

NOTE

A Conducting Nanocomposite of Polystyrene with Acetylene Black

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During recent years increasing research attention is being paid to the preparation of conducting nanocomposites of vinyl addition polymers like polystyrene (PS),¹ polypyrrole (PPY),² polyaniline (PANI),³ polymethylmethacrylate (PMMA),⁴ etc. with carbon nanotube (CNT). Most of these materials are being exploited in regard to their electrical properties including electrorheology.⁵

In view of the difficulty of availability of carbon nanotubes and their high cost any cheaper alternative for the CNT component is these composites would be indeed worth exploring. In this context we have successfully used one cheap and abundant allotrope of carbon namely acetylene black (AB) as the nanocomponent. The particle size of AB is in the nano order range and the material is highly conducting. We have reported that *N*-vinyl carbazole (NVC) monomer can be readily polymerized in bulk or in toluene in presence of AB without any extraneous catalyst; and a PNVC-AB nanocomposite can be isolated from the system. The composite possesses high dc conductivity and enhanced thermal stability compared to PNVC homopolymer.⁶

While extending the above procedures for polymerization vis-a-vis composite formation between AB and vinyl polymers such as PMMA, polyacrylonitrile (PAN)^{7,8} it was noted that unlike NVC, acrylonitrile (AN) or methyl methacrylate (MMA) monomers could not be bulk polymerized by AB alone. We, therefore, modified the procedure in which MMA or AN monomers were dissolved in aqueous medium in which acetylene black was kept dispersed by sonication and nanocomposites of PMMA-AB and PAN-AB could be isolated.

To prepare polystyrene-acetylene black nanocomposite (PS-AB) we used the emulsion polymerization process since styrene monomer is insoluble in water. Sodium dodecyl sulphate (NaDS) was used as an emulsifier and K₂CrO₄ and NaAsO₂ were used as the redox initiator. Details of these procedures and bulk property characterizations of the PS-AB nanocomposite are highlighted in this article. It may be of interest to point out here that Choi *et al.*¹ reported the preparation of carbon nanotube (CNT) adsorbed polystyrene and PMMA microspheres by using nanotubes sonicated in aqueous solutions of the surfactants to which PS or PMMA microspheres were dropped. The conductivity values of

2×10^{-4} – 3×10^{-5} S/cm were observed for CNT adsorbed on PS microspheres using cetavelon or sodium dodecyl sulphate as surfactant respectively.

EXPERIMENTAL

Materials

Styrene monomer was freed from inhibitor by washing with 5% NaOH solution, followed by distilled water, and after drying over anhydrous sodium sulphate was finally fractionated. Potassium chromate (Riedel, Germany) and sodium arsenite (Riedel, Germany) were used as the oxidant and the reductant respectively. Acetylene black (SENKA India, Chennai, India) was preheated by heating at 120 °C for 2 h in vacuum prior to use. All other solvents were of analytical grade and were freshly distilled before use.

Polymerization of Styrene Monomer with K₂CrO₄-NaAsO₂ Redox System. 0.5 gm sodium dodecyl sulphate was dissolved in 30 mL of distilled and deaerated water taken in a Pyrex flask for about 15 min. To this solution 1.5 mL of styrene was injected. Then the system was stirred at ambient temperature under nitrogen atmosphere for about 1 h. Thereafter 0.1 g of K₂CrO₄ was added and stirred for 5 min and 0.3 g NaAsO₂ was added into this solution. The polymerization reaction was continued for 3 h. The white polymer obtained was centrifuged, washed successfully with distilled water and methanol, and finally dried under vacuum for about 12 h.

Preparation of Polystyrene-AB (PS-AB) Composite. 0.5 gm sodium dodecyl sulphate was dissolved in a 30 mL of distilled and deaerated water taken in a Pyrex flask for about 15 min. To this solution 1.5 mL of styrene was injected. Then the system was stirred at ambient temperature under nitrogen atmosphere for about 1 h. To this solution, varying amounts of AB were added (Table I). The system was kept under stirring for 30 min to make a suspension of AB. Thereafter 0.1 g of K₂CrO₄ was added and stirred for 5 min and 0.3 g NaAsO₂ was added into this solution. The polymerization reaction was continued for 3 h. The whole mass was poured into an excess of MeOH. The separated black mass was filtered and washed with MeOH to remove any unreacted monomer followed by acetone successively and dried under vacuum at 100 °C for 12 h and subsequently characterized as the PS-AB nanocomposite.

