

Thermal Conductivity and Thermal Expansion Behavior of Pseudo-Unidirectional and 2-Directional Quasi-Carbon Fiber/Phenolic Composites

Donghwan Cho*, Yusong Choi¹, Jong Kyo Park², Jinyong Lee², Byung Il Yoon², and Yun Soo Lim³

Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi 730-701, Korea

¹*Propulsion Sources Team, Agency for Defense Development, Jinhae 645-600, Korea*

²*Composite Materials Team, Agency for Defense Development, Daejeon 305-600, Korea*

³*Department of Ceramics Engineering, Myong Ji University, Yongin, Gyeonggi 449-728, Korea*

(Received August 7, 2003; Revised December 23, 2003; Accepted December 30, 2003)

Abstract: In the present paper, a variety of fiber reinforcements, for instance, stabilized OXI-PAN fibers, quasi-carbon fibers, commercial carbon fibers, and their woven fabric forms, have been utilized to fabricate pseudo-unidirectional (pseudo-UD) and 2-directional (2D) phenolic matrix composites using a compression molding method. Prior to fabricating quasi-carbon fiber/phenolic (QC/P) composites, stabilized OXI-PAN fibers and fabrics were heat-treated under low temperature carbonization processes to prepare quasi-carbon fibers and fabrics. The thermal conductivity and thermal expansion/contraction behavior of QC/P composites have been investigated and compared with those of carbon fiber/phenolic (C/P) and stabilized fiber/phenolic composites. Also, the chemical compositions of the fibers used have been characterized. The results suggest that use of proper quasi-carbonization process may control effectively not only the chemical compositions of resulting quasi-carbon fibers but also the thermal conductivity and thermal expansion behavior of quasi-carbon fibers/phenolic composites in the intermediate range between stabilized PAN fiber- and carbon fiber-reinforced phenolic composites.

Keywords: Phenolic composite, Quasi-carbon fiber, Carbon fiber, Stabilized PAN fiber, Thermal conductivity, Thermal expansion/contraction

Introduction

Carbon fibers have a variety of thermal advantages for many high-temperature uses in military and civilian applications: for instance, thermal stability, high thermal conductivity, low thermal expansion, thermal shock resistance, and ablation resistance [1-3]. However, unlike phenolic resin of superb thermal and electrical insulation characteristics, carbon fibers are not often desirable for using a carbon fiber-reinforced phenolic composite in thermal insulation applications because their thermal conductivity is very high in comparison with phenolic resin. Since many advanced composite materials useful in military and aerospace applications for thermal insulation purposes need excellent thermal stability, mechanical properties, ablation resistance at elevated temperature, and lightness as well, carbon fiber is still used as one of the most attractive constitutive materials. Therefore, controlling the thermal conductivity or insulation of carbon fiber may significantly contribute to protecting a carbon fiber composite from extremely high temperature environments.

In a carbon fiber-reinforced polymer matrix composite material, thermosetting phenolic resin has caught much attention for several decades because it is highly insulative, ablation-resistant, and heat-absorbing by char formation [4,5]. It is convinced that controlling the thermal conductivity of carbon fiber is far more reasonable than controlling that of polymer matrix for thermal protection or heat-shielding of a

carbon fiber/phenolic composite. It can be accomplished by a quasi-carbonization or low-temperature carbonization process, which normally heat-treats or carbonizes stabilized PAN fibers at temperatures lower than the temperature for manufacturing commercial PAN-based carbon fibers [6-8]. The preparation and characterization of a set of quasi-carbon fibers from stabilized PAN fibers at heat-treatment temperature below 1200 °C have been reported from our research team earlier [9-12].

The aim of the present study is to fabricate quasi-carbon fiber/phenolic (QC/P) composites with quasi-carbon fibers and fabrics obtained using different quasi-carbonization processes and also to compare their thermal conductivity and thermal expansion behavior with phenolic composites reinforced with commercial PAN-based carbon fibers, stabilized OXI-PAN fiber, and their fabric forms, respectively.

Experimental

Materials

Continuous stabilized or oxidized polyacrylonitrile (OXI-PAN) fibers and commercial PAN-based carbon fibers with 6000 filaments per tow (Tae Kwang Industries Co., Korea) were used as reinforcement for pseudo-unidirectional (UD) composites. Woven OXI-PAN fabrics with plain texture (Zoltek Co., USA) and commercial PAN-based carbon fabrics with 6000 filaments per tow and 8 harness satin texture (TZ-307, Tae Kwang Industries Co., Korea) were also used as reinforcement for 2-directional (2D) composites, respectively. Resol-type phenolic resin, supplied from Kang Nam Chemical

*Corresponding author: dcho@knut.kumoh.ac.kr

Co., Korea, was used as matrix without further modification.

Quasi-Carbonization Process

The following cycles are used for quasi-carbonization processes with different heating rate and heating step below 1100 °C. The final heat-treatment temperature (HTT) was 1075 °C.

Cycle 1: Heating rate; 100 °C/h, No holding at the intermediate and final stages of HTT.

Cycle 2: Heating rate; 40 °C/h, No holding at the intermediate and final stages of HTT.

