A Conducting Composite Based on Poly(*N*-vinylcarbazole)–Formalin Resin and Acetylene Black

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ABSTRACT: A poly(*N*-vinylcarbazole) (PNVC)–formalin (FO) resin (PNVC-FO) was prepared via copolycondensation between *N*-vinylcarbazole (NVC) and FO in the presence of dry HCl gas in toluene medium at 110°C. A highly conducting composite of PNVC-FO resin with nanodimensional acetylene black (AB) was prepared by carrying out the polycondensation reaction in presence of a suspension of acetylene black (AB) in toluene. The inclusion of PNVC in the PNVC-FO-AB composite was confirmed by FT-IR analysis. Scanning electron microscopic analyses of PNVC-FO resin and PNVC-FO-AB composite revealed formation of spherical particles and aggregates of irregular shapes respectively. Thermogravimetric analyses revealed the overall stability order as: AB > PNVC-FO-AB composite > PNVC-FO resin > PNVC homopolymer. In sharp contrast to PNVC and PNVC-FO resin, which were both nonconducting (10^{-12} to 10^{-16} S/cm), the conductivity of the composites reached values between 0.75 S/cm and 6.54 S/cm corresponding to AB loading of 28–49 wt % respectively. Temperature versus conductivity studies revealed an initial increase in conductivity upto 200°C and current–voltage characteristics of the PNVC-FO-AB composite showed a linear trend consistent with Ohmic behavior. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3837–3843, 2007

Key words: *N*-vinylcarbazole; formalin; composite; thermal stability; conductivity

INTRODUCTION

Poly(*N*-vinylcarbazole) (PNVC) is a well known polymer with high thermal stability and distinctive opto-electronic properties but very low dc conductivity (10^{-12} to 10^{-16} S/cm).[1,2] Considerable research attention has been paid over the past few years on the modification of speciality, vinyl addition polymers, and condensation polymers to improve their bulk properties.[3–10] One of the important procedures used in this direction was to prepare hybrid nanocomposite materials of these polymers with selective inorganic components.[11–21] The latter included nanodimensional metal oxides such as ZrO_2, MnO_2, Al_2O_3, SiO_2, etc.,[11–15] montmorillonite (MMT) clay,[16,17] zeolites,[18] and allotropes of carbon such as carbon black (CB),[19] acetylene black (AB),[20] and Buckminster fullerene (BMF).[21]

In course of our attempts to enhance the scope of application of PNVC polymer, we were able to modify PNVC to a more thermally stable system by copolycondensation with FO to form the PNVC-FO resin. The latter possessed appreciably higher thermal stability when compared with the base polymer. However, like PNVC, the PNVC-FO resin was essentially nonconducting. We have now been able to prepare a highly conducting composite from PNVC-FO resin by using nanodimensional AB powder as one of the components in the reaction between NVC and FO. In this article, the preparative aspects and the results of evaluation of structural, morphological, thermogravimetric, and conductivity characteristics of the PNVC-FO resin and of the PNVC-FO-AB composite are highlighted. Relevantly, AB was recently used by us to prepare conducting composites with a variety of other nonconducting polymers such as polyacrylonitrile (PAN),[22] polymethylmethacrylate (PMMA),[23] polythiophene (PTP),[24] and polyfuran (PF).[24]

EXPERIMENTAL

Materials

N-vinylcarbazole (BASF, Germany) was recrystallized from *n*-hexane and kept in dark before use. Formalin, a 37–40% aqueous solution of formaldehyde gas, was supplied by BDH, India. Acetylene black (conducting grade, particle size ~ 40 nm, 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.

TABLE I
Some Typical Data on PNVC-FO Resin and PNVC-FO-AB Composite Formation[a]

Entry no.	Weight (g)			Time of reaction (h)	Weight (g) of composite	Wt % of AB loading[b] per g of composite
	NVC	AB	FO			
1	2	0	10	4	1.50	0
2	2	0.5	10	4	1.80	28
3	2	1	10	4	2.50	40
4	2	1.5	10	4	3.08	49
5	2	2	10	4	3.60	56
6	2	1	10	2	1.51	66
7	2	1	10	6	2.60	39

[a] Experimental conditions: Volume of solvent = 50 mL; Temperature = 110°C.
[b] AB loading per gram of composite = (column 3/column 6) × 100.

