

Polymerization of *N*-vinylcarbazole (NVC) by Tungsten Blues (WB) and Evaluation of a Conducting PNVC-WB Nanocomposite Isolated from the System

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ABSTRACT: Tungsten oxide and tungsten blues (WB) prepared by reducing the former with stannous chloride were capable of initiating the bulk polymerization of *N*-vinylcarbazole (NVC) at the melting temperature of the latter (65°C). The polymerizations were initiated by a η^2 -type of complex formation involving π -clouds of vinyl group and the available d-orbitals of W^{6+} ions. A composite of PNVC with WB was isolated and characterized. Formation of PNVC and its incorporation in the composite was confirmed by FTIR, NMR, and UV absorption spectroscopic studies. Scanning electron micrographic analyses of PNVC-WB composite revealed the presence of close packed aggregates comprising particles of average sizes between 100–200nm

range. TGA revealed the thermogravimetric stability trend as WB > PNVC-WB > PNVC. Dc conductivities of PNVC-WB nanocomposite were found to depend on the WB : PNVC weight ratio in the composite and varied from 3.5×10^{-4} (weight ratio 26) to 3×10^{-2} S/cm (weight ratio 100) at room temperature. The threshold WB : PNVC weight ratio for the manifestation of conductivity in the composite was around 25 under the experimental condition of this study. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1371–1377, 2010

Key words: tungsten blues; poly(*N*-vinylcarbazole); nanocomposites; cationic polymerization; solid state polymerization; thermogravimetric analysis (TGA)

INTRODUCTION

Synthesis and evaluation of polymer, transition metal oxide based nanocomposites¹ have received much research attention. Biswas et al. reported in early studies that bulk polymerization of NVC could be initiated directly by some 3d-transition metal oxides with reactivity order as: $V_2O_5 > MnO_2 > TiO_2 > Cr_2O_3 > NiO > ZnO > Cu_2O > CuO > Co_3O_4$.² In subsequent studies that aimed at preparing nanocomposites of polymers with inorganic oxides and particularly with transition metal oxides, speciality polymers like poly(*N*-vinylcarbazole) (PNVC), polypyrrole (PPY), polyaniline (PANI), and polythiophene (PTP) were used in combination with V_2O_5 , MnO_2 , TiO_2 , ZrO_2 .¹ Nanocomposites of PNVC with V_2O_5 , ZrO_2 showed dc conductivities of the order 10^{-5} S/cm, values being 10^7 to 10^{11} fold higher than the conductivity for the unmodified PNVC. A few other reported systems include PANI- MnO_2 ($1-2.5 \times 10^{-2}$ S/cm), PANI- ZrO_2 ($0.03-0.35 \times 10^{-2}$ S/cm), PANI- V_2O_5 ($\sim 10^{-4}-10^{-1}$ S/cm) and PTP- V_2O_5

(0.1 S/cm).¹ Among other novel systems, V_2O_5 -xerogel-PANI system and PPY-FeOCl composite³ via intercalative polymerization of PY monomer with FeOCl have been explored by Kanatzidis et al.⁴ The *in situ* intercalative polymerization of 2,2' bithiophene in layered V_2O_5 , nH_2O xerogel⁴ produced a film of polymer-layered oxide bronze with four orders magnitude higher conductivity with respect to pristine xerogel. Intercalated PANI- V_2O_5 -xerogel bronze⁵ also prepared by Kanatzidis et al. showed enhanced conductivity.

A prominent feature of the chemistry of molybdenum and tungsten is the formation of numerous polymolybdate and polytungstic acid and salts. V, Nb^V, Ta^V, and U^{VI} show comparable behaviour but to a limited extent. The polyacids of molybdenum and tungsten are of two types (a) isopolyacids and their related anions which contain only Mo or W along with oxygen and hydrogen and (b) the heteropolyacids and anions which contain one or two atoms of another element in addition to Mo, W, oxygen, and hydrogen.⁶

Mixed oxide-hydroxide materials called "blue oxides" are obtained by reduction of acidified solutions of molybdates or tungstates with reducing agents like Sn^{II}, SO₂.^{6,7} Because of their nanocrystalline nature the precise structures are not known and the cause of blue color is uncertain. For W^{6+} , in the pH range 5–7.8 species like WO_4^{2-} , $W_6O_{20}(OH)_2^{6-}$, $W_7O_{24}^{6-}$, $HW_7O_{24}^{5-}$ and $H_2W_{12}O_{42}^{10-}$ have been

