Composites of Polypyrrole and Carbon Black. 2. Electrosynthesis, Characterization, and Influence of Carbon Black Characteristics

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Polypyrrole (ppy)–carbon black composites with the carbon black content ranging from 10 to ~80 wt % were electrosynthesized from aqueous dispersions of carbon black containing pyrrole monomer. An electrotrapping mechanism is proposed for the composite film growth; the negatively charged carbon black particles are attracted toward the (positively charged) anode surface where they are assimilated into the growing ppy matrix. The presence of carbon black enhanced the charge-storage capacity and the electronic conductivity of the parent polymer in the resultant electrocomposite as measured by cyclic voltammetry in 0.1 M KCl. The infuence of carbon black characteristics on these two properties of the composite was explored by examining composites electrosynthesized from seven commercial blacks encompassing a wide range of surface area, porosity, void volume, and electronic conductivity. Two different carbon black solution loads (10 and 20 g/L) were employed in these experiments. The carbon black porosity and its specific surface area exerted a positive effect on the ability of the ppy–carbon black composite to store charge. Similarly, an increase in the structure of the carbon black had a positive effect on the current density (i.e., the electronic conductivity) of the resultant composite. However, the Printex XE-2 carbon black based composite showed anomalously low charge-storage capacity and current density in 0.1 M KCl despite the high porosity and structure of its carbon black component. Possible reasons for this are discussed as are data obtained by previous researchers on other types of ppy–carbon composites.

Introduction

In a recent communication,[1] we introduced an electrochemical method for synthesizing polypyrrole–carbon black composites from aqueous dispersions of carbon black containing the pyrrole monomer. In this paper, we elaborate on this approach, present materials characterization data and also explore the effect of varying the type of carbon black on the charge-storage capacity and electronic conductivity of the resultant composite.

Attempts have been made in recent years to modify or enhance the properties of the parent polymer, namely, polypyrrole (ppy), by incorporating in it other polymers,[2] metals,[3] or metal oxides.[4] It would appear that carbon black would be a logical candidate for this purpose. Composites of carbon black and other materials, e.g., polymers, have a long history especially in the rubber industry. Another important application for these materials has been in the electronics and dielectrics industries. For example, the conductivity of carbon black–elastomer composites may be easily tuned by varying the carbon black load. Thus, high-resistivity composites are useful for communication cable and optical fiber protection. The low-resistivity counterparts, on the other hand, have useful antistatic properties. It is of interest to note that electronically conductive polymers such as ppy are being targeted for very similar technological applications.[5] Consequently, there is both a fundamental and technological incentive to explore how a molecular composite of ppy and carbon black would behave, relative to its components.

Aside from our own work, we are aware of two other instances wherein ppy–carbon composites have been synthesized, and such synergisms have been discussed. Polypyrrole was electrochemically deposited on anodes comprising either carbon fibers or carbon fabric.[6] With the former, the conductivity of the resultant material was reported to be dominated by the fiber. On the other

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hand, in the case of the fabric, the ppy was thought to have enhanced the number of contacts thereby increasing the electronic conductivity of the composite. Another group codeposited ppy and carbon powder in a nonaqueous medium containing propylene carbonate and $LiClO_4$.[7] These authors attempted a correlation between the charge capacity of the resultant material and the specific surface area of the carbon black.[7a] However, they were hampered by the lack of knowledge of the relative amounts of ppy and carbon black in the resultant composite.

In this paper, we describe a range of ppy–carbon black "electrocomposites" varying in carbon black content from 10 to 80 wt %. We also tested several commercial carbon blacks encompassing a wide variation in carbon black characteristics. We show that these materials can by conveniently synthesized from aqueous media and that the resultant composites have enhanced charge-storage characteristics and electronic conductivity (at negative potentials) relative to the parent polymer. Carbon black properties such as electrical conductivity, porosity, specific surface area and void volume exert a positive effect on the ability of the electrocomposite to store and conduct charge. However, there is a limit beyond which an increase in these properties can be deleterious to the composite as exemplified by the behavior of the Printex XE-2 carbon black.

Experimental Section

Pyrrole was obtained from Aldrich (98%) and was purified by filtering through a bed of activated Al_2O_3 (150 mesh) before use. Potassium chloride was reagent grade from Mallinckrodt. Cadmium chloride was from Aldrich.

The N135, N660, SB250, and SB500 carbon blacks are manufactured by Sid Richardson Carbon Co. The XC-72 and Black Pearls (BP) 800 were obtained from Cabot Corp. The Printex XE-2 carbon black was from Degussa AG. Characterization of the various carbon blacks was done using the following equipment: a Model E absorptometer from Brabender Inc. for dibutyl phthalate (DBP)[8] and 24M4 DBP[9] absorption tests, a Micrometrics Gemini 2360 for nitrogen-specific surface area,[10] and a Philips EM 300 transmission electron microscope for the particle size measurements.[11] The electronic conductivity of the various carbon blacks was measured using the four-probe technique and a Keithley 224 programmable current source in conjunction with a Keithley 197A autoranging microvoltmeter. Disks made from each carbon black sample by compressing it at ca. 29 MPa in a KBr pellet press were utilized for this purpose. Electrochemical measurements utilized a Princeton Applied Research (PAR) Model 273 potentiostat. Scanning Auger microscopy (SAM) was performed on a Kratos XSAM-800 machine. Scanning electron microscopy (SEM) was done on a JEOL Model 6100 instrument.

