

## EFFECT OF BORON CONTENT OF HIGH-ORTHO PHENOLIC FIBERS ON THERMAL PROPERTY

by

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*High-ortho boron-containing phenolic fibers were prepared, and cured in a solution of formaldehyde and hydrochloric acids. The resulted fibers were heat-treated in N<sub>2</sub> at tiered temperature. Differential scanning calorimetry and thermogravimetric analysis were employed to characterize thermal performance. The results show that the addition of boron in the precursor resin can increase the peak of curing temperature and thermal stability.*

Key words: *high ortho, phenolic fiber, boron, copolymerization, thermal properties*

### Introduction

High-ortho phenolic fibers can be prepared by melt-spinning of high-ortho novolac resins [1, 2]. However, a high-ortho phenolic novolac resin would generate fibers with low tensile strength. To overcome the problem, the boron-containing novolac resin has been synthesized and applied [3-5], which has high thermal stability, low heat conductivity and reaction activity [6]. Meanwhile the boron-containing phenolic fibers, which are prepared by melt-spinning a mixture of novolac resin and boron acid, show an increasing of thermal stability and mechanical strength [7]. However, the spinning of the high-ortho boron-containing novolac resin has not been reported.

In this study, a linear high-ortho boron-containing phenolic resin was prepared. Based on the special structure of high-ortho phenolic resins and lower reactivity of boron-containing phenolic resins, the high-ortho boron-containing phenolic fibers (HBPF) were prepared by melt-spinning. The resultant HBPF exhibit excellent thermal properties.

### Experimental

The novolac precursor resins were prepared by the reaction of phenol, formaldehyde, and boric acid in the presence of zinc acetate catalyst. Phenol (1.0 mol), formaldehyde (0.85 mol), boric acid, and zinc acetate were added in a three-necked flask, equipped with a reflux condenser, stirrer, and thermometer. The mixture was heated and maintained boiling

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for 4 hours, and then sulfuric acid was added, followed by further heating under reflux for 50 minutes. The reaction mixture was distilled under vacuum to remove water and unreacted phenol at tiered temperature up to 120 °C for 2 hours. A range of novolac precursors with different boron contents was obtained by changing the concentrations of boric acid.

The HBPF were prepared by melt-spinning using the melting phenolic precursor resin. The filaments were cured in a combined solution of hydrochloric acid and formaldehyde in a bath equipped with a thermometer and stirrer. The solution was heated from room temperature to 95 °C. Then, the cured fibers were heated until the temperature reached 240 °C in vacuum oven, and held for 2 hours in nitrogen. Finally, the resultant samples taken out after cooled to room temperature were washed with water and dried at room temperature.

The resultant HBPF containing 3.327 g, 6.792 g, 10.404 g, 14.174 g, and 18.111 g boric acid in the reaction solution are denoted HBPF-2, HBPF-4, HBPF-6, HBPF-8, and HBPF-10, the reference fiber without additives is denoted HBPF-0.

## Results and discussion

The first heating differential scanning calorimetry (DSC) thermograms of the phenolic filaments are presented in fig. 1. From these thermograms, the following parameters are determined:  $T_g$ , the glass transition temperature determined from the inflection point;  $T_i$ ,  $T_p$ , and  $T_t$ , the gel temperature of initial, peak, and terminal position of the phenolic filament, respectively. These parameters are collected in tab. 1.

Figure 1 presents DSC thermograms recorded during heating at a rate of 10 °C min<sup>-1</sup> for the boron-containing phenolic filaments and high-ortho phenolic filament.  $T_g$  (54.6 °C), melting temperature (116 °C), and  $T_p$  (190.5 °C) of phenolic filament are observed in fig. 1. Compared with pure phenolic filament, which shows an obvious glass transition and a high and narrow curing peak, the boron-containing filaments have inconspicuous  $T_{gs}$  and  $T_{ms}$ . Table 1 shows the glass transition temperatures of phenolic filaments, as well as the gel temperatures, including initial, peak, and terminal temperature.

$T_g$  shifts to a higher temperature with increasing boron content up to 10 wt.%, and the melting peaks become faint. It means that the increasing of boron content increases the interferences among the macromolecules, including the branching and hydrogen bonds caused by B-OH. For all the filaments, the initial, peak and terminal gel temperature increase over 20 °C with increasing the boron content up to 6 wt.%. This behavior is typical of a boron-containing phenolic resin. And the addition of boron acid increases the activation energy of ortho/para for curing, and induces the increasing of the gel temperature. However, when the boron content reaches 10 wt.%, the temperatures drop. It contributes that B-OH, a catalyzer in gel reaction, plays a more important role than increasing of the activation energy, which decreases the gel temperature inversely.

