



Synthesis of Nano Conducting Polymer Based Polyaniline and it's Composite: Mechanical Properties, Conductivity and Thermal Studies

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Abstract: Polyaniline (PAn) was prepared chemically in the presence of bronsted acid from aqueous solutions. Polyaniline- nylon 6 composite (termed as PAn/Ny6) prepared via solvent casting method. The preparation conditions were optimized with regard to the mechanical properties of the polymer composite. It was found that the molar ratio of PAn to nylon have the greatest effect in determining the mechanical properties of polymer composite. Electrical conductivity was measured using standard method of four point probe. Spectrophotometric analysis (UV-Vis) was used for investigation of the effect of thermal treatment on polyaniline and it's composite.

Keywords: Polyaniline, Nano conducting polymer, Nylon 6, Conductivity, Thermal stability.

Introduction

Nano Conducting polymer films are a relatively new class of materials whose interesting metallic properties were first reported on 1977, with the discovery of electrically conducting polyacetylene¹. This chance discovery occurred when a researcher accidentally added too much catalyst while synthesizing polyacetylene from acetylene gas, resulting in shiny metallic like substance rather than the expected black powder. This shiny semi-conducting material was subsequently partially oxidized with iodine or bromine vapors resulting in electrical conductivity values of up to 10^5 S cm⁻¹, which is in the metallic range². The importance of this discovery was recognized in 2000, when the Nobel prize for chemistry was awarded to the scientists who discovered³ electrically conducting polyacetylene in 1977.

Among conducting polymers, a great deal of researches have been devoted to polyaniline (PAn) due to its good environmental stability, easy polymerization and low cost of monomer.

Polyaniline can be synthesized by the oxidation of aniline solution in bronsted acids by chemical oxidants or electrochemically^{4,5}. In order to commercialize PAn, it is possible to fabricate blends or composites with some other conventional polymers. Polyamid (for example nylon) is a good choice because of its solubility in the same solvent of PAn (formic acid). Flexible and free standing films from composites of polyaniline- nylon (PAn/Ny) can be obtained by casting method⁶. Polyaniline (PAn) has been reported to have the following idealized structure (Figure 1)⁷.

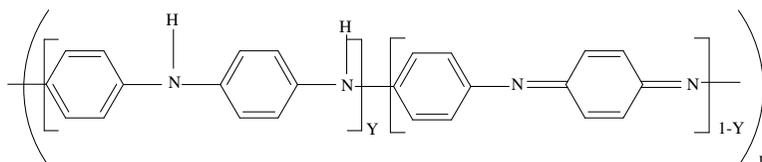


Figure 1. The general structure of PAn conducting polymers.

The structure containing Y reduced (benzenoid diamine) and (1-Y) oxidized repeat groups (quinoid diamine), where the oxidation state can be defined by the value of (1-Y). Y can be varied continuously in principle from one (the completely reduced material) to zero (to completely oxidized polymer). The completely reduced material (Y=1) is called leucoemeraldine and the completely oxidized form (Y=0) is termed as pernigraniline. Intermediate oxidation states, where Y = 0.75 and 0.25 are called protoemeraldine and nigraniline⁸. The true emeraldine oxidation state Y = 0.5 of polyaniline in which 50% of the nitrogen atoms are protonated (consists of equal numbers of reduced and oxidized repeat units) is the most highly conducting (metallic) form of the polymer⁹. The relative content of the benzenoid and quinoid forms depends on the acid concentration and the degree of oxidation of the polymer¹⁰. Chemical polymerization of aniline in aqueous acidic media can be easily performed using of oxidizing agents such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is shown in the following Figure 2. Ammonium persulfate is the most popular and frequently used chemical oxidant for polymerization of aniline in acidic aqueous solutions.

