Synthesis of BTI and Its Application in Preparation of Imide-Epoxy Resin

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Abstract

About 2 mol trimellitic anhydride react with 1 mol 4,4'-diamino-diphenyl methane in proper solvent producing the amide acid. Reflowing in xylene., the amide acid will be imidized and an imide-contained dibasic acid(BTI) can be obtained . The acidity of BTI is 200～210 mgKOH/g. Its melting point is in 355～360℃. With specific catalyst, BTI can react with epoxy resin rapidly in 155～160℃. Their product features lower acidity ≤ 1 mgKOH/g and expoxy value approaching the calculated value.

Key-Words Imide-contained dibasic Acid(BTI) Imide-Epoxy

Introduction

The following imide-contained dibasic acid (BTI see Fig 1) can be easily obtained with imidzing trimellitic anhydride and aromatic diamine in dry pyridine-acetic anhydride system.

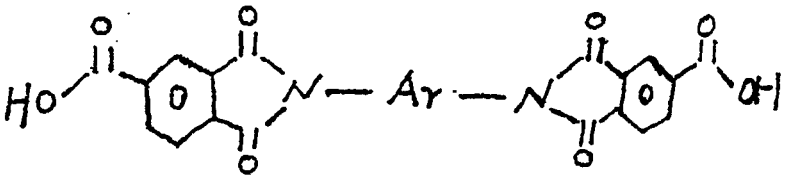

Fig 1 Imide-Contained Dibasic Acid

With two -COOH group, BTI can easily react with -OH, epoxy group and amino group, and introduce imide structure to materials of polyester, epoxy resin and polyamide, etc. That can improve the heat-resistance, high temperature performance, and chemical-resistance of these materials.

This method of modification has some application value. However, in fact, BTI as a modifier has not been directly used in industries in China. The main difficulties are caused by the high cost, the complicated seperation process, and the low purity of products in the imidization in pyridine-acetic anhydride system.

To reduce BTI's producing cost, efforts have been maken to prepare BTI in solvent of xylene or cresol.[1,2] However, the acidity of product was up to 320 mgKOH/g,[1] far higher than the calculated value of 205.3 mgKOH/g, which means uncomplete imidization or a larger amount of impurities in the products.

In this paper. We separately solve trimellitic anhydride and aromatic diamine in selected solvent in lower temperature, they produce an amide acide which is separated out in crystallinic state. Then imidization has been made by dehydrating in boiling xylene. The BTI prepared in this method features high purity. Imide group can be successfully introduced into the structure of epoxy resin after BTI reacting with epoxy resin.

Experimental

Synthesis of BTI

2.03 mol trimellitic anhydride was solved, then added in the solution of 1 mol 4,4'-diamino-diphenyl methane slowly, the temperature of reaction was controlled lower than 60℃. After the exotherm of reaction was steady, the system was kept stirring in 55～60℃ for 5 hours. A yellow powderly crystal was then obtained and the crystal was washed with pure solvent and dried in the air, the crystal was put into blow oven of 55±2℃ to dry out.

The dried crystal was then added into the react flask again, and the crystal was dehydrated during reflux in 145～150℃ in solvent of xylene for 30 hours. After filtrated, washed and dried, the BTI was obtained with a high yield of about 95%.

Synthesis of imide-Epoxy resin

Adding BTI and a catalyst into 60～80℃ epoxy resin, then heating the mixture to 160℃± 2℃, the reaction was completed in 10～15min, A transparent brown amorphous solid was yielded.

Results and Discussion

Synthesis of BTI

Some properties of the BTI obtained by this method are shown in table 1.

Table 1 Some Properties of BTI

	Properties	Results
1	appearance	Light yellow powder
2	acidity (mgKOH/g)	205～210
3	melting point (℃)	355～360

From Table 1, We can see the appearance and the melting point are very close to the results reported.[2], The measurement acidity is appoximately equal to the calculated value (205.3 mgKOH/g). Therefore, we can preliminarily estimate that the main product is BTI, and with high purity.

Since its relatively simple process and lower producing cost, this method may be used in industrial application.

Application of BTI in preparation of Imide-Epoxy Resin

In theory, with proper catalyst and suitable process BTI can equivalently react with epoxy resin to get high softening point, or partly crosslinked resins. In this paper, we heated a mixture of 20 phr BTI and 100 phr CYD 128 (bisphenol A epoxy resin, epoxy value of 0.540 mol/100g) at 180℃ for over 1 hour without catalyst, the mixture displayed no change. After 0.015 phr catalyst was added in the system released heat at once in 150～155℃, and became a homogeneous system. Some properties of the product is displayed in Table 2.

Table 2 Properties of Imide-Epoxy Resin(BTI 20 phr)

Properties	Result	
	react 10～15min at 160℃	react 60min at 160℃
Appearance	transparent brown amorphous solid	transparent brown amorphous solid
Softening Point(℃)	50～60	50～60
Acidity(mgKOH/g)	0.85	0.15
Epoxy value mol/100g	0.400 (0.388)*	0.390 (0.388)*

* Calculated epoxy value.

In Table 2 the measured epoxy value of the product is close to the calculated one. To a certain extent, prolonging the reaction time brings little difference to the softening point and the epoxy value. The result also demonstrates that the catalyst is suitable to the system and controls the side-reaction effectively.

Conclusion

1. High purity BTI can be obtained by the way of dehydration and imidizating in reflowing nonpolar slovent of low cost.
2. With proper catalyst BTI and epoxy resin can react easily and the side-reaction can be effectively controlled.

Reference

[1] Belg. patent 638,676
[2] Brit. patent 973,377