A Conducting Nanocomposite of Acetylene Black with Preformed Poly-*N*-vinylcarbazole Crosslinked by Anhydrous FeCl$_3$

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ABSTRACT: A conducting nanocomposite of crosslinked poly-*N*-vinylcarbazole (CLPNVC) with nanodimensional acetylene black (AB) was prepared by oxidative crosslinking of preformed PNVC through pendant carbazole moieties in presence of anhydrous FeCl$_3$ as an oxidant and AB suspension in CHCl$_3$ medium at 65°C. The incorporation of CLPNVC moieties in the CLPNVC-AB composite was endorsed by Fourier transform infrared analysis. Scanning electron microscopic analysis showed formation of lumpy aggregates with average sizes in the 130–330 nm ranges. The thermal stability of the CLPNVC-AB composite was appreciably higher than that of the PNVC-AB composite. The direct current conductivities of the composites were significantly enhanced relative to that of the PNVC homopolymer (10^{-12}–10^{-16} S/cm) and varied in the range of 10^{-4}–10^{-2} S/cm depending on the amount of AB loading in the CLPNVC-AB composite. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 819–824, 2006

Key words: crosslinked poly-*N*-vinylcarbazole; acetylene black; nanocomposite; conductivity; thermal stability

INTRODUCTION

Considerable research interest has been shown lately in the modification of vinyl polymers such as poly-*N*-vinylcarbazole (PNVC), polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), polyacrylamide(PAM), polystyrene (PS), and polyvinylchloride (PVC), with a view to enhance 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 vinyl polymers, such as PNVC, PMMA, and PAN, with conducting speciality polymers like polyaniline (PANI), polypyrrole (PPY), and polythiophene (PTP). Several workers reported[1,2] on the preparation of conducting polymer blends/composites of PPY-polyvinylchlchloride (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 monomer with FeCl$_3$. Ruckenstein and coworkers[4,5] described the preparation and evaluation of PANI/poly(alkylmethylacrylate) and PPY/polyalkyl(methylacrylate) composites with high electrical conductivity (6 S/cm). PTP-based composites were prepared[6] by directly electropolymerizing thiophene monomer from an electrolyte medium containing the dissolved host polymers such as PMMA, PVC, PS, etc. Transparent PVC–PMTP films thus obtained showed conductivities between 10^{-2} and 10^{-1} S/cm. Other types of PTP composites electrogenerated[7] by means of multistep methods were reported, such as PBT-PTP, PTP-PVC, PTP-PS, PTP-poly(bisphenol A carbonate), PTP-, and PMTP-Nafion.

Conducting composites were also prepared[8–10] via encapsulation of polymeric moieties onto nanodimensional metal oxide particles suspended in the reaction medium. In this context, Ray and Biswas[11,12] prepared water-dispersible conducting nanocomposites of vinyl polymer (PNVC) with nanodimentional MnO$_2$ and ZrO$_2$, without any external catalyst. Recently, Wang et al.[13] synthesized a new family of polymer–molybdenum bronze nanocomposites, using an exfoliation/encapsulation methodology. The electrical conductivities of these nanocomposites were in the range of 10^{-2}–10^{-7} S/cm.

In an alternative process, blending of polymers with conducting fillers, like natural graphite flak, carbon black and powders was adopted for preparing electrically conducting composites. In this background, Chen et al.[14] recently prepared conducting PMMA–graphite nanosheet composites via *in situ* polymeriza-

TABLE I
Some Typical Data on Composite Formation[a] Between CLPNVC and Acetylene Black