Films of ppy–carbon black electrocomposites were prepared by polymerizing pyrrole (0.1 M) at +0.85 V (vs Ag/AgCl reference; all potentials below are quoted with respect to this reference) in a 0.1 M solution of KCl containing carbon black dispersed in it. The dispersions were ultrasonicated for about 5 min prior to use. Glassy carbon sheets or disks were used as supports for the ppy–carbon black composite films, and film growth was terminated after a constant charge of 0.71 C/cm^2 had accumulated unless otherwise noted.

Solution loads of carbon black in the range 0.5–50 g/L were employed in this study. The uptake of carbon black by the ppy matrix was monitored by varying the solution load of carbon black and performing elemental analysis (Perkin-Elmer 2400 C, H, N analyzer) on the resultant films. Large (geometric area 10.5 cm^2) support electrodes were used in these experiments in order to generate milligram quantities of the electrocomposite, thereby optimizing the analytical sensitivity. A control "run" with no carbon black yielded a C:N ratio of 4.0:1 as expected for ppy. Any increase over and above this ratio was taken as the amount of carbon black present in the film.

Results and Discussion

Electrosynthesis of ppy-Carbon Black Composites. The electropolymerization of pyrrole proceeds in an aqueous dispersion containing the carbon black. Thus the carbon black particles are assimilated into the growing ppy matrix. This approach is quite general in that particles comprising any targeted material can, in principle, be incorporated into ppy. We had earlier used this approach to prepare ppy–Pt nanocomposites[3d] by employing a colloidal Pt solution and anodically polymerizing pyrrole in this medium. As in this previous case, we believe that an "electrotrapping" mechanism is also operative with carbon black. That is, the carbon black particles, because of their negative surface charge,[12] migrate toward the (positively charged) anode and are then engulfed within the growing ppy matrix. Support for this notion accrues from the fat that we observe adherence of carbon black particles at the glassy carbon electrode poised at +0.85 V *even in the absence of pyrrole monomer in the medium*. Our use of the term "electrocomposite" appears to be tenable within the context of a related technology for the fabrication of metal (e.g., Ni) matrices containing Al_2O_3, SiO_2, diamond, SiC, etc., for reinforcement and wear-resistance applications.[13] In the latter instance, the metal is electrodeposited from a slurry containing the particles to be incorporated.

Scanning Auger microscopy (SAM) using nitrogen as the probe element (specific to ppy) revealed a uniform distribution of carbon black in the electrocomposite. Thus a SAM map (at 500×) for nitrogen contained a uniform distribution of dark and light spots corresponding to ppy "rich" and "lean" regions in the matrix respectively (not shown).

Influence of Carbon Black Content on the Charge-Storage Capacity and Electronic Conductivity of ppy–Carbon Black Electrocomposite. The N135 carbon black was used as a "baseline" system for these studies. First, it was important to check how the carbon black content (in wt %) of the resultant composite scaled with the corresponding solution load of the carbon black (in g/L). Figure 1a contains the relevant data. The efficiency of carbon black incorporation into the ppy film clearly decays at solution loads greater than ca. 20 g/L.

Figure 2 contains a family of cyclic voltammograms in 0.2 M KCl for films with increasing carbon black content (Figure 2b–e); control scans for the two com-

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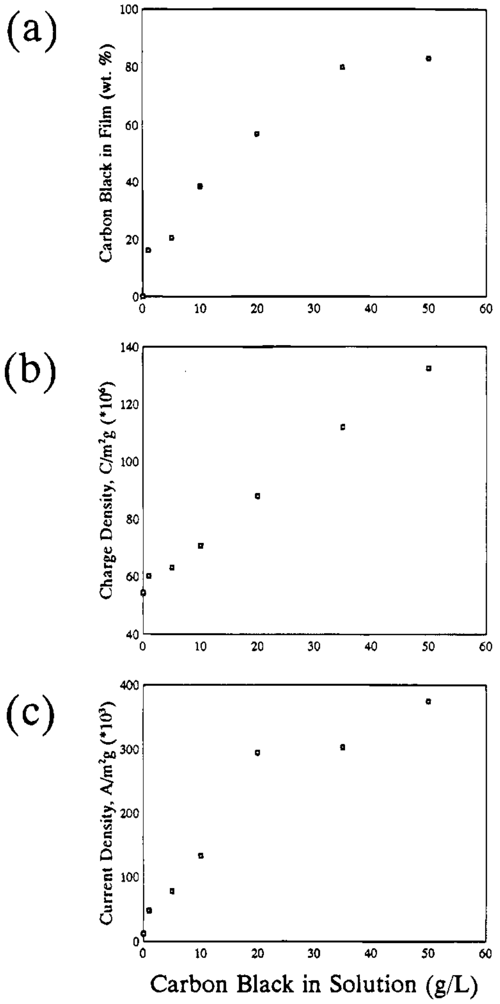

Figure 1. Plot of carbon black content of the electrocomposite film (Figure 1a), charge density (Figure 1b), and current density at −0.8 V (Figure 1c) vs the corresponding carbon black load of the solutions used for electrosynthesis. The ordinates in Figure 1b,c have been scaled to unit weight of the ppy component in the electrocomposite (refer to text). The geometric area of the support electrode (0.07 cm^2) was used for computations of the charge and current densities. The charge was obtained from integration of the cyclic voltammograms between 0.4 V and −0.8 V (cf. Figure 2 below).

ponents of the electrocomposite, namely, ppy (Figure 2a) and carbon black (Figure 2f), are also shown. All the voltammograms (except the one in Figure 2f) show a "capacitive" background, superimposed on which are redox curves. This sort of cyclic voltammogram morphology has been discussed for ppy[14] and for other conducting polymers.[15] The carbon black-containing specimens additionally show increased charge at the negative end of the potential window as well as redox features at about −0.6 V. Also worthy of note is the negligible charge for carbon black alone (Figure 2f). The enhanced charge storage characteristics of the electrocomposites becomes apparent when the parameter, charge density normalized to unit weight of the "active" ppy material (units of C/m^2·g; see below) is plotted against the carbon black load of the solution. Figure 1b contains such a plot.

