Blending Spinning to Prepare Flame Retardant Phenolic/Polybutylene Succinate Fiber

Fan Yang¹,², Angting Bian¹,², Jiuhua Liu¹,², Yanping Wang¹,² *

¹State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China
²College of Material Science and Engineering, Donghua University, Shanghai 201620, China

*Corresponding author e-mail: wyp@dhu.edu.cn, 513731024@qq.com

Abstract. In order to improve the spinnability of phenolic (PF) resin, a small amount of polybutylene succinate (PBS) was added during the melt spinning process. It was found that the spinning speed can be increased to 400m/min with only 1 wt% PBS. The glass transition temperature of the PF/PBS as-spun fiber decreased with PBS content, and the PBS melting endotherm peak disappeared after blending with PF. Crosslinking was formed after curing, which can greatly increase strength of PF fibers. The strength of PF/PBS fiber can reach 2.01 cN/dtex, which is 30% higher than pure PF fiber.

1. Introduction
Phenolic (PF) fiber has the advantages of high temperature resistance, chemical resistance, low thermal conductivity, etc. It also has the characteristics of high carbon residue and self-extinguishing from fire. Therefore, it is usually used for insulation material, flame retardant material, chemical resistant materials and fiber reinforcement [1].

In 1968, researchers in United States and Japan began researching PF fiber. However, due to the poor mechanical properties of as-spun PF fibers, the production was extremely demanding. Until the 1990s, Kynol Corporation of Japan began the industrial production of phenolic fiber. Phenolic resin has poor spinnability and the strength of its as-spun fiber is extremely low. PA6 was added in phenolic resin to improve its spinnability by Economy [2]. However, the melting point of PA6 is so high that the blending processing causes degradation of PF. Therefore, in this paper, polybutylene succinate (PBS), a low melting point polyester, was chosed to improve the spinnability of PF.

In this paper, the blending and spinning of PBS and PF were carried out, and PF/PBS blended as-spun fiber was prepared. It is aimed that the spinnability of PF can be improved by melt blending.

2. Experimental
Phenolic resin (PF), FR16, was purchased from the Chinese Academy of Sciences. Its softening point is between 100 and 110 °C. Polybutylene succinate (PBS), N9000, was purchased from BASF. Hydrochloric acid (HCl, 37%, w/w) was purchased from Shanghai test. Formaldehyde (HCHO 37%, w/w) was purchased from Shanghai test.
PF and PBS chips are dried for 12 h in vacuum oven and melt-spun to obtain PF and PF/PBS as-spun fiber. The spinning speed is adjusted between 100 and 700 m/min. The PF and PF/PBS as-spun fibers are placed in the HCHO/HCl mixed solution at a heating rate of 30 °C/h. The temperature is raised to boiling and kept for 3 h. The fiber is washed, heated from room temperature to 160 °C in a vacuum oven and kept 160 °C for 2 h.

The sample is heated from 20 °C to 180 °C at a rate of 20 °C/min using differential scanning calorimeter (Niche 214 Polyma) under nitrogen atmosphere. Heating the sample from 20 °C to 700 °C at a rate of 20 °C/min under nitrogen flow protection. The linear density of the fiber is measured by a weighing method, and the mechanical property was tested using an XQ-1A yarn strength meter.

3. Results and Discussion

![Figure 1](image)

**Figure. 1** TG and DSC curves of PF and PBS

According to Fig.1 (a), it could be seen that the mass loss of 1 wt% of PF and PBS is at 228.6 °C and 282.5 °C. Therefore, the spinning temperature only needs to consider the heat resistance of PF, and the processing temperature needs to be much lower than 225 °C.

In Fig.1 (b), that the glass transition temperature (Tg) of PF is 66.9 °C, and the softening point of the PF is around 105 °C, so the PF spinning temperature should be over 110 °C. The melting point of PBS is 116.9 °C, so the PF/PBS spinning temperature is between 120 °C and 225 °C. In order to reduce the decomposition of PF, the optimal blending temperature is 120 °C.

During the spinning process, it is found that the optimum spinning temperature of pure PF was 114 °C, and the spinning temperature of PF/PBS is 120 °C. When the temperature is low, the material is rod-shaped and discontinuous when extruded, and it is difficult to form fiber; when the temperature is high, the PF is in the form of droplets, which cannot be wound. The PF as-spun fiber is brittle, and the conventional passive winding machine crushes the PF as-spun fiber easily, so it is wound directly onto the roller using an active winder. PF as-spun fiber can only be prepared at the speed of 200 m/min, when the spinning speed is too low, the fiber is fluffy on the roll; and the spinning speed is too high, the fiber breaks frequently during the spinning process. PF/PBS as-spun fiber in which only 1wt% PBS is put can be stably got at a spinning speed of 200 ~ 400 m/min. The PF/PBS as-spun fiber of 5 wt% and 10 wt% PBS are stably wound at a spinning speed of 500 m/min. It can be found that the spinnability of PF is greatly improved by adding PBS.
Figure 2 DSC curves of PF/PBS as-spun fiber

The $T_g$ of PBS is around -30 °C [3]. It can be seen from the Fig.2 that the $T_g$ of PF is around 66.9 °C, and the $T_g$ of 3 PF/PBS fiber are 66.0 °C, 64.5 °C and 63.7 °C, respectively. The $T_g$ are decreased with the increase of PBS. At the same time, PBS melting peaks do not appear in the three ratios of PF/PBS as-spun fiber.

The as-spun fiber is put in the HCHO/HCl mixed solution, and its strength has a great promotion, because the HCHO generates $+\text{CH}_2\text{OH}$ under the action of HCl, the $+\text{CH}_2\text{OH}$ and the PF molecule have cross-linked reaction [4]. After secondary curing in the vacuum oven, the fiber’s strength becomes higher, because residual $+\text{CH}_2\text{OH}$ and the PF molecule have cross-linked reaction under high temperature [5]. The cured pure PF fiber strength is 1.56 cN/dtex, the cured PF/PBS fiber strength is 2.01 cN/dtex, increased by 30.0% than the cured PF. The PF as-spun fiber is a transparent fiber which becomes orange-pink fiber after first curing, and becomes yellow fiber after secondary curing. The as-spun fiber of PF/PBS is transparent fiber, and the fiber after first curing is light yellow, after secondary curing becomes dark yellow. In Fig.3, the surface of PF and PF/PBS are smooth and round.

Figure 3 SEM micrographs of PF and PF/PBS fiber

4. Conclusion
The PF has poor spinnability. Therefore, the effect of PBS on PF fiber is investigated by adding PBS to PF/PBS fiber in PF. The results show that with the increase of PBS, the spinnability of PF was significantly improved. Pure PF fiber could only be stably spinning at the winding speed of 200 m/min, PF/PBS fiber can be taken between 200–500 m/min with stable winding. The glass transition temperature of the PF/PBS blend decreased with the increasing of PBS, and the glass transition
temperature decreased from 66.9 °C to 63.7 °C with the PBS increased from 0% to 10%. After curing, the pure PF fiber is yellow and the PF/PBS fiber is dark yellow. The pure PF fiber strength is 1.56 cN/dtex, and the strength of the PF/PBS fiber is increased by 30.0% to 2.01 cN/dtex.

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