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TABLE I
Some Typical Data on the Polymerization of NVC by WB
and Preparation PNVC-WB Composite^a

Entry no.	Initial feed of reactants (g)			Product	
	WO ₃	WB	NVC	Total weight of the composite (g)	% PNVC ^b
1	0.45		0.3	0.56	37
2	0.30		0.3	0.43	43
3	0.10		0.2	0.19	44
4		0.30	0.30	0.47	57
5		0.30	0.15	0.38	53
6		0.65	0.1	0.69	40
7		2.00	0.2	2.06	30
8		0.75	0.05	0.76	26
9		1.00	0.05	1.01	20

^a Condition: Bulk polymerization at 65°C, time 1 hr.

^b Evaluated from the relation [(Column 5-Column 2)/Column 4] × 100.

identified. W in all these species retains +6 oxidation states. However, the blue oxides are thought to have W in oxidation state of +6 and +5 along with some OH⁻ instead of O₂⁻ to balance the charges. Such combination of mixed oxidation states is probably the reason for the high electrical conductivity of these blues. Biswas et al. have reported the use of isopolymetallates of vanadium and molybdenum in the oxidative polymerization of pyrrole and preparation of a polypyrrole-molybdenum blues nanocomposite thereof.⁸ PNVC-FeCl₃ impregnated zirconia,⁹ PNVC-Mo (VI),¹⁰ and PNVC-ZnO¹¹ systems have also been explored by these workers.

The absence of any information on tungsten based composite systems prompted us to explore NVC/WO₃/WB (tungsten blue) polymerization. In this context, we have made the interesting observation that WO₃ is able to initiate NVC polymerization in bulk at 65°C (the melting point of the monomer) without any extraneous catalyst. However, a nanocomposite of PNVC with WO₃ can be isolated from the system which is essentially nonconducting. In contrast, we have further observed that tungsten blue (WB) prepared by conventional methods discussed above can also initiate the polymerization of NVC monomer and a highly conducting composite of PNVC with tungsten blue hereinafter called PNVC-WB nanocomposite can be isolated. In this article, we intend to highlight the polymerization technique used along with details of structural and physicochemical property characterization of PNVC and PNVC-WB nanocomposite.

EXPERIMENTAL

Materials

N-Vinylcarbazole (NVC) (BASF, Germany) was recrystallized twice from methanol at 40°C, freeze

dried and stored in vacuum before use. Tungsten (VI) oxide purchased from Sigma Aldrich, USA (99% pure) was preheated at 120°C for 4 h in vacuum before use. Stannous chloride used was purchased from Merck, Germany. All other reagents and solvents were of AR grade and purified by standard method before use.

Polymerization of NVC by WO₃

Polymerization was carried out in bulk by heating a homogeneous mixture of known weights of WO₃ and NVC in a Pyrex flask at 65°C, which is the melting temperature of NVC. After a definite polymerization time, toluene was added to the contents of the reaction flask and then the total content was poured in excess of methanol. The whole mass was quantitatively filtered, repeatedly washed with boiling methanol to remove any unreacted monomer. The total mass was then dried in vacuum at 60°C for 4 h and subsequently characterized as PNVC-WO₃ composite.

The above experiment was repeated with various ratios of NVC to WO₃ and varying time of reaction (Table I).

Preparation of tungsten Blues (WB)

A known weight of WO₃ was taken in a Pyrex flask containing 6N HCl solution. It was stirred vigorously and then a known weight of SnCl₂ was added to this light-green colored suspension under stirring condition. The color of the suspension gradually turned blue followed by the appearance of a precipitate known as tungsten blues. The resultant mixture was filtered and the blue colored precipitate was collected after repeated washing with water followed by methanol. It was then dried at ~ 70°C under vacuum for 4 h.

Polymerization of NVC by tungsten blue

The polymerization was carried in bulk by heating a homogeneous mixture of known weights of WB and NVC in a stoppered conical flask at the melting temperature of NVC which is 65°C. After a definite polymerization time (1 h) toluene was added to the contents of the reaction vessel and the total mass was precipitated in excess methanol and the precipitate was quantitatively filtered, repeatedly washed with boiling methanol to remove any unreacted monomer. The bluish-white mass was then dried in vacuum at ~ 60°C for 4 h and subsequently characterized as PNVC-WB composite.

