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Synthesis of Polyaniline/Polyamide composites as membrane and investigation of its properties

M. Banimahd Keivani [1,2], M. Aghaie[3], R. Ansari [4], K.Zare[1], H. Aghaie[1,*]

[1] Chemistry Department, Science & Research Campus, Islamic Azad University, Tehran, Iran
[2] Iranian Academic Center for Education Culture & Research (ACECR) Guilan Branch, Rasht, Iran
[3] Faculty of Chemistry, North Tehran Branch, Islamic Azad University ,Tehran,Iran
[4] Chemistry Department, Guilan University, Rasht, Iran

ABSTRACT

Practical applications of conducting polymers such as polyaniline as membranes are particulary limited because of their poor mechanical properties. However by mixing polyaniline with some conventional insulating polymers such as nylon and preparation composite films through solvent casting or blending, it seems to be a suitable way in order to increase the mechanical properties of the conducting polymer films. Polyaniline/Nylons (PAn/Ny) composites were processed from formic acid. The preparation conditions were optimized with regard to the mechanical properties. The molar ratio of PAn to nylon has the greatest effect in mechanical properties of the composite membranes.Thermal stability of the PAn/Nylon composites (casted on transparent glass from formic acid) was investigated spectrotrophotometrically (Uv-Vis). Our spectrophotometric analysis shows that the polymeric composites are more thermally stable compared to pure PAn.

Keywords: polyaniline; Nylon; polyamide; conducting polymers; composite; membrane

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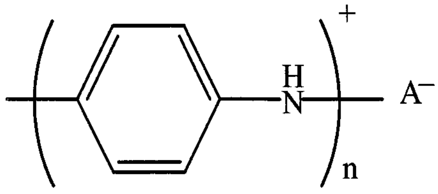
[*] .Corresponding Author;H.Aghaie
E-mail address:hn_aghaie@yahoo.com

INTRODUCTION

Polyaniline (PAn) is one of the most important electrically conducting polymers, because of its inherent combination of high conductivity and high environmental stability.

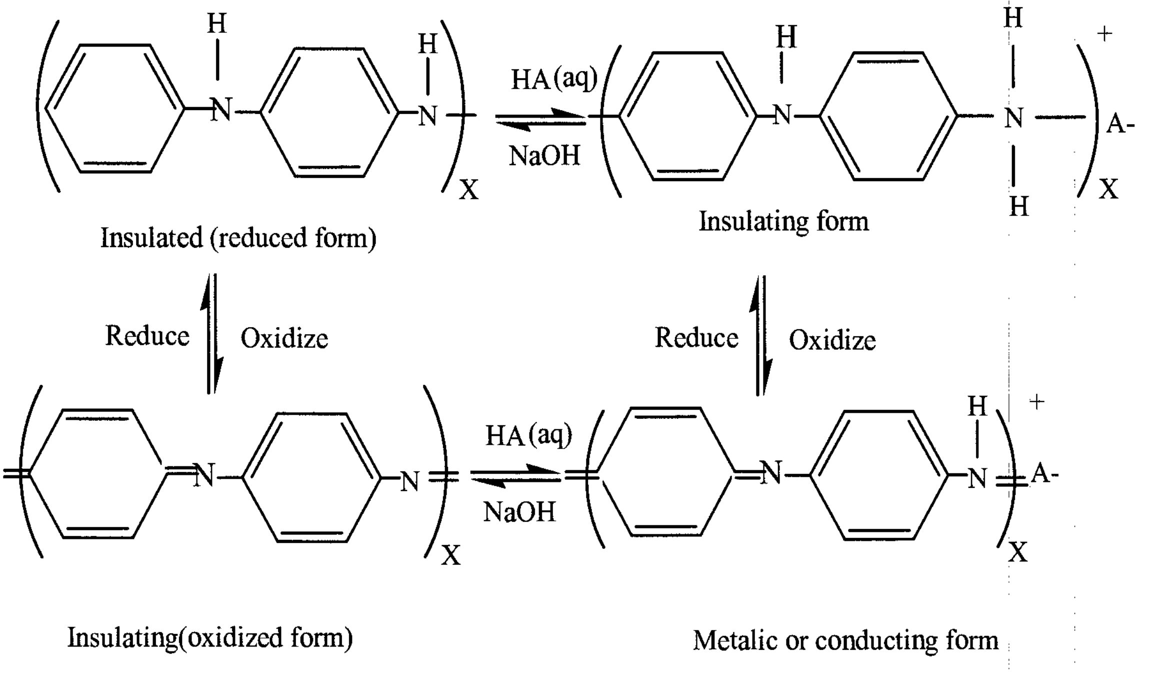


Polyaniline (PAn)

The high processibility of Polyaniline has stimulated the attention of several investigations in order to develop the role and applications of this polymer.