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Table I. Some typical data on polymerization of styrene, polystyrene-AB composite formation^a and dc conductivity values

| Entry No. | Reactants | | Weight (g) of composite | Products | | Conductivity (S/cm) |
|-----------|-------------------|------|-------------------------|--|------------------------------|-------------------------|
| | Weight (g) of | | | Weight (g) of PS in the composite ^b | AB/PS(w/w) in the composites | |
| | Styrene | AB | | | | |
| 1 | 1.57 ^a | 0 | 1.1 | — | — | 10^{-12} – 10^{-16} |
| 2 | 1.57 | 0.11 | 1.40 | 1.29 | 0.08 | 0.117 |
| 3 | 1.57 | 0.23 | 1.41 | 1.18 | 0.19 | 0.324 |
| 4 | 1.57 | 0.32 | 1.54 | 1.22 | 0.26 | 0.481 |
| 5 | 1.57 | 0.41 | 1.60 | 1.19 | 0.34 | 1.33 |

^aDensity of styrene = 1.05 g/cc; wt. of styrene = 1.575 g/cc. Experimental conditions: Wt of K_2CrO_4 = 0.1 g; $NaAsO_2$ = 0.3 g; Volume of solvent = 30 mL; Temperature = 110 °C; Time of reaction = 8 h. ^bPS loading in the composite = (column 4-column 3).

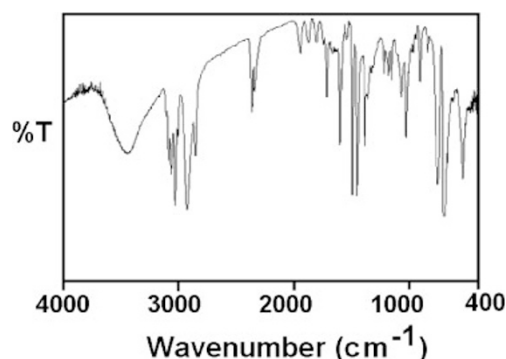


Figure 1. The FT-IR spectrum of the polymer isolated from PS-AB composite.

Characterization and Property Evaluation. The FT-IR spectrum of the mass extracted from PS-AB composite was taken on a JASCO-680 plus instrument in pressed KBr pellet. Dispersions of Free PS resin and PS-AB composites in 2-propanol were microsprayed on a mica substrate. The samples were sputter coated with gold layer and ULTRA 55-36-11 scanning electron microscope was used to take the micrographs. Direct current (dc) resistivity measurements were conducted on pressed pellets (13 mm diameter, 0.1 mm breadth) with silver coating, using four-probe technique. The unit manufactured by Scientific Equipment and Services, Roorke, India, comprised a low constant current source (Model LCS-02), a digital microvoltmeter (Model DMV-001) and a PID controlled oven (Model PID-200).

RESULTS AND DISCUSSION

The composite was isolated as a blackish powdery mass characteristically different from PS homopolymer which exist as a tacky mass. Table I presents some quantitative data on the polymerization vis-a-vis composite formation under the experimental condition used.

The incorporation of PS in the composite was endorsed by the FT-IR spectrum (Figure 1) of the mass recovered after refluxing the PS-AB composite in toluene and precipitating the polymer by methanol addition matches with the same for polystyrene homopolymer. The major characteristic vibration

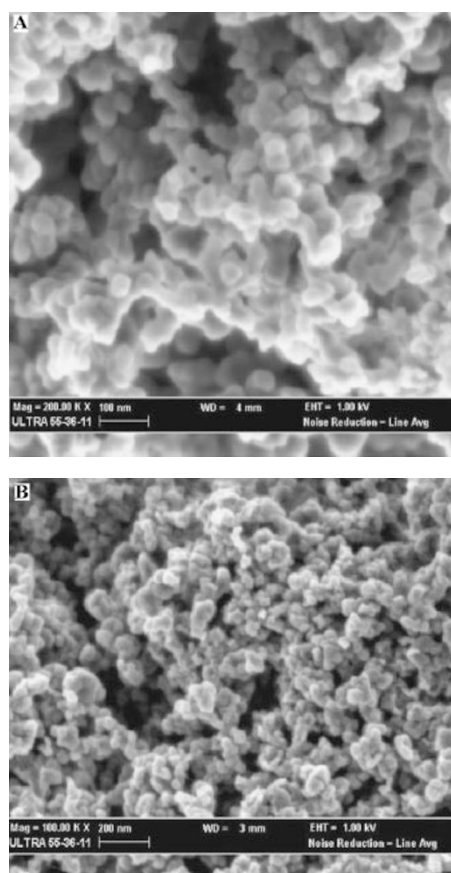


Figure 2. Scanning electron micrographs of (A) PS homopolymer, (B) PS-AB composite.