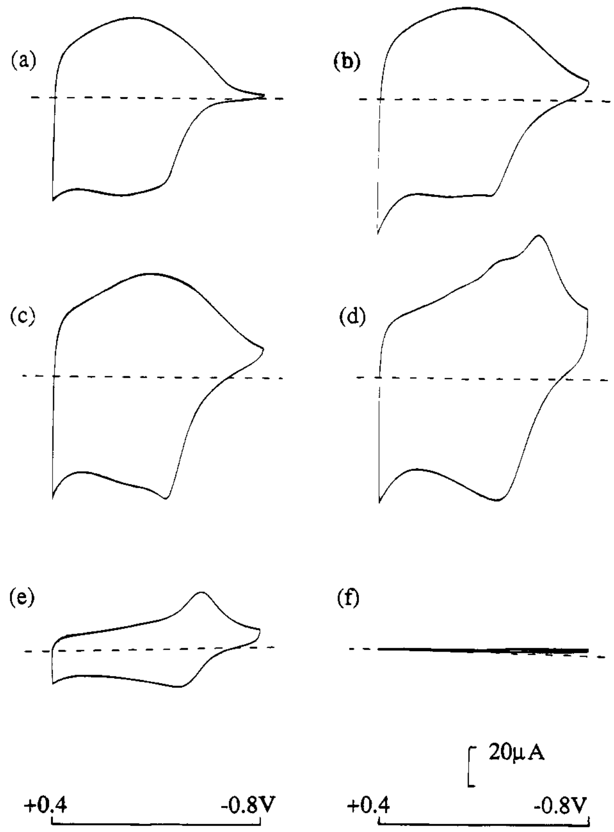

Figure 2. Cyclic voltammograms in 0.2 M KCl at a potential scan rate of 10 mV/s for (a) polypyrrole and (f) carbon black. Figure 2b−e correspond to electrocomposites synthesized from 0.1 M KCl solutions containing (b) 5, (c) 10, (d) 20, and (e) 50 g/L of carbon black. The sample in Figure 2f was electrosynthesized from 0.1 M KCl containing 35 g/L carbon black. In all the cases, the deposition potential was +0.85 V and a constant charge of 50 mC was accumulated. The geometric area of the electrode was 0.07 cm^2. The dashed line refers to zero current.

The second virtue of the ppy−carbon black electrocomposite (relative to pure ppy) is enhanced electrical conductivity, especially at negative potentials. To illustrate this, the current density at −0.8 V (a potential at which ppy is essentially electrically insulating; see below) is plotted against the carbon black load in Figure 1c. These data were obtained from the cyclic voltammograms in Figure 2a−e.

The plots in Figure 1b,c have been normalized with respect to the ppy content (in grams) of the electrocomposite as follows. The charge consumed for ppy film growth, Q_{ppy}, was obtained from the difference of the total charge (50 mC) and the background charge computed from a blank experiment. The time required for passage of 50 mC was found to systematically decrease with an increase in the carbon black load of the original solutions. Thus carbon black consumes a nonnegligible amount of charge when present as a slurry. This background charge was measured under identical conditions as above but omitting pyrrole from the solution. Using Faraday's law and the values of Q_{ppy} thus obtained, the mass of ppy in the electrocomposite could be computed. A doping level of 33% was taken for these calculations from related work.[3]

It is noteworthy that the intercepts in Figure 1b,c for the charge density and current density at 0 g/L (i.e., for a pure ppy sample) correspond closely to the slopes of

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[14] (a) Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W. Y. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *129*, 115. (b) Feldberg, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 4671. (c) Krishna, V.; Ho, Y.-H.; Basak, S.; Rajeshwar, K. *Ibid.* **1991**, *113*, 3325.

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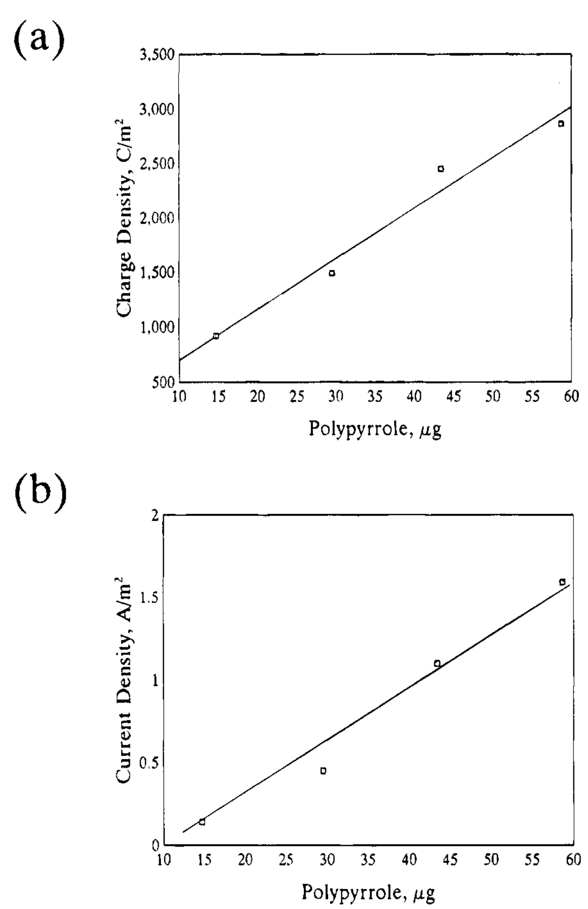

