

複合材料の強度評価と応用

Professor Kim, Yun-Hae
Department of Mechanical Engineering
Korea Maritime and Ocean University

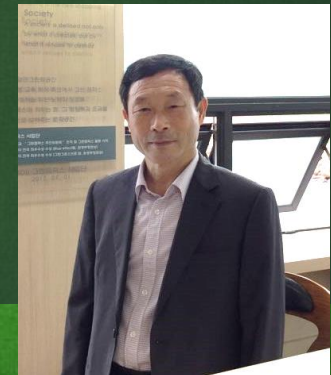
- Composites?
- Strength Evaluation of Nanocomposites
- Environmental Effect
- Application of Composites
- Conclusion

Personal History

Academic and Research Background

Department of Marine Engineering, Korea Maritime and Ocean University (B.E.)
Graduate School, Department of Marine Engineering, Korea Maritime and Ocean University (M.E.)
Graduate School, Department of Mechanical Engineering, Tokushima University, Japan (M.E.)
Graduate School, Department of Mechanical Engineering, Kyushu University, Japan (Ph.D)
Professor, Korea Maritime and Ocean University, Korea
Visiting Professor, National Institute of Standards and Technology, U.S.A.
Secretariat General of International Conference on Marine Engineering funded by Busan Metropolitan City

2004.1-2005.1 Visiting Professor, Tokushima University, Japan
2005-2008 Division Chief
2009-2012 Director of Innovation Center for Engineering Education
2010-2011 Editor-in-Chief, The Korean Society of Ocean Engineering
2012.1-present Chief Editors of Nano Hybrids, Trans Tech Publication
2014-2015 Dean of Student Affairs
2015-2016 Dean of Academic Affairs
2016. ex-Acting President
2014-2017 President of Korean Association of Green Campus Initiative



**Professor/Director
Kim, Yun-Hae**

Social Activities

2000.8-2003.11 Vice-Director of Marine Equipment Research Institute (KMOU)
2009 Founding Chairman of ACEE2009
2010-present Editor-in-Chief, Korean Society of Ocean Engineers(KSOE)
2012.11 Co-chair of the 3rd Asian Conference on Engineering Education (ACEE2012)
2013 Chair of the Asian Conference of Engineering Education (ACEE2013)
2014 Chairmen of ISMST, AEMT, ICMCE
2014 Chair of the 7th Advanced Materials Development and Performance (AMDP2014)
2015 President of the Korean Association for Green Campus Initiative
2019 Vice-president of the Korean Society of Composite Materials(KSCM)

- ❖ **Composites**
- ❖ **Mechanical Engineering**
- ❖ **Welding Engineering**
- ❖ **Engineering Education**

Prof. KIM's International Activities

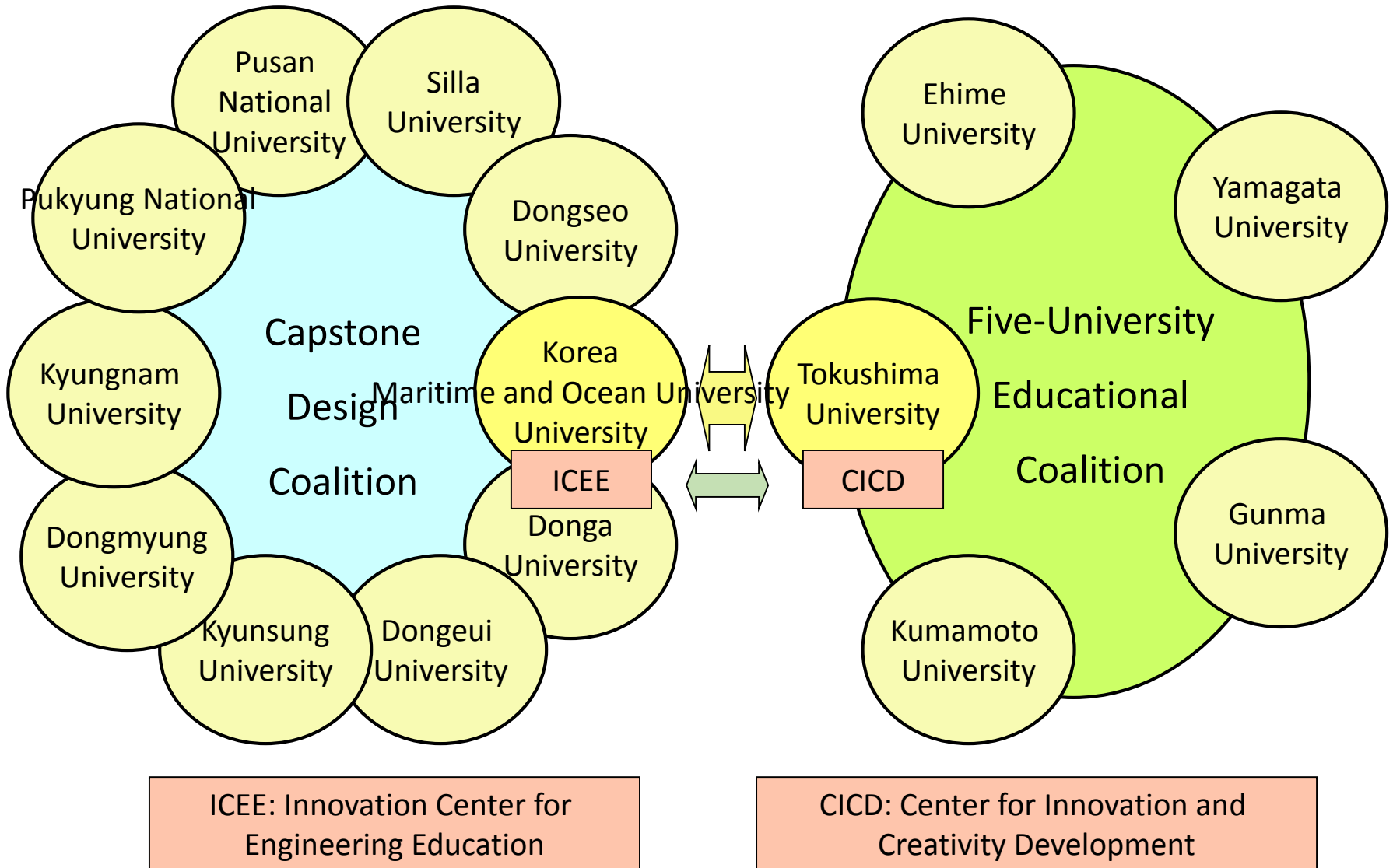
1. Founding Chair of ACEE
2. Chair of AMDP 2014
3. Founding Chair of ACCS 2015
4. Chair of PHENMA 2018



