Preparation and Some Properties of a Nanocomposite of Polyacrylonitrile with Acetylene Black

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ABSTRACT: Conducting nanocomposites of polyacrylonitrile (PAN) with acetylene black (AB) were prepared *via* K_2CrO_4–$NaAsO_2$ initiated redox polymerization of acrylonitrile in presence of AB suspension in aqueous-methanol medium at 60 °C. Prolonged extraction of PAN–AB composite by DMF failed to extract the loaded polyacrylonitrile completely from the acetylene black, as confirmed by FT IR studies. SEM analyses revealed the formation of agglomerates of particles of nonuniform sizes and shapes. TEM analysis indicated that average particle diameters of the PAN–AB composite were in the range of 120–250 nm. Thermal stability of the PAN–AB composite was appreciably improved relative to that for the unmodified base polymer. The dc conductivity of the PAN–AB composite was in the range of 10^{-4}–10^{-2} S/cm depending on the amount of AB in the PAN–AB composite, a value remarkably improved relative to that of the PAN homopolymer ($>10^{-11}$ S/cm).   [DOI 10.1295/polymj.36.812]
    KEY WORDS   Polyacrylonitrile / Acetylene Black / K_2CrO_4–$NaAsO_2$ Redox System / Thermal Stability / Conductivity /

Considerable research interest has been shown lately in the modification of fundamental polymers like polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), polystyrene (PS), etc. with a view to enhancing the scope of practical application of these materials. A widely investigated method in this direction is the preparation of conducting polymer blends and composites of the speciality conducting polymers such as polyaniline (PANI), polypyrrole (PPY), and polythiophene (PTP) with conventional polymers like PAN, PMMA, PS, etc. Several workers[1,2] reported on the preparation of conducting polymeric blends/composites of PPY–PVc and PPY–PMMA *via* electrochemical and oxidative polymerization methods respectively. Stanke *et al.*[3] synthesized a conducting graft copolymer film of PMMA and PPY by oxidative polymerization of pyrrole with $FeCl_3$. Ruckenstein[4,5] described preparation and evaluation of polyaniline/poly(alkylmethacrylate) and polypyrrole/poly(alkylmethacrylate) composites with high electrical conductivity (6 S/cm).

In an alternative process, blending polymers with conducting fillers, such as natural graphite flake, carbon black, and powders, to prepare electrically conducting composites has been extensively investigated in the past few decades. In this context, Chen *et al.*[6] prepared conducting PMMA/graphite nanosheet composites *via in-situ* polymerization of methylmethacrylate (MMA) by benzoyl peroxide in aqueous alcohol solution in presence of expanded graphite (EG). We recently reported[7] that acetylene black (AB)- the purest form of highly conducting carbon black, was capable of initiating the polymerization of *N*-vinylcarbazole. Interestingly, this system led to the simultaneous formation of a PNVC–AB composite with a conductivity in the order of 10^{-2} S/cm. Earlier, Japanese groups[8–13] reported the polymerization of vinyl monomers like styrene, α-methystyrene, isobutyl vinyl ether (IBVE), *N*-vinyl-2-pyrrolidone (NVP) in the presence of carbon black (CB) and external catalyst *vis-a-vis* formation of graft composites in the systems. Biswas *et al.*[14–17] also explored the initiation of the polymerization of the NVC by Orient black (N220), Vulcan XC-72, etc. without any external oxidant.

In this background, we wish to describe in this article a novel procedure for the preparation of a highly conducting PAN–AB composite *via* K_2CrO_4–$NaAsO_2$ initiated redox polymerization of acrylonitrile in aqueous alcoholic medium and also report some relevant properties of the PAN–AB composite.

EXPERIMENTAL

Materials and Methods

Acrylonitrile (Aldrich, USA) was freed from inhibitor by successive washings with dilute sodium carbonate solution, dilute sulphuric 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. Acetylene black (SENCO India, Chenai, India) was preheated by heating at 120 °C for 2 h in vacuum prior to use. Potassium chromate (Riedel, Germany) and sodium arsenite (Riedel) were used as

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the oxidant and the reductant respectively. All other solvents were of analytical grade and were freshly distilled before used.

