

Effect of Resin Impregnation Methods at the Early Stage of Densification on the Impregnation Efficiency, Microstructure, and Thermal Stability of Carbon–Carbon Composites

DONGHWAN CHO,¹ YOUNG SEOK AHN,¹ JIN YONG LEE²

¹ Department of Polymer Science and Engineering, Kumoh National University of Technology, Kumi, Kyungbuk 730-701, Korea

² Composite Materials Team, Agency for Defense Development, P.O.Box 35, Taejon 305-600, Korea

Received 20 March 2001; accepted 30 July 2001

ABSTRACT: The effect of impregnation methods and heat-treatment temperature at the early stage of densification on the impregnation efficiency, microstructure, and thermal stability of carbon–carbon composites prepared from carbon–phenolic green composites was studied. The results suggest that simultaneous application of pressure and heat provides better impregnation performance during densification at the early stage of carbon–carbon composite fabrication than ultrasonic impregnation and vacuum infiltration impregnation. Also, optical microscopic examination strongly supports the result of the impregnation efficiency obtained using three different resin impregnation methods. An additional heat-treatment at 2000 °C after carbonization results in better thermal stability and a denser microstructure of the fiber and matrix of the composite. For the carbonized composites, including a fully cured furfuryl alcohol resin impregnant, the weight loss measured by a thermogravimetric method quantitatively agrees with the weight loss occurred in a carbonization furnace at the corresponding temperature. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 183–192, 2002

Key words: carbon–carbon composite; resin impregnation method; impregnation efficiency; microstructure; thermal properties

INTRODUCTION

Efficient densification is of much academic and industrial interest in fabricating carbon-fiber-reinforced carbon matrix (carbon–carbon) composites, which are increasingly used in aerospace and extremely high temperature materials applications, because it is closely related with the cost of

processing and final products. A liquid phase impregnation method rather than a vapor phase impregnation method has been utilized as the common technology to densify carbon–carbon composites. The choice of the liquid phase is likely because of its economic cost as well as the ease and efficiency of the process.^{1, 2}

Using a liquid phase resin impregnation method, the densification of a carbon–carbon composite from a green composite or preform composed of carbon fiber and thermosetting resin or thermoplastic pitch is generally achieved through

Correspondence to: D. Cho (dcho@kmut.kumoh.ac.kr).

Journal of Applied Polymer Science, Vol. 85, 183–192 (2002)
© 2002 Wiley Periodicals, Inc.

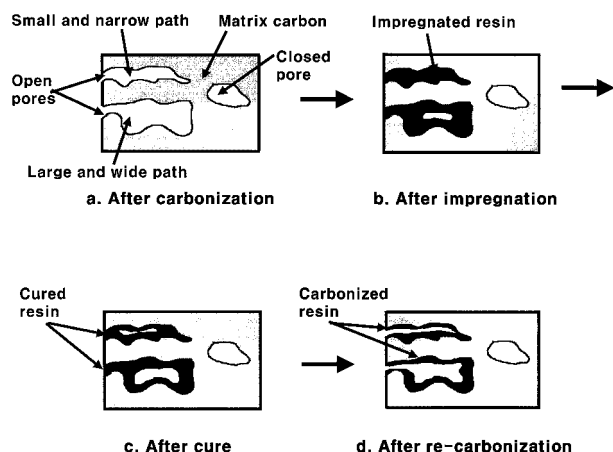


Figure 1 A schematic representation of pore-filling by resin impregnation, resin shrinkage, and resin-to-char conversion occurring during a series of densification processes.

a series of carbonization \rightarrow resin impregnation \rightarrow cure \rightarrow re-carbonization processes. During these processes, the open pores or voids resulting from the weight loss and thermal shrinkage of polymeric matrix on carbonization can be impregnated with low viscosity resin under proper processing conditions. A series of densification steps of pore-filling by resin impregnation into a carbonized composite, resin shrinkage by cure, and then resin-to-char conversion by re-carbonization is schematically represented in Figure 1. The effect of a series of resin impregnation \rightarrow cure \rightarrow re-carbonization steps on the densification of a carbonaceous composite is most profound at the second and the third carbonization stages. The densification efficiency gradually decreases with increasing the number of re-carbonization steps^{3, 4} because many large pores or voids remain in the carbonized matrix that has experienced the early stage of carbonization.

Success in filling macro- and micro-pores or voids may determine the quality of carbon-carbon composites because their properties, performance, and the lifetime are strongly influenced by density. Much research has been done to develop and understand the mechanism of pore-filling by resin impregnation and chemical vapor infiltration (CVI) techniques.⁵⁻⁹ The densification mechanism depends on the structure of voids or pores in a carbonaceous composite. Recently, Gao et al.¹⁰ investigated the change of the void structure in carbon-carbon laminates during densification by multiple resin impregnation, multiple CVI,¹¹ and their alternative techniques¹² and also

pointed out the importance of an optimum densification technique.

