論文

Thermal Anisotropy Factor of Mesophase Pitch-based C-type or Hollow Carbon Fibers Reinforced Composites

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메조페이스 핏치계 C형 및 중공형 탄소섬유 강화복합재의 열이방성 계수

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ABSTRACT

A comparison was conducted of the thermal conductivity; anisotropy factor and diffusivity ratio of unidirectional mesophase pitch-based round, C-type and hollow carbon fibers reinforced epoxy composites. Their thermal conductivities parallel and perpendicular to the reinforcing fibers were measured by means of steady-state method. It was found that the thermal conductivity greatly depended on the cross-sectional form of the reinforcing fibers. Especially, the anisotropy factors ($\kappa_{\parallel}/\kappa_{\perp}$) of C-type and hollow carbon fibers reinforced composites revealed about two time higher values, 110-130, than those of round carbon fiber reinforced ones, which showed about 44-55. also their thermal diffusivity factors ($\alpha_{\parallel}/\alpha_{\perp}$) showed higher values, about 7-8, than those of round carbon fiber reinforced ones which have about 6.

초 록

메조페이스 핏치계 일방형(UD) 원형, 중공형, C형 탄소섬유 강화 에폭시 복합재가 가열 가압법에 의해 제조하여, 강화섬유의 축(0°) 방향과 횡방향(90°)의 상호 열전도도를 정상 상태법에 의해 측정하였으며, 또한 이들의 열이방성계수 그리고 열확산 계수를 비교하였다. 그 결과 강화섬유 단면형상에 크게 의존하였다. 특히, C형과 중공형 탄소섬유 강화 복합재의 열이방성계수가 원형 강화재의 경우, 45~55에 비해 약 2배, 110~130를 나타냈다. 그들의 열확산도 또한 중공과 C형 강화인 경우, 7, 8로 원형, 6보다 다소 큰값을 보였다.

1. Introduction

Carbon materials(carbon film, carbon fiber, C/C-composites) have been known to possess an excellent thermal conductivity[1]. Sometimes they require a high directional thermal conductivity to distribute heat and to insulate rocket nozzles or nose cones[2]. One of the carbon materials is quasi-crystalline pyrolytic carbon which shows very high anisotropy factor, about 1250[3]. But, it is difficult to use as thermal structural materials due to process problem. Among the carbon materials with easy preparation process, it is carbon fiber that has thermal property and can be made

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structural materials. Especially, a graphitizable pitch-based carbon fiber also reveals very high anisotropic characteristics and is used as ablative materials of aerospace nose cone, rocket nozzles and so on. The thermal conductivity as well as the mechanical properties of the fibers reinforced composites greatly depend on the micro molecular orientation controlled by precusors and cross-sectional geometry or the cross-section structures of the reinforcements[4]. Therefore it may be possible to control the thermal conductivity according to the direction of the reinforcement through the macro-modification of fiber form or fiber micro-textures. In the previous researches[5] we were able to produce C- and H-CF in the laboratory scale and obtained the result that their mechanical properties were more excellent than that of R-CF[6]. It was shown that H-CF has an excellent flexibility and that C-CF offers better reinforcing effects for the matrix precursor than that of R-CF[7]. Particularly, H-CF/EP-composite has a lower density because numerous holes in H-CF/EP system are kept intact[7]. It is expected that the deformation of the reinforcing fiber will show a high anisotropic property and, thus use for cooling the mini-component of electronic parts.

So the concerns of this research are to examine the charateristics of heat transfer for mesophase pitch-based round, hollow or C-type carbon fibers reinforced composite materials. Finally, this paper will also describe the future prospects of hollow carbon fibers.

2. Experimental And Materials

The reinforcements used were carbon fibers which are produced as coal tar pitch converted into mesophase pitch[8~10]. The fiber forming conditions and appearances were shown in Table 1.