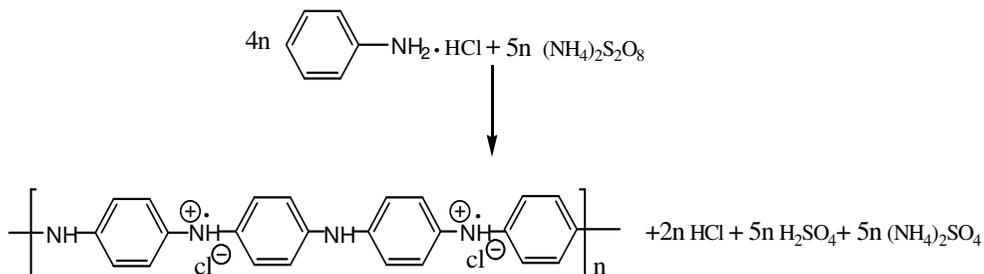


Figure 2. Overall polymerization reaction of PAn using ammonium persulfate.

Unfortunately, practical application of conducting polymers such as polypyrrole, polythiophene and polyaniline is limited particularly because of their poor mechanical properties. However, the composites prepared by mixing of conducting polymers with conventional polymers can be used in order to improve mechanical properties for all potential usages significantly¹¹.

Experimental

Aniline (Merck) was used after distillation. Nylon 6 (KN 136, Kopa co. Korea) was obtained as granules form. The other chemicals used were of high purity and AR grade.

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 a home made 4-point probe device. 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. Mechanical tests (Tensile strength) were carried out using S.D.L. Micro 250 (manufactured by Shirley co. England).

Preparation of PAn and Pan/Ny6 composite

25 mL of Freshly distilled aniline (0.2M) was added into 500 mL of 2M HCl in a beaker. 250 mL of 0.25 M ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) solution, was added from a burette into the well-stirred monomer solution during 40 min. Polymerization was carried out at 0 ~5 °C. The molar ratio of monomer to oxidant was selected 1:1. The solution was continued stirring about 2 h after the complete addition of the oxidant. Then the green dark powder (polymer) was filtered, washed with dilute HCl solution, distilled water and methanol respectively in order to remove impurities and remainder monomers. Then the product was dried at 50-60 °C in an oven for 2 h at ambient conditions. The synthesized polymer powder (PAn/HCl) was treated with a solution of ammonia (0.5M) for 4 hours at room temperature in order to change the polymer into emeraldine base (EB) state, which is the only processable form of polyaniline. PAn composite films were then prepared using co-dissolution method employing formic acid (88%) as solvent. For fabrication of PAn/Ny composites, EB and nylon 6 were separately dissolved in formic acid (1% w/v). Then they were mixed together with different proportions. Free standing films (40-50 μm) were prepared by casting these solutions in petri dishes, placed in an oven at 60 °C overnight. The films obtained were removed from petri dishes by immersion in dilute HCl solution for few minutes. The membranes dried at room temperature after washing with distilled water.

Results and Discussion

Conductivity and morphology

Electrical DC-conductivity of PAn composite films (doped with HCl) was measured using conventional 4-point probe technique¹². In order to measure conductivity, the polymer samples were cut into 1×4 cm strips for conductivity. Conductivity measurements were carried out after doping the polymer samples with 0.2 M HCl solution for 2 h at room temperature after drying at ambient conditions. 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/Ny6 was 0.009 S/cm in weight ratios of 1:2. With increasing the percentage of nylon, conductivity of polymer composite σ (S/Cm) decreased gradually (Table 1).

PAn/Ny6 composites were changed into insulator when treated with a dilute ammonia solution (0.2 M). The conductivity was recovered completely when redoped with HCl solution (0.2 M). It was also found that chemical treatment of PAn/Ny6 composites films with chemical reductants such as sodium thiosulfate and oxidants such as potassium permanganate leads to increasing resistivity of polymers significantly. The conductivity was recovered when the samples were redoped in a dilute HCl solution. For doping of PAn/Ny composite dilute solution of HCl was employed since nylons are not usually chemically stable in strong HCl solution because of hydrolysis reaction. As our results showed conductivity of the polymer is changed when treated in different media and the changes are reversible.

Table 1. Electrical conductivity of PAN/Nylon6 composite prepared in different weight ratio.

