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Study on Amino Modification of Waste Polystyrene

1st Kang Wang
School of Chemical Engineering
Xuzhou University of technology
Xuzhou 221018, China
531301852@qq.com

2nd Haijie Guo
School of Chemical Engineering
Xuzhou University of technology
Xuzhou 221018, China
785671758@qq.com

3rd Jie Yang
School of Chemical Engineering
Xuzhou University of technology
Xuzhou 221018, China
1947269851@qq.com

4th Guizhen Gong *
School of Chemical Engineering
Xuzhou University of technology
Xuzhou 221018, China
ggz72@163.com

***Abstract*—Amino modification of waste polystyrene was investigated. Polystyrene is nitrated with concentrated sulfuric acid and nitric acid, reduced with iron powder and hydrochloric acid. The best raw ratios of the nitrification reaction and reduction reaction are nPS: nHNO3: nH2SO4=1: 6: 2, NPS-NO2: nFe=1: 8, respectively. FTIR and XRD suggest that the success of the amination of polystyrene.**

Keywords—Waste Polystyrene, Amino, Modification, FTIR, XRD

I. Introduction

Polystyrene, thermal insulation, good cushioning performance, low price and so on, has taken up a large proportion in modern production and life. Although its large use has brought convenience to people, because of its good chemical stability, it is not easy to aging, difficult to degrade naturally, resulting in a lot of waste pollution [1]. How to solve the waste polystyrene has become one of the problems urgently to be solved in the society. Polystyrene can be made into coatings, dyes and adhesives through chemical modification [2-4]. The aminated modification of PS is an important way to prepare dyes. The preparation of dye intermediates by aminated modification has an important contribution to the research and development of dyes. The research of dye chemistry is in line with the purpose of green development. PS amination can not only solve the problem of environmental pollution, but also make related research for the preparation of dyes from waste PS [5-7].

In this paper, waste polystyrene was used as the raw material to modify by amino group, which was added to the benzene ring by the route of nitrification and reduction. The reaction conditions are optimized and the products are analyzed by FTIR and XRD.

II. Experimental

A. Materials.

Polystyrene used is discarded polystyrene. It was washed with de-ionized water, and dried in a vacuum oven at 80 oC for 5 h, then stored in a desiccator at room temperature before using. All chemical reagents used in the experiment are analytical grade, obtained from the commercial source, and were used without further purification.

B. Nitrification of polystyrene.

After 5.00 g waste polystyrene dissolve in 40 mL chloroform, a mixture of concentrated sulfuric acid and nitric acid were slow dropped at ice water bath. After the dripping was completed, the mixed liquid reacted at room temperature for 5 h, followed to removal water and mixed acid with separatory funnel. The residual solution was precipitated with ethanol to give nitrified polystyrene (PS-NO2).

C. Reduction of nitro polystyrene.

60 mL concentrated hydrochloric acid and 8.96 g Fe power added into three neck bottle, then mixture of 5.88 g PS-NO2 dissolved in 30 mL dimethyl sulfoxide was dropped into at 65~75 oC. After dropping, heating to 100 oC for 3 h, then 60 mL concentrated hydrochloric acid and 8.96 g Fe power were added again, continue to react for 6 h. After reaction, the product were filtered from the solution, followed to wash with 5% NaOH solution, then wash to neutral with deionized water to gain pale yellow power amino polystyrene (PS-NH2), yield 77.5%. The reaction route is shown in Figure 1.

The raw and products gained were analyzed by FTIR spectroscopy (Alpha, Bruker company, German) using potassium bromide tableting method over a scan range of 500 to 4000 cm−1.

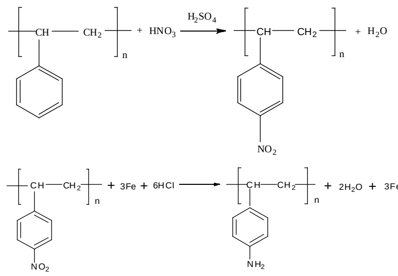

Figure 1 Reaction route of amino modification of waste polystyrene

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III. RESULTS AND DISCUSSION

A. Reactant ratio of nitrification.

The ratio of the reactant in nitrification is an important factor. Such as the amount of sulphuric acid has an effect on the form and yield of the product, as shown in Table 1. According to the mechanism of nitrification, the greater the amount of concentrated sulfuric acid, the more NO2+ will produce, which is beneficial to the nitrification. However, too much concentrated sulfuric acid will also have an adverse effect on the experiment. It can be seen from the results of table 1 that excessive amount of concentrated sulfuric acid will cause excessive viscosity of the system, and become colloidal or even caking. When nPS: nHNO3: nH2SO4 is 1: 6: 2, the effect of the experiment is the best, not only good rotation, but also can be statically stratified, easy to remove excess acid and precipitate yellowish floc in ethanol, and the yield is the highest value in all experimental data. Therefore, the best reactant ratio of the nitrification reaction is nPS: nHNO3: nH2SO4=1: 6: 2.