Table 1. Fiber forming conditions and its appearence

Fibers	Treat Temperature, ℃			Diameter, μm	Thickness, μm
	Spinning	Stabilization (Holding time)	Carbonization		
H−CF	315± 5	295(40)	1000	45± 3.2	12± 1.4
C−CF	318± 5	295(40)	1000	32± 4.0	10± 0.7
R−CF	318± 5	295(40)	1000	18± 2.6	18± 2.6

These procedures and methods were already patented by one of the authors. The matrix used in this research was epoxy resin produced by Kook-Do Chem, Co., in Korea which has a bi-functional group. At first, we prepared prepregs with these carbon fibers and epoxy resin. These prepregs were cut and laid unidifrectionally into a mold which has a dimension of 6×3×1(cm). The system of fiber and matrix was pressed and cured under 45[kg/cm^2] pressure for 1 hour at 80℃ and 150℃, respectively by a hot press technique described previously[11]. The sample for the measurement of thermal conductivity was a disk of 2.5cm in diameter and 0.5mm in thickness. The mass fraction of carbon fiber in the composites was 0.15, 0.35 or 0.45, although higher carbon fiber content in the CFRP was possible.

The principle of the measurement is based on the heat transfer of Fourier's law. The instrumentation for measuring the thermal conducitivity provides accurate measurement of temperature and power supply as a steady-state method. Fast response temperature probes(thermocouples), with a resolution of 0.1℃, give direct digital readout in ℃. The power control circuit provides a continuously variable electrical output of 0~100 Watts with direct readout[12]. The measurements of the thermal conductivity were made on a cylindrical sample of 2.5cm in diameter and 0.5mm in thickness at the temperature range of 40℃ to 120℃. The calculations of thermal conductivity, specific heat and thermal diffusivity values follow the equations below :

$$\kappa = \frac{q \cdot t}{A\,(T_2 - T_1)} \quad \cdots\cdots\cdots\cdots\cdots (1)$$

$$C_p = \frac{-q}{m\Delta T} \quad \cdots\cdots\cdots\cdots\cdots (2)$$

$$\alpha = \frac{\kappa}{C_p \cdot \rho} \quad \cdots\cdots\cdots\cdots\cdots (3)$$

κ : Thermal conductivity
A : Area of heat conduction
$T_2 - T_1$: Temperature difference between heating and cooling part
t : Sample thickness
C_p : Specific heat
m : Sample weight
ρ : Sample density
α : Thermal diffusivity,
ΔT : Temperature differences at steady-state
q : Watts applied

3. Results And Discussion

3-1. Characteristics of the hollow and C-type carbon fibers reinforced epoxy composites(H-CF/EP and C-CF/EP)

In structural mechanics, as the optimization of the stress distribution of a material, design engineer found out that tube or non-circular(for example, I-beam) shape is more available than solid(round) one in the mechanical and other properties. In this section, we mentioned about the mechanical properties of the epoxy composites reinforced with isotropic round-type, C-type or hollow-type carbon fibers at 70 wt%. And the reinforcing effects of pitch-based isotropic hollow-type of C-type carbon fibers were studied as comparing to typical round-type carbon fibers. All specific mechanical properties of the composites reinforced with three types of isotropic pitch-based carbon fibers are collected in Fig. 1 : flexural

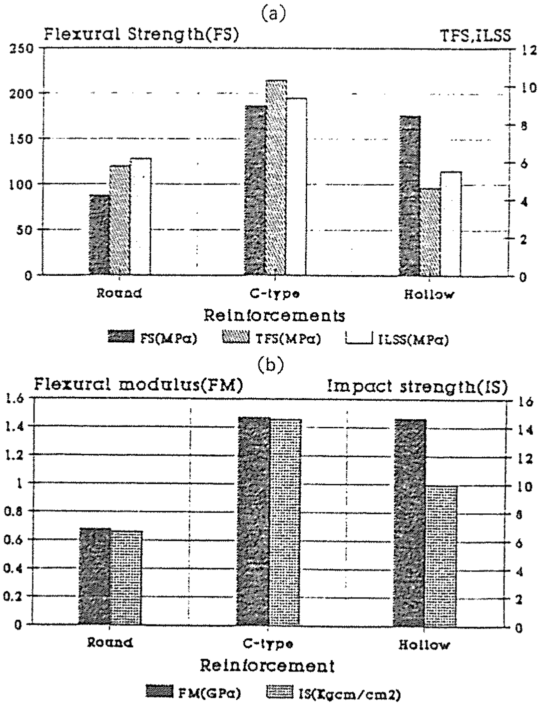


Fig. 1. Specific properties of the composites reinforced with three types of isotropic carbon fibers.

strength(FS), flexural modulus(FM), interlaminar shear strength(ILSS), transverse flexural strength(TFS) and impact strength(IS) of R-CF/EP, C-CF/EP and H-CF/EP composites. C-CF/EP composite shows the highest values in all mechanical properties, while R-CF/EP the lowest values.