Characterization and property evaluation

The FTIR spectrum of the composite was taken on a JASCO-410 instrument in pressed KBr pellet. UV-visible and emission spectra for WB and PNVC-WB composite were determined with a Hitachi U-4100 model spectrophotometer and Hitachi F-4010 Fluorescence Spectrophotometer, respectively. ¹H-NMR analysis of PNVC was performed with Bruker 500 MHz model. Thermal stability of WB and PNVC-WB composite was determined using a thermogravimetric analyzer (NETZSCH, Germany, model: STA 449C) under N₂ flow at a heating rate of 10°C per minute. Differential scanning calorimetric analyses of WB and PNVC-WB composite were carried out on agarose gel by an Exstar 6000 of Seiko Instruments Incorporation with a heating rate of 1°C per minute. Molecular weight of PNVC homopolymer was determined viscometrically in toluene¹² at 27°C using the relation

$$[\eta]_{\text{PNVC}} = 7.62 \times 10^{-4} [M]^{0.5}$$

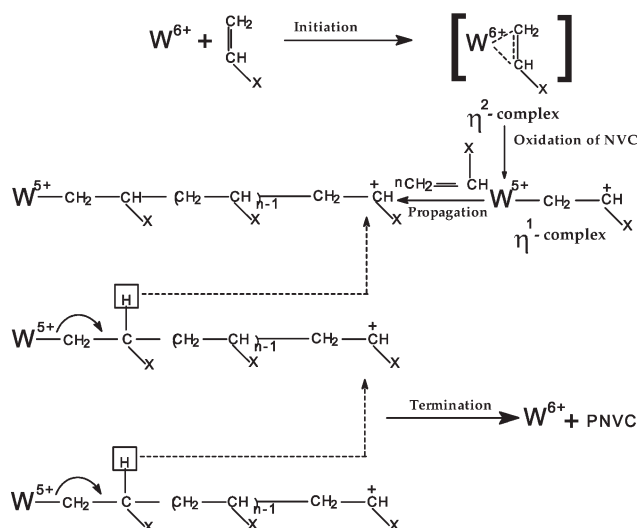
where $[\eta]$ is the intrinsic viscosity and M is the molecular weight.

Direct current (dc) resistivity measurements were conducted on pressed pellets of PNVC-WB composite (13 mm diameter, 0.1 mm breadth) with silver coating using the conventional four-probe technique. The unit manufactured by Scientific Equipment and Services, Roorkee, India, comprised a low constant current source (Model DMV-001) and a PID controlled oven (Model PID-200). Scanning electron micrographic studies of WB and PNVC-WB composite were performed in a Vega Tescan Digital Microscopy Imaging.

RESULTS AND DISCUSSION

General features

Table I presents some typical data on the polymerization of NVC by WO₃ and WB. The data suggests



Scheme 1 A tentative mechanism for the polymerization of NVC by W^{VI}.

that both WO₃ and WB are capable of initiating NVC polymerization with no major fluctuation in the extent of polymerization at a fixed time. The PNVC-WO₃ and PNVC-WB composites were isolated in the form of greenish-yellow and bluish-white powder, respectively. Mechanistically, the yield data imply a similar initiation mode involving interaction of NVC with W⁶⁺ moieties followed by normal propagation and termination via proton transfer mode (Scheme I) shown below. Incidentally, for cationic polymerization of NVC these proposed termination and transfer steps are considered very important as revealed in various systems.^{9-11,14} The viscometric molecular weight of the polymer recovered from the composite was 8.8×10^4 .

FTIR characteristics

Figure 1 presents the FTIR spectrum for PNVC-WB composite. The spectrum for the PNVC-WB composite reveals the following characteristic peaks: ~ 765.6 cm⁻¹ is because of >CH₂ rocking vibration; 1157 cm⁻¹ out of plane deformation of vinylidene group; 1222.65 cm⁻¹ C-H in-plane deformation of aromatic ring; 1331.6 cm⁻¹ plane deformation of vinylidene group; 1451.2 cm⁻¹ ring deformation of NVC moieties; 1624.7 cm⁻¹ C=C stretching vibration of vinylidene group. The observed FTIR peaks match convincingly with the FTIR spectra of the authentic PNVC sample.¹⁴ The appearance of a shoulder around 984 cm⁻¹ in the spectrum is characteristic of W=O bond present in the PNVC-WB composite. These results clearly endorse the formation of PNVC and its incorporation in the NVC-WB polymerization system.

