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Influence of precursor preparation on the synthesis of boron carbide from glutinous rice flour

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Abstract

Boron carbide is a promising candidate for a variety of applications, including blasting nozzles, neutron moderators, and lightweight armor. Using of inexpensive and readily available starting materials which can react with boric acid to form B-O-C bonds, e.g., glutinous rice flour, is one of alternative means to produce high purity boron carbide powder at low temperature. In this study, boric acid and glutinous rice flour, boron and carbon sources, were used for synthesizing B_4C powder by the carbothermic reduction. The mole ratios of boric acid to glutinous rice flour ranging from 1:1 to 2.5:1 were formulated and mixed by continuous stirring at 80°C for 2 h to 8 h. The influence of reaction time during the mixing process on the phase formation of the synthesized powder was investigated. It was found that appropriate reaction time for condensation of 4 h facilitated the B_4C phase formation during synthesis. The precursors were synthesized under Ar flow at 1350°C to 1450°C for 5 h without calcination. B_4C powder with the purity of 90 wt% was successfully synthesized from this study. Chemical bonding, phase analysis, and morphology of the synthesized powder were identified by Fourier-transform infrared spectroscopy, X-ray diffraction, and scanning electron microscope, respectively. The influences of starting composition and synthesis temperature on the characteristics of the synthesized powders were also discussed.

1. Introduction

Boron carbide (B_4C) is known as the hardest material, next only to diamond and cubic boron nitride. Its excellent properties, e.g., low density (2.52 g·cm^{-3}), high melting point (2540°C), high elastic modulus (445 GPa), good chemical stability, high neutron capture cross-section, make B_4C an outstanding candidate for numerous advanced applications in military, abrasive, aerospace, and nuclear industries [1-2].

A number of synthesis processes to produce various forms of boron carbide powders have been reported [2], including magnesiothermic reduction, synthesis from elements, chemical vapor deposition, ion beam synthesis, plasma dynamic synthesis, and carbothermic reduction. Among these methods, the most widely used process for synthesizing B_4C powder on an industrial scale is carbothermic reduction. Normally, this process is carried out in an electric arc furnace using boron oxide (B_2O_3) and carbon black or petroleum coke as boron and carbon sources. The overall carbothermic reduction reaction can be presented as the following equation:

$$2B_2O_3\ (l,g) + 7C\ (s) \rightarrow B_4C\ (s) + 6CO\ (g) \qquad (1)$$

However, this process is strongly endothermic and usually completed after heat treatment at a high temperature of approximately 2000°C, resulting in the agglomeration of the synthesized powder and this causes difficulty with the grinding process required for further fabrication steps due to the extreme hardness of B_4C powder.

During the recent years, many researchers have been searching for the alternative techniques to synthesize B_4C powder at lower temperature. One of them is the use of polymer precursors to provide more homogeneous dispersion between boron and carbon species in the mixed precursor, leading to a reduction in synthesis temperature. Low temperature syntheses of B_4C powder from boric acid and various kinds of polymer precursors such as polyvinyl alcohol [3], citric acid [4], glycerin [5], sucrose [6], cellulose, and starch [7] have been proposed. By these processes, B_4C powder can be synthesized at a much lower temperature (1000°C to 1600°C) in vacuum or inert atmosphere than that of the traditional process [8-9]. This may be caused by the formation of borate ester bonds during the condensation process which facilitates the reaction kinetics to form boron carbide at a lower temperature. However, the obtained product usually contains a large amount of residual carbon derived from the polymer precursor. Generally, the main factors those affecting the purity of the powder product were molar ratio of starting materials, type of carbon source, precursor preparation, calcination, and synthesis temperature. Numerous attempts to produce fine B_4C powder with less free carbon content at low temperature have been reported. Khanra [10] synthesized micron-sized B_4C powder with free carbon content of 9.8 wt% at 1600°C from boric acid-citric acid gel. Vijay *et al.* [6] synthesized B_4C nanopowder with the average particle size of 35 nm in vacuum at 1600°C by using boron oxide and sucrose as starting materials. The product contained 2.5 wt% residual carbon. The obtained high purity nanosized powder was resulted from appropriate starting composition and synthesis condition. Pilladi *et al.* [11] synthesized B_4C powder with 3.5 wt%