Polyaniline conducting polymers have been considered as good candidates for commercial applications such batteries, sensors, separation and electro-chromic devices [1-3].Other advantages are their ease of synthesis in both aqueous and non-aqueous solutions, low cost of monomer, relatively high conductivity (1-20 S/cm) and environmental stability. Regarding conducting polymers,one can find out that many researches have been devoted to polyaniline during the last quarter of century [4-6].

The noble prize for chemistry has been awarded in 2000 for the discovery and development of conducting polymers [7].It has been reported that polyaniline structure is as follow[8]:



Polyaniline can be synthesized by the oxidation of aniline in the solution phase in bronsted acids by chemical oxidants or electrochemically [8-11]. PAn is changed into a base form called emeraldine base (EB) by treatment with dilute aqueous alkali solutions. EB is insoluble in water but soluble in some aqueous and non-aqueous mixed solvents such as concentrated sulphuric acid, aqueous acetic acid (80%) and formic acid (88%), dimethylsulfoxide (DMSO), dimethylformamide (DMF), and 1-methyl 2-pyrrolidinone (NMP). This permits it to be solution processed to produce large, flexible, free standing films of the emeraldine base polymer which can be protonated (doped) with a non-oxidizing protonic acid such as HCl to films having conductivities of ~10 S/cm [12-13]. Electrical conductivity of PAn is strongly dependent on pH of the polymer or solution. It changes into an insulator material by simple base treatment or at pH above 4. Practical application of conducting polymers such as polypyrrole, polythiophene, and polyaniline is limited particulary because of their poor mechanical properties. However, the composites prepared by mixing of conducting polymers with conventional polymers can be used with improved mechanical properties for many usages.

It has been reported [14] that organic acid dopants produce more thermal (in air) and environmental (water) stability than small size dopants. This stability can be due to immobility of the larger size counterions. Therefore the large size dopants anions contrast to Cl^- do not migrate or removed when the polymer immersed in water. In generally doped polyanilines are less thermally stable than undoped form. EB (undoped, oxidized base form) of PAn is the most thermally stable form of polyanilne (up to 500°C) with regard to structural integrity [15].

Thermal studies of polyaniline conducting polymers are particularly important when one considers the use of elevated temperatures to process polyaniline and its blends into technologically useful forms. In any practical application, knowledge of the stability and degradation mechanism of this class of conducting polymer is also of primary importance. The high thermal stability of the neutral form of polyaniline (EB) has brought about the possibility for newer dopants in order to prepare heat stable doped PAn[16].

EXPERIMENTAL

Chemicals

Aniline (from Merck company) was used after distillation. Nylon 6 (KN 136, Kopa co. Korea), Nylon 66 (S 293-E Akzo co., Holand) was obtained as granules form. The other chemicals were of high purity and AR grade.

Instrumental

Mechanical tests (Tensile strength) were carried out using S.D.L. Micro 250 (manufactured by Shirley co. England). Uv-vis spectroscopy was carried out using Uv-2100 (Shimadzu). Electrical conductivity was measured using 4-point probe technique [16]. A digital coulometer (ZAG chem. Iran) as current source, digital micrometer for measuring thickness of films and an accurate digital voltmeter (ALDA) for measuring potential during conductivity measurement were employed.

Procedures

Aniline (Merck) was distilled before polymerization as a white liquid and stored in fridge before polymerization. 25 mL of freshly distilled aniline was added into 500 mL of HCl 2M in a beaker. 250 mL of 0.25 M ammonium persulfate $(NH_4)_2S_2O_8$ solution, was added from a burette into the well-stirred monomer solution during 40 min. Polymerization was carried out at ~5°C. The solution was continued stirring about 2 hours after the complete addition of the oxidant. Then the polymer (green dark powder) was filtered, washed with dilute HCl solution, distilled water and methanol respectively in order to remove impurities. Then the product was dried at 50- 60°C in an oven for 2 hour at ambient conditions.

The polyaniline powder (2.0 g) was treated with 500 mL of ammonia solution (0.1M) for 12 hours in order to change the polyaniline into emeraldine base salt (EB). For preparation of composite membrane or free standing films, solutions of EB in formic acid (1%) and Nylons in formic acid (1%) were prepared separately, then they were mixed together in different proportions. The resulted solutions (EB/Nylon) were poured in petri dishes and casted in an oven at temperature about 60°C. The casted films were socked in distilled water for a while and then were removed from the dish with the help of a surgery knife. The films were dried at room temperature after washing with distilled water.

