

Article

Strong Effect of Process Parameters on the Properties of Boron-Containing Phenolic Resins with High Char Yield

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Abstract: This work is focused on the optimization of critical process parameters for preparation of boron-containing phenolic resin (B-containing PR), including the molar ratios of formaldehyde/phenol and potassium borate/phenol, reaction time; and measurement of surface tension of B-containing PR solution and wettability between B-containing PR solution and carbon fibers. The effects of the formaldehyde/phenol and potassium borate/phenol molar ratios on the char yield of the B-containing PR was studied. The highest char yield of B-containing PR could be as high as 71% under optimal conditions (molar ratios of formaldehyde/phenol = 1.8 and potassium borate/phenol = 0.2, and reaction time = 13 h). The effect of concentration and tested temperature on the surface tension of B-containing PR solution was investigated, and the wettability between B-containing PR solution and carbon fibers was evaluated for the first time, providing useful theory and experimental data for the preparation of B-containing PR-based composites.

Keywords: boron-containing phenolic resin; molar ratio; reaction time; char yield; surface tension; wettability

1. Introduction

Rapid developments in space science and technology have resulted in the introduction of a large variety of spacecraft. Thermal protection systems (TPSs) that offer excellent performance are, therefore, required to shield spacecraft from high temperatures generated during atmospheric entry in the stagnation region [1–3]. TPSs can be of two types—non-ablative and ablative systems [1,4]. Non-ablating TPSs are usually employed in reusable hypersonic vehicles that are not subjected to intense entry conditions. Ablative TPSs, on the other hand, are used in hypersonic vehicles under harsh environmental conditions due to numerous heat dissipation mechanisms, such as phase transition and chemical reaction [1,5]. Among ablative TPSs, carbon/phenolic systems have attracted much interest, particularly with the closure of the Space Shuttle program and renewed focus on Apollo-style spacecraft [6,7]. The Phenolic Impregnated Carbon Ablator (PICA) developed at NASA Ames Research Center is a state-of-the-art carbon/phenolic ablator, which exhibits low mass per unit volume and superior ablation property. Research results have confirmed that PICA offers outstanding anti-ablation performance, along with a low-density property (about 0.2–0.4 g/cm³) [7–10].

PICA is a highly porous fibrous carbon substrate partially impregnated with phenolic resin (PR) that has high thermal stability, excellent ablation resistance, and low cost; this phenolic resin is used as an ablation-resistant matrix [11,12]. With rapid developments in aerospace technology, PRs with better heat resistance and stronger mechanical properties are required to create advanced ablation-resistant composite materials [13]. The literature reports that introducing boron (B) into the PR molecular structure is an effective way to enhance its thermal and mechanical properties. Various approaches

have been adopted to synthesize B-containing PR, including methods using polyformaldehyde and salicyl alcohol, and copolymerization blending [13–16]. Several process parameters, including reaction time and raw material ratio, influence the properties of final products, especially for organic materials. Zhang et al. and co-workers have confirmed that boric acid content plays an important role in the properties of B-containing phenolic fibers prepared by melt-spinning a mixture of novolak resin and boron acid, followed by curing the filaments with formaldehyde solution in the presence of an acid catalyst [17–19]. Thus, it is reasonable to believe that the critical process parameters strongly affect the properties of B-containing PR before the composites are created. In addition, there is very little research on the surface tension of PR solutions, thus limiting guidance on impregnation of B-containing PR into carbon fiber braids and further preparation of PICA materials.

The work presented here builds on the creation of B-containing PR through a polyformaldehyde method using phenol and formaldehyde with catalyst potassium borate to investigate the effects of the formaldehyde/phenol and potassium borate/phenol molar ratios on the char yield of the B-containing PR. Measurements of wettability and surface energy between carbon fibers and B-containing PR were also performed for the first time. The analysis results can provide useful experimental data for the creation of high-performance PICA materials.

