工學博士 學位論文

생체재료용 Carbon/PEEK 복합재료의 기계적 특성의 향상에 관한 연구

Improvement of Mechanical Properties of Carbon/PEEK Composites for Bio-Materials

指導敎授 金 允 海

2014年 1月

韓國海洋大學校 大學院

材 料 工 學 科

尹 晟 源

本 論文을 尹晟源의 工學博士 學位論文으로 認准함.

委員長 :	工學博士	文 慶 萬	(인)
委　員 :	工學博士	李 柄 雨	(인)
委　員 :	工學博士	裵 昌 原	(인)
委　員 :	工學博士	金 國 鎭	(인)
委　員 :	工學博士	金 允 海	(인)

2014年 1月

韓國海洋大學校 大學院

Contents

List of Tables -- iv

List of Figures -- v

Abstract -- viii

1. Introduction

1.1 Background -- 1

1.1.1 Artificial joint surgery -- 8

1.1.2 Patient-customized artificial joint ---------------------------------- 11

1.2 Purpose of Study -- 13

2. Introduction of Artificial Joint

2.1 History --- 20

2.2 Manufacturing --- 23

2.3 Market Trends --- 26

3. Materials and Experiment Method

3.1 Preparation of the Materials -- 30

3.2 Removal of Sizing --- 34

3.3 Moisture Absorption Theory -- 37

3.4 Specimens --- 39

3.5 Experiment Method -- 43

4. Results and Discussion

4.1 Effect of Sizing Removal -- 49

4.1.1 Mechanical properties -- 49

4.1.2 Fracture surface -- 56

4.2 Behavior of Moisture Absorption -------------------------------------- 63

4.2.1 Mechanical properties -- 67

4.2.2 Fracture energy -- 68

4.2.3 Fracture surface -- 72

4.3 Friction and Wear Behavior --- 76

4.3.1 Tribological properties --- 76

4.3.2 Fracture surface -- 83

4.4 Finite Element Analysis -- 90

4.4.1 Design and modeling method -------------------------------------- 90

4.4.2 FEA models and load --- 96

4.4.3 Principal stress -- 98

4.4.4 Shear stress -- 104

5. Conclusion -- 107

References --- 112

List of Tables

Table 1 International comparison of the speed of population aging --------- 4

Table 2 Properties of fiber and resin for tests ----------------------------------- 31

Table 3 Standard of shape for femur --- 91

Table 4 Mechanical properties of carbon/PEEK composites ----------------- 94

Table 5 Details of the meshes for models --------------------------------------- 97

List of Figures

Fig. 1	World population prospects --	3
Fig. 2	Life expectancy (over the age of 65) --------------------------------	5
Fig. 3	The aging of the major advanced country in 2040 -----------------	6
Fig. 4	Elderly population rate --	7
Fig. 5	Various operation cases ---	10
Fig. 6	Artificial joint --	10
Fig. 7	Artificial hip joint --	18
Fig. 8	Plane for manufacturing of stem -------------------------------------	19
Fig. 9	The problem of artificial hip joint and solution --------------------	24
Fig. 10	A step of development for artificial hip joint ----------------------	25
Fig. 11	The medical device market --	28
Fig. 12	Korea market of artificial joint ---------------------------------------	29
Fig. 13	Manufacturing method of PEEK film --------------------------------	32
Fig. 14	Images of carbon fiber and PEEK film -----------------------------	33
Fig. 15	SEM images of carbon fiber ---	35
Fig. 16	Degradation mechanism of composites by moisture absorption -	38
Fig. 17	Curing conditions for specimen preparation -----------------------	40
Fig. 18	Ply configuration for carbon fiber -----------------------------------	41
Fig. 19	Shape of specimens for friction and wear test ----------------------	46

Fig. 20 Images of method for each test -- 47

Fig. 21 Result of the mechanical strength according to sizing removal -- 51

Fig. 22 Result of the mechanical strength according to fiber ply orientation -- 54

Fig. 23 SEM observations -- 58

Fig. 24 SEM observations -- 61

Fig. 25 Moisture absorption behavior according to immersion time ----- 65

Fig. 26 Change of mechanical strength by moisture absorption ----------- 66

Fig. 27 The S-S curve of the composites ------------------------------------ 70

Fig. 28 Fracture energy for carbon/PEEK composites ---------------------- 71

Fig. 29 SEM observations -- 73

Fig. 30 Effect of ply configuration on friction coefficient ----------------- 78

Fig. 31 Effect of sliding velocity and pressure on friction coefficient ---- 82

Fig. 32 SEM observations -- 84

Fig. 33 SEM observations -- 87

Fig. 34 Standard of shape for femur --- 92

Fig. 35 Design concept and load direction of the stem and Ti stem composites -- 93

Fig. 36 Meshed shape of the stem -- 95

Fig. 37 Principal stress by ply configuration --------------------------------- 100

Fig. 38 Principal stress according to load ------------------------------------ 102

Fig. 39 Shear stress for Ti --- 105

Fig. 40 Shear stress by ply configuration ------------------------------------ 106

생체재료용 Carbon/PEEK 복합재료의 기계적 특성의 향상에 관한 연구

Yoon, Sung Won

Department of Materials Engineering

Graduate School of Korea Maritime and Ocean University

Abstract

The purpose of this study is to determine the correct estimation of the mechanical properties of carbon/PEEK composites and its validity has been tested with the alternative materials of the metal-based materials for artificial hip joint.

This study evaluated the mechanical properties according to the temperature of heat treatments for the sizing removal of carbon fiber and the fiber ply orientation.

First, the sizing removal of carbon fiber were conducted at 300℃ for 4 hours and 400℃ for 2 hours respectively. The fractured surface in the specimen of tensile test made from PEEK and epoxy resin was observed by SEM. The fracture surface of the tensile test specimen of the carbon/epoxy

composites heat-treated to 400℃ showed that the resin did not adhere nearly in the fiber surface and pull out was observed. It is considered that 400℃ is suitable heat treatment temperature for the sizing removal of the carbon fiber. The mechanical test results represent that there was no significant differences in short beam strength. However, the tensile strength and compressive strength of the carbon/PEEK composites were higher than those of the carbon/epoxy composites in the case of the vacuum bag process. Furthermore, this result indicated that the sizing material did not have a significant effect on the strength of the carbon/PEEK composites.

Second, the specimens for the carbon/PEEK and carbon/epoxy composites were manufactured based on the ASTM standard. The specimens were immersed in distilled water at 37℃ for 100 days and the coefficient of moisture was measured in accordance with Fick's law. Moreover, the fracture energy according to the fiber ply orientation was evaluated in this study. The result exhibited that the coefficient of moisture-absorption of carbon/PEEK composites was the lowest because the interface coherence between the fiber and resin are the strongest. As a result, the fracture energy of the carbon/PEEK composites was superior to the carbon/epoxy composites.

Third, the effect of Carbon/PEEK composites on the tribological properties has been investigated. The unidirectional composites had higher friction coefficients than those multidirectional composites. This was caused by the debonding between the carbon fiber and the PEEK sheet, which was

proportional to the contact area between the sliding surface and the carbon fiber. The friction test results showed that there was no significant differences in relation to the fiber ply orientation. However, the friction properties of the carbon/PEEK composites were higher than those of the carbon/epoxy composites. As a result, it seemed that when the carbon/PEEK composites slid in a direction normal to the prepreg lay-up direction, its friction coefficient may be represented a smaller value compared to sliding in a direction parallel to the prepreg lay-up direction. In a case where the speed was 2.5 m/s, the friction coefficient was relatively large for configuration I. The friction surface of the specimen was analyzed using an electron microscope. In all cases, the debonding of the fiber and PEEK could be confirmed.

Finally, it is suggested that a new concept design of the stem and aims to determine the suitability of various carbon/PEEK composite should be designed for artificial hip joints. Shear stress and principal stress tested with alternative materials of the Ti-based stem for artificial hip joints. In addition, FEA is conducted according to the fiber ply orientation and the load condition for carbon/PEEK composites.

KEY WORDS: Artificial joint 인공관절; Carbon fiber 탄소섬유; Composites 복합재료; FEA 유한요소해석; PEEK 폴리에테르에테르케톤; Thermoplastic 열가소성 수지; Stem 스템.

1. Introduction

1.1 Background

In presently, the aged population ratio is globally enlarged. The aged population above 65 years old is about 7.4% of the total population according to "World Population Prospects" data of UN in 2005. The world population prospects were shown in Fig. 1. According to the statistics of UN, the aged population was expected to close in about 16.1% of the total population in 2050. The life expectancy over the age of 65 was shown in Fig. 2. [1]

In the case of Korea, beginning in 2000, the aged population above 65 years old exceeded 7% of the total population and Korea got into the real aging society. The aged population above 65 years old exceeded 14% and it was likely to enter the aged society in 2018. The period that the elderly population ratio reaches 14% from 7% is 18 years, and the period that the elderly population ratio reaches 20% from 14% is just 8 years. So, aging rate of Korea is faster than the aging rate which the advanced country experiences. The aging of the major advanced country in 2040 was shown in Fig. 3. The international comparison of the speed of population aging was shown in Table. 1. [2]

The geriatric disease including the senile dementia, cerebral hemorrhage, arthritis and etc. is naturally increased together according to the increase in the population of old people. The elderly population rate was shown in Fig. 4. In addition, the solution about the geriatric disease becomes the critical matter of the society because as the society develops, the desire for the quality of the life is increased. Particularly, the senile articulation disease in which the articular function is degraded due to the degeneration of the joint of arthritis of which loses the function is together increased. [3]

The artificial joint was developed in order to treat this senile articulation disease. In the human body, there are the various joints. There is the hip joint and shoulder, including the knee joint and finger joint and there is the articulationes vertebrales. The biological and the physical structure of these various kind joints and function is complicate and is not still understood completely. However, the use of artificial joint will be increased for the treatment of the arthritis, osteoporosis and fracture, increased inevitably according to the aging trend of the population. Therefore, engineering technology applied to the manufacture of the artificial joint and the improved problem need to be looked into. [4]

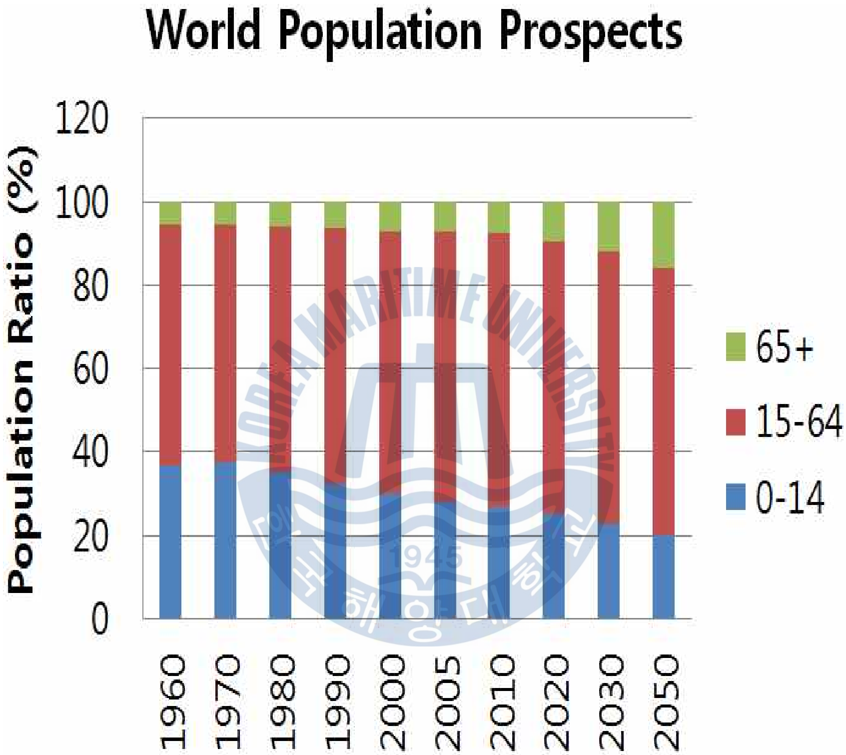


Fig. 1 World population prospects

Table 1 International comparison of the speed of population aging

	The reach year			The increase need life	
	7%	14%	20%	7% - 14%	14% - 20%
France	1864	1979	2018	115	39
Norway	1885	1977	2024	92	47
Sweden	1887	1972	2014	85	42
Australia	1939	2012	2028	73	16
U.S.A	1942	2015	2036	73	21
Canada	1945	2010	2024	65	14
Italy	1927	1988	2006	61	18
U.K	1929	1976	2026	47	50
Germany	1932	1972	2009	40	37
Japan	1970	1994	2006	24	12
Korea	2000	2018	2026	18	8

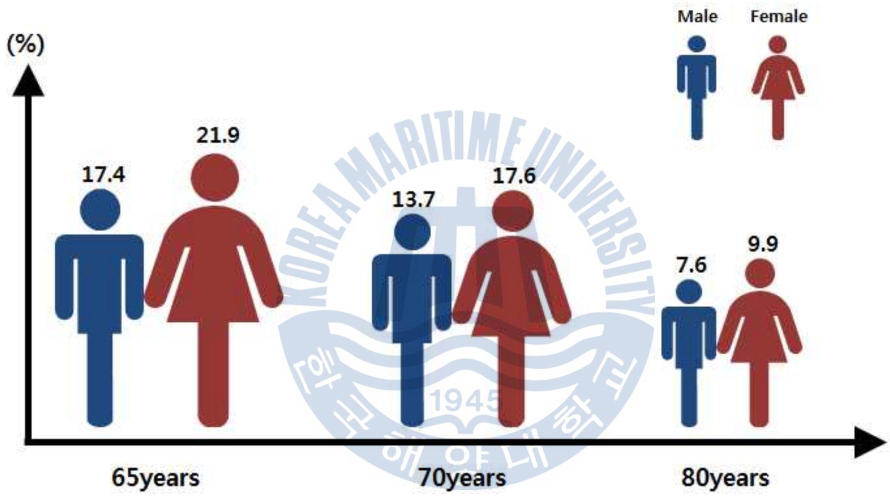


Fig. 2 Life expectancy (over the age of 65)

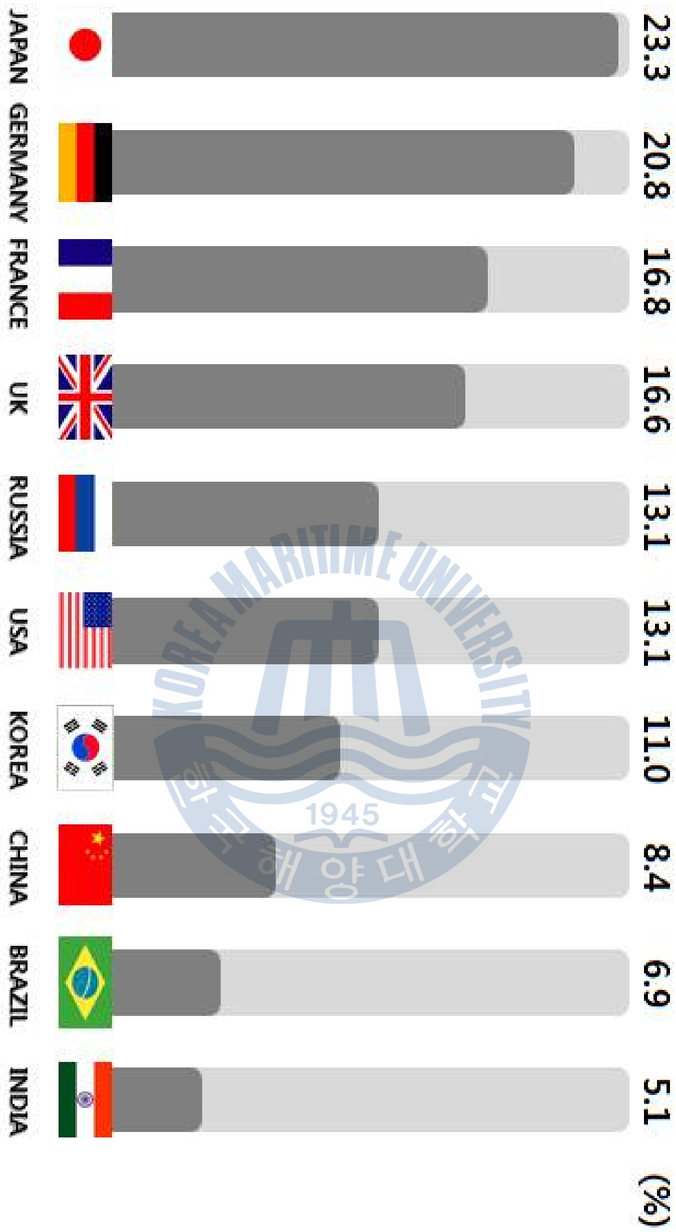


Fig. 3 The aging of the major advanced country in 2040

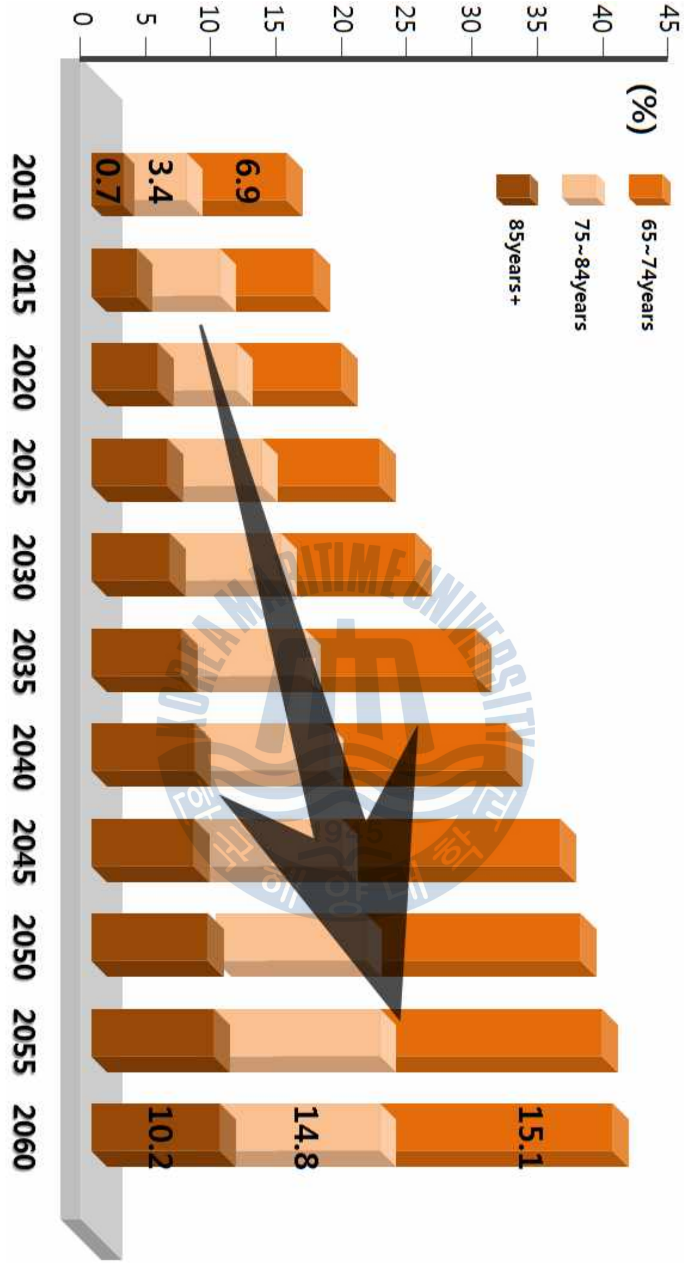


Fig. 4 Elderly population rate

1.1.1 Artificial joint surgery

The artificial joint replacement is the operation replacing the destroyed joint of the human body with a plastic or metal device called an artificial joint. The various operation cases were shown in Fig. 5. One of the most common causes of artificial joint replacement is arthritis. The artificial joint was shown in Fig. 6. The cause for the arthritis is various. [5]

- Osteoarthritis - Osteoarthritis (OA) also known as osteoarthrosis, degenerative joint disease or degenerative arthritis because it is a wearing out condition involving the breakdown of cartilage in the joints. Symptoms may include joint pain, tenderness, stiffness, locking, and sometimes an effusion.

- Rheumatoid arthritis - Rheumatoid arthritis (RA) is an autoimmune disease that results in a chronic, systemic inflammatory disorder but principally attacks flexible joints. The result is cartilage loss, pain, and stiffness.

- Avascular necrosis - Avascular necrosis (AVN) is a disease where there is cellular death of bone components due to interruption of the blood supply. Without blood, the bone tissue dies and the bone collapses. If avascular necrosis involves the bones of a joint, it often leads to destruction of the joint articular surfaces.

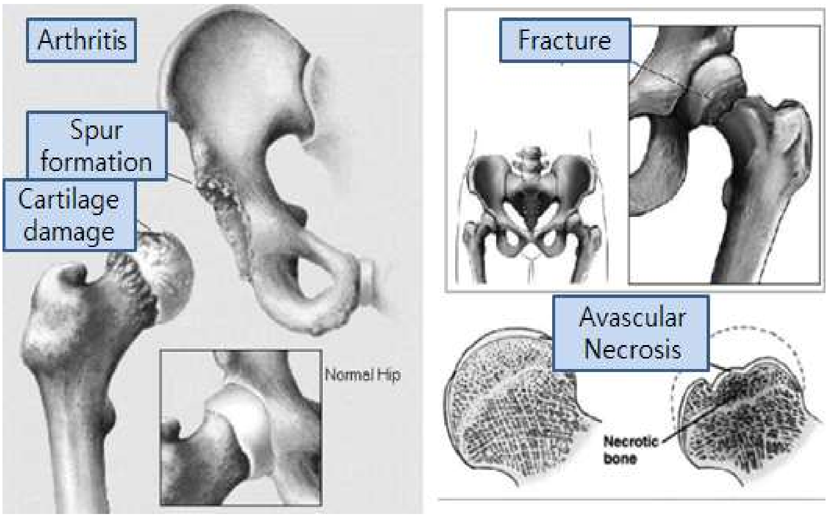


Fig. 5 Various operation cases [5]

Fig. 6 Artificial joint [5]

1.1.2 Patient-customized artificial joint

The artificial joint has the excel function called the pain settlement and exercise function security. However, relatively the lifetime of the artificial joint being used currently is short. The problem of the artificial joint is various.

- Stress shielding phenomenon - The shrinkage of the bone and resorption phenomenon is generated in the change of the stress distribution and the femur or acetabulum is removed according to the process of the time.

- Loosening - The artificial joint becomes loose.

- Osteolysis - The bone of the artificial joint surrounding melts due to the wear of the polyethylene and it sways.

The miss ratio of the artificial joint is considerably increased due to this kind of phenomenon. There are nearly no femur, acetabular or hard bone to support the artificial joint in the artificial joint re-surgery. So, the re-surgery is difficult. The lifetime of the re-surgery is shorterer than the lifetime of the first operation. It is in the tendency that the number of patient who has to receive for rerevision surgery is increased. [6]

Therefore, it has to be designed for the life prolongation of the artificial joint in order to be suitable for the human body framework and life pattern of the patient. In addition, the development of the new patient-customized artificial joint satisfying the shape optimization technique is requested with for biomechanic and kinematics.

1.2 Purpose of Study

Composite materials are designed to display properties that are superior to those of the individual materials. Of these composite materials, fiber-reinforced plastics have a high specific strength and specific rigidity. [7-11] They have been increasingly and consistently used as alternatives to the metallic materials used in the aerospace, ship building, automobile, and sports-related leisure product industries because they show excellent chemical resistivities and formabilities. [12-16]

The average span of human's life has increased by the development of the medical technology. Therefore, health problems in the older generation have emerged as social problem. In particular, activities become more difficult because of deformations in the skeletal system and the development of disease, which lower the quality of life. For this reason, the artificial hip joint was developed to regain lost functions. The artificial hip joint was shown in Fig. 7. [17-20]

Recently, there has been active progress in the research on new medical devices because of the health concerns and population problems that arise from a rapidly aging society. However, in general, metal materials are the mainstream, and it is relatively difficult to apply composites to medical devices, despite of their excellent characteristics.

[21, 22]

An artificial hip joint consists of a cup, head, and stem. Most of the stems are manufactured from Ti, Co-chrome, or stainless steel alloys. However, metal materials deliver small scale stress to an arbitrary area of the bone as a result of the difference in rigidity. Metal materials also atrophy the femur, causing bone loss. In addition, a problem arises whereby the implant device loosens as a result of the stress shielding between the metal material and the bone, shortening the life of the joint. [23-26]

In addition, there has been a surge in the number of patients with articular disease because of the increase in the human lifespan. Therefore, more than one joint is often required using a resubstitution technique. However, the success rate is drastically decreased in a resubstitution operation. Therefore, the development of a patient-customized artificial hip joint is urgently required in order to improve the useful life of the artificial hip joint. Thus, a substitute composite material needs to be found to resolve this problem. [27-31]

Epoxy resin is the most widely used matrix material for composite materials because of its comparatively low cost. However, because it is harmful to the human body, the development of a substitute material is urgently required.