Cycle 3: Heat-treated up to 800 °C with a heating rate of 40 °C/h (10 min holding at 800 °C) and subsequently up to 1075 °C with a heating rate of 20 °C/h (No holding at 1075 °C).

After each quasi-carbonization process, the heat-treated fibers and fabrics were naturally cooled down to ambient temperature in the furnace. All quasi-carbonization processes were performed purging a high purity (99.999 %) of nitrogen gas in a mullite tube-type Siliconit furnace.

The reason for choosing 1075 °C in the present work is substantially based on the results reported by Cho *et al.* [10]. In the paper, the fundamental characteristics of quasi-carbon fibers have been reported and their potential applications have also been suggested. Also, others [2,11] have reported that composites made with carbon fibers processed at low carbonization temperature show higher thermal insulation and ablation resistance than those with commercial carbon fibers.

Prepreg Preparation

All the 'as-received' and the heat-treated OXI-PAN fibers and fabrics were individually sized with 1.0 wt% poly(vinyl alcohol) by a dip-coating method and then dried at 125 °C for 20 min in an oven. The commercial carbon fibers and carbon fabrics were used as received without any further treatment because they are already proprietarily sized. The sized fibers and fabrics were impregnated with phenolic resin to be an equivalent content of fiber reinforcement and phenolic resin and then heated at 80 °C for 3 min in an oven to prepare prepregs composed of B-stage resin.

Composite Fabrication

The prepared prepregs were cut to be 50 mm × 50 mm in size to fit into a steel mold and then stacked in the mold applying the manual pressure. 40~50 plies of the prepregs were stacked to fabricate a composite of 10 mm thickness, depending on the heat-treatment process. In the middle of stacking, the prepregs were compacted several times using a press at ambient temperature in order to minimize possibly entrapping air in the mold. The fiber contents in the pseudo-unidirectional (pseudo-UD) and 2-directional (2D) composites were about 50 % by weight. Figure 1(a) represents the pseudo-UD arrangement of fiber/phenolic prepregs placed in

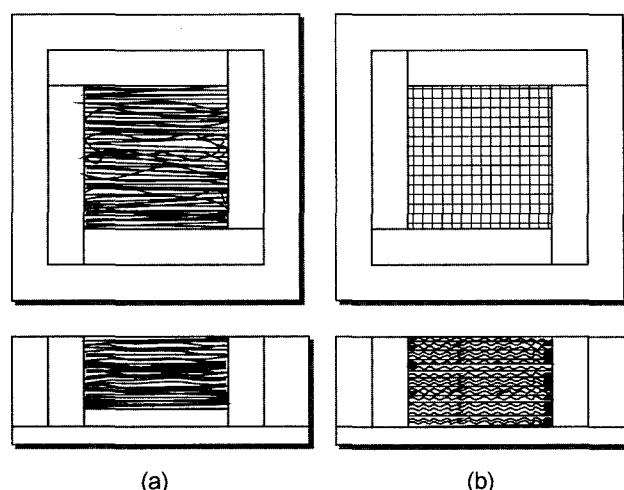


Figure 1. Schematic illustration of stacking patterns of (a) quasi-carbon fiber/phenolic molding compounds and (b) quasi-carbon fabric/phenolic prepregs placed in a compression mold.

the mold. The reason for designating it as pseudo-UD is that 'as-received' OXI-PAN fibers are consisted of a huge number of fiber bundles with uncountable filaments, which is not possible to make uniform UD prepregs as normally prepared by a filament-winding method. The resulting phenolic composites reinforced with the 'as-received' OXI-PAN fiber and quasi-carbon fibers of pseudo-UD arrangement are all referred to as 'pseudo-UD composites' in this study. Figure 1(b) represents the 2D arrangement of fabric/phenolic prepregs in the mold. The resulting phenolic composites reinforced with the 'as-received' OXI-PAN fabric, quasi-carbon fabric and commercial carbon fabric are all referred to as '2D composites'.

All the composites used here were fabricated by a compression molding method using a hot-press (Carver 2518). The mold with the stacked prepregs was pre-heated at 70 °C for 1 h, cured at 110 °C for 2 h, at which the gelation of phenolic resin used vitally takes place, and then further cured at 150 °C for 3 h. The pressure of 1250 psi was applied at the elapsed time of 20 min at 110 °C, which phenolic resin flows most actively. The applied pressure was remained constant until each composite was naturally cooled down to ambient temperature.

Characterization

Elemental Analysis

The elemental compositions for the quasi-carbon fibers processed according to different quasi-carbonization cycles were examined by an elemental analyzer (EA 1110, Thermoquest Co.). Carbon (C), hydrogen (H) and nitrogen (N) compositions were directly obtained. Oxygen composition was determined by subtracting the C, H and N compositions from the total amount of a measuring fiber, assuming that other possible ingredients of a very tiny amount in it are negligible. The

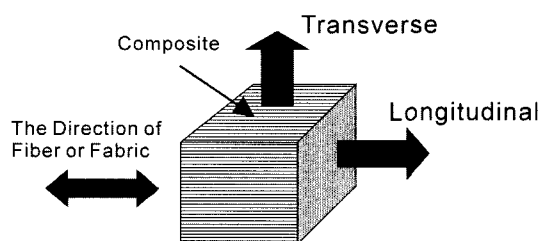


Figure 2. Schematic illustration indicating the transverse and longitudinal directions of reinforcing fibers aligned in a composite.

result was compared with the result obtained for the 'as-received' OXI-PAN and commercial carbon fibers.

