

Conducting Nanocomposites of Polyacrylamide With Acetylene Black and Polyaniline

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A conducting nanocomposite of polyacrylamide (PAA) with acetylene black was prepared via $\text{Na}_2\text{AsO}_3\text{-K}_2\text{CrO}_4$ redox initiated polymerization of acrylamide in water containing a suspension of acetylene black. FTIR analyses confirmed the presence of PAA in the nanocomposites. The composite possessed lower thermal stability than AB and exhibited three stages of decomposition upto 430°C . DSC thermogram revealed three endotherms due to minor thermal degradation (at $\sim 100^\circ\text{C}$), melting and decomposition (at $\sim 230^\circ\text{C}$) and major decomposition (at $\sim 430^\circ\text{C}$). TEM analyses indicated the formation of globular composite particles with sizes in 30–70 nm range. In contrast to the very low conductivity of the base polymer the composite showed a dramatic increase in conductivity (0.19–6.0 S/cm) depending upon AB loading. Log (conductivity) $-1/T$ plot showed a change in slope at $\sim 127^\circ\text{C}$ indicating the manifestation of an intrinsic conductivity region and an impurity conductivity region. The activation energy for conduction as estimated from the slope of region I was 0.008 eV/mol. The C–V plot was linear showing a metallic behavior. For comparison in conductivity PAA-polyaniline composite was also prepared which however displayed much lower conductivity values. POLYM. COMPOS., 30:490–496, 2009. © 2008 Society of Plastics Engineers

INTRODUCTION

Polymer based nanocomposite materials have been receiving wide research attention in view of their many unique and distinctive physico-chemical and opto-electronic properties [1]. In this regard mostly speciality polymers-like polyaniline(PANI), polypyrrole (PPY), polythiophene (PTP), polyfuran (PF), and poly-*N*-vinylcarbazole (PNVC) have been extensively used as the polymer component with montmorillonite clay (MMT) [2], nanodimen-

sional metal oxides such as silica [3], manganese(iv)dioxide[4], alumina [5, 6], and vanadium pentoxide xerogel [7–10] as the other components.

Further improvement of the properties mainly conductivity of many of these polymer-metal oxide/MMT nanocomposites was achieved via loading of conducting polymers on the already formed composites. PANI or PPY encapsulated binary polymer composites, of PNVC-MMT/oxide, PF-MMT/oxide are some typical examples in this respect [1, 5, 6, 11].

Among the carbon allotropes, expensive varieties like Buckminsterfullerene (BMF) [12] and more recently carbon nanotubes [13] (MWNT and SWNT) were used for nanocomposite preparation with PNVC. These composites exhibited high dc conductivity values and improved thermal stability compared to the respective base polymer. Nanocomposites of polystyrene (PS) or poly methylmethacrylate (PMMA) with MWNT and SWNT were prepared and explored for their electro rheological properties [14].

In view of the difficulty of ready availability of CNTs and BMF, vis-a-vis their high processing cost any cheaper alternative for the CNT component would be worth exploring. In this regard, we have successfully used one cheap and abundant variety of carbon namely acetylene black (AB) as the nanocomponent in place of CNTs to prepare conducting nanocomposites of polymers-like PNVC [15], PMMA [16] or polyacrylonitrile (PAN) [17]. Earlier Ray and Biswas [18] reported on the composites of PNVC with carbon black (CB) but AB is preferable being reportedly the purest form of CB with well-defined particle sizes in the nanometer range [15, 16, 19].

Polyacrylamide (PAA) is another water soluble polymer with a wide range of industrial applications as flocculants, rheology-control agents, drag-reducing polymers, and adhesives [20]. However, attempts to broaden the scope of application of this polymer appear to be meager. A relevant work [21] described the preparation of PAA-PANI composite by polymerizing ANI in aqueous medium containing ammonium perdisulfate. The composite could be used as electrodes in secondary batteries. Conductive (10^{-5} S/cm) blends of PAA-PANI were also prepared [22].

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TABLE 1. Some typical data on PAA homopolymer formation.^a

Entry no.	Initial feed weight (g)			Yield of polymer	
	K ₂ CrO ₄	AA	NaAsO ₂	g	%
1	0.03	1.4	0.03	0.14	10
2	0.03	1.4	0.06	0.41	29
3	0.03	1.4	0.09	0.60	43
4	0.03	1.4	0.12	0.87	62
5	0.05	1.4	0.05	0.374	27
6	0.05	1.4	0.10	0.61	43
7	0.05	1.4	0.15	0.98	70
8	0.05	1.4	0.20	1.1	79
9	0.05	1.0	0.20	0.75	75
10	0.05	1.0	0.20	0.74	74

Viscometric molecular weight = 7.6×10^4 (in water).