PEEK (Polyetheretherketon) is well known as the thermoplastic resin and it is possible application to various industrial fields by the remarkable properties including the excellent mechanical strength, dimensional stability, wear resistance and so on. Particularly, PEEK is usable with the implant device as the biocompatibility material getting the approval in FDA. [32-35]

The carbon fiber has the characteristic including the high strength, high tensile, high elastic modulus and thermal resistance and so on. Therefore, it has the excellent properties as the material of composites and it is applied in many industrial fields. The carbon fiber processes the sizing treatment at the surface of the fiber in order to enhance the adhesive strength of interface with the resin. This does the effect that it protects the surface of the carbon fiber and gives the lubrication and does the resin-impregnation easily. However, the epoxy used as the sizing material is harmful to the human body and cannot be used in the implant device. [36-40]

However, in the internal of the person, the artificial joint is exposed to the long term moisture under 37℃ environment. If the fiber-reinforced composite materials are exposed to moisture environmental, the moisture penetrated and diffused into the resin which is the base, and as a result, the degradation of the fiber-reinforced composite materials appears. In other words, the absorbed moisture makes not only to occur the crack by causing the expansion of the volume while plasticizing the resin, but also by changing the internal stress state. In addition, the swelling moisture can degrade the bond strength by separating the chemical bonding of the composite materials at the interface between the resin and the fibers. The interface between the fiber and resin deteriorates due to such damage and the mechanical properties of the composite materials are degraded.

In addition, fiber-reinforced composites significantly differ in their mechanical properties according to the ply orientation of the fiber. Currently, in the case of carbon/epoxy composites, various studies are being conducted in relation to the ply orientation of the fiber. However, in the case of carbon/PEEK composites, there is a lack of objective data.

Moreover, in the human body, an artificial hip joint is placed in a constant friction environment for a long period. Particularly, the neck part of the stem becomes weak due to the friction from the interaction of the head and cup. Moreover, artificial joint needs to be investigated in terms of the change in intensity according to the fiber ply orientation of the carbon/PEEK composites because of the stress it receives at various ply orientation. [41-46]

Also, composites can minimize the stress shielding phenomenon because the design shape may be more variously transformed than the existing metal material. However, with composites, it is not easy to implement a design shape because of the different mechanical properties according to the laminating direction of the fiber. In addition, the thickness setting is difficult due to the complicated shape of the stem. [47-50]

Therefore, in this study, carbon/PEEK composites were fabricated, and the different mechanical properties according to the fiber ply orientation were investigated. The plane for manufacturing of stem was shown in Fig. 8. From these results, it were investigated that the carbon/PEEK composites were applicable to artificial hip joints.

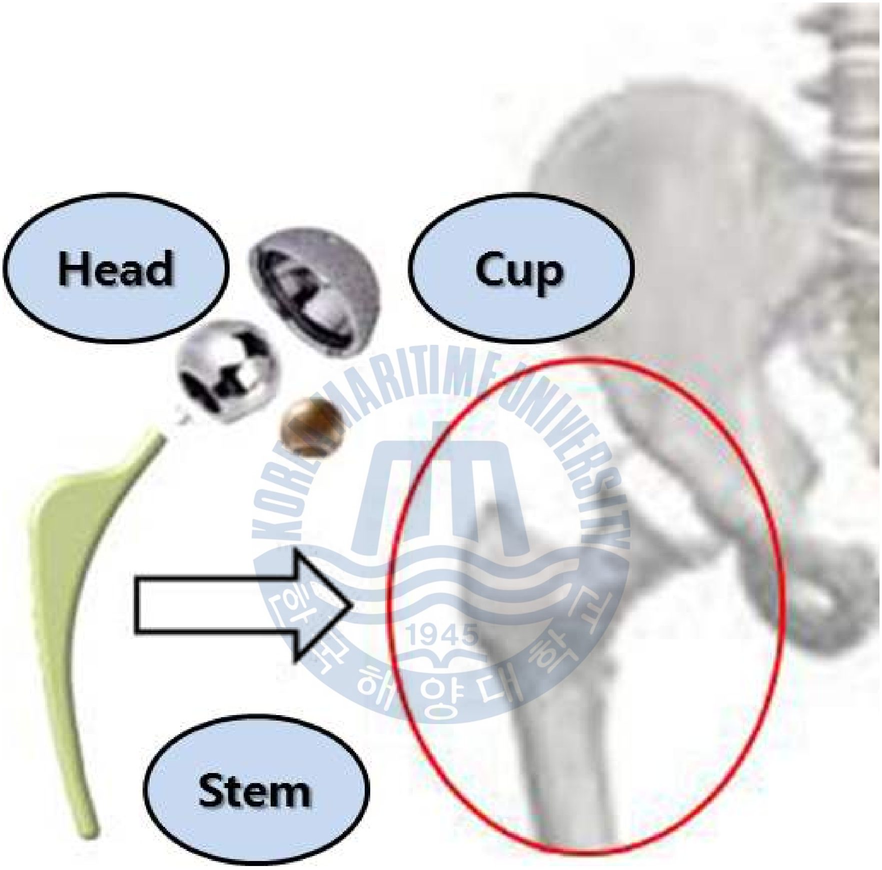


Fig. 7 Artificial hip joint

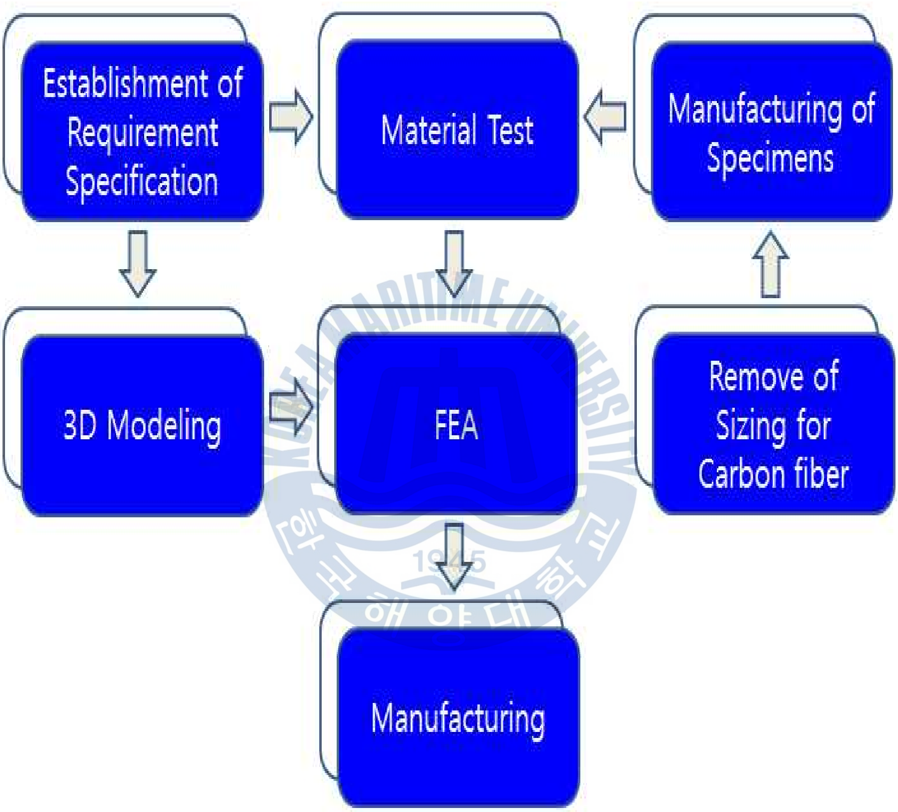


Fig. 8 Plane for manufacturing of stem

2. Introduction of Artificial Joint

2.1 History

The artificial joint surgery is one of the clinical treatment for restoring of function when the problems are occurred on the joint caused by diseases or accidents. The Total Hip Replacement and Total Knee Replacement are typical example of artificial joint.

The study of artificial joint has begun designing and manufacturing the artificial hip joint in 1930. The femoral component and acetabular component manufactured of stainless steel are failed. And from 1950 until 1960, artificial joint introduced by Charnley got great success. Charnley replaced the polytetrafluoroethylene which reduces the friction in order to solve the problem of being generated due to the friction between caput femoris and acetabulum part with the material of acetabulum part. However, this material having low friction property rised to the clinical problem and is replaced with the high density and high molecular weight polyethylene. This became the basic model of the artificial hip joint being used currently. Presently, the titanium alloys and cobalt chrome alloy in which the toughness is excellent and the bio compatibility is excellent is used in the femur and acetabulum part instead of the stainless steel, and the caput femoris of the ceramic material is used. It was generalized that using the Ultra High Molecular Weight Polyethylene (Ultra High Molecular Weight Polyethylene: UHMWPE) cup having excellent friction properties instead of Polytetrafluoroethylene.

Meanwhile, in 1960's, the using of metal-metal artificial hip joint that manufactured from the titanium and stainless steel, introduced by MeKee, was low by the abrasion problem because of the excessive friction. However, recently, it is again in the limelight as the minimization of the abrasion through the alloy material development and ultraprecision machining.

In the case of the artificial joint of the Charnley, the fixing of the bone of the artificial joint used the polymethyl methacrylate (PMMA) bone-cement. In 1970's, the loosening phenomenon that the artificial hip joint is broken away from of the osseous tissue was reported by many patients. As a result of the biopsy, the necrosis of the osseous tissue caused from PMMA particle has been found to be major factor. The wide research about the bone-cement was activated. On the other hand, the new fixed method replacing this was introduced in 1980's. By using the Porous coating for the junction with the osseous tissue of the femur and acetabulum part, the porous area is created. This new fixed method started from the concept which did not use the bone-cement and in which the osseous tissue fixes artificial joint and bone physically by burrowing into the porous area. For this purpose, the artificial hip joint operations were performed closely to the osseous tissue. In 1980's, the quite amount of artificial hip joint operation were performed without using the bone-cement. However, whereas about 10~40% of non-cement artificial hip joint surgery treated patients complained of the initial pain, the case of using the improved PMMA bone-cement is not passed by about 1%. In the case of the porous coating artificial hip joint, whereas the fixing of the hour is improved increasingly, in the case of the bone-cement artificial hip joint, the probability that this opposite phenomenon is generated is high. Presently, the use of the porous coating and bone-cement artificial hip joint is approximately presumed as 50:50. The problem of artificial hip joint and solution were shown in Fig. 9.

2.2 Manufacturing

The difference of the mechanical and biological function exists between the artificial joint and natural joint. The purpose of the artificial joint design and manufacture is minimized this difference. For this reason, the close cooperation of the doctor and engineer is essential. When the artificial joint manufacture the consideration is like under.

(1) The prediction of the load and kinematic velocity

(2) The friction and wear

(3) The requirement of mechanical function

(4) The fixed method of artificial joint

(5) Surgical instrument

(6) Manufacturing process

(7) The material's choice

The clinical consideration and standard which the commercial enterprise will have to consider exists much and the product is manufactured in the condition that it satisfies the standard. In the Fig 10, the production process of the artificial joint is shown.

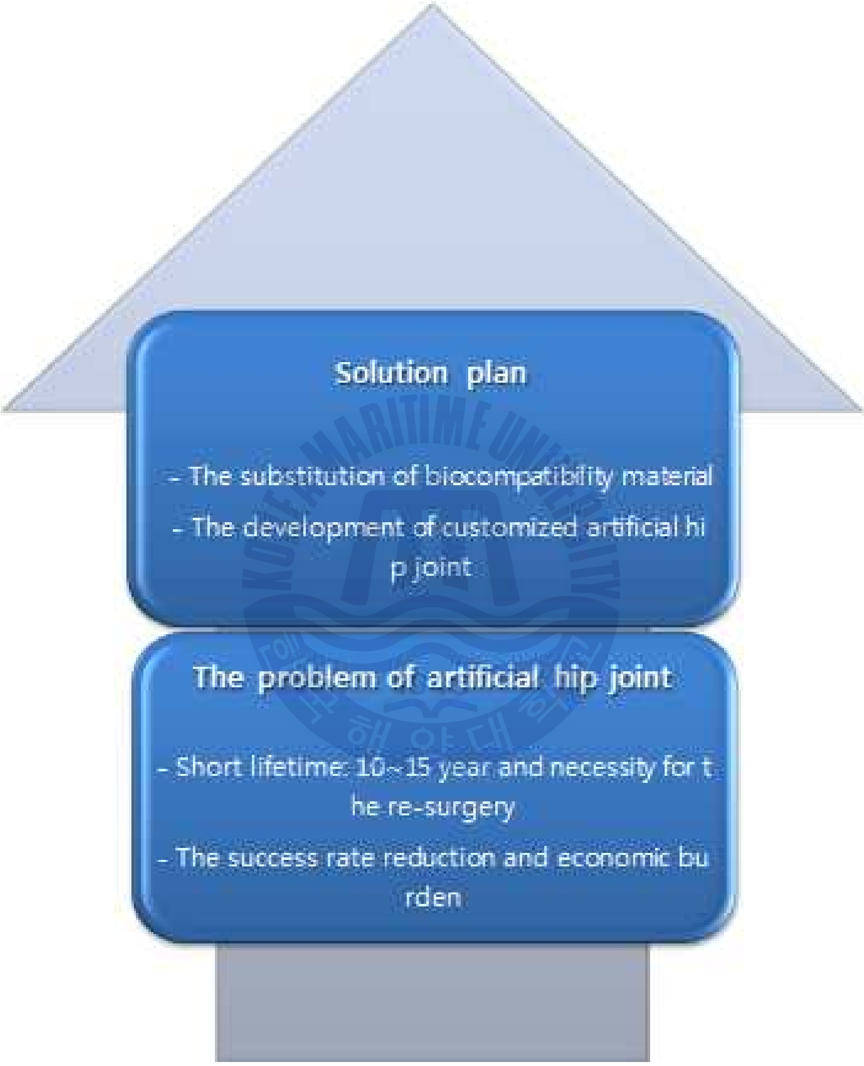


Fig. 9 The problem of artificial hip joint and solution

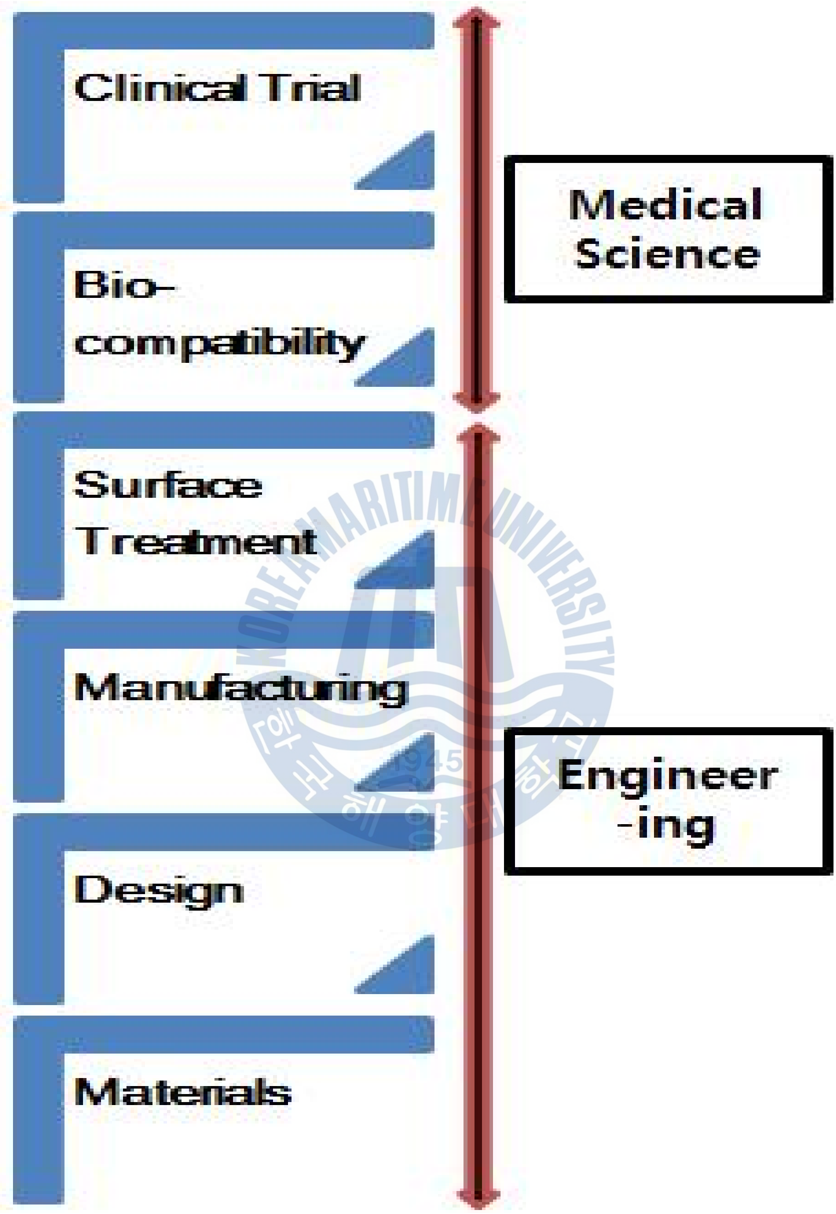


Fig. 10 A step of development for artificial hip joint

2.3 Market Trends

The increase in the arthritis the number of patients can become the growth promotive factor of the artificial hip joint market. The medical device market was shown in Fig. 11. According to the result of examination which HA Wieland reports, it forecasts that the U.S., Europe, and Japanese arthritis the number of patients increases to 40 million people in 2007 and 42 million people in 2012 at 37 million people in 2002. The increase in the rest surgical treated patient number, product diversification according to the patient, age group degradation of the arthritic and etc. can become the promotive factor.

On the other hand, because of acting in the patient position as the burden, the specific product preference tendency of the medical team or the surgical operation example of experience deficit and expensive cost of surgery is the factor making slowed the growth.

The arthritis is not disease threatening the life and is the disease giving the inconvenience to the daily life. The leisure use of the old people becomes the social problem and the desire growth about the improvement of quality of the life of the old-age generation including the leisure activity is expected to increase the artificial joint prosthesis.

However, the artificial joint product has to pass the medical device confirmation and permission process. Accordingly, the expensive cost for the clinical test and long development period is needed. Besides, the monopolistic market structure of the multinational corporation can become the growth inhibitor. Korea market of artificial joint was shown in Fig. 12.

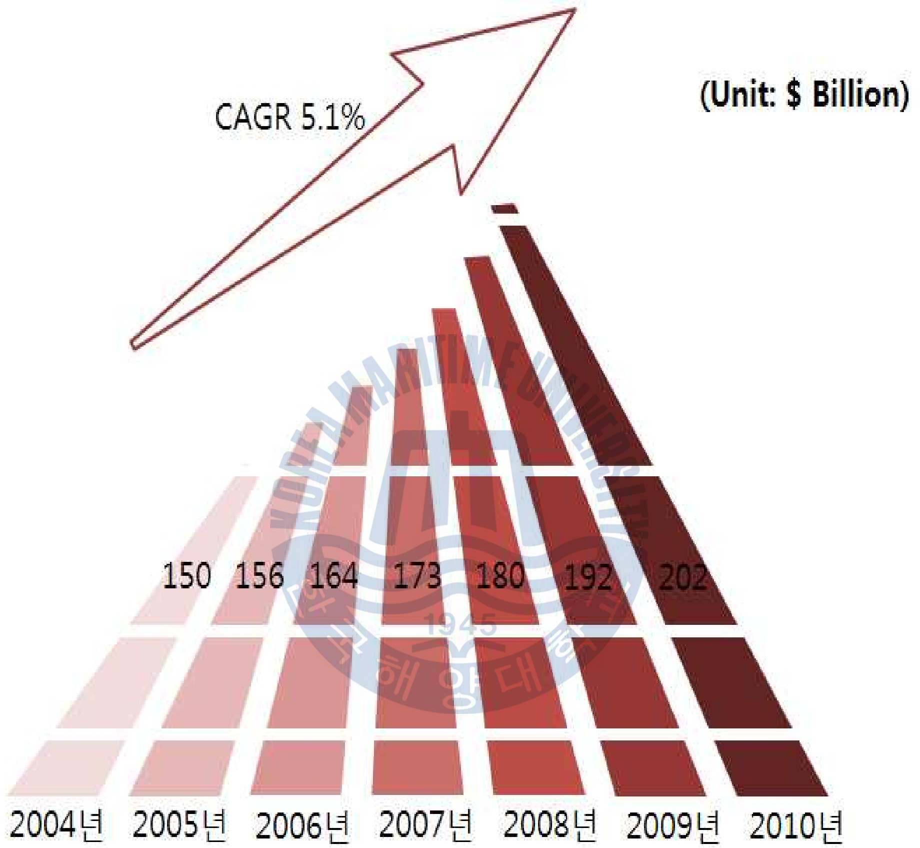


Fig. 11 The medical device market

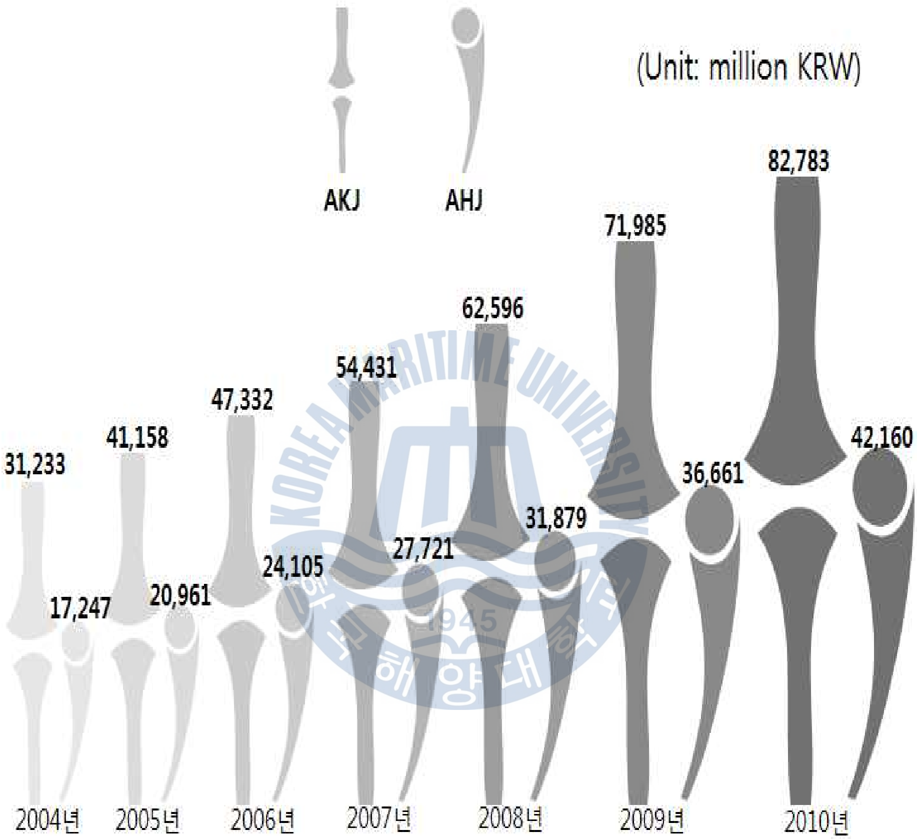


Fig. 12 Korea market of artificial joint

3. Materials and Experiment Method

3.1 Preparation of the Materials

Experimental materials were prepared to measure the tribological properties of carbon/PEEK composites and carbon/epoxy composites. The manufacturing method of PEEK film was shown in Fig. 13. The images of carbon fiber and PEEK film were shown in Fig. 14. The carbon fiber of PAN-based UD tape was used for the reinforcing material. In addition, a thermoplastic PEEK film in from the Victrex Company was used as a matrix material. Also, KFR121/KFH141 epoxy resin from the Kukdo Company was selected to compare the mechanical properties with PEEK film. The properties of the fiber and resin used in the experiment are shown in Table 2.

