

NOTES

Polyaniline / Polymeric Acid Composite, a Novel Conducting Rubber

INTRODUCTION

Organic conducting polymers have attracted much attention in recent years.¹⁻⁷ Many technological applications of these interesting conducting materials such as in molecular electronics,⁸ light-weight batteries,³ and displays,² etc., have been forecast. However, a major problem relating to the successful utilization of such organic materials pertains to their inherent poor mechanical properties. Consequently, vigorous efforts are still continuing towards the search of new conducting polymers with desired physical and chemical properties. In this context, polyaniline has recently been considered to be a highly promising material because it can be conveniently switched in aqueous acid solutions and it does not lose its electroactive character when stored in an ambient environment.^{6,7} A unique observation made in case of undoped polyaniline is the fact that its electrical conductivity increases to several orders of magnitude (10^{10}) on being treated with an inorganic acid⁷ (e.g., HCl, HF, or H₂SO₄). This phenomenon has been described to involve a new concept of doping in that the number of electrons associated with the conducting polyaniline does not change during the doping process.⁶ In order to further establish this phenomenon of doping, we have carried out experiments on electrochemically undoped polyaniline with polystyrene sulfonic acid, a polymeric acid. Another principal reason which motivated us toward undertaking this work has been the pressing technological need to improve upon the mechanical properties of conducting polyaniline. In this paper, we report preliminary results of a composite of polyaniline with polystyrene sulfonic acid.

EXPERIMENTAL

Polyaniline samples used in the present study were electrochemically prepared using an apparatus described previously.^{3,5} The electrolyte consisted of 10 mL of HCl (10M concn), 2 mL of distilled aniline, and 40 mL of distilled water. Loosely bound black aggregates of polyaniline formed on anode consisting of indium-tin-oxide glass plate (area = 2×3 cm²; sheet resistance $\sim 20 \Omega/\square$). A piece of platinum foil served as counter electrode. A current density of 1 mA/cm² at 1 V was found to be sufficient for initiating the polymerization of aniline. A constant supply of nitrogen gas was maintained through the electrolyte during the electropolymerization. Polyaniline deposit removed from the conducting glass were undoped by treating these with aqueous ammonia. This undoped polyaniline after satisfactory drying was turned into pellets and further utilized for doping with a polymeric acid.

Polystyrene sulfonic acid was prepared using a procedure followed by Kato et al.⁹ A mixture comprising of 3 g of polystyrene pellets, 0.034 g of silver sulfate, and 44 mL of sulfuric acid was heated at 90°C for 2 h until it became dark brown and highly viscous. This viscous liquid when poured into excess of ice-cold distilled water on constant stirring resulted into a white gummy mass which was quickly washed with water several times until heat emergence was no longer felt. The precipitate of polystyrene sulfonic acid was dissolved in distilled water to make 100 mL of solution of polystyrene sulfonic acid.

A known amount of polystyrene sulfonic acid solution was taken in a Petrie dish to which a predetermined quantity of undoped polyaniline dried previously at 50°C was added. At least four such different compositions of undoped polyaniline and polystyrene sulfonic acid were prepared. In each case, a paste dark green in color was obtained which was dried in an oven at about 120°C and later in vacuum, respectively. Interestingly, this paste could be homogenized by addition of a few drops of acetone.

The electrical conductivity of this rubbery mass was measured in air using a four-point probe method. The elongation measurements on different samples of the conducting rubber were made on a specially designed mechanical tester.

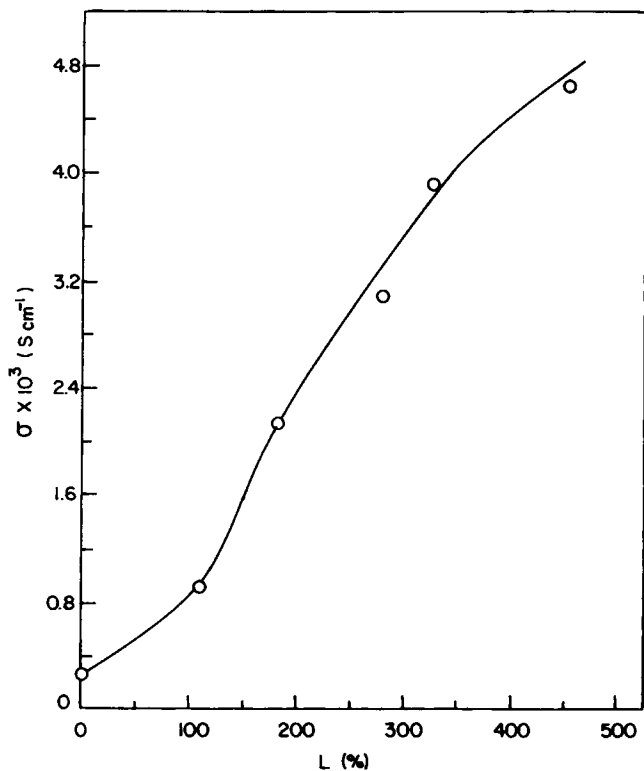


Fig. 1. Variation of electrical conductivity σ as a function of percentage of elongation L of polyaniline-polystyrene sulfonate composite in polystyrene sulphonic acid.