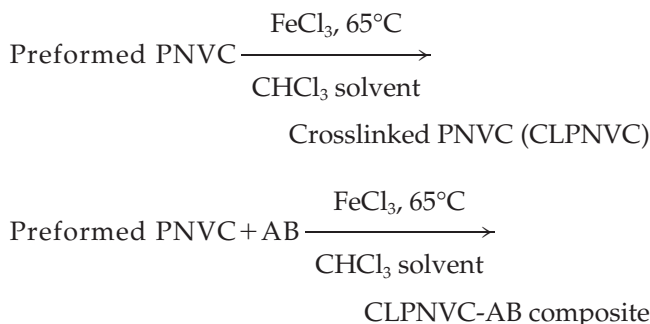| Entry no. | Weight (g) | | Weight (g) of composite | | % Polymer loading[b] per gram of composite |
	PNVC	AB	before reflux with benzene	after reflux with benzene	
1.	0.05	—	0.05	0.05	—
2	0.10	—	0.10	0.095	—
3	0.10	0.04	0.14	0.13	69
4	0.10	0.06	0.16	0.15	60
5	0.10	0.10	0.20	0.195	48
6	0.10	0.20	0.30	0.30	33
7	0.10	0.30	0.40	0.40	25
8	0.05	0.10	0.15	0.15	33
9	0.20	0.10	0.30	0.27	62
10	0.30	0.10	0.40	0.35	71

[a] Composite formation conditions: volume of solvent = 30 mL; temperature = 65°C; weight (g) of $FeCl_3$ for each set = 2 g.
[b] % polymer loading per gram of composite = (Column 5 − Column 3) × 100/Column 5.

tion of methylmethacrylate by benzoyl peroxide in aqueous alcohol mixture in presence of expanded graphite. Biswas et al.[15–18] explored the initiation of the polymerization of the NVC by Orient black (N220), Vulcan XC-72, and carbon black (CB), without any external catalyst. Japanese group reported[19–24] on the preparation of graft vinyl polymer-CB composites in presence of external catalyst. More recently, Maity and Biswas[25,26] also prepared PAN/PMMA–AB conducting composites via K_2CrO_4–$NaAsO_2$ redox polymerization of respective monomers in aqueous–alcohol mixture in which the AB particles were suspended by sonication.

In this background, recently we reported[27] that AB could directly polymerize NVC without any extraneous catalyst, and a nanocomposite of PNVC with AB could be isolated from the system. Although the PNVC-AB composite showed high conductivity value, it was somewhat unstable in the sense that the PNVC could be extracted away by repeated solvent extraction, and furthermore the composite was of limited thermal stability.

We have now been able to improve the above drawbacks of the PNVC-AB composite by deploying a modified procedure schematically shown below

$$\text{Preformed PNVC} \xrightarrow[\text{CHCl}_3 \text{ solvent}]{\text{FeCl}_3, 65°C} $$

Crosslinked PNVC (CLPNVC)

$$\text{Preformed PNVC+AB} \xrightarrow[\text{CHCl}_3 \text{ solvent}]{\text{FeCl}_3, 65°C} $$

CLPNVC-AB composite

The formation of CLPNVC was consistent with the observations of Block et al.,[28,29] Sarac et al.[30] and Bis-

was and Ballav[31,32] CLPNVC exhibited appreciably improved thermal stability over the range 200–1000°C relative to PNVC homopolymer and to PNVC-AB composite. Details of the preparation and the results of evaluation of bulk properties of the CLPNVC-AB composite are highlighted in this article.

EXPERIMENTAL

Materials

N-Vinylcarbazole (BASF, Germany) was recrystallized from *n*-hexane and kept in dark. Acetylene black (SENCO India, Chennai, India) was preheated by heating at 120°C for 2 h in vacuum prior to polymerization. Anhydrous $FeCl_3$ (Merck, Germany) was used as an oxidant. All other solvents were of analytical grade and were freshly distilled before use.

Preparation of PNVC

N-Vinylcarbazole (2 g) was dissolved in 50 mL of $CHCl_3$ and 3 g of anhydrous $FeCl_3$ was added. The system was kept under stirring at room temperature for 3 h, and then the solution was poured into an excess of MeOH. The white mass was filtered and washed abundantly with boiling MeOH[33] in turn, until the washings were free of monomer and of any $FeCl_3$ solution color, followed by acetone and dried at 70°C for 5 h in vacuum. The white PNVC thus obtained was fractionated several times in a benzene–methanol solvent system.