Table 2 Properties of fiber and resin for tests

Fiber	Density [g/cm^3]	Tensile strength [MPa]	Young's Modulus [GPa]	Poisson's ratio [ν]
Carbon Fiber (UD)	1.7	4,400	245	0.2
Resin	Density [g/cm^3]	Tensile strength [MPa]	Elastic Modulus [GPa]	Elongation at Break [%]
Epoxy Resin	1.1	70	3.0	60
PEEK Film	1.3	130	2.5	150

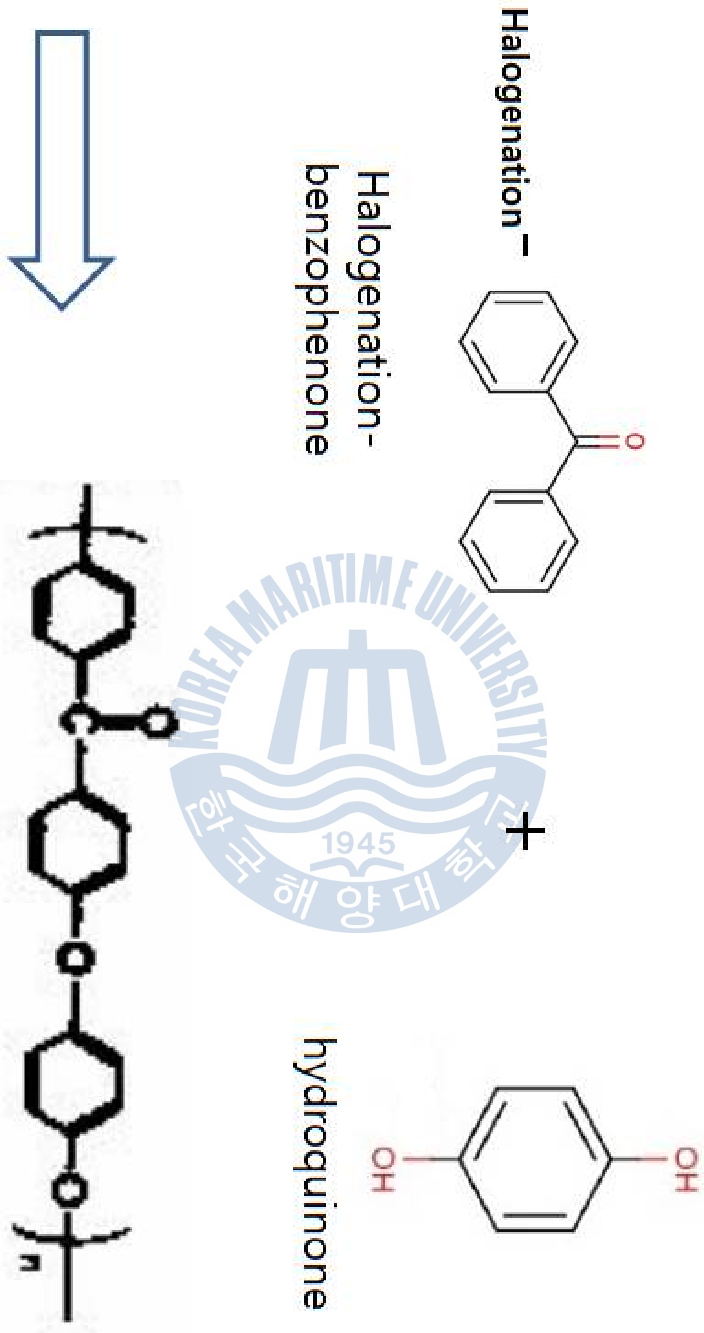


Fig. 13 Manufacturing method of PEEK film

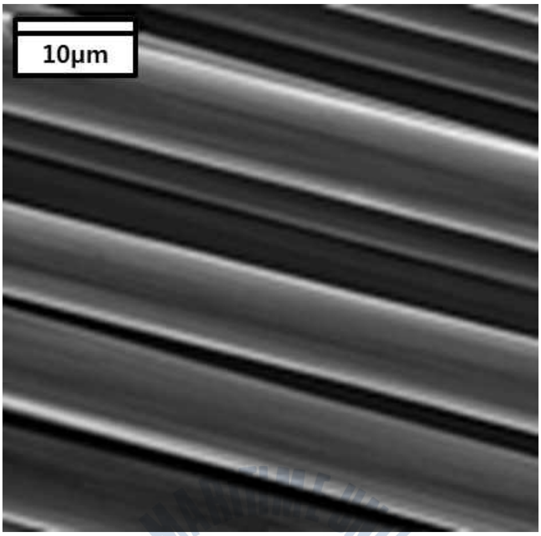
(a) Carbon Fiber

(b) PEEK Film

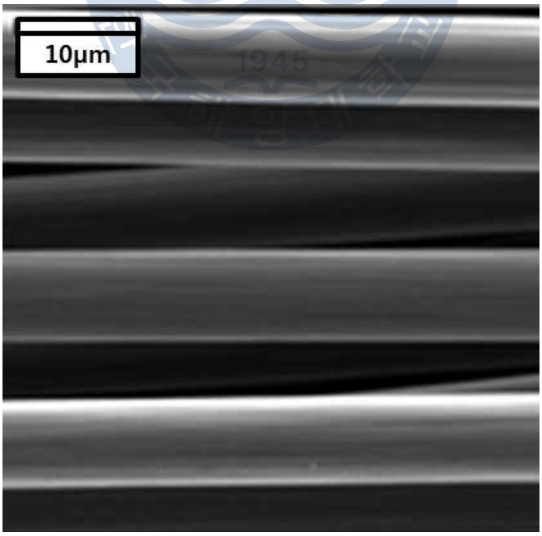
Fig. 14 Images of carbon fiber and PEEK film

3.2 Removal of Sizing

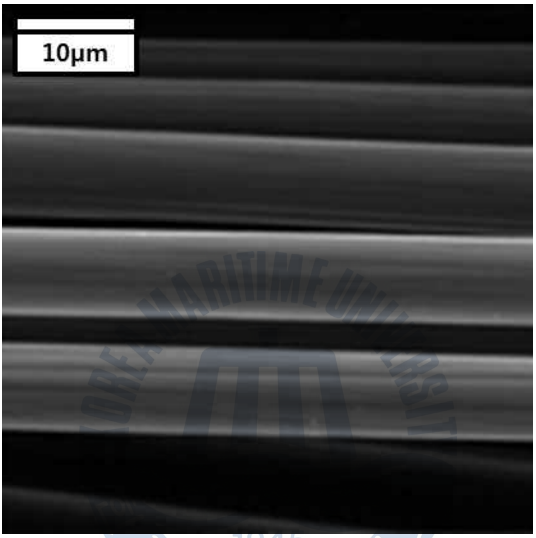
The carbon fiber protects the surface of fiber and enhances the adhesive strength with the resin through the sizing treatment. However, the sizing materials such as epoxy are harmful to the human body and cannot be used in the implant device. Therefore, the coated sizing on the surface of the carbon fiber was removed through the heat treatment. Thereafter, the carbon fiber surface was observed by using SEM (Scanning Electron Microscopy). The experimental condition was performed through the temperature change for 4 hours at 300℃ and 2 hours at 400℃. The surface of the carbon fiber observed by SEM was shown in Fig. 15. The clear image could be confirmed at surface of heat-treated carbon fiber than before through the experimental results. This is considered that the coated sizing material on the carbon fiber was removed due to the heat treatment of high-temperature.



(a)



(b)



(c)

Fig. 15 SEM images of carbon fiber: (a) before sizing removal, (b) after sizing removal for 4 hours at 300℃, (c) after sizing removal for 2 hours at 400℃

3.3 Moisture Absorption Theory

If fiber-reinforced composite materials are exposed under high temperature and high humidity environment for a long time, absorbed moisture makes the glass transition temperature to reduce by weakening the structure of resin. In other words, the moisture absorption of the fiber-reinforced composite materials follows Fick's diffusion law. The moisture content applied in this study was calculated from the following equation (1).

$$W(\%) = \frac{W_i - W_a}{W_a} \times 100 \qquad (1)$$

Where, W = Moisture Content (%)

W_i = weight of specimen after moisture absorption

W_a = weight of specimen before moisture absorption

Figure 16 shows step by step the degradation mechanism of material properties due to the moisture absorption of fiber-reinforced composite materials.

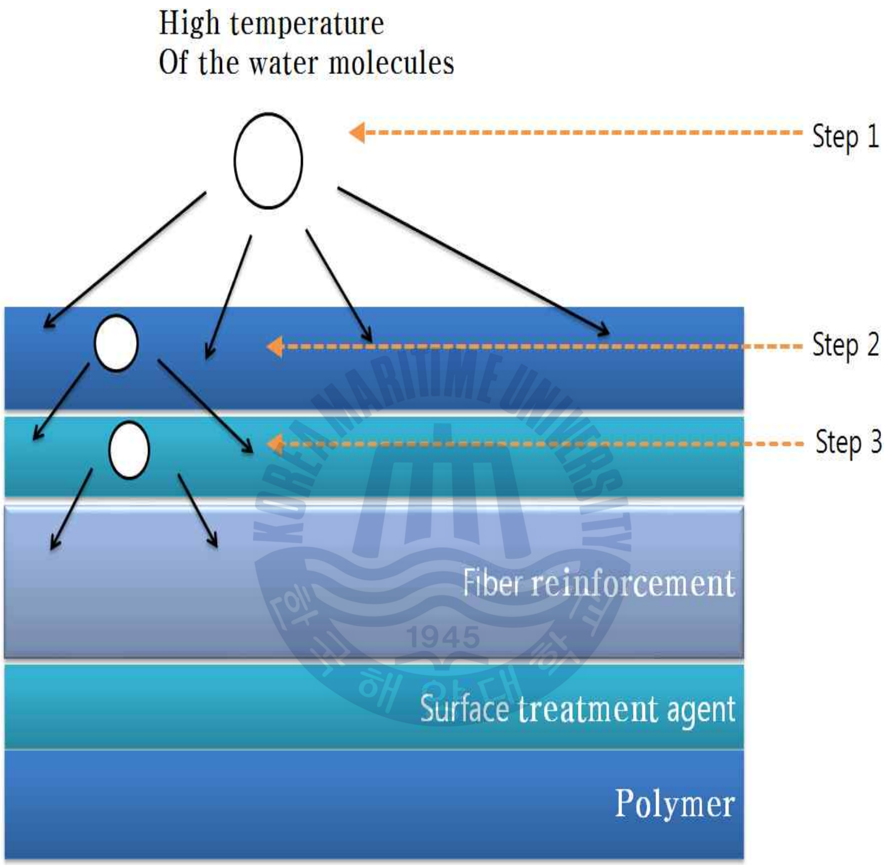


Fig. 16 Degradation mechanism of composites by moisture absorption

3.4 Specimens

The PEEK film and epoxy resin were used as the matrix materials for manufacturing the prepreg. In the case of the PEEK prepreg, the prepreg sheet was made using PEEK film of the same size and was laminated on both surfaces of the carbon fiber in a hot press with a pressure of 10 MPa at 400℃. The curing conditions for specimen preparation were shown in Fig. 17. Thereafter, the carbon fiber prepreg was laminated at various angles in order to confirm the change in the mechanical properties according to the ply orientation angle of the fiber. Subsequently, composite materials were fabricated by operating the hot press at 380℃ using the hot press molding method with the prepreg.

In the case of the epoxy prepreg, the epoxy resin (KFR121) and hardening agent (KFH141) were impregnated by mixing at a 100:30 ratio according to the table of mixing ratios provided by the resin manufacturing company. The direct impregnation method used a beaker and roller for the resin impregnation. The resin impregnation ratio was 45%. The resin impregnated fiber was dried for 3h at 50℃ inside a vacuum drying oven, and refrigeration was maintained by attaching a release film to both sides. An autoclave was operated using a vacuum bag molding method at 174℃ for 1h, and the composites were made.

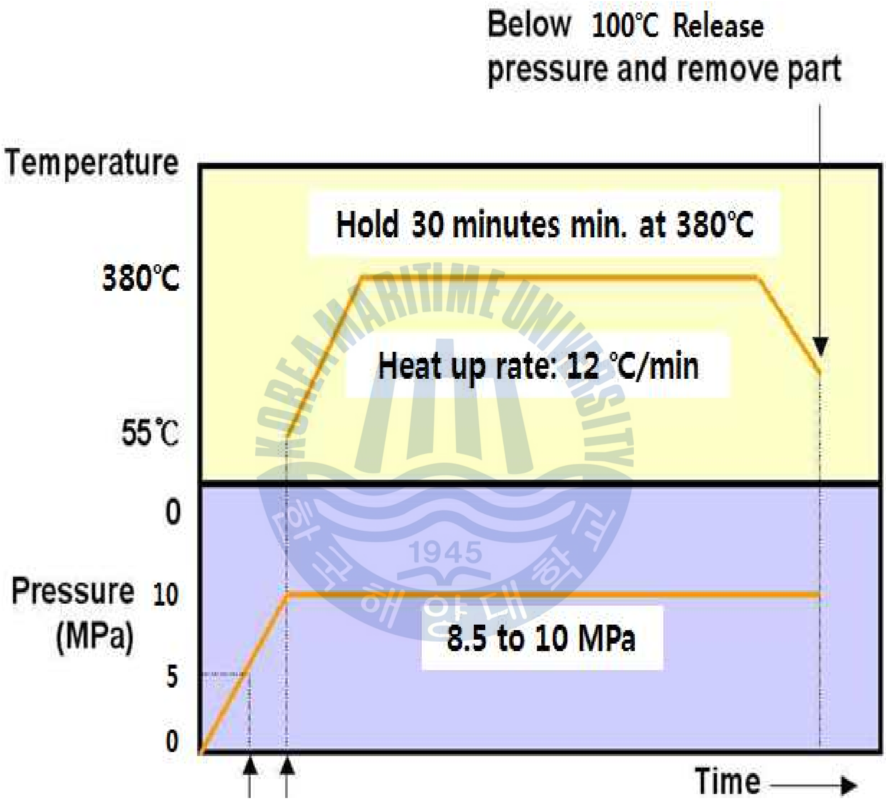
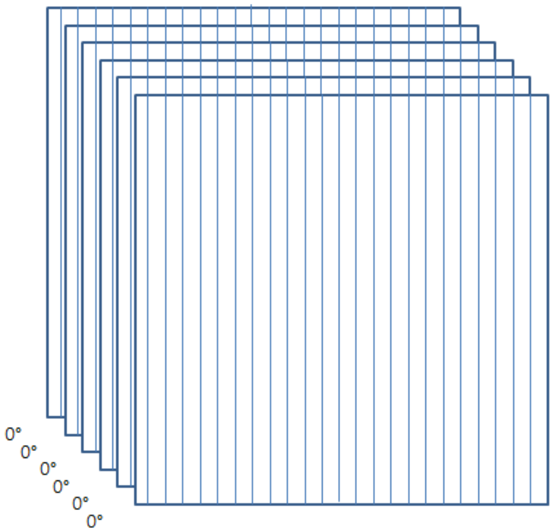
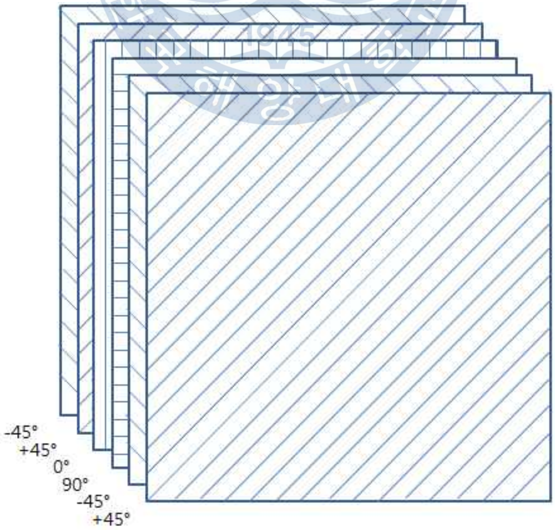


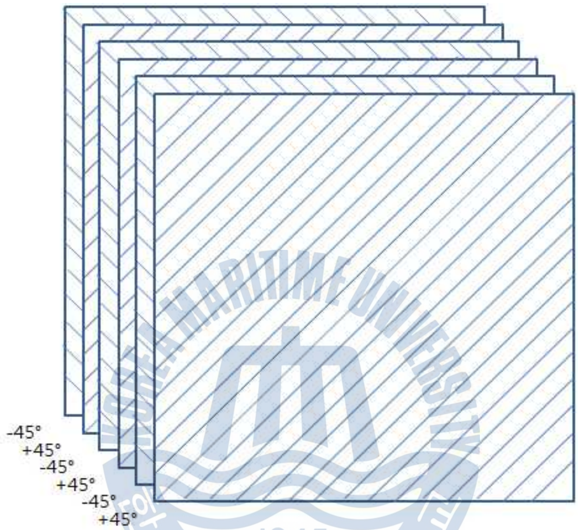
Fig. 17 Curing conditions for specimen preparation



(a) Configuration I



(b) Configuration II



(c) Configuration III

Fig. 18 Ply configuration for carbon fiber: (a) [(0°)$_6$], (b) [(±45°)$_1$(0°/90°)$_1$(±45°)$_1$], (c) [(±45°)$_3$]

3.5 Experiment Method

The tensile, compressive, bending and short-beam test has been made to evaluate the mechanical properties of the carbon/PEEK composites. The ply configuration for carbon fiber was shown in Fig. 18. The tensile test, compressive test and bending test were conducted according to the ASTM D 638, ASTM D 695 and ASTM D 790 standards, respectively. Seven specimens were made for each test. The average result data was taken from the 5 specimens, excluding the highest and lowest data from the measurement. The specimens were used to investigate the effect of moisture absorption on the mechanical degradation of fiber-reinforced composite materials. The specimens were sufficiently immersed in the distilled water in the moisture absorption device, and tensile and bending tests were conducted depending on the moisture content; the specimens were maintained at 80 ℃ for 100 days. The Universal Test Machine (KDMT-156) of Kyung-Do Company was used for the test. The cross head speeds were set at 5mm/min for the tensile test and 5.5mm/min for the bending test according to the related specification. The images of method for each test were shown in Fig. 20. The short-beam test has been made as it is indicated in Fig. 20 (c) after making the test specimen according to the standard of ASTM D 2344. The short beam strength has been obtained from the following equation (2).

In addition, the fracture surfaces were observed in order to confirm the interface bonding of the fiber and resin by using SEM after cutting the fraction surrounding.

$$F^{sbs} = 0.75 \times \frac{P_m}{(b \times s)} \qquad (2)$$

Where, F^{sbs} : Short-beam strength [MPa]

P_m : Max load observed during the test [N]

b : Measured specimen width [mm]

h : Measured specimen thickness [mm]

A pin-on-disc device was used to observe the frictional properties of the carbon/PEEK composites. The shapes of specimens for friction and wear test were shown in Fig. 19. Stainless steel was used as the relative friction surface, and the normal load was fixed at 20 N and 40 N. The friction coefficient was investigated according to the fiber ply orientation. The friction angles were separated into the parallel and normal directions. The friction velocity was 2.5m/s and 5m/s. The condition of temperature was maintained 37℃ in the experiment. At the same time, the damaged the specimen of the composites were observed using scanning electron microscope.

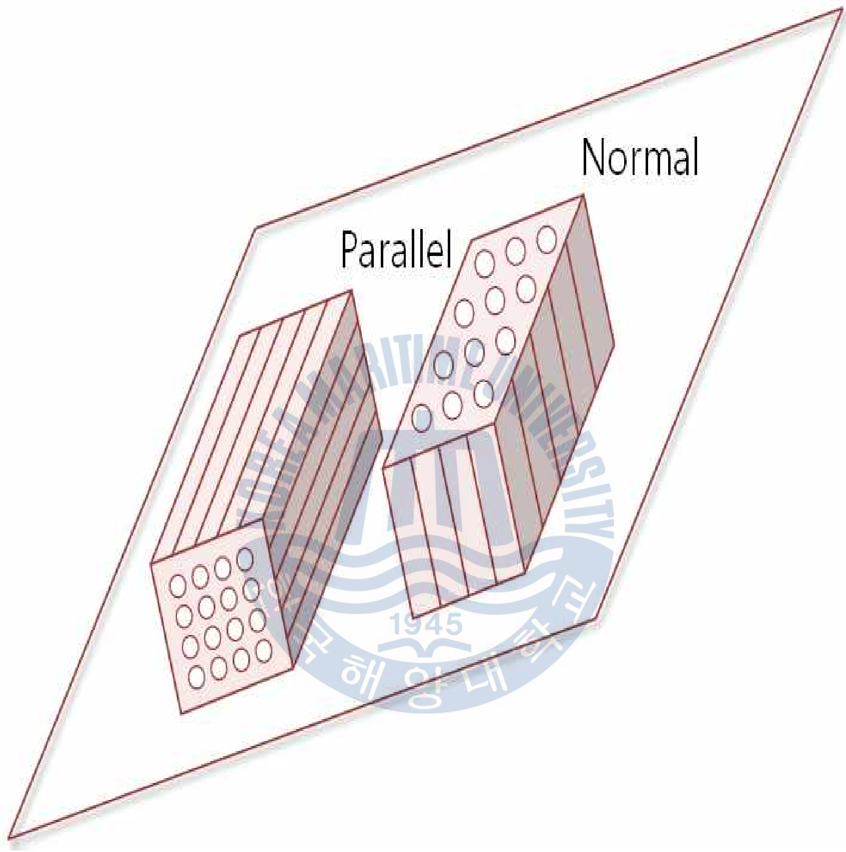


Fig. 19 Shape of specimens for friction and wear test

(a) Tensile test

(b) Compression test

(c) Short beam test

Fig. 20 Images of method for each test

4. Results and Discussion

4.1 Effect of Sizing Removal

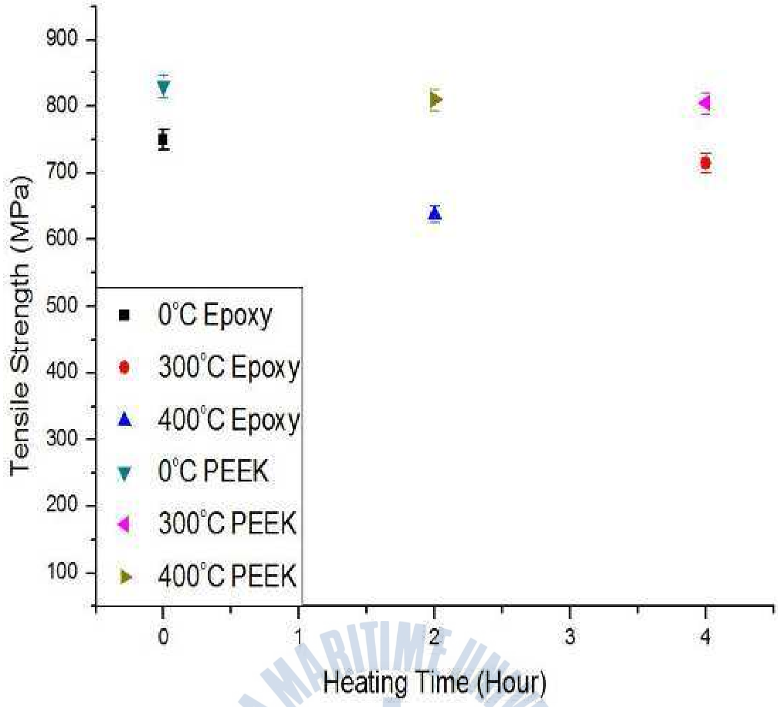
4.1.1 Mechanical properties

The results of mechanical property test according to the sizing treatment or not of carbon/epoxy composites was known that the strength of the composites was excellent in the case of sizing treatment. This indicates the value in which the interface bonding between the surface of carbon fiber and epoxy resin is excellent and the strength is high. In the case of carbon/PEEK composites, the mechanical property value of the sizing treatment former and after did not have the noticeable difference. This is considered because PEEK resin did not have an effect as to the sizing material in chemical combination.

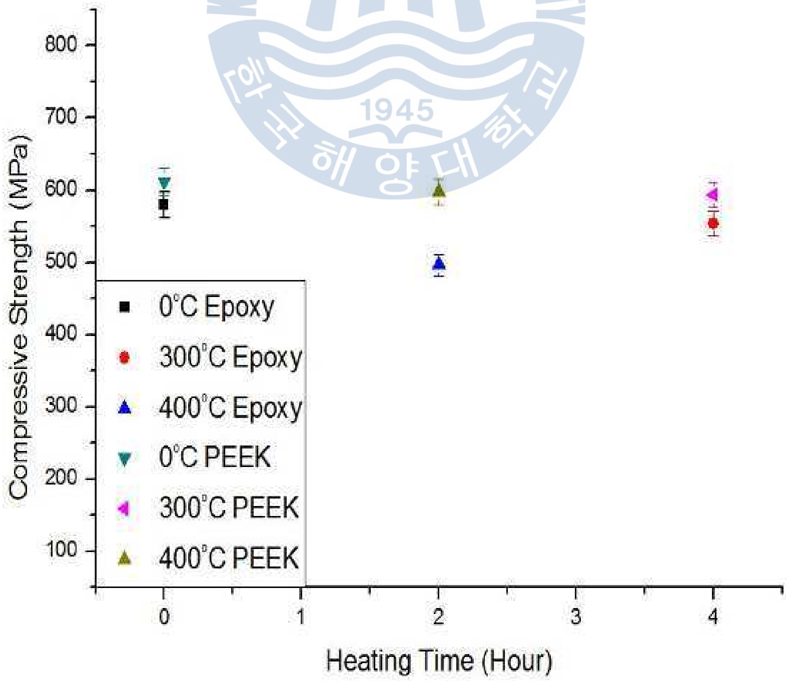
The result of the tensile test according to the sizing processed or not was shown to the Fig. 21 (a). There is a difference in its strength according to the result, but it is shown that the carbon/PEEK composites displayed more excellent strength than carbon/epoxy composites. Especially, the carbon/PEEK composites showed higher data for strength by 100 ~ 200 MPa approximately in the case of sizing removal. It is considered that the physical properties of the PEEK resin itself were more excellent than that of epoxy resin. The strength of the sizing treatment former and after did not have the noticeable difference in the case of carbon/epoxy composites. It is considered that the delamination was maximized by the decreased inter-layer coupling between carbon fiber from which the sizing treatment is removed and the epoxy resin.

It is displayed the aspect which is similar to the result of the tensile test in the case of the compressive test. Particularly, The strength of the specimen heat-treated at 400℃ shows the noticeable difference. It seems that the surface of the sizing removal carbon doesn't like the adhesive strength with the epoxy resin. However, it doesn't reach the noticeable effect to the adhesive strength with PEEK resin.