^a Experimental conditions: Volume of solvent = 7.5 mL; Room temperature = 23°C. Time of polymerization = 1.5 hr.

In the above background we have now developed appropriate procedures for the modification of PAA via composite formation with AB. Significantly, our methods produce a highly conducting nanocomposite of PAA-AB (6 S/cm), the conductivity depending upon the AB loading. Further for comparing the relative efficiency of modification of PAA by AB on conductivity in specific we have also prepared a PAA-PANI composite by an interesting and simple technique. Details of these preparations along with the results of evaluation of structural, morphological, and conductivity characteristics of these composites are highlighted in this article.

EXPERIMENTAL

Materials

Acrylamide (AA) (Aldrich, 97%) was dried at 70°C in vacuum for 12 hr prior to use. Aniline (Merck, Germany) was distilled at the boiling temperature under reduced pressure and stored in a dark cool place before use. Acetylene Black (SENKA India, Chennai, India) was preheated by heating at 120°C for 2 hr in vacuum prior to use for polymerization and composite formation with polymers. Potassium chromate (K₂CrO₄) (Riedel, Germany) and sodium arsenite (NaAsO₂) (Riedel, Germany) were used as such. All other solvents were of analytical grade and were freshly distilled before use.

Polymerization of AA by K₂CrO₄-NaAsO₂ Redox System

A known amount (Table 1) of K₂CrO₄ was dissolved in 10 mL deaerated distilled water taken in a 50 mL Pyrex flask to which a known amount of AA was added. The system was kept under stirring at ambient temperature for 5 min. To this solution, a known amount of NaAsO₂ was dissolved. The induction periods were within

3–5 min and the polymerization was allowed to continue for 2–3 hr without stirring. Thereafter, the liquid was poured in excess of methanol, when a white polymer was obtained which was filtered under suction and washed with methanol and finally, dried in vacuum for 12 hr.

Preparation of Polyacrylamide-Acetylene Black Composite by K₂CrO₄-NaAsO₂ Redox System

Deaerated distilled water (7.5 mL) were taken in a 50 mL Pyrex flask along with 1 mL of methanol. To this, varying amount of AB was added (for detailed data vide Table 2). The mixture was stirred to make a good suspension of AB. One gram of AA was added and stirring was continued. Then 0.05 g K₂CrO₄ was added and the system was stirred at ambient temperature. Finally 0.20 g NaAsO₂ was added and the solution was stirred for 5 min. The polymerization was continued for 1.5 hr without stirring. The whole mass was poured into an excess of methanol. The precipitated black mass was filtered under suction, washed with methanol followed by acetone and finally dried under vacuum at 70°C for 12 hr to constant weight.

Preparation of Polyacrylamide-Polyaniline Composite

K₂CrO₄ (0.05 g) was dissolved in 7.5 mL of deaerated distilled water taken in a 50 mL Pyrex flask. To this, 1.0 g AA was added and the solution was stirred to homogenize. Finally, 0.20 g NaAsO₂ was dissolved. The induction periods were within 3–5 min and the polymerization was allowed to continue for 1.5 hr without stirring. After completion of polymerization of AA, a known volume (~1.5 mL) of HCl was added to the solution to maintain 2(N) acid strength. Then varying amounts of ANI (for detailed data vide Table 3) were injected into the solution. The solution mixture was then continuously stirred for 1.5 hr at ambient temperature. The whole green mass was poured into an excess of methanol. The precipitated mass was filtered under suction and washed with methanol followed by acetone and dried under vacuum at 70°C for 12 hr to constant weight.

TABLE 2. Some typical data on the PAA-AB composite formation.^a

Entry no.	Initial feed		Weight (g) of composite	wt % of AB loading ^b per g of the composite
	Weight of AA (g)	Weight of AB (g)		
1	1.0	0.10	0.54	18
2	1.0	0.15	0.63	24
3	1.0	0.20	0.64	33
4	1.0	0.30	0.66	45

^a Experimental conditions: Wt. of K₂CrO₄ = 0.05 g; NaAsO₂ = 0.2 g; Reaction time = 3 hr; Volume of solvent = 9 mL; Room temperature = 23°C.

^b AB loading per g of composite = (column 3/column 4) × 100.

