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Analysis of Densification Process of Carbon/Carbon Composites with Pitch as an Impregnant

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The analytical method was developed to calculate efficiency of densifying carbon/carbon (C/C) composites using coal tar pitch as a matrix precursor at each cycle. Three factors were defined in analyzing the densification process: impregnation efficiency, retention efficiency, and overall densification efficiency. The relationships developed were applied to the experimental results for three densification cycles of C/C composites with pitches as an impregnant to evaluate the factors which may depend on the impregnant and on the route of carbonization. The impregnation efficiency increased with the repeated process cycles whereas the retention efficiency decreased irrespective of the impregnant and carbonization route. Carbonization route P+A+G, in which pressure carbonization (P) and graphitization (G) were done before and after atmospheric pressure carbonization (A) respectively, using impregnant of high carbon yields was the most effective method in densifying C/C composites.

Key words : Carbon/carbon composites, Density, Pitch, Impregnation

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I. Introduction

Pitches are an attractive material as the matrix precursor of carbon/carbon (C/C) composites because they can have high carbon yields and are graphitizable. The pitch-based processing of C/C composites usually comprises complicated processes, namely, preparation of a preform, followed by sequential densifications that are repeated a few times until the desired density is attained.[1-3] The densification process which consists of impregnation, carbonization and sometimes graphitization is directly related to the manufacturing cost. However, little work has been published on the analysis of the densification process.

In the densification of C/C composites, pores within the composites are filled with pitch by impregnation and then a part of the pitch may be lost by an exudation from the pore structures as a liquid phase and/or by an evaporation of volatile components of the pitch during carbonization.

Moreover, the density of pitch itself increases during the conversion to carbon which leaves an empty space again within the pores. The shrinkage or expansion of the composite dimension also should be considered depending on the carbonization temperature.

In this work, we tried to analyze the densification process of C/C composites by defining some factors, which may depend on the process parameters such as carbon yield of pitch impregnant, pressure and final heat treatment temperature of the process.

II. Procedure of Analysis

To develop a series of relationships between bulk densities of C/C composites and various parameters in each step of densification processes, the starting composite shows a rigid but still porous which was formed by an initial impregnation of pitch and carbonization. The bulk density of the porous composite sample which consists of carbon fiber with density ρ_f and carbon matrix with density ρ_m can be expressed by

$$\rho_{C,o}=\rho_f V_f+\rho_m V_{m,o} \tag{1}$$

where V_f and $V_{m,o}$ are the initial volume fractions of fiber and matrix, respectively.

$V_{m,o}$ can be calculated from eqn (1) as V_f is easily obtained during the fabrication of the preform and the others are measurable values. An initial porosity P_o is also calculated by definition as

$$P_o=1-(V_f+V_{m,o}) \tag{2}$$

If the composite is initially graphitized before densification process, the volume fractions of fiber and matrix change due to an evolution of volatile matters, density variations of each component and dimensional changes of the composite. The new volume fractions of fiber V_f' and matrix $V_{m,o}'$ after the initial graphitization are thus

$$V_f' = y_f \frac{\rho_f}{\rho_f'} \frac{V_f}{1+\delta} \tag{3}$$

and

$$V_{m,o}' = y_m \frac{\rho_m}{\rho_m'} \frac{V_{m,o}}{1+\delta} \tag{4}$$

where y_f and y_m are yields of fiber and matrix, ρ_f' and ρ_m' are densities of fiber and matrix after graphitization, respectively, and δ is a fractional volume change of the composite. Thus the porosity of graphitized composite changes due to variations in V_f and $V_{m,o}$.

Now we consider successive densification cycles of the composite which may or may not have been graphitized. The bulk density of composite impregnated with pitch in the i-th cycle is given by

$$\rho_{I,i} = \rho_{C,i-1} + w_i P_{i-1} \rho_p \tag{5}$$

where $\rho_{C,i-1}$ and P_{i-1} are the density and porosity of the composite in the (i-1)-th cycle respectively, ρ_p is the density of pitch impregnant and w_i is defined as an impregnation efficiency of the i-th cycle which means a filling ratio of the pore with pitch impregnant.