2. Experimental Section

2.1. Materials

The chemical materials were of analytical grade and used without further purification. The raw materials, including phenol (molecular weight: 94.11, purity: $\geq 99.5\%$, Aladdin), formaldehyde (solution concentration: 37%), and potassium borate (purity $\geq 99.5\%$) were purchased from Aladdin (Shanghai, China) and Harbin Jierui Chem. Co. The carbon fiber (Toray T700) braid with final density of 0.15 g/cm^3 was fabricated by needle punching of nonwoven carbon fiber cloth.

2.2. Preparation of B-Containing PR

B-containing PR was prepared by a catalytic synthesis method. Phenol and formaldehyde were stirred evenly for 20 min in a reaction bottle with volume of 250 mL. Then, a certain amount of potassium borate was added as a catalyst. The formaldehyde solution weighed 150 g (containing 55.5 g formaldehyde), and the weights of the added phenol and potassium borate were calculated according to the formaldehyde/phenol molar ratio (1.0–2.0) and potassium borate/phenol molar ratio (0.1–0.4), respectively. Under action of the catalyst, the reactant was found to be fully dehydrated when the reaction system was heated to 85°C ; it was then held at this temperature for several hours (10–15 h). The effects of the molar ratios of formaldehyde/phenol and potassium borate/phenol, and reaction time on the carbon residue rate of B-containing PR were studied. For comparison, common PR was also fabricated under the same optimization conditions, just without potassium borate.

2.3. Sample Characterization

To confirm successful introduction of B, the chemical bonding of the as-prepared samples was identified by Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer, Shanghai, Spectrum Two, USA; wavenumber range: $400\text{--}4000 \text{ cm}^{-1}$, resolution: 0.4 cm^{-1} , scanning rate: $10 \text{ cm}^{-1}/\text{s}$, KBr/sample ratio: 100:1). The residual carbon after pyrolysis was attached to the conductive tape and further analyzed by a field-emission scanning electron microscope (SEM, FEI Company, Hillsboro, HELIOS NanoLab 600i, USA) equipped with Energy Dispersive X-ray (EDX) to confirm presence of the B element. The accelerating voltage used in SEM analysis was 20 kV. The B content within B-containing PR was measured as per related literature and National Standards (GB/T 24411—2009). The thermal stability, along with residual carbon content, was evaluated by thermogravimetric analysis (TGA, SDT Q600, TA Instruments, TA Instruments, Wilmington, USA) with a heating rate of 5°C min^{-1} up to a temperature of 1200°C under protection of flow Ar atmosphere (flow rate 40 mL/min). The starting

sample weight was 10 mg for TGA. The surface tension of PR and B-containing PR solutions as well as the wettability between B-containing PR solution and carbon fibers were recorded by an optical contact angle meter (SDC-100S, Shengding Precision Instrument Co., Ltd., Dongwan, China). PR or B-containing PR solutions at different concentrations (0.4 and 0.8 g/mL) and temperatures (25 °C, 35 °C and 45 °C) were prepared and placed into a syringe that was part of an optical contact angle meter. The status of PR or B-containing PR solution droplets (squeezed from the syringe) and the wetting state of B-containing PR solution droplet on the surface of carbon fibers were imaged and analyzed by the optical contact angle meter. The system automatically calculates surface tension on assessing the status of solution droplets.

3. Results and Discussion

3.1. The Effect of Formaldehyde/Phenol Molar Ratio on the Char Yield of B-Containing PR

Previous studies have shown that the formaldehyde/phenol molar ratio affects the crosslinking density of PR after curing, and then leads to a different char yield. Generally, the larger the crosslinking density in the curing process of PR is, the higher the char yield is [20,21]. The formaldehyde/phenol molar ratio ranges from 1.0 to 2.0 in traditional preparation of PR, and the largest cross-linking density in the curing process is achieved when the formaldehyde/phenol molar ratio is proper, resulting in the highest char yield [20–22]. Thus, the influence of formaldehyde/phenol molar ratio within 1.0–2.0 on the char yield of B-containing PR was investigated, while the molar ratio of potassium borate/phenol was kept at 0.2 and reaction time was 13 h. The char yields of B-containing PR obtained with different formaldehyde/phenol molar ratios were evaluated; the results are shown in Figure 1. In addition, as a comparison, the char yields of common PR achieved with different formaldehyde/phenol molar ratios were also fabricated under the same conditions, just without potassium borate.

