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One-Step Densification of Carbon/Carbon Composites Impregnated with Pyrolysis Fuel Oil-Derived Mesophase Binder Pitches

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Abstract: Carbon/carbon (C/C) composites are conventionally manufactured by liquid-phase impregnation (LPI), in which the binder pitches and phenolic resins are impregnated into the composites, and by chemical vapor infiltration (CVI). However, CVI has certain limitations in that expensive gases, such as methane and propane, are used and a long reaction time is required. Therefore, LPI is more widely used, as it employs economical pitches. In this study, the effects of one-step preparation on mechanical properties of C/C composites impregnated with mesophase binder pitches and phenolic resins have been investigated. The C/C composites containing four types of 20 wt.% mesophase binder pitches had differences in softening point (SP) and quinoline insoluble (QI) contents. After conducting trials on mesophase formation using different heat treatment temperatures and times, the best density and mechanical properties of the C/C composites were achieved using the mesophase binder pitches with 170 °C SP. However, when SP 200 °C was used, the density of the C/C composites was not further improved. This is because the binder pitches were not properly impregnated into the composites due to the high viscosity and QI of the binder pitches. Furthermore, the C/C composites fabricated with 20 wt.% pitch 2 exhibited the highest mechanical properties.

Keywords: C/C composites; mesophase binder pitches; phenolic resins; softening point; quinolone insoluble

1. Introduction

Carbon/carbon (C/C) composites are carbon materials comprising carbon fibers and carbon matrix resins. The specific strengths and thermal characteristics of such composites are excellent, but high-density C/C composites must be fabricated via repetitive carbonization treatments, reimpregnation, and carbonization at high-temperatures to achieve these characteristics [1–3]. Many pores and cracks form in C/C composites owing to gas evolution resulting from pyrolysis of the matrix during carbonization. These pores and cracks degrade the thermal and mechanical properties of the materials [4–6]. To fill them, the C/C composites must undergo multiple cycles of liquid reimpregnation and recarbonization until the desired density is obtained. Densification has a direct impact on processing cost. Several studies have been conducted with the goal of fabricating C/C composites via a single manufacturing process [7–9].

Petroleum and coal tar pitches are excellent carbon matrix precursors or binders for manufacturing C/C composites; high density and coke yield can be obtained with these binders [10,11]. The coke yield depends on the pyrolysis conditions and pitch composition. Owing to the pitch plasticity and the devolatilization during the early carbonization stages, as well as further coke shrinkage during pyrolysis, many voids and cracks are observed in the C/C composites after the first impregnation and carbonization cycle [2,8–10]. In addition, any pores can be produced inside the C/C composites after carbonization because the raw or binder pitches have a carbon yield of less than 50%, and it is thus necessary to repeat the impregnation and carbonization processes several times to manufacture the C/C composites for high density. The initial void structure that results from the processing of pitch-based C/C composites significantly affects their mechanical properties. And coplanar interlayer flaws caused by processing are clearly expected to affect the interlaminar shear strength (ILSS) of phenolic resin-based C/C composites [11–13]. This is a major limitation of this method, and many studies have recently conducted impregnation using a mesophase pitch obtained by pitch deformation. However, although this mesophase pitch has a high carbon yield, it also has a high melt viscosity; therefore, densification of the C/C composites is limited [10,14].

In this study, C/C composites were fabricated via a single process by adding a pyrolysis fuel oil-based mesophase binder pitches to the phenolic resins of the C/C composites. Binder pitches were dispersed in phenolic resins and impregnated within prepreg to improve the impregnation and density of C/C composites that had been manufactured using the one-step densification process with blends of phenolic resins and binder pitches. The impregnated green bodies were carbonized at 1100 °C to produce the C/C composites and the effects of impregnating the blends of phenolic resins and binder pitches on density and mechanical properties of the C/C composites were investigated.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN)-type high strength carbon fibers produced by Taekwang Industrial Co., Ltd., (Ulsan, Korea) and long fibers which were not surface treated or unsized, were used as carbon fiber-reinforcements for C/C composites and the physical properties of carbon fibers are shown in Table 1. A resole-type phenolic resins (Kolon Chemical Co., Ltd., Gwacheon, Korea) containing approximately 60% of solids was used as the matrix precursor in the fabrication of hardened materials and carbides [15]. Pyrolyzed fuel oil (PFO) (GS Caltex Co., Ltd., Daejeon, Korea) was used as raw material for manufacturing of binder pitches.

Table 1. Physical properties of carbon fibers.

Product	Number of Filaments	Tensile Strength (MPa)	Tensile Modulus (GPa)	Density (g/cm^3)	Elongation (%)	Diameter (μm)
Carbon fibers	12,000	4410	245	1.78	1.8	7

2.2. Preparation of Mesophase Binder Pitches

The mesophase binder pitches were prepared by a two-step heat treatment method in the batch-type reactor. The heat-treated binder pitches of the C/C composites had different softening points (SP) and quinoline insoluble (QI) contents (Table 2) [16]. The properties of mesophase binder pitches are summarized in Table 3. The mesophase binder pitches were crushed to a size less than 100 mesh using a ball mill to achieve an even distribution in the phenolic resins. Furthermore, approximately 20 wt.% of milled binder pitches were added to the phenolic resins, and the combination was thoroughly stirred using a mechanical stirrer to promote homogenization.