Furfuryl alcohol has been popularly used not only as an impregnant¹³ but also as a matrix precursor¹⁴ for carbonaceous composites. Furfuryl alcohol has some advantages over phenolic resin as an impregnant: It does not include solvents, so a weight loss by solvent volatilization can be avoided. It is of very low viscosity, therefore it can be infiltrated into internally deep open pores in a composite during impregnation under proper conditions. It can be converted into furan resin or polyfurfuryl alcohol by heat. The cured resin has the carbon yield of 50–55%.⁴ The extent of carbon residue formed from an impregnated resin as well as from a thermosetting resin matrix at carbonization temperature significantly contributes to the density and properties of a carbon-carbon composite. If better impregnation efficiency can be achieved, it would be desirable for fast and economic densification of carbon-carbon composites.

The aim of this work is to present results on our research to improve the resin impregnation efficiency for carbon-carbon composites at the early stage of densification where is mostly affected by thermal shrinkage and pore formation. In the present work we studied the dependence of impregnation efficiency on three different resin impregnation methods utilizing ultrasonic energy, simultaneous pressure/heat, and vacuum infiltration, respectively. The extent of impregnation is discussed with the results from microscopic and thermogravimetric examinations.

EXPERIMENTAL

Materials

The material used as reinforcement was a 12K PAN-based carbon fabric with an 8-harness satin texture (manufactured by Tae Kwang Industries Company). No surface-treatment or sizing was done on fiber before use. The areal density of the fabric is $\sim 0.450 \text{ kg/m}^2$. The fabric counts were 25×25 per square inches. The average diameter of a single filament is $6.8 \mu\text{m}$ and the density is $\sim 800 \text{ kg/m}^3$. Resole-type phenolic resin with a solids content of $\sim 60\%$ (supplied by Kolon Chemical Company) was used as precursor for the formation of carbonaceous matrix. Furfuryl alcohol catalyzed by *p*-toluene sulfonic acid (*p*-TSA) of 0.05 wt% was used as impregnant for carbon-

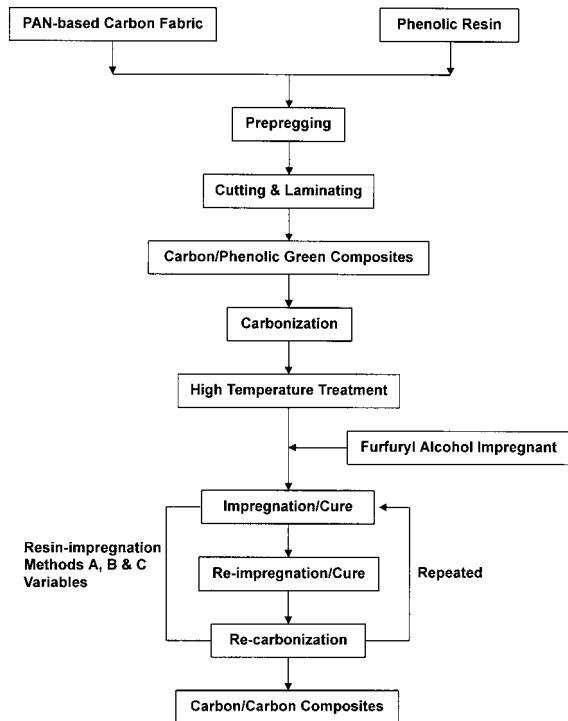


Figure 2 A flow chart of processing steps for fabrication of carbon-carbon composites used in the present study.

carbon composites. Furfuryl alcohol and *p*-TSA were purchased from Aldrich Chemical Company and used as-received.

Preparations of Carbon-Carbon Composites

Industrially carbon-carbon composites are fabricated according to the flow chart seen in Figure 2. The specimens for individual examinations were taken at each processing step during the preparation of carbon-carbon composites. The focus of this work is in the later half of the flow chart, including resin impregnation, cure, and carbonization. The following description gives the experiment in detail.

Carbon-Phenolic Green Composites

Carbon-phenolic prepregs with 34 plies were placed in a mold of 50×50 mm size, and heated with a hot-air gun applying manual pressure to minimize air entrapment and to enhance the adhesion between the cross-plies. A three-step cure cycle (at 80°C for 30 min, at 110°C for 30 min, and at 160°C for 120 min) was chosen for an optimal compression molding. The pressure applied with a plunger was $\sim 8.8 \times 10^5 \text{ kg}_f/\text{m}^2$ (8.6

$\times 10^4 \text{ Pa}$). The thickness of the composite obtained was 17 mm. The bulk density and apparent porosity of the green composite molded were $\sim 1450 \text{ kg}/\text{m}^3$ and 8%, respectively.

Carbonization and High-Temperature Treatment

The prepared green composites were carbonized in a tube-type furnace at a heating rate of $20^\circ\text{C}/\text{h}$ up to 1000°C under a nitrogen atmosphere, holding for 2 h at the final temperature, and then were furnace cooled to ambient temperature. Re-carbonization was performed under the corresponding condition to the first carbonization. All composites used in this work were additionally heat-treated up to 2000°C at ambient pressure under an argon atmosphere right after the first carbonization, using a graphitization furnace. Such a high-temperature (HT) treatment was conducted to transform closed pores in the carbonized composite into open pores and to enhance densification performance. The composite specimen obtained at this stage is designated as 1C/C+HT.