Thermal Conductivity

The dimensions of a composite specimen for thermal conductivity measurement were 10 mm × 10 mm × 10 mm in a regular tetrahedron shape. A tailor-made thermal conductivity testing apparatus was used. The instrumental lay-out and description are referred to elsewhere [11,13]. The measurements were performed at ambient temperature in the transverse and longitudinal directions of a composite, respectively. Figure 2 shows a schematic illustration indicating the transverse and longitudinal directions of a fiber- or fabric-reinforced composite. The measurable range of thermal conductivity in the apparatus is 0.2–450 W/m·K. To obtain the reliable and reproducible thermal conductivity data, a set of tests were done and the results were averaged. For calculating the thermal conductivity of a measuring composite, the cross-sectional area and the height of each specimen were input and the instrumental factors such as electrical power input, resistance and voltage changes, and instrumental constant were considered. The detailed explanation has been described in the earlier paper [11].

Thermal Expansion Behavior

The thermal expansion behavior of each composite specimen was examined using a thermomechanical analyzer (TMA 2940, TA Instrument). The dimensions of a specimen for the thermomechanical test were exactly same as that for the thermal conductivity test. The expansion mode was used throughout the test. The measurements were performed from ambient temperature to 800 °C purging a nitrogen gas with 100 cm³/min. A heating rate of 2 °C/min, which is slow enough to thermally equilibrate the specimen during the test, was used. The tests were conducted in the transverse and longitudinal directions of a composite specimen, respectively.

Results and Discussion

Table 1 summarizes the change of the chemical compositions examined during heat-treatment processes from stabilized PAN fiber to carbon fiber via quasi-carbon fiber. The stabilized PAN fiber and the commercial PAN-based carbon fiber show typical chemical compositions of carbon, nitrogen, oxygen and

Table 1. Variations of the chemical compositions from stabilized OXI-PAN fiber to carbon fiber through quasi-carbon fibers

Chemical composition (%)	'As-received' stabilized OXI-PAN fiber	Quasi-carbon fiber		Commercial PAN-based carbon fiber
		Cycle 2	Cycle 3	
Carbon	62	83	86	95
Nitrogen	22	10	11	4
Oxygen	11.8	6.4	2.5	0.9
Hydrogen	4.2	0.6	0.5	0.1

hydrogen, as reported in the literature [14]. It is found that the contents of N, O and H are significantly decreased by quasi-carbonization while the carbon contents are largely increased. The carbon contents depend on the quasi-carbonization cycle used and are about 10 % lower than those of the commercial carbon fiber. This is because quasi-carbonization process was performed at lower temperature than in the carbonization process commercially producing carbon fibers. The oxygen contents of stabilized PAN fiber are relatively high because there are a number of oxygen-containing functional groups on the surface such as hydroxy, carbonyl, and carboxyl groups [1,15]. Such the chemical groups may contribute to developing the aromatic structure in the fiber by the fusion between the aromatic groups in the ladder-like polymer chains of stabilized PAN fiber during quasi-carbonization or carbonization process.

Comparing quasi-carbonization Cycles 2 and 3, the conversion from C, O and H into C increases with decreasing heating rate and holding heat-treatment time at 800 °C. The result of chemical composition analysis suggests that the contents of the key elements like carbon, oxygen, nitrogen and hydrogen in the quasi-carbon fiber may be effectively controlled by using proper quasi-carbonization processing parameters on purpose to be in between stabilized PAN fiber and commercial carbon fiber.

Figure 3 shows the result of the (a) transverse and (b) longitudinal thermal conductivities for pseudo-UD phenolic composites reinforced with differently heat-treated fibers. Hereinafter, the transverse and longitudinal thermal conductivities or thermal expansion behaviors indicate the thermal conductivity or thermal expansion independently measured along the transverse (perpendicular) and longitudinal (parallel) directions of the reinforcing fibers or plies in a composite, respectively. As seen in Figure 3, the transverse and longitudinal thermal conductivities of the pseudo-UD composite reinforced with stabilized OXI-PAN fibers have a lowest value. The composites reinforced with quasi-carbon fibers processed by Cycles 1 and 3 exhibit 30–40 % lower transverse and longitudinal thermal conductivities than that with commercial carbon fibers. Comparing the values in Figures 3(top) and 3(bottom) notes that the thermal conductivity of the composite is 2–6 times greater in the longitudinal direction than in the transverse one,