Table 2. Heat treatment conditions of binder pitches [16].

Samples	1st Heating Rate (°C/min)	1st Heat Treatment (°C)	Holding Time (h)	2nd Heating Rate (°C/min)	2nd Heat Treatment (°C)	Holding Time (h)	Amount of Gas (L/min)
Pitch 1	2	200	0.5	2	360	4	N_2, 1
Pitch 2	2	360	4	2	380	3	
Pitch 3	2	360	4	2	400	3	
Pitch 4	2	360	4	2	420	1	

Table 3. Properties of binder pitches.

Samples	SP (°C)	QI (%)	Carbon Yield (%)	Elemental Analysis (%)				C/H Ratio
				C	H	N	S	
Pitch 1	135	0	35	93.73	6.00	0.11	0.75	1.30
Pitch 2	168	10.74	50	94.30	5.41	0.09	0.27	1.45
Pitch 3	227	35.93	67	94.78	4.75	0.11	0.28	1.66
Pitch 4	250	50.19	68	94.71	4.72	0.10	0.28	1.67

2.3. Preparation of C/C Composites

After adding 20 wt.% of mesophase binder pitches to the phenolic resins by thorough stirring, the prepregs were fabricated using the unidirectional drum winding method in which the carbon fibers were impregnated by a continuous process. The solvent was removed from the prepregs by drying for two days at room temperature, after which the resins impregnated into the prepregs were partially hardened (B-stage). After cutting the partially cured prepregs into 150 mm × 60 mm pieces to fit in the mold, the 15-ply laminated sample was cured using a self-manufactured hot press via the vacuum bag molding method and the green body was formed and cured at 220 °C for 2 h.

Unidirectional C/C composites were fabricated by carbonizing each green body under a nitrogen atmosphere at 1100 °C for 2 h. The fiber volume fraction of the C/C composites was 60% (± 2%) [15,17].

2.4. Characterizations

2.4.1. Density and Porosity

To examine the effects of mesophase binder pitches on the C/C composites, the average density values were calculated from five sequential analyses of the composites using a densitometer (XS204, METTLER TOLEDO Co., Columbus, OH, USA). The porosity was calculated using Equation (1) based on measurements conducted using the water displacement method described in ASTM C20-83 [18,19]:

$$\text{Open porosity } (\%) = \frac{W_{sat} - W_d}{W_d} \times 100, \quad (1)$$

where W_d is the weight of the specimen measured at room temperature after drying, and W_{sat} is the weight of the saturated specimen after removing the surface moisture.

2.4.2. Structural Characteristics

An X-ray diffractometer (X'pert Powder, PANalytical, NLD) was used to analyze the crystal sizes (L_c (002)) and surface separations (d (002)) of the C/C composites. The crystal sizes and surface separation values were determined using the Brown–Ladner and Bragg equations, respectively.

2.4.3. Mechanical Properties

The interlaminar shear strength (ILSS) of C/C composites was measured using the universal test machine (LR5K Plus, Lloyd Co., London, UK). The short beam test was performed in accordance with ASTM D2344. The span-to-depth ratio and crosshead speed were set to 4:1 and 2 mm/min, respectively. The average values were calculated after measuring the ILSS of five specimens for each condition [18,20].

To evaluate the flexural strength and modulus of the C/C composites, a three-point bending test was performed with a span-to-depth ratio of 16:1 using a crosshead speed of 2 mm/min in accordance with ASTM D790 [18].

2.4.4. Morphology

After platinum coating, the fracture surface structures of the C/C composites were observed using a scanning electron microscope (SEM, S-4800, Hitachi Ltd., Tokyo, Japan).

3. Results and Discussion

3.1. Effect of Mesophase Binder Pitches on C/C Composites

Figure 1 shows the densities of the C/C composites as a function of the amount of mesophase binder pitches added. C/C composites with mesophase binder pitches show larger increase in density than those with only the conventional phenolic resins. The densities of C/C composites without mesophase binder pitches are low (approximately 1.17 g/cm^3), owing to the single-process manufacturing without reimpregnation. However, the C/C composite impregnated with pitch 2, which has a SP of 168 °C, exhibits the highest density (1.45 g/cm^3) among all the mesophase binder pitches. As the mesophase binder pitches undergo liquid-phase carbonization and pores are generated within the composites, the mesophase binder pitches fully infiltrate the composites, thus increasing their densities [21–23].