Preparation of PNVC-FO resin

Two g of NVC were dissolved in 50 mL of toluene in a two necked Pyrex Flask. To this solution, a measured quantity of formalin was added (Table I). Thereafter, dry HCl gas, generated by adding dropwise concentrated H_2SO_4 to solid NaCl in an appropriate glass assembly, was passed through the solution at 110°C for different hours and the entire reaction product was poured into an excess of MeOH. The separated white mass was filtered, washed successively with boiling MeOH to remove any unreacted monomer[25] followed by acetone and finally dried under vacuum at 100°C for 6 h.

Preparation of PNVC-FO-AB composite

In a two necked Pyrex Flask, 2 g of NVC were dissolved in 50 mL of toluene to which a measured quantity of formalin was added. To this solution, varying amounts of AB were added (Table I). The system was kept under stirring for 1 h to make a suspension of AB. Thereafter, dry HCl gas, generated by adding dropwise concentrated H_2SO_4 to solid NaCl in an appropriate glass assembly was passed through the solution at 110°C for different hours and the reaction product was poured into an excess of MeOH. The separated black mass was filtered and washed with boiling MeOH to remove any unreacted monomer[25] followed by acetone successively and dried under vacuum at 100°C for 6 h.

The resulting PNVC-FO-AB composite thus obtained was refluxed with benzene for 12 h at 65°C. The separated black mass was filtered and washed with MeOH and acetone successively and dried under vacuum at 100°C for 6 h.

Characterization and property evaluation

The FTIR spectra of PNVC-FO resin and PNVC-FO-AB composite were taken on a JASCO-410 instrument in pressed KBr pellet. Dispersions of PNVC-FO resin and PNVCFO-AB composites in 2-Propanol were microsprayed on a mica substrate. The samples were sputter-coated with gold layer and a Hitachi S-415A scanning electron microscope was used to take the micrographs. Thermogravimetric (TGA/DTA) analyses were performed on a Shimadzu DT-40 instrument with a heating rate of 10°C per minute. XRD patterns of resin and of the composite were obtained from Philips X-ray diffractometer (Cu LFF;40 kV, 20 mA). 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

General features

PNVC-FO resin formation

The material finally isolated from the reaction mixture was a nearly colorless mass insoluble in common solvents for PNVC homopolymer. Further, the resin was refluxed with toluene and filtered. The filtrate did not produce any precipitate in MeOH because of any PNVC homopolymer. A tentative scheme of resin formation[26] is given in Figure 1.

Composite formation between resin and AB

The composite was isolated as a black mass intractable in usual organic solvents. Table I presents some typical data on formation of PNVC-FO resin and PNVC-FO-AB composite respectively. At fixed initial weight of NVC and FO in the initial feed total weight of the composite increased consistently (entries 1–5). The results of entries 3, 6, and 7 indicate that at fixed amount of NVC, AB, and FO in the initial feed, the total weight of the composite increased with increasing time of reaction. Interestingly, percentage of poly-
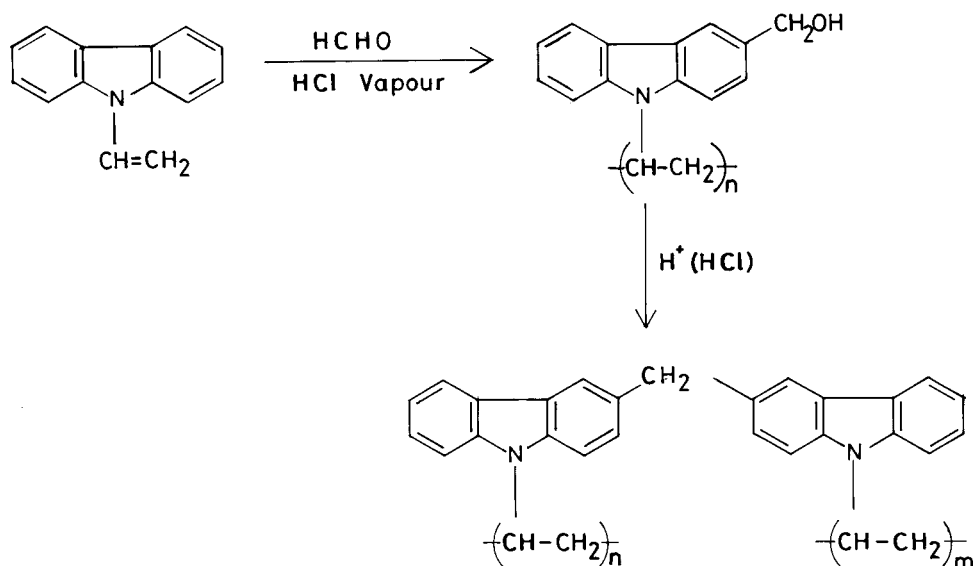
Figure 1 A tentative scheme for the formation of crosslinked resin from *N*-vinylcarbazole and formalin.