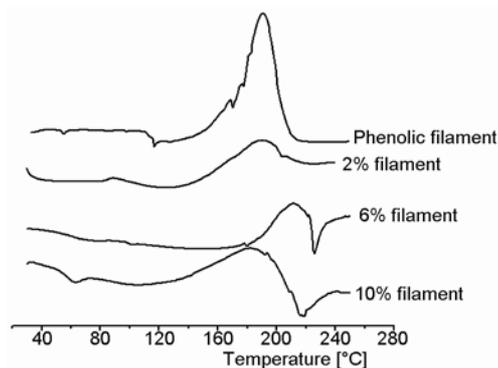


Figure 1. DSC thermograms of phenolic filaments with different boron contents

Table 1. Thermal parameters of high-ortho phenolic filament fiber with different boron contents

Polymer code	$T_g$ [°C]	$T_i$ [°C]	$T_p$ [°C]	$T_t$ [°C]
HBPF-0	54.6	126.4	190.5	198.1
HBPF-2	–	128.2	190.5	222.0
HBPF-6	60.9	158.8	211.7	225.6
HBPF-10	61.5	113.4	181.6	218.4

To determine the thermal stability of the polymers, thermogravimetric analysis (TGA) of HBPF was carried out under nitrogen at  $20\text{ }^{\circ}\text{C min}^{-1}$  (fig. 2). In the temperature range of 110-300  $^{\circ}\text{C}$ , the total weight loss for all the samples may correspond to the loss of some small, end groups and weaker bonds in the chains of the HBPF, further curing between them and B-OH [5]. As shown in fig. 2(a), similar weight losses are observed in HBPF which were prepared with novolac precursors with boron or free. The terminal temperature of the fiber with boron content under 6 wt.% at the first weight loss does not beyond 300  $^{\circ}\text{C}$ . During the heating, the weight loss increases with increasing the content of the phenol borate B-O linkage. The curing processing in oven was applied from room temperature to 240  $^{\circ}\text{C}$  slowly, and then kept for 2 hours. The fact that the processing increases the thermal stability of the boron-containing fibers with increasing the phenol borate B-O linkage of the HBPF, and the carbonyls converted from the methylene links, leads to lower weight loss, fig. 2(b). At the same time, the curves in fig. 2(b) are similar to the curves in fig. 2(a) when the temperature is higher than 300  $^{\circ}\text{C}$ . It suggests that the 2 hours curing at 240  $^{\circ}\text{C}$  in oven induces the reactions mentioned above under 300  $^{\circ}\text{C}$  completely.

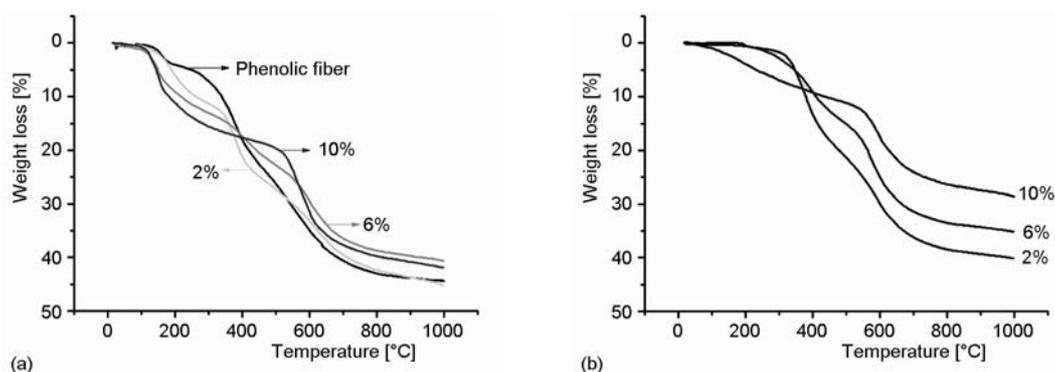


Figure 2. TGA curves of HBPF cured in solution (a), and then cured in oven (b)

While TGA curve of the HBPF-10 contains a wider weight loss from 153  $^{\circ}\text{C}$  to 430  $^{\circ}\text{C}$  in fig. 2(a), and below 456  $^{\circ}\text{C}$  in fig. 2(b), which does not present in all other samples. It may be due to that the free boric acid in the sample reacts further with phenolic molecule to produce water [5].

## Conclusions

High-ortho boron-containing novolac resins have been synthesized by copolymerization among phenol, formaldehyde, and boric acid in the presence of zinc acetate and sulfuric acid catalyst. The fibers were prepared by melt-spinning the resin, followed by curing the filaments with the mixture of hydrochloric acid and formaldehyde solution, and curing the fibers with heat-treated in  $\text{N}_2$  at elevated temperature. HBPF show a higher curing temperature and thermal stability than boron-free phenolic fiber.

## Acknowledgment

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