No.	weight ratio PAn : Ny 6	σ , S/Cm $\times 10^{-3}$
1	1:2	9
2	1:3	7
3	1:4	5

Characterisation of PAn and PAn/Ny6 composite was also carried out using scanning electron microscopy (SEM). All the electron micrographs were obtained from powder (for PAn and EB form) and film (for PAn/Ny6) specimens of this materials. SEM observations have shown the differences in morphology of PAn (or EB form) and PAn/Ny6 composites. The SEM pictures are given in Figure 3.

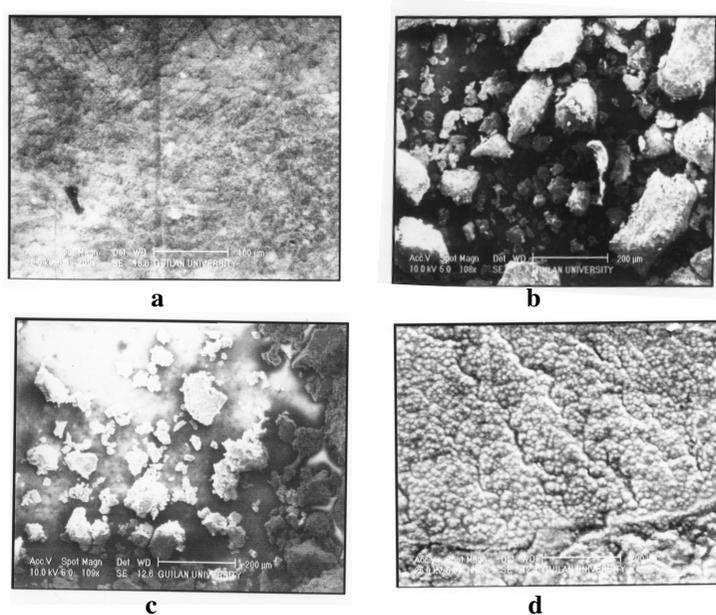


Figure 3. Scanning electron micrographs (SEM) of (a) EB/Ny6, (b) EB powder, (c) PAn/HCl powder, (d) EB/Ny6, HCl 0.2 M was used for doping of the polymer.

Mechanical properties

In order to perform mechanical test, polymer samples were prepared as free standing films using casting technique. Free standing films with adequate mechanical properties of PAn composites with nylons can be easily prepared by casting from formic acid. The results obtained in this investigation have been summarized in Table 2.

Table 2. Mechanical properties of PAn /Nylon 6 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

Thermal stability studies

In order to find out the effect of thermal treatment on electrical conductivity and also to investigate the reversibility of conductivity upon thermal treatment, the polymer samples (PAn/Ny 6) were prepared as a thin film deposited on the surface of lambs. It was observed that when the polymer was thermally treated, its dry state conductivity was increased upon thermal treatment up to 100 °C and upon subsequent cooling, conductivity back to its initial value.

Effect of thermal treatment on the polymer structure was also studied using UV-Vis analysis (Figure 4). As our results show PAn (EB form) is thermally stable up to 130 °C under air atmosphere. Some minor structural changes (without decomposition) may occur even after mild heat treatment but not any important changes were observed in the UV-Vis spectrum of the polymer before and after heat treatment up to 130 °C. However, when the polymer is treated at more elevated temperatures ($T > 150$ °C), some irreversible changes such as cross-linking might be occurred. In the case of PAn/Nylon6 polymer composites showed more thermal stability (up to 180 °C) in air than pure PAn (Figure 5).

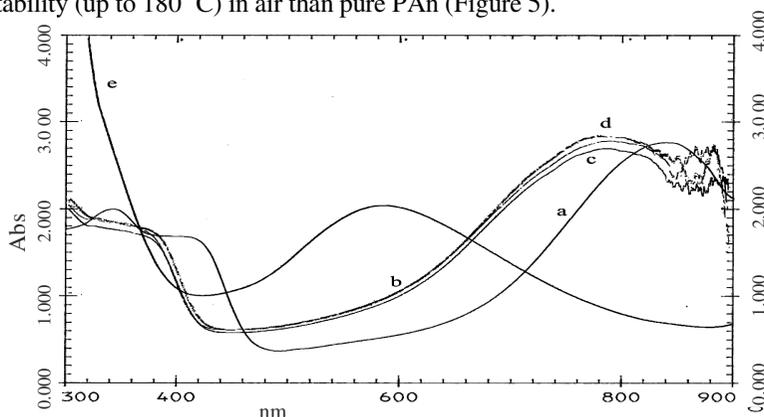


Figure 4. UV-Vis spectra of PAN (EB); (a) Before thermal treatment, (b) After heat treatment at 80 °C, (c) After heat treatment at 100 °C, (d) After heat treatment at 130 °C, (e) After heat treatment at 150 °C, the time of exposure at maximum temperature was 30 min.