Figure 3. Plots of the mass of ppy vs (a) charge density in C/m^2 from a cyclic voltammogram between +0.4 and −0.8 V at 10 mV/s in 0.1 M KCl and (b) current density at −0.8 V in A/cm^2 from the voltammogram used in (a) above. The amount of ppy was varied by applying a potential of +0.85 V to a glassy carbon electrode in a 0.1 M pyrrole/0.1 M KCl solution until charges of 0.71, 1.42, 2.13, and 2.84 C/cm^2 accumulated which correspond to ppy masses of 14.6, 29.3, 43.4, and 58.6 µg, respectively.

the plots of charge density and current density vs. the thickness (or equivalently the mass) of a series of ppy films electrosynthesized in the absence of carbon black (Figures 3a and 3b). This eliminates the possibility that the inclusion of carbon may lead to a thicker film than the pure ppy leading to the enhanced behvavior. The amount of ppy on the support electrode was varied by applying a potential of +0.85 V to it until increasing amounts of anodic charge had accumulated. The polymerization charge density was converted to ppy mass using previous electrochemical quartz crystal microgravimetry data[3] from this laboratory.

It must be noted that the current density enhancement at −0.8 V persists at scan rates lower than 10 mV/s indicating that the higher currents in Figure 1c cannot simply be due to *iR* (ohmic) drop effects in the film.

Electrical conductivity measurements (using a four-probe dc technique) on these ppy−carbon black electrocomposites were hampered by the fact that the films were too thin and uneven in thickness. Therefore, cyclic voltammetry was performed on a series of samples similar to those in Figure 2, with the $Cd^{2+/0}$ redox couple being used as a conductivity probe in these experiments. The idea is that provided the film is *impermeable to Cd^{2+} ions* over the time scale of the experiment, manifestation of waves due to $Cd^{2+} \rightleftharpoons Cd^0$ redox process (which then is constrained to take place at the outer film surface/electrolyte boundary) would depend on the ability of the intervening film to shuttle electrons back and forth between the solution and the glassy carbon support electrode. Figure 4 contains the data for 5 mM $CdCl_2$ in 0.1 M KCl.

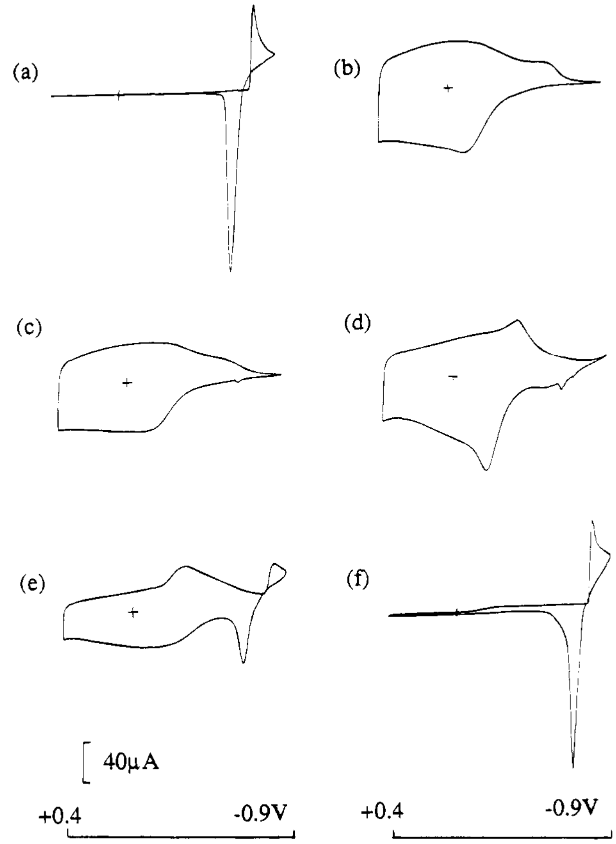

Figure 4. Cyclic voltammograms in 5 mM $CdCl_2$/0.1 M KCl (potential scan rate: 10 mV/s) for (a) glassy carbon electrode and (b) polypyrrole. The scans in Figure 4c−e correspond to carbon black loads of 5, 20, and 35 g/L, respectively. The scan in Figure 4f is for a carbon black sample similar to the one in Figure 2f.

The voltammogram in Figure 4a is for the bare glassy carbon electrode and shows the waves attributable to the $Cd^{2+/0}$ couple. The corresponding scan in Figure 4b is for the parent ppy. Note that the $Cd^{2+} \rightleftharpoons Cd^0$ redox feature is now absent attesting to (a) the impermeability of ppy to Cd^{2+} ions and (b) the poor electronic conductivity of ppy at ca. −0.8 V. With increasing loading of carbon black (Figure 4c−e), the probe redox feature is systematically more prominent. The carbon black clearly is effective in shuttling electrons between the outer film surface and the support electrode. The voltammogram in Figure 4f is for the carbon black alone (i.e., not containing any ppy). A comparison of this scan with the one in Figure 4a reveals two features: (a) a current plateau at potentials less than about −0.1 V; (b) a slight shift of the $Cd^{2+} \rightleftharpoons Cd^0$ redox waves which are attributable to carbon black.