TABLE 3. Some typical data on the PAA-PANI composite formation.^a

Entry No.	Initial feed		Product			wt % of PANI loading ^d per g of the composite
	Weight of AA (g)	Weight of aniline (g)	Weight of composite (g)	Weight of PAA ^b (g)	Weight of PANI ^c (g)	
1	1.0	0.10	0.83	0.74	0.09	11
2	1.0	0.20	0.88	0.74	0.14	16
3	1.0	0.30	0.92	0.74	0.18	20
4	1.0	0.40	0.98	0.74	0.24	24
5	1.0	0.50	0.99	0.74	0.25	25

^a Experimental conditions: Wt. of K₂CrO₄ = 0.05 g; NaAsO₂ = 0.2 g; Reaction time = 3 hr. Volume of solvent = 9 mL; Room temperature = 24°C.

^b Vide entry nos. 9 and 10 of Table.1.

^c Wt of PANI(g) = (column 4 – column 5).

^d PANI loading per g of composite = (column 6/column 4) × 100.

Physicochemical Characterizations

The prepared polymer and the composites were characterized in respect of their structure and physicochemical properties. Fourier Transform Infra-Red (FTIR) Spectral Analysis was performed on a JASCO –680 PLUS instrument using KBr (dried at 100°C prior to use) pellets. The intrinsic viscosity (η) of PAA homopolymer was determined with an Ostwald viscometer in water for PAA at 22°C. The molecular weight of the homopolymer was calculated by using Ueberreiter–Springer equation [23].

$$[\eta]_{\text{PAA}} = 4.9 \times 10^{-3} \times [M]^{0.8} \text{ (water)}$$

Thermogravimetric (TG/DSC) analyses were performed on a Netzsch, Germany model STA 449C instrument under nitrogen at a heating rate of 10°C min⁻¹. The direct current (dc) conductivity values of the pressed pellets (13 mm diameter, 0.1 mm breadth) of the various samples (homopolymer, composites) were measured at room temperature and also at higher temperature using four-probe technique. The unit manufactured by the 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

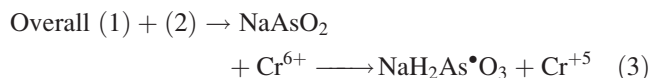
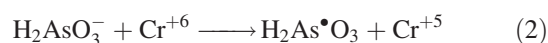
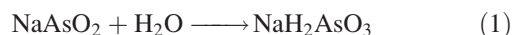
General Features

Polymerization of Acrylamide. Among many redox combinations, K₂CrO₄-NaAsO₂ system afforded a kinetically feasible system for the facile polymerization of AA in aqueous medium. An additional reason for choosing Cr⁺⁶ as an oxidant was our observation that the aqueous polymerization of some specialty monomers such as pyrrole (PY) and aniline (ANI) could be induced by this oxidant. This feature was in fact utilized for the preparation of PAA-PANI composite. Table 1 presents some typical data on the PAA homopolymer formation.

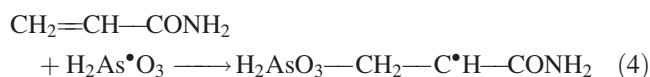
Mechanism of Polymerization of AA. The aqueous polymerization of AA could not be induced by Cr⁺⁶ or AsO₂⁻ alone under ambient and higher temperature condition. Polymerization occurred only when both constituents were present in the reaction mixture. At the end of polymerization the liquid was poured in excess of methanol to get a precipitate of the homopolymer and the conversion percentage was determined gravimetrically. According to Smedley and Kinniburgh [24] when NaAsO₂ is dissolved in water, the reaction occurs as shown in Eq. 1, in the pH range of 8–9.

It has been well established [25] that the anion H₂AsO₃ possesses a pyramidal structure with one lone pair on the arsenic (As) atom. On addition of Cr⁺⁶, reduction activation [26] via the oxidizing metal ion Cr⁺⁶ and the reducing H₂AsO₃⁻ ion leads to a single electron-transfer reaction, as shown in Eq. 2 with the free radical on the As atom. Thus the probable polymerization pathway may be represented as follows.