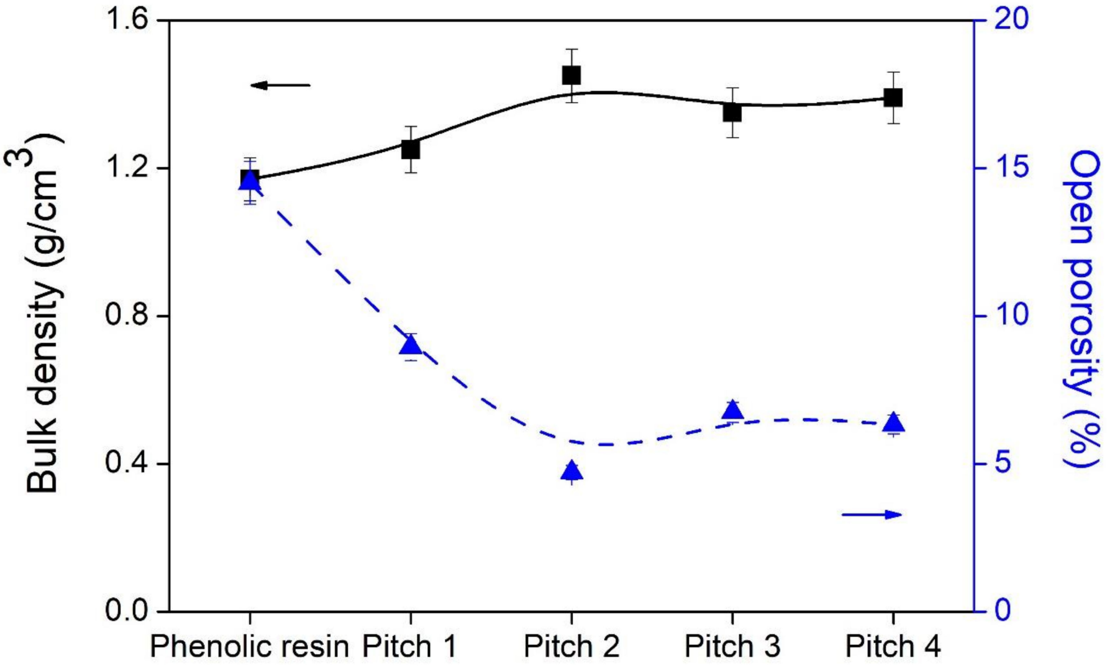

Figure 1. Bulk density and open porosity of C/C composites with phenolic resin and binder pitch blends.

Figure 2 shows a schematic of the pore filling mechanism associated with liquid impregnation using mesophase binder pitches and phenolic resins. As the impregnated phenolic resins become carbonized, they separate from the open pores, and the matrix contracts. And the phenolic resins are suitable for micropore filling, but it cannot easily achieve densification, because the liquid phase matrix contracts and blocks the pore entrances [5]. Also, the carbon yield is very low when impregnated pitches of C/C composites are carbonized alone under an atmospheric pressure. However, the yield increases significantly when the mesophase pitches are carbonized and thus the density of C/C composites increases with impregnation. The liquid impregnation using mesophase binder pitches and phenolic resins is high and densification becomes possible with only a few cycles. Also, pressurized carbonization is not required with the phenolic resins and mesophase binder pitches owing to the pore closing mechanism [1,4].

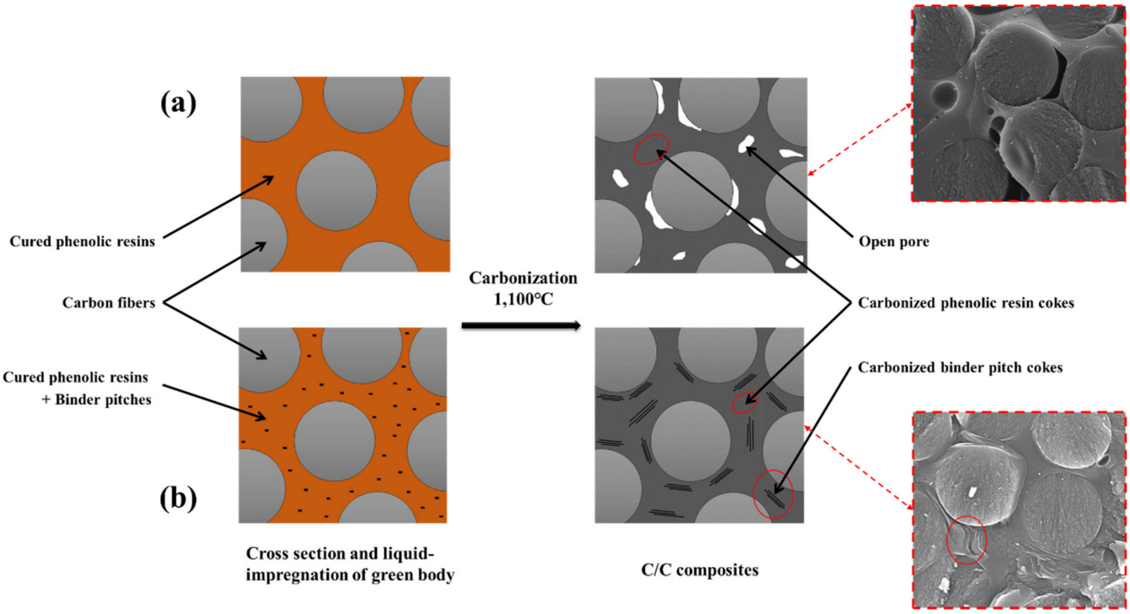

Figure 2. A schematic of the pore filling mechanism; (**a**) phenolic resins impregnated and (**b**) phenolic resin and mesophase binder pitch blends impregnated.

As shown in Figure 1, the porosity is inversely proportional to the density, and it decreases when the mesophase binder pitch materials are added. When C/C composites are prepared using the phenolic resins with a density similar to that of pitch 1, more pores are produced, as more volatile substances are released compared to the mesophase binder pitches. Thus, their porosity levels are higher than those of the pitch 1-impregnated composites. Mesophase binder pitches with SP in the range of 160~170 °C are easy to use in the manufacture of C/C composites, and for improving the density, because composite pore formation is reduced. Furthermore, pitches 3 and 4, which have SP above 200 °C, improve the composite density more than pitch 1. However, they influence the density and porosity of the C/C composites to a lesser extent than pitch 2, because their infiltration into the center of the composites is inadequate [5,24].