Unfortunately, it is difficult to compare the present data with those reported[7] by another research group for ppy−carbon black electrocomposites synthesized from a nonaqueous medium. Specifically, only one solution load of carbon black (3.5 g/L) was employed by these authors, and the corresponding carbon black content of

Table 1. Characteristics of the Various Carbon Blacks Used in This Study[a]

	carbon black						
parameter	N135	N660	SB250	SB500	XC-72	BP 800	Printex XE-2
specific surface area,[b] m^2 g^{-1}	145.9	35.3	266.9	505.0	243.9	247.6	982.0
particle diameter, nm	22.7	88.2	24.9	23.7	28.3	28.1	38.1
microscopic surface area, m^2 g^{-1}	142.9	36.7	130.3	136.8	114.6	115.4	85.1
porosity,[d] m^2 gl$-^1$	3.0	0	136.6	368.2	129.3	132.2	896.9
DBP no., 10^{-5} m^3 kg^{-1}	135.3	90.7	145.7	157.8	170.2	68.1	346.0
24M4 DBP no., 10^{-5} m^3 kg^{-1}	117.8	75.1	99.1	109.1	129.1	61.5	319.6
electrical conductivity,[e] S m^{-1}	206	116	167	194	240	109	549

[a] The values shown for the various parameters are those averaged from replicate measurements. [b] Measured by the N_2 adsorption BET technique. [c] Computed from the equation: surface area = $3/\varrho R$, where R is the average radius of the carbon black particle as determined by TEM (cf. row 2), and ϱ is its density (1.85 g cm^{-3}). Spherical particle geometry is assumed here. [d] Taken as the difference between the two sets of values in rows 1 and 3, respectively. [e] Values from pressed pellets (29 MPa).

the electrocomposite was not reported. The cyclic voltammogram presented by these authors for one ppy–carbon black composite sample in propylene carbonate/1 M $LiClO_4$, however, does reveal an impressive enhancement of the charge envelope relative to the parent ppy trace.[7] In this regard, there appears to be broad agreement between our results and theirs. There also have been attempts by other researchers to improve the electronic conductivity of ppy at negative potentials. For example, treatment of ppy with NaOH was reported to result in an enhancement of the polymer conductivity at negative potentials up to ~1.1 V.[16]

Influence of Carbon Black Characteristics. A total of seven different carbon blacks were included for this portion of the study. Table 1 contains a listing of these blacks and their morphological attributes as measured by various tests (Experimental Section). All of these carbon blacks are produced by the furnace process.[17] However, as seen from Table 1 their morphological attributes (and hence their targeted applications) are quite different. The N135 grade is intended for use in the manufacture of rubber compounds in tire treads. On the other hand, the N660 black has relatively large particle size that finds use for tire sidewall manufacture as well as for various mechanical goods made of rubber. Thus the N660 is much less reinforcing in rubber than the N135 counterpart. The XC-72 and BP 800 are conductive carbon blacks which are used for applications related to antistatic coatings, electromagnetic shielding, etc. The Printex XE-2 has extremely high surface area. This high surface is mostly due to its porosity which is induced during its production under a severe oxidizing environment. Other than applications that require high electronic conductivity, this carbon black also has found a niche in the xerographic printing process, hence its name. The SB 250 and SB 500 are experimental carbon blacks that were produced at a pilot plant.

Correlations of the carbon black characteristics in Table 1 with the corresponding properties of the composite utilized two parameters for the latter, namely, charge density and the current density at −0.8 V. These parameters were extracted from cyclic voltammetry data on the composite electrodes in 0.1 M KCl. The charge density and current density as before were normalized with respect to the amount of ppy in the composite.

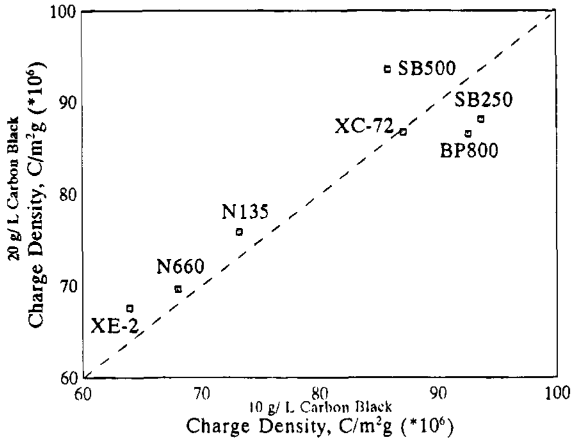

Figure 5. Plot of charge density (C/m^2·g) for electrocomposites prepared from carbon black solution loadings of 10 vs 20 g/L. The charge density was calculated from cyclic voltammetry data in 0.1 M KCl from +0.4 to −0.8 V at a potential scan rate of 10 mV/s. The various carbon blacks (Table 1) are indicated on the figure.

In discussing these data, it must be noted at the outset that the performance of all the composites was superior to ppy itself in terms of the two parameters, namely, charge density and current density. Interestingly enough, a plot of the charge density data at the two loads against each other shows some scatter as exemplified by Figure 5, indicating that the different carbon blacks do not exert the same effect on a chosen composite property at a given loading. In other words, the dashed line in Figure 5 has a slope of unity. Points lying above this line correspond to carbon blacks for which the higher loading affords better characteristics. The opposite is true for SB 250 and BP 800.