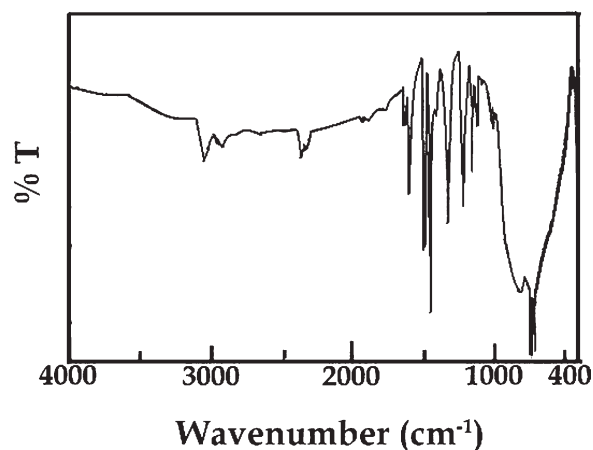


Figure 1 FTIR spectrum for PNVC-WB composite.

UV-vis spectral characteristics

Figure 2(a,b) show the UV-absorption spectrum for WB and PNVC-WB composite, respectively. The absorption pattern for WB reveals the appearance of a

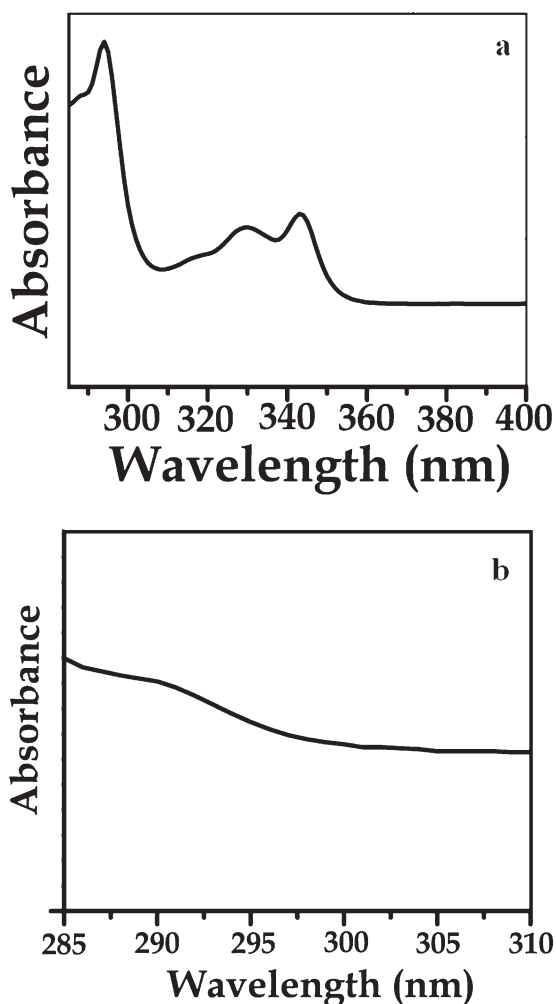


Figure 2 UV-Vis absorption spectra of (a) PNVC-WB and (b) WB.

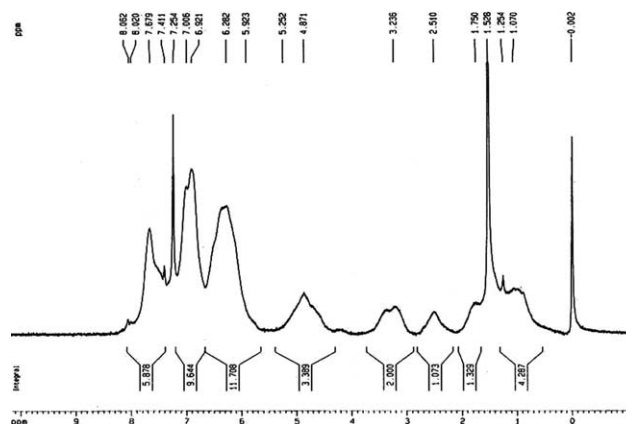


Figure 3 $^1\text{H-NMR}$ spectrum of PNVC homopolymer.