mer formed per gram of the composite showed a consistent increase with time of reaction.

FTIR spectral characteristics

Table II summarizes the major FTIR peaks observed with PNVC-FO-AB composite along with their probable assignments. The presence of PNVC in the PNVC-FO-AB composite was supported by the appearance of FTIR peaks (cm^{-1}) at 725, 747, 1210, 1327, 1490, 1625, and 2921 cm^{-1} in the region 600–4000 cm^{-1}

which matched with the FTIR peaks for PNVC synthesized by other ways.[19–21]

Scanning electron micrographic analysis

Figures 2(a,b) present the scanning electron micrographs for PNVC-FO resin and PNVC-FO-AB composite respectively. The SEM morphology for AB particles showed the presence of small nearly spherical particles with the tendency to form larger aggregates randomly distributed on the surface.[20] The morphol-

TABLE II
FTIR Band Assignments of the PNVC-FO Resin and PNVC-FO-AB Composite

| Material	Observed 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 vibration of NVC moiety
	1630	C=C stretching vibration of vinylidene gr
	3060	Aromatic C—H stretching vibration
PNVC-FO resin	723	Ring deformation of substituted aromatic structure
	747	>CH$_2$ rocking vibration
	1237	Out of plane deformation of vinylidene gr
	1384	>CH$_2$ deformation of vinylidene gr
	1451	Ring vibration of NVC moiety
	1615	C=C stretching vibration of vinylidene gr
	2930	Aromatic C—H stretching vibration
PNVC-FO-AB composite	725	Ring deformation of substituted aromatic structure
	747	>CH$_2$ rocking vibration
	1210	Out of plane deformation of vinylidene gr
	1327	>CH$_2$ deformation of vinylidene gr
	1490	Ring vibration of NVC moiety
	1625	C=C stretching vibration of vinylidene gr
	2921	Aromatic C—H stretching vibration
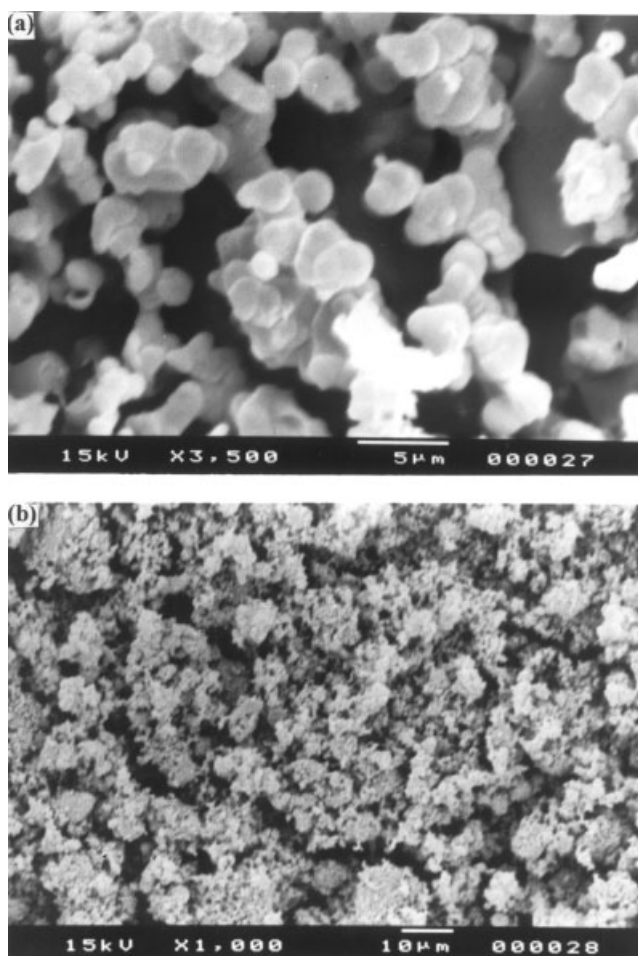
Figure 2 SEM images of (a) PNVC-FO resin (b) PNVC-FO-AB composite.