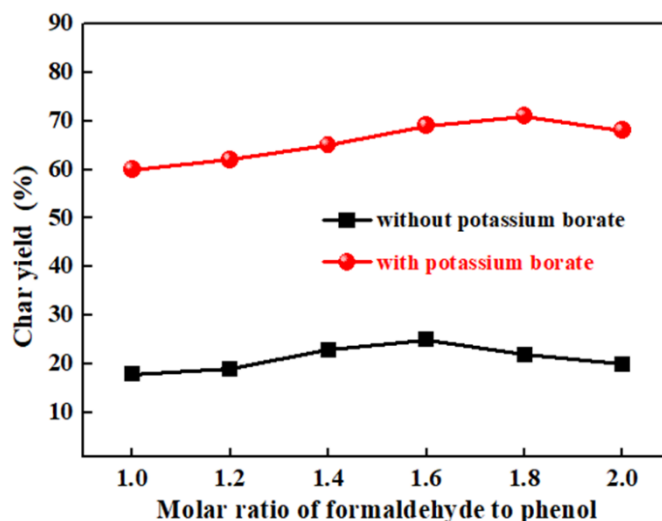


Figure 1. The effect of formaldehyde/phenol molar ratio on the char yield of B-containing PR and common PR.

As per Figure 1, the char yields of common PR exhibit an increasing trend, followed by a decrease, as the formaldehyde/phenol molar ratio increases; the values of char yield range from 18% to 25%, and the highest value is about 25% when the formaldehyde/phenol molar ratio is 1.6. On introduction of potassium borate, the char yields of B-containing PR are significantly improved, while the values of char yield increase at first and then decrease, similar to the results of common PR. Notably, the char yields of B-containing PR are between 60% and 71%, and maximum char yield is acquired when the formaldehyde/phenol molar ratio is 1.8. The reason for introduction of the B element in char yield can be concluded in the following sentences: Some of the pristine carbon-carbon bonds in PR

are replaced by boron-oxygen and boron-carbon bonds, and the chemical binding energies of both (515 kJ/mol for B-O and 393 kJ/mol for B-C) are much higher than that of the carbon-carbon bond (332 kJ/mol for C-C), resulting in higher thermal properties [13–15,23]. In addition, the formation of boron-oxygen and boron-carbon bonds further affects the carbon-forming structure and property of PR at high temperatures, shortens the interatomic spacing, increases the cross-linking degree of PR, and improves the compactness of carbon.

3.2. The Effects of Potassium Borate/Phenol Molar Ratio and Reaction Time on the Char Yield of B-Containing PR

According to the above results, a higher char yield of B-containing PR was achieved when the formaldehyde/phenol molar ratio was 1.8. We further investigated the effect of potassium borate/phenol molar ratio on the char yield of B-containing PR under this optimal condition. Figure 2 reveals the char yields of B-containing PR obtained with different potassium borate/phenol molar ratios and reaction times. From the results, it is obvious that the char yield of B-containing PR clearly increases first and is then relatively constant with increase of reaction time when the potassium borate/phenol molar ratio is determinate, which should be ascribed to the saturated cross-linking reaction in the system with sufficient reaction time. Moreover, the char yield of B-containing PR under the condition of formaldehyde/phenol = 0.1 is distinctly lower than those of products prepared when the formaldehyde/phenol = 0.2 or 0.4, suggesting that the B element content should not reach the optimal value in the reaction system. When the molar ratio of potassium borate/phenol is 0.2 or 0.4, the B-containing PR possesses a high char yield ranging from 60% to 71%, and char yield increases first and then tends to stabilize with the extension of reaction time. Notably, the char yield of B-containing PR with potassium borate/phenol = 0.2 is slightly higher than that of products fabricated with a potassium borate/phenol molar ratio of 0.4 when reaction time was 12–15 h, indicating that excessive potassium borate did not contribute to the char yield, and the highest char yield of 71% was acquired under the conditions of potassium borate/phenol = 0.2 and reaction time = 13 h, respectively. In order to further confirm B content within the B-containing PR, the B content of the optimized B-containing PR with highest char yield was tested according to previous literature and related National Standards (GB/T 24411—2009); the average value was found to be about 6 wt.%, similar to results reported in previous literature [24].

