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Experimental Studies on the Synthesis and Performance of Boron-containing High Temperature Resistant Resin Modified by Hydroxylated Tung Oil

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Abstract: In this work, hydroxylated tung oil (HTO) modified high temperature resistant resin containing boron and benzoxazine was synthesized. HTO and ethylenediamine was used to toughen the boron phenolic resin with specific reaction. The structure of product was studied by Fourier-transform infrared spectroscopy(FTIR), and the heat resistance was tested by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis(TGA). The results indicated that the conjugated triene structure of HTO was involved in the crosslinking of the heating curing progress, and in addition, the open-loop polymerization reaction of benzoxazine resin during heating can effectively reduce the curing temperature of the resin and reduce the release of small molecule volatiles, which is advantageous to follow-up processing. DSC data showed that the initial decomposition temperature of the resin is 350-400 °C, the carbon residue rate under 800 °C was 65%. It indicated that the resin has better heat resistance than normal boron phenolic resin. The resin can be used as an excellent ablative material and anti-friction material and has a huge application market in many fields.

1. Introduction

High temperature resistant resin has been widely used in the fields of refractory materials, super hard materials, abrasives, friction materials, aerospace materials and adiabatic materials[1,2]. The existing high temperature resistant materials include polyimide resin, polysulfone resin, polyether resin, polyphthalocyanine resin, phenolic resin and so on[3-5]. Phenolic resin was the first synthetic resin which was discovered and industrialized in the world, and it has a long history so far. Due to the cheap reactants, simple production process and low capital investment, high mechanical strength and excellent heat resistant performance, phenolic resin has been widely used in many fields [6]. The improvement of phenolic resin is one of the important topics in the field of the high temperature resistant resin [7,8].

Main methods of improving thermal stability of phenolic resin include alkyl phenol or phenyl phenol modification, vegetable oil modification, rare elements (such as molybdenum, tungsten and organic boron) modification, organic silicon modification, and other impurity atoms of polymer materials (such as polyimide and polyamide) copolymerization modification and blending

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modification, etc[9-12]. Above all, organic boron modification is one of the most effective and economic methods. Due to the introduction of boron atoms, C-O-B bong and C-O→B ligand bond were formed in the molecules of resin. Since the B-O bond enthalpy is 523 kJ/mol and it is higher than that of 347 kJ/mol of C-O bond enthalpy, the heat-resistant performance of boron-containing resin is excellent, and the thermal decomposition temperature is significantly improved[13,14]. Additionally, the introduction of vegetable oil into the phenolic resin could also increase the thermal stability and toughness of the resin[15,16]. As the existing boron phenolic resin was brittle and easy to absorb moisture, the curing temperature was high and the release of small molecule volatiles in curing was large, it is necessary to improve the performance of resin continually.

Therefore, this work adopted HTO through derivative processing. The modified high temperature resistant resin containing boron and benzoxazine was synthesized with specific reaction. The HTO and ethylenediamine were used to toughen the boron phenolic resin. Through researching the effects of reaction conditions on the properties of modified resin, the optimum process conditions of high temperature resistant resin was selected to meet the requirement of market. It would provide effective reference basis for the production and application of novel high temperature resistant resin.

2. Experimental

Certain amount of boric acid, phenol and HTO were added in 500 mL of four-necked flask with electric mixer. Esterification was carried out when oil bath was heated highter than 140 ℃, and water was steamed out. Then the system was cooled to 60 ℃, a certain amount of paraformaldehyde and ethylenediamine were added. The material was heated to 105 ~ 110 ℃ and refluxed 1h.

Vacuum-dewatering process was conducted up to the required viscosity at the temperature of 80 ℃, and then the product was discharged. Figure 1 shows the pathway for the preparation of boron phenolic resin.

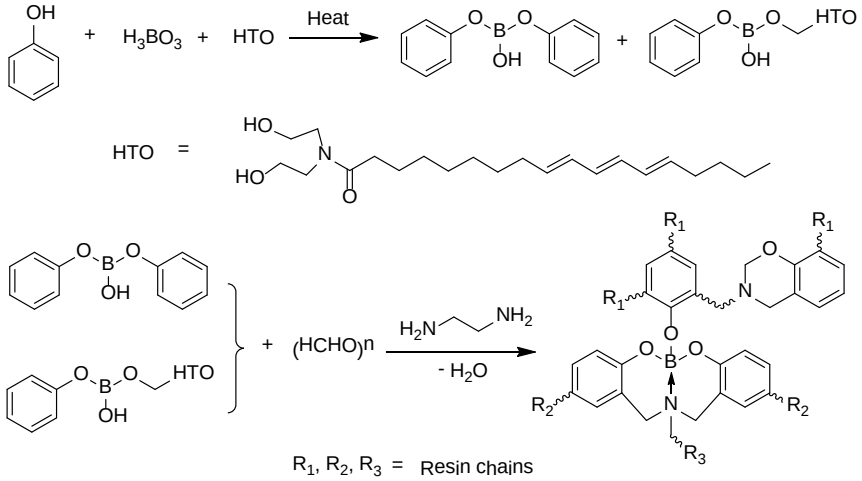


Figure 1. Synthesis routes of boron phenolic resin modified by HTO

3. Results and discussion

In this work, the reaction conditions were optimized by many experiments. The suitable ratio of the raw materials is n(phenol): n(boric acid): n(paraformaldehyde)=1:0.3:1.3. Ethylenediamine was used as alkaline catalyst, and it can also participate in the reaction to generate the benzoxazine structure. Since the vacant orbital of the boron atom can coordinate with the lewis base, the coordination of nitrogen atoms and boron atoms could enhance the water resistance of the resin. The boron phenolic resin was modified by HTO, which was better than the direct use of tung oil. In the synthesis process, esterification reaction went ahead between the hydroxyl of HTO and boric acid. The retained conjugate triene structure was cross-linked in the process of resin curing, and it was beneficial to improve the heat resistance of resin.