Thermal stability of the PAn/Nylon composites (casted on transparent glass as a thin film acid) was investigated spectrotrophotometrically (uv-vis). Thermal treatment was carried out for 30 minutes at considered temperature. For mechanical test, the polymer films were cut into 1cm× 4cm strips.

RESULTS AND DISCUSSIONS

Polyaniline (EB) can be processed with formic acid (Ka = 1.8×10^{-4}, bp = 105°C). Formic acid is a good solvent for both polyamides (Nylons) and polyaniline. So composites of PAn with polyamides (Nylons) can be easily prepared by solution processing. Polyaniline (EB) can be readily dissolved in formic acid. However, the casted films are too weak to be removed from the dish. The polymer films were very fragile. Preparation of the PAn as composite with conventional polymers can be used to improve the mechanical properties. It was found in this research that PAn/Nylon composite casted from formic acid (suitable solvent for both components) could be prepared with adequate mechanical strength in order to be used as membrane or freestanding films. Some decrease in mechanical properties (tensile strength) was observed when the polymer prepared as composite via solvent casting.

Thermal treatment

Uv-vis study on polymer samples (Fig.1) revealed that PAn (EB form) is thermally stable up to 130°C under air atmosphere. Not any important changes were observed in the Uv-Vis spectrum of the polymer before and after heat treatment till 130°C. The results obtained from our Uv-Vis analysis reveal that some structural changes (without decomposition) occur even after mild heat treatment. However, when the polymer was treated at above this temperature, some irreversible changes such as cross-linking occured.

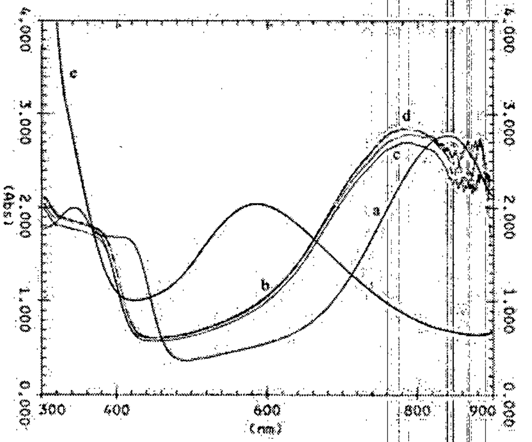


Fig.1. Uv-Vis spectra of PAn (EB),(a)Before thermal treatment, (b)After treatment at 80°C, (c) After treatment at 100°C, (d)After treatment at 130°C, (e)After treatment at 150°C, The time of exposure at maximum temperature was 30 min. Thermal treatment was carried out in laboratory conditions.

In the case of PAn / Nylon 6 (Fig.2) and PAn / Nylon 66 (Fig.3), the polymer is composites were more thermally stable (up to 180°C) in air than pure PAn.

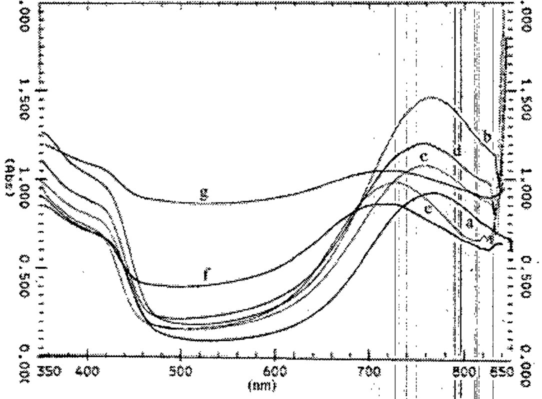


Fig.2. Uv-Vis spectra of PAn (EB)/Nylon6, (a)Before thermal treatment, (b)After treatment at 80°C, (c)After treatment at 100°C, (d)After treatment at 130°C, (e)After treatment at 150°C, (f)After treatment at 200°C, (g)After treatment at 250°C. The conditions were the same as Fig.1.