RESULTS AND DISCUSSION

The electrical conductive rubber essentially resulted with the evaporation of water from a mixture containing known amounts of undoped polyaniline and polystyrene sulfonic acid respectively. Compared to HCl-doped polyaniline wherein we observed a decrease in its value of electrical conductivity at 40°C, no such decrease of electrical conductivity was found in case of polyaniline/polystyrene sulfonic acid composite. This conductive rubber having an elongation at break of about 500% could be stretched up to 150%. The variation of electrical conductivity σ measured in case of a typical composition of polyaniline (12.6%) contained within the matrix of polystyrene sulfonic acid with change in elongation length L has been shown in Figure 1. The increase in the value of electrical conductivity of the stretched samples of composite can be attributed to the orientation of the molecules in the direction of stretching.

The electrical conductivity σ of each of the different compositions of polyaniline/polystyrene sulfonic acid composite was determined and its variation as a function of weight percentage W of polyaniline contained within the polystyrene sulfonic acid is shown in Figure 2. Such a variation of electrical conductivity is characteristic of a polymer composite. At low loadings, the electrical conductivity increases slowly up to the percolation threshold ($\sim 11.6\%$) after which it suddenly increases. It appears as if the conductive particles of polyaniline-polystyrene sulfonate get close to each other, leading to the formation of a continuous conductive network in polystyrene sulfonic acid.

The rubbery characteristics of conducting polyaniline/polystyrene sulfonic acid composite can be interpreted by considering the fact that only equivalent amounts of undoped polyaniline will react with the polystyrene sulfonic acid resulting into the formation of polyaniline-polystyrene sulfonate. Since the acid added was in excess, the conductive particles of polyaniline-polystyrene sulfonate get distributed into the matrix of polystyrene sulfonic acid. As a result, a polyaniline molecule may be linked to many polystyrene sulfonic acid molecules via ionic bonds. That means

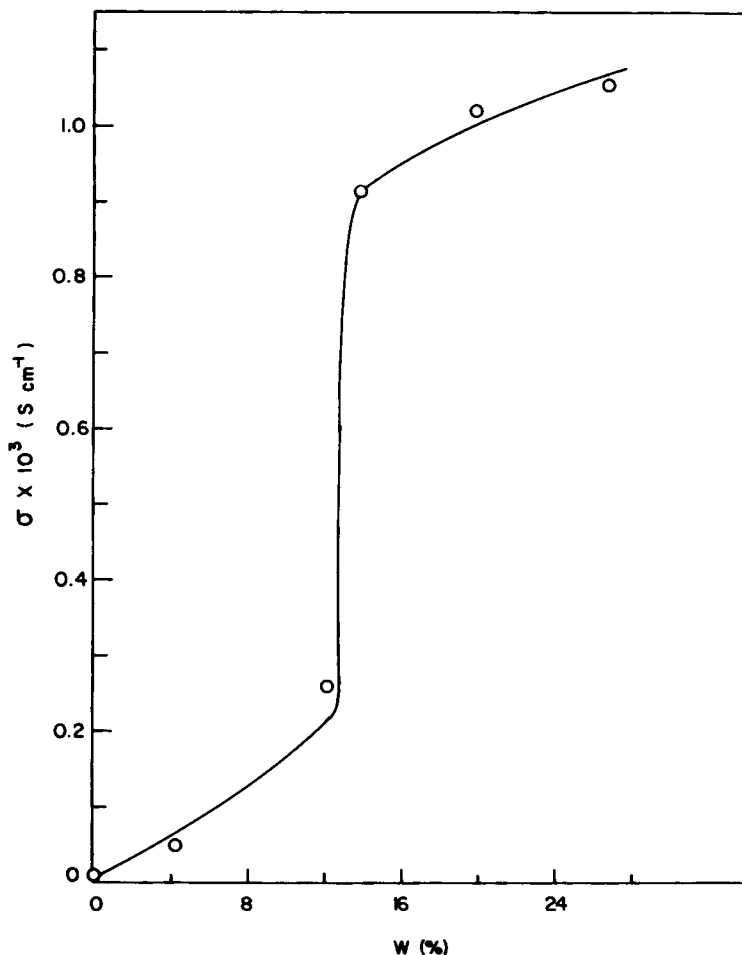


Fig. 2. Variation of electrical conductivity σ as a function of weight percentage W of polyaniline in polyaniline/polystyrene sulfonic acid composite.

some sulfonate groups from a given polystyrene sulfonic acid molecule are ionically bonded to a polyaniline molecule whereas others may get attached to other polyaniline chains. Some remain as sulfonic acid groups. Similarly, it may also happen that one polystyrene sulfonic acid molecule gets ionically bonded to several polyaniline molecules. The net result is that both the polyaniline chains and the polystyrene sulfonic acid molecules are occasionally crosslinked to each other resulting into the observed rubbery behavior of the composite. The experimental observation that this conducting rubber hardens when containing a lower percentage ($\sim 2\%$) of polystyrene sulfonic acid further testifies the important role played by the polymeric acid in its elastic behavior. An important consequence of the existing ionic bonds within the composite is that the particles of polyaniline will not get detached from the conducting rubber thus formed. However, it is difficult to ascertain at this stage if this interesting polymeric composite constitutes either a two-phase system or the aniline oligomers are molecularly dispersed into the matrix of polystyrene sulfonic acid.

In view of the observed value of the lower percolation threshold of the composite when compared to those of the conventional conducting rubber such as polybutadiene blends¹⁰ which typically exhibit the elastic properties of the host rubber, the systematic investigations including morphological studies of this novel conducting rubber are in progress.

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