3.1. Structural characterization

Figure 2 is the FTIR spectrum of HTO modified boron phenolic resin (HTO-BPF). It can be observed that the characteristic bands of boron phenolic resin are very obvious, including the *v*OH band at 3354cm^{-1}, the amide band at 1595cm^{-1}, the *v*BO band at 1388cm^{-1}, the *v*Ph-O band at 1226cm^{-1}, as well as the *v*C-B-N band at 1080cm^{-1}. It is also seen that there is a small band at around 990cm^{-1} [17,18], showing the triene structure from HTO remains in boron phenolic resin.

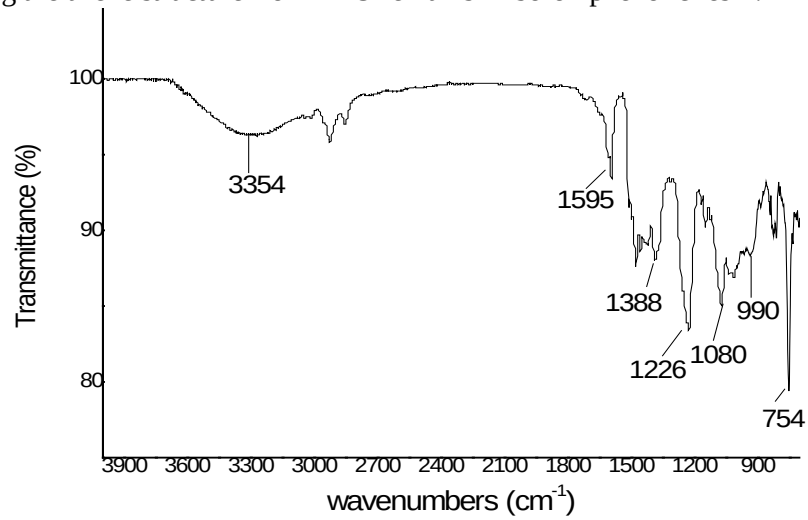


Figure 2. FTIR spectrum of HTO modified boron phenolic resin (HTO-BPF)

3.2. Heat-resistant properties

Figure 3 was the TG spectra of HTO modified boron phenolic resin (BPF) (here referred to as HTO-BPF) and common BPF. It can be seen that although the initial heat resistance of HTO-BPF (146 ℃, 98%) is lower than that of common BPF (196 ℃, 98%), the heat resistance in the high temperature zone of HTO-BPF is excellent. The char yield of HTO-BPF is 86 % at 500 ℃, and the ratio is 65% at 800 ℃. The results indicated that the conjugated triene structure of HTO was involved in the crosslinking of the heating curing progress and it may improve the heat resistance of the resin in the high temperature zone. In addition, the open-loop polymerization reaction of benzoxazine structure in the resin during heating could effectively reduce the curing temperature of the HTO-BPF.

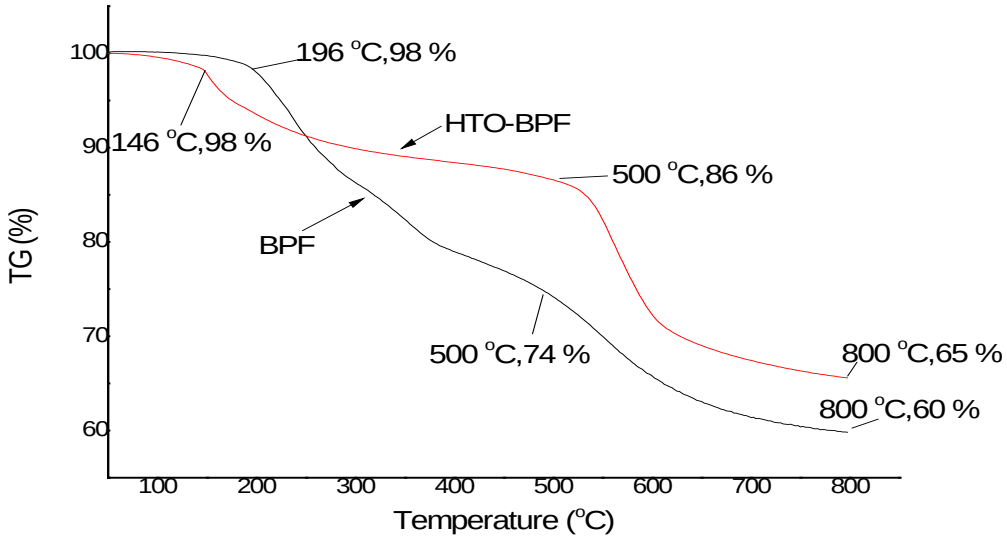


Figure 3. Comparative TG curves between HTO modified boron phenolic resin (HTO-BPF) and common boron phenolic resin(BPF)

4. Conclusions

In summary, HTO modified high temperature resistant resin containing boron and benzoxazine was synthesized. The structure of product was studied by FTIR, and the heat resistance was tested by DSC and TGA. The data indicated that the conjugated triene structure of HTO was involved in the product, and the benzoxazine structure was also formed. DSC data showed that the initial decomposition temperature of the resin is 350-400 ℃, the carbon residue rate under 800 ℃ was 65%. It indicated that the resin has better heat resistance than normal boron phenolic resin. The results can provide a good theoretical basis for the preparation of novel high temperature resistant resin.

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