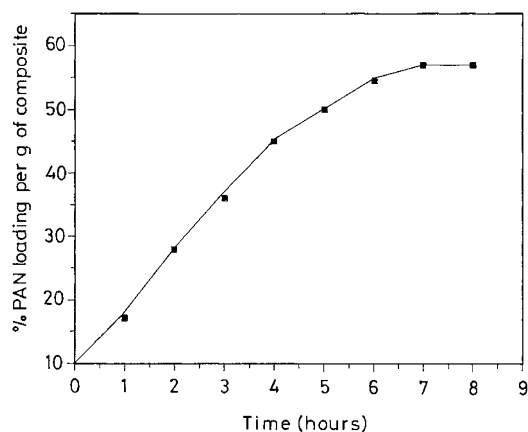
Figure 1 shows that % PAN loading per g of composite increased with the square root of the product of  $[\text{K}_2\text{CrO}_4]$  and  $[\text{NaAsO}_2]$  at fixed amount of SiO<sub>2</sub> in the initial feed. This trend would be expected since the overall yield of PAN (inset of Figure 1) and hence its % loading in the composite with fixed SiO<sub>2</sub> was found to increase with an increase in the product of  $[\text{K}_2\text{CrO}_4]$  and  $[\text{NaAsO}_2]$ .

Figure 2 shows that % PAN loading per g of compos-

ite increased progressively to a limiting value with the time of the polymerization at fixed initial feed composition of the polymerization. This trend was parallel to the variation of the % conversion to PAN with time.

#### Scanning Electron Microscopic Analysis

Several scanning electron micrographic images of the PAN-SiO<sub>2</sub> nanocomposite are presented in Figure 3(a)–3(d) which clearly revealed that the PAN-SiO<sub>2</sub> composite particles were made up of lumpy masses of irregular shapes and sizes (25–105 nm). The



**Figure 2.** Dependence of % PAN loading per g of composite on the reaction time; [AN] = 0.75 mol L<sup>-1</sup>, [K<sub>2</sub>CrO<sub>4</sub>] = 0.06 mol L<sup>-1</sup>, [NaASO<sub>2</sub>] = 0.05 mol L<sup>-1</sup>.

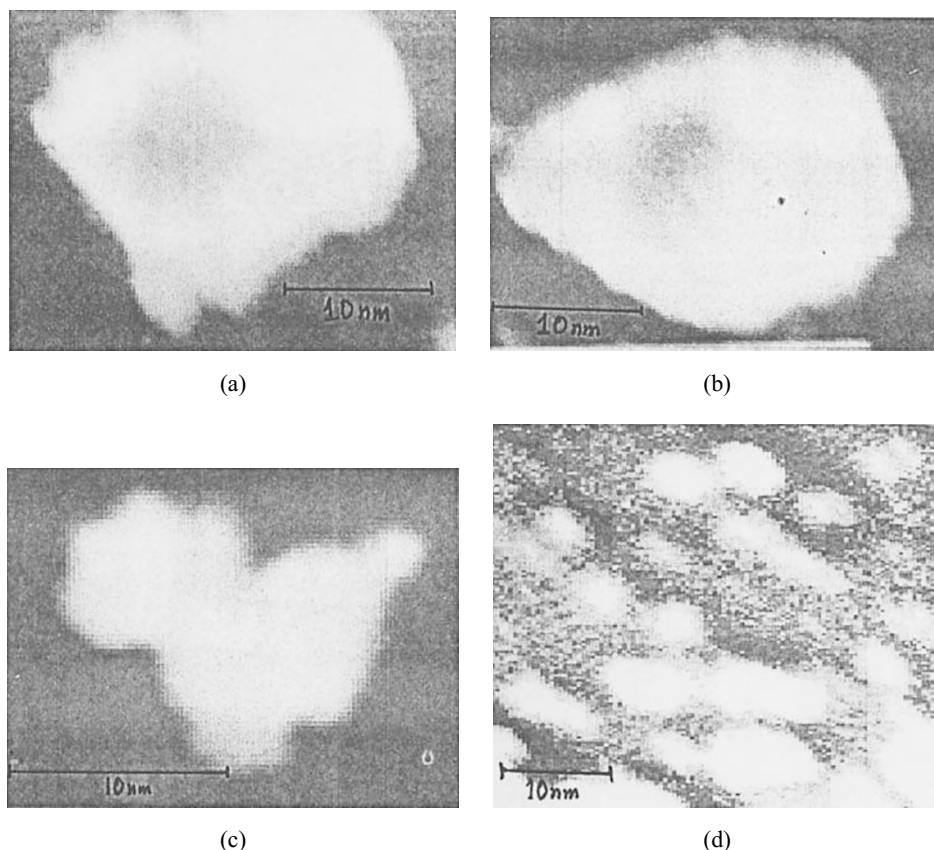
morphology pattern appeared to be similar to the typical ‘raspberry’ morphology pattern reported by Armes *et al.*<sup>12</sup> for PPY-SiO<sub>2</sub> or PANI-SiO<sub>2</sub> nanocomposites and subsequently by Biswas *et al.* for PNVC-SiO<sub>2</sub>,<sup>10</sup> PNVC-Al<sub>2</sub>O<sub>3</sub>,<sup>6</sup> and PTP-Al<sub>2</sub>O<sub>3</sub><sup>7</sup> systems. Such a morphology could develop through aggregation of silica particles glued together<sup>13</sup> by the precipitating polymer moieties acting as a binder.