XRD analysis is used to examine the crystallinity variations in the C/C composites when mesophase binder pitches are added, and the results are summarized in Table 4. As shown in Figure 3, the (002) peak at around $2\theta = 24°$ indicates a graphitic structure. Peaks representing (100) or (101) are found at around $2\theta = 43°$, and little difference is found between the peak phases. The (100) and (101) peaks at around $2\theta = 43°$ cannot be distinguished. Warren et al. [25] asserted that the laminated structure might comprise several layers stacked with three-dimensional regularity, as with graphite, or there might be several disorderly layers stacked in an irregular manner. In other words, the (100) and (101) diffraction lines are not separated in the XRD profile of the turbostratic structure. The diffraction lines are found separated as the graphite content increases. In our experiments, the graphitic structure is not well developed after heat treatment at temperatures up to 1100 °C [26].

Table 4. Structural parameters of C/C composites with phenolic resin and binder pitch blends.

Samples	d_{002} (Å)	L_c (Å)
Pitch 1	3.58	13.66
Pitch 2	3.57	14.41
Pitch 3	3.56	16.26
Pitch 4	3.56	16.49

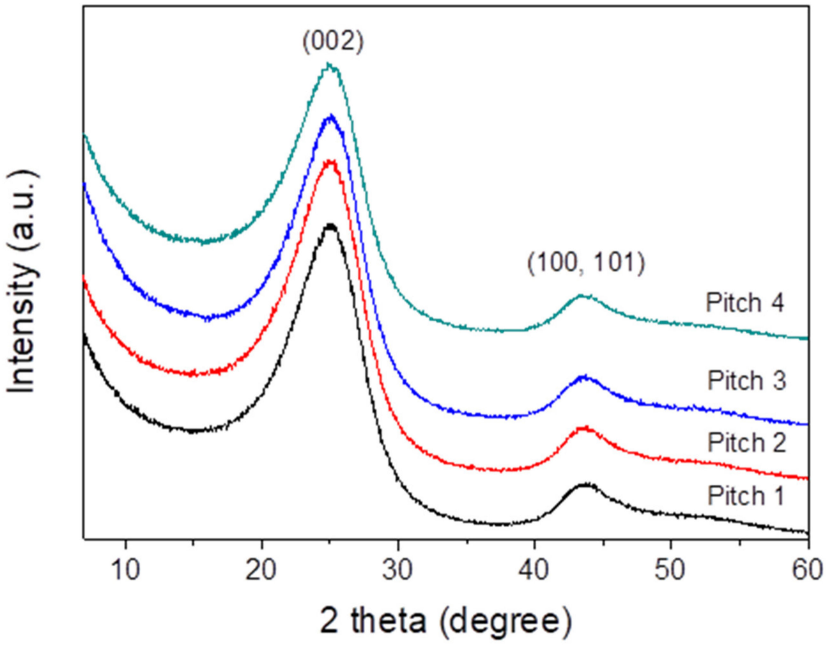

Figure 3. X-ray diffraction patterns of C/C composites with phenolic resin and binder pitch blends.

It can be observed in Table 4 that the composite crystallite sizes (L_c) increase with impregnation by mesophase-forming binder pitches. However, there is little change in the interlayer distances d(002). Thus, the crystallite size is insufficiently developed after heat treatment at temperatures up to 1100 °C, but the composite crystallinity increases depending on the extent of mesophase formation by the binder pitches during carbonization.

Figure 4 shows the flexural strengths of the C/C composites manufactured using mesophase binder pitches with various SP via a single process. It can be seen that the increase in flexural strength of these composites is more than the increase in the case of the composites impregnated with only the phenolic resins. The composite impregnated with phenolic resins exhibits a flexural strength of approximately 112 MPa, while the composite impregnated with pitch 2 exhibits a flexural strength of 176 MPa, which is the highest value achieved with the mesophase binder pitches used in this study. It appears that adding a mesophase binder pitches increases the crystallization or particle area in the matrix. During carbonization, the binder pitches help decrease the number of pores or defects produced inside the composites. As in the case of bending strength, the flexural modulus increases more with the mesophase binder pitches than with the phenolic resins. As discussed previously, the pitches are apparently more effective owing to closure of the voids. The graphitic structure between the fibers and the matrix resins is good, and the carbon fiber surface is oriented satisfactorily [8,9,27,28].

To examine the interfacial bonding force, the changes in ILSS of the C/C composites were observed as a function of the SP of the mesophase binder pitches. As in the case of the flexural strength, the C/C composites impregnated with mesophase binder pitches exhibit higher ILSS than those impregnated with phenolic resins (Figure 5). The composite made with pitch 2 exhibits the highest ILSS (approximately 20 MPa). The ILSS of the composites impregnated with mesophase binder pitches with SP above 200 °C are higher than those of the composites made with phenolic resins, but extension of this trend cannot be confirmed. Mesophase formation from pitches with SP above 200 °C can improve the mechanical properties of the composites; however, their direct influence on density is limited owing to their high viscosities [29–33].