The impregnated composite lose its weight on carbonization due to an exudation of molten pitch and/or an evaporation of volatile products from the preform. If we define a retention efficiency x_i, which is a measure of the efficiency of retaining the molten pitch in pores without the exudation, the bulk density of carbonized composite in the i-th cycle is expressed by

$$\rho_{C,i} = \rho_{C,i-1} + w_i x_i y_p P_{i-1} \rho_p \tag{6}$$

where y_p is a carbon yield of pitch, which is a measure of efficiency of keeping the pitch components without the gaseous evaporation. The carbon yield depends on the pressure and final heat treatment temperature as well as on the chemical components of pitch itself.

If we define a densification efficiency E_i, which is a measure of pore filling with carbon matrix after impregnation and carbonization in the i-th cycle, another expression of $\rho_{C,i}$ other than eqn (6) is given by

$$\rho_{C,i} = \rho_{C,i-1} + E_i P_{i-1} \rho_m \tag{7}$$

Comparing eqn (6) with eqn (7) produces a following relationship among E_i, w_i, and x_i:

$$E_i = w_i x_i y_p \frac{\rho_p}{\rho_m} \tag{8}$$

The porosity after i-th densification cycle is obtained as

$$P_i = P_{i-1}(1-E_i) \tag{9}$$

III. Experimental

1. Preparation of C/C preforms

Porous two-dimensional C/C composite samples were prepared using commercial 8-harness satin weave fabrics as a reinforcement and coal tar pitch as a matrix precursor. The fabric consisted of high tenacity (HT) polyacrylonitril (PAN)-based carbon fibers which have a density (ρ_f) of 1.80 g/cm^3 and a diameter of 5.5 μm. The density of carbon fibers after graphitization (ρ_f') at 2500°C increased to 1.90 g/cm^3 with a yield (y_f) of 98%.

The fabrics were impregnated with coal tar pitch by heating, then stacked and molded to produce preforms by hot pressing and cooling. Two different methods were applied to carbonize them. Low-density samples were formed by heating the preforms in a matched die to 600°C with 3°C/min for a one-hour soak time. The matched die was made to be locked with bolts to protect the composites from swelling during the heat treatment. The composites were then carbonized at 1200°C for an hour. Both of the treatments were carried out under nitrogen atmosphere. High-density preforms were formed by an in-situ pyrolysis of the preforms at 480°C for 1.5 hours in a hot-press die followed by pressing.[4,5] The composites were then carbonized at 1200°C for an hour under nitrogen atmosphere. Some of the carbonized preforms were graphitized at 2,500°C for an hour under helium atmosphere.

The density of carbon matrix was obtained by measuring the density of pitch coke by a sink-float method after carbonization and graphitization. The densities of the carbonized matrix (ρ_m) and the graphitized matrix (ρ_m') were 2.00 g/cm^3 and 2.20 g/cm^3, respectively. The yield of the matrix (y_m) was 95% after the graphitization.

Table 1 summarizes initial parameters of six samples. Some parameters were calculated by taking measurable values into eqns (1) through (4). The first three samples have low densities about 1.30 g/cm^3 and fiber volume fractions about 57%, whereas the others have high densities of 1.43 to 1.48 g/cm^3 and fiber volume fractions of 60 to 62%. An initial graphitizaton was performed on four samples c through f, which showed about 2% volume shrinkage after the graphitization. Some parameters such as $V_{m,o}$, P_o, $V_{m,o}'$, and P_o' were calculated by taking

Table 1. Initial Parameters of the C/C Composite Samples Before and after Graphitization

Sample	Before graphitization				After graphitization				
	$\rho_{C,o}$	V_f	$V_{m,o}$	P_o	δ	$\rho_{C,o}'$	V_f'	$V_{m,o}'$	P_o'
a	1.303	0.565	0.143	0.292					
b	1.301	0.573	0.135	0.292					
c	1.288	0.569	0.132	0.299	-0.018	1.274	0.521	0.120	0.359
d	1.431	0.620	0.158	0.222	-0.020	1.418	0.569	0.144	0.287
e	1.476	0.601	0.197	0.202	-0.023	1.466	0.562	0.180	0.258
f	1.482	0.599	0.202	0.199	-0.020	1.469	0.550	0.184	0.266

Table 2. Pitch Impregnants and Carbonization Routes in the Densification Processes

Sample	Impregnant*	Carbonization route**
a	J	A
b	J	P+A
c	J	P+A+G
d	J	P+A+G
e	S	P+A+G
f	M	P+A+G

* J : Raw pitch from Jung-Woo Coal Chemical Co.
S : Chemically modified pitch with sulfur.
M : Mesophase pitch.
** A : Atmospheric-pressure carbonization (1,200°C).
P : Pressurized carbonization (10 MPa, 500°C).
G : Graphitization (2,500°C).

measurable values into eqns (1) through (4).