Figure 6a,b show the influence of carbon black porosity on the charge density of electrocomposites prepared from 10 and 20 g/L carbon black solutions respectively. It appears that starting at essentially no porosity (N135, N660), increasing porosity increases the charge density up to a point at which further increases are detrimental. At the higher carbon black load (20 g/L) the limit of usefulness of porosity is shifted to a higher level. A very similar trend is seen for the influence of the carbon black surface area on the charge density of the composite (Figure 7a). In this case also the higher carbon black load shifts the limit of usefulness of surface area to a higher level (Figure 7b).

Figure 8a,b illustrate the influence of carbon black conductivity on the charge density and current density of the resultant composite, respectively. An increase of the electronic conductivity of the black translates to a

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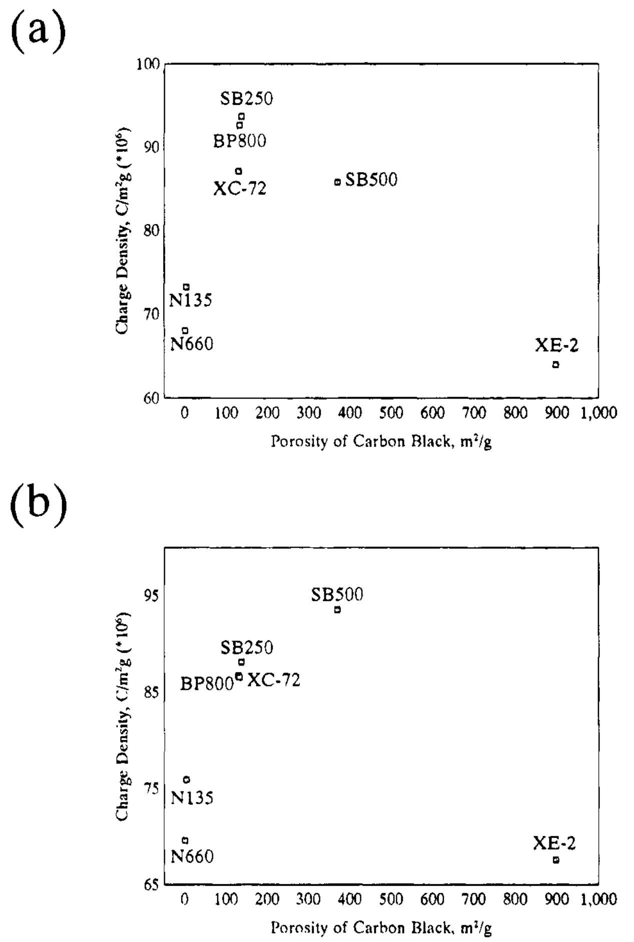

Figure 6. Plots of the charge density as described in Figure 5 vs the porosity of the carbon black used to prepare the electrocomposite for solution carbon black loads of (a) 10 and (b) 20 g/L.

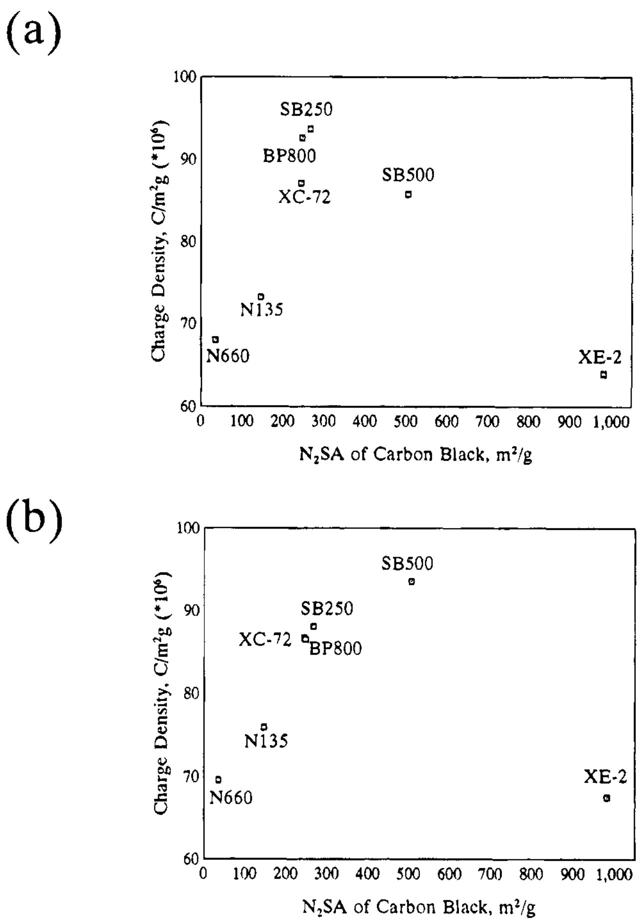

Figure 7. Plots of the charge density of the electrocomposite vs the N_2 specific surface area of the carbon black for solution carbon black loads of (a) 10 and (b) 20 g/L.