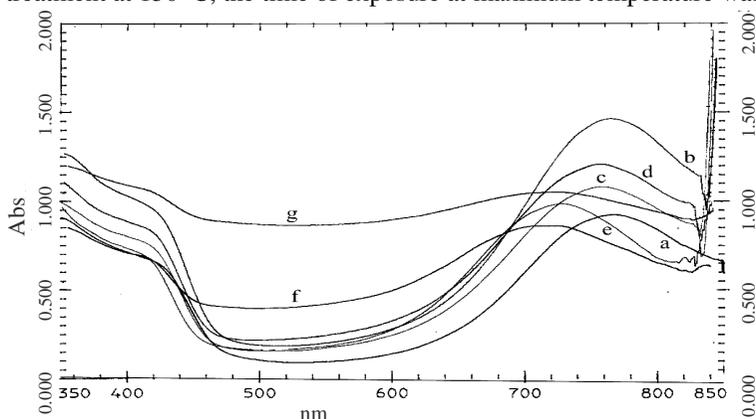


Figure 5. UV-Vis spectra of PAN (EB)/Nylon 6, (a) Before thermal treatment, (b) After heat treatment at 80 °C, (c) After treatment at 100 °C, (d) After heat treatment at 130 °C, (e) After heat treatment at 150 °C, (f) After heat treatment at 200 °C, (g) After heat treatment at 250 °C. The conditions were the same as Figure 4.

Conclusion

Polyaniline and its composites with conventional polymers such as nylons can be easily processed from formic acid via cast method (bp = 105 °C) producing desired thickness of the film. It was found the percentage of the nylon 6 has very important effect on mechanical, electrical and thermal stability of the polyaniline composite. The best weight ratio for PAn/Nylon6 was found to be 1:3 with regard to mechanical. Electrical conductivity is decreased with increasing of the nylon percentage in polymer composite. According our UV-vis investigation the polymer composites are more thermally than pure polyaniline.

References

1. Shirakawa H, Louis E J, MacDiarmid A G, Chiang C K and Heeger A J, *J Chem Soc; Chem Commun.*, 1977, 578.
2. Herbert Naarmann, *Polymers to the Year 2000 and Beyond*, John Wiley & Sons, 1993, Chapter 4.
3. Wallace G G and Spinks G M, *Conductive Electroactive Polymers; Intelligent Material Systems*, 2nd Edn., CRC Press, 2003, 1.
4. Angelopoulos M, Austurias G E and Ermer S P and Ray A, *Mol Cryst.*, 1988, **160**, 151-163.
5. Pasquali M, Pistoia G and Rosati R, *Synthetic Metals*, 1990, **53**, 1-15.
6. Malmong J A and Compoli C S, *Synthetic Metals*, 2001, **119**, 87-88.
7. Ansari R, *E J Chem.*, 2006, **3(4)**, 186-201.
8. Angelopoulos M, Rarnd A, MacDiarmid A G and Epstein A J, *Synthetic Metals*, 1987, **21**, 21-30,
9. MacDiarmid A G, Richter J C, Somasiri A F and Epstein A G, in *Conducting polymers*, (Ed.L.Alcacer), Reidel Publishing Co. Dordrecht, 1987, 105.
10. Bhadani S N, Gupta M K and Gupta S K S, *J Appl Polym Sci.*, 1993, **49**, 397-403.
11. Ansari R, Price W E and Wallace G G, *Polymer*, 1996, **37(6)**, 917-923.
12. ASTM, Designation: D 4496.



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