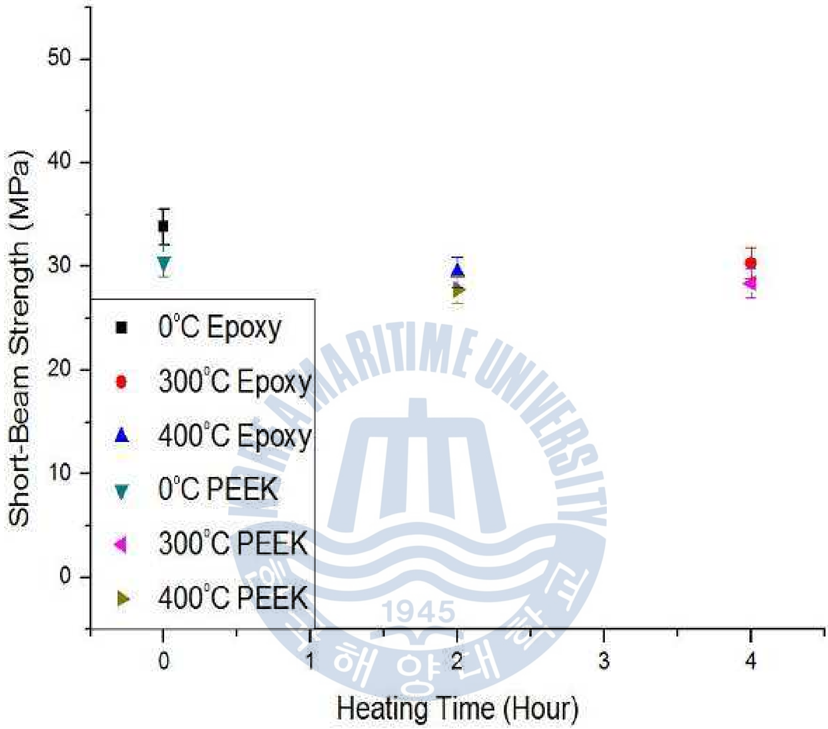
The mechanical properties of carbon/PEEK composites and carbon/epoxy composites were nearly similar and the high property value was shown in short-beam test. This is considered to display the relatively high property value because of enhancing the fiber content ratio in the process of making prepreg.



(a) Tensile test



(b) Compressive test

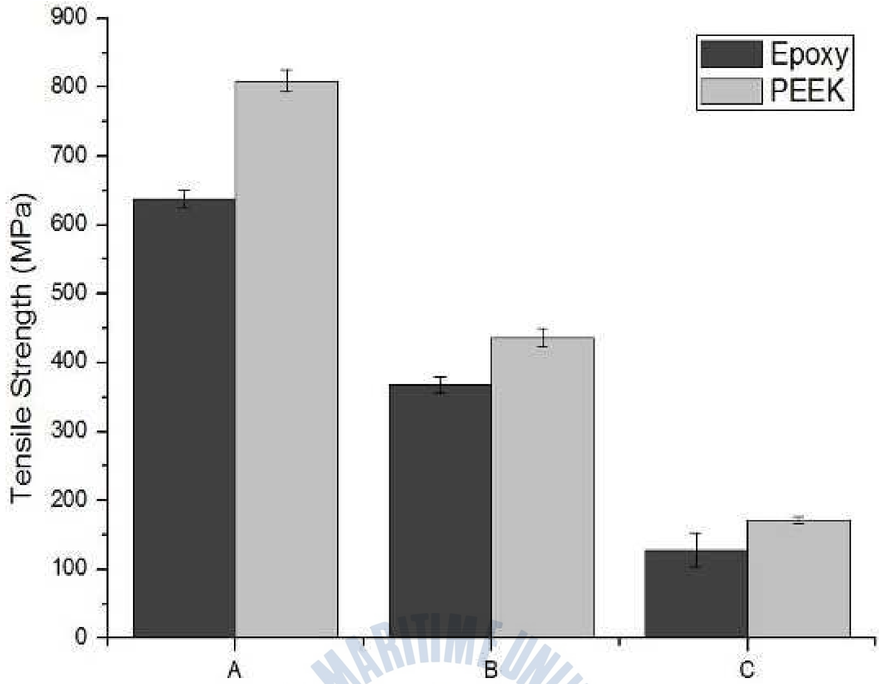


(c) Short-beam test

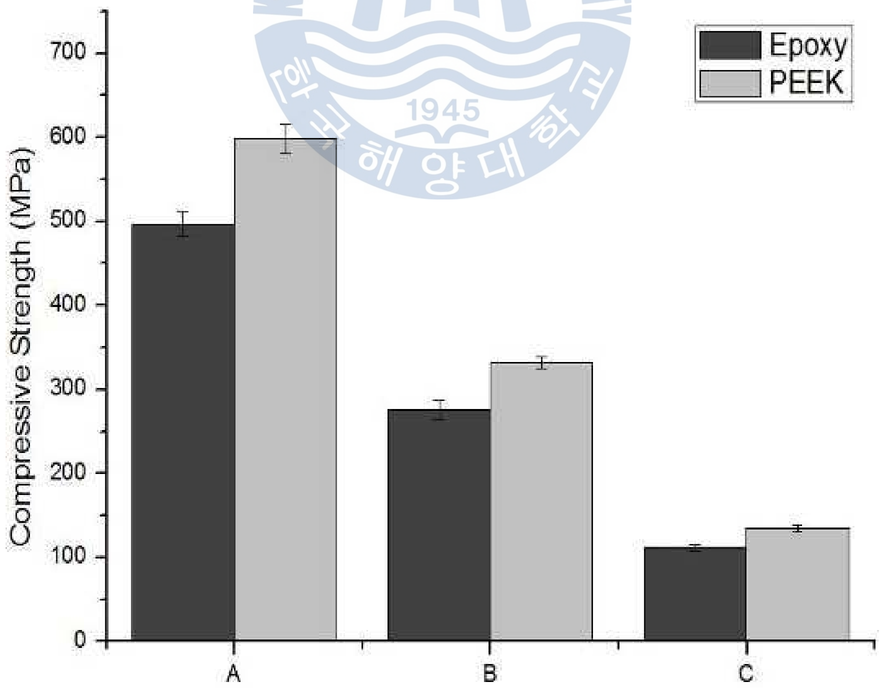
Fig. 21 Result of the mechanical strength according to sizing removal

Meanwhile, the results of the mechanical property test according to the alignment angle of the carbon fiber was known that the strength of the composites was excellent in the case of same $[(0°)_6]$ specimens as the axial direction. This is considered due to absorb the imposed energy because the direction of the fiber and direction of force coincides. On the other hand, the mechanical properties were reduced in case of the fiber ply orientation angle of 45°. This is considered that mechanical properties are decreased because of absorbing the imposed energy by the matrix materials. The result of the mechanical property test according to the fiber ply orientation angle was shown in Fig. 22.

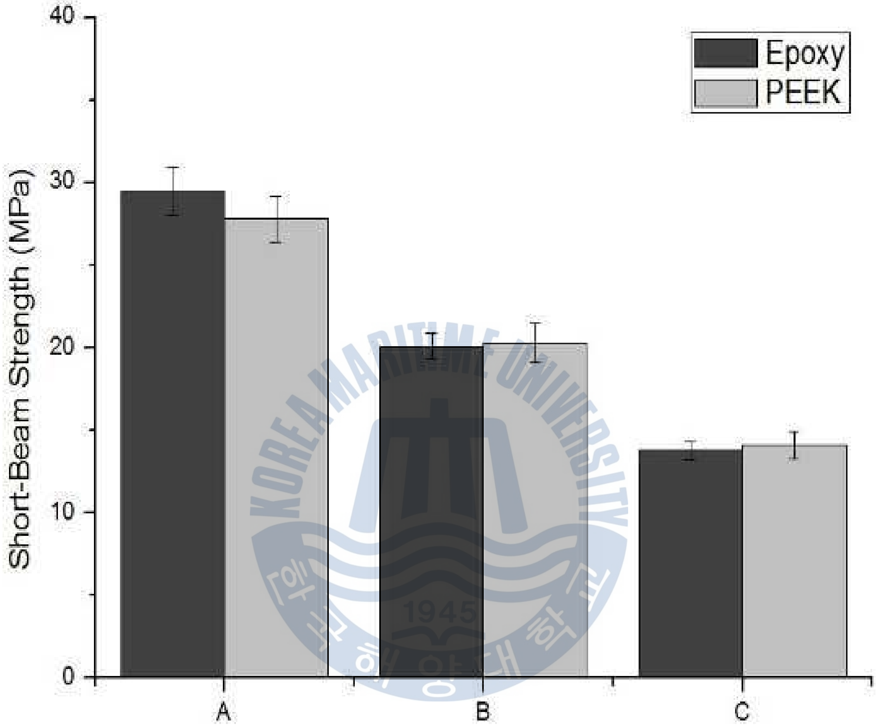
The mechanical properties of carbon/epoxy composites were shown high property value in the short-beam test. The carbon fiber and matrix material are the discontinuity surface. Preferentially the crack occurs in the side where these are contacted and it is the delamination phenomenon generated. Therefore, it is considered that the mechanical properties are high in case of the carbon/epoxy composites.



(a) Tensile strength



(b) Compressive strength



(c) Short-beam strength

Fig. 22 Result of the mechanical strength according to fiber ply orientation

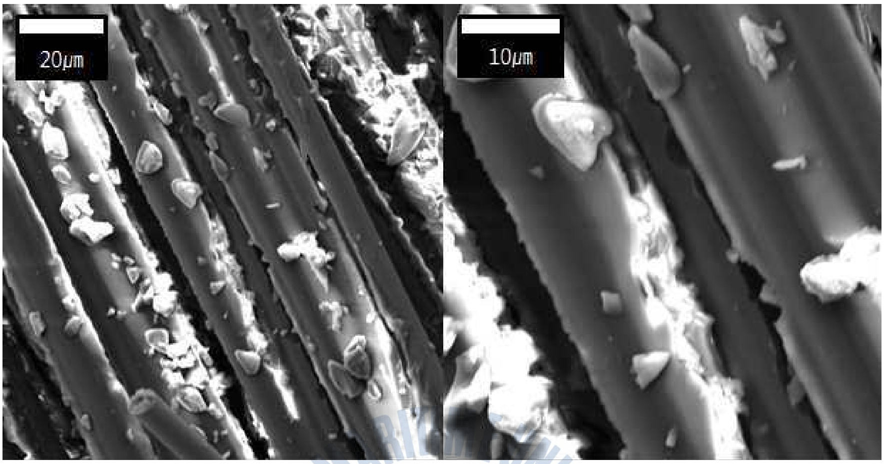
4.1.2 Fracture surface

It was revealed out from the experiment result that the carbon/PEEK composites have the higher strength than the carbon/epoxy composites. The fractured surface in the specimen of tensile test made from PEEK and epoxy was observed in order to identify this phenomenon. Fig. 23 is a photo observed from the fracture surface of the carbon fiber composites specimen by SEM. It can be checked that a lot of resin is adhered on the surface of fiber without the pull out phenomenon as the interface bonding strength between the carbon fiber and the epoxy resin was excellent when the carbon/epoxy composites photo of 0℃ heating is observed. In addition, the similar aspect on the fracture surface of the carbon/PEEK was checked without noticeable difference with the case of the carbon/epoxy. It shows that the bonding between the resin and the fiber was excellent as the fiber was intensively hardened at the forming.

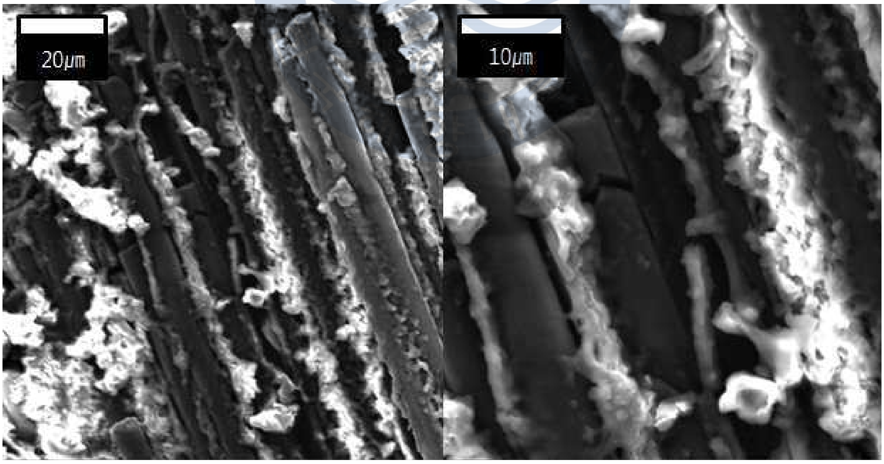
On the other hand, the fracture surface of the tensile test specimen of the carbon/epoxy composites heat-treated to 400℃ could know that the resin did not be stained nearly in the fiber surface and pull out was observed. This is considered that the effect reached to the chemical combination between surface of the carbon fiber and the epoxy resin caused by the sizing removal.

However, the tensile test specimen of the carbon/PEEK composites could not find the noticeable difference in comparison with none heat-treatment. This is considered because the sizing treatment did not have an effect on PEEK resin.

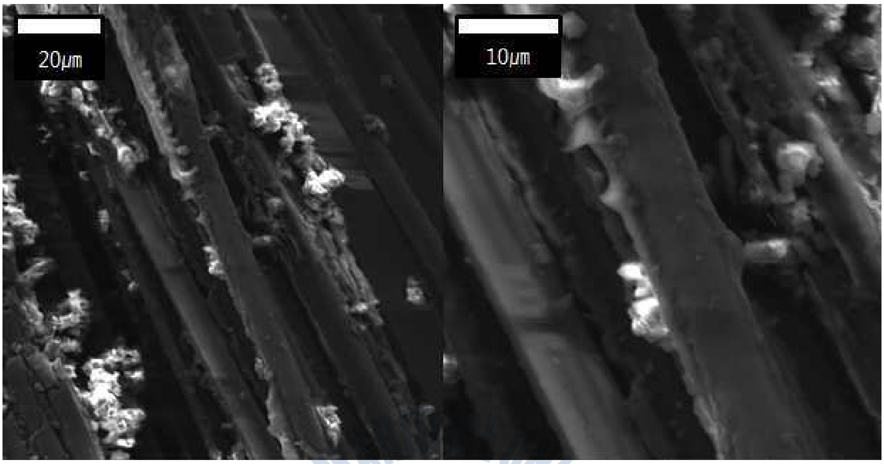
The fracture surface of the tensile test specimen manufactured with the ply orientation angle of the carbon fiber was checked. It could confirm that pull out phenomenon showed conspicuously in case of the fiber ply orientation angle of 45°. The picture of fracture surface was shown in Fig. 24. The pictures of the fracture surface of fiber ply orientation angle of 0° are equal to the Fig. 23 (e), (f). Particularly, the pull out phenomenon showed conspicuously in the case of the carbon/epoxy composites. It is considered that the delamination was maximized by the decreased inter-layer coupling between carbon fiber from which the sizing treatment is removed and the epoxy resin.



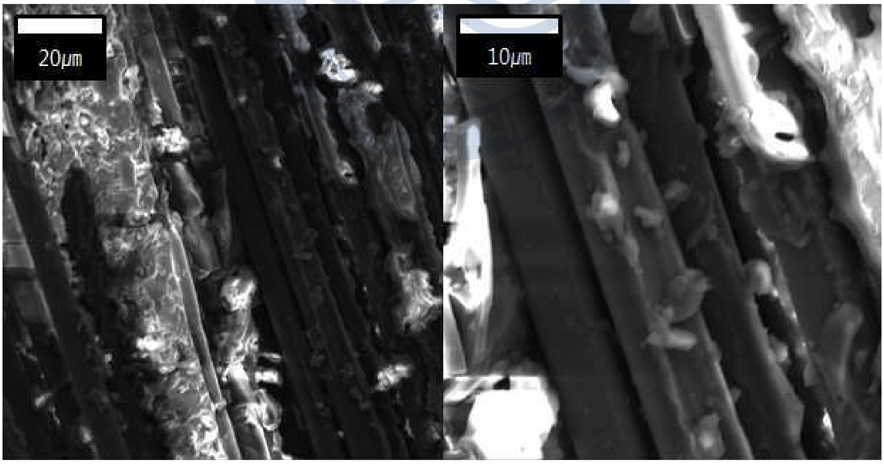
(a) 0℃ Heating for carbon/epoxy composites



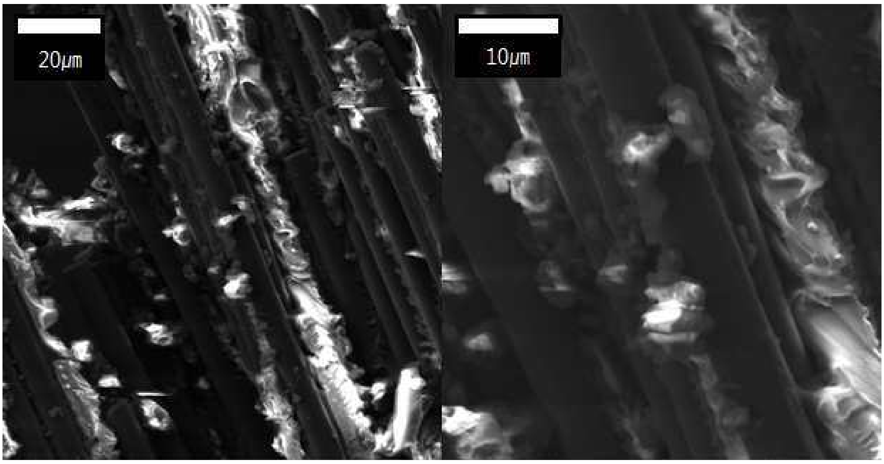
(b) 0℃ Heating for carbon/PEEK composites



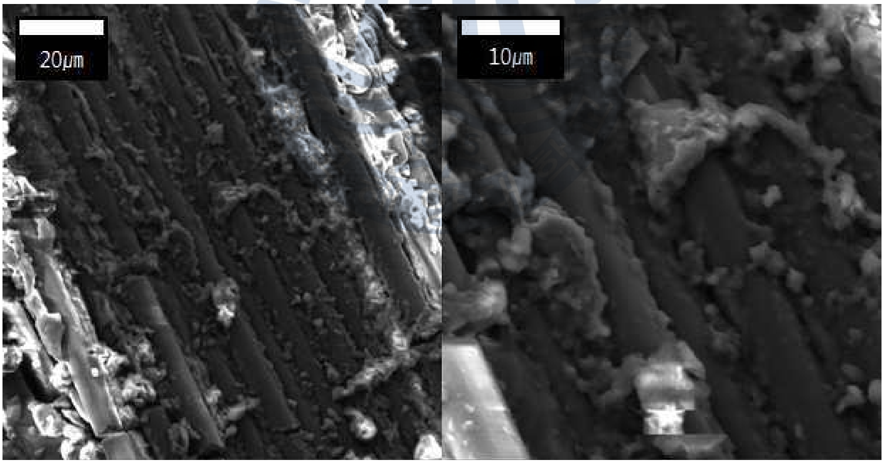
(c) 300℃ Heating for carbon/epoxy composites



(d) 300℃ Heating for carbon/PEEK composites

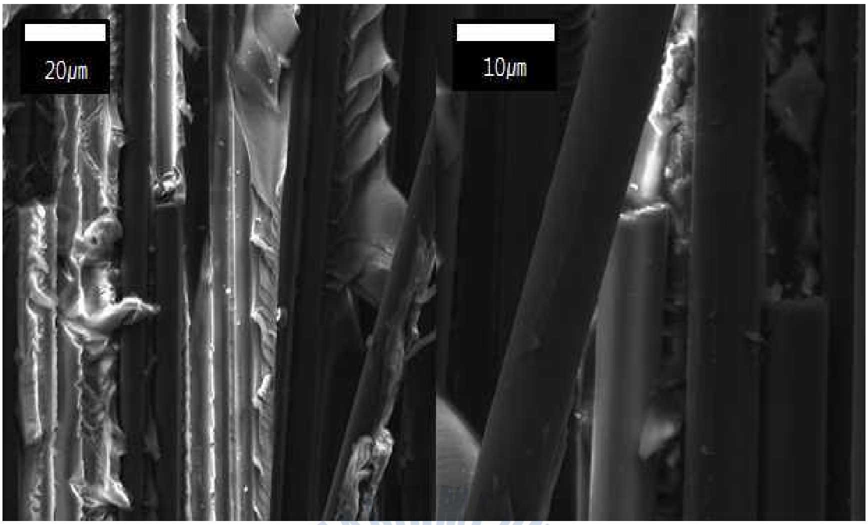


(e) 400℃ Heating for carbon/epoxy composites

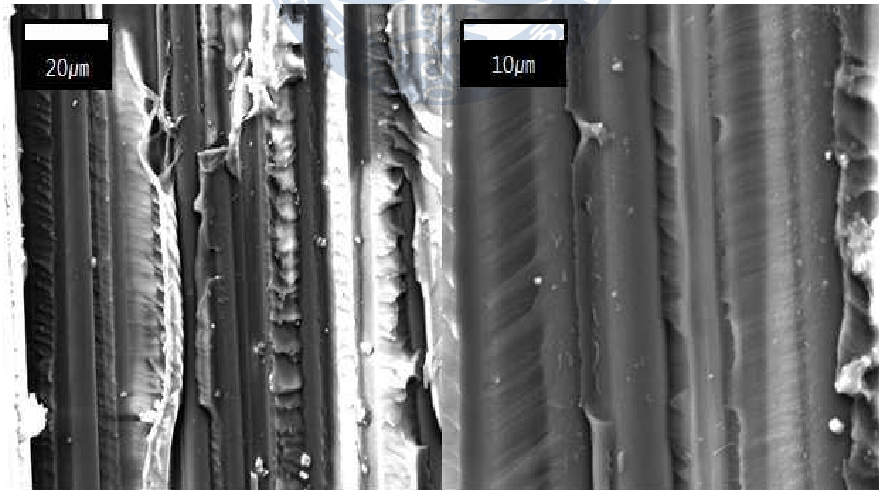


(f) 400℃ Heating for carbon/PEEK composites

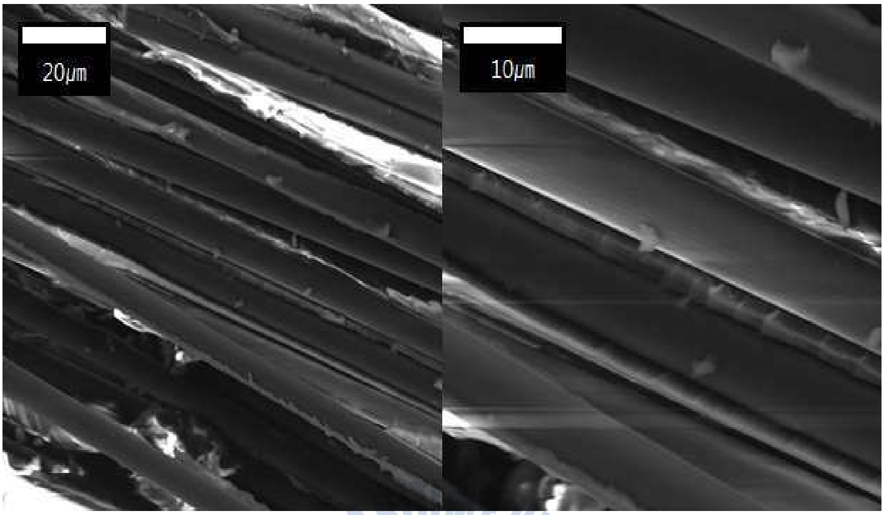
Fig. 23 SEM observations



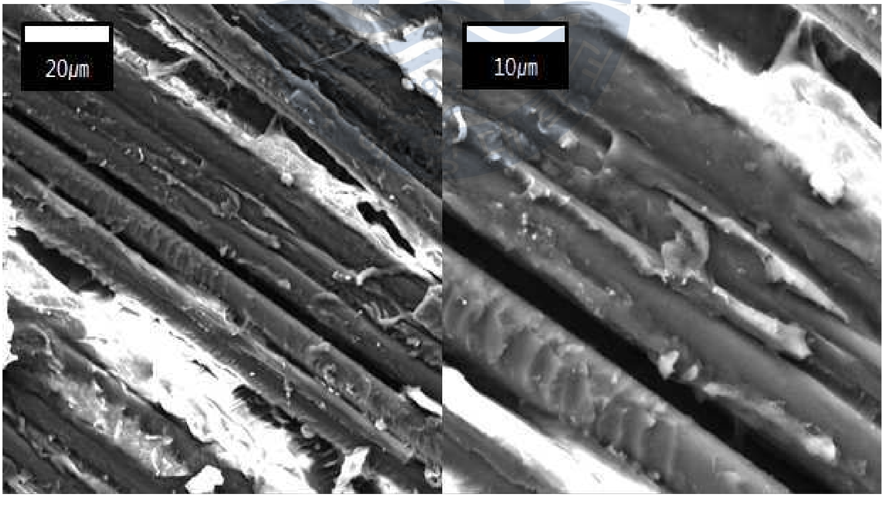
(a) Configuration II – epoxy



(b) Configuration II – PEEK



(c) Configuration III – epoxy



(d) Configuration III – PEEK

Fig. 24 SEM observations

4.2 Behavior of Moisture Absorption

In all specimens, the sudden increase of moisture content was confirmed before 20 days, and the gradual increase of moisture content was shown on the graph after 20 days. The theory that the behavior of the moisture of most polymeric materials follows Fick's diffusion law at the temperature below the glass transition temperature (Tg) was verified by the moisture content graph of this study. In addition, the moisture content of each specimen appeared to repeatedly increase and decrease when the immersion time was more than 100 days; it is considered that further moisture absorption did not occur due to the saturated moisture content.