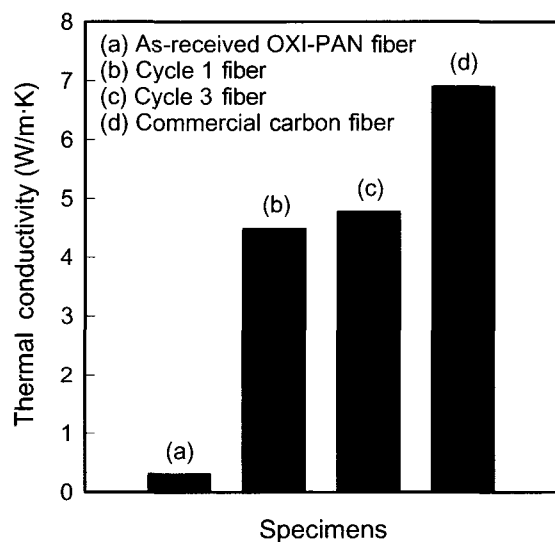
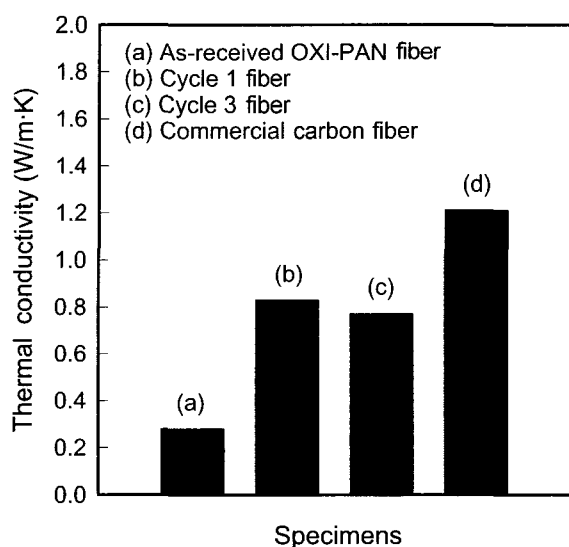


Figure 3. Transverse (top) and longitudinal (bottom) thermal conductivities measured for pseudo-UD composites made with four different types of reinforcing fibers.

depending on the reinforcing fibers. The result demonstrates that use of quasi-carbon fibers largely reduces the thermal conductivity of pseudo-UD composite reinforced with commercial carbon fibers. However, the variation of heating rate and heating step during the quasi-carbonization process does not significantly influence their conductivities. This is probably explained by that the microstructural change like thermal shrinkage and fiber diameter is more significantly influenced by final heat-treatment temperature than by heating rate or heating step during carbonization process. It is also explained by that the aromatic structure and molecular alignment can be less developed in the fiber processed at low carbonization temperature, as studied earlier [10] with quasi-carbon fibers.

Figure 4 shows the result of the (a) transverse and (b)

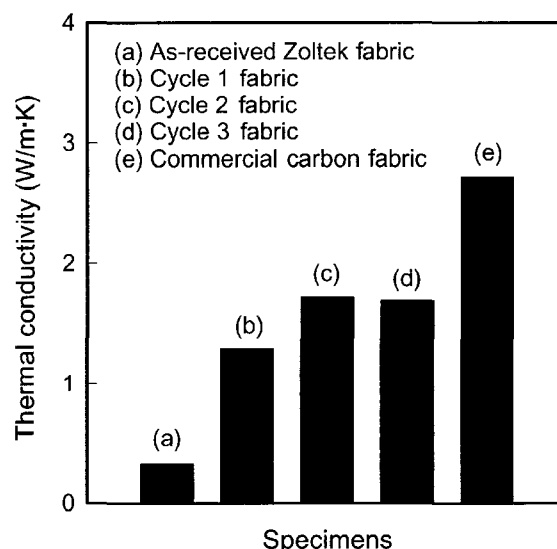
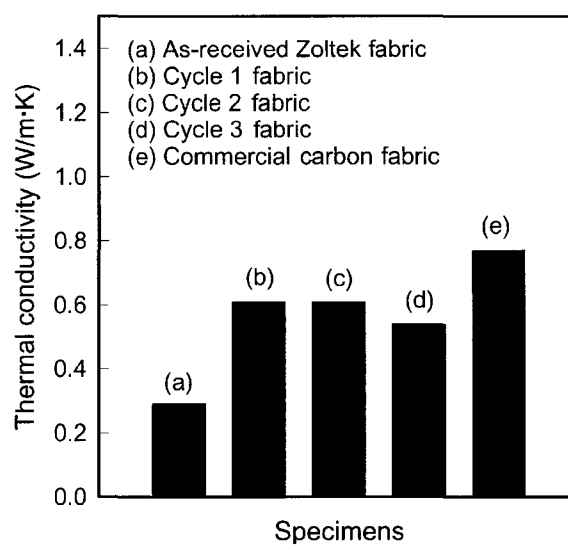


Figure 4. Transverse (top) and longitudinal (bottom) thermal conductivities measured for 2D composites made with four different types of reinforcing fibers.

longitudinal thermal conductivities for 2D phenolic composites reinforced with differently heat-treated fibers. It is found that the thermal conductivities obtained for 2D composites in the two directions are much lower than those for pseudo-UD counterparts, especially in the longitudinal direction. This is because the reinforcing fibers in the pseudo-UD composite are better arranged along the longitudinal direction than those in the 2D composite. In the 2D composite, the longitudinal thermal conductivity is greater than the transverse one, as similarly observed in Figure 3. Use of quasi-carbon fabrics in fabricating the 2D QC/P composite also significantly diminishes both the transverse and longitudinal thermal conductivities of the 2D C/P composite. As compared with the result of 2D C/P composites reinforced with commercial carbon fabrics, the

