Effect of the Nano-cellulose on the Preparation and the Conductivity Properties of the Polyaniline

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Abstract

Polyaniline is widely used as a kind of conductive polymer. The preparation of polyaniline has been studied mainly by the methods of chemical synthesis and electrochemical synthesis. In this paper, polyaniline was synthesized by chemical oxidation under acidic conditions using ammonium persulfate as oxidant. And then, the polyaniline was doped with a certain concentration of protonic acid to make it conductive. Finally, Nano-cellulose and polyaniline were combined to obtain composite products. The optimum conditions were discussed in the experiment and the composite with good electrical conductivity was achieved. The results shown that the conductivity of the conductive polyaniline was 9.98 S/cm under the optimum experimental condition (reaction temperature was 0℃, the amount of material APS:AN was 1:1, HCL concentration was 2 mol/L). The best compound effect was that Nano-cellulose and polyaniline were mixed by in situ polymerization and ultrasonic treatment of the combined effect and the composite ratio was 3:2. This work provide a new method to prepare conductive polymer of polyaniline.

Key words: *polyaniline; conductive polymer; Nano-cellulose*

1. Introduction

Since MacDiarmid et al. synthesized conductive polyaniline(PANI) in acidic conditions in 1984, conductive polyaniline has attracted much attention because of its easy synthesis, remarkable environmental stability, simplicity in doping, high electrochemical activity and low cost. Polyaniline is widely investigated in many fields because of its excellent properties. For a long time, the study of polyaniline is mainly based on the control of polyaniline morphology, such as Nanotubes, Nanoballs, Nanoparticles and so on.

Various methods have been used to synthesize PANI, such as emulsions, template synthesis, self-assembly, interfacial polymerization and electrochemical oxidative polymerization. Electrochemical oxidative polymerization is the use of a certain principle of the original battery, containing aniline monomer in the electrolyte solution, so the original cell structure is formed, making the anode aniline monomer oxidation polymerization reaction, which polymerization into polyaniline powder. Although the electrochemical synthetic products with high purity, excellent performance, but only for laboratory synthesis, industrial production is more waste. Chemical synthesis method is the reaction of aniline monomer under the action of an acidic medium and an oxidizing agent to produce polyaniline. As the chemical synthesis process is relatively simple and the conditions are easier to achieve, this method is the main preparation of polyaniline [1].

Polyaniline is widely used in electrochemical catalysis, electrochromic, corrosion protection, sensors and so on, and polyaniline is the most promising one of the conductive polymer [2]. But its coral-like molecular structure determines the insoluble, has become a bottleneck restricting its development and application. Solving its insoluble is the prerequisite for the application of polyaniline.

In the global energy and environmental needs of increasingly tense situation, Nano-Cellulose is well known as a completely new material from nature. Nano-cellulose comes mainly from wood, cotton, linen, plants and other agricultural products, that is a very rich in natural reserves of renewable resources [3]. Due to its excellent physical and chemical properties, unique organizational structure, the depletion of energy and resources in recent years, Nano-cellulose has become a new research field. Currently Nano-Cellulose in the application of the matrix composite has been a research focus.

This paper studied the preparation of polyaniline by chemical oxidation with ammonium persulfate as oxidant under acidic conditions. And then, the polyaniline was doped with a certain concentration of protonic acid to make it conductive. Nano-Cellulose and the conductive material Polyaniline were complexed via some means, the complex experiments and the applications of the composite were explored.

2. Experimental

2.1 Materials and Instruments

Materials: Aniline(AN), AR, Damao Chemical Reagent Factory, Tianjin. Hydrochloric acid (HCL), 36%AR, Fine Chemical Factory, Economic and Technological Development Zone, Laiyang. Ammonium persulfate(APS), AR, Damao Chemical Reagent Factory, Tianjin. Nano-cellulose, 0.86%, Homemade.

Instruments: Four probe tester, RTS-8, Guangzhou, China. Ultrasonic signal generator, BILON-500, Shanghai BINLON Instrument Co. Ltd.

2.2 The Method of Composite

Firstly, the conductive polyaniline was prepared by chemical oxidation. Secondly, the composite ratio and the composite conditions were discussed. Finally, the conductivity of the composite product was discussed.

2.2.1 Preparation of Conductive Polyaniline

① Polymerization

Hydrochloric acid and a certain amount of aniline monomer were added to a four-necked flask and stirred at 0 ° C for 1 h. And then, a certain concentration of ammonium persulfate hydrochloric solution was dropped into the reaction system. Stirring for 3 h, the reaction was over. Finally, the resulting solution was filtered and washed.

② Doping

The prepared powder was mixed with hydrochloric acid and stirred for 4 h. After completion of the reaction, the test product was filtered and washed. The mixture was placed in a culture dish and dried at 60 ℃ for 24 h to get conductive polyaniline.