#### Transmission Electron Microscopic Analysis

TEM analysis of the SiO<sub>2</sub> dispersion revealed the presence of stringy particles of average diameter 20 nm.<sup>17</sup> The TEM micrograph (Figure 4) of a PAN-SiO<sub>2</sub> nanocomposite dispersion in the 1000 ppm dilution range clearly indicated the formation of spherical particles with average particle diameter in the 28–100 nm range. A similar trend was also observed by Armes *et al.*<sup>17</sup> for the PPY, PANI, and SiO<sub>2</sub> nanocomposite systems.

#### Thermogravimetric Stability

Wt% retained versus temperature studies for PAN homopolymer, PAN-SiO<sub>2</sub> nanocomposite and dried SiO<sub>2</sub> (Figure 5) revealed the following trend in the order of thermogravimetric stability: dried SiO<sub>2</sub> (12% weight loss at 799 °C) > PAN-SiO<sub>2</sub> nanocomposite (76% weight loss at 997 °C) > PAN homopolymer

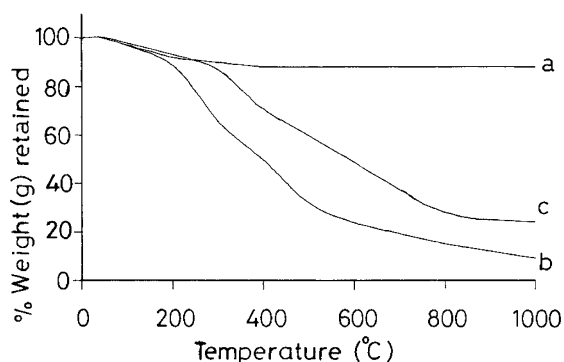


**Figure 3.** Scanning electron micrographs of a PAN-SiO<sub>2</sub> composite.

**Table I.** D.c conductivities of various PAN-based composites.

Entry No	Materials	Conductivity(S cm <sup>-1</sup> )	Reference
1	PAN homopolymer	>10 <sup>-7</sup> –10 <sup>-8</sup>	this study
2	PAN-SiO <sub>2</sub> nanocomposite	2.1 × 10 <sup>-6</sup>	this study
3	PAN-SiO <sub>2</sub> (Doped with FeCl <sub>3</sub> for one week)	1.2 × 10 <sup>-5</sup>	this study
4 <sup>a</sup>	PANI-(PAN-SiO <sub>2</sub> )	3.5 × 10 <sup>-3</sup>	ref 31
5 <sup>b</sup>	PANI-(PAN-SiO <sub>2</sub> )	2.5 × 10 <sup>-3</sup>	ref 31
6 <sup>a</sup>	PPY-(PAN-SiO <sub>2</sub> )	2.8 × 10 <sup>-4</sup>	ref 31
7 <sup>b</sup>	PPY-(PAN-SiO <sub>2</sub> )	1.5 × 10 <sup>-4</sup>	ref 31