This is due to wider interficial contact area between reinforcement and matrix which can effectively transfer the applied stress. That is, when the open degree and the ratio of equivalent outside to equivalent inside diameter, $d_2/d_1 = \xi$, of C-type carbon fiber are 90° and 1.25, respectively, the theoretical contact surface ratio between the C-type carbon fiber and the matrix is 2.72[12].

Fig. 2 shows scanning electron microphotos (SEM) of cross-sectional and longtudinal fracture surfaces in the three types of carbon fibers reinforced composites. From three photos of cross-sectional fractures on the left, we can easily see that the matrix phase around these fibers was impartially contributed and had a good wettability. Especially, we can see that holes in the H-CF/EP composites(a) were hardly filled which gives the resistanace to heat transfer. And Fig. 2(c) shows the fracture surfaces of the fiber sides and matrix sides of C-CF/EP system. With this texture observation we can expect a special mechanical property and better insulation(thermal resistance wall) of heat transfered from the matrices in the direction perpendicular to the reinforcements. These phenomena are inferred from the fact that the contact surface of C-type carbon fiber is greater than that of round or hollow-type fiber. The above mechanical properties are the results for only isotropic pitch-based carbon fibers reinforced composites. The results of mesophase pitch-based hollow and C-type fibers could be inferred from the above results. That is to say, mesophase pitch-based hollow and C-type carbon fiber can simultaneously possess the merits of microtexture (better molecular orientation along the fiber axis) as well as macrostructure(shapes of the fibers), which contribute to both improved mechanical properties and thermal conductivity.

3-2. Thermal properties of the composites

High thermal conductivity materials are very

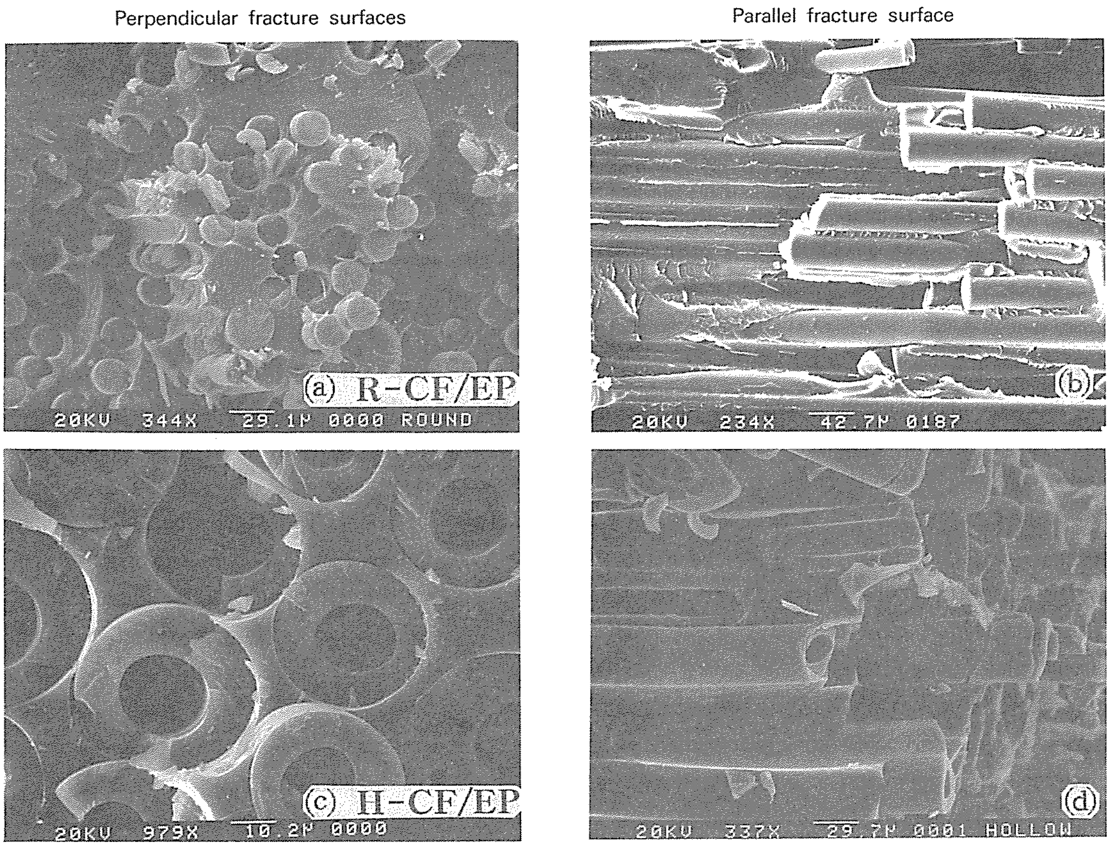
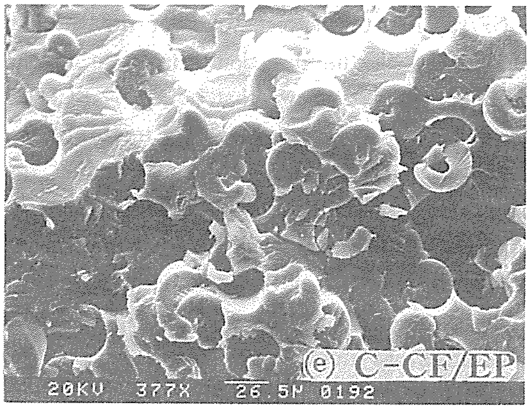
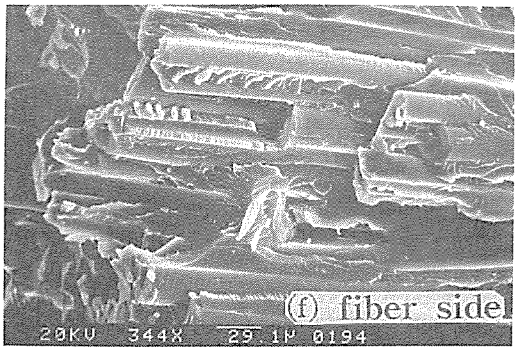