bands in Figure 1 agree very convincingly with the literature data for polystyrene;⁹ ~ 3025 – 3060 cm^{-1} (aromatic C-H stretching); ~ 2920 – 2850 cm^{-1} (Aliphatic C-H stretching); 1450 – 1490 cm^{-1} (in plane bent-stretching phenyl ring) and 700 cm^{-1} (out of plane phenyl ring); 750 cm^{-1} (out of plane hydrogen). The broad absorption around 3500 cm^{-1} is due to some contamination. (alcohol)

Scanning electron micrographs of PS (Figure 2A) show existence of spherical particles with average sizes in 50–70 nm range calculated over a wide cross-section of the micrograph. The corresponding SEM for PS-AB (Figure 2B) shows the

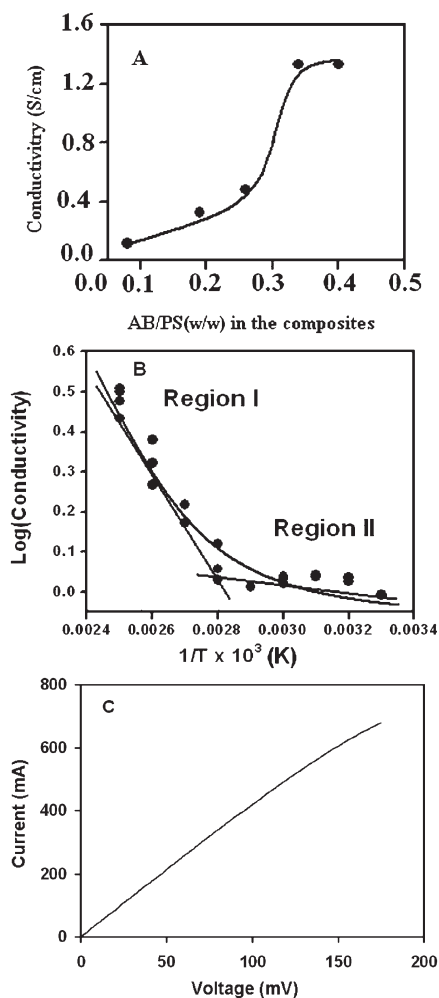


Figure 3. Conductivity characteristics of (A) PS-AB composite as a function of AB loading, (B) Log (Conductivity)- $1/T$ (Kelvin) curve of the PS-AB composite, (C) Current-voltage (I-V) curve for PS-AB composite.

formation of discrete aggregates of particles with sizes in the 140–160 nm range. Evidently in the composite AB nanoparticles must have been cemented together by the PS moieties during polymerization. This is reflected in the larger aggregate sizes manifesting in the composites.

Figure 3A shows that the room temperature conductivity of the PS-AB composites increases initially with increasing AB:PS (w/w) ratio in the composite and tends to level off with AB amounts 0.4 to 0.5 in the initial feed under the conditions followed in the experiments. Since PS is highly non-conducting the conductivity of pure AB (3.7 S/cm) will never be realized in the composite. Log (conductivity) vs. $1/T$ plot (Figure 3B) for PS-AB (entry 4 in Table I) shows a change of slope implying presence of intrinsic conduction (region I) and

extrinsic conduction (region II).¹⁰ The latter is usually observed in semiconductor systems due to impurity defects.¹¹ The activation energy of intrinsic conduction as calculated from the slope in region I is estimated to be 0.008 eV/mol. Relevantly we recently realized¹² a similar activation energy value for a polyacrylamide-AB nanocomposite. For graphite, literature suggests a value of 0.005 eV/mol.¹¹ Hence the value realized in AB based nanocomposites of PS or PAA systems appears to be reasonable. As observed with other AB based systems and also metal oxides/13X-zeolite based systems of PPY, PANI, PF⁸ and PNVC^{6,13} the current-voltage variation (Figure 3C) in PS-AB composite is linear implying metallic behaviour.¹⁰ It may be relevant to add here that the conductivity of the PS-AB composites prepared in this work is significantly higher than the CNT-PS composites reported by Choi *et al.*¹

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