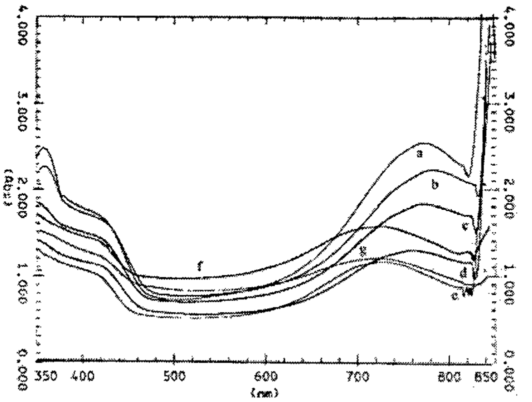


Fig.3. Uv-Vis spectra of PAn (EB)/Nylon 66, (a)Before thermal treatment, (b)After treatment at 80°C, (c)After treatment at 100°C, (d)After treatment at 130°C, (e)After treatment at 150°C, (f)After treatment at 200°C, (g)After treatment at 250°C. The conditions were the same as Fig.1.

Mechanical properties

PAn cannot be prepared as free standing film when casted from formic acid as solvent. The casted films were very brittle. For preparation of PAn membranes N-methyl pyrolidone (NMP) is a popular solvent. However, Nylons are not soluble in NMP. Free standing films or membrane with adequate mechanical properties of PAn composites with Nylons can be easily prepared by casting from formic acid.

In order to prepare polyaniline composites with Nylons, the optimum weight ratio was found to be 1:2, 1:3 and 1:3 for PAn/Nylon 66, PAn/Nylon 6 respectively (Table1& Table2).

Table1. Mechanical properties of PAn /Nylon66 composite

No.	weight ratio PAn : Nylon 66	ΔL (mm)	F (N)	Tensile strength (MPa)
1	1:2	0.23	8	19.5
2	1:3	0.40	5.5	15.7
3	1:4	5	3	5.3
4	Pure Ny66	3.25	10	16

Table 2. Mechanical properties of PAn /Nylon6 composite

No.	weight ratio PAn : Nylon 6	ΔL (mm)	F (N)	Tensile strength (MPa)
1	1:2	0.20	2.4	6
2	1:3	0.30	8.4	19
3	1:4	0.7	1.4	3
4	Pure Ny6	1.53	6.4	15

Electrical conductivity

The polymer samples were cut into 1cm×6cm strips for conductivity measurement. The average thickness was 50μm. Conductivity measurements were carried out after doping the polymer samples in a 0.5 M HCl solution for 2 hour at room temperature. DC conductivity of polymers was measured using 4- point probe technique. The current applied in this technique was 20 μA.

It was found that conductivity of PAn/Nylon composites after doping with HCl, was much lower than pure PAn but is much higher than Nylons (insulator). The highest conductivity for PAn/Ny 66 composite film was 0.008 S/cm and for PAn/Ny 6 was 0.009 S/cm in weight ratios of 1:2.

With increasing the percent of nylon, conductivity of polymeric composite decreased gradually (Table3 & Table4). PAn/Ny composites were changed into insulator when treated with a dilute ammonia solution(0.2M).The conductivity was recovered completely when redoped with HCl solution(0.2M).It was also found that chemical treatment of PAn/Nylon composites films with chemical reductants such as sodium thiosulfate and oxidants such as potassium permanganate leads to increasing resistivity of polymers.The conductivity is recovered after redoping in HCl solution. Dilute HCl solutions are suitable for protonation of PAn composites.Nylons are not chemically stable in strong HCl solution because of hydrolysis reaction.

Table3. Electrical conductivity of PAn/Nylon66 composite by using 4- point probe technique

No.	weight ratio PAn : Nylon 66	E(mV)	σ_v (S/Cm) $\times 10^{-3}$
1	1:2	630	8
2	1:3	900	6
3	1:4	1000	5

Table4. Electrical conductivity of PAn/Nylon6 composite by using 4- point probe technique

No.	weight ratio PAn : Nylon 6	E(mV)	σ_v (S/Cm) $\times 10^{-3}$
1	1:2	600	9
2	1:3	800	7
3	1:4	1000	5

Conclusions

We have found that it is possible to synthesis polyaniline composites with some conventional thermoplastic polymers such as nylons with improved mechanical properties, with superior thermal stability as free standing films or membranes. The molar ratio of PAn to nylon has the greatest effect on mechanical properties of the composite membranes.

Many applications of PAn conducting polymers may demand it to be prepared as membranes. Formic acid is a good solvent for preparation of polyaniline/Nylon composites as membranes. Formic acid is an odorous material, so it should be handled cautiously. Conductivity of PAn/Nylon composites after doping with HCl is much lower than pure PAn but it is much higher than Nylons (insulator). PAn/Ny composites change into insulator when they are treated with a dilute ammonia solution. The conductivity recoveres completely when redope with HCl solution.

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