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residual carbon at 1500°C using condensed gel precursor prepared from boric oxide and sucrose. The high yield of B_4C (60 wt%) were reported due to the utilization of sucrose as a gel forming agent. Zahid *et al.* [12] reported the B_4C phase formation starting at 1100°C in the powder synthesis using mixed precursor of boric acid, cellulose, and ethylene glycol. The reaction to form B_4C was completed at 1200°C where a small amount of free carbon remained in the powder product. The authors explained such low temperature synthesis as a result of dispersibility of B_2O_3 in cellulose structure. The B_4C equiaxed particles with the average size of 5 μm were observed. Kakiage *et al.* [5] synthesized 1.1 μm sized B_4C powder with no residual carbon from boric acid and glycerin. The B_4C phase formation firstly appeared at 1150°C and the reaction was completed at 1250°C. The authors explained that high degree of homogeneity in the precursor including the formation of B-O-C bonds in the mixed starting materials, is an important factor to gain small sized and high purity B_4C powder. Avcioglu *et al.* [13] synthesized high purity B_4C powder by sol-gel process from boric oxide, glycerol, and citric acid. The powder synthesized at 1500°C consisted of rhomboid-flake, plate, and rod like B_4C particles with the size ranging from 50 nm to 100 mm. Recently, the utilization of saccharides, e.g., flour starch as a carbon source for B_4C synthesis has gained attention from several researchers. Maqbool *et al.* [7] synthesized B_4C powder for structural and electronic applications from boric acid and pure starch. The formation of B_4C was accomplished at 1450°C for 4 h and a certain amount of free carbon still persisted in the final product. The authors explained that high residual free is a result of interaction between boron and carbon species in the mixed precursor. Kozień *et al.* [14] synthesized a 50 μm sized B_4C powder by carbothermic reduction process using boric acid and hydroxyethyl starch. The formation of crystalline B_4C was observed at 1400°C with a large amorphous carbon content in the final product. Most of the mentioned studies employed calcination process prior the synthesis for controlling the mole ratio between carbon to boron oxide in the precursor to reach the stoichiometric value of 3.5.

Glutinous rice flour is an interesting alternative precursor for the B_4C synthesis because it is an inexpensive and readily available carbon source with high content of –OH functional groups in its structure. These –OH functional groups can interact with boric acid, resulting in the formation of B-O-C bonds which facilitates the reaction between B and C species to form B_4C, enhancing low temperature synthesis [7,15-16].

In this study, low cost and low temperature synthesis of B_4C powder was attempted using carbothermic reduction method without calcination process prior the synthesis. Boric acid and glutinous rice flour were used as sources of boron and carbon, respectively. The influences of process parameters, i.e., starting composition, precursor mixing time, and synthesis temperature on phase formation of the synthesized powders were investigated. In addition, the process approaches to improve the purity of the powder product were discussed.

2. Experimental

2.1 Material preparation

Boric acid (99.5%, Fisher Chemical) and glutinous rice flour ($d_{(50)}$ 13 μm, food grade, Thailand) were used as boron and carbon sources, respectively. The XRD patterns of boric acid and glutinous rice flour are shown in Figure 1. In this study, four precursor compositions were prepared with molar ratios of boric acid to glutinous rice flour of 1:1, 1.5:1, 2:1, and 2.5:1. These compositions were named as P1.0, P1.5, P2.0, and P2.5, respectively. Boric acid and glutinous rice flour were separately dissolved in 100 mL of distilled water at 80°C. The suspensions were homogeneously mixed together by continuously stirring (hotplate stirrer: C-MAG HS7, Merck) speeds 200 rpm at 80°C for 2, 4, 6, and 8 h in open system. After mixing, the suspensions were dried in an oven at 100°C for 24 h. Dried precursors were hand ground and passed through a 100-mesh screen. The obtained precursors were placed in a graphite crucible and synthesized in a tube furnace at 1350°C to 1450°C for 5 h at a heating rate of 5°C·min^{-1} with an Ar flow 3 L·min^{-1}.