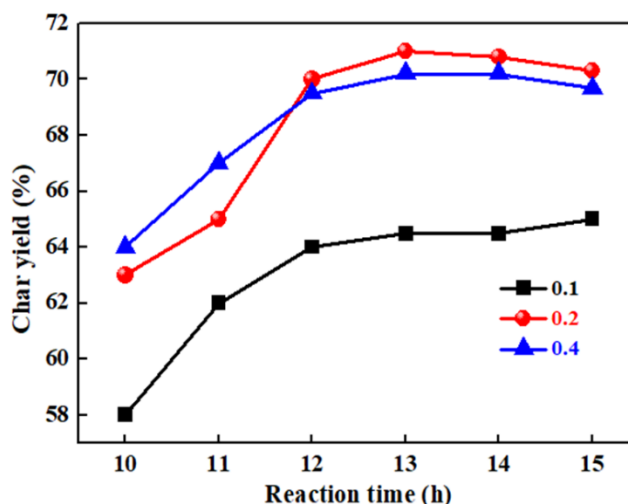


Figure 2. The effects of potassium borate/phenol molar ratio and reaction time on the char yield of B-containing PR.

3.3. Comparison of Thermal Stabilities of Common PR and B-Containing PR

Combined with the above analysis, the optimal process parameters (molar ratios of formaldehyde/phenol and potassium borate/phenol were 1.8 and 0.2, and reaction time was 13 h) were carried out to synthesize B-containing PR. The thermal stabilities of common PR and B-containing PR were investigated by TGA, and the TG curves of common PR and B-containing PR are exhibited in Figure 3. When the temperature is below 400 °C, the two kinds of PR show a similar trend with slight weight loss, in which curing and polycondensation reactions occur to release small solvent molecules. When compared to common PR, there was an additional downtrend at about 200 °C for B-containing PR, which might be a result of the excess reactant used to react and generate water [19,25]. Notably, the two kinds of PR display a close temperature range for maximum weight loss within 400–800 °C, which should be ascribed to the unstable characterization of terminal benzene rings; weight loss still occurs for common PR when the temperature is larger than 800 °C, while the weight of B-containing PR is relatively stable [19,26]. Finally, the char yield of B-containing PR is about 71%, which was about 2–3 times that of common PR, demonstrating that the incorporation of B elements could effectively improve char yield. The residual pyrolytic carbon of B-containing PR was observed by SEM; elemental area scanning under SEM was also carried out to confirm successful introduction of the B element, as presented in Figure S1 (See Supplementary Materials for details). It is obvious that the residual pyrolytic carbon of B-containing PR is in the form of nanoparticles with average size of about 200 nm, while the nanoparticles agglomerate easily. From the elemental area scanning images, the composition of residual pyrolytic carbon of B-containing PR is found to contain C, O, and B, thus confirming the successful incorporation of B element in PR.