Impregnation and Cure

Three different resin impregnation methods were used to investigate the effect of the methods on the impregnation efficiency of carbonaceous composite as follows.

Ultrasonic Impregnation (Method A) This method uses ultrasonic energy applied to a composite in a resin bath to increase the infiltration of the resin into the composite. The impregnation time in the bath was ~ 2 h at ambient temperature. The impregnated resin was partially cured in a carbonization furnace at 50°C for 120 min and then at 100°C for 120 min. The required cure condition was determined from previous work¹⁵ by thermal analysis.

Simultaneous Application of Pressure and Heat (Method B) The simultaneous application of pressure and heat, called Method B, involves immersion of the composite in a resin bath while applying pressure at 20 atm. After applying pressure for 5 h, the pressure vessel including the composite specimen and impregnant used here, as shown in Figure 3, is turned upside down to separate the impregnated composite from the uncured. The impregnated resin, while under pressure, is then partially cured at 50°C for 180 min and then at 100°C for 10 h.

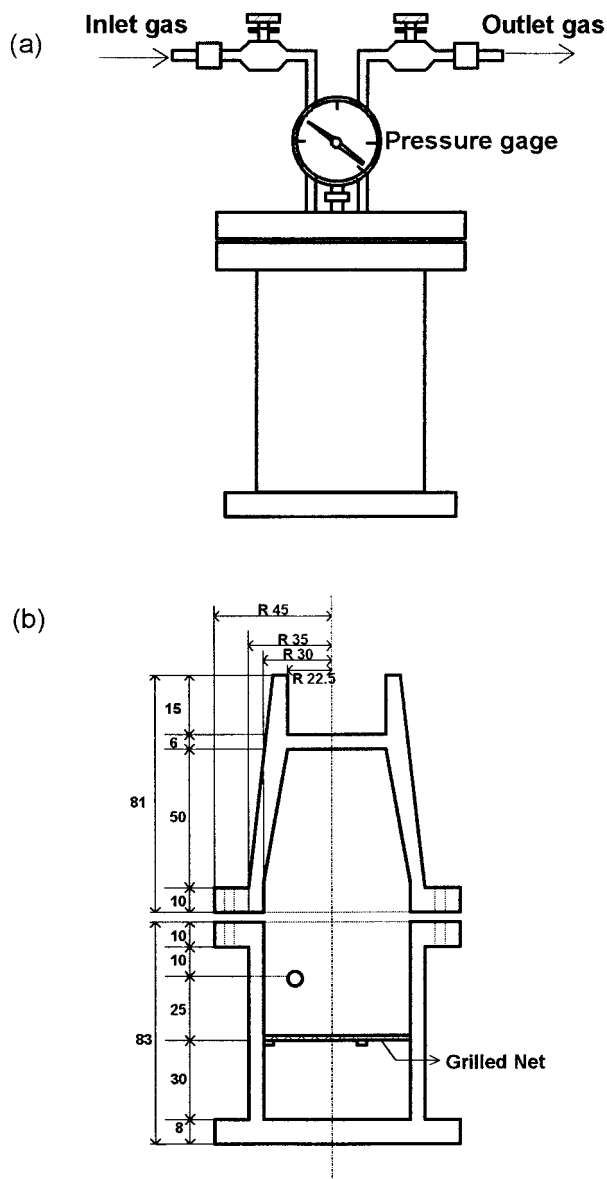


Figure 3 A schematic illustration of the impregnation bath used for impregnation and cure processes during fabrication of carbon–carbon composite: (a) overall view; (b) internal structure and dimension.

Vacuum Infiltration Impregnation (Method C) Method C involves the complete immersion of the composite in the resin while under vacuum at ambient temperature for 120 min. The vacuum applied was 1 Torr and is used to remove air trapped in the open pores and interstices so that the resin can infiltrate the composite. After vacuum infiltration, it was found necessary to tightly wrap the composite specimen in foil to minimize the loss of excess resin that flows out to the surface of the specimen at ambient pressure. This

step was completed as quickly as possible to avoid even the small loss of the excess resin. The cure was then conducted under the conditions used in Method A.

In all the three methods, two impregnation–cure steps were conducted to enhance the extent of impregnation before re-carbonization. All the partially cured composite specimens obtained from Methods A, B, and C were completely cured at 160 °C for 120 min in an oven after each impregnation process.

Analysis

The thermal stability for starting materials, carbon–phenolic green composites and carbon–carbon composites was measured using a thermogravimetric analyzer (DuPont 951 TGA) up to 1100 °C under an inert atmosphere with a heating rate of 10 °C/min. Dry nitrogen gas was purged at 80 cc/min to provide an inert atmosphere during cure and carbonization.

The change of weight, bulk density, and apparent porosity in the composites obtained at each processing step was evaluated according to ASTM C20-87.¹⁶ A percent impregnation efficiency in the present study was calculated as follows:

$$\text{Impregnation Efficiency (\%)} = [(W_{rc} - W_o)/W_c] \times 100 \quad (1)$$

where W_c and W_{rc} designate the weights of the first carbonized composite and the corresponding re-carbonized composite, respectively.