Polymerization of Acrylonitrile with K_2CrO_4–$NaAsO_2$ Redox System

K_2CrO_4 (0.2 g) was dissolved in 30 mL of water–methanol mixture (3 mL MeOH) in a Pyrex flask to which 1.5 mL of acrylonitrile was injected. The system was kept under stirring at room temperature under N_2 atmosphere for 10 min and thereafter, 0.3 g of $NaAsO_2$ was dissolved into this solution. Then the total system was kept at 60 °C for 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.

Preparation of PAN–AB Nanocomposite

In a Pyrex flask, 0.02–5 g of AB was added to 30 mL of water–methanol mixture (3 mL methanol) under sonication for 1 h to make a suspension of AB in which 0.2 g of K_2CrO_4 was dissolved and 1.5 mL of acrylonitrile was injected. Thereafter, 0.3 g of $NaAsO_2$ was added to it. The system was kept at 60 °C with stirring for 6 h under N_2 atmosphere. The total black mass was washed in succession with distilled water, methanol and acetone and finally dried in vacuum for 12 h.

The total PAN–AB composite thus obtained was extracted with DMF through continuous refluxing for one week at 50 °C. The total separated mass was centrifuged, a process repeated at least four times until the extract did not yield any precipitate with methanol due to any residual surface adsorbed PAN. This residue was finally dried at 60 °C for 12 h under vacuum. After various physicochemical characterizations, the composite was confirmed to contain PAN along with AB.

Characterization and Property Evaluation

Intrinsic viscosity of PAN homopolymer was determined with an Oswald viscometer in DMF solution at 25 °C and molecular weight was calculated using the Ueberreiter–Springer equation $[\eta] = 1.66 \times 10^{-5} \times M^{0.81}$.[18] The FT IR spectrum of PAN–AB composite was taken on a JASCO-410 instrument in pressed KBr pellet. Dispersion of PAN–AB composite in 2-propanol was microsprayed on a mica substrate. The sample was sputter coated with gold layer and a Hitachi S-415 A scanning electron micrograph was used to take the micrograph. Thermogravimetric analyses were performed on a Shimadzu DT-40 instrument. Direct current (dc) conductivity measurements were made on pressed pellets with a silver coating, using the conventional four-probe technique.

RESULTS AND DISCUSSION

General Features of Composite Formation

Table I presents some results on the polymerization of AN *vis-a-vis* composite formation of polyacrylonitrile with acetylene black. 85% PAN homopolymer was formed when the polymerization was conducted under conditions summarized in Table I. Entries 1–8 indicate that the percent conversion of PAN homopolymer decreased with increasing weight of AB at fixed amount of redox system and monomer in the initial feed. A notable feature was that after prolonged extraction of PAN–AB composites with DMF at 60 °C, some residual amount of PAN (last column, Table I) was found to be present in the PAN–AB composite. This could be due to fact that PAN homo-
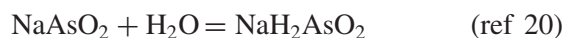
Table I. Some typical data on composite formation[a] of polyacrylonitrile with AB

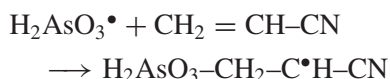| Entry No	Weight of AB (g)	Weight of composite (g)		% polymer formed[b]	% of polymer grafted[c] per g of composite
		before reflux with DMF	after reflux with DMF		
1	0.02	0.73	0.09	57	78
2	0.03	0.63	0.14	50	78
3	0.04	0.56	0.15	45	73
4	0.05	0.53	0.18	40	72
5	0.10	0.50	0.25	33	60
6	0.20	0.45	0.36	21	44
7	0.30	0.52	0.365	18	35
8	0.50	0.73	0.70	19	28

[a]Experimental conditions: weight of AN = 1.2 g, weight of K_2CrO_4 = 0.1 g, weight of $NaAsO_2$ = 0.3 g, total volume = 30 mL (water = 27 mL and MeOH = 3 mL), temperature = 60 °C, time of polymerization = 6 h; [b]% polymer formed in the control experiment (without AB; using same experimental conditions mentioned above) was 85%; % polymer in the composite = [(column 3 − column 2)/1.2] × 100 [c]% grafting = [(column 4 − column 2)/column 4] × 100
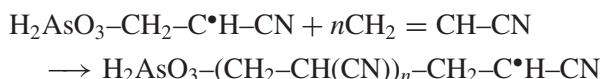
polymer was grafted on the acetylene black surface.