2. *Densification*

The samples were densified by consecutive three cycles of impregnation and carbonization. Three kinds of pitch impregnants and three route of carbonization, as shown in Table 2, to evaluate their effects on the densification process were used in this study.

Table 3 shows some properties of the pitch impregnants J, S, and M. Isotropic pitch S was chemically modified from pitch J by heat-treatment with sulfur as an additive.[6] The addition of sulfur is known to improve carbon yield of pitch.[1] Partial mesophase pitch M was thermally modified from pitch J by heat-treatment with nitrogen gas blowing. Carbon yields of the pitch (y_p) also varied with the carbonization route. Application of pressure during carbonization serves to improve the carbon yield by restricting the evolution of volatile molecules present in the pitch.[1,7]

The composite samples were vacuum impregnated with molten pitches at the temperatures of 100°C higher than their softening points. The molten pitch was transferred to the impregnation bath to ensure penetration of all available porosity in the composite and then pressurized to 0.5 MPa. The impregnated composites were carbonized along three routes A, P+A and P+A+G. Each carbonization step, P, A and G designates 10MPa-pressure carbonization at 500°C, atmospheric-pressure carbonization at 1,200°C, and graphitization at 2,500°C, respectively. All of the carbonization steps were carried out for an hour at each temperature under an inert atmosphere.

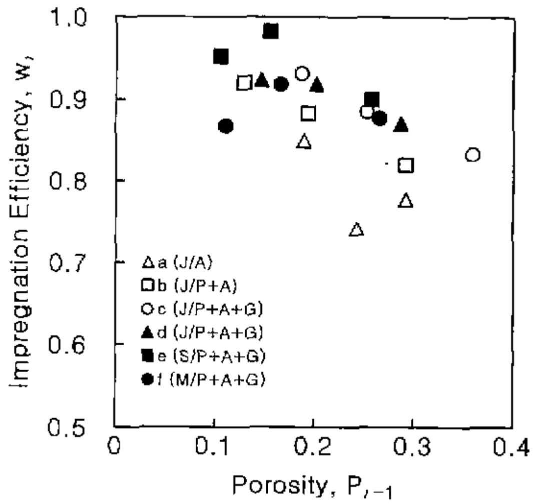

Fig. 1. Plot of impregnation efficiency versus porosity.

Bulk densities of impregnated composites (ρ_I), and those of carbonized ones (ρ_C) were measured at each cycle of densification, and then the impregnation efficiency (w), retention efficiency (x), densification efficiency (E), and porosity (P) were obtained from eqns (5), (6), (8) and (9), respectively.

IV. Results and Discussion

Plot of impregnation efficiency at each cycle against porosity of the sample at the former cycle is shown in Fig. 1. The impregnation efficiency increases with decreasing porosity irrespective of the sample. It is interesting to note that extrapolation of the data to zero porosity makes a perfect impregnation.

At the same porosity range, the samples graphitized before each impregnation step (samples c through f) show higher impregnation efficiencies than others (samples a and b). At 30% porosity range, the graphitized sample d shows about 90% efficiencies but the non-graphitized sample b shows about 80%. The highest efficiencies of graphitized samples approach 95% at 10% porosity. Graphitization is well known to open up porosity and aids impregnation.[8] Comparing samples d through f, which are different in the impregnant pitch but have the same carbonization route, the variations of impregnation efficiency against porosity lie on almost the same line. This implies that the type of impregnant did not affect

Table 3. Some Properties of Pitch Impregnants

Impregnant	Density (g/cm^3)	Softening point (°C)	Anisotropic content (%)	Carbonization yield (%)		
				route A	route P+A	route P+A+G
J	1.32	111	0	50	63	59
S	1.34	180	0	-	-	74
M	1.37	215	40	-	-	79