The microstructures of the composites obtained in the three different impregnation methods and at the heat-treatment temperature of 2000 °C were observed with an optical microscope (OLYMPUS BH-60M) after mounted and polished with 0.05- μm -sized alumina powder.

RESULTS AND DISCUSSION

Thermal Stability of Starting Materials

The thermal stability and carbon yield of starting materials for carbon–carbon composites (i.e., carbon fiber reinforcement, matrix precursor, and impregnating resin) play a significant role in fabrication and properties of the final composites. Figure 4 represents the thermogravimetric result for PAN-based carbon fabric, cured phenolic resin, and cured furfuryl alcohol resin in an inert

atmosphere. The carbon fabric exhibits a weight loss of $\sim 13\%$ at $1100\text{ }^{\circ}\text{C}$, which reflects a carbon yield of $\sim 87\%$. The cured phenolic resin used here has a char residue of $\sim 70\%$ at $1100\text{ }^{\circ}\text{C}$. This result indicates that $\sim 70\%$ of phenolic matrix in the green composite can be transformed into carbonaceous matrix after carbonization. The cured furfuryl alcohol resin has a carbonaceous carbon yield of $\sim 55\%$ at $1100\text{ }^{\circ}\text{C}$, which is consistent with the literature value.⁴ However, the furfuryl alcohol used as impregnant may be thermally shrunk to a large extent during a curing process done after impregnation. Therefore, the amount of the impregnant remaining cured in pores and voids of carbon-carbon composite through a sequence of impregnation, cure, and then re-carbonization will be much less than that of the uncured impregnant, as illustrated in Figure 1. As seen in Figure 4, the carbon yield of the fully cured furfuryl alcohol resin is $\sim 15\%$ lower than that of the fully cured phenolic resin. It is noted that a control of weight loss below $600\text{ }^{\circ}\text{C}$ is important to an overall carbon residue, which is critical in densifying a carbonaceous matrix as impregnant as well as matrix precursor. Consequently, developing an efficient impregnation method and intrinsically introducing an impregnant with high carbon yield will contribute to enhancing the densification efficiency during fabrication of carbon-carbon composites. The present study focuses only on the former approach, but a preliminary report on the latter approach has been given earlier.¹⁵

Effect of Heat-Treatment Temperature on Microstructure

The effect of heat treatment temperatures (1000 and $2000\text{ }^{\circ}\text{C}$) on the microstructure of a carbon-

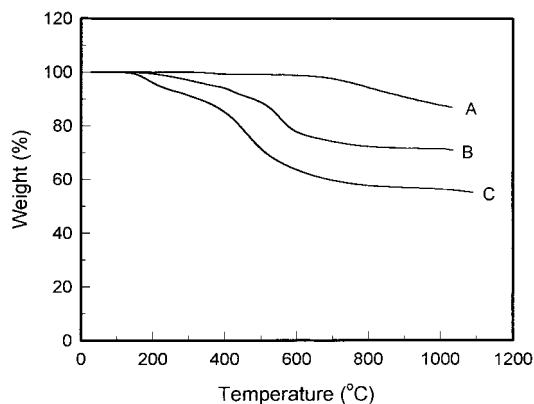


Figure 4 Thermal stability of (A) PAN-based carbon fabric, (B) cured phenolic resin, and (C) cured furfuryl alcohol resin, measured in N_2 .