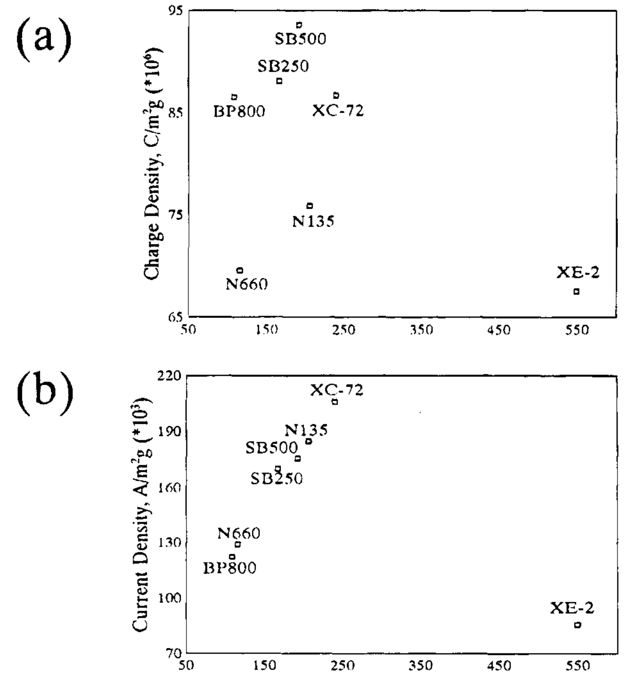

Figure 8. Plots of (a) charge density and (b) current density at −0.8 V of electrocomposites (synthesized from a 20 g/L carbon black solution) vs the electronic conductivity of the parent black (cf. Table 1).

better performance composite although as with the other parameters tested, the XE-2 based material shows "anomalous" behavior.

Geometric characteristics are responsible for what is called the "structure" of carbon black. Rigid, connected, irregularly shaped entities called aggregates predominately exist in carbon black. Their shapes make their effective volumes typically greater than the volumes of specific surface-area-equivalent spheres. The aggregates as a rule are not convex bodies but have indentations and concavities that effectively make them occupy or pervade volumes of space considerably greater than their solid volumes. It is virtually impossible to pack most carbon blacks to fill a fraction of space anywhere near that obtainable in random dense packings of monodispersed spheres. Intuitively, it is to be expected that a measurement of the ratio of void space (volume) to matter in a carbon black sample would reflect the departure from simple spherical geometry. Indeed, this is the rationale behind the so-called DBP absorption measurements that are used in the specification of carbon blacks.

The DBP absorption test may be described as a titration carried out in an internal mixer equipped with a means for sensing the torque on the mixing blades. The DBP is metered into the mixing chamber containing the black under test until the void space in the mixture is just filled. The endpoint is sensed as a sharp increase in torque, which terminates the process, and the result is reported as the volume of liquid (DBP) per unit mass of carbon black required to reach the end point.[8] The

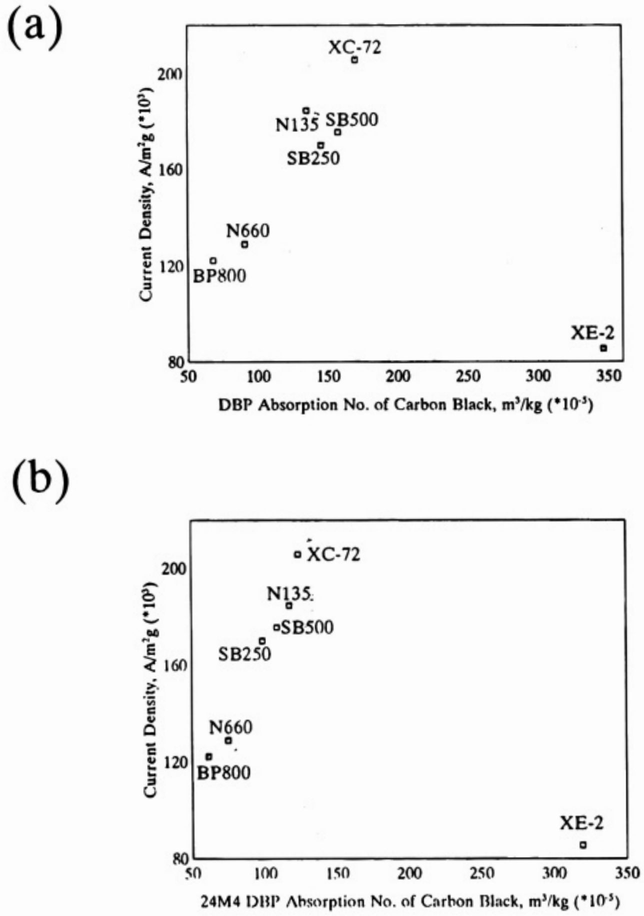

Figure 9. Plots of the current density at −0.8 V for the electrocomposite vs (a) DBP and (b) 24 M4 DBP absorption numbers of the carbon blacks listed in Table 1. The data are for a solution carbon black load of 20 g/L.

24M4 DBP absorption test entails compressive treatment of the sample before the measurement.[9] This is done to minimize differences due merely to mechanical history variations of the carbon black sample. Table 1 contains a listing of both DBP and 24M4 DBP absorption numbers for the various blacks.

Figure 9a,b contain plots of the current density of the composite against DBP and 24M4 DBP absorption number, respectively. These are shown for the 20 g/L carbon black solution case although similar trends were obtained at the lower carbon black load. An increasing structure of the carbon black (as probed by both DBP and 24M4 DBP absorption) translates to a corresponding increase in the current density of the electrocomposite except for the high-porosity Printex XE-2 sample. An increasing DBP and 24M4 DBP value would mean that the carbon black aggregates and agglomerates are more highly branched, causing more voids in the material. In a composite, this higher degree of branching ought to lead to increased contacts of the carbon black material to itself leading to higher conductivity and thus higher current density at potentials at which the ppy is in the reduced (insulating) state.