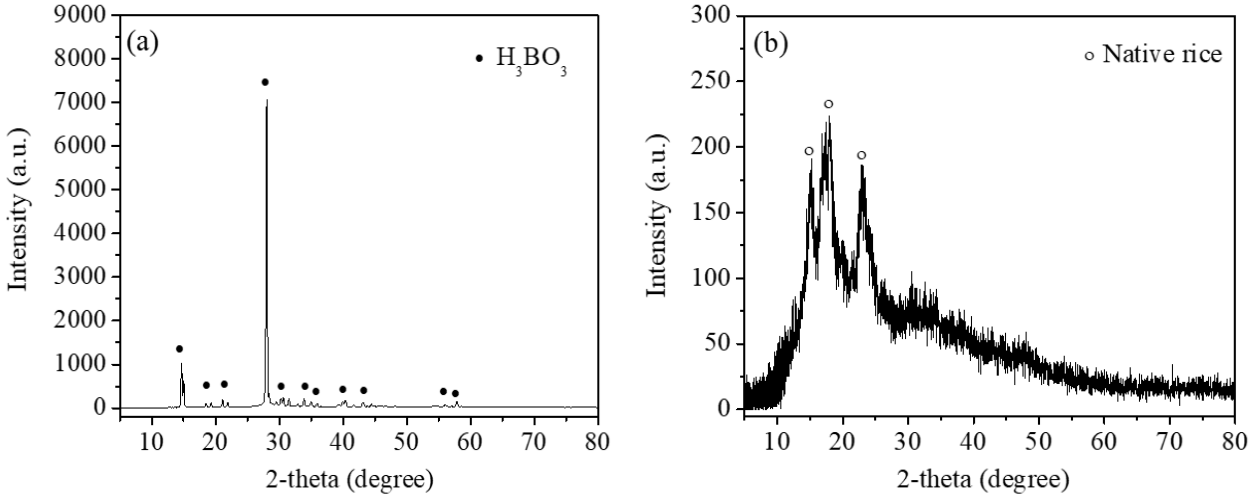

Figure 1. XRD patterns of starting materials (a) boric acid (b) glutinous rice flour.

2.2 Characterizations

Viscosities of the suspension of mixed precursors were determined at 80°C by Viscometer (Brookfield, Programmable DV-II$^+$ Viscometer) using spin number LV-1 in water bath. Chemical functions in the starting materials and precursors were analyzed by Fourier transform infrared spectroscopy (FTIR: Nicolet, model Impact 400, USA) using KBr tablets at a spectra range of 400 cm^{-1} to 4000 cm^{-1}. Phase analysis of precursor and synthesized powder was performed by X-ray diffractometer (XRD: Bruker, D8 Advance, Germany) operated at 40 kV and 40 mA with monochromatized Cu-Kα (λ = 1.5418 Å) radiation in the 2θ range 5° to 80° at the scan speed of 0.01° per second. The B_4C peak intensity ratios of each component (I_{B_4C}, I_C, and $I_{B_2O_3}$) in the XRD patterns were estimated by using Equation. (2);

$$B_4C\ peak\ intensity\ ration\ =\ \frac{I_{B_4C}}{I_{B_4C}+I_C+I_{B_2O_3}} \tag{2}$$

where I_{B_4C}, I_C, and $I_{B_2O_3}$ denote the main peak intensities in an XRD pattern of B_4C ((021) reflection at 2θ ~37.8°), carbon (amorphous halo at 2θ ~26°), and B_2O_3 ((310) reflection at 2θ ~ 27.8°), respectively. The free-carbon content remained in the synthesized powder was determined using a quantitative X-ray diffraction - Rietveld refinement method using Topaz version 2.1 software (Bruker, D8 Advance, Germany). All results have been calculated with the Chi- squared (χ^2) ≈1. The Chi-squared (χ^2) can be determined from the weighted profile R factor (R_{wp}) and the expected profile R factor (R_{exp}) by using Equation (3);

$$\chi^2\ =\ \frac{R_{wp}}{R_{exp}} \tag{3}$$

The morphology of the synthesized powder was observed by scanning electron microscope (SEM: JOEL, JSM-6480LV, Japan) operated at 15 kV in secondary electron mode.

3. Results and discussions

3.1 Effect of starting composition and mixing time

XRD patterns of the powders synthesized from precursors prepared using different mixing times are shown in Figure 2. It was found that at the synthesis temperature of 1450°C, XRD peaks corresponding to rhombohedral B_4C structure (JCPDS #00-035-0798) were observed as a major phase in all samples but these intensities were varied with the starting compositions and mixing times. Considering the influence of mixing time, all four compositions showed similar tendency in the phase formation of synthesized powder. The B_4C peak intensities increased with the increasing precursor mixing time from 2 h to 4 h and started to decrease when the mixing time increased from 6 h to 8 h. The influence of starting composition on the phase formation of the synthesized powders was also observed. B_4C major phase was appeared with the large amount of amorphous carbon (JCPDS #00-026-1076) in P1.0 synthesized powder which derived from starting composition with the highest carbon proportion. As the boron content in the starting compositions increased, the broad peak belonging to amorphous carbon in the XRD patterns of synthesized powders became smaller while the B_4C peak intensities were increasing. The highest B_4C peak intensities along with the lowest carbon content were found in the XRD pattern of P2.0 synthesized powder. Further reduction of carbon content in the starting composition, P2.5, caused the unreacted B_2O_3 (JCPDS #00-013-0570) to appear in the phase composition of the powder product. These relationships showed a similar tendency in the phase formation of synthesized powder for all conditions (Figure 2(a), (b), (c), and (d)).