Table 2. A summary of the thermal conductivities calculated for three reinforcing fibers and measured for the phenolic composite specimens reinforced with them, respectively

Thermal conductivity Heat-treatment	Calculated for fibers (Fiber contents: 50 % by weight) (W/m · K)			Measured for Composites (W/m · K)
	$K_m = 0.20$	$K_m = 0.25$	Average	
Commercial carbon fiber	16.62	16.55	16.59	6.90
Quasi-carbon fiber cycle 3	11.16	11.09	11.13	4.78
Quasi-carbon fiber cycle 1	10.46	10.39	10.43	4.49

thermal conductivities of 2D QC/P composites are 20~30 % lower in the transverse direction and 40~50 % lower in the longitudinal direction, depending on the quasi-carbonization cycles.

Therefore, it can be concluded that use of quasi-carbon fibers or fabrics importantly contributes to reducing the thermal conductivity of a carbon fiber reinforced phenolic composite. The transverse contribution to the reduction is greater in the pseudo-UD composite than in the 2D composite. The longitudinal contribution is greater in the 2D direction than in the pseudo-UD direction. In the case of the 2D composite, the thermal conductivity of the QC/P composite using the Cycle 3 fabrics is lower in the transverse direction but higher than in longitudinal direction than that of the QC/P composite using the Cycle 1 fabrics prepared with higher heating rate and without heating step. In the pseudo-UD and 2D composites reinforced with stabilized OXI-PAN fibers and fabrics, respectively, their transverse and longitudinal thermal conductivities are almost similar. This is due to very low thermal conductivity of the stabilized OXI-PAN fiber itself regardless of the fiber direction.

Table 2 summarizes the result of the thermal conductivity for quasi-carbon fibers and a commercial carbon fiber, which is estimated from the longitudinal thermal conductivity values obtained for pseudo-UD QC/P and C/P composites, as shown in the bottom of Figure 3. Once a composite is simply composed of a single reinforcing fiber and a single polymeric matrix, the thermal conductivity of the composite can be calculated by the following expression.

$$K_{\text{comp}} = V_f \cdot K_f + V_m \cdot K_m \quad (1)$$

where K_{comp} , K_f , and K_m are the thermal conductivities of the composite, the fiber, and the matrix, respectively. V_f and V_m are the volume fractions of the fiber and the matrix, respectively. If one knows the weight fraction and the density of the fiber and the matrix of a composite, the volume fractions of the fiber and the matrix can be calculated using the following relationship.

$$V_f = (\omega_f/\rho_f)/\{(\omega_f/\rho_f) + (\omega_m/\rho_m)\} \text{ and } V_m = 1 - V_f \quad (2)$$

For the composite components used in the present work, the density of commercial PAN-based carbon fiber is 1800 kg/m³, the density of cured phenolic resin matrix is 1240 kg/m³ and the thermal conductivity of the matrix is 0.20~0.25

W/m·K [16], depending on the extent of cure of phenolic matrix used. One can determine the thermal conductivity of the fiber (K_f) from the known volume fraction of the fiber and the matrix in a composite and the measured thermal conductivity of a composite using the equation (1).

The last column in Table 2 represents the longitudinal thermal conductivity for pseudo-UD C/P and QC/P composites. The three columns in the middle of the table represent the values of thermal conductivity calculated for three different reinforcing fibers. Once the fiber contents in the pseudo-UD C/P composite are 50 % by weight, the thermal conductivity of the commercial carbon fiber composing of the composite is estimated to be about 16.6 W/m · K in this work. This value is very consistent with the thermal conductivity (17.0 W/m · K) for the commercial one provided by the manufacturer. The reason for the slightly lower value than the commercial value is that the reinforcing quasi-carbon fibers are aligned in pseudo-unidirectional form in the composite. Such a comparable result with the thermal conductivity of carbon fiber reflects that the thermal conductivity values obtained for quasi-carbon fibers consisting of the pseudo-UD QC/P composites in this work are reliable. The thermal conductivity of quasi-carbon fiber is about 63~67 % lower than that of carbon fiber. It also increases at a slow heating rate to the final HTT. This is because well-aligned aromatic structure can be formed in the longitudinal direction of the fiber during quasi-carbonization process at a slower heating rate, which allows a longer period of heat-treatment time.

Figures 5 and 6 represent the thermal expansion and contraction behavior in the (a) transverse and (b) longitudinal directions for pseudo-UD and 2D composites reinforced with stabilized PAN fibers, quasi-carbon fibers, and commercial carbon fibers, respectively. Comparing the dimensional changes against temperature, the results obviously show that the transverse thermal expansion is much greater than the longitudinal one. The reason for that is that the thermally stable aromatic structure with ordered alignment has been developed along the fiber axis (in the longitudinal direction) during heat-treatment. Also, there are a number of matrix resin layers between the interplies through the thickness (in the transverse direction) of the composite. It is generally found that the thermal expansion of phenolic matrix resin is much greater than that of carbon fiber or quasi-carbon fiber.