If the composite materials are exposed to moisture for a long time, moisture diffusion into the base material occurs, causing interfacial debonding and destruction due to the swelling phenomenon and the destruction of the three-dimensional network. The analysis of the behavior of moisture content in this study demonstrates that the moisture content of carbon/PEEK composites showed a lower measured value of about 2% in comparison with the carbon/epoxy composites. It is believed that this is because the penetration of water molecules in the moisture environment is relatively low because the interfacial bonding strength between carbon fiber and PEEK resin is superior to that between carbon fiber and epoxy resin. The behavior of the moisture content according to the immersion time of each fiber-reinforced composite material is shown in Figure 25.

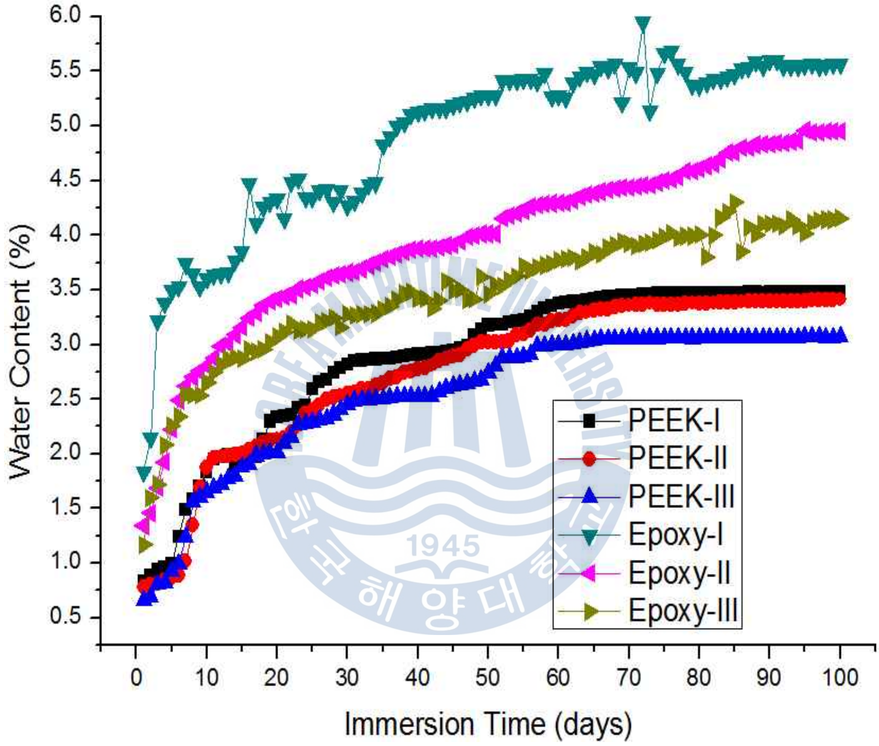
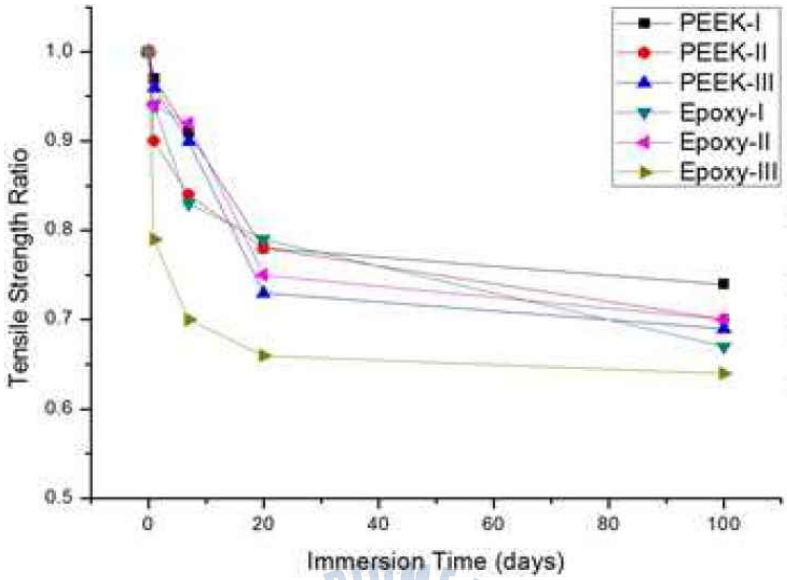
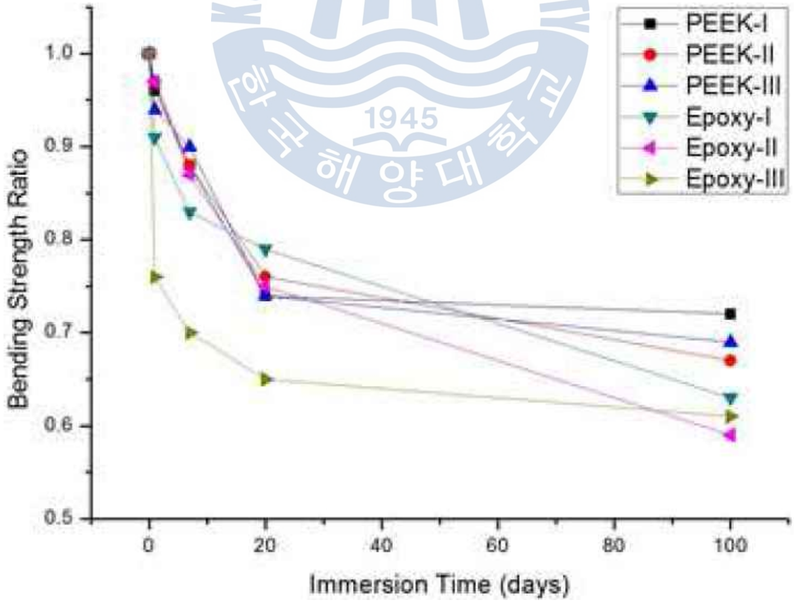


Fig. 25 Moisture absorption behavior according to immersion time



(a) Tensile test



(b) Bending test

Fig. 26 Change of mechanical strength by moisture absorption

4.2.1 Mechanical properties

The change of mechanical properties due to moisture absorption is shown in Fig. 26. Generally, the curves in the graph of tensile strength and bending strength decreased according to the lapse of immersion time, and especially a sharp reduction of the graph curve was shown before 20 days. This seems to be because the interfacial adhesion weakens due to the penetration of moisture into the fiber-reinforced composite materials. The reduction of the tensile strength according to the immersion time was measured according to the type of composites: carbon/PEEK composites of configuration I was 28%, carbon/epoxy composites was 37% and carbon/PEEK composites of configuration II was 33%, carbon/epoxy composites was 41% and carbon/PEEK composites of configuration III was 31%, and carbon/epoxy composites was 39%. Also, the reduction of the bending strength according to the immersion time was similar to the tensile strength. From the results of tensile strength and bending strength tests, it was verified that the reduction of mechanical properties of carbon/PEEK composites was the lowest. In conclusion, from the results of the mechanical properties tests of moisture absorption, it is considered that the increase of the moisture content influences the reduction of mechanical properties by weakening the adhesion between the interfaces.

4.2.2 Fracture energy

In the stress-strain curve, if the area is calculated, the fracture energy per volume (J/cm^3) can be calculated. The bending fracture energy per volume (J/cm^3) shows the toughness of the material. The fracture toughness is the capability of absorbing the energy generated among the plastic deformation and crack processes. The fracture energy depends on its mechanical properties or processing method. The possibility of brittle fracture of the material reduces as the toughness increases. The fracture energy is the area of the S-S curve of the specimen. The S-S curve of the carbon/PEEK composites of the Configuration I was shown to Fig. 27. The area was calculated from the following equation (3).

$$\frac{Energy}{Volume} = \int_0^{\epsilon_f} \sigma d\epsilon \qquad (3)$$

Where, σ = Moisture Content (%)

ε = weight of specimen after moisture absorption

ε_f = weight of specimen before moisture absorption

The fracture energy of each specimen is shown in Fig. 28. The exponential function of $y=ae^{bx}$ was used. The fracture energy of each specimen was verified. The fracture energy of the carbon/PEEK composites shows that the property's value was higher than the fracture energy of the carbon/epoxy composites. It is considered that this is because the energy in which the fracture toughness of the carbon/PEEK composites was excellent and which it endures in the cracking of the material was stronger.

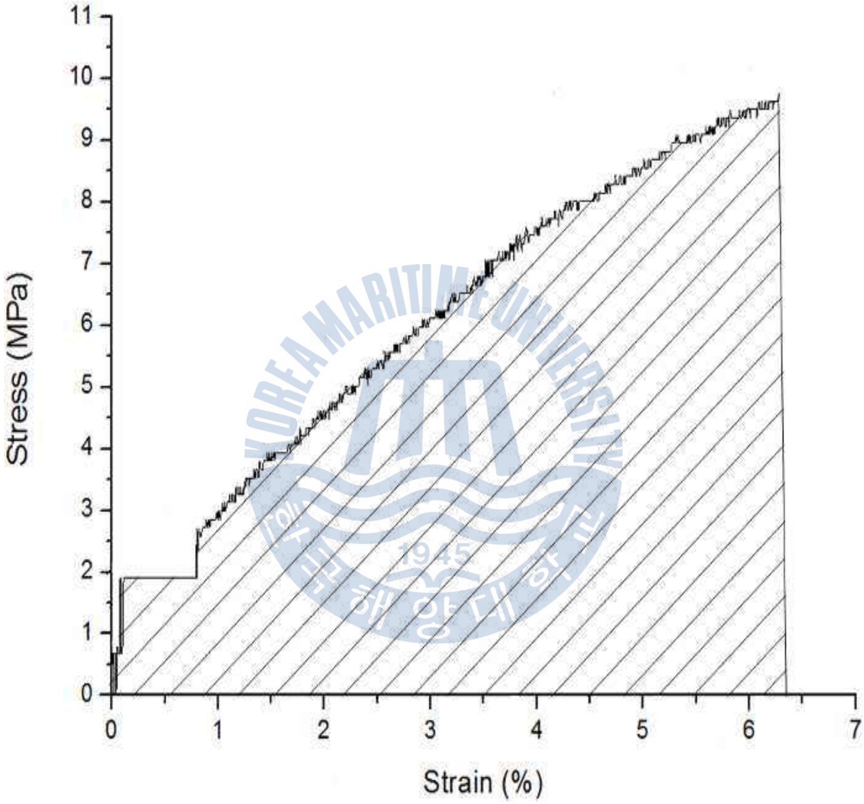


Fig. 27 The S-S curve of the composites.

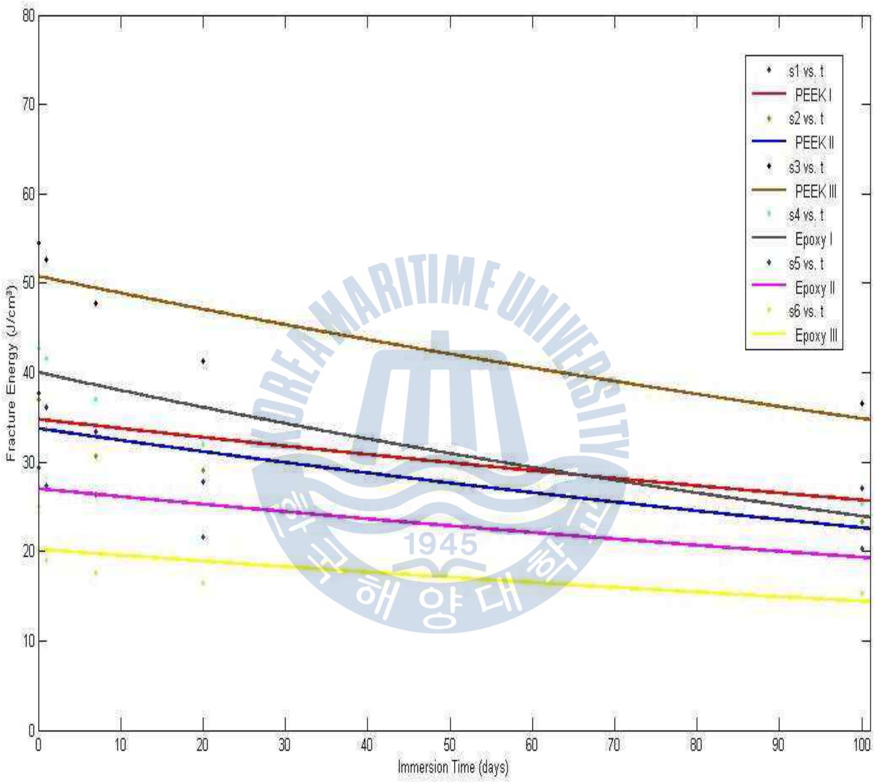
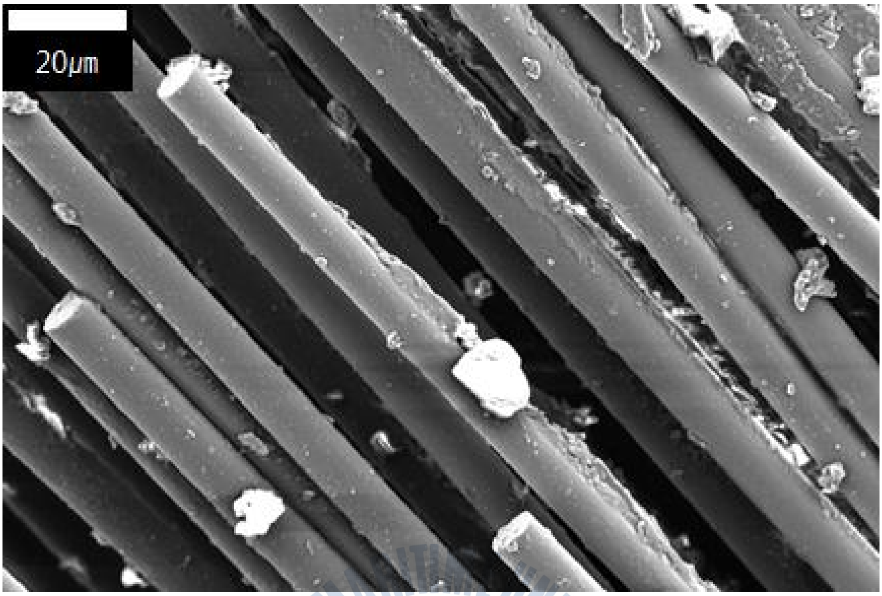


Fig. 28 Fracture energy for carbon/PEEK composites

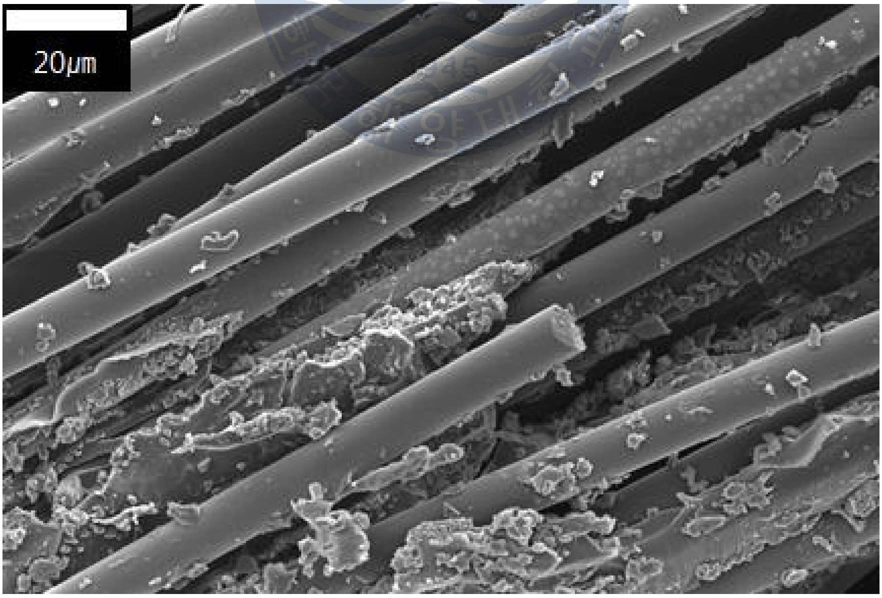
4.2.3 Fracture surface

The tensile and bending test were carried out to observe the destroyed morphology in the interface between the resin and fiber, and the fracture plane of the destroyed specimen was analyzed using an electron microscope. Figure 29 shows the fracture shape for each specimen according to the immersed period. Inspecting the specimen, the brittle fracture that typically indicates the unique failure modes of fiber-reinforced composite materials has not occurred, and it could be confirmed that the pull out phenomenon occurs because the resin cannot play the role due to the water molecules penetrating inside the fiber-reinforced composites.

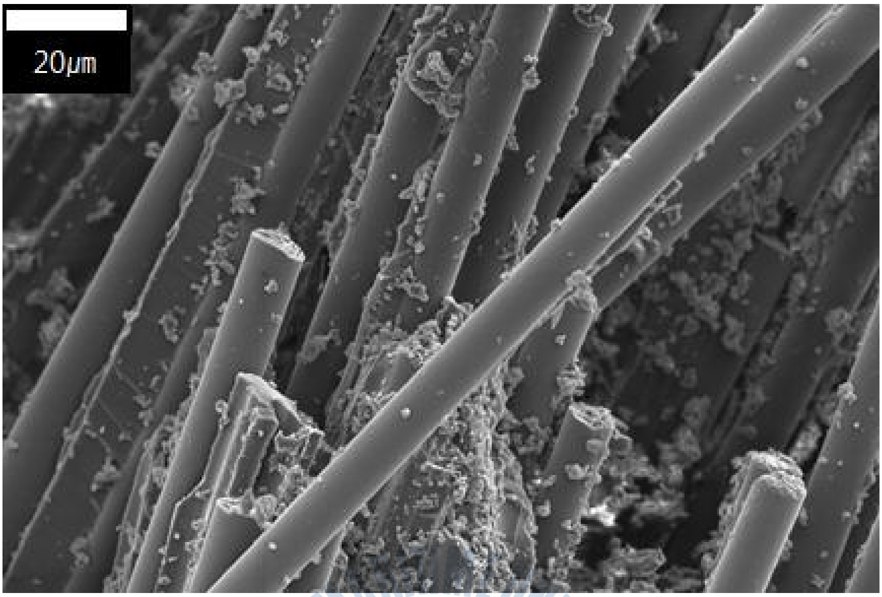
On the other hand, it could be confirmed that the breakdown shape of the specimens undergoing a short immersion time showed brittle fracture due to the powerful bonding between the resin and reinforced fiber. In conclusion, it is believed that as the time that the fiber is immersed in water increases, the length of the fiber pulled-out also increases, and the amount of resin is reduced due to the weakening of the interfacial bonding force between the resin and fiber.



