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Synthesis of Polyaniline Nylon 66 Conducting Composites

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Composites of polyaniline conducting polymers (polyaromatic amines) with synthetic polymers such as polyamides (nylons) can be processed from formic acid solvent through cast method. Formic acid was found to be a good solvent for preparation of polyaniline/nylon composites (PAn/Ny) as free standing films or coating on the surface of different inert substrates. The preparation conditions of PAn/Ny composite were optimized with regard to the mechanical properties and electrical conductivity. Chemical polymerization of polyaniline polyamide (nylon) composites with the procedure described in this paper provides the best way in order to prepare PAn/Ny composite membranes with high conductivity, uniformity and homogeneity. The procedure described can also be considered the only way for preparing PAn/Ny composites as coated on the surface of inert and conducting substrates such as glass or paper in order to make them conductors or semiconductor materials.

Key Words: Polyaniline, Nylon 66, Composite, Conductivity, Casting.

INTRODUCTION

Polyaniline (PAn) is a well known and one of the most potentially useful conducting polymers that has been extensively investigated in the last two decades[1–6]. The Nobel prize for chemistry was awarded in 2000 to MacDiarmid and his co-workers Shirakawa and Heeger for the discovery and development of conducting polymers.

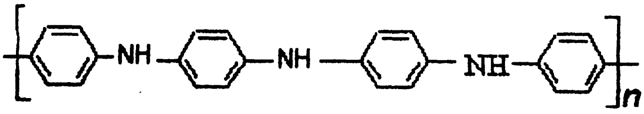
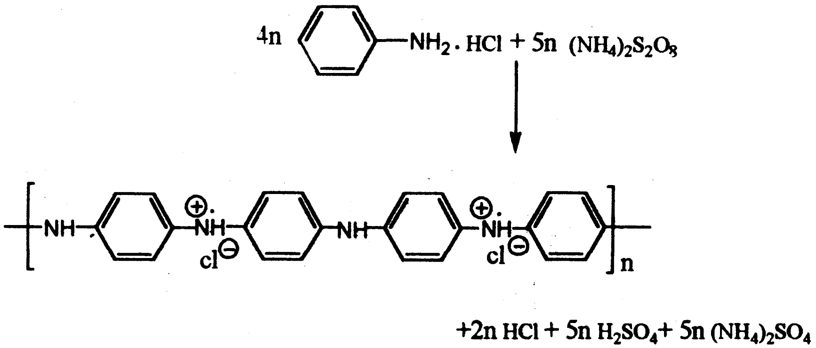


Fig. 1. Chemical structure of polyaniline (PAn) which beocmes electrically conducting afte: doping.

The important feature is the extended domain of conjugated double bonds. Good conductivity ($\sigma = 10^{10}-10^{1}$ S/cm), unique electroactivity, excellent environmental stability, insolubility in the common solvents, easy polymerization, low cost of monomer and the superior processibility have stimulated several investigations for potential applications of polyaniline in the last two decades. Electronic properties of conducting polymers are the same as semiconductors and they are characterized by a conjugated structure of alternating single and double bonds. PAn can be synthesized by the oxidation of aniline solution in bronsted acids by chemicals or electrochemically[5,6]. The efficient polymerization of aniline is achieved only in an acidic medium (bronsted acid). On the basis of conductivity, HCl and H_2SO_4 have been found the best dopants for protonation of polyaniline.



The oxidation process is accompanied by the insertion of anion to maintain the charge neutrality. The electrical conductivity of PAn is strongly dependent on pH of the polymer or solution. Acid doped oxidized polyaniline (EB/HCl) is simply converted to a base form called emeraldine base (EB) by treatment with dilute aqueous alkali solutions ($\sigma < 10^{-8}$ S/cm). Polyaniline exists in different oxidation states.

Of the different oxidation states of polyaniline the emeraldine salt (50% oxidized) is the only electrically conducting form while all other forms are insulating[5]. Polyaniline is not soluble in common solvents. Melt processing of PAn is also not possible, since the polymer decomposes at temperatures below its softening or melting point. Emeraldine base form (EB) is the only conducting and soluble form of polyaniline in few solvents.

The solubility of polyaniline (EB form) in some specified solvents (such as N-methylpyrrolidone, formic acid 88%) opens the opportunity for solution processing of PAn with other conventional insulator polymers[7–10]. This permits it to be solution processed to produce large, flexible, free standing films of the polyaniline composites with electrical and improved mechanical properties. These composite materials have introduced conducting polymers to practical applications such as electrochromic devices, rechargeable batteries, sensor materials, anticorrosion protection and membrane separations[11–13, 16]. Various chemical and electrochemical methods have been employed for preparation of polyaniline composites or blends with different common polymers, properties and characterization techniques have been excellently reviewed by Jayashree *et al*[14].

EXPERIMENTAL

All reagents were used as purchased. Poly[(hexamethylene adipamide)] [—$NH(CH_2)_6NHCO(CH_2)_4CO$—] or nylon 66 (S 293-E Akzo Co., Holland) was obtained as granules form. Aniline, formic acid (88%) and N-methylpyrrolidone solvents were procured from Merck. The other reagents used were of high purity and AR grade. Electrical conductivity of the polymers in doped state was measured using standard 4-point probe technique[14, 15]. A digital coulometer (Zac. Chem., Iran) was used as current source. An accurate digital multimeter (Alda) was used for measuring potential drop during 4 point probe test.

