A conductive poly(*N*-vinylcarbazole)–carbon black composite

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Carbon black initiated poly(*N*-vinylcarbazole) yields a composite which exhibits a conductivity as high as $1\,\Omega^{-1}\,\mathrm{cm}^{-1}$. The value is the highest ever reported for poly(*N*-vinylcarbazole)-based systems.

(Keywords: poly(*N*-vinylcarbazole); carbon black; conductive composite)

Introduction

Poly(*N*-vinylcarbazole) (PNVC) obtained by conventional methods is essentially an insulator (conductivity = 10^{-10}–$10^{-16}\,\Omega^{-1}\,\mathrm{cm}^{-1}$)[1]. Biswas and Roy[2] reported an improved conductivity range of 3.7×10^{-6}–$7.2 \times 10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ for a copolymer of *N*-vinylcarbazole (NVC) and pyrrole prepared in an ether medium with $FeCl_3$ as a catalyst. More recently[3], these authors reported a further enhancement in the conductivity of PNVC ($1.1 \times 10^{-4}\,\Omega^{-1}\,\mathrm{cm}^{-1}$) prepared in the presence of $FeCl_3$ in aqueous medium. In this context, we wish to report the preparation of a PNVC–carbon black (CB) composite which exhibits a conductivity as high as $1\,\Omega^{-1}\,\mathrm{cm}^{-1}$. This value is the highest ever reported for PNVC-based systems. Although our procedure does not lead to the formation of PNVC with improved inherent conductivity, it does offer a simple yet novel technique of producing a highly conductive composite with the distinctive properties of PNVC.

The grafting of some vinyl monomers on CB in the presence of cationic, anionic or free radical catalysts has been reported by several workers[4,5]. Biswas and Haque[6] showed that CB (N220) without any external catalyst can induce the cationic polymerization of NVC. In this work, we have utilized this simple CB initiation procedure to produce a PNVC–CB composite using a conductive variety of CB.

Experimental

Materials. Vulcan XC 72 (Cabot Corporation), a conductive variety of CB, was pretreated by heating at 120°C for 2 h *in vacuo* prior to polymerization. NVC (BASF, Germany) was recrystallized following a published procedure[7]. All solvents were AR grade materials and purified by standard methods.

Polymerization. The polymerizations were carried out in Pyrex vessels (50 ml) at 60°C under nitrogen. A known amount of NVC was added in toluene (15 ml) or any other solvent to a weighed amount of CB with continuous stirring. After 2 h, the total contents of the flask were added to a requisite volume of methanol, filtered on a Gooch crucible and the precipitate was repeatedly washed with boiling methanol[7] and finally dried at 80°C for 8 h under vacuum.

Characterization. The i.r. spectra were recorded on a Perkin-Elmer 883 i.r. spectrophotometer using KBr pellets. Thermogravimetry was performed on a Stanton–Redcroft STA 625 instrument. Scanning electron micrographs were taken by a CAM SCAN series 2DV. Electrical conductivity measurements were performed on a Keithley 617 solid state electrometer using a four-probe technique.

Results and discussion

Table 1 shows some conversion and conductivity data which suggest the following features. (1) Conversion increases with increasing amount of CB in the initial feed. Elemental analysis data for PNVC (after separation of toluene solution from CB and subsequent methanol precipitation and purification): C 87.5 (87.0); H 6.0 (5.7); N 8.0 (7.3). The η_{rel} values of the polymers were in the range 1.1–1.3 as determined in toluene. Thermogravimetric analyses indicated initial decomposition temperatures to be around 200°C followed by a weight loss of ~20–60% in the range 250–450°C with complete weight loss at 600°C. (2) The conductivity shows almost a 10-fold jump corresponding to a four-fold increase in the amount of CB in the initial feed, with a fixed amount of NVC. (3) Use of $FeCl_3$ as a cocatalyst as well as a dopant does not help in realizing conductivities of $> \sim 1\,\Omega^{-1}\,\mathrm{cm}^{-1}$. (This was the maximum value realized with the NVC–CB polymerization system under the experimental conditions used here.) (4) The NVC–CB polymerization system is totally inhibited in basic solvents including ether and dioxane, which are however, effective solvents for the NVC–CB–$FeCl_3$ system. Conversion is highest in dioxane while the conductivity is the lowest.