Biswas and Maity recently reported[19] that the polymerization of acrylonitrile by K_2CrO_4–$NaAsO_2$ redox system occurred *via* free radical pathway as follows:

$$NaAsO_2 + H_2O = NaH_2AsO_2 \qquad \text{(ref 20)}$$

$$H_2AsO_3^- + Cr^{6+} = H_2AsO_3^\bullet + Cr^{5+} \quad \text{(ref 21)}$$

Initiation

$$H_2AsO_3^\bullet + CH_2 = CH–CN$$
$$\longrightarrow H_2AsO_3–CH_2–C^\bullet H–CN$$

Propagation

$$H_2AsO_3–CH_2–C^\bullet H–CN + nCH_2 = CH–CN$$
$$\longrightarrow H_2AsO_3–(CH_2–CH(CN))_n–CH_2–C^\bullet H–CN$$

It is well established[8–17] by ESR studies that carbon black systems have unpaired electrons. Tsubokawa *et al.*[22,23] reported on the grafting of some vinyl monomers on CB in the presence of free radical initiators. Relevantly, Biswas *et al.*[14,16] found that simultaneous precipitation of PNVC by methanol addition to the polymerizing solution (NVC+CB+benzene) was effective in producing a PNVC–CB graft composite. In this background, we believe that the proposed grafting between growing PAN moieties and AB could be *via* free radical coupling as the following equation.

$$H_2AsO_3–(CH_2–CH(CN))_n–CH_2–C^\bullet H–CN + AB^\bullet$$
$$\longrightarrow H_2AsO_3–(CH_2–CH(CN))_n–CH_2–CH(CN)–AB$$
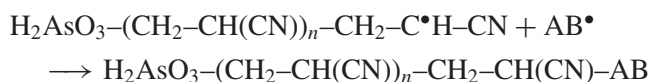
One of the reviewers pointed out that free radicals in CB are unable to trap radicals. In this context, we wish to submit that we observed[7,14–17] direct initiation of NVC polymerization by CB, AB and fullerene without any external initiators *via* electron transfer reaction between nitrogen lone pair of NVC and free electron in CB/AB/fullerene. In the latter system, our contention was endorsed by Chen *et al.*[24] who obtained ESR evidence for the electron transfer reaction. Secondly, in this particular system we failed to obtain any PAN–AB graft composite from preformed PAN and AB suspension. The PAN–AB graft composite was only obtained during *in-situ* polymerization of AN in presence of AB and redox system.

FT IR Absorption Characteristics of PAN–AB Composite

Table II summarizes the FT IR peaks for the PAN-based composites along with their probable assignments. The presence of PAN in the PAN–AB composite recovered after repeated extraction with DMF was supported by the appearance of FT IR peaks (cm^{-1}) at 2924, 2260 and 1460 which matched with the reported FT IR spectra for PAN.[25–27]

Table II. FT IR absorption characteristics of PAN–homopolymer and of PAN–AB composite