Preparation of crosslinked poly-*n*-vinylcarbazole (CLPNVC)

Preformed PNVC (0.05–0.1 g; entries 1, 2 in Table I) was dissolved in 30 mL of $CHCl_3$. The system was heated to 65°C for 3 min and followed by the addition

of $FeCl_3$ (2 g). The system was kept under reflux at 65°C for 3 h. Then, the separated mass was filtered and washed thoroughly with MeOH and dried at 70°C in vacuum for 5 h.

Preparation of a crosslinked poly-*n*-vinylcarbazole-acetylene black composite (CLPNVC-AB composite)

Preformed PNVC (0.05–0.3 g; entries 3–10 in Table I) was dissolved in 30 mL of $CHCl_3$. To this solution, 0.04–0.3 g of AB was added. The system was kept under stirring for 3 h to make AB suspensions. Thereafter, the system was heated to 65°C for 3 min, followed by the addition of 2 g of $FeCl_3$. The system was kept under reflux at 65°C for 3 h. Then, the separated black mass was filtered and washed thoroughly with MeOH and dried at 70°C in vacuum for 5 h.

The total CLPNVC-AB composite thus obtained was extracted with benzene through continuous refluxing for 1 week at 65°C. The total separated mass was filtered, and the process was repeated at least three times until the extracts did not yield any precipitate with MeOH because of any residual surface adsorbed homopolymer. This residue was finally dried at 80°C for 6 h in vacuum. After various physicochemical characterizations, the composite was confirmed to contain CLPNVC along with AB.

Characterization and property evaluation

The FTIR spectrum of the CLPNVC-AB composite was taken on a JASCO-410 instrument in pressed KBr pellet. Dispersion of CLPNVC-AB composite in 2-propanol was microsprayed on a mica substrate. The samples were sputter-coated with gold layer, and Hitachi *S*-415A scanning electron microscope was used to take the micrographs. Thermogravimetric (TGA/DTA) analyses were performed on a Shimadzu DT-40
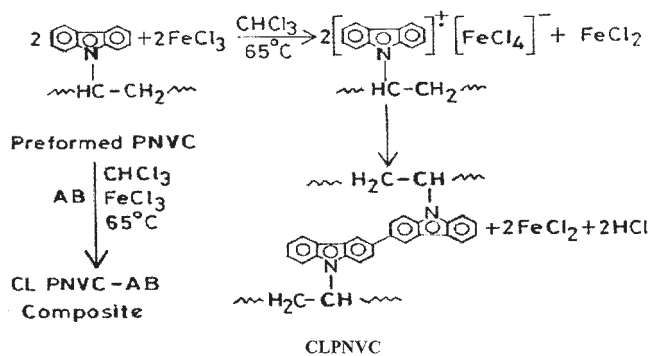
Scheme 1 Formation of CLPNVC and CLPNVC-AB composite.

instrument. XRD pattern of the CLPNVC-AB composite was obtained from a Philips X-ray diffractometer (Cu LFF; 40 kV, 20 mA). Direct current (dc) conductivity measurements were conducted on pressed pellets with silver coating, using four-probe technique.

RESULTS AND DISCUSSION

General features of composite formation

Table I presents some relevant data on the composite formation comprising preformed PNVC and AB particles in presence of $FeCl_3$ as an oxidant in $CHCl_3$ solvent at 65°C. Entries 1, 2 indicate that upon heating in $CHCl_3$ solvent in presence of $FeCl_3$, preformed PNVC normally soluble in common solvents yielded an intractable mass of practically the same weight as that of the polymer in the initial feed. This was due to crosslinking of PNVC via 3–3′ coupling. This feature was fully consistent with the recent observations of Sarac et al.[30] and Biswas and Ballav[31–32] Entries 3–7 indicate that the percent of CLPNVC loading per gram of composite decreased with increase in the amount of