small hump in the wavelength range 285–295 nm and a broad absorption tail above 350 nm, a feature that matches with the literature data.¹⁵ The composite reveals the manifestation of two sharp peaks at 329 nm and 342 nm, respectively, because of PNVC moiety. PNVC homopolymer exhibits two UV peaks between 290–320 nm which is endorsed by literature data.¹⁶

$^1\text{H-NMR}$ characteristics

Figure 3 presents the $^1\text{H-NMR}$ peaks for PNVC homopolymer. The proton assignments are as follows: aromatic carbazole $\delta = 8\text{--}6.5$; methyne $\delta = 3.5\text{--}2.5$, and methylene $\delta = 2\text{--}1$ ppm. The large and unusual up field shift of one of the aromatic protons, $\delta = 5$, is attributed to the restricted internal rotation of the bulky carbazole group. Thus the proton NMR features are perfectly consistent with the values reported in the literature for PNVC homopolymer.¹²

Thermal stability studies

Figure 4(a,b) show the TGA plots for WB and PNVC-WB, respectively. The overall thermal stability trend appears to be: WB > PNVC-WB. It is to be

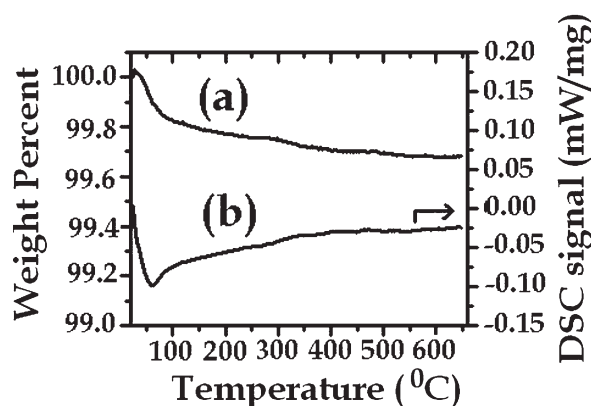


Figure 4 (a) TGA and (b) DSC curves of WB.

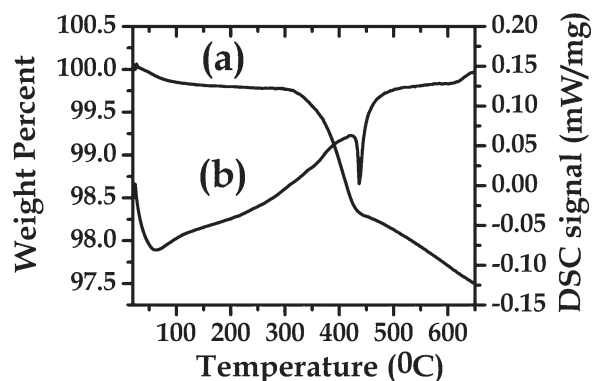


Figure 5 (a) TGA and (b) DSC curves of PNVC-WB.

noted that PNVC homopolymer reportedly^{10,17} shows complete weight loss between 500–600°C and is stable initially up to 300°C. An analysis of the