<sup>a</sup>ANI/PY was added to PAN-SiO<sub>2</sub> suspension in aqueous medium to which FeCl<sub>3</sub> was added. <sup>b</sup>ANI/PY was added to PAN-SiO<sub>2</sub> suspension in aqueous medium containing excess CrO<sub>4</sub><sup>=</sup> in presence of HCl.

**Figure 4.** Transmission electron micrograph of a PAN-SiO<sub>2</sub> composite.**Figure 5.** TGA thermograms of (a) Dried Silica (b) PAN homopolymer (c) PAN-SiO<sub>2</sub> nanocomposite.

(91% weight loss at 997 °C). Such enhancement of thermal stability after polymer-oxide nanocomposite formation was a typical feature of a majority of reported polymer metal oxide composite systems.<sup>4–9,12,17</sup> This trend could manifest from the formation of a compact polymer- metal oxide nanoaggregates which would require higher thermal energy for degradation.

The DTA scans for both PAN homopolymer and PAN-SiO<sub>2</sub> nanocomposite revealed manifestation of

a sharp exothermic peak in the temperature range 487 ± 20 °C corresponding to the region of maximum weight loss (300–600 °C). In this range, PAN suffered massive oxidative degradation.

#### Conductivity Characteristics

Table I presents the d.c. conductivity values for some PAN-based composites. PAN homopolymer produced in this research did not show any attractive conductivity value. On composite formation with SiO<sub>2</sub> somewhat higher conductivity value could be realized in PAN-SiO<sub>2</sub> systems. External doping with FeCl<sub>3</sub> further improved the conductivity (10<sup>-5</sup> S cm<sup>-1</sup>) as was to be expected.

It occurred to us that an interesting way of improving upon the conductivity of the PAN-SiO<sub>2</sub> composite would be to deposit conducting polymers like PPY or PANI on the preformed PAN-SiO<sub>2</sub> suspension in the aqueous medium. Results of our preliminary experimentations<sup>31</sup> in this direction (entries 4–7, Table I) were encouraging. Further work is in progress in this direction.

#### Stability of PAN-SiO<sub>2</sub> Nanocomposite Suspension in Water

As mentioned earlier PAN homopolymer separated out as a coagulum in the aqueous medium. However, in presence of nanodimensional SiO<sub>2</sub> particles suspended in the aqueous medium the separated PAN particles encapsulated the SiO<sub>2</sub> particles and thereby formed the composite which remained suspended in the aqueous medium. This process was widely followed by previous workers<sup>4–9,11–24</sup> for the preparation of processable dispersions of intractable speciality polymers. The method presented here is expected to be of wide scope since these studies can be extended to miscellaneous water insoluble fundamental polymers including vinyl polymers as well as copolymers of these polymers with the speciality polymers like PPY, PANI, or PTP.

## CONCLUSIONS

The aqueous polymerization of acrylonitrile was initiated by  $\text{CrO}_4^{=}/\text{AsO}_2^-$  redox pair. The same polymerization in presence of nanodimensional  $\text{SiO}_2$  particulate dispersants in the aqueous medium resulted in the formation of PAN- $\text{SiO}_2$  nanocomposite as a permanently stable suspension. Polymer loading in the composite could be controlled by adjusting  $[\text{CrO}_4^{=}]/[\text{AsO}_2^-]$ . Conductivity of otherwise non-conducting PAN ( $\sim 10^{-11} \text{ S cm}^{-1}$ ) could be enhanced to  $10^{-6} \text{ S cm}^{-1}$  through nanocomposite formation with  $\text{SiO}_2$  and to  $\sim 10^{-5} \text{ S cm}^{-1}$  by  $\text{FeCl}_3$  doping.

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