2018 International Conference on
Physics and Mechanics of New Materials and Their Applications
PHENMA2018
Date : August 9~11th, 2018
Venue : Korea Maritime and Ocean University, Busan, Republic of Korea
Organized by  한국해양대학교  韩国海洋大学
Sponsored by  bt  bt



Background of ACEE



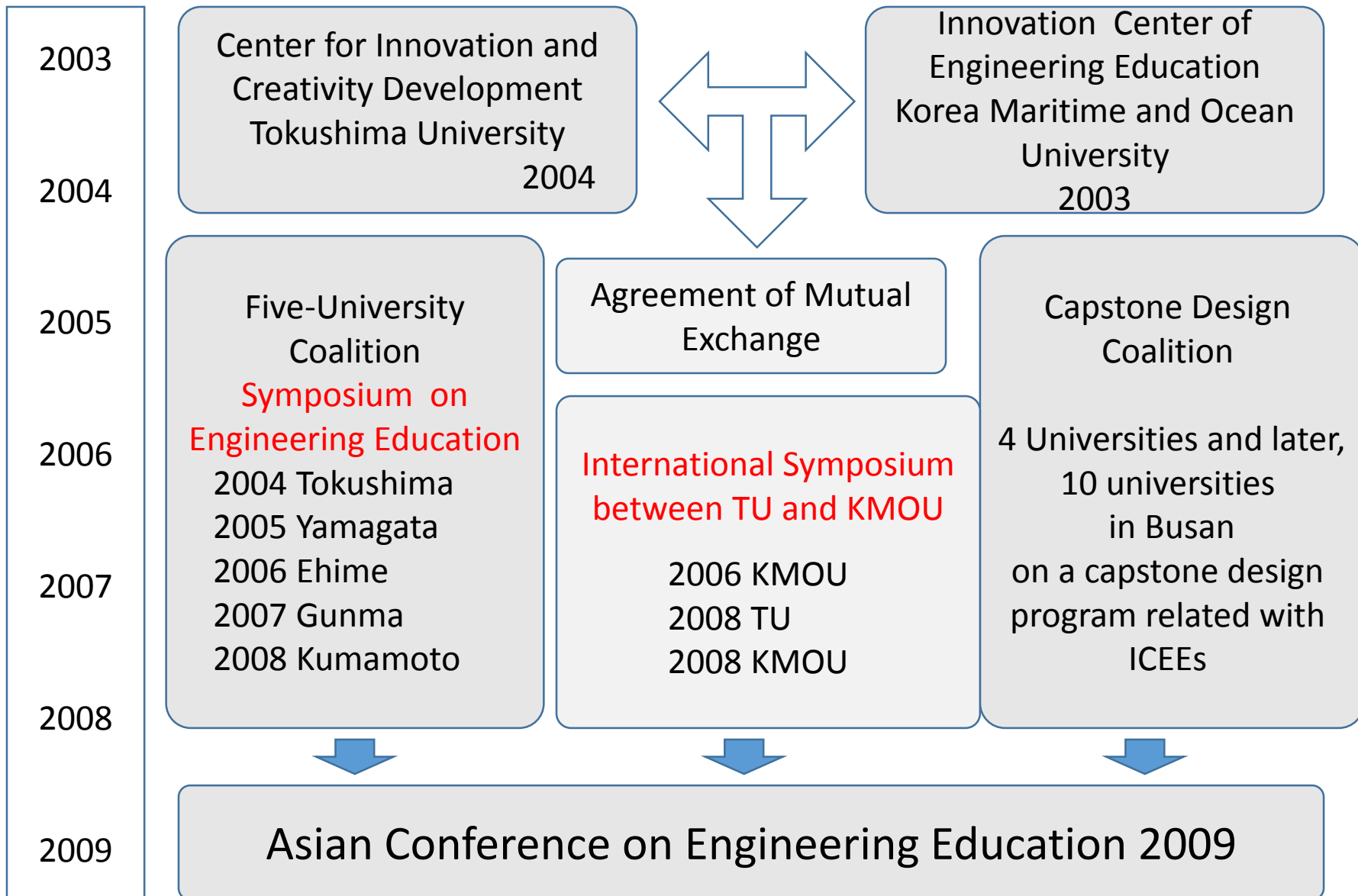
Visiting the Universities in **Japan** for the ACEE 2009

2009.01. (**Director Meeting, Tokyo in Japan**)

Director meeting of five-university coalition
in Japan



Background of ACEE



Brief History of ACEE

- | | |
|------|--|
| 2009 | 1 st ACEE Korea Maritime and Ocean University, Busan, Korea |
| 2011 | 2 nd ACEE The University of Tokushima, Tokushima, Japan |
| 2013 | 3 rd ACEE Joint Conference with KSEE, Jeju, Korea |
| 2014 | 4 th ACEE Kumamoto University, Kumamoto, Japan |
| 2015 | 5 th ACEE Dalian Maritime University, Dalian, China |
| 2017 | 6 th ACEE Dali University, Yunnan, China |
| 2018 | 7 th ACEE Niigata University, Japan |
| 2019 | 8 th ACEE UMS, Kota Kinabalu, Malaysia |

1st ACEE

2009, Korea Maritime University, Busan



2nd Asian Conference on Engineering Education (ACEE 2011)

- Challenges and Innovations in Engineering Education -



The University of Tokushima, Tokushima, Japan

October, 7-9, 2011

3rd ACEE

2013 , Jeju, Korea



Asian Conference on Engineering Education(ACEE)

4th ACEE

2014, Kumamoto University, Japan



5th ACEE

2015, Dalian Maritime University, China



6th ACEE

2017, Dalian University, China



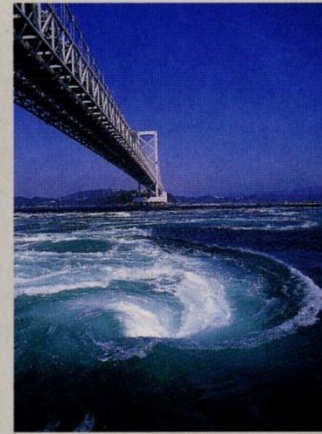


The 1st ACEE 2009



2nd Asian Conference on Engineering Education (ACEE 2011)

– Challenges and Innovations in Engineering Education –



The University of Tokushima, Tokushima, Japan

October, 7-9, 2011

3rd Asian Conference on Engineering Education (ACEE 2013)
(In Conjunction with KSEE's 20th Anniversary)

Nov. 7th (THU.) – 8th (FRI.), 2013 / Ramada Plaza Jeju Hotel, Korea



明德 明辨笃实 创新育人



中国大理学院
Dali University



韩国海洋大学
Korea Maritime University

手拉手 2011 新年晚会

Hand in Hand 2011 New Year Party



**1st Asian Conference
on Engineering Education**
October 28-30, 2009, Korea Maritime University, Busan



**2nd Asian Conference
on Engineering Education
(ACEE 2011)**

– Challenges and Innovations in Engineering Education –



The University of Tokushima, Tokushima, Japan

October, 7-9, 2011

3rd Asian Conference on Engineering Education (ACEE 2013)

November 7- 8, 2013 Jeju, Korea





Dreams to the Future

The dream of having Asian Conference on Engineering Education has come true.