The peak intensity ratios of B_4C can be estimated from the relation between B_4C, B_2O_3, and amorphous carbon intensities, according to Equation (2). The evolution of B_4C peak intensity ratios of the powders synthesized at 1450°C for 5 h is shown in Figure 3. The results confirmed that the composition P2.0, prepared by mixing the starting materials at 80°C for 4 h, showed the highest B_4C peak intensity ratio.

The weight loss of the synthesized P2.0, P1.5, and P1.0 powders at 1450°C for 5 h was 88.38, 81.82, and 80.17 wt%, respectively. The quantitative phase analysis of the synthesized P2.0, P1.5, and P1.0 are shown in Table 1. The B_4C powder with the purity of 90 wt% could be synthesized in this study. The accuracy indexes of the expected R-factor (R_{exp}), weighted profile R-factor (R_{wp}), and Chi-squared (χ^2) of the quantitative X-Ray diffraction-Rietveld refinement method were 9.49, 11.90, and 1.25, respectively which closely fit in a model.

3.2 Influence of mixing time on the homogeneity of precursor

Variation of the B_4C phase formation observed in this study was not only caused by the starting composition but also by the precursor preparation, as the precursor mixing time had an effect on the viscosity and homogeneity between B and C species within the precursor suspension. Figure 4 shows the viscosity of boric acid, glutinous rice flour aqueous suspension, and P2.0 precursor suspensions that have been continuously stirred for 2, 4, 6, and 8 h at 80°C. It was found that all suspensions showed shear thickening behavior as the viscosity increased starting at a certain shear rate. And the precursor suspensions exhibited higher viscosities than that of the flour aqueous suspension. Generally, when glutinous rice flour particles are heated in the presence of water, they undergo irreversible changes. The first set of changes during heating is termed as gelatinization where the flour particles are swollen resulting in the increase of suspension viscosity. In addition, the occurrence of crosslinking reaction between glutinous rice flour and boric acid caused an increase in the viscosity of the precursor suspensions [17]. Similar result has been reported by Gadhave *et al.* [18] who studied on crosslinking between boric acid and polyvinyl alcohol (PVA). The authors explained that the created crosslinks caused the difficulty for the PVA chains to move along in the suspension so that the viscosity increased. In Figure 4, the precursor suspension that has been stirred for 8 h showed the highest viscosity. Mixing of the starting materials by continuous stirring at 80°C for longer time may also cause some water loss, cluster formation, and jamming, resulting in the higher viscosity. These could hinder the esterification or crosslinking process, leading to the non-uniform mixture.