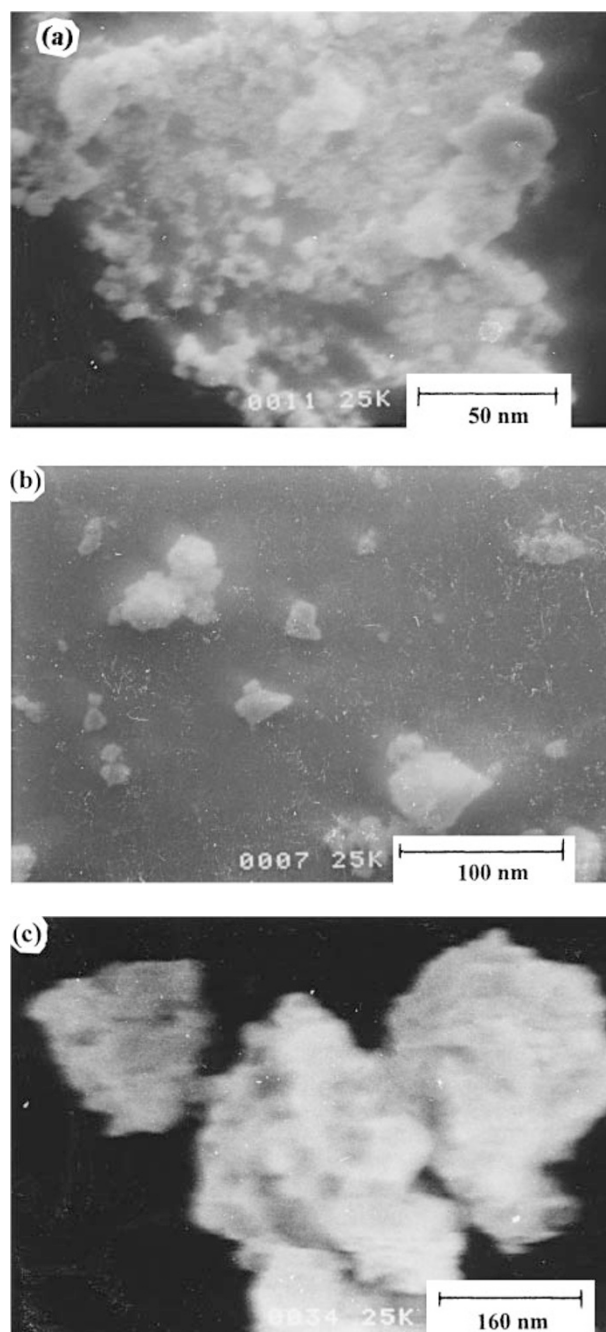| PAN	Absorption of PAN–AB composite (cm^{-1})	Assignments
2939	2924	C–H stretching vibration
2245	2260	C≡N stretching vibration
1454	1460	C–H bending vibration

Figure 1. Scanning electron micrographs of (a) AB (b) PAN homopolymer (c) PAN–AB composite (entry 8; Table I).

Scanning Electron Micrographic Characterization

The SEM morphology for AB (Figure 1a) showed presence of small nearly spherical AB particles with

the tendency to form larger lumps (40 nm) randomly distributed on the surface. The morphology for PAN homopolymer (Figure 1b) was essentially indicative of the formation of lumpy aggregates of mixed sizes ranging from 10–70 nm with definite pattern. In contrast, SEM photograph of the PAN–AB composite suggested the formation of lumpy agglomerates of much larger particles with nonuniform sizes (130–300 nm) and shapes. The formation of such microaggrgates could result through cementation of nano-sized AB particles with the precipitating PAN homopolymer—a situation similar to the scenario described by Armes and Maeda[28] in their PPY–metal oxide nanocomposite systems where the nanocomposites were considered to be made up of microaggregates "glued" together by the precipitating PPY component. Such morphology was believed[29] to be the reason for the manifestation of attractive conductivity value. In the light of this concept the high conductivity of the PAN–AB composite is consistent with the compact interparticle morphology in PAN–AB composite.