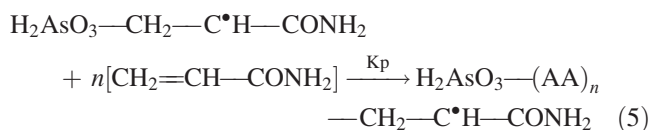
Radical Formation



Initiation



Propagation



Termination can involve either coupling

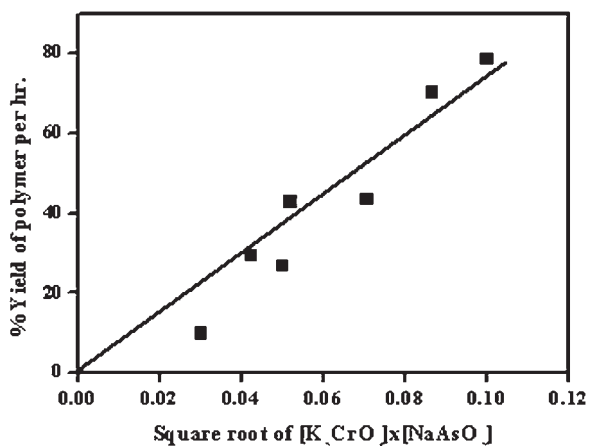
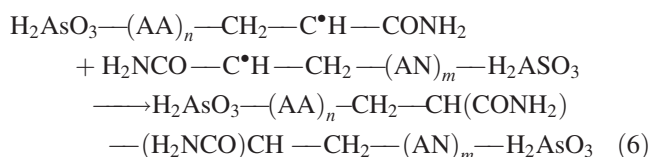
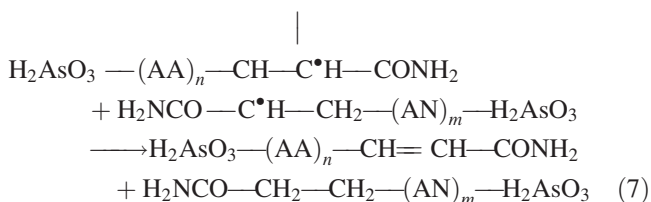


FIG. 1. Plot of initial rate versus the square root of the product of $[K_2CrO_4]$ and $[NaAsO_2]$.



or Disproportionation



Kinetics of Polymerization. On the basis of the aforementioned mechanism, the following expression for R_p may be derived for steady-state conditions:

$$R_i = \text{constant } [NaAsO_2][Cr^{+6}] \quad (8)$$

$$R_t = \text{constant } [H_2AsO_3-CH_2-CH^{\bullet}-CONH_2]_n^2 \quad (9)$$

Under steady-state conditions

$$R_i = R_t$$

$$\text{So that } [H_2AsO_3-CH_2-CH^{\bullet}-CONH_2]_n^2 = \text{constant } [NaAsO_2][Cr^{+6}]$$

$$\text{or } [H_2AsO_3-CH_2-CH^{\bullet}-CONH_2]_n = \text{constant } \sqrt{[NaAsO_2][Cr^{+6}]} \quad (10)$$

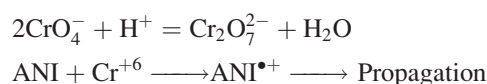
At constant AA concentration

$$R_p = \text{constant } \sqrt{[NaAsO_2][Cr^{+6}]}$$

Figure 1 shows the plot of initial rate versus the square root of the product of $[NaAsO_2][K_2CrO_4]$.

Composite Formation Between Polyacrylamide-Acetylene Black. Table 2 presents some results on the polymerization of AA vis-a-vis composite formation of PAA with AB. It was possible to vary the composite composition hence the percentage of conductive component loading in the composite by altering the initial feed composition.

Composite Formation Between Polyacrylamide-Aniline. Table 3 presents some relevant data on polymerization and composite formation in the AA-ANI polymerization system. It should be pointed out in this context that Pron et al. [27] reported the oxidative polymerization of ANI in 2M HCl solution of K_2CrO_4 . In the present system the observed polymerization of ANI by K_2CrO_4 could occur via $Cr_2O_7^{2-}$ ions formed in the system as follows:



FTIR Spectral Characteristics

The FTIR spectroscopic analyses (Fig. 2) of the prepared homopolymer showed the presence of strong carbonyl peaks at $1,679 \text{ cm}^{-1}$ and the broad amide peak at $3,422 \text{ cm}^{-1}$ which matched with the reported FTIR spectrum for PAA [28]. The presence of PAA in the PAA-AB was supported by the appearance of FTIR (Fig. 2) peaks