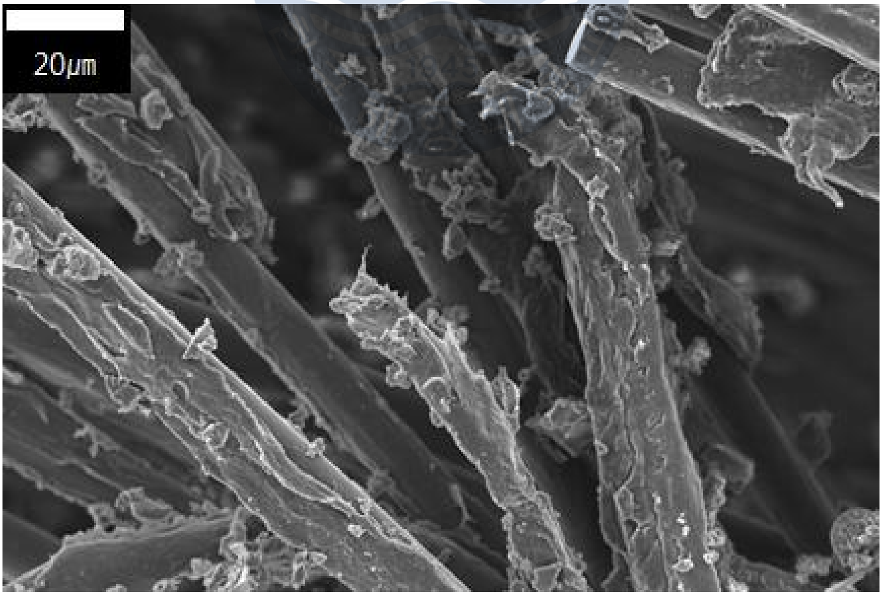
(a) Configuration I – epoxy



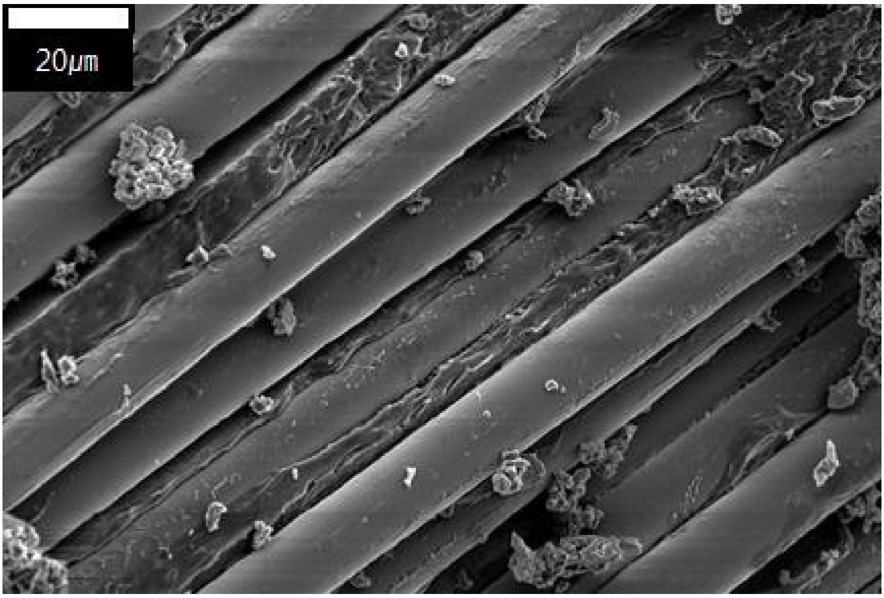
(b) Configuration I – PEEK



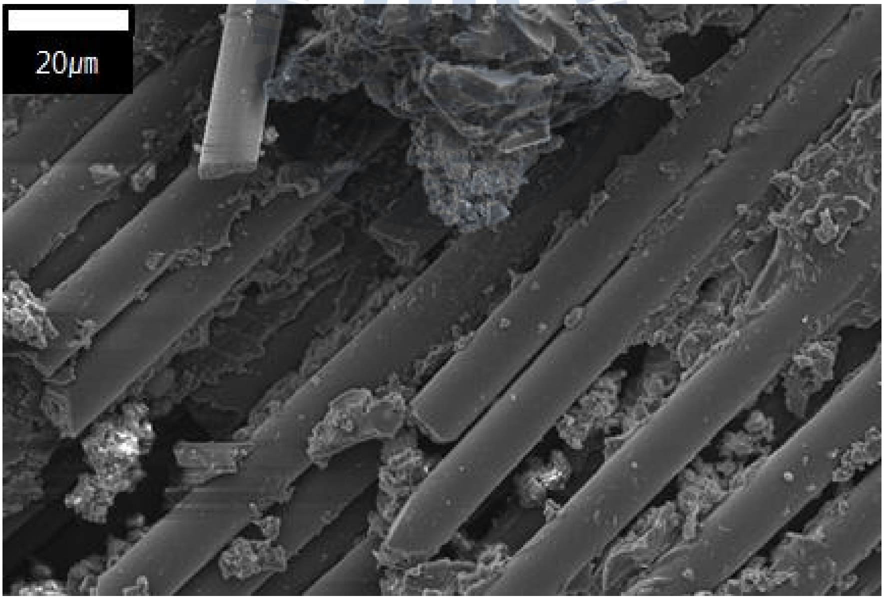
(c) Configuration II – epoxy



(d) Configuration II - PEEK



(e) Configuration III – epoxy



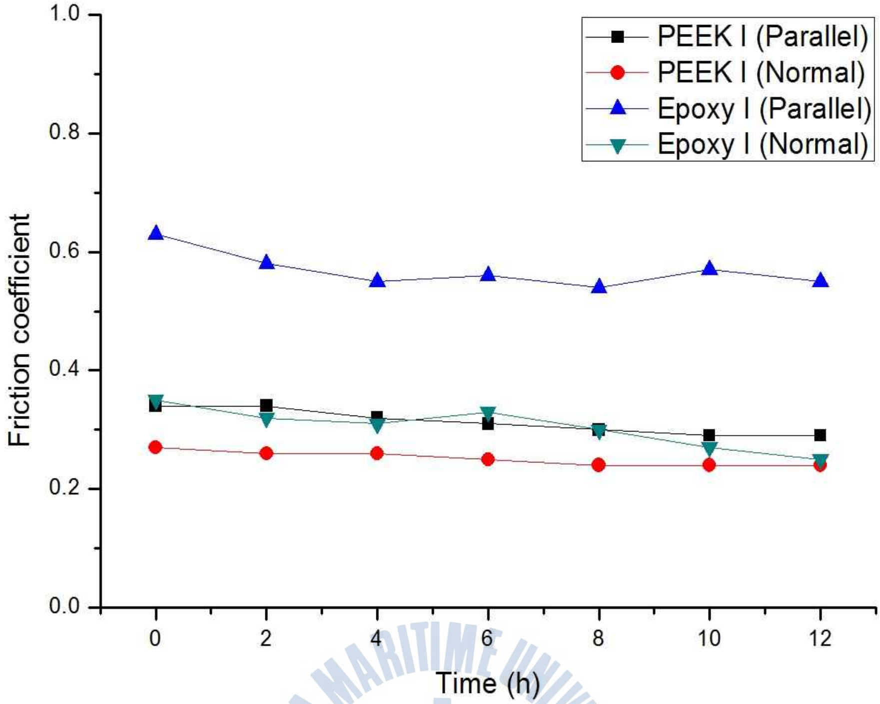
(f) Configuration III - PEEK

Fig. 29 SEM observations

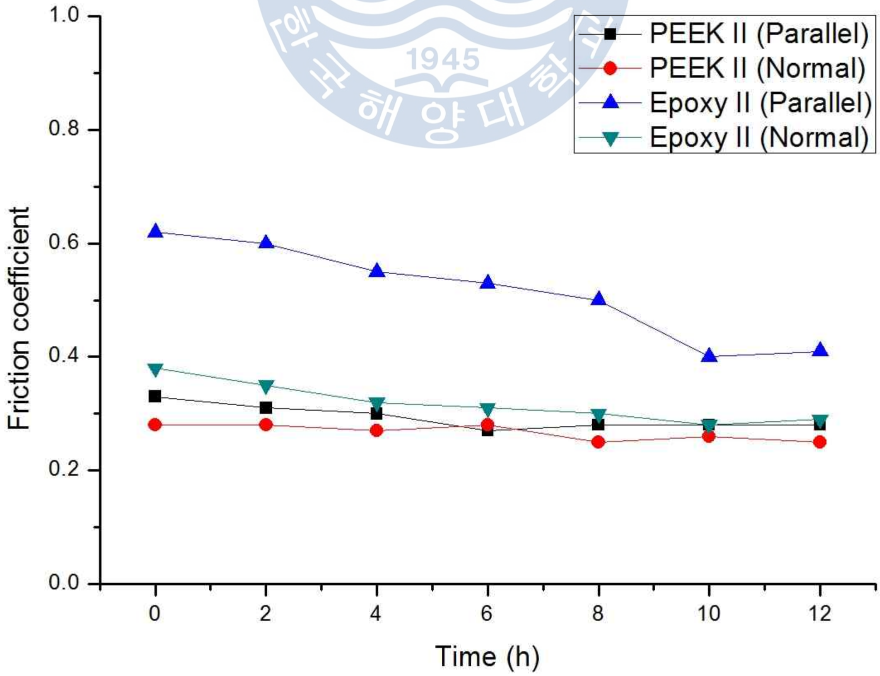
4.3 Friction and Wear Behavior

4.3.1 Tribological properties

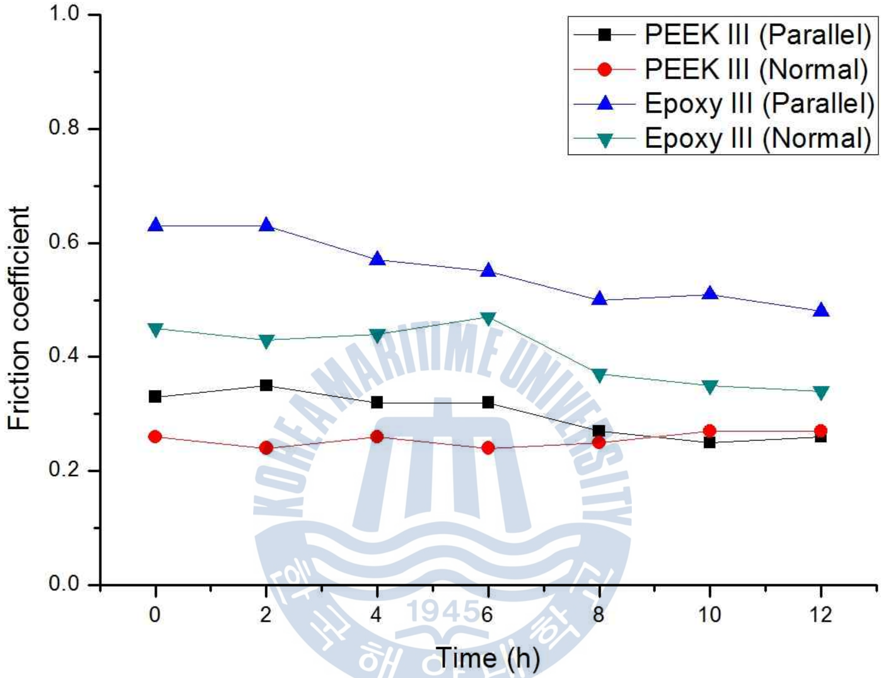
The test was progressed for the friction coefficients according to the fiber ply orientation. The results of the friction coefficient are shown in Fig. 30. The carbon/PEEK and carbon/epoxy composites showed similar trends. As shown in the figure, the friction coefficient was larger in the direction parallel to the relative friction surface. In addition, no clear difference in the friction coefficient was found in relation to the carbon fiber ply orientation. However, in the case of the direction parallel to the relative friction surface, the sizes of the friction coefficient had the order of configurations I, III, and II. In the case of the normal direction, the friction coefficients had the order of configurations I, II, and III. The carbon fiber and matrix material showed a surface with discontinuity. Preferentially, a crack occurred on the side where these were in contact, and a delamination phenomenon was generated. In the case of the direction normal to the relative friction surface, debonding occurred between the carbon fiber and the resin at the friction surfaces, and this was directly affected by the fiber ply orientation. However, in this case, the debonding was unable to increase before the length of the carbon fiber was reduced by wear. In the case of the direction parallel to the relative friction surface, the debonding was considered to be a result of the increase in the friction coefficient because the contact area of the relative friction surface and carbon fiber was relatively wide.



(a) Configuration I



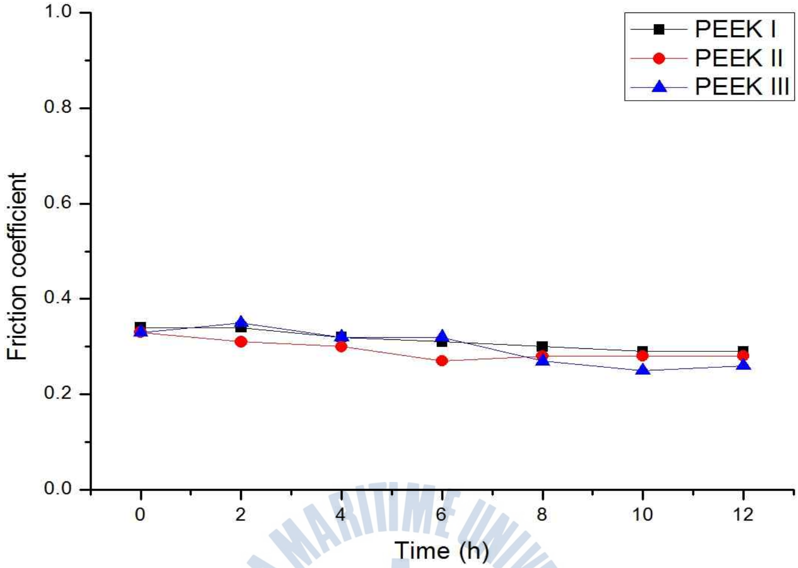
(b) Configuration II



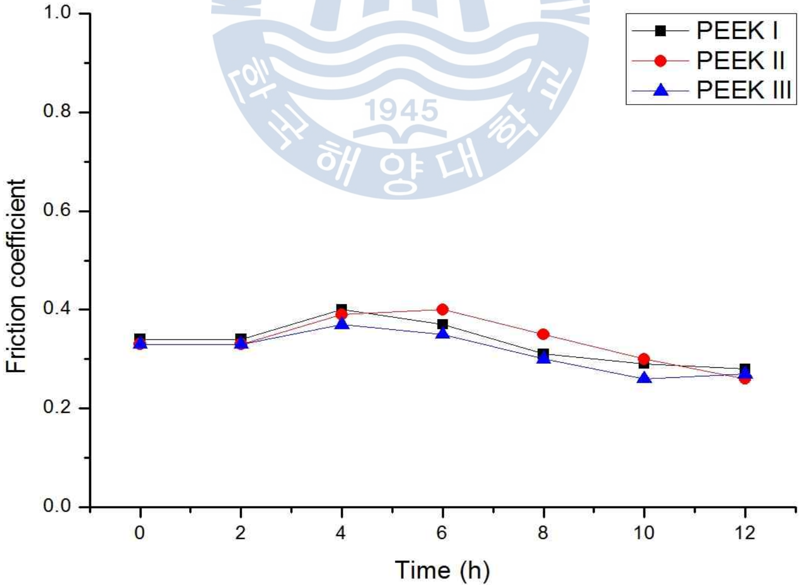
(c) Configuration III

Fig. 30 Effect of ply configuration on friction coefficient

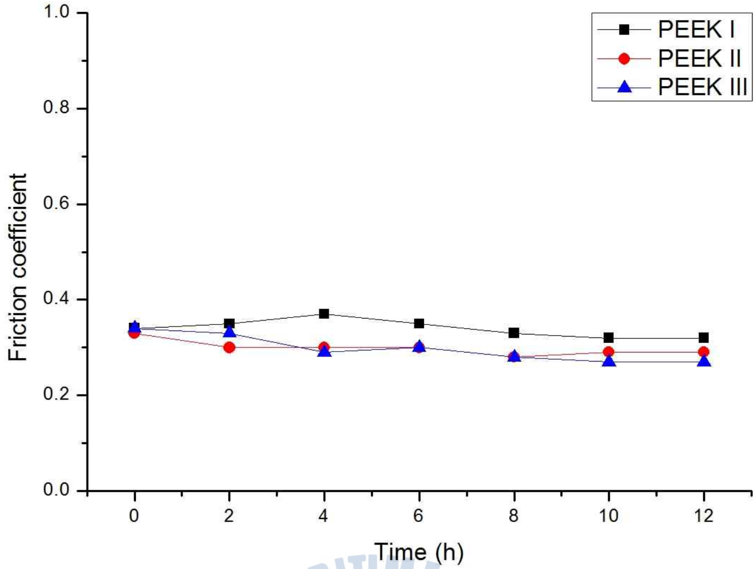
The friction coefficients were compared according to the fiber ply orientation. The changes in the friction coefficient are shown in Fig. 31. As shown in the figure, the friction coefficient did not show a large-scale change according to the sliding distance at a low pressure and speed. However, the friction coefficient was increased and reduced when the pressure and speed increased. The carbon fiber and matrix material had a surface with discontinuity. Preferentially, a crack occurred at the side where these were in contact, and the delamination phenomenon was generated. In other words, the matrix part wore out as the pressure increased. Thus, it is considered that the fiber received the repeated load. Therefore, it was determined that the pressure and speed had an effect on the friction coefficient. In addition, in the case where the speed was 2.5 m/s, a relatively large friction coefficient was found for configuration I. This appears to be a phenomenon where the bending stress acted on the carbon fiber. However, in a case where the speed was 5 m/s, no definite difference was seen in the friction coefficient according to the carbon fiber ply orientation. Thus, it could be said that the fiber ply orientation was unable to have an effect on the frictional property when the friction velocity was high.



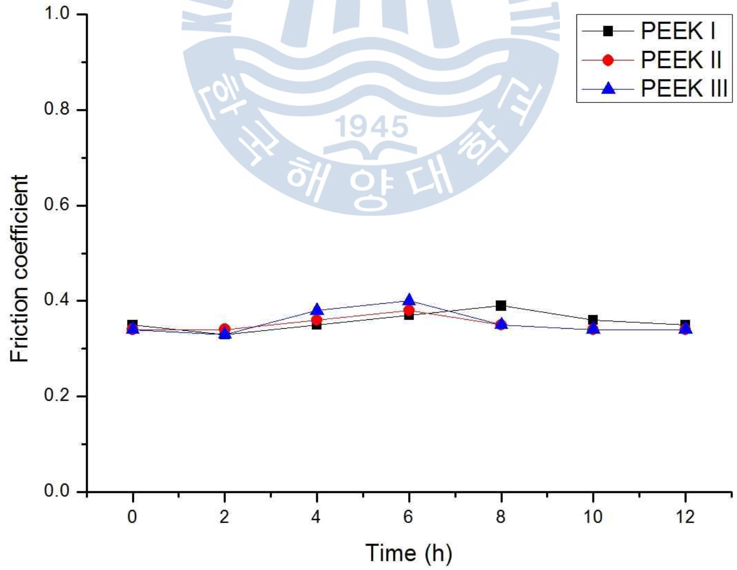
(a) V = 2.5 m/s, P = 20 N



(b) V = 5 m/s, P =20 N



(c) V = 2.5 m/s, P = 40 N

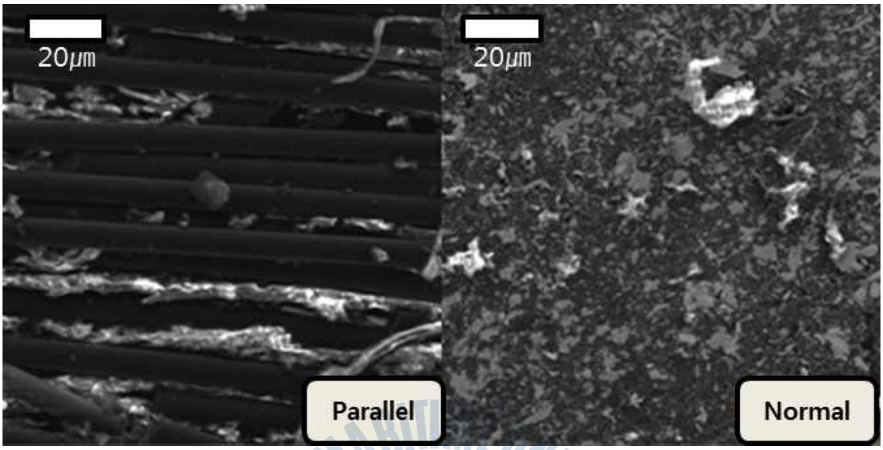


(d) V = 5 m/s, P = 40 N

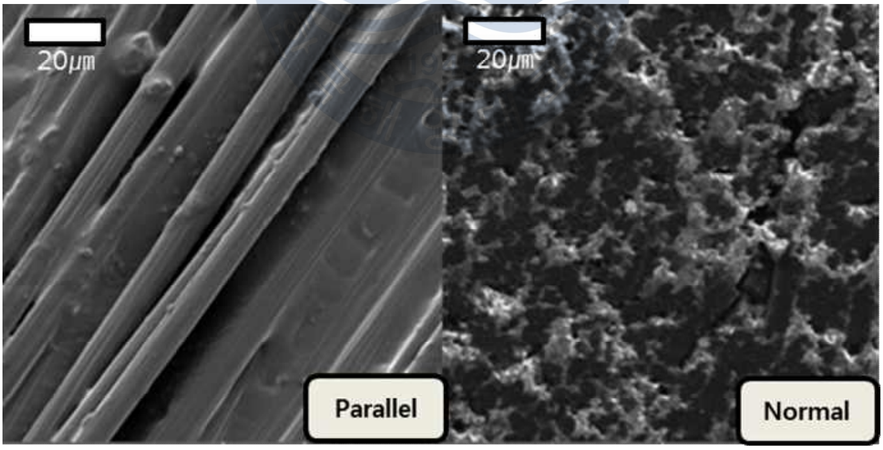
Fig. 31 Effect of sliding velocity and pressure on friction coefficient

4.3.2 Fracture surface

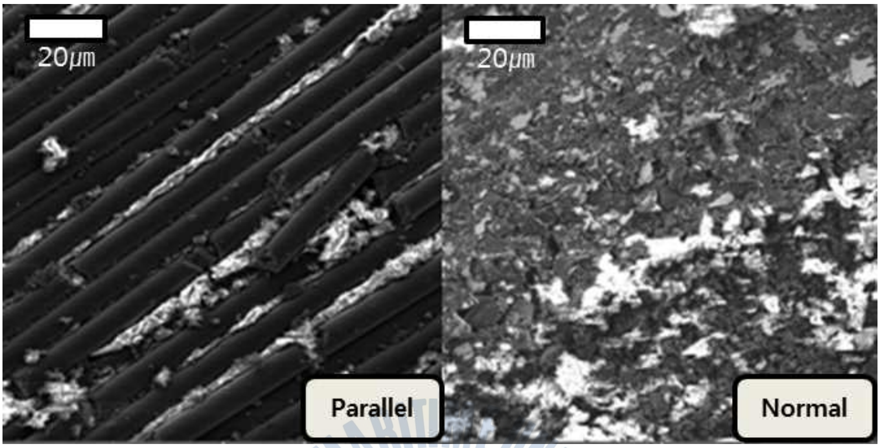
Friction tests were carried out to observe the destroyed morphology in the interface between the resin and fiber, and the friction surface of the specimen was analyzed using an electron microscope. The friction shape for each specimen was shown in Fig. 32. First, in the case of the direction normal to the relative friction surface, extreme breaks in the carbon fiber occurred in the specimens with configuration II and III. In addition, in case of the direction parallel to the relative friction surface, the extreme breaks in the carbon fiber occurred in the specimens with configuration I. This appears to be a phenomenon where the bending stress acts on the carbon fiber. On the other hand, in the specimens with configurations I and II, the tensile stress and bending stress acted on the carbon fiber. Thus, the grinding fiber and breaking fiber could be confirmed. Fig. 33 shows the friction shape for each specimen. In all cases, the debonding of the fiber and PEEK could be confirmed. The carbon fiber was subjected to more repeated loads at high speed. Thus, the debonding seemed to be generated by the degradation of the material.



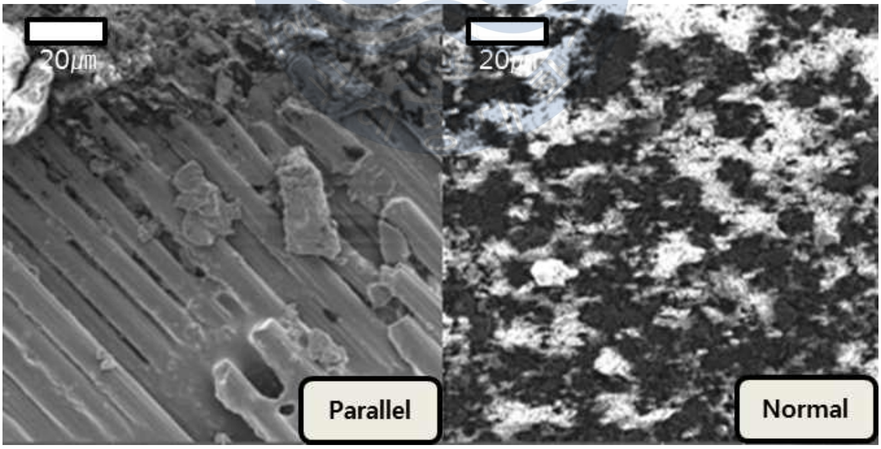
(a) Configuration I for carbon/epoxy



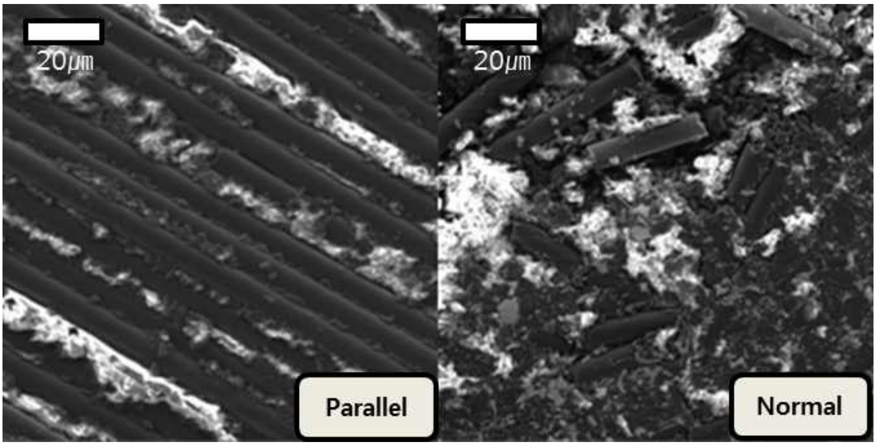
(b) Configuration I for carbon/PEEK



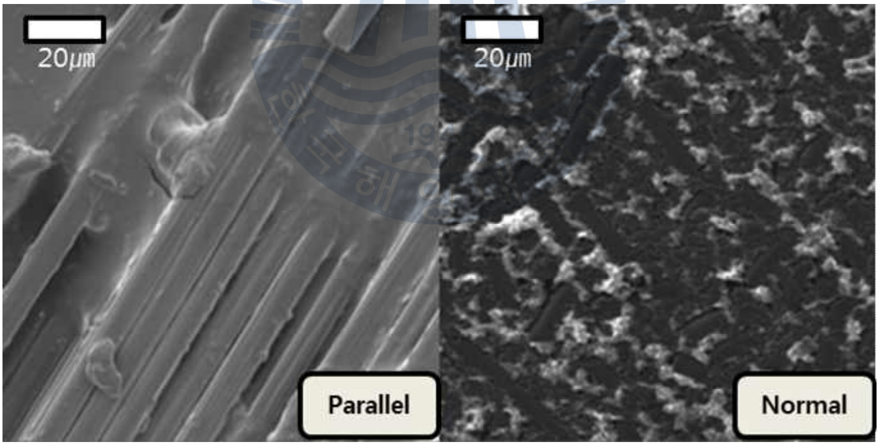
(c) Configuration II for carbon/epoxy



(d) Configuration II for carbon/PEEK

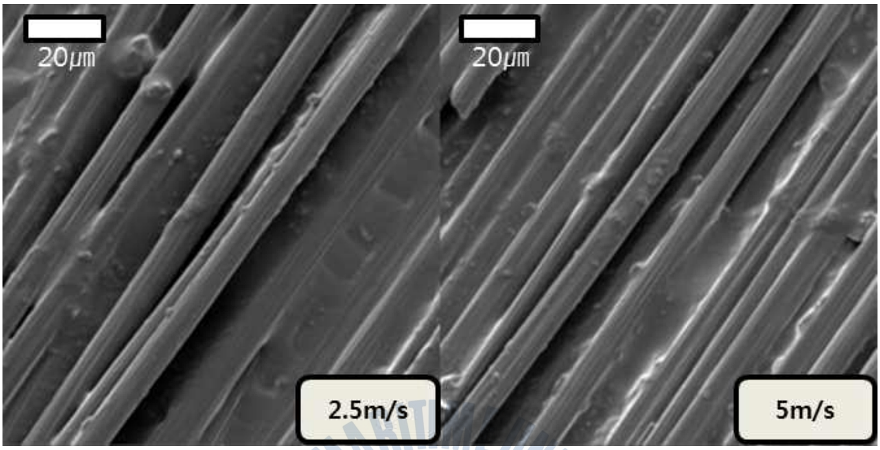


(e) Configuration III for carbon/epoxy

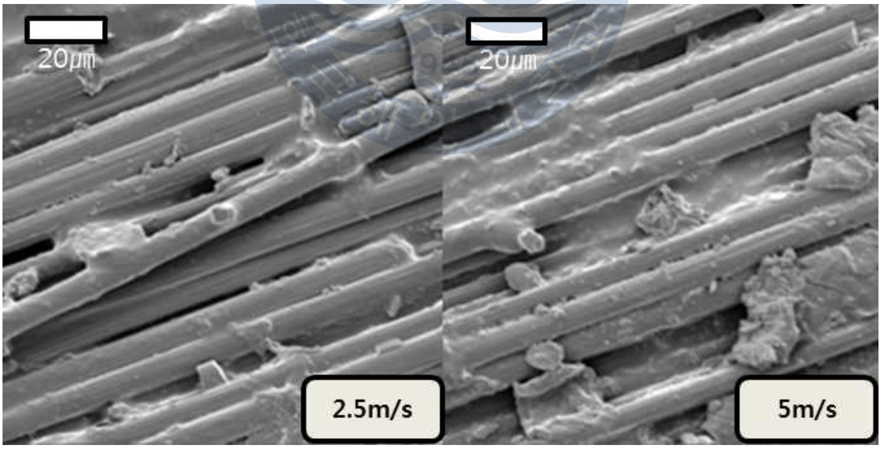


(f) Configuration III for carbon/PEEK

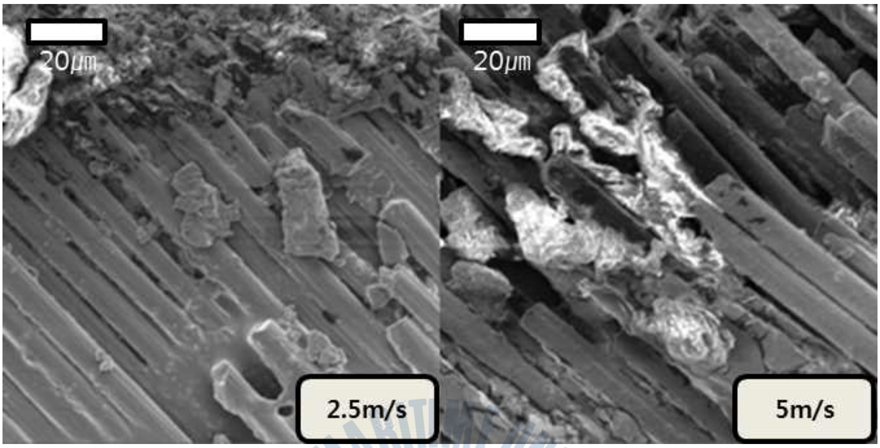
Fig. 32 SEM observations



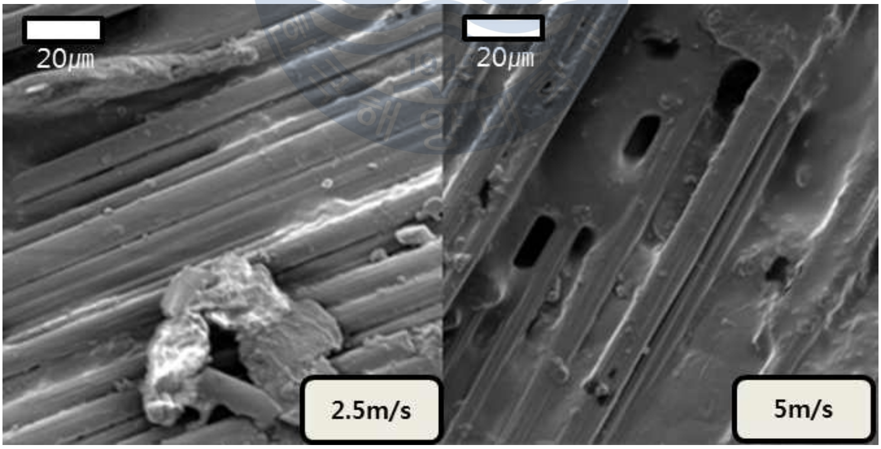
(a) Configuration I (20 N)