The result also indicates that the thermal expansion of

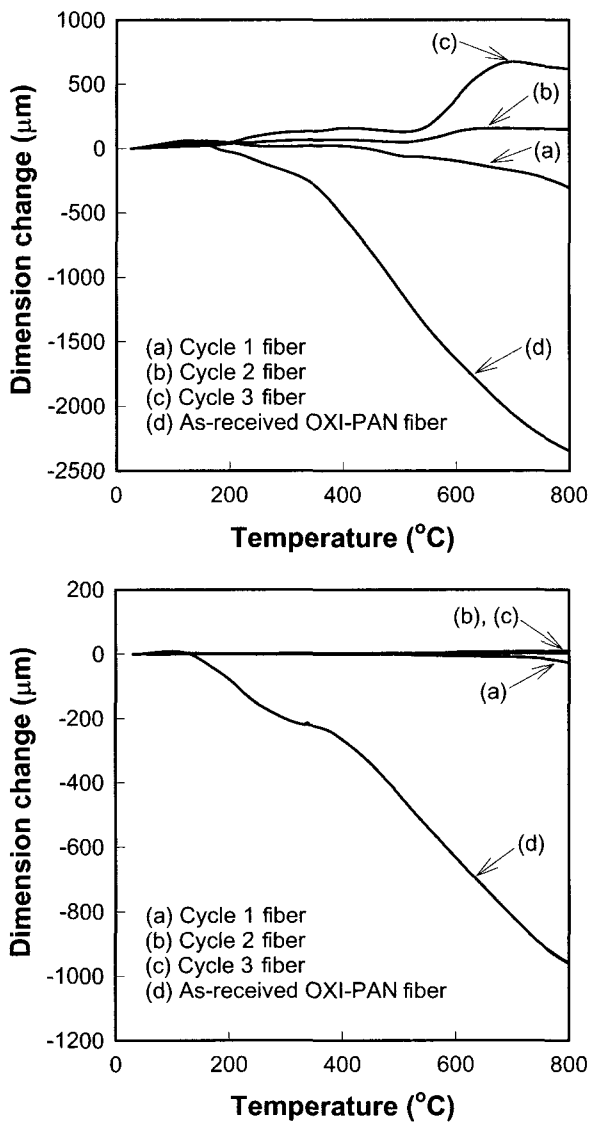


Figure 5. Thermal expansion and contraction behavior observed in the transverse (top) and longitudinal (bottom) directions for pseudo-UD composites.

pseudo-UD composites is much smaller than that of 2D composites. Especially, above 500 °C, the thermal expansion of woven 2D composites is greater than that of pseudo-UD counterparts. This is mainly because the matrix region located not only between the interplies in the 2D composite but also between the intersections of warps and fills in the fabric is more thermally expanded than the reinforcing fiber region. It is believed that the matrix layers in the pseudo-UD composite are uniformly distributed in the fibers without considerable intersections by warps and fills or resin-rich spots so that the thermal expansion is more or less restricted.

In the case of 2D C/P composite seen in Figure 6(e), the thermal expansion below 500 °C is very low and similar with that of pseudo-UD QC/P. However, it largely expands above

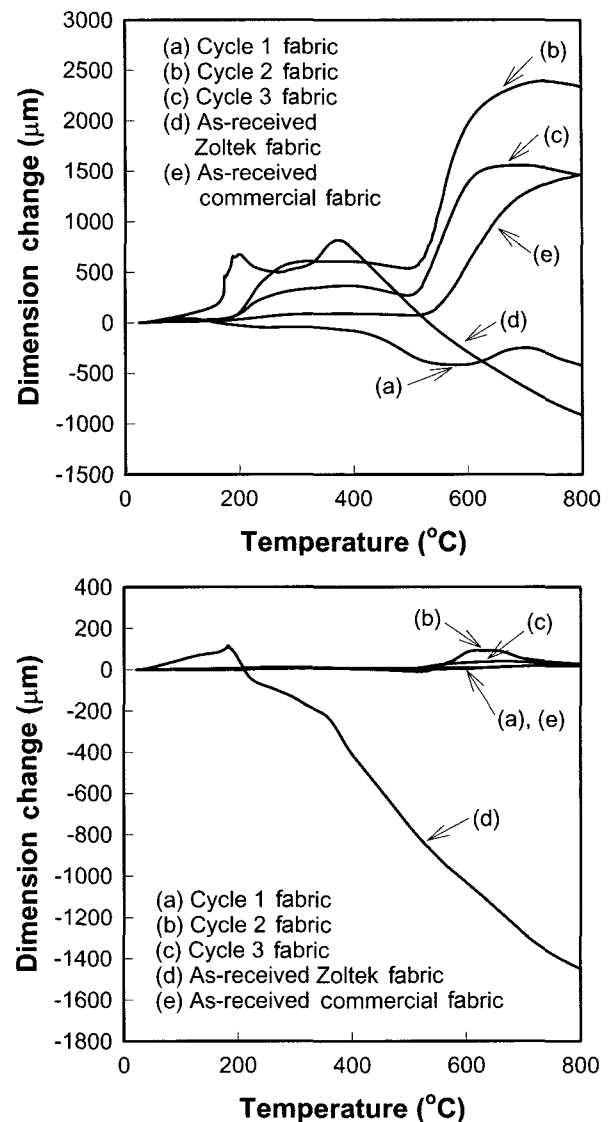


Figure 6. Thermal expansion and contraction behavior observed in the transverse (top) and longitudinal (bottom) directions for 2D composites.