It is to be emphasized that coprecipitation of PNVC in CB during polymerization is important in isolating pelletizable PNVC–CB composites of high conductivity. A mechanical mixture of preformed PNVC and CB produces materials of lower conductivities than the PNVC–CB composite and, unlike the latter, the pellet is readily breakable. $FeCl_3$ when used with CB

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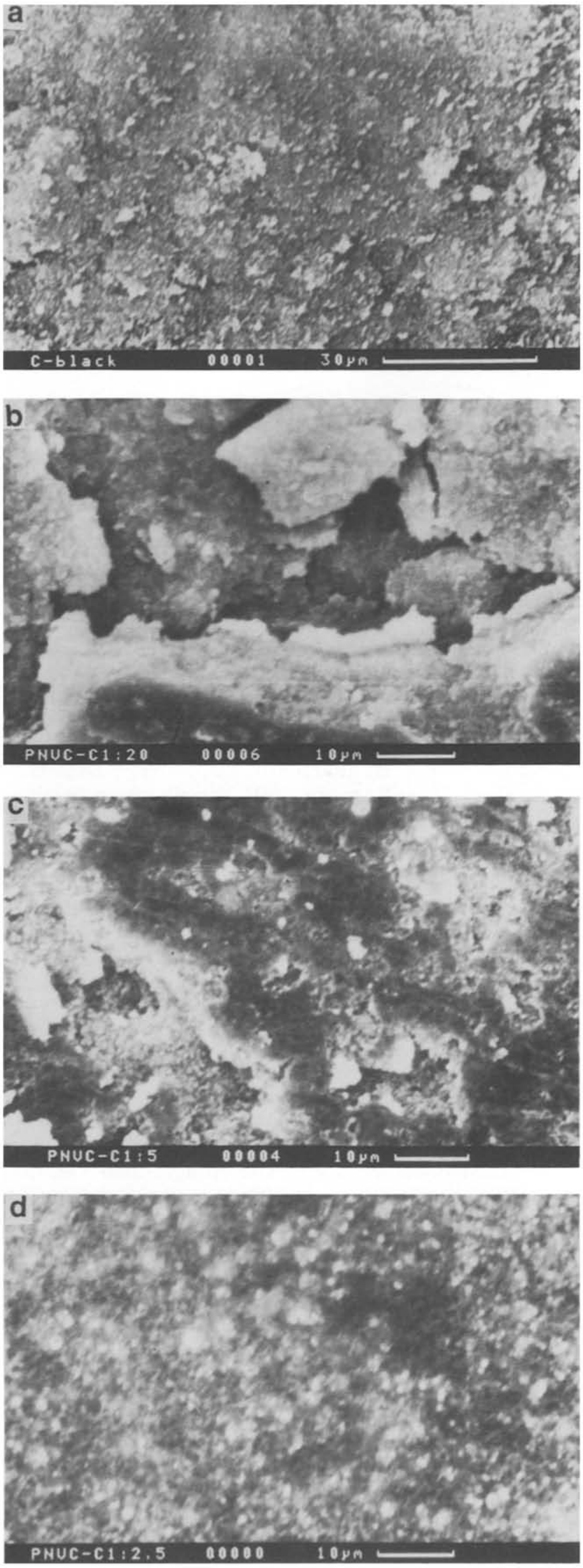

Figure 1 Scanning electron micrographs of: (a) pure carbon black; (b) PNVC–CB composite (2.5:0.125); (c) PNVC–CB composite (2.5:0.50); (d) PNVC–CB composite (2.5:1.00)

Table 1 Preparative conditions for PNVC–CB composites and conversion and conductivity data

No.	NVC:CB ($g\,g^{-1}$)	Solvent	Conversion of PNVC[a] (%)	Conductivity ($\Omega^{-1}\,cm^{-1}$) 30°C	130°C[b]
1	2.5:0.125	Toluene	50	0.11	0.55[b]
2	2.5:0.25	Toluene	54	0.19	0.81[b]
3	2.5:0.50	Toluene	65	0.98 0.99	1.14
4	2.5:1.00	Toluene	67	0.99	1.19
5	2.5:2.50	Toluene	65	1.0	1.13
6[c]	2.5:0.50	Ether	55	0.20	–
7[c]	2.5:0.50	Dioxane	99	0.045	–

[a] Calculated on the basis of weight of NVC in the feed
[b] Conductivity increases with temperature to a relatively larger extent for composites containing low amounts of CB
[c] The polymerization system contains 0.69 $FeCl_3$

(run nos 6 and 7 in *Table 1*) leads to the formation of PNVC in addition to that formed by CB. Since the inherent conductivity of PNVC is very small, the overall conductivity of the mixture of PNVC ($FeCl_3$) and the PNVC–CB composite system is decreased. A higher yield in dioxane relative to ether should therefore imply a lower conductivity, as is actually observed.

The SEM micrographs (*Figure 1*) of PNVC–CB and CB reveal the formation of large granules in PNVC–CB composites as distinct from a more or less featureless CB surface. With an increasing amount of CB in the system, the micrographs show a change to the surface similar to that of CB with dispersed spherical PNVC moieties.

In conclusion, the procedure may be regarded as novel for NVC since the monomer is characteristically very susceptible to cationic initiation by CB without any external cocatalyst or catalyst added.

In terms of the solubility of the composite with respect to its general processability, it should be noted that PNVC–CB composites are not completely soluble in toluene or other solvents[6]. However, the PNVC part may be dissolved after repeated solvent extraction, though complete separation from the CB component is extremely difficult. PNVC–CB composites can be processed from the powdery state by pressing or by dispersion in toluene or any suitable solvent.

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