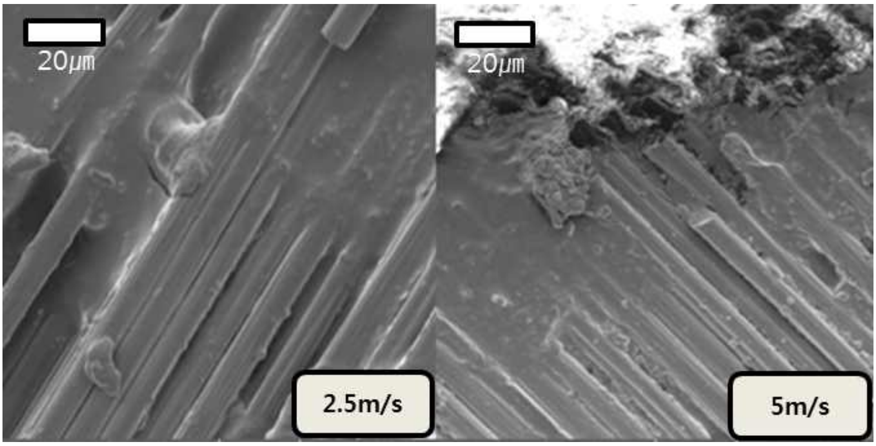
(b) Configuration I (40 N)



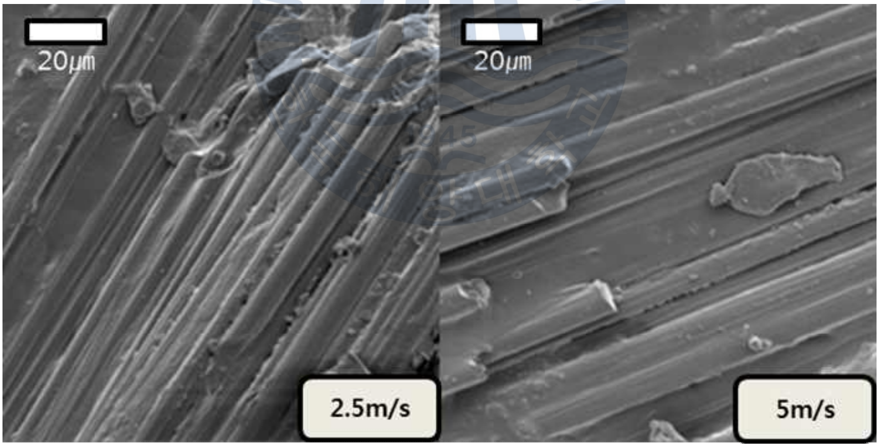
(c) Configuration II (20 N)



(d) Configuration II (40 N)



(e) Configuration III (20 N)



(f) Configuration III (40 N)

Fig. 33 SEM observations

4.4 Finite Element Analysis

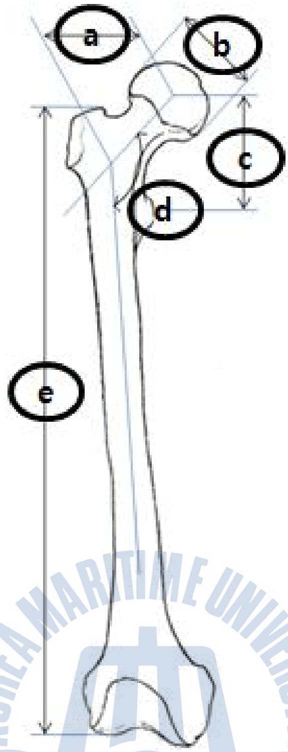
4.4.1 Design and modeling method

The shape of the femur is extracted through the patient's CT image in order to accurately implement the shape of the customized artificial hip joint stem and the stem needs to be designed according to this shape. However, the size of the femur differs and the different activity environments for each patient. The standard of shape for femur was shown in Fig. 34. Therefore, it is not appropriate to progress the research by extracting the shape from the CT image of one particular patient. In this paper, the stem was designed from the normal shape of the femur. The normal shape of the femur was shown in Table 3. In addition, 3 types of fiber layered structures were established in order to confirm the distribution of stresses phenomenon and implement the optimum design of the stem according to the fiber laminating direction. The mechanical properties of carbon/PEEK composites were shown in Table. 4.

The 3D modeling of both stem types of artificial hip joints was designed based on the normal shape of the femur. The first shape follows the shape of the stem made of the existing metal material. The second stem shape is designed for the bottom part of the stem with the curve shaped for an even load dispersion. The designed shape and load direction of the stem are shown in Fig. 35.

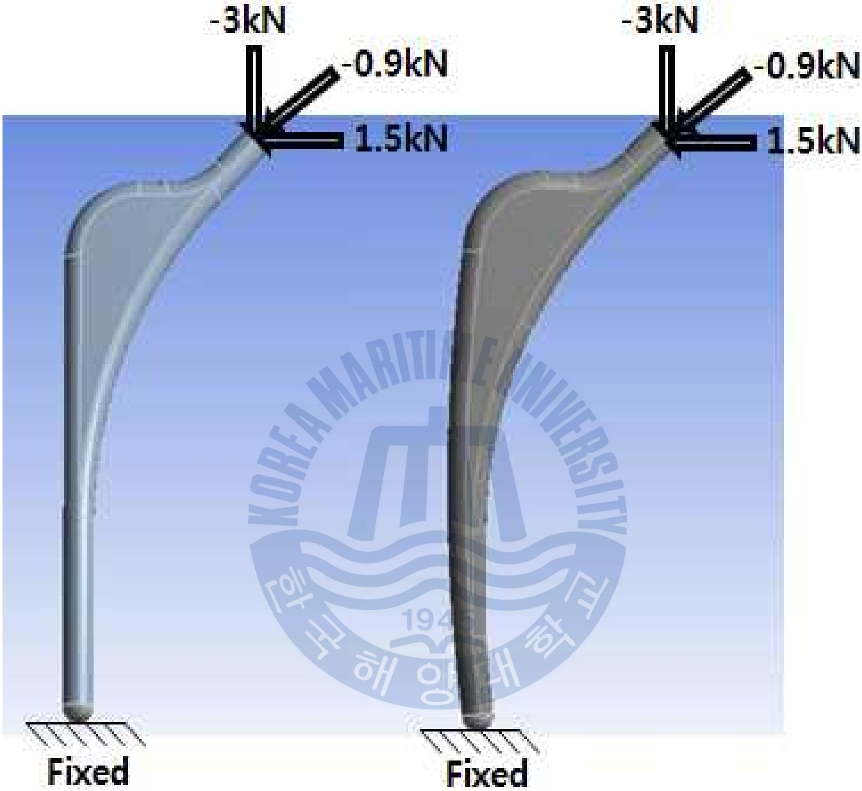
Table 3 Standard of shape for femur

Parameters	Standard			
	Average	Deviation	Maximum	Minimum
Femoral head offset (mm)	37.4	5.1	49.1	26.4
Femoral head diameter (mm)	45.1	3.8	50.3	36.7
Femoral head position (mm)	49.5	6.0	59.8	35.9
Neck-shaft angle (°)	127.1	5.0	135.9	115.5
Femoral length (mm)	420.9	28.9	470.1	363.6



	Parameters	Standard
ⓐ	Femoral head offset (mm)	37.4
ⓑ	Femoral head diameter (mm)	45.1
ⓒ	Femoral head position (mm)	49.5
ⓓ	Neck-shaft angle (°)	127.1
ⓔ	Femoral length (mm)	420.9

Fig. 34 Standard of shape for femur

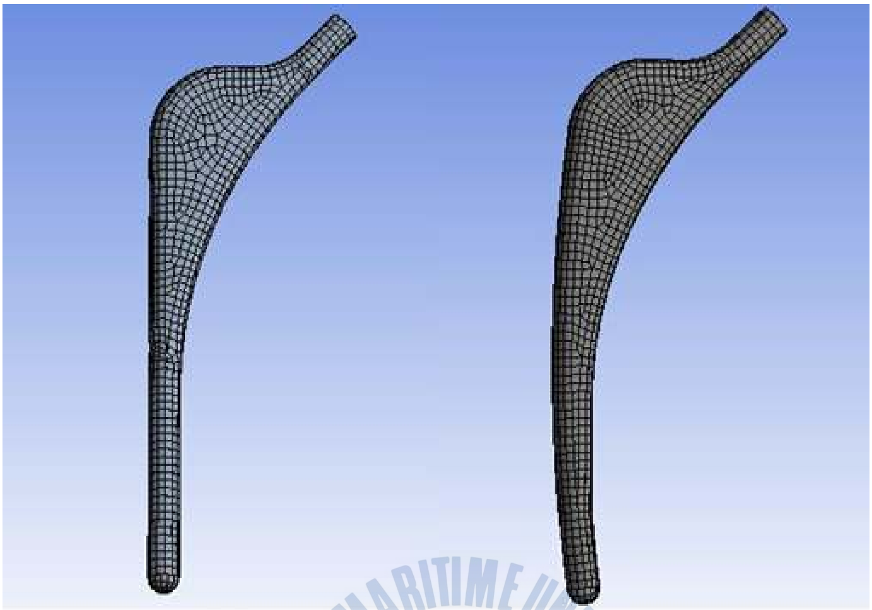


(a) General shape (b) Curved shape

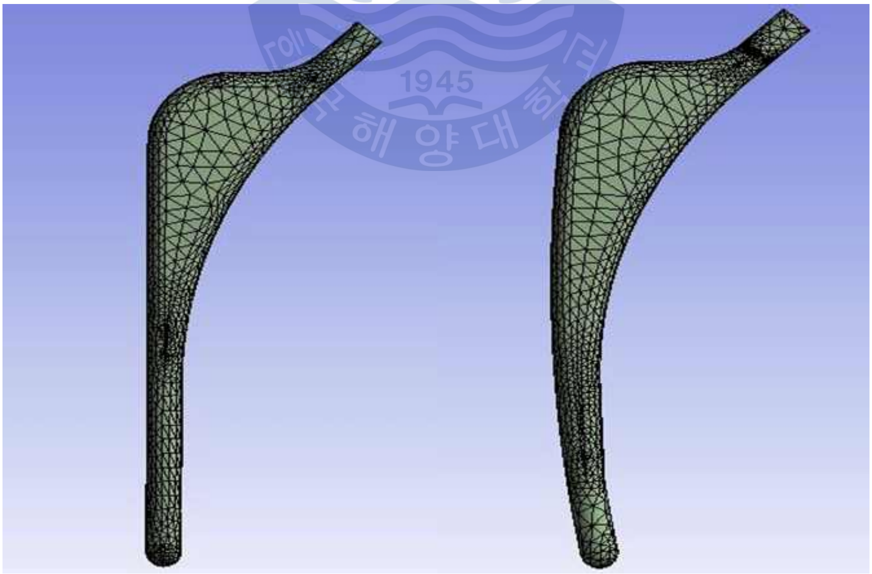
Fig. 35 Design concepts and load direction of the stem and Ti stem composites

Table 4 Mechanical properties of carbon/PEEK composites

Constants		Configuration I	Configuration II	Configuration III	Ti
Modulus of Elasticity (GPa)	E_x	95	4.5	4.0	96
	E_y	8.5	15.5	9.8	
	E_z	8.5	15.5	9.8	
Shear Modulus (GPa)	G_{yz}	2.5	3.5	3.0	35.3
	G_{zx}	4.5	4.0	3.5	
	G_{xy}	4.5	4.0	3.5	
Poisson Ratio (ν)	yz	0.3	0.3	0.3	0.36
	zx	0.3	0.3	0.3	
	xy	0.3	0.3	0.3	



(a) Composites



(b) Metal

Fig. 36 Meshed shape of the stem

4.4.2 FEA models and load

The meshed shape of the stem is shown in Fig. 36. Details of the model meshes are shown in Table 5. The finite element analysis models were meshed and analyzed using a commercially available program. It is very important to analyze the bio-mechanical characteristics of the geometric design variables before designing the customized artificial hip joint. The femur undergoes various stresses depending on the the lifestyle and posture of the patient. However, it is difficult to reproduce these conditions completely in the simulation. Therefore, the loading condition is applied to the area of neck where the break in the stem mainly occurs. The geometric design variables of the stem were confirmed by using the finite element method. The shear stress of the composites and metal are compared for the artificial hip joint.

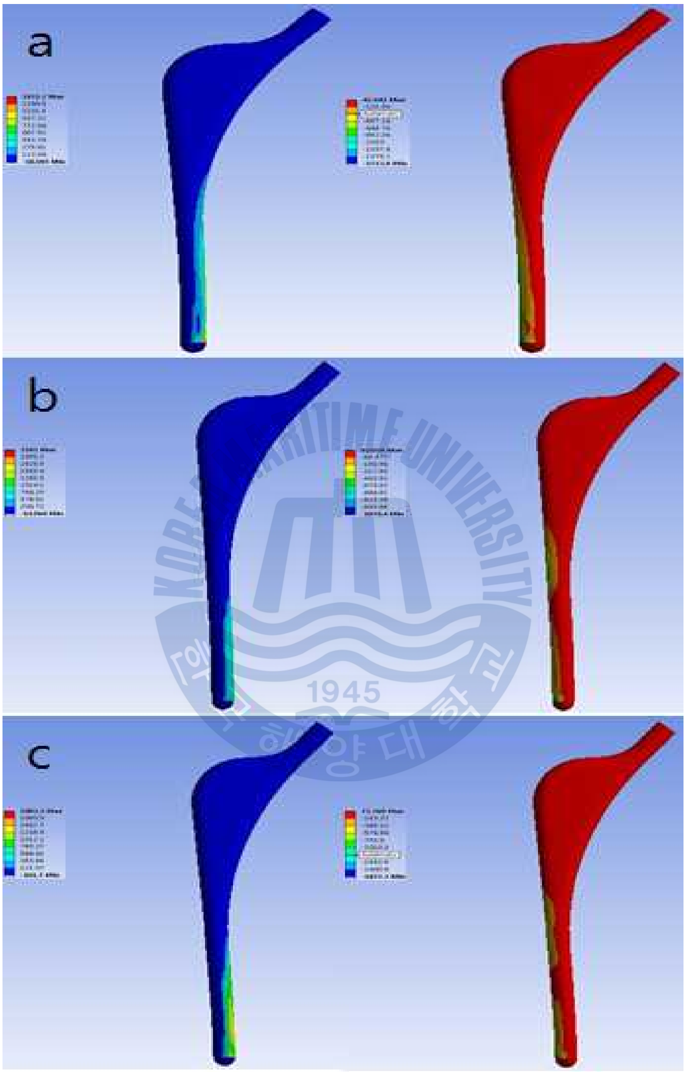
The stem receives various loads from the muscle. First, three load cases of 1kN, 2.5kN and 5kN were used for each of FEA models. Second, the load condition was determined as shown in Fig. 35 for each of the FEA models. The load applied to the stem head with an angle of 20° was used to verify the FEA results obtained in the present study by comparing the stresses in the stem and in the Ti stem model with those reported by previous researchers. The loads were distributed over several nodes to avoid stress concentration and the displacement of all nodes at the distal end of the stem was rigidly constrained.

Table 5 Details of the meshes for models

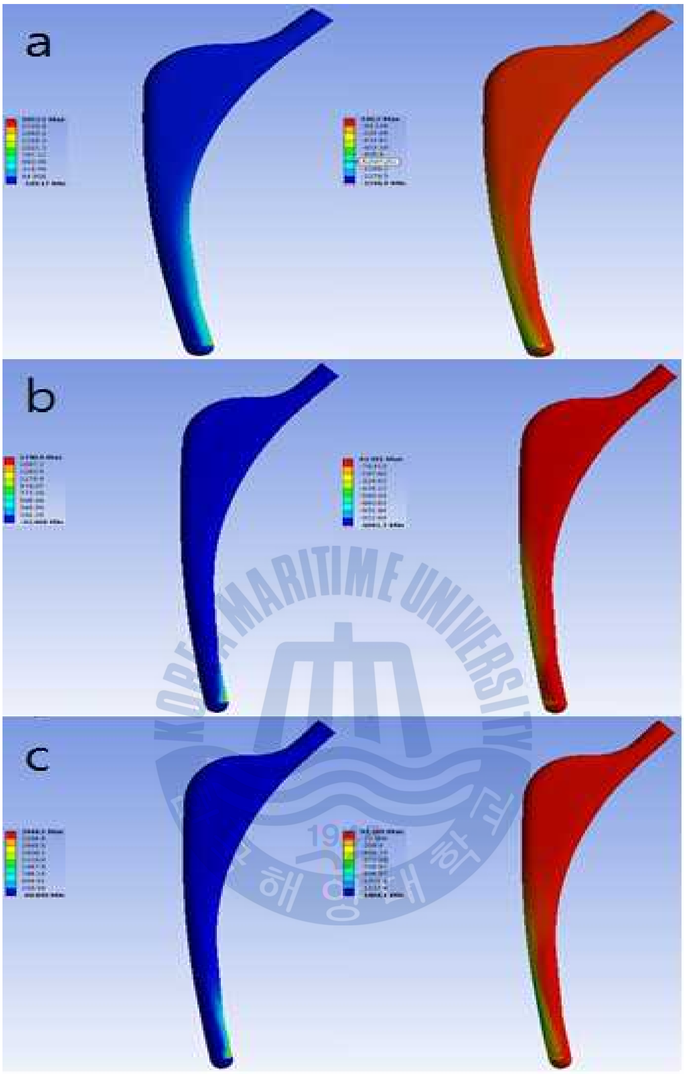
Part	Number of Nodes	Number of Elements
General Shape (Composites)	9,715	7,836
Curved Shape (Composites)	10,409	8,456
General Shape (Metal)	7,382	3,555
Curved Shape (Metal)	9,824	4,721

4.4.3 Principal stress

The new concept design of the stem using composites was described. Finite element models were used to evaluate the potential of the proposed design concept. The principal stress according to the ply configuration is shown in Fig. 37. The condition of loading used in the experiment was 1kN. In the case of general shape, the results according to ply configuration showed that the stress of ply configuration I were 24.8%~39.5% lower than ply configurations II and III. On the other hand, in the case of the curved shape, ply configuration II was 8.51%~26.7% lower than ply configurations I and III. It is considered that this is because the mechanical property of ply configuration II was superior to ply configuration I laminated with 0° because of the curve. On the other hand, the general shape of the stem receives stress perpendicularly. Therefore, it seems that the stress applied to the stem was low in the case of ply configuration I. The distribution of stress effect on the general shape of ply configuration I and the curved shape of ply configuration II were checked in this paper. The principal stress according to load is shown in Fig. 38. The load applied to the stem was 2.5kN and 5kN. The result showed that the stress of the curved shape was 20% higher than the general shape in the 2.5kN load. A similar phenomenon in the condition of 5kN load was confirmed. However, in the case of ply configuration II, the stress of the curved shape was about 32% lower than the stress of the general shape. The distribution of stresses applied to the stem therefore differed according to the fiber ply orientation. Therefore, the fiber ply orientation and the shape of the stem need to be determined by measuring the load accurately because the load applied to the stem differs for each patient.

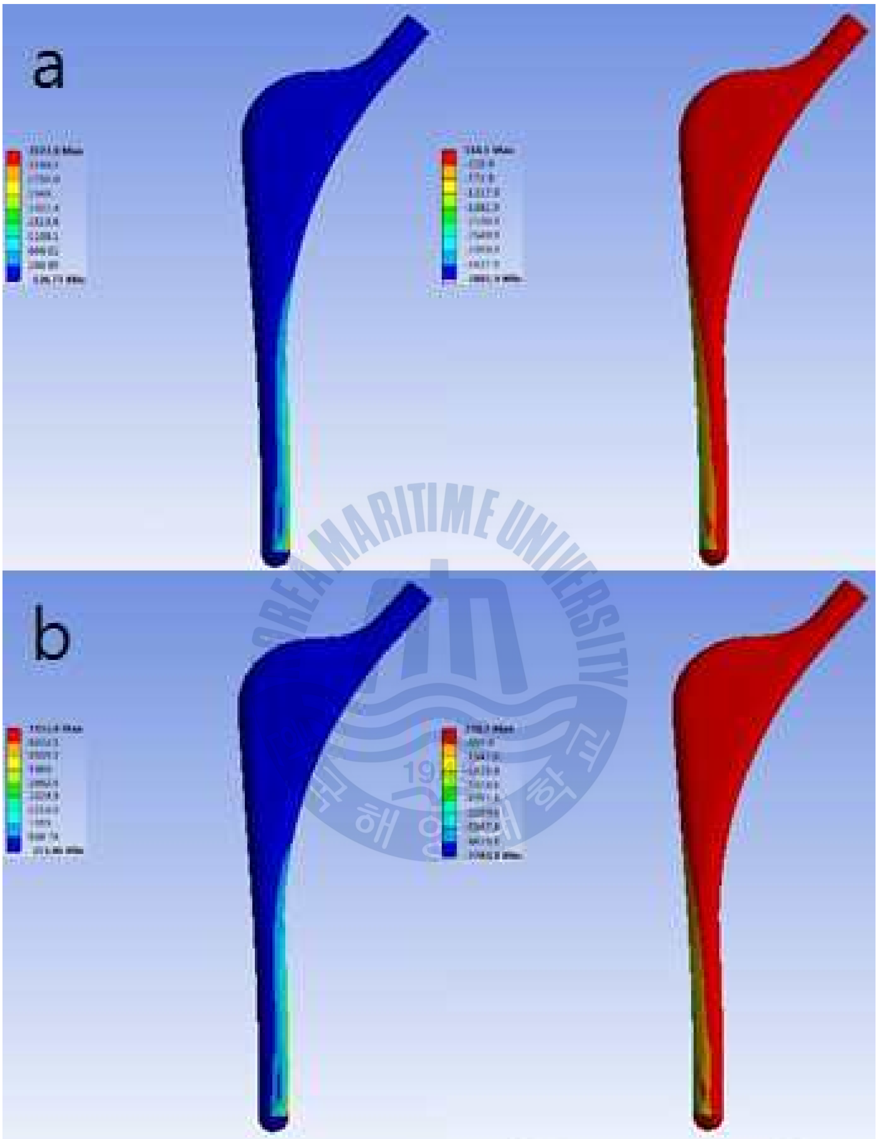


(a) General shape

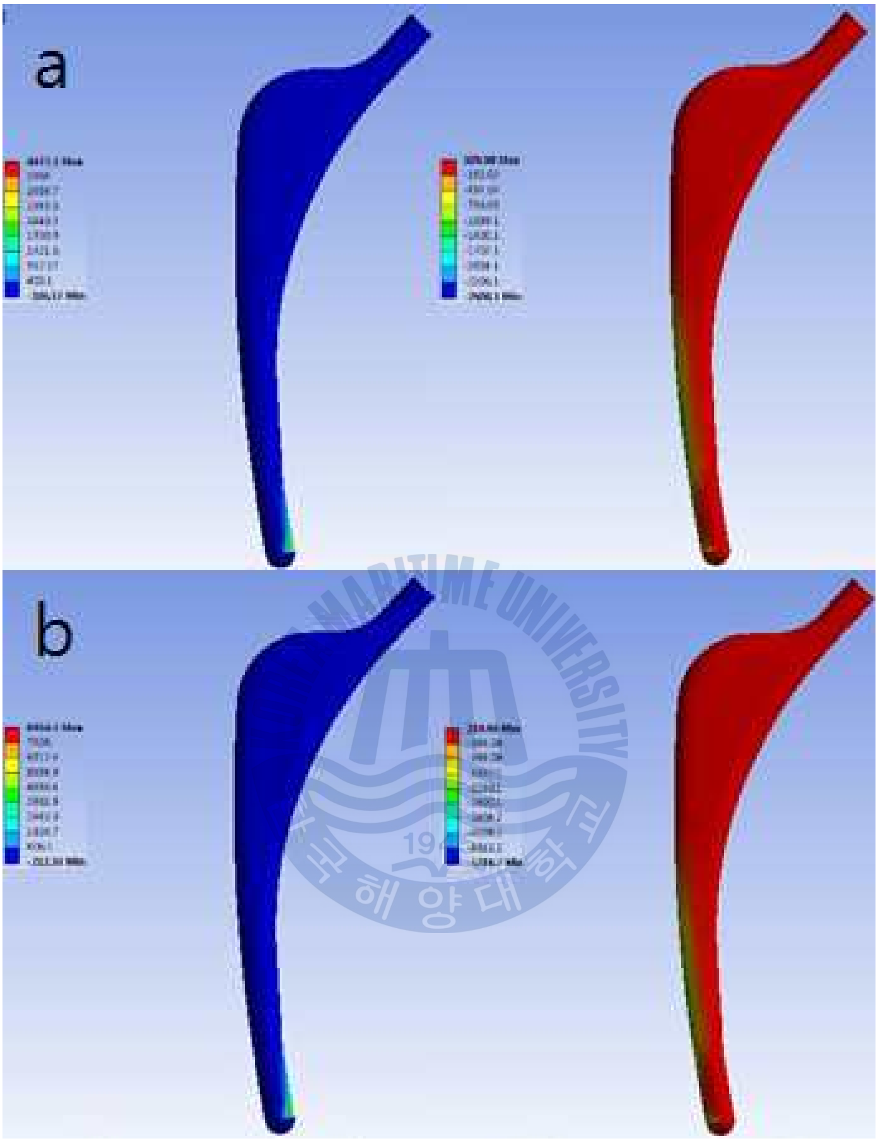


(b) Curved shape

Fig. 37 Principal stress by ply configuration: a. maximum and minimum stress of ply configuration I, b. ply configuration II, c. ply configuration III.