③ Measurement of Conductivity

The polyaniline powder was compressed with YP-2 table, and the sheet thickness was about 0.5mm. The conductivity of the sheet was analyzed by the RTS-8 four-probe instrument, and the average was measured several times.

2.2.2 Polymerization of Nano-cellulose with Polyaniline

① Composite Method of Nano-cellulose with Polyaniline

No.1:

The freeze-dried Nano-cellulose and conductive polyaniline were added to deionized water for ultrasonic compounding, the reaction was over. After freeze-drying, the composite product was obtained.

No.2:

In the preparation of conductive polyaniline process, the amount of freeze-dried Nano-cellulose was added. So Nano-cellulose involved in the formation of polyaniline process.

NO.3:

In the preparation of conductive polyaniline process, the amount of freeze-dried Nano-cellulose was added. After the doping reaction, the appropriate amount of deionized water was added. Under certain ultrasonic conditions, the reaction was over. After freeze-drying, the composite product was obtained.

② Composite Ratio of Nano-cellulose with Polyaniline

The conductivity of the three methods was measured to determine the highest conductivity of the experimental method. To determine the optimum compound ratio，the composite ratio of polyaniline to nanofibers was changed, and the performance of the composite product was analyzed.

3. Results and Discussion

3.1 Effect of Composite Method on Conductivity

No.1: The ratio of polyaniline to Nano-cellulose was 1:1and the ultrasonic frequency was 300W.

No.2: According to yield of polyaniline preparation process, the mass ratio of polyaniline to Nano-cellulose was 1:1.

No.3: According to yield of polyaniline preparation process, the mass ratio of polyaniline to Nano-cellulose was 1:1, and the ultrasonic frequency was 300W.

As shown in the following table:

Table 1 Effect of Composite Method on Conductivity

Number	Approach	The conductivity of composite products (S/cm)
1	Ultrasonic treatment	0.25
2	In situ polymerization	0.54
3	In situ polymerization and ultrasonic	0.83

As shown in the table, it was the highest conductivity that the composite product of polyaniline and Nano-cellulose was obtained by the No.3, and the conductivity of product can reach 0.83 S/cm. Because the No.3 used ultrasonic treatment for No.2. A certain time of ultrasonic treatment make the dispersion of Nano-cellulose in the reaction system more uniform. The polyaniline produced by the reaction can be more uniformly adsorbed on the Nano-cellulose molecule. Therefore the composite product has better conductive effect. And the No.3 used the in situ polymerization more than No.1, which was more advantage. During the reaction, the aniline monomer was continuously polymerized to form polyaniline

3.2 Effect of Composite Ratio on Conductivity

After determining the composite scheme, the effect of the composite ratio on the conductivity of the composite product was discussed. The composite ratio of polyaniline and Nano-cellulose was changed，and the conductivity of the product was measured several times.

The effect of composite ratio on the conductivity is showed in Table 2.

Table 2 Effect of Composite Ratio on Conductivity

Number	The mass fraction of polyaniline	The mass fraction of Nano-	The conductivity of composite
1	0	100%	-
2	10%	90%	0.01
3	20%	80%	0.10
4	30%	70%	0.47
5	40%	60%	0.65
6	50%	50%	0.79
7	60%	40%	0.96
8	70%	30%	1.65
9	80%	20%	3.56
10	90%	10%	6.34
11	100%	0	9.98

As shown in the table, the composite product was dissolved in deionized waster, stirred with a glass rod and placed in a petri dish. The composite product was dried in an oven at 60℃ to observe the film forming properties.

When the content of polyaniline was about 40% in the composite product, the composite product could be formed into a brittle film. This is because the Nano-cellulose content was too low, and the composite product cannot be effectively connected to form a conductive film.

4. Conclusions

Conductive polyaniline was prepared by chemical oxidation method using ammonium persulfate as oxidant and hydrochloric acid as dopant.

The prepared products had suitable molecular mass and good conductivity, and the conductivity of polyaniline synthesized was 9.98 S/cm under the best experimental conditions.

When the composite ratio of polyaniline to Nano-cellulose was controlled to be 2: 3, the composite product has the highest conductivity and can be formed into a film, and the conductivity was 0.65 S / cm.

The composite product of polyaniline and Nano-Cellulose was intended for use in the field of conductive ink, which was used as conductive substrate such as circuit board, membrane switch and flexible electrode. However, taking into account the poor performance of the composite product film, the composite product needs to epoxy resin and other materials with better film forming performance. So that it has a certain conductivity, while achieving the required conductivity of the conductive film. Therefore, the study in this article were meaning in theoretical research and significance in practical application.

References

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