Fig. 2. Fracture surface of epoxy composites with three types of isotropic carbon fibers[13].

Parallel fracture surface



Perpendicular fracture surfaces



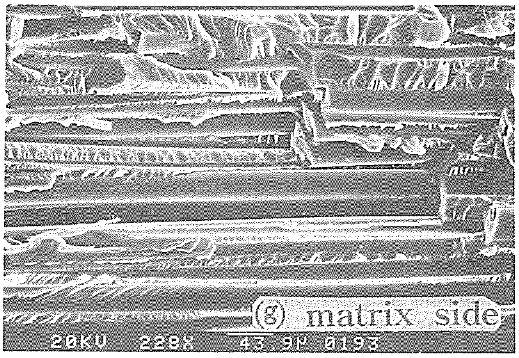


Fig. 2. (Continued)

important in system where high heat loads must be managed(transported or dissipated). High specific thermal conductivity materials are critical in many applications to minimize weight and volume. One of them is the composite material with high thermal conductivity fibers. The growing needs for materials dedicated to thermal management applications has led to the design of new composite materials. Indeed, with appropriate combination of selected matrices and reinforcements, it is now possible to tailor composite materials with almost the desired thermal conductivity as to the fiber direction. That is, it is possible to put the greater difference between parallel and perpendicular to the fiber direction than that of typical fiber reinforced one. These materials are the same composites reinforced with hollow-type or C-type carbon fibers. In this section, it is investigated how thermal transfer characteristics of

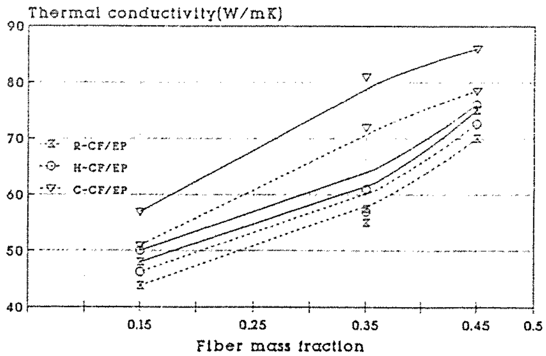


Fig. 3(a). Thermal conductivity in the direction perpendicular to the reinforcement according to fiber mass fraction, measuring temperatures and fiber types. dotted line (……) : 40℃, solid line(——) : 120℃.