(a) General shape



(b) Curved shape

Fig. 38 Principal stress according to load: a. maximum and minimum stress of 2.5kN load, b. 5kN load

4.4.4 Shear stress

The proposed stem design using carbon/PEEK composites and Ti was described. Finite element models were used to evaluate the potential of the proposed new design concept. The shear stress of Ti is shown in Fig. 39. The same load was applied to the stem and to the composites. The stress of the curved shape was 18% lower than the general shape. The proposed stem design is superior to the existing shape as to the stress distribution.

The shear stress according to the ply configuration is shown in Fig. 40. The loading was identical for all experiments. In the case of general shape, the results according to ply configuration show that the shear stress of ply configuration II were lower than ply configuration I and III.

On the other hand, in the case of the curved shape, ply configuration I was lower than the ply configuration II and III. The mechanical property of ply configuration I was superior to ply configuration II and III due to the curve. Because the stem receives stress perpendicularly the stress applied to the stem was low in ply orientation case I. The distribution of stresses applied to the stem therefore differed according to the fiber ply orientation.

Therefore, the fiber ply orientation and the shape of the stem need to be determined by measuring the load accurately since the load applied to the stem differs for each patient.

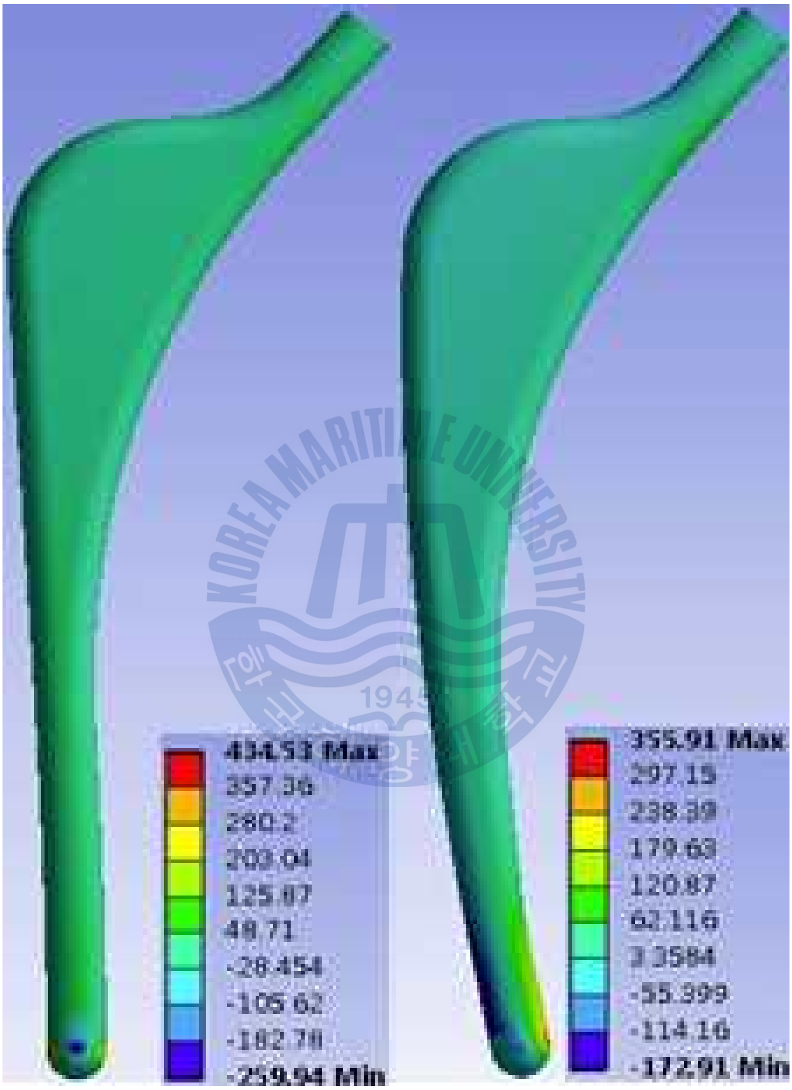
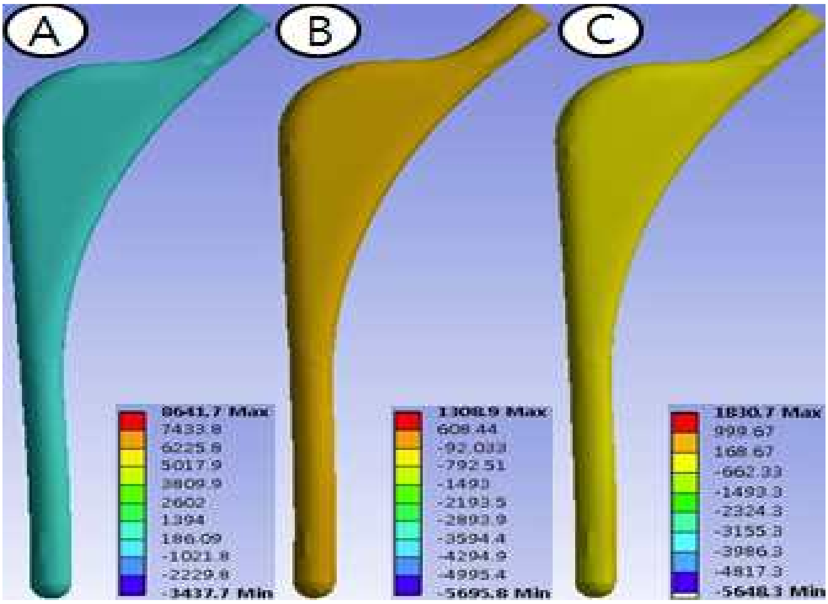
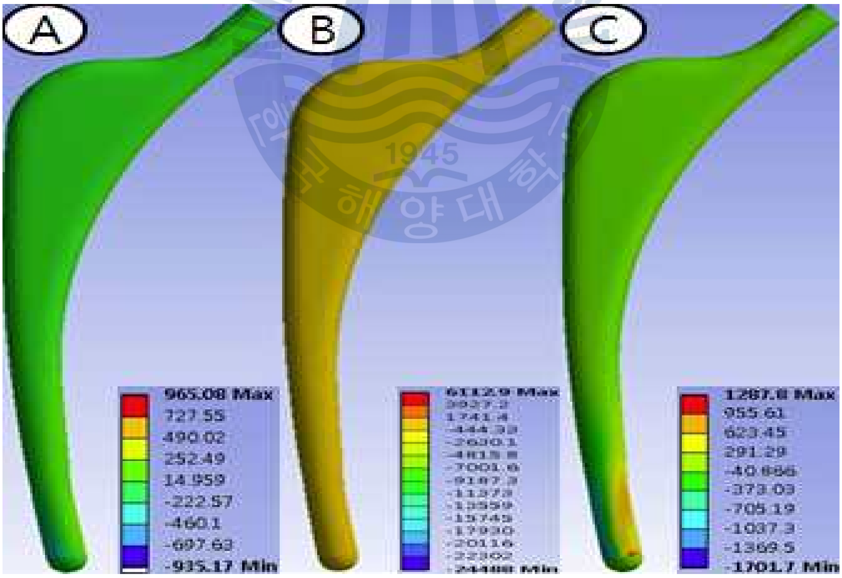


Fig. 39 Shear stress for Ti



(a) General shape



(b) Curved shape

Fig. 40 Shear stress by ply configuration: ⓐ configuration I, ⓑ configuration II, ⓒ configuration III

5. Conclusion

In this study, the composites were manufactured carbon/PEEK composites and carbon/epoxy composites. The mechanical properties according to the fiber ply orientation were also investigated. Also, this study analyzed the effect of the design on the composites for artificial hip joint. The following results were obtained from these data.

(1) The mechanical property of the specimens manufactured as the respectively different matrix material was tested. It is seen that carbon/PEEK composites shows more excellent properties than those of the carbon/epoxy composites. This is determined that properties of PEEK resin itself was more excellent than Epoxy resin.

(2) In the case of the epoxy, the strength of the sizing removal former and after had the noticeable difference. It is considered that the delamination was maximized by the decreased inter-layer coupling between carbon fiber from which the sizing treatment is removed and the epoxy resin.

(3) In the case of PEEK resin, the change of strength according to the sizing treatment was not large. This shows that influence that sizing treatment of the carbon fiber reaches to the interfacial bond strength with PEEK resin is not strong.

(4) The strength of the composites was excellent in the case of same $[(0°)_6]$ specimens as the axial direction. This is considered due to absorb the imposed energy because the direction of the fiber and direction of force coincides.

(5) The mechanical property of carbon/epoxy composites was shown high property value in the short-beam test. The carbon fiber and matrix material are the discontinuity surface. Preferentially the crack occurs in the side where these are contacted and it is the delamination phenomenon generated.

(6) It was revealed out from the experiment result that a lot of resin is adhered on the surface of fiber without the pull out phenomenon as the interface bonding strength between the carbon fiber and the epoxy resin was excellent. On the other hand, the fracture surface of the tensile test specimen of the carbon/epoxy composites heat-treated to 400℃ could know that the resin did not bury nearly in the fiber surface

and pull out was observed. This shown that 400℃ were suitable for the sizing removal of the carbon fiber.

(7) Pull out phenomenon showed conspicuously in case of the fiber ply orientation angle of 45°. This is considered that it is unable to receive the interference according to the laminating direction of the carbon fiber because the stress applied to the specimen is concentrated to the matrix material.

(8) In the composite material, if the water molecules due to moisture absorption penetrate into the composite materials, the swelling phenomenon and the destruction of the three-dimensional network occurred, causing the weakening of the interfacial bonding force and the interfacial separation and destruction between the resin and fiber. The moisture content in this study showed a rapid increase up to 20 days in all fibers, followed by a slow increase. From the results of analyzing the behavior of moisture content, the measured values of the moisture content of carbon/PEEK composites were about 2% lower than those of the carbon/epoxy composites. It is believed that because the interfacial bonding force between the resin and fiber of the carbon/PEEK composites is superior to other composites, the penetration of water molecules was relatively lower.

(9) The fracture energy of each specimen was calculated. The fracture energy of the carbon/PEEK composites shows the value of the property is higher than the fracture energy of the carbon/epoxy composites. It is considered that this is because the energy in the fracture toughness of the carbon/PEEK composites was excellent and it endures in the cracking of the material.

(10) It is believed that with an increase in the time immersed in water, the length of the fiber pulled-out increases and the amount of resin is reduced due to the weakening of the interfacial bonding force between the resin and fiber.

(11) The friction coefficient did not show a large-scale change according to the sliding distance at a low pressure and speed. The pressure and speed had an effect on the friction coefficient. No clear difference was found in the friction coefficient according to the carbon fiber ply orientation. A larger friction coefficient was generally displayed in the case of the direction parallel to the relative friction surface. In the SEM results, the tensile stress and bending stress were found to act on the carbon fiber.

(12) The stress of the curved shape was 18% lower than the general

shape. Thus, the proposed stem design is superior to the existing shape as to the distribution of stresses. In the case of general shape, the shear stress of ply orientation case II was lower than ply orientation cases I and III. In the case of the curved shape, ply orientation case I was lower than ply orientation cases II and III. The fiber ply orientation and the shape of the stem need to be determined by measuring the load accurately, because the load applied to the stem differs for each patient.

Thus, it was confirmed that the carbon/PEEK composites had sufficient mechanical properties to replace the materials used in the existing artificial hip joint.

Recently, the research about the new medical device is actively progressed by the request for the healthy life and the population problem that becomes old age rapidly. However, the generalized metal material is the mainstream relatively and the difficulty is in the medical device application in spite of the excellent characteristic of the composites. Even though the competitiveness of the carbon/PEEK composites are price lags behind the existing metal materials currently, but it is considered that the improvement in the reliability of carbon/PEEK composites which has excellent mechanical properties comparatively will substitute the metal materials for artificial hip joint if the consistent demand and technology development are made.

References

[1] G.. I. Jung, J. S. Kim, J. H. Choi, and J. H. Jun, “The Trend and Prospect of Biomedical Engineering Field”, *KIC News*, Vol. 13, No. 6, 2010, pp. 18

[2] Data of Statistics Korea

[3] H. J. Kim, “Study of the Development of Customized Hip Implant in Total Hip Replacement(THR)”, Yonsei University Graduate School, 2010, pp. 1

[4] K. Choi, “Joint Prostheses and Engineering Technology”, *Journal of the Korean Society of Precision Engineering*, Vol. 17, No. 11, 2000, pp. 17-18

[5] The image and data of the google web site

[6] S. G. Kim, “Korean-type artificial joint”, *Journal of the Korean Medical Association*, Vol. 13, No. 2, 2000, pp. 154

[7] Parnas, R. S., A. J. Salem, T. A. K. Sadiq, H. P. Wang and S. G. Advani, "The Interaction Between Micro- and Macro- Scopic Flow in RTM Preforms", *Composite Structures*, Vol. 27, 1994, pp. 93

[8] Pears, N. R. L., F. Guild and J. Summerscales, "An Investigation into the Effects of Fabric Architecture on the Processing and Properties of Fibre Reinforced Composites Produced by Resin

Transfer Moulding", *Composites Part A: Applied Science and manufacturing (Incorporating Composites and Composites Manufacturing)*, Vol. 29, 1998, pp. 19

[9] Lundstrom, T. S. R. Stenberg, R. Bergstrom, H. Partanen and P. A. Birkeland, “In-plane Permeability Measurements: A Nordic Round-robin Study", *Composites Part A: Applied Science and Manufacturing (Incorporating Composites and Composites Manufacturing)*, Vol. 31, 2000, pp. 29

[10] Binetruy, C. and J. Pabiot, "Effect of Fabric Architectural Heterogeneities on Effective and Saturated Permeabilities in RTM Processing”, *Intergrated Design and Manufacturing*, 1997

[11] Binetruy, C., B. Hilaire and J. Pabito, "The Influence of Fiber Wetting in Resin Transfer Molding: Scale Effects", *Polymer Composites*, Vol. 21, 2000, pp. 548

[12] S. H. Um, “in Honeycomb Sandwich”, Korea Maritime University Graduate School, 2004, pp. 3

[13] Y. H. Kim et al., “Glass Fiber Permeability Using the VARTM Process”, *Advanced Materials Research*, Vol. 97-101, 2010, pp. 1772

[14] L. B. Vogelesang, and J. W. Gunnink, “A Materials Challenge for the Next Generation of Aircraft”, *Materials & Design*, Vol. 7, No. 2, 1986, pp. 287

[15] J. H. Son, "Evaluation of the Physical and Mechanical Properties of Advanced Composites by VaRTM Process and It's Application", Korea Maritime University Graduate School, 2006, pp. 2

[16] S. C. Kwon, "A Study on the Analysis of Causes & Minimizing of Defects at Composite Materials Sandwich Structure Reinforced with Honeycomb Core in Autoclave Processing", Korea Maritime University Graduate School, 2001 pp. 2

[17] Y. H. Kim et al., "Design of Artificial Hip Joint by Carbon/PEEK Composites", *Advanced Materials Research*, Vol. 774-776, 2013, pp. 1336

[18] M. Rahman, S. Ramakrishna and H. C. Thoo, "Machinability Study of Carbon/PEEK Composites", *Machining Science and Technology: An International Journal*, Vol. 3, 1999, pp. 49

[19] J. Denault and T. Vu-Khanh, "Fiber/Matrix Interaction in Carbon/PEEK Composites", *Journal of Thermoplastic Composite Materials*, Vol. 6, No. 3, 1993, pp. 190

[20] Kenzora JE, McCarthy RE, Lowell JD and Sledge CB, "Hip Fracture Mortality. Relation to Age, Treatment, Preoperative Illness, Time of Surgery, and Complications", *Clin Orthop Relat Res.*, Vol. 186, 1984, pp. 45

[21] Y. H. Kim et al., "Effect of Moisture Absorption and Fiber Ply Orientation for Artificial Hip Joint on the Mechanical Properties of

Carbon/PEEK Composites", *Advanced Materials Research*, Vol. 774-776, 2013, pp. 1326

[22] Y. H. Kim et al., "Mechanical Properties of Carbon/PEEK Composites According to the Fiber Ply Orientation and Sizing Removal of Carbon Fiber for Artificial Hip Joint", *Advanced Materials Research*, Vol. 750-752, 2013, pp. 164

[23] Ikeda M, Komatsu SY, Sowa I, and Niinomi M, "Aging Behavior of the Ti-29Nb-13Ta-4.6Zr New b Alloy for Medical Implants", *Metall Mater Trans A*, Vol. 33, 2002, pp. 487

[24] Niinomi M, "Recent Research and Development in Titanium Alloys for Biomedical Applications and Healthcare Goods", *Sci. Technol. Adv. Mater.*, Vol. 4, 2003, pp. 445

[25] Bania PJ, Lenning GA, and Hall JA, "Development and Properties of Ti-15V-3Al-3Sn-3Cr", *AIME*, 1984, pp. 209

[26] Kamachi Mudali U, Sridhar TM, and Baldev R, "Corrosion of Bioimplants", *Sadhana*, Vol. 28, 2003, pp. 601

[27] Fujihara K, Huang ZM, Ramakrishna S, Satknanantham K and Hamada H, "Performance Study of Braided Carbon/PEEK Composite Compression Bone Plates", *Biomaterials*, Vol. 15, 2003, pp. 2661

[28] Kurtz SM and Devine JN, "PEEK Biomaterials in Trauma, Orthopedic, and Spinal Implants", *Biomaterials*, Vol. 32, 2007, pp.

4845

[29] Abu Bakar MS, Cheng MH, Tang SM, Yu SC, Liao K, Tan CT, Khor KA and Cheang P, "Tensile Properties, Tension-tension Fatigue and Biological Response of Polyetheretherketone-hydroxyapatite Composites for Load-bearing Orthopedic Implants", *Biomaterials*, Vol. 13, 2003, pp. 2245

[30] Ning C and Dai K, "Research Development of Hydroxyapatite-based Composites Used as Hard Tissue Replacement", *Journal of Biomedical Engineering*, Vol. 3, 2003, pp. 550

[31] Wang R, Wen D, Xie X and Zhong Y, "Development of nanohydroxyapatite composites as bone grafting materials", *Journal of Biomedical Engineering*, Vol. 5, 2008, pp. 1231

[32] Frank Adam et al., "Early Failure of a Press fit Carbon Fiber Hip Prosthesis with a smooth surface", *The Journal of Arthroplasty*, Vol. 17, No. 2, 2002, pp. 217

[33] Katoozian H et al., "Material Optimization of Femoral Components of Total Hip Prosthesis using Fiber Reinforced Polymeric Composites", *Medical Engineering & Phisics*, Vol. 23, 2001, pp. 503

[34] Kawamura T, Zako M et al., "On a Design Method of Composite Stem Based on CT Images", *Proceedings of 16th International Conference on Composite Materials*, 2007

[35] Shunichi B, Takashi U et al., "The Development of Composite Stem for Hip Joint, an Application of Composite Materials for Medical Implant Device", *Proceedings of 16th International Conference on Composite Materials*, 2007

[36] S. W. Chun, Y. M. Kim, and H. J. Kang, "Tribological Properties of Laminated Fiber Orientation in Carbon Fiber/Epoxy Composites for Reflecting Material of the Electromagnetic Wave", *J. Korean Ind. Eng. Chem.*, Vol. 10, No. 5, 1999, pp. 778

[37] S. K. Ryoo and K. W. Kim, "A Study on Friction and Wear Behavior of Carbon Fiber Reinforced Polyetheretherketone", *The Korean Society of Mechanical Engineers*, Vol. 25, No. 6, 2001, pp. 930

[38] G. Theiler, W. Hubner and T. Gradt, "Friction and Wear of PTFE Composites at Cryogenic Temperatures", *Tribology International*, Vol. 35, No. 7, 2002, pp. 449

[39] H.Y. Kim, "A Study on Friction and Wear of Porous PTFE", Pukyong National University Graduate School, 2011, pp. 1

[40] M. Wegener, W. Wirges and B. Tiersch, "Porous Polytetrafluoroethylene (PTFE) Electret Films: Porosity and Time Dependent Charging Behavior of the Free Surface", *Journal of porous materials*, Vol. 14, No. 1, 2007, pp. 111

[41] R. Frake, D. Lehmann and K. Kunze, "Tribological Behaviour of

New Chemically Bonded PTFE Polyamide Compounds", *Wear*, Vol. 262, No. 3, 2007, pp. 242

[42] M. H. Seo, D. W. Kim, S. J. Lee and K. Y. Lee, "Evaluation and Analysis of Relation Between Wear and Friction Characteristics of UHMWPEs against Materials in Total Joint Replacement", *Korean Society of Tribologist and Lubrication Engineers*, Vol. 51, 2010, pp. 157

[43] M. T. Manley, "Bearings of the Future for Total Hip Arthroplasty", *J. Arthroplasty*, Vol. 23, 2008, pp. 47

[44] Tsukizoe T. and Ohmae N., "Friction and Wear of Advanced Composite Materials", *Flbre Sc. Tech.*, Vol. 18, 1983, pp. 265

[45] J. K. Lancaster, "Polymer Based Bearing Materials, the Role of Fillers and Reinforcement", *Tribology*, Vol. 5, 1972, pp. 249

[46] J. P. Giltraw and J. K. Lancaster, "The Role of the Counterface in the Friction and Wear of Carbon Fiber Reinforced Thermosetting resins", *Wear*, Vol. 16, 1970, pp. 359

[47] Y. Wang and F. Tan, "Tribology Properties to Transfer Films of PTFE-based Composites", *Wear*, Vol. 261, No. 11, 2006, pp. 1359

[48] F. Su, Z. Z. Zhang and K. Wang, "Friction and Wear Properties of Carbon Fabric Composites Filled PTFE and MoS2", *Tribology*, Vol. 25, No. 4, 2005, pp. 338

[49] V. Banchet, "Wear and Friction Characterization of Materials for

Hip Prosthesis", *Wear*, Vol. 263, 2007, pp. 1066

[50] M. J. Fagan and A. J. C. Lee, "Material Selection in the Design of the Femoral Component of Cemented Total Hip Replacements", *Clinical Materials*, Vol. 1, No. 3, 1986, pp. 151