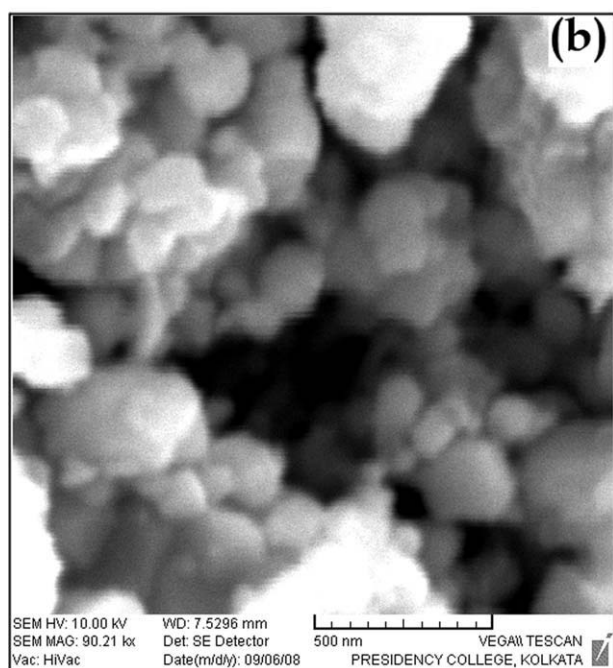
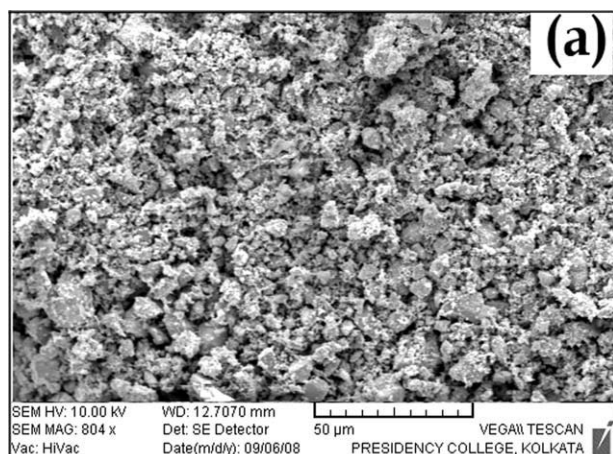


Figure 6 SEM images of (a) WB and (b) PNVC-WB.

TABLE II
Dc Conductivity Values

Entry no.	Material	Conductivity (S/cm)
1	WO ₃	No conductivity in measurable range
2	PNVC-WO ₃	No conductivity in measurable range
3	WB	0.1
4	PNVC-WB ^a	0.035×10^{-2}
5	PNVC-WB ^b	2.4×10^{-2}
6	PNVC-WB ^c	3×10^{-2}

^a WB : PNVC (Weight : Weight) = 26.

^b WB : PNVC (Weight : Weight) = 57.7.

^c WB : PNVC (Weight : Weight) = 100.

weight percent–temperature plot [Fig. 4(a)] suggests practically no loss of weight (~ 0.2 in the temperature range 70–110°C and ~ 0.4 up to 600°C) for the WB component, which accounts for its high stability. TGA plot of PNVC-WB composite [Fig. 5(a)] reveals minor weight losses ($\sim 0.5\%$) up to 310°C and $\sim 1.5\%$ in the temperature range 310–430°C, thereafter the composite suffers a weight loss of $\sim 2\%$ up to 600°C. Henceforth, the composite does not exhibit any major difference in thermal stability. The observed thermal stability characteristics for WB and PNVC-WB appears to be justified as incorporation of WB moieties of high thermal stability in polymer matrix should be expected to impart high stability of the composite system. Similar observation has been consistently observed by Biswas et al. in various polymer-metal oxide nanocomposite systems.¹

Differential scanning calorimetric curve for PNVC-WB [Fig. 5(b)] shows a glass transition for the PNVC component at $\sim 229^\circ\text{C}$.¹² This PNVC-WB component shows the manifestation of endothermic peaks in the range of 450–550°C, a feature that agrees convincingly with the reported temperature of minimal endothermic effect for PNVC at 450°C¹⁸ because of intensive degradation of the polymer starting from 300–350°C.

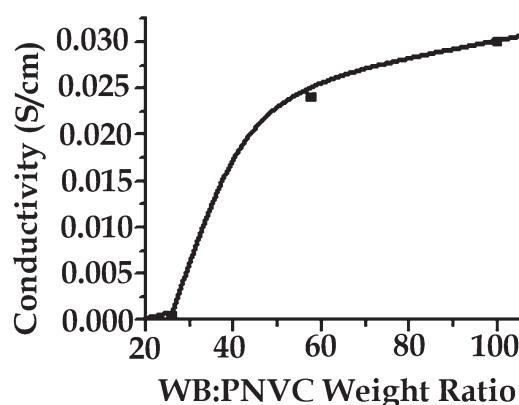


Figure 7 Plot of conductivity-WB : PNVC weight ratio.