TABLE II
FTIR Bands of CLPNVC-AB Composite with Their Assignments

System	Peaks (cm^{-1})	Assignments
PNVC	721	Ring deformation of substituted aromatic structure
	742	>CH_2 rocking vibration
	1220	Out of plane deformation of vinylidene gr
	1329	>CH_2 deformation of vinylidene gr
	1450	Ring deformation of NVC moieties
	1630	C=C stretching vibration of vinylidene gr
	3060	Aromatic C—H stretching vibration
CLPNVC-AB	724	Ring deformation of substituted aromatic structure
	746	>CH_2 rocking vibration
	1234	Out of plane deformation of vinylidene gr
	1329	>CH_2 deformation of vinylidene gr
	1471	Ring deformation of NVC moieties
	1659	C=C stretching vibration of vinylidene gr
	2939	Aromatic C—H stretching vibration

AB at a fixed amount of preformed PNVC in the initial feed. Further entries 5, 8–10 indicate that the percent of CLPNVC loading per gram of composite increased with increase in weight of preformed PNVC at a fixed amount of AB in the initial feed.

The formation of the CLPNVC-AB composite in the present system may be visualized as follows. The PNVC moieties initially soluble in the reaction medium became insoluble via crosslinking.[28–32] The probable pathway is shown schematically in Scheme 1. In course of the separation of the CLPNVC moieties in the reaction medium in which nanoparticles of AB were finely suspended, the former would quite likely be deposited on the AB suspensoids, thereby forming the CLPNVC encapsulated AB nanocomposite particles. The scenario is essentially similar to what was proposed by Armes and coworkers[8–10] for explaining the formation of PPY/PANI-SiO$_2$ nanocomposites and by Biswas and coworkers[34–40] for the PNVC-SiO$_2$/AlO$_3$, PTP/PPY/PANI-Al$_2$O$_3$, PNVC-PTP/PPY/PANI-Al$_2$O$_3$, PAN/PMMA-SiO$_2$ nanocomposite systems.

FTIR absorption characteristics of CLPNVC-AB composite

Table II summarizes the FTIR spectrum of the PNVC homopolymer and CLPNVC-AB composite along with their band assignments. FTIR peaks at 2939, 1659, 1471, 1329, 1234, 746, and 724 cm^{-1} confirmed the presence of CLPNVC moieties in the composite recovered after repeated extraction with benzene. These observed peaks matched with those reported in the FTIR spectrum for PNVC.[11,12]

Scanning electron micrographic characteristics

Figures 1(a), 1(b), and 1(c) show the scanning electron micrographs (SEM) of the AB, CLPNVC, and CLPNVC-AB composites, respectively. The SEM morphology for AB shows (Fig. 1(a)) the presence of small nearly spherical AB particles with the tendency to form larger lumps (40 nm) randomly distributed on the surface. The formation of discrete lumps with irregular shapes and sizes was clearly visible from the SEM of CLPNVC (Fig. 1(b)). The micrograph of the CLPNVC-AB composite (Fig. 1(c)) revealed the formation of lumpy agglomerates of much larger particles with nonuniform sizes (130–330 nm) and shapes. The formation of such agglomerates could result through cementation of nanosized AB particles with the CLPNVC- a situation similar to the scenario described by Armes and coworkers[8–10] in their PPY/PANI–metal oxide systems in which the nanocomposites were considered to be made up of microaggregates "glued" together by the precipitating PPY/PANI moieties.

(a)

(b)

(c)

Figure 1 SEM of (a) acetylene black (b) CLPNVC, and (c) CLPNVC-AB composite.