The further dream we have:

- To promote a coalition of engineering education in a large scale in Asian area.
- To develop educational ability in Asia
- To enhance the creative force of students
- To contribute to the education of engineers

We hope that the ACEE will grow in larger scale and broaden in all Asian countries in order to educate excellent young people.

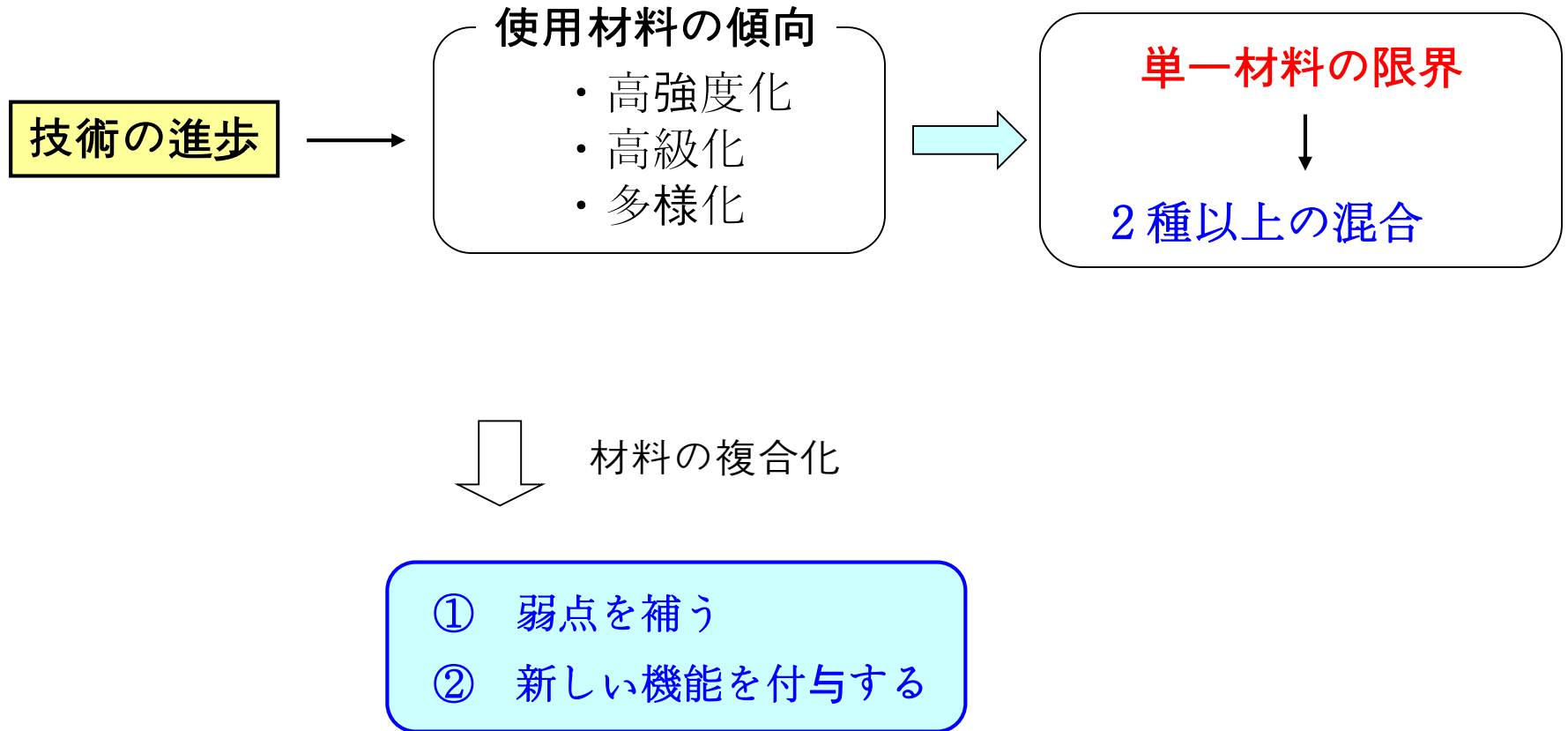
Future Work of ACEE

- **8th ACEE 2019 in Malaysia**

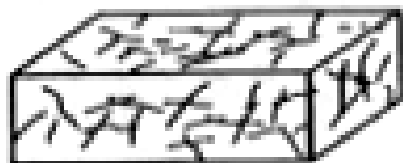
➤ 8th ACEE 2019 in Malaysia



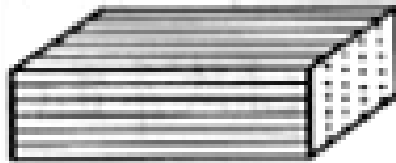
複合材料(Composites) ?