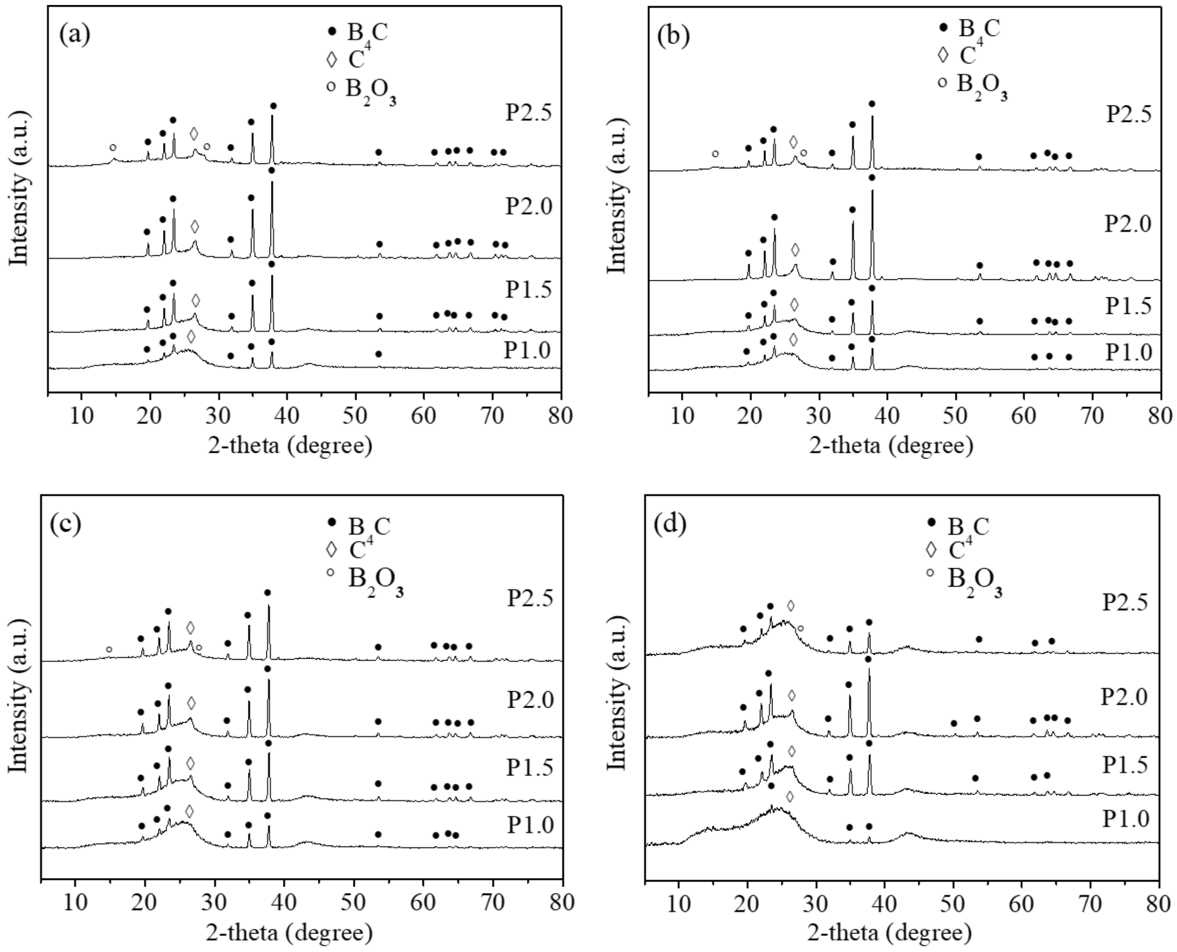

Figure 2. XRD patterns of powders synthesized at 1450°C for 5 h from the precursor prepared using different mixing times of (a) 2 h, (b) 4 h, (c) 6 h, and (d) 8 h.

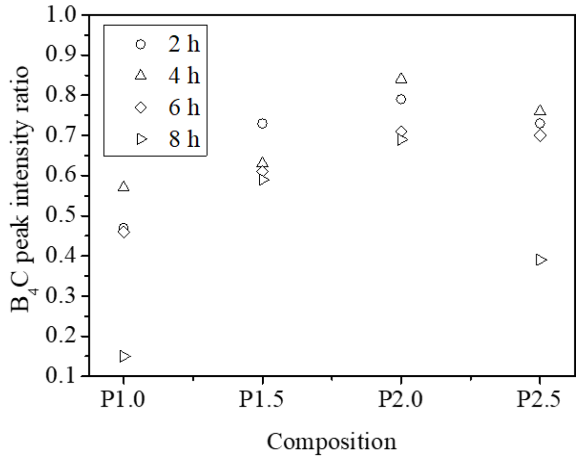

Figure 3. B_4C peak intensity ratios of powders synthesized at 1450°C for 5 h prepared using different precursor mixing times.

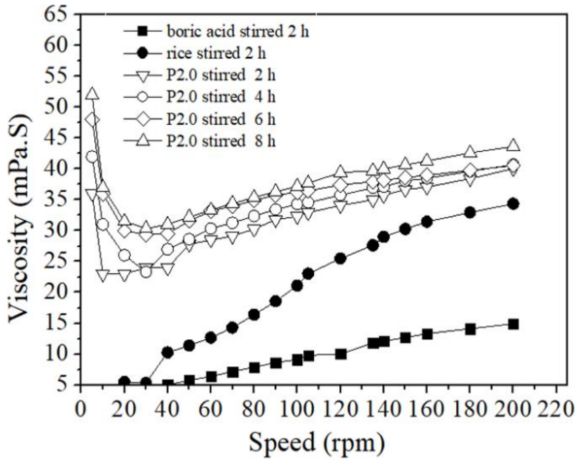

Figure 4. Viscosity of boric acid, glutinous rice flour aqueous suspension, and P2.0 precursors prepared by stirring at 80°C for 2, 4, 6, and 8 h.

Table 1. Quantitative phase analysis of powders synthesized at 1450°C for 5 h.