TABLE 1 EFFECT OF RAW RATIO ON NITRIFICATION

No.	$nPS:nHNO_3:nH_2SO_4$	Phenomenon	Product form	Yield [%]
1	1:1.5:2	Minor caking	Pale yellow powder	80.67
2	1:2:3	Colloid	—	—
3	1:2:4	Colloid	—	—
4	1:3:5	Severe caking	—	—
5	1:4:3	Minor caking	Pale yellow powder	50.34
6	1:4:4	Colloid	—	—
7	1:5:3	Good rotation	Pale yellow floc	78.93
8	1:5:4	Colloid	—	—
9	1:6:2	Good rotation	Pale yellow floc	87.65
10	1:6:4	Severe caking	—	—

B. Reactant ratio of reduction reaction.

The effect of raw ratio on reduction reaction is shown in Table 2. When nPS-NO2: nFe=1: 6, the yield is low. But it is too high to cause a large amount of ferric mud in the product and can not be treated. When NPS-NO2: nFe=1: 8 is the best.

TABLE 2 EFFECT OF RAW RATIO ON REDUCTION REACTION

$nPS-NO_2:nFe$	Yield [%]
1:6	59.90
1:8	77.52

FTIR analysis of extracts.FTIR of PS, PS-NO2 and PS-NH2 is shown in Figure 2. The absorption peak at 1618 cm-1 is benzene ring skeleton C=C stretching vibration. The sharp 3125 cm-1 absorption peak is the C-H telescopic vibration peak of the benzene ring. The strong absorption peak 1395 cm-1 represents the symmetrical stretching vibration peak of the N=O bond of the nitro. The absorbance from PS-NO2 is much stronger than that from PS and PS-NH2. The peak 3483 cm-1 is ascribed to NH2 group, there is no the absorption. This fact suggests that the success of the amination of polystyrene.

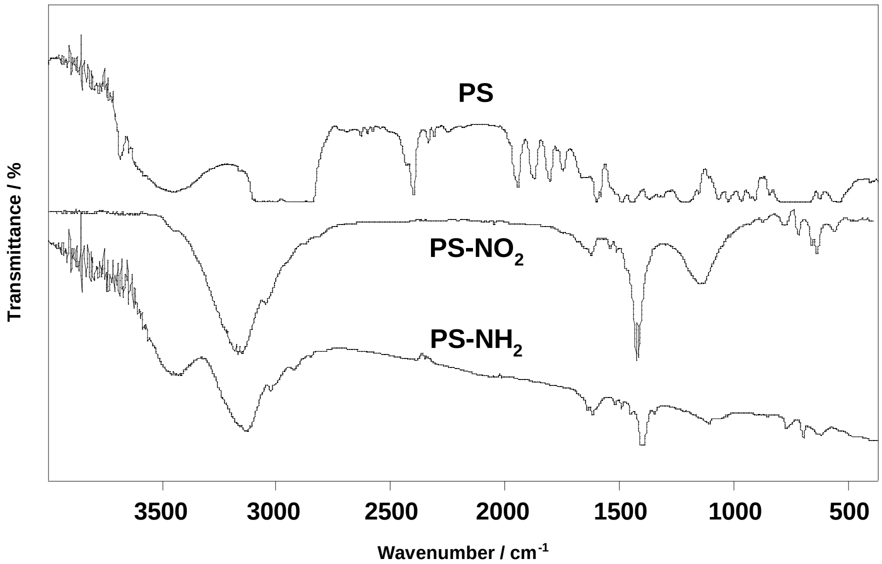

Figure 2. FTIR spectra of PS, PS-NO2 and PS-NH2

XRD analysis. XRD of PS-NO2 and PS-NH2 are shown in Figure 3. Diffraction peak at 2θ 20o is peak of polystyrene in PS-NO2 and PS-NH2 XRD. There is a diffraction peak at 2θ 35o in PS-NO2 , While disappear in PS-NH2 XRD.

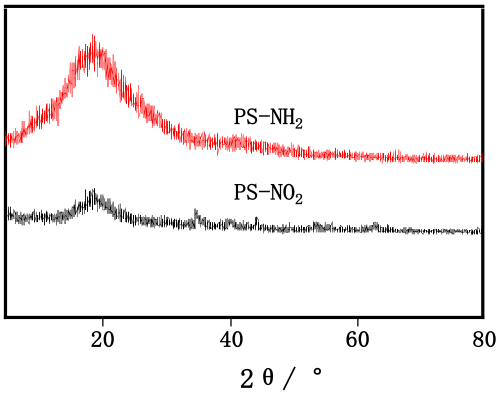

Figure 3. XRD of PS-NO2 and PS-NH2

IV. SUMMARY

To improve the utilization of high added value of waste polystyrene, amino modification was investigated. Polystyrene is nitrated with concentrated sulfuric acid and nitric acid, reduced with iron powder and hydrochloric acid. The best raw ratios of the nitrification reaction and reduction reaction are nPS: nHNO3: nH2SO4=1: 6: 2, NPS-NO2: nFe=1: 8, respectively. FTIR and XRD suggest that the success of the amination of polystyrene.

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