複合材料 (C = M + R) の分類



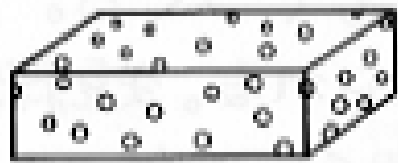
不連続繊維強化複合材料



連続繊維強化複合材料



ランダム方向連続繊維強化
複合材料



粒子分散型複合材料



積層型複合材料

機械用材料として使われるためには

■ 条件

使用材料の条件



- ・強度特性
- ・機能性
- ・加工性
- ・経済性

* 材料力学？

= 安全で、しかも経済的に設計する。

一方向強化複合材料

- 連続繊維の場合

長繊維

繊維強化複合材料の強化

混合則

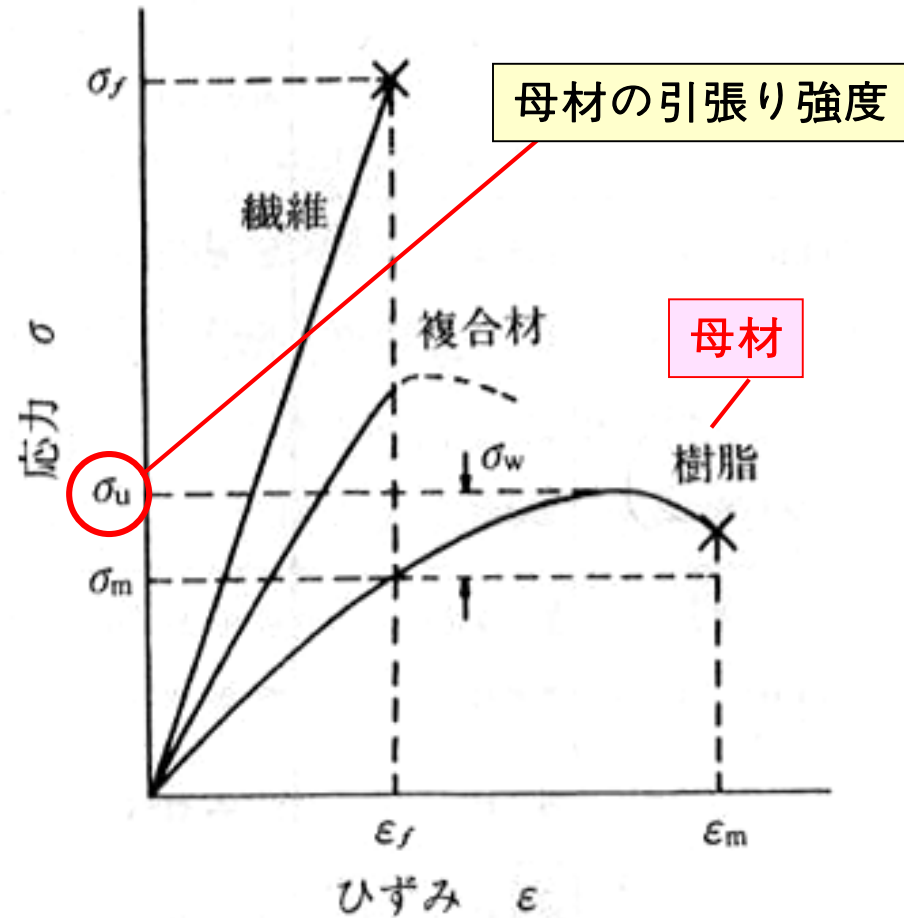
$$\sigma_c = \sigma_f V_f + \sigma_m (1 - V_f)$$

σ_c : 複合材料の引張り強度

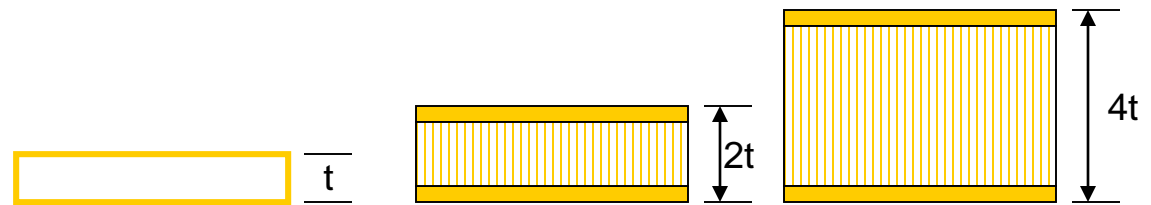
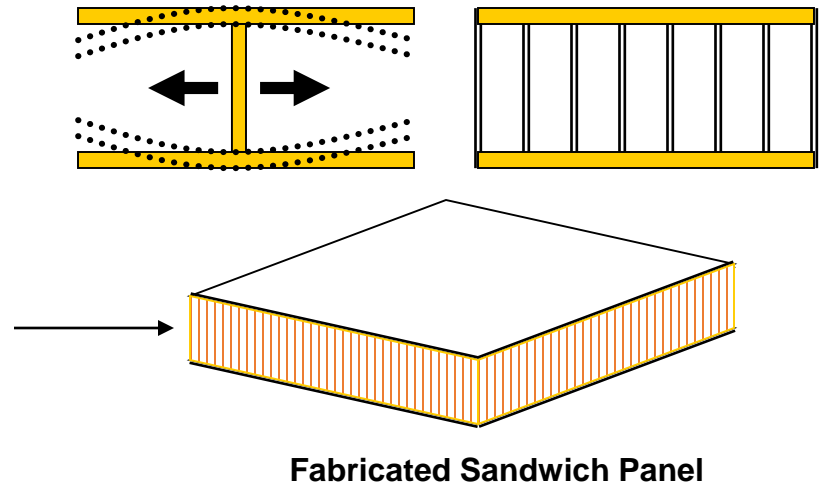
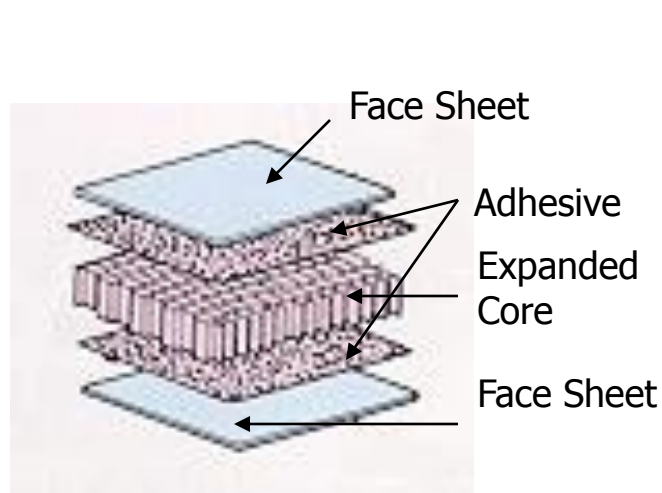
σ_f : 繊維の引張り強度

σ_m : 母材の強度

V_f : 繊維の体積含有率



複合材料のメリット



Relative Stiffness(D)	100	700	3700
Relative Strength	100	350	925
Relative Weight	100	103	106

A striking example of how honeycomb stiffens a structure without materially increasing its weight.

Impact Property of Unsaturated Polyester Containing Halloysite Nanotubes Heat-treated at Various Temperatures

Soo-Jeong, PARK, Antonio Norio NAKAGAITO, Yun-Hae KIM, Hitoshi TAKAGI

Presenter, Soo-Jeong Park

**Eco-Materials Lab.,
Tokushima Univ. Dept. of Mechanical Engineering**
Korea Maritime and Ocean Univ. Dept. of Marine Equipment Engineering

CONTENTS

1. INTRODUCTION

2. EXPERIMENTAL WORK

2-1 Materials and Samples Preparation

2-2 Property Evaluation

3. RESULT AND DISCUSSION

3-1 Structural Changes of HNTs by Heat Treatment

3-2 Impact Strength of UPR/HNTs Nanocomposites

4. CONCLUSION

01 Comprehension of Main Material used

INTRODUCTION

In accordance with **structure of reinforcement**

1. Particle-Reinforced Composites

; Suppress Deformation of the Matrix around the Particles,
Mechanical Property Improvement

Halloysite nanotube Reinforced Unsaturated Polyester Matrix Nanocomposite

In accordance with **material of reinforcement**

2. Polymer Matrix Composites (PMC's)

- Polymer Plastic Resin
- Fiber Reinforcement as Glass, Carbon, Aramid and etc..