500 °C. It means that the thermal expansion above 500 °C is due predominantly to the phenolic matrix because the commercial carbon fibers do not expand in the temperature range of the TMA measurement performed. Therefore, it is concluded that the matrix part in the composite is most responsible for the thermal expansion above 500 °C. The thermal expansion behavior of a composite reinforced with stabilized OXI-PAN fibers is quite different from that of other composites. The hump-like peaks or a shoulder in the temperature range below about 400 °C observed for the 'as-received' Zoltek fabric (curve d) in the top of Figure 6 may be ascribed to the evaporation of volatiles and the pyrolysis of stabilized OXI-PAN fiber. The volatile compounds of low molecular weight in the stabilized OXI-PAN fiber are removed

in the range of 200 °C~400 °C. As a result, the fiber markedly contracts both in the transverse and longitudinal directions. It has been reported earlier [10] that the thermal contraction of the fiber causes a significant weight loss of about 40~45 %. Such the contraction is normally greater than the degree of thermal expansion of phenolic matrix. Therefore, the composite exhibits the negative dimensional change having a negative coefficient of thermal expansion (CTE), as seen in Figures 5 and 6.

In the pseudo-UD and 2D QC/P composites reinforced with quasi-carbon fibers processed by Cycle 1, the quasi-carbon fibers may contain some unreacted or volatile components remaining even after quasi-carbonization process since the heating rate of 100 °C/h to 1075 °C in the Cycle 1 is relatively high. Therefore, the composite specimen may undergo additional contraction due to the unreacted components remaining in the fiber. In addition, the thermal expansion of phenolic matrix occurs competitively below 500 °C. It is likely that above 500 °C the degree of fiber contraction is slightly greater than that of matrix expansion. In the pseudo-UD and 2D QC/P composites reinforced with quasi-carbon fibers by Cycle 3, the thermal expansion below 500 °C is likely to be relatively small. This is because the additional fiber contraction may be compensated by the matrix expansion. However, as seen in the top of Figure 6, the thermal expansion behavior above 500 °C predominantly relies on the phenolic matrix in the 2D QC/P composite.

In the longitudinal measurements for 2D and pseudo-UD QC/P composites in the bottom of Figures 5 and 6, the thermal expansion and contraction do not take place significantly, with the exception of the composites composed of stabilized OXI-PAN (curve d in Figure 5) and Zoltek (curve d in Figure 6) fabrics without heat-treatment. It seems that the longitudinal thermal expansion due to the phenolic matrix in the composite may not be significant, considering the very low dimensional

change above 500 °C.

Table 3 summarizes the coefficients of transverse thermal expansion for 2D and pseudo-UD composites reinforced with 'as-received' stabilized fabrics, with quasi-carbon fibers and fabrics processed at different quasi-carbonization cycles, and with a commercial carbon fabric, respectively. The CTE was measured in three different temperature regions of expansion behavior: low temperature (room temperature to 200 °C), intermediate temperature (200 °C to 500 °C), and high temperature (500 °C to 700 °C). The result provides useful quantitative information on understanding the thermal expansion and contraction behavior of a variety of the pseudo-UD and 2D composite materials described in detail earlier.

The CTE values of the composites measured in the transverse direction are more largely varied in three temperature regions than those in the longitudinal direction due to the greater contribution of the phenolic matrix in the composite to their thermal expansion behavior. In the low temperature region below 200 °C, the phenolic matrix composing of the composite is thermally and dimensionally stable, but the stabilized fibers or fabrics therein are somewhat less stable accompanying additional chemical reaction in this temperature region. The quasi-carbon/phenolic and carbon/phenolic composites are quite stable having low CTE values. In the temperature region between 200 °C and 500 °C, the phenolic matrix in the composite begins to decompose. The stabilized fiber reinforcement is much less stable with the applied heat, showing a large change in the thermal expansion behavior with negative CTE value, because the temperature in this region is normally higher than heat-treatment temperature (200 °C~250 °C) for stabilization. The quasi-carbon/phenolic composites show some thermal expansion or contraction depending on the applied cycle for quasi-carbonization, due to combined effect between the phenolic matrix and quasi-carbon fiber or fabric consisting of the composite, which both are subject to be influenced by the exposed temperature. In the temperature region between 500 °C and 700 °C, the phenolic matrix is pyrolyzed and largely expanded. The CTE values of quasi-carbon/phenolic and even carbon/phenolic composites become greater due to the phenolic matrix effect depending on the applied cycle. The stabilized fiber/phenolic composites exhibit large negative CTE value because the fibers therein are also pyrolyzed in the temperature and largely shrunk. It is, of course, expected that there is a combined effect between the matrix with positive CTE and the stabilized fabric with negative CTE in the composite. The detail description is also referred to the explanation on the expansion behavior in Figures 5 and 6 earlier.