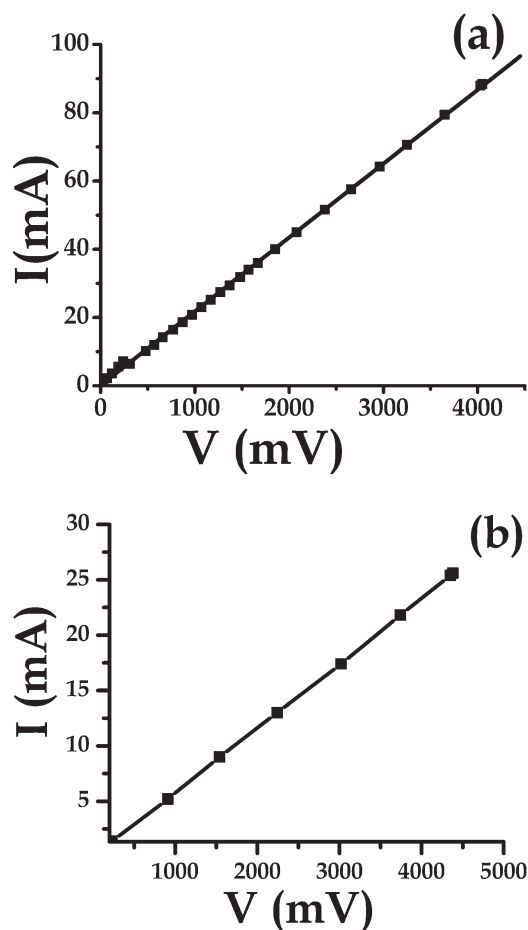


Figure 8 Current(I)-Voltage(V) plots of (a) WB and (b) PNVC-WB.

Scanning electron micrographic analysis

The scanning electron microstructure of PNVC-WB composite [Fig. 6(b)] reveals close packed aggregates of polymer coated WB moieties with spherical shape. The average sizes of the aggregates selected over a wide cross-section of the micrograph have been evaluated to be around 150 nm.

SE micrograph of WB [Fig. 6(a)] shows presence of granules of irregular sizes and shapes. Evidently, the heterogeneous composition of WB appears to be reflected in the micrograph. In contrast, PNVC-WB composite morphology [Fig. 6(b)] exhibits distinct globular phases of polymer encapsulated WB particles. Such encapsulation of WB particles by participating PNVC moieties is not homogeneously achieved in a single polymerization experiment.

Conductivity characteristics

Table II suggests that WO_3 and PNVC- WO_3 do not exhibit any conductivity, whereas WB and PNVC-WB composite exhibit appreciably high conductivity.

For the latter composite the conductivity increases from the semiconducting to the conducting range (Fig. 7) depending upon the weight ratio of WB : PNVC in the composite. The threshold value for this weight ratio for the manifestation of dc conductivity in the composite appears to be ~ 25 . The current-voltage variation for WB [Fig. 8(a)] is linear and reveals ohmic nature. The conductivity of WB and PNVC-WB composite is in the order of 10^{-1} S/cm 10^{-2} S/cm, respectively. Significantly, this value is many folds greater than the conductivity for PNVC homopolymer (10^{-12} – 10^{-14} S/cm). The enhancement in the conductivity of the composite from the base polymer is attributed to the formation of WB impregnated PNVC matrix. The presence of W^{5+} ions along with W^{6+} ions in the PNVC-WB composite facilitates local charge separation, and thereby an increase in the conductivity of the composite. At the same time formation of PNVC in the PNVC-WB system tends to decrease the conductivity of the composite from that of the freshly prepared WB. The current-voltage variation for PNVC-WB composite [Fig. 8(b)] is linear and reveals ohmic nature of the material.

CONCLUSIONS

A nanocomposite of poly(*N*-Vinylcarbazole) and tungsten blue was prepared by *in situ* bulk polymerization of NVC in presence of WB at 65°C . The formation of PNVC in the system was endorsed by FTIR, UV-Vis, emission, and $^1\text{H}^1$ -NMR spectroscopic analyses. Thermal stability studies indicated the stability trend as WB > PNVC-WB > PNVC. DSC analysis of the composite indicated a glass-transition break at $\sim 229^\circ\text{C}$ for the PNVC component. SEM analysis revealed a globular morphology for the composite with average particle sizes of ~ 150 nm. In contrast to PNVC ($\sim 10^{-12}$ – 10^{-10} S/cm), PNVC-WB exhibited high dc conductivity (3.5×10^{-4} – 3×10^{-2} S/cm) depending upon WB : PNVC (25–100) w/w in the composite.

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