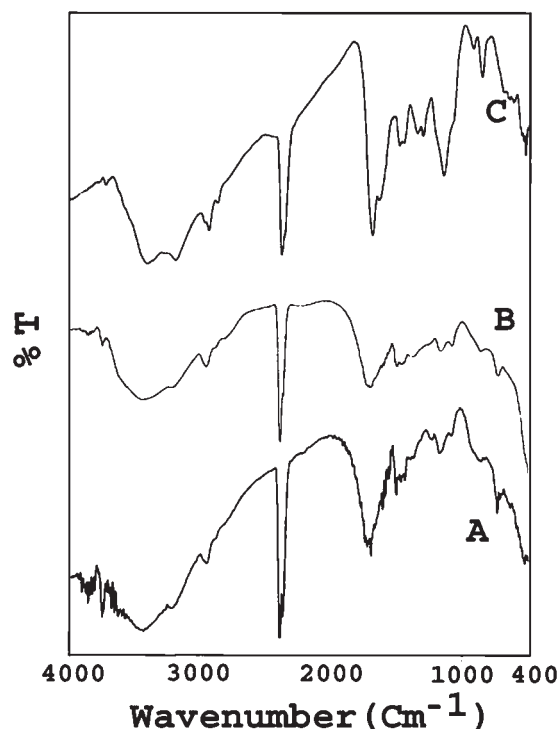


FIG. 2. The FTIR spectrum of (A) PAA homopolymer, (B) PAA-AB composite, (C) PAA-PANI composite.

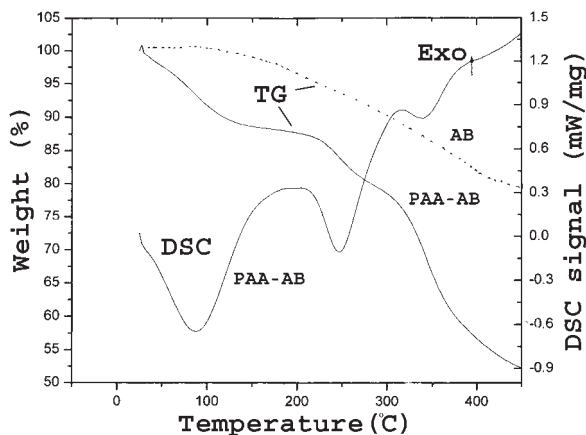


FIG. 3. TG and DSC thermograms of PAA-AB composite.

(cm^{-1}) at 1,679 (carbonyl) and 3,422 (amide) which matched with the reported FTIR spectrum for PAA. Figure 2 also presents the FTIR spectrum for the PAA-PANI composite. The peaks in cm^{-1} at 1,240–1,384 (C–N stretching vibration), 1,487–1,590 (N–H bending vibration), 3,425 (NH stretching vibration) confirmed the formation vis-a-vis presence of PANI [29, 30] in the PAA-PANI composite.

Thermogravimetric Stability

Figure 3 shows TGA and DSC thermograms of PAA-AB composite. TG clearly shows that weight loss occurs in three stages located between 0 and 150°C (~12% wt loss), 150 to 230°C (~10% wt loss) and between 230 and 450°C (~40% wt loss). The observed trend is consistent with the reported 3 step weight loss of PAA homopolymer around 100, 200, and 340°C respectively [31]. The DSC thermogram shows the occurrence of three endotherms at ~ 100, 250, and at 330°C respectively. The first endotherm should imply some degradation apart from any moisture loss which should not produce any DSC peaks. In line with the observation of Beretta and coworkers [32], the sharp endotherm at 250°C is due to melting and decomposition, the reported T_m for PAA being 270°C [32]. The third DSC peak at 330°C is attributable to extensive thermal degradation process accounting for major weight loss (~40%).

The thermogram for AB is shown in the dotted line in Fig. 3. The composite PAA-AB exhibits lower stability because of presence of less stable PAA moiety in the system. This feature is a typical one as observed in many systems [1].

Morphological Features of PAA-AB and PAA-PANI Composite Systems

Transmission electron micrograph of PAA-AB (Fig. 4A) reveals the presence of spherical aggregate of particles which resulted from the encapsulation of nanosized

AB particles by the precipitating PAA moieties. The average size of the particle as estimated from the measurement of the sizes of the composite particles present across the entire cross-section of the micrograph has been estimated to be in the range of 30–70 nm, which endorse the claim of nanocomposite formation in PAA-AB composite.

TEM pattern for PAA-PANI is shown in Fig. 4B. The composite is seen to comprise PAA chain of spherical particles covered by the dark shaded PANI moieties precipitated on to the PAA moieties. Such morphology is more clearly visible in the enlarged section of the micrograph (inset of Fig. 4B). The scenario corresponds to a PANI loading during one single experiment. The encapsulation is not homogeneous as seen in the micrograph.