Preparation of polyaniline composites: Polyaniline was prepared chemically as described in literature[2]. Aniline was distilled before polymerization. A solution of 0.20 M of aniline in HCl (1 M) was used for polymerization. Ammonium persulfate (0.2 M) was used as oxidant (the molar ratio of monomer to oxidant was 1 : 1.25). The reaction temperature was adjusted about 0°C. In order to change PAn/HCl to EB form, the synthesized polymer powder was treated with a solution of ammonia solution (0.5 M). For preparation of composite as free standing films, the separately prepared solutions of EB and nylon in formic acid (1% w/w), were mixed together in different weight ratios. The resulting solutions were poured in evaporating petri dishes. The solvent (formic acid, $k_a = 1.8 \times 10^{-4}$, b.p. = 105°C) was evaporated from the cast film in an oven at temperature about for 48 h with air circulation. The cast films were peeled off from the dishes after soaking in distilled water for a while. The films were dried at room temperature after washing with copious distilled water. The higher temperatures should be avoided because of structural changes such as cross-linking which occurs at elevated temperatures[6, 16].

RESULTS AND DISCUSSIONS

The preparation conditions were optimized with regard to the mechanical properties and electrical conductivity. The optimum weight ratio for preparation of flexible conducting films of PAn/Ny composites by solution processing was found to be 1 : 3 for PAn/Ny66. The maximum conductivity obtained for PAn/Nylon composite membranes was 0.10 S/cm. With increasing percentage of Nylon, conductivity of polymer composite decreased gradually. Increasing percent of PAn may increase the conductivity in composite films but the mechanical properties deteriorate with increasing PAn percentage. The conductivity of PAn/Ny composite films prepared in this investigation with cast method is both higher and more uniform than previously reported PAn Composites prepared with other techniques[7]. Flexible and free standing PAn/Ny composite films with adequate mechanical properties were also produced successfully in this investigation (tensile strength = 20 MPa). Almost the same results were obtained when we used nylon-6 instead of Nylon-66. Therefore, thermoplastic polymers such as polyamides (nylons) seem to be good candidates for preparing PAn conducting polymer composites. Therefore, it seems that the composite films of PAn/Ny are suitable, sensitive and inexpensive chemiresistor or sensors for detection of even low concentrations of acid or base gases in air of plants or in aqueous solutions.

The colour of PAn/Ny composites coated as a thin film from formic acid on the surface of transparent glass plates is changed from deep blue by acid treatment (conducting state) into brown by subsequent base treatment (*e.g.*, ammonia vapour or HCl). The colour changes with pH were also reversible upon pH changes or acid/base treatments. Better adherent coating of PAn/Ny film can be obtained on glass surface. Therefore, the PAn/Ny composites coated on transparent glass plates can be used as very cheap chemical sensors (*e.g.*, pH sensors). The electrical conductivity of PAn/Ny composites is also changed reversibly with pH changes or exposing to acidic or basic vapours. Therefore PAn/Ny composites coated as thin film on glass plates can be used as gas sensor materials. PAn/Ny was very sensitive to Bronsted or Lewis acid/base gases or vapours. Quantitative determination of acid or base gases, oxidant or reductant chemicals may be possible by measuring the optical absorption spectrum or conductivity of the PAn/nylon film.

It was also observed that the conductivity of PAn/Ny composite coated on the surface of a glass plate doped with HCl, changes reversibly by heat treatment up to 100°C. The temperature-dependence behaviour was the same as semiconductors. It can be envisaged that the PAn/Ny composites may be suitable materials for fabrication of thermal sensors. However, more quantitative investigations are needed for accurate conclusions.

Conclusions

The optimum weight ratio for preparation flexible conducting films of PAn/Ny composites by solution processing was found to be 1 : 3 for PAn/Ny66. The maximum conductivity obtained for PAn/Nylon composite membranes was 0.10 S/cm. Preparation of polyaniline composites with polyamides from formic acid through solution cast method produces more uniform and homogeneous composites than other techniques. It could be possible to cast PAn/Ny from solution on the surface of dense solid insulating substrate in order to fabricate relatively inexpensive acid-base sensors (even disposable). Electrical conductivity of PAn/Ny composite films prepared in this investigation was reversibly changed from insulator to conductor when exposed to acid and base treatments (protonation/deprotonation) in both the vapour and aqueous phases. Flexible and semiconducting PAn composites as fibres or membranes can be readily prepared with polyamides from formic acid as solvent. Polyamides (nylons) seem to be very suitable materials (cheap and structurally consistent with PAn) for preparing PAn composites in different shapes. Since melt processing is not possible for PAn (decomposes at melting point), so formic acid is the best solvent for preparation of polyaniline/nylon composites as membranes or coating. However, it is an odorous material and should be handled cautiously. Although, N-methyl pyrrolidone (NMP) has been reported the best solvent for PAn, but this popular solvent cannot dissolve nylons.

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