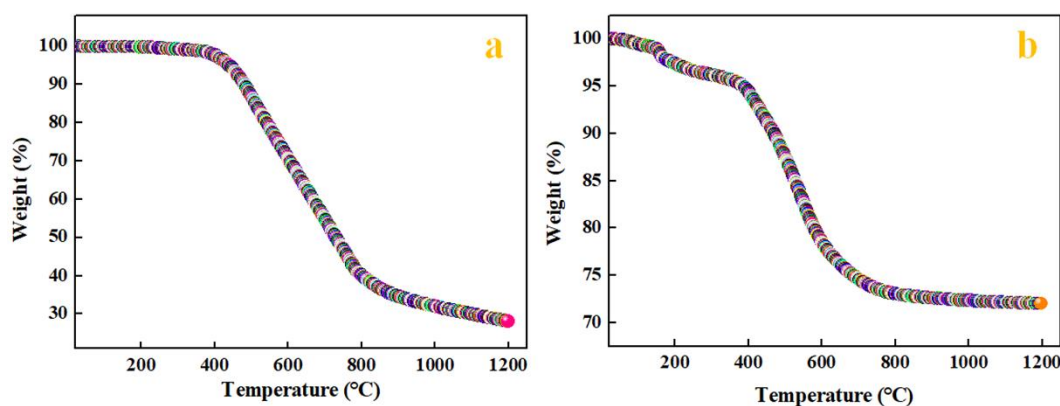


Figure 3. The thermal stabilities of (a) common PR and (b) B-containing PR.

3.4. Structure of Common PR and B-Containing PR

The chemical structures of common PR and B-containing PR prepared under optimal process parameters were investigated by FTIR spectroscopy. The FTIR spectra of all samples were displayed in Figure 4. From the FTIR spectra, the characteristic absorption peaks at 3326 cm^{-1} for common PR and 3217 cm^{-1} for B-containing PR ascribe to the presence of hydroxyl; the characteristic absorption peaks of benzene skeleton occur at 1594 and 1510 cm^{-1} for common PR and B-containing PR. The characteristic absorption peaks around 1237 cm^{-1} for common PR and 1222 cm^{-1} for B-containing PR correspond to the C-O bond of phenolic hydroxyl, and the stretching vibration peak of C-O bond for residual phenol hydroxyl is weakened visibly. The characteristic absorption peak of the C-O bond for benzyl hydroxyl is located at about 1100 cm^{-1} [27,28]. Notably, the B-containing PR exhibits a new strong absorption peak at about 1455 cm^{-1} , which is attributed to the characteristic peak of the B-O bond compared with that of common PR, indicating successful incorporation of the B element by the current simple method [13,27]. In addition, there are two characteristic peaks of para-substituted and ortho-substituted of benzene for common PR at about 812 and 756 cm^{-1} , while the characteristic peak

at 812 cm^{-1} is weakened significantly (almost disappeared), suggesting the high ortho-substituted characteristic of the as-prepared B-containing PR [29–31].

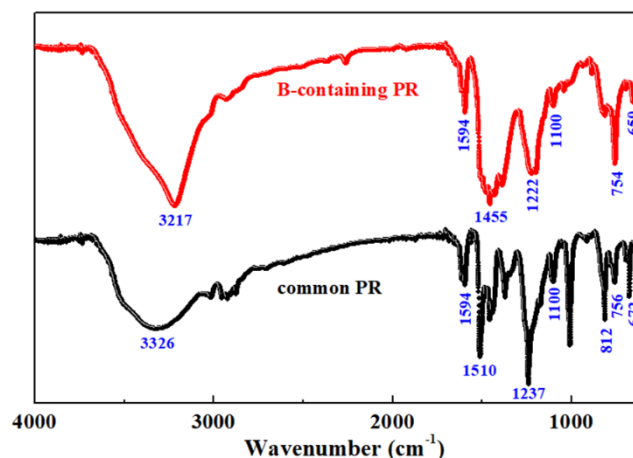


Figure 4. FTIR spectra of common PR and B-containing PR.