Composition	**B_4C (wt%)**	**Carbon (wt%)**
P 2.0	90.08	9.92
P1.5	67.34	32.66
P1.0	57.10	42.89

The hypothetically proposed illustration of the interaction between boric acid and glutinous rice flour during the mixing process in the present work is illustrated in Figure 5. When boric acid is dissolved in aqueous solution, it forms tetrahydroxyborate anion and a proton upon reaction with water whereas boron in aqueous system is naturally in the form of borate ion ($B(OH)_4^-$) [19]. During the mixing process, hydroxyl groups could be easily reacted with boric acid and produce a condensed product, i.e., borate ester (B-O-C) [16].

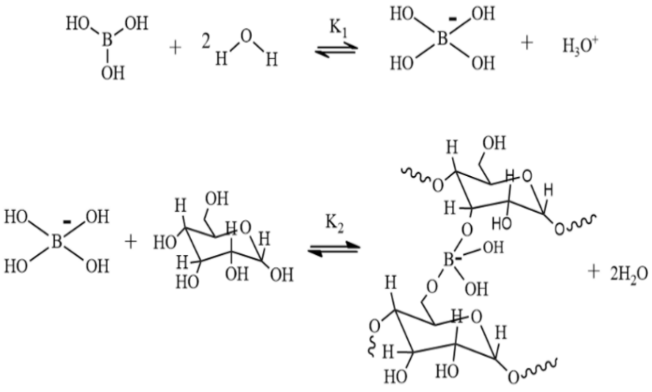

Figure 5. Hypothetical illustration of interaction between boric acid and glutinous rice flour.

FTIR spectra of glutinous rice flour, boric acid, and P2.0 precursors prepared by mixing the starting materials for various times were analyzed in order to identify the change in chemical bonding after mixing process. For the boric acid spectrum shown in Figure 6(a), the broad bands at 3000 cm^{-1} to 3500 cm^{-1} and 1300 cm^{-1} to 1600 cm^{-1} corresponded to the O-H and B-O stretching vibration, respectively whereas the sharper band at 1100 cm^{-1} to 1200 cm^{-1} was assigned to B-OH bending vibration. In addition, the narrow bands appeared at 640 cm^{-1} and 546 cm^{-1} were attributed to BO_3 and O-B-O vibrations, respectively [15, 20-21]. The FTIR spectrum of glutinous rice flour revealed the appearance of bands at 3000 cm^{-1} to 3600 cm^{-1}, 2800 cm^{-1} to 2900 cm^{-1}, and 1000 cm^{-1} to 1200 cm^{-1} which were attributed to the O-H, C-H, C-O, and C-O-C stretching vibrations, respectively [15,22-23]. Compared to the starting materials, FTIR spectra of the precursors showed some different features. The smaller intensity of C-H and C-O stretching vibration peaks those found in precursors spectra further verified the condensation reaction. In addition, the peak intensity assigned to the B-O stretching and B-OH bending vibration in the precursors those have been prepared by mixing for 4 h were found to be smaller than the precursor that has been stirred for 2, 6, and 8 h indicated that the precursors were homogeneous as shown in Figure 6(b) and overlayed image in Figure 6(c). The intensity of peaks assigned to the B-O stretching and B-OH bending vibration decreased indicates that boron species could well interact with hydroxyl groups of glutinous rice flour during the mixing [15]. The dispersion of the B_2O_3 and carbon components is a dominant factor in the formation of B_4C. The diffusion of reacting species readily occurs for the precursor with high dispersion and high homogeneity, supporting the XRD results of synthesized powder.

3.3 Effect of synthesis temperature

XRD patterns of powders synthesized from the precursors prepared by mixing the starting materials for 4 h are present in Figure 7. At 1350°C, rhombohedral B_4C phase was detected as a minor phase in all compositions. Unreacted phases of amorphous carbon appearing at $2\theta = 26.6°$ and B_2O_3 co-existed with B_4C in P1.0, P1.5, and P2.5. B_2O_3 was not detected in the phase composition of P2.0. The results indicated that the synthesis temperature of 1350°C was not sufficient to complete the reaction to form B_4C. As the synthesis temperature increased to 1450°C, B_4C became a main phase in all compositions. Amorphous carbon and B_2O_3 peak intensities decreased with the increasing B_4C phase formation indicating the improvement in reactivity between B and C species to form B_4C. P2.0 showed the highest peak intensity of B_4C with a little bump of amorphous carbon in the final product. The presence of carbon residue in P2.0 synthesized powder implies that a slight volatilization loss of B_2O_3 may occur during the heat treatment [9].