Conclusions

Comparing the thermal conductivity and thermal expansion behavior of a variety of phenolic composites reinforced with stabilized OXI-PAN fibers, quasi-carbon fibers, commercial

Table 3. A summary of the coefficient of thermal expansion (CTE) in three temperature regions measured in the transverse direction for pseudo-UD and 2D composites reinforced with different fibers and fabrics

Composite	R.T. to	200 °C to	500 °C to
	200 °C	500 °C	700 °C
	($\mu\text{m}/\text{m} \cdot ^\circ\text{C}$)	($\mu\text{m}/\text{m} \cdot ^\circ\text{C}$)	($\mu\text{m}/\text{m} \cdot ^\circ\text{C}$)
Stabilized Zoltek fabric	391	-26	-394
Stabilized OXI-PAN fabric	-9	-359	-470
Commercial Carbon fabric	15	10	733
Cycle 1 fiber	27	26	348
Cycle 2 fiber	34	-21	-61
Cycle 3 fiber	18	5	67
Cycle 1 fabric	-18	-72	81
Cycle 2 fabric	40	97	1350
Cycle 3 fabric	41	48	931

carbon fibers, and their fabrics, we have concluded the results as follows.

Use of quasi-carbon fibers or fabrics importantly contributes to reducing the thermal conductivity of a carbon fiber/phenolic composite, depending on quasi-carbonization processes. The contribution to the reduction in the transverse direction of reinforcing fiber in a composite is greater in the pseudo-UD composite than in the 2D composite. The longitudinal contribution is greater in the 2D composite than in the pseudo-UD composite. The pseudo-UD composites reinforced with quasi-carbon fibers exhibit 30~40 % lower transverse and longitudinal thermal conductivities than that with commercial carbon fibers. The thermal conductivities of 2D QC/P composites are 20~30 % lower in the transverse direction and 40~50 % lower in the longitudinal direction. Also, it has been estimated that the thermal conductivity of quasi-carbon fiber is about 63~67 % lower than that of commercial carbon fiber.

The thermomechanical results inform that in both pseudo-UD and 2D composites the transverse thermal expansion is much greater than the longitudinal one and the thermal expansion of pseudo-UD composites is much smaller than that of 2D counterparts, especially above 500 °C. In the C/P composite, the phenolic matrix part is most responsible for the thermal expansion above 500 °C. However, in the QC/P composite, it is noted that some additional contraction of quasi-carbon fibers may be compensated by the matrix expansion since above 500 °C the degree of fiber contraction is slightly greater than that of matrix expansion.

Consequently, the present study suggests that use of proper quasi-carbonization process may control effectively not only the chemical compositions of resulting quasi-carbon fibers but also the thermal conductivity and thermal expansion behavior of quasi-carbon fibers/phenolic composites in the intermediate range between stabilized PAN fiber- and carbon fiber-reinforced phenolic composites.

Acknowledgement

This work has been supported by research fund from the Agency for Defense Development (ADD) in 2001.

References

1. J.-B. Donnet, T. K. Wang, J. C. M. Peng, and S. Rebouillat Eds., "Carbon Fibers", 3rd ed., Marcel Dekker, New York, 1998.
2. D. L. Schmidt and R. D. Craig, "Advanced Carbon Fabric/Phenolic for Thermal Protection Applications", *AFWAC-TR-81-4136*, AFWAL (1982).
3. D. Cho and B. I. Yoon, *Comp. Sci. Tech.*, **61**, 271 (2001).
4. A. B. Strong, "Fundamentals of Composites Manufacturing: Materials, Methods, and Applications", Chap. 9, SME, Dearborn, 1989.
5. A. Gardziella, L. A. Pilato, and A. Knop, "Phenolic Resins", Springer-Verlag, Berlin, 2000.
6. G. Pan, N. Muto, M. Miyayama, and H. Yanagida, *J. Mater. Sci.*, **27**, 3497 (1992).
7. H. A. Katzman, P. M. Adams, T. D. Le, and C. S. Hemminger, *Carbon*, **32**, 379 (1994).
8. L. R. Zhao and B. Z. Jang, *J. Mater. Sci.*, **30**, 4535 (1995).
9. D. Cho, Y. Choi, J. K. Park, and J. Y. Lee, *Polym. Sci. Tech.*, **11**, 717 (2000).
10. D. Cho, Y. Choi, and J. K. Park, *Polymer (Korea)*, **25**, 575 (2001).
11. J. K. Park and T. J. Kang, *Carbon*, **40**, 2125 (2002).
12. J. K. Park, D. Cho, and T. J. Kang, *Carbon*, **42**, 795 (2004).
13. J. K. Park, Ph. D. Dissertation, Seoul National University, Seoul, 2002.
14. A. K. Gupta, D. K. Paliwal, and P. Bajaj, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **C31**, 1 (1991).
15. D. D. L. Chung, "Carbon Fiber Composites", Chap. 6, Butterworth-Heinemann, Boston, 1994.
16. N. L. Hancox and R. M. Mayer Eds., "Design Data for Reinforced Plastics", Chap. 7, Chapman & Hall, London, 1994.