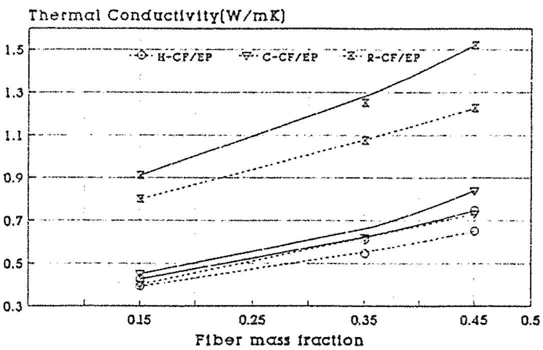


Fig. 3(b). Thermal conductivity in the direction perpendicular to the reinforcement according to fiber mass fraction, measuring temperatures and fiber types. dotted line (……) : 40℃, solid line(——) : 120℃.

the fibrous composites are effected by fiber cross-sectional shapes.

As the mechanical properties of the fiber reinforced composites depend on the fiber shapes and the fiber contents, the thermal conductivity also shows the same tendency, as shown in Fig. 3 (a, b).

From the figure we can see that thermal conductivities of the composites depend on the three parameters, ① measuring temperature, ② fiber contents and ③ their cross-sectional forms. Our interests are forcused on the anisotropy factor of the carbon fibers reinforced composites. C-CF/EP has the highest value of the thermal conductivity in the direction parallel to the fiber, $\kappa_{\parallel}$, while H-CF/EP has the lowest value of the thermal conductivity in the direction transverse to the fiber, $\kappa_{\perp}$. Fig. 4 shows that holes in H-CF/EP are still intact. The cross-sectional texture is the radial-folded structure toward centerline of the fiber. This structure is induced during spinning anisotropic pitch. It is found that these line-origin structures have higher thermal conductivity than radial or onion structure. So, it is inferred that H-CF itself has a developed molecular orientation along the fiber axis based on the center line which is in accord with the heat transfer.

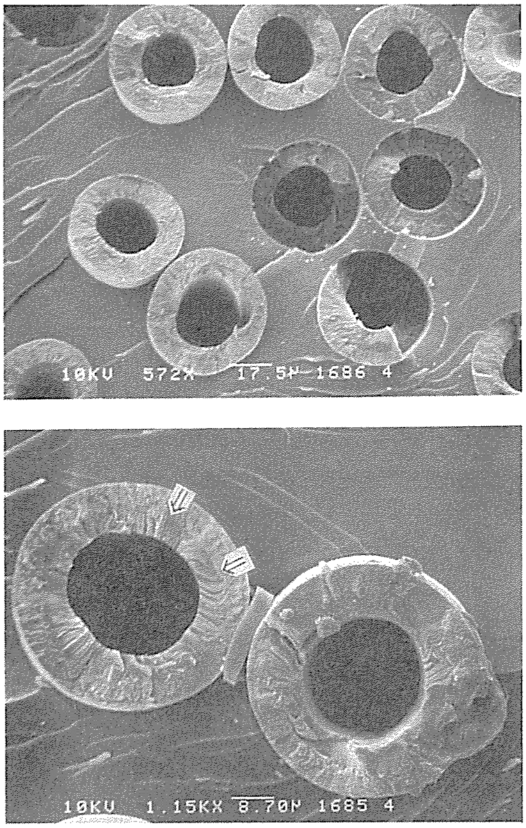


Fig. 4. Fracture surface of mesophase pitch-based hollow carbon fiber reinforced epoxy composites. Note the microstructure centering around center line.