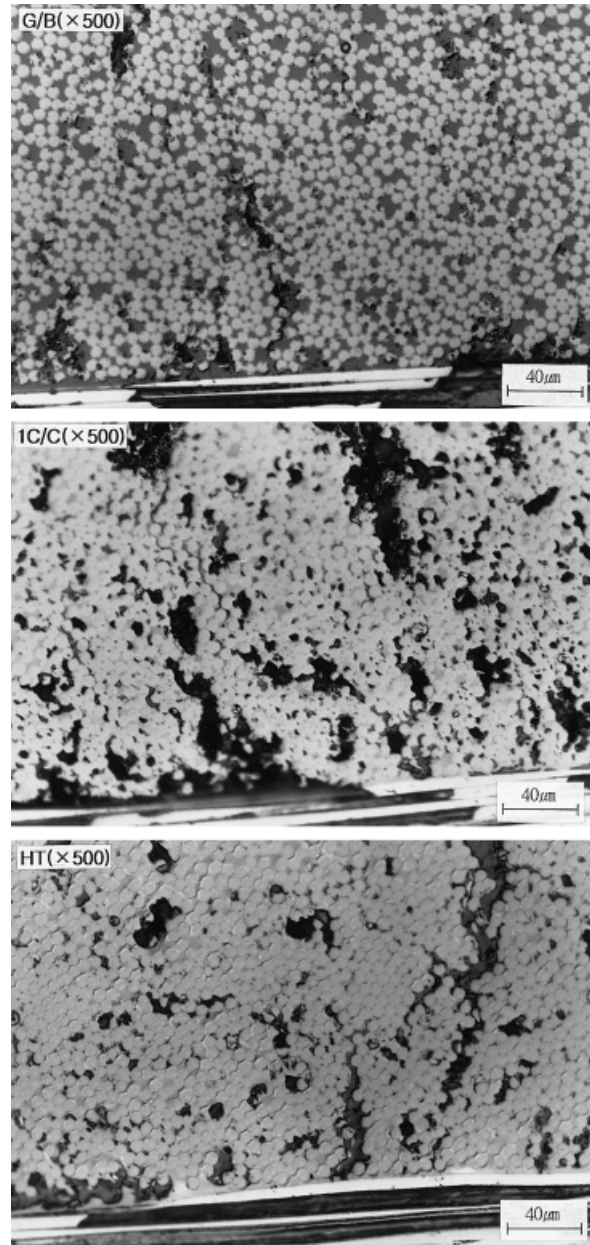


Figure 5 Optical microphotographs showing the heat-treatment temperature effect on the microstructure of carbon-phenolic green (G/B), carbonized (1C/C), and carbonized and additionally heat-treated (HT) composites. The carbonization temperature was $1000\text{ }^{\circ}\text{C}$ and the additional heat-treatment temperature was $2000\text{ }^{\circ}\text{C}$.

phenolic green composite is shown in Figure 5. The green composite has relatively uniform distribution and good bonding between fiber and phenolic matrix. Also, there are some micropores or voids in the matrix region that are generated on molding and that are hardly removed com-

pletely in such a carbon fabric–phenolic system, which has a harness satin texture that is possibly created by air entrapped during processing. On carbonization, the phenolic matrix part in the green composite experiences much higher thermal shrinkage than the fiber part, so the micropores are extended and increased. As seen in the middle of the photos in Figure 5, there are some new macropores resulting from a large volume of volatiles released from the resin-rich area between fibers due to pyrolysis. A large number of micropores may be caused by volatilization and shrinkage of the matrix resin at fiber–matrix interfaces. During this process, thermal shrinkage barely occurs in the fiber part because of almost negligible thermal contraction of carbon fiber at the given carbonization temperature.

After an additional heat treatment at 2000 °C, the interstices between the fiber and matrix are reduced so that the HT composite specimen has a denser distribution of the fiber and matrix than the 1C/C counterpart. This reduction is ascribed to additional matrix shrinkage and small thermal contraction in the transverse direction of carbon fiber, resulting in an overall volumetric shrinkage of the composite, especially through the thickness. As a result, the number and size of micropores and macropores, not only between the fibers but also between the cross-plyes, become smaller. Consequently, the bulk density of the composite becomes greater. The bulk density of 1C/C composite heat treated at 1000 °C is increased from 1375 to 1420 kg/m³ by an additional heat treatment at 2000 °C. Such microstructural changes probably contribute to some extent to promoting the efficiency of impregnation and densification.

Effect of Resin Impregnation Methods on the Impregnation Efficiency

Among the resin impregnation methods used in this work, the specimens prepared by Methods A and C are exposed to ambient pressure during handling before being cured whereas the specimen in Method B can be cured under the given vessel pressure without releasing to ambient pressure; that is, the impregnated resin can be solidified under the condition that both pressure and heat are applied simultaneously. A comparison of how the different methods influence the weight change in 1C/C+HT, 2C/C and 3C/C composites at each processing step is shown in Figure 6. In this figure, 1C/C+HT designates the composite carbonized at 1000 °C and subsequently

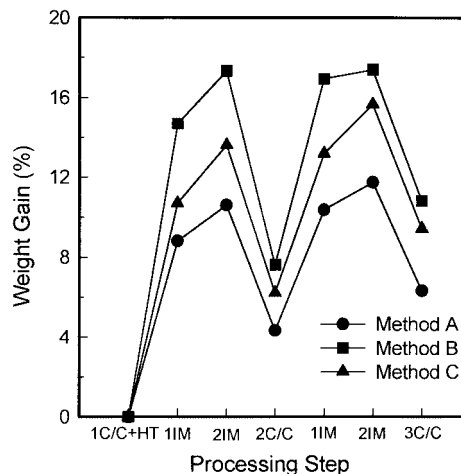


Figure 6 Variations of percent weight gain by the furfuryl alcohol resin impregnant at each processing step performed using three different resin impregnation methods.

heat treated at 2000 °C, 2C/C and 3C/C designate the second and the third carbonization composites, respectively, and 1IM and 2IM designate the composites finished with the first and the second impregnation/cure processes after a given carbonization step, respectively. The weight gain or loss at each step is only caused by the amount of the resin infiltrated or carbonized. In Method B, the weight of composite is increased ~14.7% by one impregnation/cure step and ~17.3% by two steps. This result can be explained as follows: first, the impregnated resin is cured directly in the vessel without any pressure loss, and second, the impregnant under 20 atm pressure can be easily forced into deep pores or voids in the carbonaceous matrix. A weight increment by the impregnated resin after the second carbonization is less than that after the first carbonization. Even after the second carbonization, Method B shows a slightly higher weight gain than other methods, obviously because most of the open pores in the carbonaceous matrix are filled with the impregnant and the fewer pores of smaller size regenerated by re-carbonization are filled by the ensuing impregnation steps.