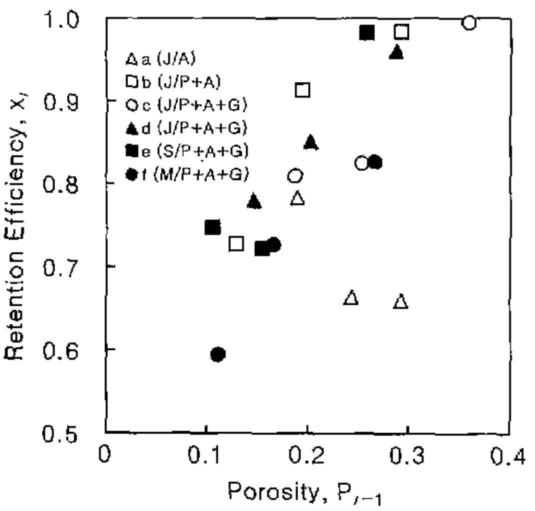

Fig. 2. Plot of Retention Efficiency Versus Porosity.

the impregnation efficiency, though a higher softening point of pitch is supposed to produce a higher melt viscosity.[9]

Fig. 2 shows that the retention efficiency decreases as the densification cycle is repeated in each sample. It is apparent that the samples carbonized under pressure after the impregnation step (samples b through f) show a similar trend and higher retention efficiency than that of sample a. The retention efficiencies of some samples reach almost 100% in their first cycle of densification (near 30% porosity) while that of sample a is no more than 70%. The pressure not only increases the carbon yield but also prevent molten pitch from being forced out of the pores by pyrolysis products.[10] Again, the dependence of retention efficiency on the impregnant is not seen, though there is some scattering in data.

The variations of the efficiencies against porosity shown in Fig. 1 and 2, which seem to be contradictory to each other, may be related to the variation in pore structure as the densification proceeds. Fig. 3 shows the microstructures of composite samples which were densified with pitch J, S and M. Small pores within fiber bundles are well filled with carbon matrix whereas large pores in loosely packed regions especially between fiber bundles or between laminae are still empty irrespective of pitch type. Pitch can flow out of the composite if it is not kept within the pore by capillary action, which, however, may only be sufficient to allow the pitch to be retained within small space and not in large one.[11] Most part of the pitch, which initial filled the large space, has been drawn by capillary action into the more tightly packed space of the composite when it passes through the molten state during carbonization. Therefore, smaller pores were filled at earlier cycle of densification while larger pores were still remained empty even after the repeated cycles. The variation in the pore size distribution may have made the impregnation easier but the retention of pitch

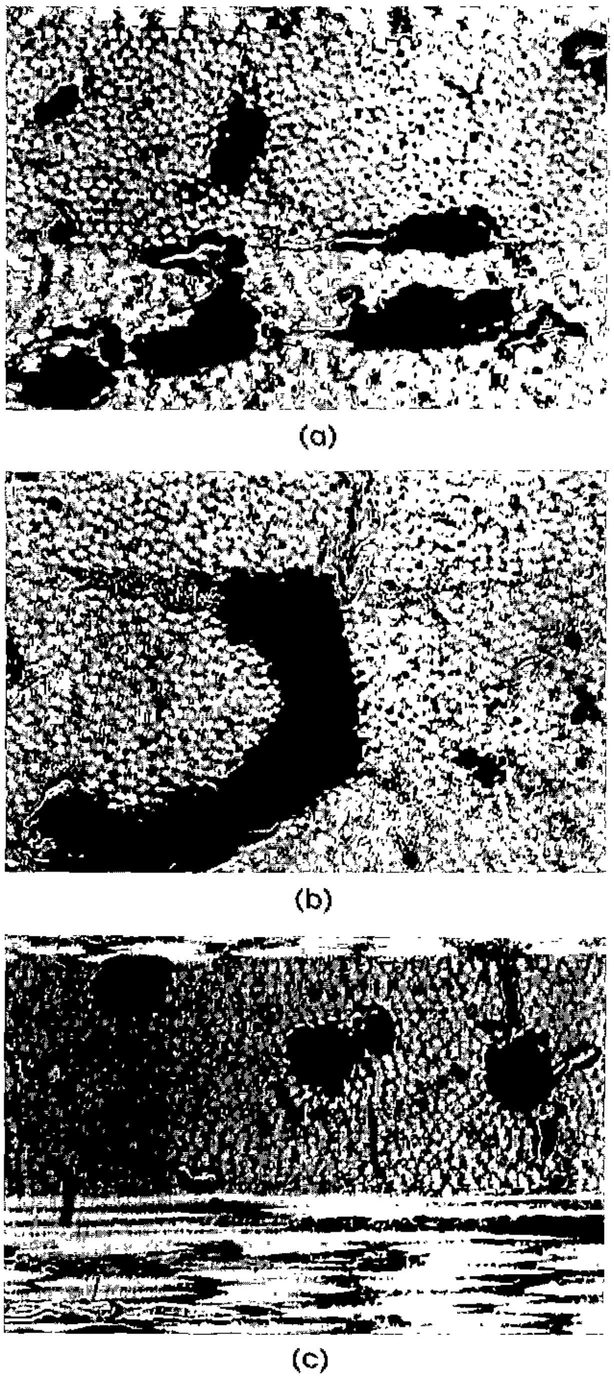
(a)
(b)
(c)

