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INTRODUCTION

Attempts have been made in recent years to modify or enhance the properties of conducting polymers, e.g., polypyrrole, by incorporating it in other polymers¹, metals², or metal oxides³. Carbon black appears to be a logical candidate for use in such a composite. Composites of carbon black with other materials, e.g., polymers, have found many uses in the rubber industry. Another important application is the electronics and dielectric industry where the conductivity of these composites may be easily tuned by varying the carbon black type and load. High resistivity composites are useful for communication cable and optical fiber protection. On the other hand, the low resistivity counterparts have useful anti-static properties. Conductive polymers such as polypyrrole are being targeted for very similar technological applications. Thus there is both a fundamental and technological interest in exploring how a composite of polypyrrole and carbon black would behave relative to its components.

Polypyrrole had been studied previously as a composite with carbon fiber and carbon fabric⁴, but this was only an electrochemical deposition of polypyrrole onto the carbon. Another group synthesized polypyrrole in the presence of carbon powder in a non-aqueous medium and found the composite to have enhanced charge capacity⁵; however, many details such as actual composition of the composite were not studied. In this work composite of carbon black and polypyrrole were prepared by three methods: (1) electrochemical oxidation of pyrrole monomer in the presence of carbon black to form an "electrocomposite", (2) chemical oxidation of pyrrole monomer in the presence of carbon black to form a "chemical composite", and (3) simple physical mixing of polypyrrole with carbon black to form a "physical composite." All three types of composites showed enhanced characteristics relative to their individual components, which include higher charge storage capacity and better electronic conductivity (especially at negative potentials).

EXPERIMENTAL

Films of polypyrrole-carbon black electrocomposites were prepared by polymerizing pyrrole (0.1M) at +0.85V (vs. Ag/AgCl) in a 0.1M 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 polypyrrole-carbon black composite films, and film growth was terminated after a constant charge of 0.71 C/cm² had accumulated. Solution loads of carbon black in the range of 0.5-50g/L were employed and the uptake of carbon black was

monitored by elemental analysis (Perkin Elmer 2400 CHN analyzer). Electrochemical measurements were made on a Princeton Applied Research (PA) Model 273 potentiostat.

Chemical composites were prepared by adding varying amounts of carbon black to a well-stirred 250 ml of 0.1M pyrrole and then adding 250 ml of 0.15M K₂S₂O₈ (the oxidizing agent). Stirring was continued for 30 minutes before filtering, washing and drying steps. Conductivity measurements were made on pressed pellets (4000 psi). Physical composites were prepared by mixing chemically synthesized polypyrrole with carbon black in a mortar and pestle.

Seven different carbon blacks were studied, which included N135, N660, XC-72, Black Pearls 800, Printex XE-2, SB250, and SB500. The last two are experimental pilot plant carbon blacks. The carbon black samples represented a wide range of specific surface area and structure.

RESULTS AND DISCUSSION

In the case of the electrocomposites, an electrotrapping mechanism is proposed for the composite film growth; the negatively charged carbon black surfaces are attracted toward the (positively charged) anode surface where they are assimilated into the growing polypyrrole matrix. The presence of carbon black enhanced the charge storage capacity and the electronic conductivity of the parent polymer in the electrocomposite as measured by cyclic voltammetry in 0.2M KCl. The effects were increased with carbon black loading. Increasing specific surface area of the carbon black used exerted a positive effect on the ability of the composite to store charge; whereas, the structure of the carbon black had a positive effect on the charge density at negative potentials.

Polypyrrole-carbon black "chemical composites" were successfully synthesized and characterized. The polymer encapsulates some of the carbon black while the rest remains adhered to the surface of the polymer. As carbon black loading in the polymer is increased there is first a small drop in conductivity before the carbon black is percolated, which is believed to be due to the carbon black occupying volume but not contributing to charge transport at these low concentrations. At a critical concentration (the percolation point) the conductivity rises sharply with increasing carbon black concentration. The most important carbon black feature that will affect the conductivity of the composite appears to be the "structure" of the

carbon black. The physical composites behave quite similarly.

The usefulness of these chemical and physical composites was demonstrated in an environmental remediation project to convert toxic Cr (VI) to Cr (III). Both components have the ability to reduce hexavalent chromium, but the composite has enhanced reduction ability over the individual materials (Figure 1).

CONCLUSIONS

Polypyrrole-carbon black composites have been successfully synthesized by various methods in aqueous medium. The composites have been demonstrated to exhibit a synergism for certain properties over the individual components. The composites produce a material with enhanced charge storage capacity, better conductivity at negative potentials, and increased ability to reduce hexavalent chromium in an environmental remediation project.

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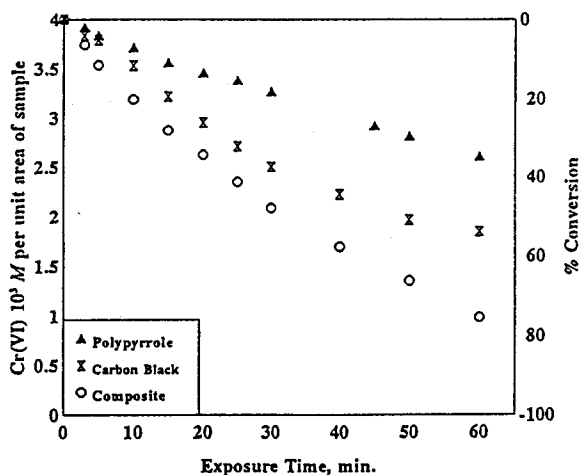


Figure 1. A comparison of equal concentrations (40% by weight) of polypyrrole N135 carbon black, and a polypyrrole-N135 carbon black chemical composite in PVC for plots of molarity of Cr (VI) per cm² of surface versus exposure time of sample to a 1mM K₂Cr₂O₇ solution in acidic medium.