So we can expect a high anisotropy factor from these two composites. The differences between $\kappa_{(\parallel),120}$ and $\kappa_{(\parallel),40}$ of C-CF/EP were relatively larger as compared with those of R-CF/EF and H-CF/EP, while the differences between $\kappa_{(\perp),120}$ and $\kappa_{(\perp),40}$ of R-CF/EP were larger than that of C-CF/EP and H-CF/EP. That means simply that the higher thermal conducitivity has the higher temperature effect. Fig. 5(a) shows anisotropy factor of the composites as a function of temperatures. At first we can see that C- and H-CF/EP have higher anisotropy factor than that of R-CF/EP. All composites have the decreasing thermal anisotropy factors with increasing temperature, because the thermal conductivities of the composites in the direction transverse to the reinforcements were more increasing with increasing temperature. As the more dependency of carbon fiber content than that of temperature difference on the thermal conductivity, the same tendency on the thermal anisotropy factor is shown in Fig. 5(b). The actual difference between C-CF/EP or H-CF/EP and R-CF/EP shows more than two times. The highest factor of C-CF/EP was 130, the lowest one of R-CF/EP was 45.

In order to calculate the thermal diffusivity, specific heats of the composites were required.

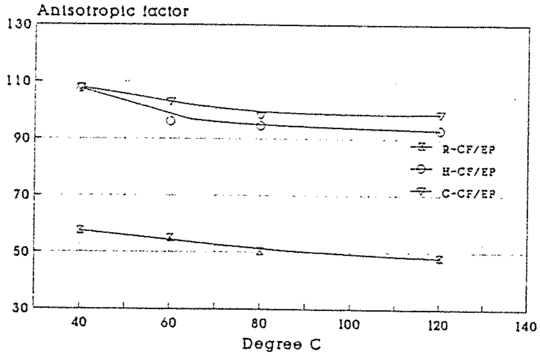


Fig. 5(a). Thermal anisotropy factor as measuring temperatures and fiber types.

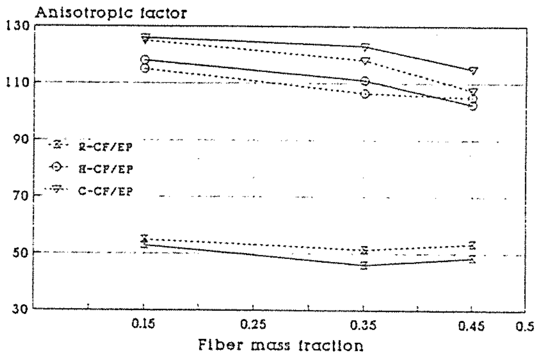


Fig. 5(b). Thermal anisotropy factor as fiber mass fractions, measuring temperatures and fiber types. dotted line(……) : 40℃, solid line(——) : 120℃.

Fig. 6 shows the specific heat of transverse direction, $C_{p(\perp)}$, in three different types of composites. All specific heats are increasing with temperature and show somewhat difference between R-CF/EP and the others (C-CF/EP and H-CF/EP). R-CF/EP has about 8×10^{-2} [J/kg·℃], while H-CF/EP and C-CF/EP, about 5×10^{-2} [J/kg·℃].

These results can be expected because the specific heat of hollow of C-type fiber able to be easily approached to graphite structure by wall shear stress of the spinnerette during spinning a mesophase pitch is less than that of round carbon fiber. In general, the direction of the graphite basal plane(c-axis) has lower specific heat than that of the a-axis[14].

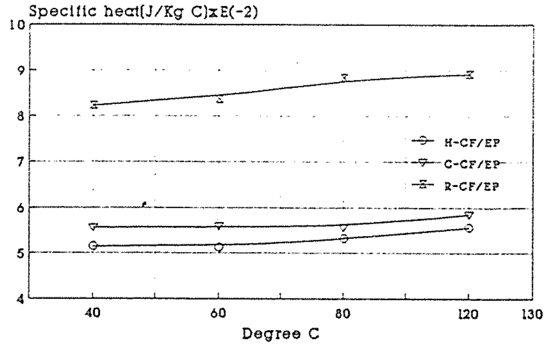


Fig. 6. Specific heat of the three types of composites reinforced with round, C-type or hollow cross-section, respectively.