3.4 Morphology of synthesized B_4C powder

Figure 8 displays the SEM images of powders synthesized from the precursors prepared by mixing the starting materials for 4 h. Polyhedral shaped B_4C particles were observed in all compositions. In addition, the partially transformed precursor particles those revealed an evidence of nucleation and growth of B_4C crystals starting from the inside of carbon matrix were detected in P2.5. Large, agglomerated particles (>100 µm) were also observed in this composition (Figure 8(a-b)). Compared to other compositions, the particle size of B_4C in P2.0 (Figure 8(c-d), ranging from 5 µm to 10 µm, was significantly more uniform with higher amount of B_4C particles. Moreover, higher amount of plate like structure of carbon with the size larger than 100 µm was observed in P2.5, P1.5, and P1.0 (Figure 8(a-b) and (e-h)).

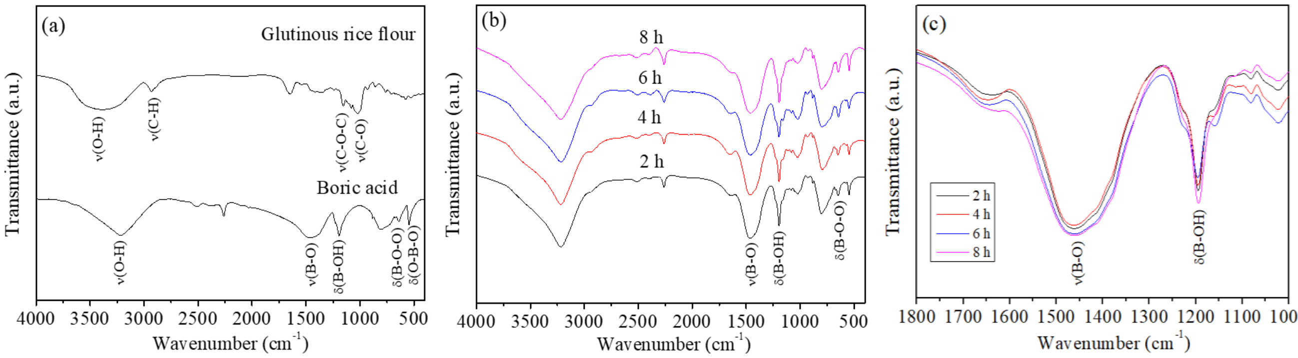

Figure 6. FTIR spectra of (a) starting materials, (b) P2.0 precursors prepared using various mixing times, and (c) overlayed image of the precursor at B-O stretching and B-OH bending vibration of (b).

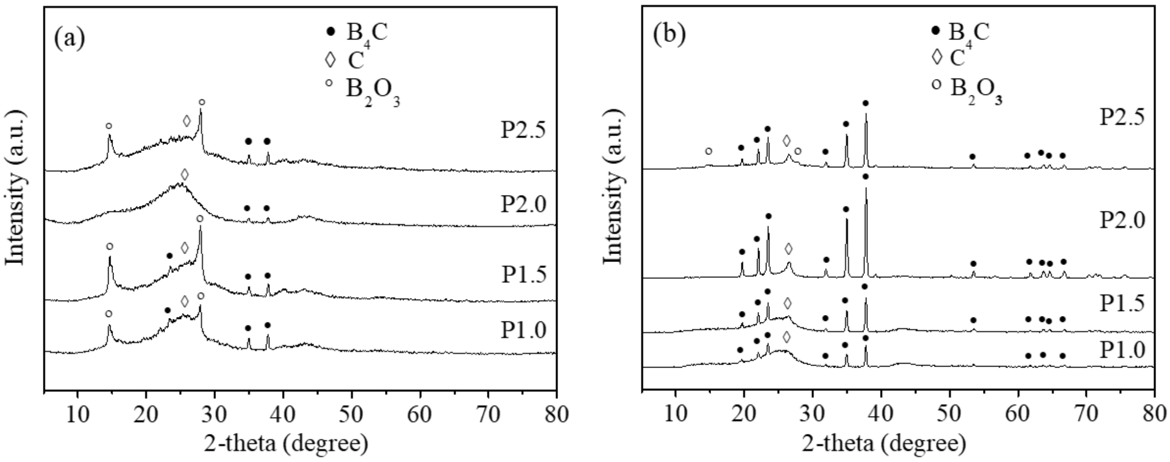

Figure 7. XRD patterns of powders synthesized at (a) 1350°C and (b) 1450°C for 5 h.