01 INTRODUCTION

Composite;
Consisting of two or more distinct materials
Composite property value is not defined.

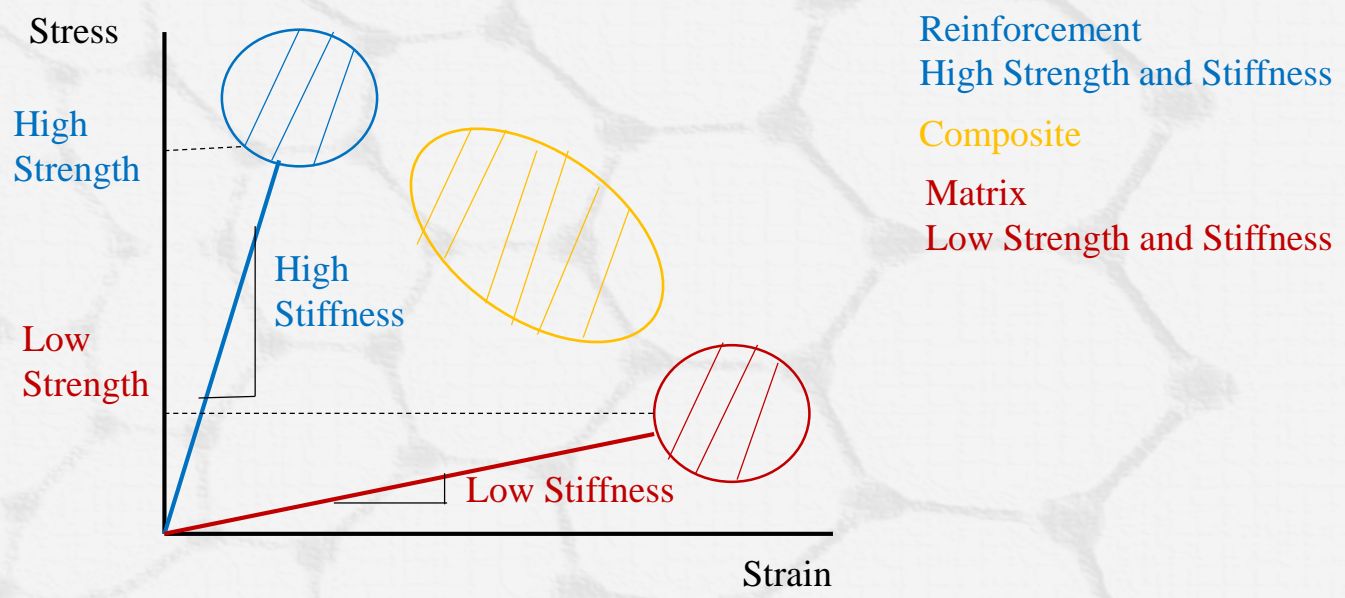


Fig. 1. Analysis Graph about designing physical property of composite

Composites can be designed for various physical properties depending on the combination and the mixing ratio of materials having different properties.

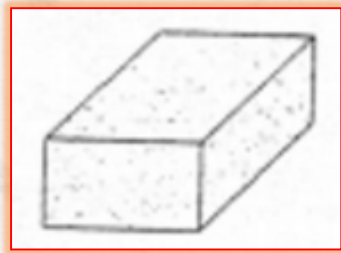
Particle Reinforced Composites

INTRODUCTION

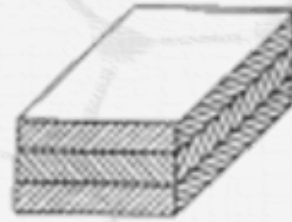
1. Layered Composites
2. **Particle Reinforced Composites**
3. Fiber Reinforced Composites



Fiber Composite



Particulate Composite



Laminar Composite



Flake Composite



Skeletal Composite

* Dispersion-Strengthened Composites

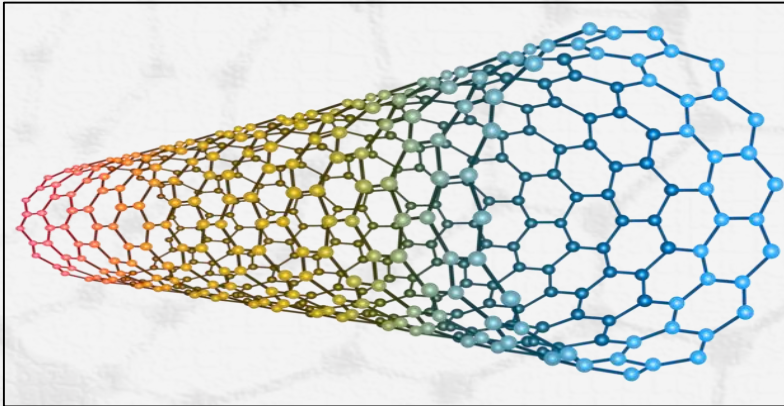
; Limitation of Deformation, Improvement of Yield Strength, Tensile Strength and Hardness

01 Nanoparticle Reinforced Composites

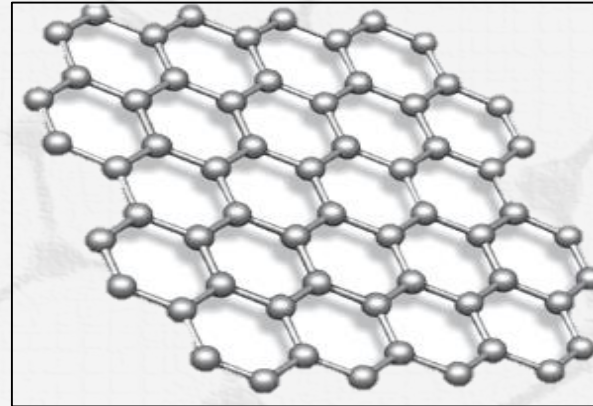
; Enhance Functionality by the Addition of Nanoparticles to the Polymer

INTRODUCTION

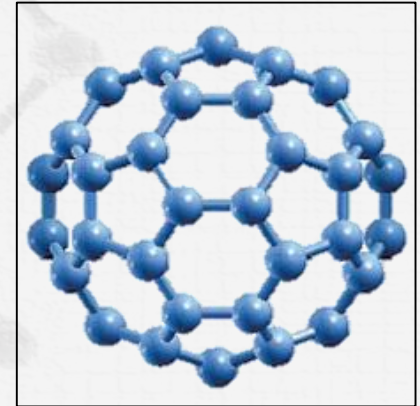
- Excellent properties can be obtained with the addition of small amounts due to a wide surface area of nanoparticles.
- A variety of reinforcements which is light and has greater strength is used to create by nanoparticles.