Method C is more effective in filling pores than Method A; that is, the impregnation can be better operating under vacuum, although both Methods A and C may be subjected to exposure to ambient pressure in the middle of impregnation process. The resin impregnant of low viscosity may infiltrate more deeply inside the composite under vacuum than under an ultrasonic condition at ambi-

ent temperature. Once the specimens in Methods A and C are taken out of an impregnation bath or a vacuum chamber, the impregnated resin can flow backward to the surface of specimen. The deeply infiltrated resin will not readily flow out because of a capillary effect. The capillary effect plays an important role in filling narrow channels of pores or voids so that wider channels are not readily filled in the early stage of densification process.¹²

The impregnation efficiency at the early stage of densification for the carbon-carbon composites with an intermediate density, obtained from the first to the third carbonization steps, is shown in Figure 7. It is clear that the efficiency in Method B is increased by a factor of 1.2 to 1.7, compared with that in Methods A and C. It is also seen from the slope of the plot that an increase of the impregnation efficiency at the first carbonization stage is greater than that at the re-carbonization stage, as demonstrated elsewhere.^{3, 4} Therefore, it can be concluded that filling open pores or voids in the carbonaceous composite is more effective in the order Methods B, C, and A.

The change in the bulk density and apparent porosity from the green composite to the third carbonization composite according to different impregnation methods is shown in Figure 8. The density of the green (G/B) composite significantly decreases from 1450 to 1370 kg/m³ due to noncarbon volatiles in the polymeric matrix accompanying some thermal shrinkage on carbonization. During this process, detrimental physical changes

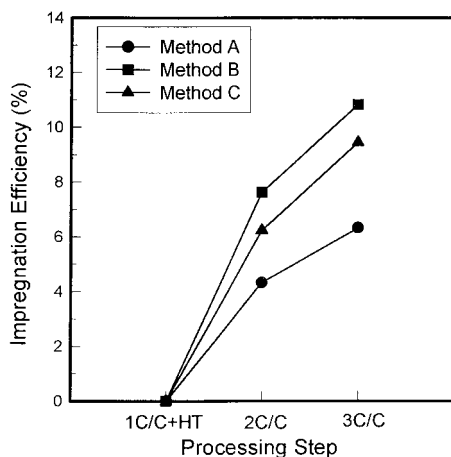


Figure 7 A comparison of the impregnation efficiency in the carbon-carbon composites prepared at each carbonization step among three different resin impregnation methods.

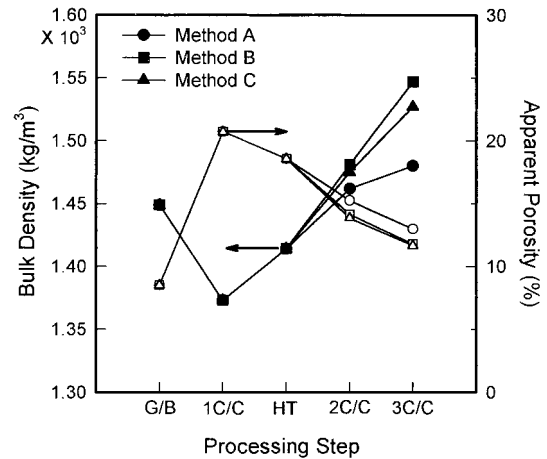


Figure 8 Variations of bulk density and apparent porosity in the carbon-carbon composites prepared at each processing step.

can also be involved; a number of micropores and macropores can be increased and/or newly generated and their size may be extended, especially in the resin-rich area in the green composite, as seen in Figure 5. As a result, the apparent porosity increases from 8.5 to 20.7%. After a subsequent heat treatment at 2000 °C, the density of the 1C/C composite increases from 1370 to 1410 kg/m³ and the porosity decreases comparably. This result is attributed to the secondary shrinkage of the matrix and the thermal contraction in the transverse direction of carbon fabric, which results in the slight volume shrinkage of the composite, as described in Figure 5. In accordance with the results seen in Figures 6 and 7, the bulk densities of 2C/C and 3C/C composites obtained by Method B are greater than those obtained by Methods A and C.

Effect of Resin Impregnation Methods on Microstructure

Optical microphotographs often provide useful information on the extent of the resin impregnated into the micro- and macropores in a carbonized composite. The microscopic result observed for three carbonized and additionally heat-treated composites (1C/C+HT) after two impregnation and cure processes by Methods A, B, and C using a furfuryl alcohol impregnant are shown in Figure 9. In the photos, the light gray or white color surrounding the carbon fibers indicates a carbon matrix region existing prior to impregnation and the dark gray color around micro- and macropores indicates a polymeric region impregnated and cured by furfuryl alcohol. The black color indi-