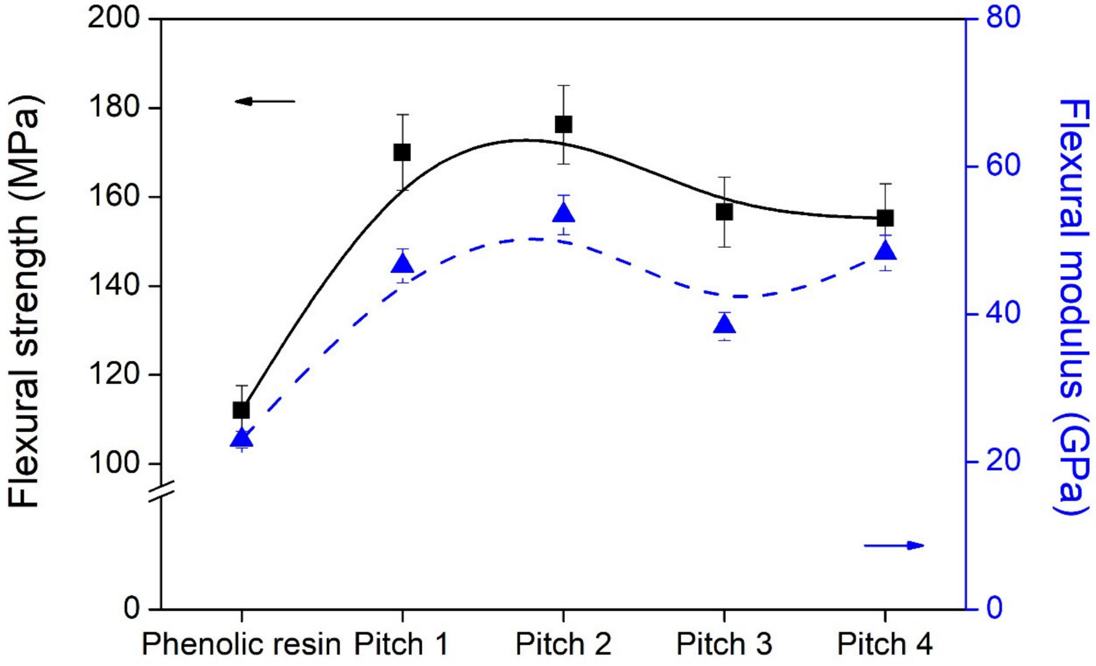

Figure 4. Flexural strengths and modulus of C/C composites with phenolic resin and binder pitch blends.

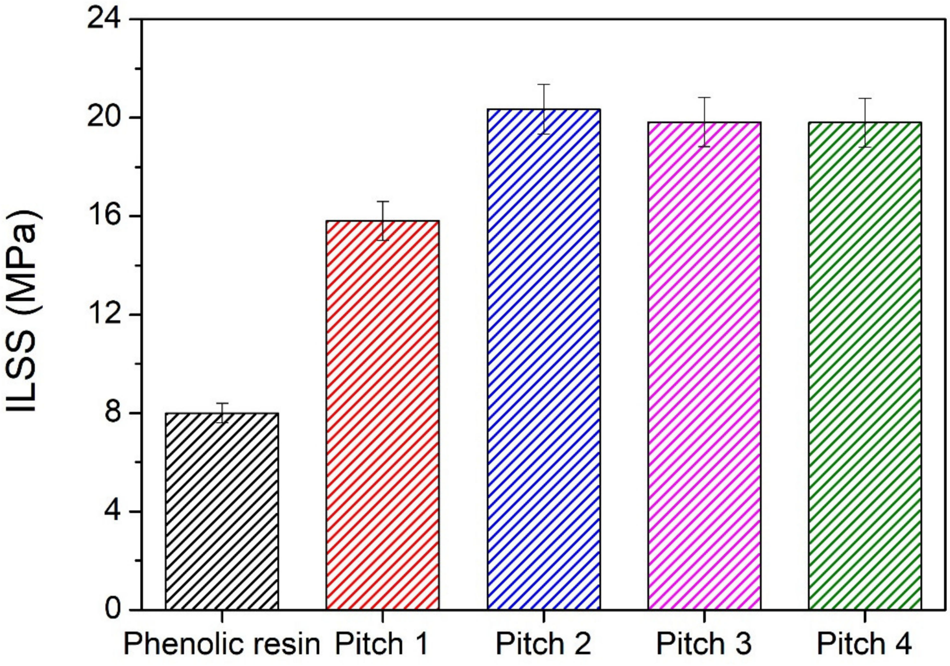

Figure 5. Interlaminar shear strength (ILSS) of C/C composites synthesized with phenolic resin and binder pitch blends.

The fracture surfaces of the C/C composites were observed via SEM after ILSS testing and the SEM images are shown in Figure 6. Pore generation during carbonization is confirmed in the C/C composites that contain phenolic resins or mesophase binder pitches. The "pull-out" phenomenon is confirmed using a material synthesized with the phenolic resins. A bundle of carbon fibers used as reinforcements is pulled out from the surface. This may occur because of the decrease in the bonding force between the fibers and the matrix resins. A few cracks are observed in the C/C composites that contain mesophase binder pitches. Their porosity levels decrease as the mesophase binder pitches fill the pores effectively. Furthermore, graphitic structure from the mesophase binder pitches develops between the fibers and matrix resins, thereby affecting the densities and mechanical properties of the composites. The main factors affecting the mechanical properties of the C/C composites are considered to be the interfacial bonding force between the fibers and matrix resins, development of graphitic structure, density, and porosity. The development of graphitic structure improves when mesophase binder pitches are added, thus affecting the mechanical properties of the composite. However, mesophase binder pitches with high SP cannot infiltrate the composite centers sufficiently [29,34–36].