ogy for PNVC-FO copolycondensate was essentially indicative of the formation of nearly spherical particles of mixed sizes ranging from 1.5–4.5 μm. In contrast, SEM image of the PNVC-FO-AB composite suggested the formation of bulging agglomerates of much larger particles with nonuniform sizes (4.4–9 μm). The formation of such aggregates could result due to the inclusion of nanosized AB particles in the PNVC-FO resin. Relevantly, Armes et al. suggested[26–28] similar cementation between nanodimensional SiO_2 suspensions and precipitating polymeric moieties in aqueous system leading to the formation of stable suspension of conducting composites. Biswas and coworkers also reported similar morphological features with a variety of polymer based nanocomposite with clay,[16,17] nano-dimensional metal oxides[11–15] and zeolite.[18]

Thermal stability studies

Figure 3(a–d) present the thermograms of AB, PNVC-FO-AB, PNVC-FO and PNVC homopolymer respectively, and Table III compares the thermogravimetric

stabilities of AB, PNVC-FO-AB, PNVC-FO and PNVC homopolymer at some selective temperatures. These data indicated that the overall thermal stability upto 1000°C followed the trend: AB > PNVC-FO-AB > PNVC-FO > PNVC.

The overall thermal stability of PNVC was found to be improved after resin formation with FO as a result of the formation of a crosslinked network structure between PNVC and FO in the PNVC-FO resin (vide Fig. 1). This contention is in line with the fact that at 600°C maximum weight loss for the resin was 56% as against 100% for PNVC homopolymer. Due to incorporation of AB particles—which were thermally more stable compared with both PNVC and PNVC-FO resin—in the composite, the overall stability of the composite would be evidently higher than that of the PNVC and PNVC-FO resin but lower than that of AB—as actually observed (vide Table III). A similar trend was also reported for a variety of polymer—metal oxide,[11–15,27–29] zeolite[18] and clay based[16,17]nanocomposite systems of several speciality and conventional vinyl polymers.

DTA scans showed exothermic peaks at 332, 576°C for AB, at 411, 488°C for PNVC-FO resin and at 440, 515°C for PNVC-FO-AB composite. The observed peaks at 411°C and 515°C in the PNVC-FO-AB composite were possibly due to overlapping of peaks between 411°C (for PNVC-FO) and 332°C (for AB) and of those between 488°C (for PNVC-FO) and 576°C (for AB), respectively.

X-ray diffraction analysis

XRD analyses confirmed amorphous nature for AB, PNVC-FO and PNVC-FO-AB composite. Interestingly, we observed earlier that PNVC-AB composite, prepared by bulk polymerization of NVC by AB alone, showed manifestation of several crystalline peaks.[20] Possibly formation of a crosslinked network
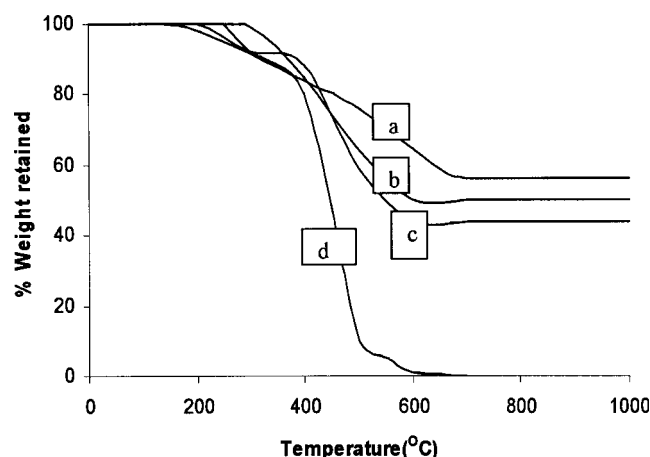

Figure 3 TGA scans of (a) AB (b) PNVC-FO-AB composite (c) PNVC-FO resin, and (d) PNVC homopolymer.