Thermal stability characterization

Figure 2 shows the thermograms of CLPNVC-AB and PNVC-AB composites. Interestingly, the former showed a consistently higher thermal stability (less than 10% at 250°C and 50% at 1000°C) than the latter (less than 10% at 250°C and 70% at 1000°C). This trend was justified, since CLPNVC would be expected to
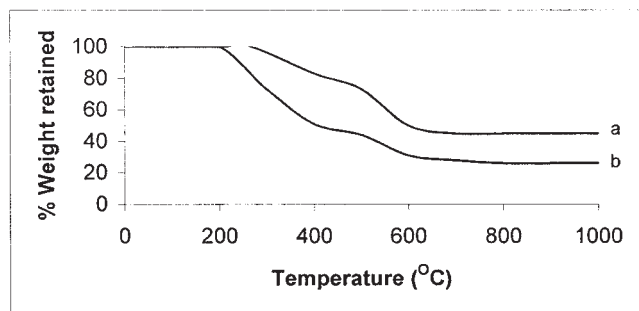
Figure 2 TGA of (a) CLPNVC-AB composite and (b) PNVC-AB composite.

require more thermal energy for degradation of the crosslinked network relative to the uncrosslinked PNVC. Accordingly, the overall stability of the CLPNVC-AB composite would be higher compared to that of the PNVC-AB composite.

XRD studies

XRD analysis for CLPNVC-AB composite prepared in this system revealed that it was essentially amorphous. This is an interesting feature, since PNVC-AB composite reported earlier[27] by us exhibited a highly crystalline pattern. This difference might be due to loss of any crystallinity in PNVC during crosslinking process.

Conductivity characteristics

Table III summarizes the dc conductivity values of the CLPNVC-AB composite along with the corresponding literature data for unmodified PNVC and some modified PNVC-based composites. The dc conductivity values for the unmodified PNVC and CLPNVC-AB composite were in the order of 10^{-12}–10^{-16} S/cm[41] and 10^{-2} S/cm respectively. It is interesting to note that the dc conductivity of the CLPNVC-AB composite

exhibited 10^{10}–10^{14}-fold enhanced conductivity value compared with the base polymer. Entries 2–5 (Table III) show that the dc conductivity of the CLPNVC-AB composite increased with increase in percentage of AB loading in the composite. Thus, at 3% loading of AB in the composite (entry 2), the conductivity increased by 10^7–10^{11}-fold compared to that of PNVC homopolymer while the value progressively increased by 10^3-fold corresponding to a 10-fold increase in the percent of AB loading (entry 4) in the CLPNVC-AB composite. This feature is quite consistent with the reported conductivity enhancement of polymers blended with conducting fillers.

The observed conductivity enhancement in CLPNVC-AB composite is indeed a distinctive feature of the system. It may be recalled that metal oxide (MnO_2 and Al_2O_3) based composite systems of PNVC[11,35] exhibited much lower conductivity values (10^{-5}–10^{-7} S/cm). The metal oxide composites with binary polymers (entries 9, 10, 11, Table III) also showed lower conductivity orders.

CONCLUSIONS

The work establishes that it is possible to improve the thermal stability and dc conductivity of a composite of PNVC with acetylene black via refluxing preformed PNVC and acetylene black in $CHCl_3$ medium in the presence of AB and $FeCl_3$ as an oxidative crosslinking agent. Acetylene black is cheap and abundantly available compared to other conductive fillers and, as such, this procedure should be expected to be of wide scope and potentiality.

TABLE III
Conductivity Values of Some PNVC-Based Composites

Entry	Materials	% of AB loading	Conductivity (S/cm^{-1})	References
1	PNVC (Unmodified)	—	10^{-12}–10^{-16}	[41]
2	CLPNVC-AB	3	10^{-5}	This study
3	CLPNVC-AB	10	10^{-4}	This study
4	CLPNVC-AB	32	10^{-2}	This study
5	PNVC-PPY blend	—	3.3×10^{-6}	[42]
6	PNVC-PPY composite	—	5.0×10^{-2}	[7]
7	PNVC-MMT composite	—	10^{-6}–10^{-5}	[43]
8	PNVC-PTP	—	10^{-4}	[28]
9	PNVC-PPY-Al_2O_3	—	10^{-6}	[33]
10	PNVC-PANI-Al_2O_3	—	10^{-5}	[34]
11	PNVC-PTP-Al_2O_3	—	10^{-7}	[28]

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