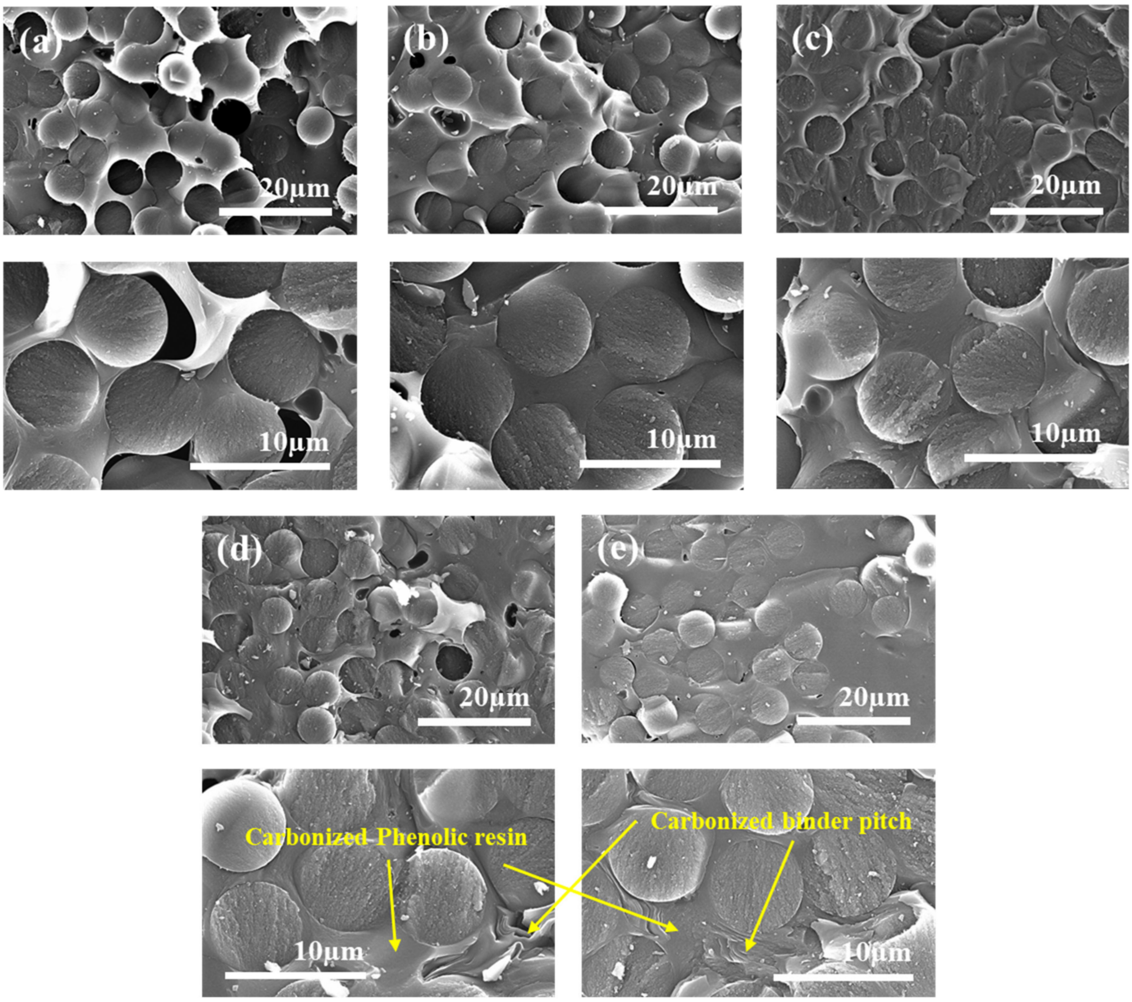

Figure 6. Cross-sectional SEM images of C/C composites with phenolic resin and binder pitch blends; (**a**) phenolic resins; (**b**) pitch 1; (**c**) pitch 2; (**d**) pitch 3; and (**e**) pitch 4.

3.2. Effect of Binder Pitch Content on C/C Composites

The C/C composites impregnated with pitch 2 exhibit better mechanical properties than their counterparts. Thus, C/C composites with various concentrations of pitch 2 were prepared. As shown in Figure 7, composites fabricated with 20 wt.% of pitch 2 exhibit the highest densities, but the density gradually declines when the concentration reaches 30 wt.%. When excess mesophase binder pitches are added, pyrolysis during carbonization releases volatile matter, thus increasing the composite porosity, which causes internal defects [37–39]. In addition, addition of excess binder pitches lowers the impregnation and densification as the viscosity of the blends of phenolic resins and binder pitches increases, and it is known that large amounts of gases such as H_2, CH_4, and C_2H_6 are discharged to the outside during the carbonization process [40,41].