TABLE III
Thermal Stability Data of AB, PNVC^a-FO Resin, and PNVC-FO-AB Composite

Materials	Temperatures (°C) (% weight loss)			DTA peaks (°C)
	200	400	600 (maximum weight loss)	
AB	0	10	15	332, 576
PNVC-FO	0	12	56	411, 488
PNVC-FO-AB	0	15	50	440, 515

^{a} PNVC suffered complete weight loss at $\sim 600°C$.

would not encourage the development of any crystalline order in the resin.

Conductivity characteristics

Table IV presents the conductivity values of the PNVC-FO-AB composites along with the values reported for some metal oxide based nanocomposites of PNVC and unmodified PNVC (10^{-12} to 10^{-16} S/cm).[30] Entries 2–5 in Table IV show that the PNVC-FO-AB composite exhibited attractively high conductivity values relative to other PNVC based nanocomposite systems and PNVC-FO resin (10^{-12} to 10^{-16} S/cm)—which increased with increasing weight percentage of AB loading in the composite (Fig. 4a). It is interesting to note that the dc conductivity values of the PNVC-FO-AB composite material exhibited 10^{12} to 10^{16} fold enhanced conductivity value relative to the same for the resin or the base polymer.

Figure 4(a) also shows that the rapid increase in conductivity occurred when AB content exceeded 40 wt %. At this threshold, enough AB moieties were present in the matrix for continuously conducting chains to be formed.

Figure 4(b) shows that the dc conductivity of the composite increased by about 30% in the temperature range 27–200°C. This could be ascribed to more favorable charge transfer interaction between the lone pair of N and π electron systems present in carbazole moieties in

the resin and AB particles. Significantly, this feature is similar to those exhibited by a composite of polypyrrole with another allotrope of carbon MWCNT. Thus, Long et al. proposed[31] for PPY-MWCNT nano cable system an enhanced charge transfer possibility between the polymer and CNT moieties with increase in temperature. Long et al. also proposed[31] a change in CNT conductive path with temperature which was responsible for the enhancement of the electrical properties in CNT-PPY composite system.

Current-voltage curve (Fig. 4c) for PNVC-FO-AB composite was linear and Ohmic in nature reflecting the metallic character of the composite. Relevantly, Wang et al. observed[32] that the current–voltage curve of a CNT doped PPY nanowire followed Ohm's law. Macroscopic PANI-CNT and PPY-CNT films also were found to display metallic characters.[33,34] Apparently the electron flow within the composite would be enhanced by the entrapped CNTs serving as ''conducting bridges'' favoring degree of electron delocalization.[33,34] A similar situation might be responsible for the display of higher conductivity in the PNVC-FO-AB composite system.

CONCLUSIONS

A highly conducting and thermally stable composite of PVNC-FO resin with acetylene black was prepared