No correlation was observed between the charge density of the composite vs either the DBP or 24M4 DBP absorption number of the carbon black. This was true for either load of the carbon black. Thus the charge storage characteristic of the composite appears to be essentially controlled by the carbon black porosity (cf Figure 6) rather than on its void volume (or structure).

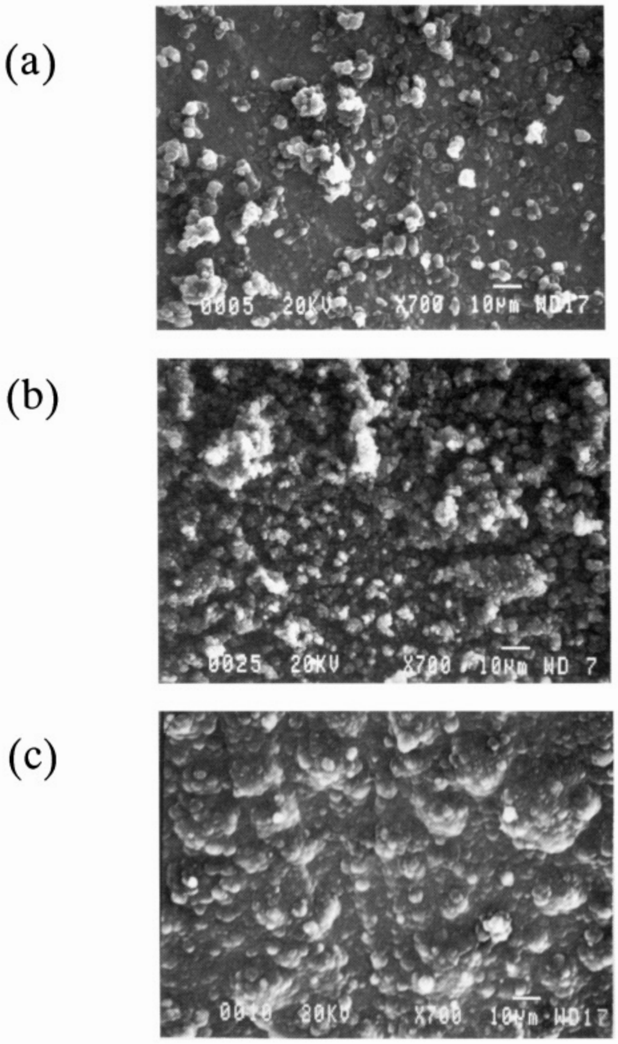

Figure 10. Scanning electron micrographs (700×) for ppy–carbon black electrocomposites synthesized from a 10 g/L solution: (a) N135 and (b) Printex XE-2, compared with the corresponding morphology of a ppy sample (Figure 10c).

Finally, Figure 10 compares scanning electron micrographs for electrocomposites prepared from a 10 g/L carbon black solution for ppy + N135 (Figure 10a) and ppy + Printex XF-2 (Figure 10b); these are compared to the morphology of ppy itself (Figure 10c). The electrocomposites clearly are more fine-grained than ppy itself and the Printex XE-2 based sample shows a high degree of dispersion consistent with its high surface area (Table 1).

Nagashima et al.[7a] have compared the characteristics of ppy-based electrocomposites prepared from five different types of carbons or carbon blacks, namely Tokai Carbon 8500, 4500, Nippon Carbon BP-1000, and Ketjen EC-600JD and SP-20 graphite. The average particle diameters of the blacks varied from 14 to 40 nm, and the surface area varied from 60 to 343 m²/g. The charge capacity (as probed by cyclic voltammetry) was found to vary with the latter parameter, but no correlation was found with carbon particle size or oil absorbability. However, it must be noted that these authors did not take into account the contribution of ppy in their composite (i.e., the composite property was not normalized with respect to its ppy content). Interestingly enough, the Ketjen black with extremely high specific surface area and electronic conductivity was found to yield an inferior composite much like the Printex-based composite behavior in this study. Poor mechanical contact between the ppy and the carbon particle was attributed by these authors[7a] for the inferior behavior of the Ketjen black-based composite relative to the other specimens. Taken as a unit, our new data on a broader range of carbon blacks are in agreement with these earlier results.

The anomalous behavior of the Printex XE-2 based composite in this study is probably related to the poor physical quality of the higher surface area composites (e.g., the Printex XE-2) which were very brittle and more likely to have fractures in the film. This was confirmed by microscopic examination of the Printex XE-2 based specimens. It must be borne in mind that the Printex XE-2 black itself has very high electrical conductivity relative to the other blacks (Table 1). Thus, the anomalous behavior of the composite specimens based on this black must be attributed to the poor film characteristics rather than to intrinsic limitations of the carbon black component.

In conclusion, ppy–carbon black composites have been electrosynthesized from an aqueous medium for the first time. We have extended our earlier preliminary study[1] to include a more complete characterization of these new materials as well as built upon the studies of earlier researchers[7] to explore the influence of carbon black characteristics on the properties of the resulting electrocomposites. In future papers in this series, we shall present aspects related to electronic percolation in these materials as well as demonstrate the use of ppy–carbon black composites in applications related to toxic waste treatment.[18]

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(18) (a) Wampler, W. A.; Rajeshwar, K. To be published. (b) Wampler, W. A.; Basak, S.; Rajeshwar, K. Manuscript in preparation.