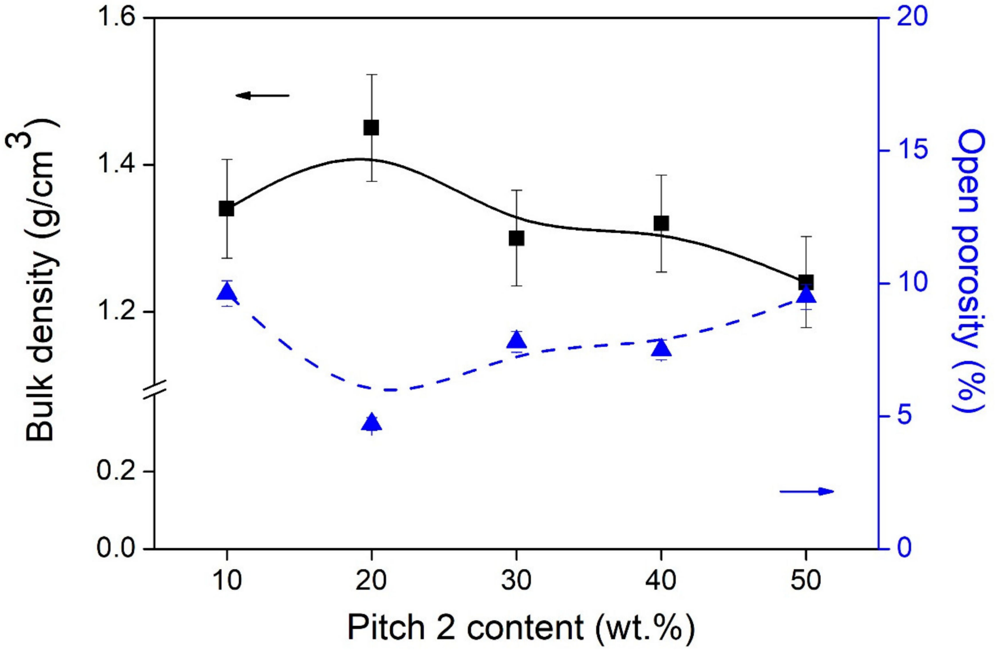

Figure 7. Bulk density and open porosity of C/C composites with pitch 2.

Furthermore, the flexural strength and eventually the bonding strength decrease when excess mesophase binder pitches are added, as shown in Figures 8 and 9. The addition of a mesophase pitches to the phenolic resins during the single-process fabrication of C/C composites effectively improves the density and mechanical properties of the composite. However, excess mesophase pitches lead to the formation of many pores and defects inside the composites, as shown in Figure 10. The optimal concentration of mesophase binder pitches is found to be 20 wt.% [33,42–44].

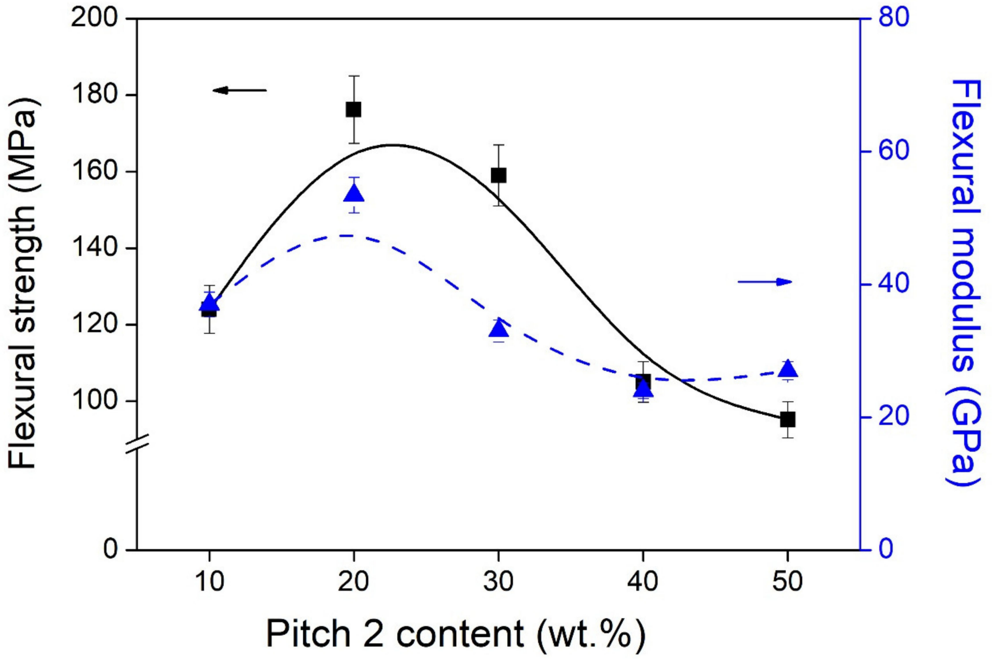

Figure 8. Flexural strength and modulus of C/C composites with pitch 2.