Fig. 7 shows thermal diffusivity ratio, $\alpha_{(\parallel)}/\alpha_{(\perp)}$, as a function of temperature, which shows slow increase with temperature. That is due to the more sensitive thermal diffusivity parallel to the reinforcement than that of perpendicular direction as to a measuring temperature. That is, it is determined as the effect of the fiber orientation(macrostructure). C-CF/EP and H-CF/EP have similar diffusivity, and R-CF/EP has relati-

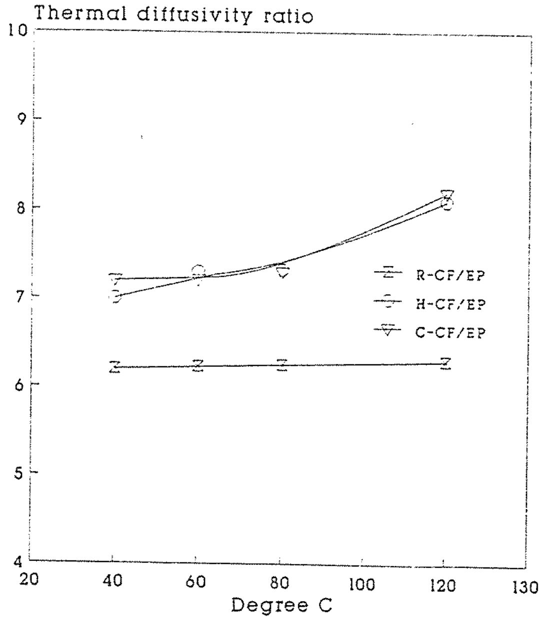


Fig. 7. Thermal diffusivity ratio versus measuring temperatures in 45wt% fiber reinforced composites.

vely lower diffusivity than that of non-circular fiber reinforced composites. Also the increasing rate of H-CF/EP and C-CF/EP is somewhat greater than that of R-CF/EP due to the microstructure of the fibers.

In general, thermal diffusivity ratios of C- and hollow-type fibers reinforced composites were 0.8 to 1.8 greater than that of round cross-sectional carbon fiber reinforced one. For three types of composites, the major contributing factor for the higher thermal diffusivity ratio is that the axis of hollow and C-type carbon fibers comparing with that of round carbon fiber coincides with the graphite basal plane which as indicated by corresponding data for pyrolytic graphite coincide with the direction of maximum thermal conductivity or diffusivity in the graphite crystal structure. Especially C-CF/EP shows a high increasing tendency with increasing temperature due to its high anisotropic factor. The reason was that C-shape has the hollowed-out surface area along the axis which offers greater contact area with matrix, and greater resistance to the heat transfer perpendicular to the reinforcements.

4. Conclusion

The thermal conductivity of carbon fibers reinforced composites greatly depends on the cross-sectional form of the fibers. Particularly, C-shaped carbon fiber reinforced composite showed the highest thermal conductivity in the direction parallel to the fibers and low conductivity in the direction perpendicular to the reinforcements. On the other hand, hollow carbon fibers reinforced composites showed a little higher conductivity than that of round carbon fiber reinforced composite, but the lowest conductivity in transverse direction. And C-CF/EP composite has the highest anisotropic factor, about 130 and H-CF/EP composite, about 120, while R-CF/EP composite the lowest factor, about 50, Like this C and H-CF/EP composites show also higher thermal diffusivity ratio than that of R-CF/EP composites.

As a result, an excellant mechanical strength and high thermal anisotropy factor of C-CF/EP and H-CF/EP could be applied as advanced materials of aerospaces and space shuttle, including thermal structural materials.

5. Future Prospects

The cross-sectional shapes like C-shape and hollow-shape carbon fibers can be tailored to maximize mechanical or other properties. The hollow carbon fibers embeded in the polymer matrix form oriented microchannels, which, like free-standing tubes, can contain solids, liquid, and gases, or act as conduits for all types of electromagnetic energy. When the holes of hollow fibers are filled with another type of material, it can become a sensor, detector, or an element in an electron multiplier. Depending on the application, the walls of hollow fibers can range from non-porous to extremely porous. Specific applications for hollow type fibers include composite reinforcement, heat exchanger, insulation, flow control, pinpoint lubrication, heat pipes, microprobes, plumbing for micromotors, optical wave guide, detector and so on.

Also, hollow-shape carbon fiber will provide the oppotunity to miniaturize numerous products and devices that are currently in existence, as well as allow the fabrication of products that have to data been impossible to product. For example , as electronic circuits become smaller and more compact, there is a greatly increased need for cooling on a microscopic scale. Hollow-shape carbon fiber can satisfy this need in the form of microscopic heat pipes or heat exchangers.

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