3.5. Surface Tensions of Common PR and B-Containing PR Solutions

The surface tensions of common PR and B-containing PR solutions were measured, which strongly depended on the concentrations of the PR solution and tested temperatures; the results are presented in Table 1. Two concentrations of common PR and B-containing PR solutions were compounded with absolute ethanol, and three temperatures selected. For common PR solution with concentration of 0.40 g/mL, surface tensions at 25–45 °C are about 32.10–25.06 mN/m, and at 25–45 °C are about 29.45–23.12 mN/m when the concentration of common PR solution is 0.8 g/mL. As for 0.40 g/mL B-containing PR solution, the surface tensions at 25–45 °C are about 28.45–22.71 mN/m, and at 25–45 °C are about 25.62–20.01 mN/m when the concentration of the B-containing PR solution is 0.8 g/mL. From the above results, it is reasonable to believe that concentration of the PR solution and the tested temperature seriously affect the surface tension of the solution. This surface tension decreases with increase in concentration of the PR solution. Low concentration means a high content of absolute ethanol, while the surface tension of absolute ethanol is larger than that of PR, leading to a high surface tension, compared with that of high concentration of PR solution [32–34]. In general, the surface tension of PR solution increases as the temperature increases, due to the curing of PR and evaporation of the solvent. However, when the temperature is relatively lower than the cured temperature of PR, increasing the temperature is found to be favorable for the mixing of PR and solvent, resulting in a lower value of surface tension of PR solution, similar to results revealed in Table 1 [32–34]. In addition, the value of surface tension of the B-containing PR solution is lower than that of common PR solution under the same conditions, demonstrating that the introduction of B element could decrease surface tension of the PR solution, which is beneficial for infiltration into the fiber braid. The reason for surface tension of the B-containing PR solution being lower than that of the common PR solution is that incorporation of the B element improves electrical conductivity of the system and decreases whole surface energy, resulting in the reduction of surface tension [35,36].

3.6. Wettability Between B-Containing PR Solution and Carbon Fibers

Although increasing temperature could decrease the surface tension of the B-containing PR solution, absolute ethanol is extremely volatile to increase in viscosity of the solution, which is unfavorable for impregnation. Thus, B-containing PR solution with 0.8 g/mL at 35 °C could be selected to impregnate the carbon fiber braid from the points of char yield and impregnation effect. To make preparations for future impregnation of a B-containing PR solution, the wettability process with B-containing PR solution at a concentration of 0.8 g/mL and carbon fibers treated at 500 °C for 1 h to remove the polymer surface

sizing agent was tracked by a surface tension tester at 35 °C. Figure 5 shows the whole wetting process at different times; it can be clearly seen that B-containing PR solutions can spread out quickly on the surface of carbon fibers, taking only 7.5 s to reach an equilibrium state, along with the contact angle reaching 0°. The above results indicate good wettability between B-containing PR solution and carbon fibers, laying a solid foundation for subsequent successful impregnation of B-containing PR into carbon fiber braids.

Table 1. The surface tensions of common PR and B-containing PR solutions at different concentrations and temperatures.

Sample	Temperature (°C)	Concentration (g/ML)	Surface Tension (mN/m)
Common PR	25	0.40	32.10
	25	0.80	29.45
	35	0.40	29.23
	35	0.80	26.23
	45	0.40	25.06
	45	0.80	23.12
B-containing PR	25	0.40	28.45
	25	0.80	25.62
	35	0.40	26.02
	35	0.80	23.17
	45	0.40	22.71
	45	0.80	20.01