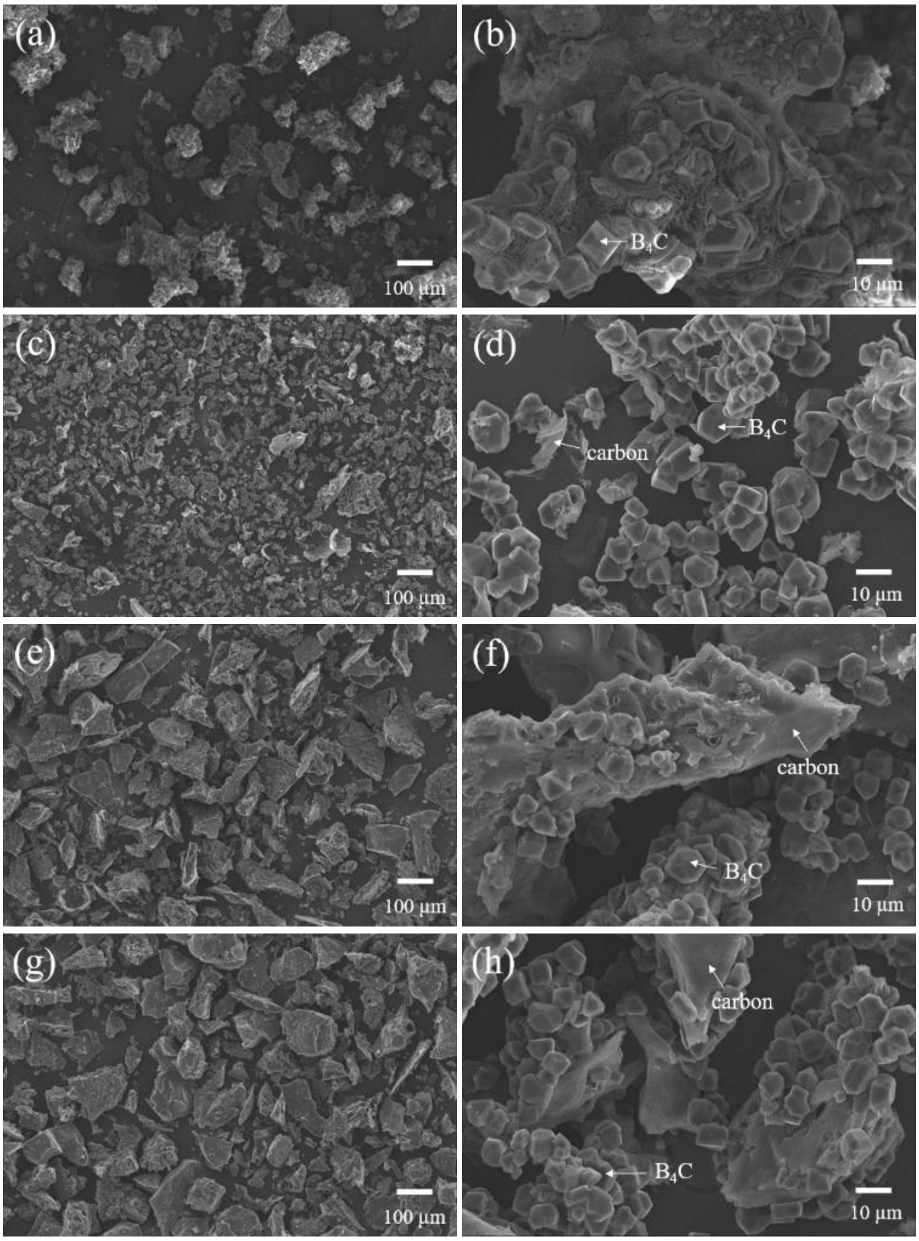

Figure 8. The SEM images of powders synthesized at 1450°C for 5 h; (a-b) P2.5, (c-d) P2.0, (e-f) P1.5, and (g-h) P1.0 with magnification of 100x and 1000x.

4. Conclusions

B_4C powder was synthesized by means of carbothermic reduction without calcination process. Boric acid and glutinous rice flour were used as boron and carbon sources for the synthesis. The homogeneity degree of precursor played an important role on the phase formation of B_4C. In this study, an appropriate precursor mixing times led to the crosslinking between polymer chains in the mixed starting materials which promoted the formation of borate ester bonds (B-O-C). The composition P2.0 prepared using precursor mixing time of 4 h showed the highest peak intensities of B_4C phase formation with low residual carbon contents 9.92 wt% at the synthesis temperature of 1450°C for 5 h under Ar flow. Microstructure of the synthesized powder consisted of polyhedral particles with the size ranging from 5 μm to 10 μm. This study assured the potentiality of Thai glutinous rice flour as a promising starting material for low temperature synthesis of B_4C powder.

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