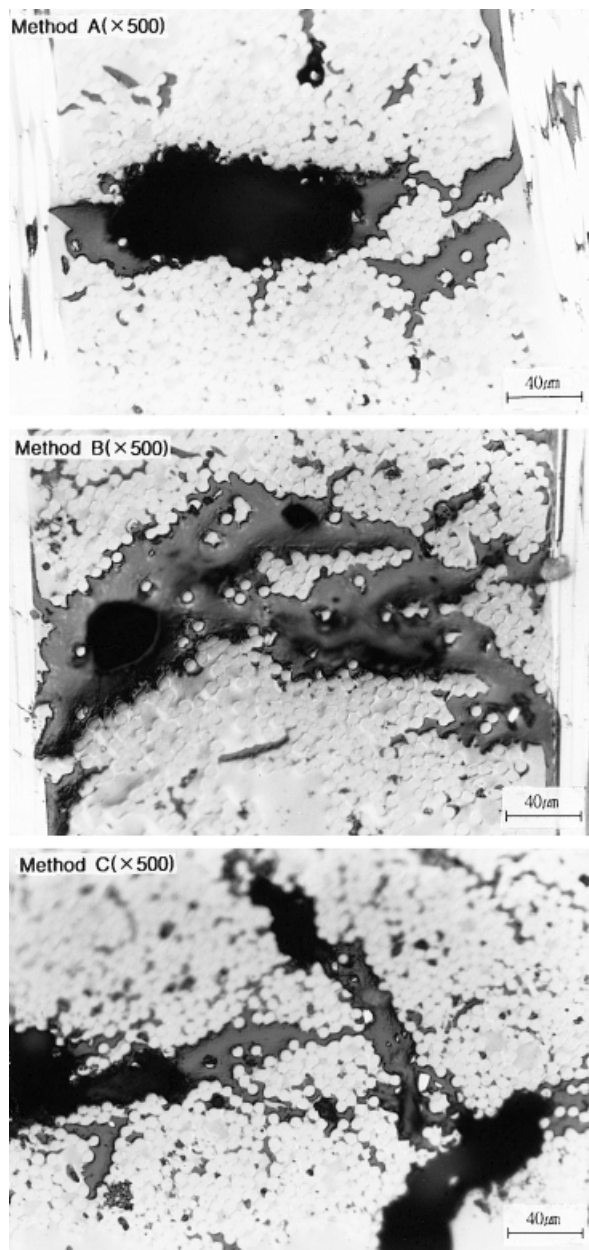


Figure 9 Optical microphotographs observed for the carbonized and additionally heat-treated composite after performing impregnation and cure processes ($\times 500$).

cates pores and voids that have not been impregnated. From the photos for Methods A and C, it is found that most of the micropores $< 20 \mu\text{m}$ in size are impregnated regardless the length and shape of the pore formed, but the impregnant is not fully filled into the macropores. This result can be explained by exposure of the impregnant to ambient air as it flows into the composite and by some backward flow of the impregnant to the surface of

the specimen while the specimen is moved from an ultrasonic bath or a vacuum chamber to a curing oven. Therefore, this procedure should be done very quickly to avoid a possible loss of the small amount of the impregnated resin as described in the Experimental section. The pores of a narrow and long path are infiltrated by the impregnant because of a capillary effect. Generally, more micropores are impregnated by Method C than by Method A.

It has been demonstrated that a large portion of the macropores is impregnated with the cured furfuryl alcohol resin by Method B, in which both pressure and heat are simultaneously applied to the impregnant. The result indicates that Method B is more effective in impregnating the $40\text{--}50\text{-}\mu\text{m}$ size pores than the other two methods because, with Method B, the impregnated resin placed in the macropores can be solidified under the applied 20 atm pressure without significantly flowing back out. However, the 20 atm pressure is not high enough to efficiently impregnate the resin into the macropores $> 50 \mu\text{m}$. This explanation of the microstructural behavior agrees with the results seen in Figures 6–8.

Effect of Resin Impregnation Methods on Thermal Stability

The effect of heat treatment temperatures and impregnation methods on the thermal stability of the composites used in this study was examined. The thermogravimetric result measured in an inert atmosphere is shown in Figure 10. The G/B composite exhibits a primary weight loss of ~ 300

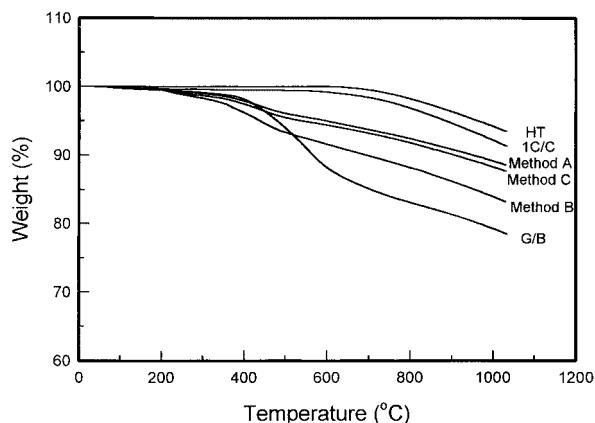


Figure 10 A comparison of thermal stability measured for one carbon–phenolic green, two heat-treated, and three impregnated composites in N_2 (HT indicates the 1C/C+HT composite specimen).