Carbon Nanotube



Nanographene



Fullerene

Fig. 2. Variety of Nano Reinforcements

01 Polymer Matrix Composites (PMC's)

; The Most Common Composite Materials

INTRODUCTION

Generally, it consists of a resin and reinforcing fibers.

* The Role of the Matrix

1. Disperse the load applied to composites from each fiber consisting inside
2. Prevent damage of the fiber from abrasion and impact
3. These properties, high strength and rigidity, easy mold-ability of a complicated shape, excellent environmental resistance, a low density, are superior to the composite materials as compared to metal in many applications.

01 Polymer Matrix Composites (PMC's)

; The Most Common Composite Materials

INTRODUCTION

Generally, it consists of a **resin** and reinforcing **fibers**.

* Polymer Additives

1. **Fillers** : Added to improve the properties such as tensile and compressive strength of the polymer, the abrasion resistance, toughness, dimensional and thermal stability
2. Plasticizers : Improving the flexibility, ductility and toughness
3. Stabilizers : Clean the oxidation of the polymer
4. Colorants : Color grant to the polymer material
5. Flame Retardants : Improved combustion and storability

01

INTRODUCTION

The **OBJECTIVE** of this research is

To observe *the reinforcement effect* of heat treated HNTs in the matrix
To analyze *structural properties*

By comparing HNTs contents



Halloysite Nanotube and Unsaturated Polyester Resin

02

■ Halloysite Nanotube ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$) ;

- a naturally occurring aluminosilicate nanotube
- a two-layered aluminosilicate with a predominantly hollow tubular structure in the submicron range.
- chemically similar to kaolin.

EXPERIMENTAL WORK
MATERIALS

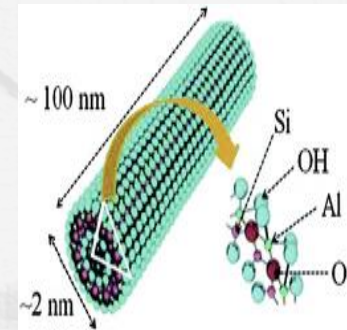


Table 1. Description of Main Materials

Materials	Provider (Title & Company)	Specifications
Halloysite Nanotubes (HNTs)	Sigma-Aldrich Japan G.K. Product Number : 685445 CAS-NO. 1332-58-7	Formula : $H_4Al_2O_9Si_2 \cdot 2H_2O$ Molecular Weight : 294,19 g/mol
Unsaturated Polyester Resin (UPR)	SHOWADENKOK K.K. Product : Srider BP-1055 (Lot. KE 624PL01)	Gelation Time : 19 minutes Optimum Hardening Time : 33 minutes Maximum Heat-generating Temperature : 138 °C
Methyl Ethyl Ketone Peroxide (MEKP)	NOF CORPORATION CAS-No. 1338-23-4	Hardner Specific Gravity : 1.146 g/ml at 20 °C
Cobalt Naphthenate	Sigma-Aldrich Japan CAS-No. 61789-51-3	Accelerator Specific Gravity : 0.921 g/ml at 25 °C

Halloysite Nanotube and Unsaturated Polyester Resin

02

EXPERIMENTAL WORK
MATERIALS

■ Unsaturated Polyester Resin (Thermosetting Resin) ;

- is made by acid, glycol, monomer
- has a limited storage time
- since the it is hardened by itself over a long period time (Gell Reaction)
- consists of polyester solution in styrene monomer
- can be molded without pressure thus referred to a as 'contact' or 'low pressure' resin

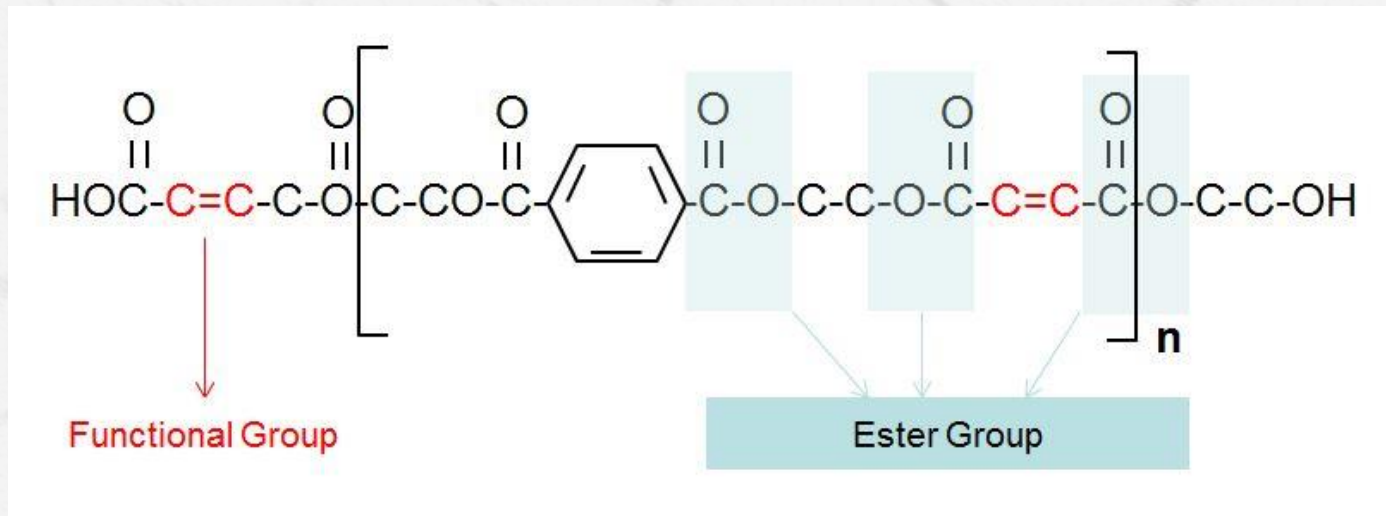


Fig. 3. An Ideal Chemical Structure of Typical Unsaturated Polyester Resin

Heat Treatment Process of HNTs

Heat Controller (Model SU02-110, CHINO Ltd.)
Ar Gas (SHIKOKU ASECHIREN Ltd.)