TABLE IV
DC Conductivity Values of Some PNVC-Based Composites

| Entry no.	Materials	Conductivity (S/cm)	References
1	PNVC	10^{-12} to 10^{-16}	30
2	PNVC-FO-AB (28 wt % AB loading)	0.75	This study
3	PNVC-FO-AB (40 wt % AB loading)	1.69	This study
4	PNVC-FO-AB (49 wt % AB loading)	6.54	This study
5	PNVC-FO-AB (56 wt % AB loading)	6.54	This study
6	PNVC-AB	10^{-2}	20
7	PNVC-CB	8×10^{-2}	19
8	PNVC-BMF	10^{-1}	21
9	PNVC-MnO$_2$	3.5×10^{-5}	12
10	PNVC-PTP	1.5×10^{-4}	35
11	PNVC-Al$_2$O$_3$	1.4×10^{-7}	14
12	PNVC-SiO$_2$	10^{-6}	15
13	PNVC-PPY-Al$_2$O$_3$	1.7×10^{-5}	36
14	PNVC-PANI-Al$_2$O$_3$	10^{-4}	37
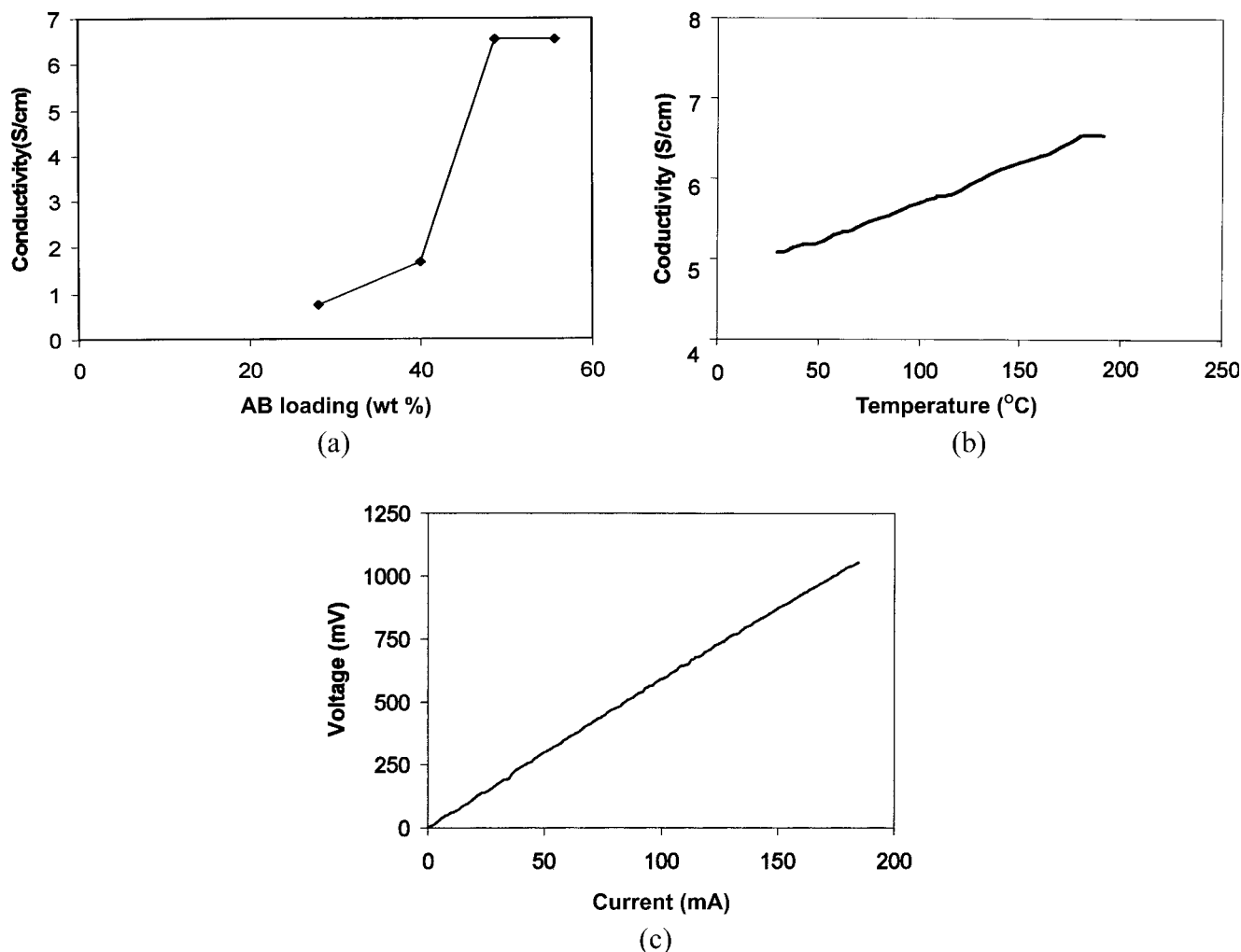
Figure 4 (a) Conductivity versus AB loading (wt %) in the composite 4(b). Conductivity–temperature curve of the PNVC-FO-AB composite 4(c). Current–voltage curve of the PNVC-FO-AB composite.

via copolycondensation reaction between NVC and FO in presence of HCl gas in toluene-acetylene black suspension at 110°C. The conductivity of the composite at 49 wt % acetylene black loading was 6.54 S/cm, which was remarkably higher than that of the PNVC-FO resin and NVC.

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