Transmission Electron Micrographic Characterization

Transmission electron micrograph of PAN–AB composite presented in Figure 2, revealed the appearance of spherical particles with sizes varying between 120–250 nm. The observed presence of dark globular particles along with the lighter once is reminiscent of the TEM micrograph realized with PPY–metal oxide and PANI–metal oxide nanocomposite systems reported earlier.[28–30]

Thermal Stability Characteristics

Percent weight retained versus temperature studies (Figure 3) for AB, PAN–AB composite and PAN
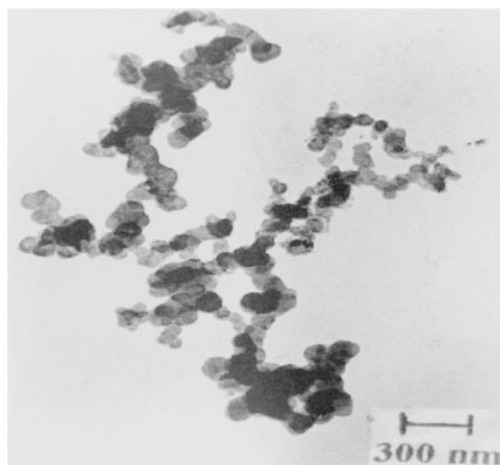

Figure 2. Transmission electron micrograph of PAN–AB composite (entry 8; Table I).
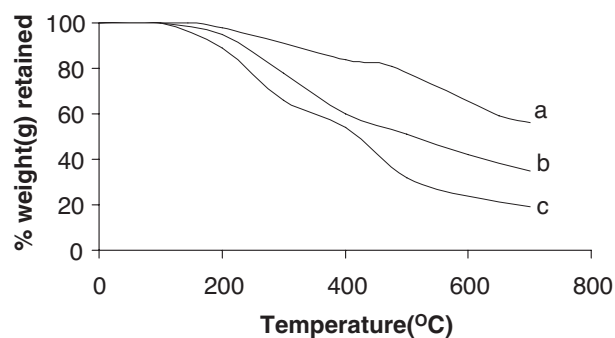
Figure 3. TGA of (a) AB (b) PAN–AB composite (entry 8; Table I) (c) PAN–homopolymer.

homopolymer revealed the following trend in the order of thermogravimetric stability: (a) initial decomposition temperature varied as AB > PAN–AB > PAN (b) temperature for 50% decomposition varied as AB > PAN–AB > PAN (c) limiting decomposition temperature varied as AB > PAN–AB > PAN. The intermediate stability of PAN–AB composite could manifest from the incorporation of less stable PAN moieties, in more stable AB in the PAN–AB composite. A similar trend was also reported for a variety of polymer–metal oxide nanocomposite systems.[31–33]

The DTA scan for the PAN–AB composite revealed exothermic peaks at 335, 518 and 550 °C respectively. The peak at 550 °C did not manifest in the TGA of PAN homopolymer.[19] Probably this peak resulted from the oxidative degradation of various functional groups (–OH, –COOH, >C=O, –CHO, etc.)[10,12,34] known to be present in various types of carbon black.

Conductivity Characteristics

The dc conductivity value of PAN homopolymer was in the order of 10^{-11} S/cm.[19] Interestingly, conductivity of the PAN–AB composite increased with increasing weight per centage of AB in the composite (Table III). However, at 3% AB content, the conductivity was increased $\sim 10^7$ fold compared to that of PAN homopolymer while the value progressively increased by 10^2 fold corresponding to a 10 fold increase in the per cent of AB in the PAN–AB compo-

Table III. Conductivity values of PAN–AB composites

Entry No	Materials	% of AB content in the composite	Conductivity (S/cm)
1	PAN homopolymer[a]	0	$>10^{-11}$
2	PAN–AB composite	3	2.1×10^{-4}
3	PAN–AB composite	6	1.9×10^{-3}
4	PAN–AB composite	10	2.5×10^{-2}
5	PAN–AB composite	31	8×10^{-2}

[a]See ref 19.

site (entries 3 and 5, Table III). This feature is quite consistent with the reported conductivity enhancement of polymers blended with conductive fillers.[6]

CONCLUSIONS

Conducting nanocomposites of PAN–AB were prepared *via* K_2CrO_4–$NaAsO_2$ redox initiated polymerization of AN in presence of AB in aqueous-alcohol dispersions. The conductivity of the PAN–AB composite increased by 10^7 to 10^9 fold relative to that of PAN homopolymer corresponding to AB loading of 3% to 31% respectively.

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