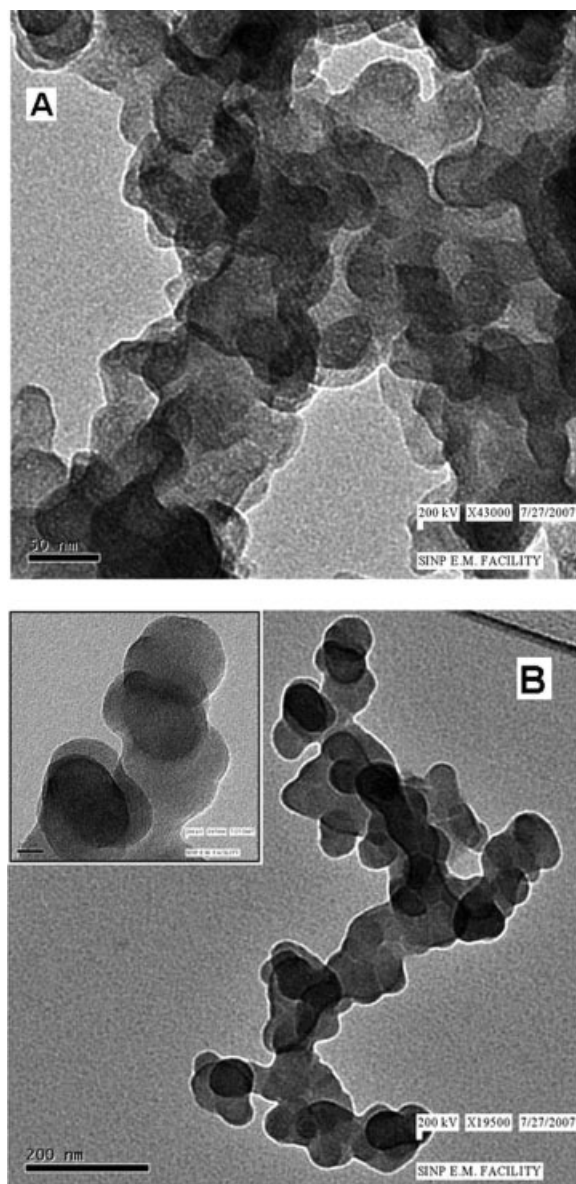


FIG. 4. Transmission electron micrographs of (A) PAA-AB composite, (B) PAA-PANI composite (Inset: an enlarged section of the micrograph of B).

However, repeated loading by PANI in multiple polymerization of ANI onto the PAA moieties could render the loading more uniform. The average size of the PAA-PANI composite particle evaluated as before with measurement across the entire micrograph fall in the range of 70–100 nm. The higher particle size of PAA-PANI compared to PAA-AB is reasonable because the particle size of PANI is larger than that for AB. Literature values for the particle size from TEM analysis of PANI-SiO₂/ZrO₂/MnO₂ composites are in the range 100–300 nm [1].

Conductivity Characteristics

Table 4 presents the dc conductivity values of PAA-AB and PAA-PANI composites with varying AB and PANI loading respectively. PAA homopolymer is essentially a nonconducting polymer. Interestingly, conductivity of the PAA-AB composite increased with increasing weight percentage of AB in the composite (Table 4). At ~18% AB content, the conductivity of the PAA-AB composite was increased ~10¹³-fold compared to that of PAA homopolymer. Figure 5A presents current-voltage variation in the composite which confirms the Ohmic behavior of the composite at room temperature. Figure 5B shows the log(conductivity) versus 1/T plot for the PAA-AB composite. The region of intrinsic conductance for PAA-AB extends upto ~127°C (region I in Fig. 5B) beyond which (region II in Fig. 5B) the conductance is possibly attributable to impurity conductivity [33]. The activation energy for conduction (intrinsic) as given by the slope of region I in Fig. 5B has been estimated to be ~0.008 eV/mol. Interestingly literature value [33] for activation conduction energy in graphite is in the order of 0.005 eV/mol [33].

Table 4 presents some DC conductivity data for the various PAA-PANI composites. Entries 5–8 confirmed that the conductivities of the PAA-PANI composite increased with increasing PANI loading in the composite. Figure 6 shows the Ohmic behavior of the PAA-PANI composite.

TABLE 4. DC conductivity values of some PAA-AB and PAA-PANI composites.

Entry no.	Composites		Conductivity (S/cm)
	Polymer	Components ^a	
1	PAA	AB ^b (18)	0.19
2	PAA	AB (24)	0.90
3	PAA	AB (33)	2.82
4	PAA	AB (45)	5.79
5	PAA	PANI (11)	3.2×10^{-4}
6	PAA	PANI (16)	1.8×10^{-3}
7	PAA	PANI (20)	3.8×10^{-3}
8	PAA	PANI (24)	5.3×10^{-3}

^a Values in parenthesis represent respective weight percent of the components in the composites.