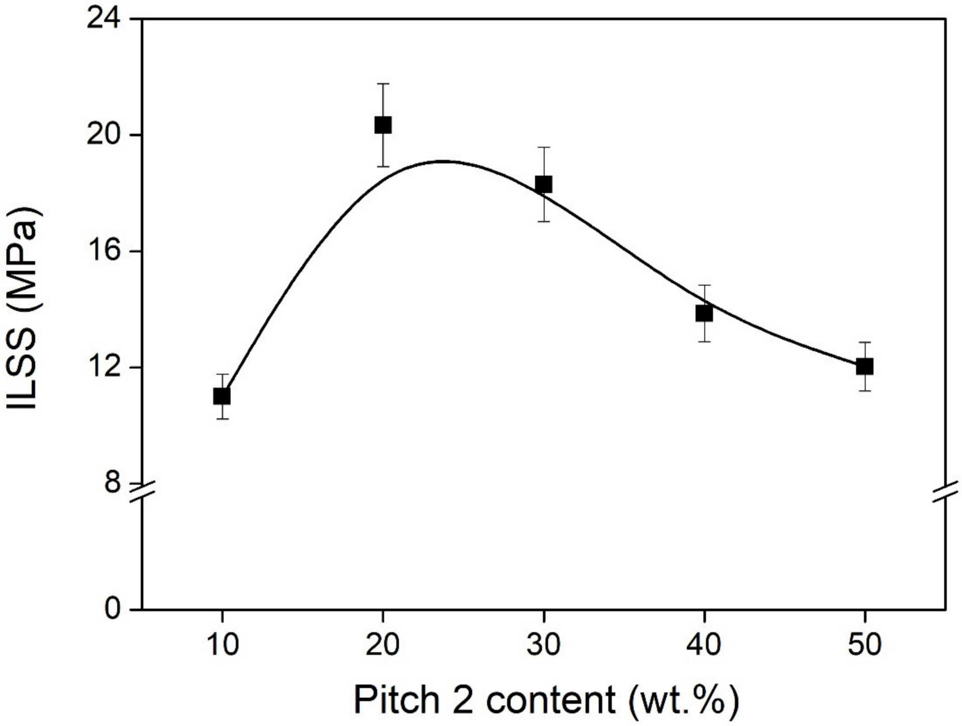

Figure 9. ILSS of C/C composites with pitch 2.

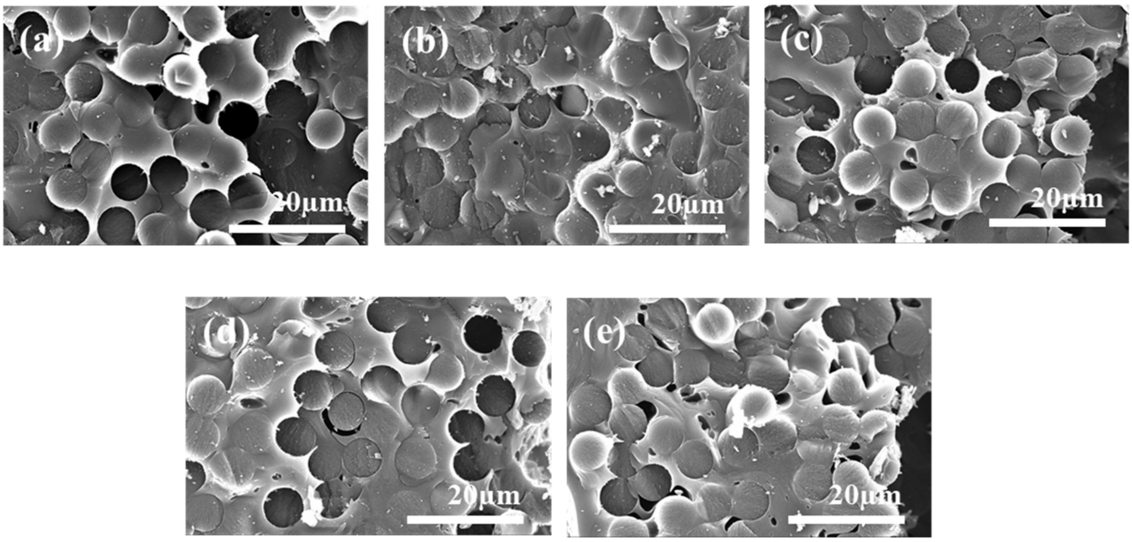

Figure 10. Cross-sectional SEM images of C/C composites with pitch 2; (**a**) 10 wt.%; (**b**) 20 wt.%; (**c**) 30 wt.%; (**d**) 40 wt.%; and (**e**) 50 wt.%.

4. Conclusions

Petroleum-based mesophase binder pitches with various SP and QI contents were added to phenolic resins to prepare C/C composites. When the mesophase was manufactured via secondary heat treatment of binder pitches, the increase of SP and QI content occurred actively as the reaction temperature and time increased. In addition, for temperatures below 360 °C, the isotropic structures comprising low SP and carbon yield appeared, while for temperatures above 380 °C coalescence into mesophase formation was observed. At the same time, heat treatment of binder pitches by temperature above 380 °C strongly affects their SP and carbon yield. Also, heat treatment temperature induced a marked increase in the C/H ratio and QI content. Finally, the density (1.45 g/cm^3) of the composites manufactured with pitch 2 (SP 168 °C) was better than that of C/C composites manufactured with phenolic resins. The ILSS and flexural strength of the C/C composites synthesized with pitch 2 were 12 MPa and 64 MPa, respectively. These values were higher than those of the composites made with phenolic resins. In contrast, pitches 3 and 4 decreased the physical properties of the composites. These pitches exhibited SP higher than 200 °C, and could not effectively impregnate the composites owing to their high viscosity. Furthermore, the C/C composites fabricated with 20 wt.% of pitch 2 exhibited the highest mechanical properties. Increasing the concentration of mesophase binder pitches beyond this value decreased the mechanical properties of the C/C composites owing to the hindrance of mesophase growth and structural uniformity because of QI in the pitches during carbonization.

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