EXPERIMENTAL WORK
MATERIALS

Operating System ;

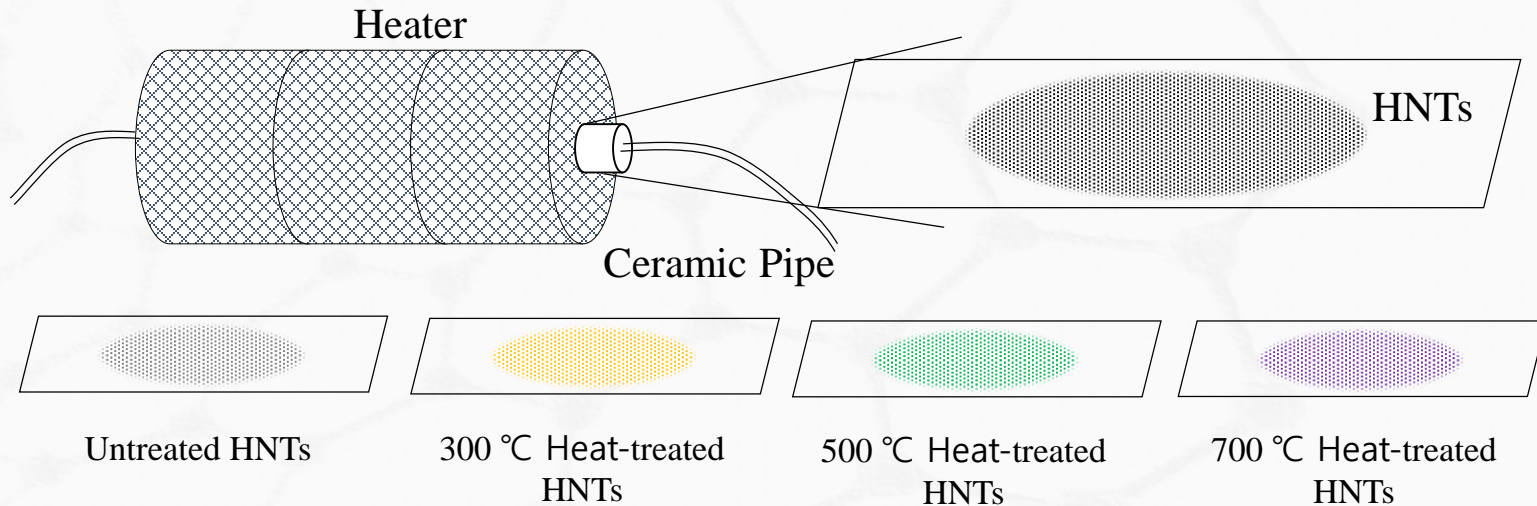


Fig. 4. Process Diagram of Heat Treatment

Ultrasonic Homogenization for Dispersion of HNTs in UP

EXPERIMENTAL WORK
SAMPLES PREPARATION

02

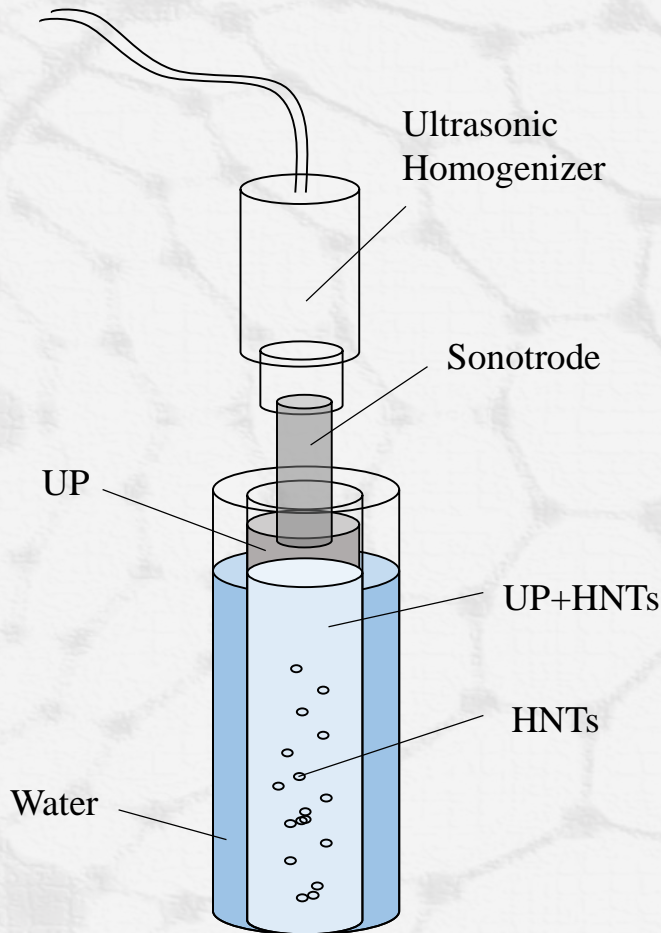


Fig. 5. Process Schematic Diagram
of Ultrasonic Homogenization

1. *Maximum Power : 150 W ;
Real Input Power : 60 W*
2. *Operating Time : 300 seconds*
3. *Pulsed at 80 % ;
Energy Pulse Lasted 0.8 seconds*
4. *Use of Capacity : 18 mL*

Powerful Dispersion Method ; Ultrasonication

- The production and disaggregation of nano-sized materials
- Ultrasonic cavitation in liquids cause fast and complete degassing

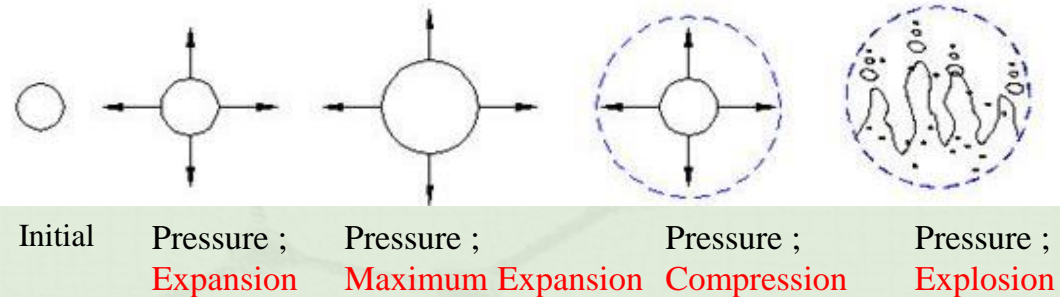


Fig. 6. Principle of Ultrasonic Dispersion

Izod Impact Test (JIS K 7062)

1. Izod Impact Tester

(YASUDA SEIKI SEISAKUSHO LTD., No. 12353)