Fig. 3. Optical Micrographs of Composite Samples d through f densified with pitch J (a), S (b) and M (c) Respectively.

more difficult, resulting the increase of impregnation efficiency and the decrease of retention efficiency with densification cycle.

Fig. 4 shows plot of densification efficiency against porosity. Samples e and f which were impregnated with high-yield pitches S and M respectively and carbonized by route P+A+G have the highest efficiency, which is decreasing as the densification proceeds. The efficiencies of both samples are about 40% in their first cycles (30%

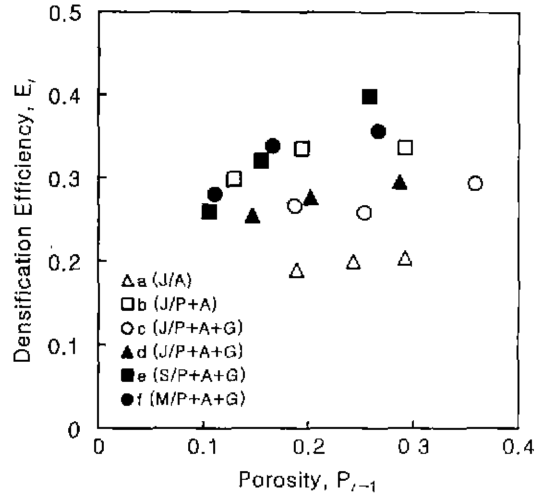

Fig. 4. Plot of Densification Efficiency Versus Porosity.

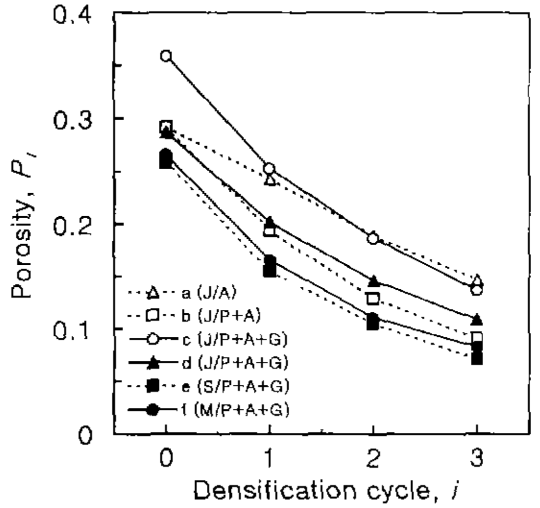

Fig. 5. Porosity Variations of Composite Samples During Densification.

porosity) but they drop to 30% in their third cycles (10% porosity). The efficiency of sample a is only 20% throughout the cycles. Considering the definition of E_i in eqn (8), E_i is mainly dependent on y_p rather than w_i and x_i because the latters are not much dependent on pitch type as shown in Fig. 1 and 2.

The porosity changes of the samples e and f show the most effective in Fig. 5.

The samples e and f were impregnated with modified pitches S and M respectively, which have higher yields than pitch J.

V. Conclusions

As the densification cycle of C/C composites with pitch proceeds, the impregnation efficiency increases while the retention efficiency decreases. This seems to result from the variation in pore structure in the composites. Small pores are well filled with pitch by capillary action but large pores remain empty after repeated cycles.

The type of pitch did not have much influence on both of the efficiencies, but the overall densification efficiency was dependent on the carbon yield of pitch.

Graphitization and pressure carbonization were found to be very effective steps during densification. The graphitization increases the impregnation efficiency by opening up the porosity and the pressure applied during carbonization not only increases the carbon yield of pitch but also increases the retention efficiency by preventing pitch from being forced out of the pores.

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