^b DC conductivity (RT) for AB = 3.6 S/cm.

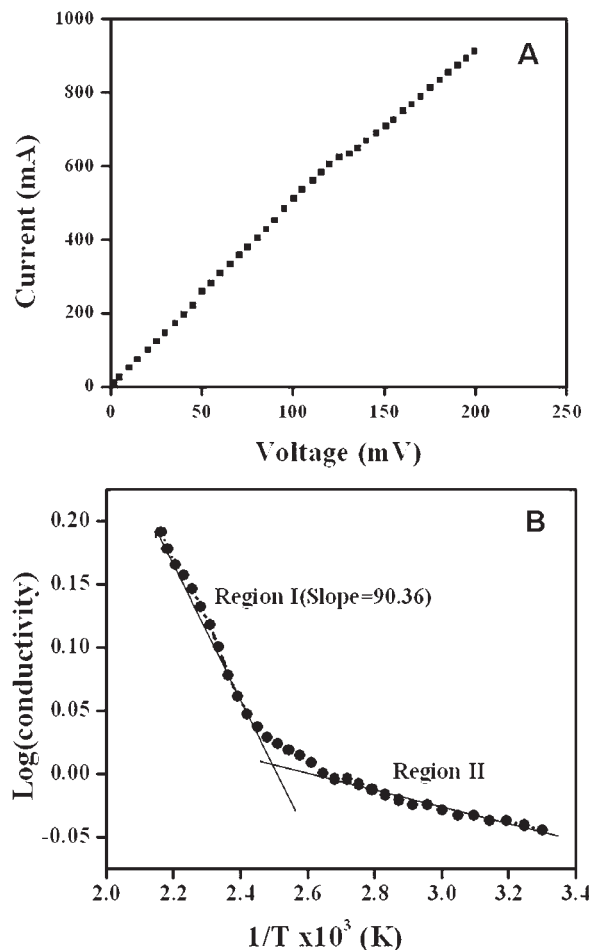


FIG. 5. (A) Current-voltage curve of the PAA-AB composite, (B) Log (Conductivity)-1/T (Kelvin) curve of the PAA-AB composite.

CONCLUSIONS

Suitable procedures were developed for the preparation of nanocomposites of PAA with acetylene black (PAA-AB) and with polyaniline (PAA-PANI) respectively. TG

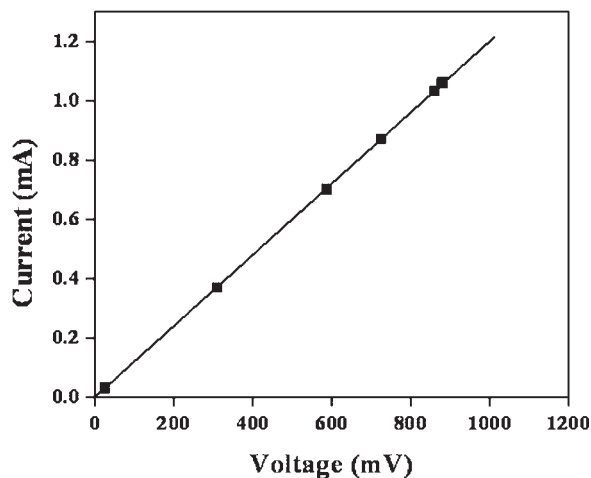


FIG. 6. Current-voltage curve for PAA-PANI composite.

analysis indicated a three stage decomposition mode for the PAA component in the composite. DSC analysis confirmed three endotherms signifying minor degradation and moisture loss, melting and major degradation of the PAA component in the nanocomposite. The dc conductivity of PAA-AB composite varied in the range of 0.19–6.0 S/cm depending upon AB loading. Activation energy for conduction (intrinsic in PAA-AB) was estimated to be 0.008 eV/mol. The magnitude of conductivity of PAA-AB was appreciably higher than that for PAA-PANI composite ($0.3\text{--}5.3 \times 10^{-3}$ S/cm) which also depended on the extent of PANI loading.