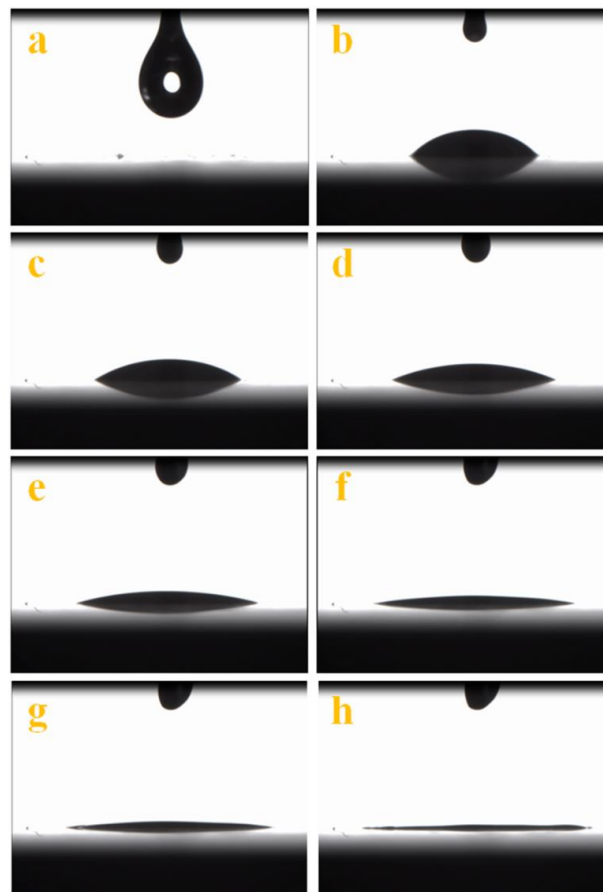


Figure 5. Shape of B-containing PR droplet on carbon fibers at different times. (a) 0 s, (b) 0.15 s, (c) 0.3 s, (d) 0.6 s, (e) 1.2 s, (f) 1.95 s, (g) 2.4 s and (h) 7.5 s, respectively.

4. Conclusions

In this paper, a polyformaldehyde method using phenol and formaldehyde as raw materials with the catalyst potassium borate was proposed to prepared B-containing PR. The critical process parameters for preparation of B-containing PR, such as the molar ratios of formaldehyde/phenol and potassium borate/phenol, and reaction time, was optimized. The measurement of surface tension of B-containing PR and wettability between B-containing PR solution and carbon fibers was taken, providing useful theory and experimental data for the preparation of B-containing PR-based composites.

The influence of formaldehyde/phenol molar ratio within 1.0–2.0 on the char yield of B-containing PR was investigated, with the molar ratio of potassium borate/phenol kept at 0.2 and reaction time at 13 h. The char yields were found to be between 60% and 71%, and maximum char yield was acquired when the formaldehyde/phenol molar ratio was 1.8. The effects of potassium borate/phenol molar ratio ranging between 0.1 to 0.4 and reaction time on char yield of B-containing PR was evaluated in the condition of formaldehyde/phenol molar ratio = 1.8. The char yield of B-containing PR in the condition of formaldehyde/phenol = 0.1 was distinctly lower than those of products prepared when the formaldehyde/phenol = 0.2 or 0.4. When the molar ratio of potassium borate/phenol was 0.2 or 0.4, the B-containing PR possessed a high char yield ranging from 60% to 71%, and the char yield increased first and then stabilized with the extension of reaction time. By optimization of critical process parameters, the highest char yield of B-containing PR could be as high as 71%, with molar ratios of formaldehyde/phenol = 1.8 and potassium borate/phenol = 0.2, and reaction time = 13 h, respectively. In addition, the surface tension of B-containing PR solution was measured under different concentrations and tested temperatures; its value was found to decrease with increase in concentration and tested temperature. Finally, the wettability between B-containing PR solution and carbon fibers was investigated for the first time, and B-containing PR solution with 0.8 g/mL at 35 °C was found to spread on to the surface of carbon fibers within 7.5 s to reach an equilibrium state, along with contact angle of 0°, indicating good wettability between B-containing PR solution and carbon fibers.

In conclusion, the results of this study indicate that the high char yield of B-containing PR with good wettability between B-containing PR solution and carbon fibers could be used to prepare B-containing PR-based composites, which can be used as thermal insulation materials. Our next research will concentrate on the design and fabrication of B-containing PR-based composites in an effort to characterize their microstructures and properties.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2076-3417/10/4/1408/s1>.

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