Table I Comparison of Weight Losses of Furfuryl Alcohol Resin Impregnant at 1000 °C among Different Resin Impregnation Methods^a

Resin Impregnation Method	Weight Gain by Impregnation (%)	Weight Loss at 1000 °C by Carbonization (%)	Weight Loss at 1000 °C by TGA (%)
A	10.6	4.8	5.2
B	17.3	7.8	9.3
C	13.6	6.1	5.9

^a Measured in a carbonization furnace by thermogravimetric analysis.

°C, due to decomposition and volatilization of cured phenolic matrix, which increases between 500 and 600 °C. A secondary weight loss at ~600 °C is due to char formation by pyrolysis of the matrix. The 1C/C+HT composite shows the highest thermal stability, with a carbon yield of ~95%. Because of its thermal history that was experienced during heat treatment at 2000 °C. The temperature of 2000 °C is expected to be high enough to develop further the crystal structure with preferred orientation and higher carbon content. Even though the phenolic matrix is not perfectly graphitized at this temperature, it can be transformed into a well-developed glassy carbon with denser aromatic layers, which is responsible for higher thermal stability than the matrix heat treated at lower temperature.

The carbon residues obtained at 1000 °C after two impregnation and cure processes using different impregnation methods are 89.1% for Method A, 85.0% for Method B, and 88.4% for Method C. Increasing the amount of the impregnated resin increases the weight loss. The initial weight loss starting at ~200 °C is due to decomposition of the impregnant. It is useful to quantitatively compare the weight loss of the impregnant at 1000 °C measured by a thermogravimetric method with the weight lost by carbonization at 1000 °C in a furnace after the impregnation and cure process. The two results are quite comparable to each other, as summarized in Table I. Comparing the percent weight gain by the impregnation and cure process in the second column with the percent weight loss by carbonization in the third column indicates that these values are consistent with the result of the carbon yield for the cured furfuryl alcohol resin measured by a thermogravimetric method in Figure 4. In the last column, the weight loss at 1000 °C determined by a thermogravimetric analysis experiment is obtained by subtracting the carbon residues (89.1, 85.0, and 88.4%) at 1000 °C in Methods A, B, and C curves,

respectively, from the carbon residue (94.3%) at 1000 °C for the 1C/C+HT composite in Figure 10; that is, the values represent the weight loss by the impregnated resin only.

CONCLUSIONS

In this work the effect of impregnation method and heat-treatment temperature on the impregnation efficiency, microstructure, and thermal stability of carbon-carbon composites prepared at the early stage of densification was investigated. The results give the following conclusions:

1. Among three resin impregnation methods that were investigated to improve impregnation performance during fabrication of carbon-carbon composite, Method B, in which both pressure and heat are simultaneously applied to cure the impregnated resin, is the most effective in comparison with Method A, which is based on an ultrasonic impregnation, and Method C, which is based on a vacuum infiltration.
2. An additional heat treatment at 2000 °C after carbonization at 1000 °C causes the composite to have a denser fiber and matrix microstructure. The number and size of micropores and macropores formed in the resin-rich region located between the fibers in a carbonized composite are decreased. As a result, the bulk density of the composite increases and the apparent porosity decreases.
3. Optical microscopic observations of the composites prepared by the three different resin impregnation methods are in agreement with the results of impregnation efficiency.
4. The thermal stability of all the composites used in this work were examined. For the

carbonized composites finished with the impregnation and cure process, the weight loss at 1000°C, measured by a thermogravimetric method, and the weight loss at 1000 °C, which occurred in a carbonization furnace, are quite comparable.

REFERENCES

1. Savage, G. *Metals Materials* 1988, September, 544.
2. Ha, H.S.; Kim, D.G.; Cho, D.; Yoon, B.I. *J Korean Soc Comp Mater* 1993, 6, 1.
3. Savage, G. *Carbon-carbon composites*. Chapman & Hall: London, 1993, Chapter 1.
4. Thomas, C.R. *Essentials of carbon-carbon composites*. The Royal Society of Chemistry: Cambridge, 1993, Chapter 1.
5. Diefendorf, R.J. *Proceedings of the 10th Annual ASME Symposium on Carbon Composite Technology*, New Mexico, 1970, p. 125.
6. Fitzer, E. *Carbon* 1987, 25, 163.
7. Rellick, G. *Carbon* 1990, 28, 589.
8. Chlopek, J.; Blzewicz, S. *Carbon* 1991, 29, 127.
9. Lee, K.H.; Choe, C.R.; Yoon, B.I. *J Mater Sci Lett* 1993, 12, 199.
10. Gao, F, Patrick JW, Walker A. 1993. *Carbon* 31:103.
11. Gao, F.; Patrick, J.W.; Walker, A. *Carbon* 1994, 32, 1215.
12. Gao, F.; Patrick, J.W.; Walker, A. *Comp Sci Technol* 1997, 57, 483.
13. Cho, D. *Bull Korean Cer Soc* 1997, 12, 182.
14. Monocha, L.M. *Carbon* 1994, 32, 213.
15. Ahn, Y.S.; Cho, D. *Korean J Mater Res* 1998, 8, 299.
16. ASTM C20-87 Standard test methods for apparent porosity, water absorption, apparent specific gravity, and bulk density of burned refractory brick and shapes by boiling water.