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REFERENCES

1. A. Maity and M. Biswas, *J. Ind. Eng. Chem.*, **12**, 311 (2006) and references cited therein.
2. S.S. Ray and M. Biswas, *Adv. Polym. Sci.*, **155**, 167 (2001), and references cited therein.
3. S.P. Armes, S. Gottesfeld, J.G. Beery, F. Garzon, and S.F. Agnew, *Polymer*, **32**, 2325 (1991).
4. S.S. Ray and M. Biswas, *Synth. Met.*, **105**, 99 (1999).
5. (a) N. Ballav and M. Biswas, *Polym. Int.*, **52**, 179 (2003); (b) N. Ballav and M. Biswas, *Polym. Int.*, **53**, 1467 (2004).
6. (a) A. Maity and M. Biswas, *J. Appl. Polym. Sci.*, **88**, 2233 (2003); (b) A. Maity and M. Biswas, *J. Appl. Polym. Sci.*, **94**, 803 (2004).
7. M.G. Kanatzidis, C.G. Wu, H.O. Marcy, D.C. DeGroot, and C.R. Kannewurf, *Chem. Mater.*, **2**, 222 (1990).
8. M.G. Kanatzidis and C.G. Wu, *J. Am. Chem. Soc.*, **111**, 4139 (1989).
9. C.G. Wu, D.C. DeGroot, H.O. Marcy, J.L. Schindler, C.R. Kannewurf, Y.J. Liu, W. Hirpo, and M.G. Kanatzidis, *Chem. Mater.*, **8**, 1992 (1996).
10. J. Hartreld, H.P. Wong, B.C. Dave, B. Dunn, and L.F. Nazar, *J. Non-Cryst. Solids.*, **225**, 319 (1998).
11. N. Ballav, P. Saha Sardar, S. Ghosh, and M. Biswas, *J. Mater. Sci.*, **41**, 2959 (2006).
12. M. Biswas and S.S. Ray, *Synth. Met.*, **123**, 135 (2001).
13. A. Maity and M. Biswas, *J. Nanosci. Nanotechnol.*, in press.
14. H.J. Jin, H.J. Choi, S.H. Yoon, S.J. Myung, and S.E. Shin, *Chem. Mater.*, **17**, 4034 (2005).
15. N. Ballav, A. Maity, and M. Biswas, *Mater. Chem. Phys.*, **87**, 120 (2004).
16. A. Maity and M. Biswas, *Polym. J.*, **36**, 1 (2004).
17. A. Maity and M. Biswas, *Int. J. Polym. Mater.*, **55**, 175 (2006).
18. A. Ray and M. Biswas, *Polymer*, **34**, 2903 (2004).
19. G.T. Austin, Ed., *Shreve's Chemical Process Industries*, 5th ed., McGraw Hill International Edition, Singapore, 135 (1985).
20. (a) M.B. Hocking, K.A. Klinchuk, and S. Lowen, *J. Polym. Sci. A: Polym. Chem.*, **38**, 3128 (2000); (b) S.T. Lim, H.J. Choi, S.Y. Lee, J.S. So, and C.K. Chan, *Macromolecules*, **36**, 5348 (2003).
21. N.V. Bhat and N.V. Joshi, *J. Appl. Polym. Sci.*, **50**, 1423 (1993).
22. B. Das, S. Kar, S. Chakraborty, D. Chakraborty, and S. Gangopadhyay, *J. Appl. Polym. Sci.*, **69**, 841 (1998).
23. J. Klein and K.-D. Conrad, *Die Macromol. Chemie.*, **181**, 227 (1979).
24. P.L. Smedley and D.G. Kinniburgh, *Appl. Geom.*, **17**, 517 (2002).
25. R. Sarkar, *General and Inorganic Chemistry, Part II*, Books and Allied, India 417 (2001).
26. C.H. Bamford, W.G. Bard, A.D. Jenkins, and P.F. Onyon, *The Kinetics of Vinyl Polymerization by Radical Mechanism*, Butterworths, London, 223 (1958).
27. A. Pron, F. Genoud, C. Menardo, and M. Necheiu, *Synth. Met.*, **18**, 291 (1987).
28. I. Fortenberry and J.A. Pojman, *Polym. Sci.*, **38**, 1129 (2000).
29. A. Maity and M. Biswas, *Polym. J.*, **36**, 10 (2004).
30. G. Socrates, *Infrared Characteristics Group Frequencies*, Wiley, Chichester (1980).
31. S. Shukla, A.K. Bajpai, and R.A. Kulkarni, *J. Appl. Polym. Sci.*, **95**, 1929 (2005).
32. O.G. Freddi, M. Taukada, and S. Beretta, *J. Appl. Polym. Sci.*, **71**, 1653 (1999).
33. A. Tager, *Physical Chemistry of Polymers*, Mir Publishing, Moscow 303, 310 (1972).