2. Room Temperature

3. Hammer's Work : 5.5 J

4. Sample Type : Unnotched Specimens

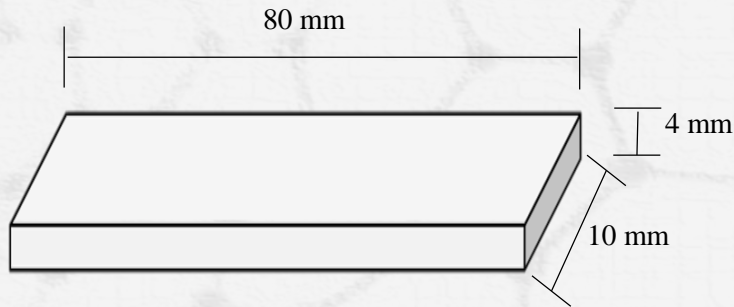


Fig. 7. Specification of Unnotched Specimens
(4.0 mm x 10.0 mm x 80.0 mm)

EXPERIMENTAL WORK
PROPERTY EVALUATION

$$E_c = WR[(\cos\beta - \cos\alpha) - (\cos\alpha' - \cos\alpha) \left(\frac{\alpha + \beta}{\alpha + \alpha'}\right)]$$

$$a_{iV} = \frac{E_c \times 10^3}{b \times h}$$

E_c : The Corrected Energy (J)

WR : The Moment around the Axle of the Hammer (2.949040 N · m)

α : The Initial Lift Angle of the Hammer (150.0°)

β : The Hammer after Breaking the Specimen (°)

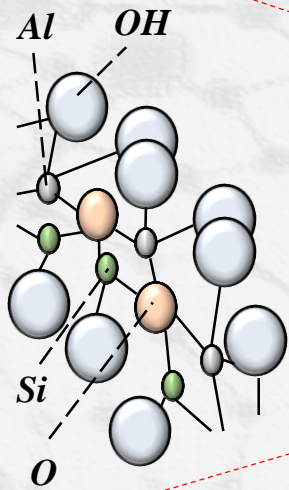
α' : The Real Lift Angle of the Hammer (148.8°)

a_{iV} : The Izod Impact Strength (KJ/m²)

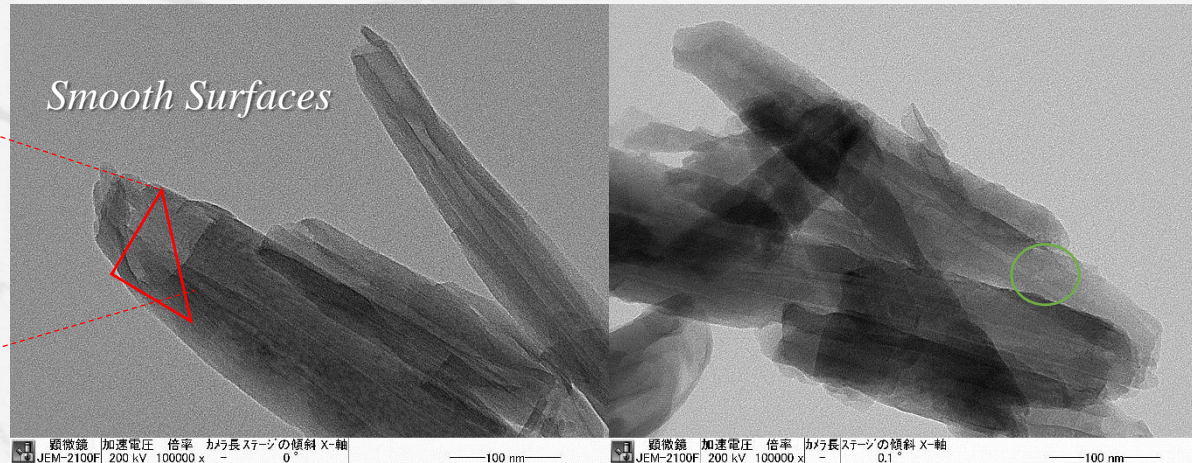
b : The Width (mm)

h : The Thickness (mm)

Structural Changes of HNTs by Heat Treatment



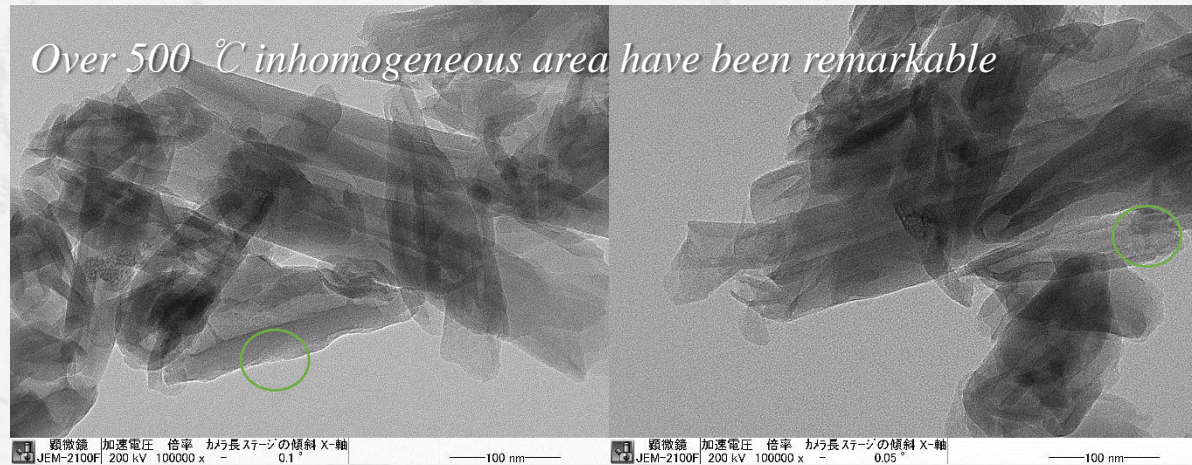
have water molecules between Al-OH (O) octahedral plates



Untreated HNT

300 °C Heat-treated HNT

- *Rough Surfaces*
- *Structure was destroyed by dehydration*
- *No difference in shape*
- *Turn to amorphous when temperature is raised up to 500 °C*



500 °C Heat-treated HNT

700 °C Heat-treated HNT

RESULTS AND DISCUSSION
STRUCTURE CHANGES

Fig. 8. TEM micrographs of UP/HNTs nanocomposites

Impact Strength of UP/HNTs Nanocomposites

Observation Point

1) HNTs Contents ;

Compared to Impact Strength

→ Relatively UP/1 wt.% HNTs Nanocomposite is much higher than one using 3 wt.% HNTs

2) The Rheological Property of Resin

Was affected by nanoparticles

→ The more nanoparticles added,
the more the aggregation occurred

→ **High Viscosity, Stress Concentration**

3) Reinforcement Effect of HNTs

Partially caused

4) The Ideal Levels under Given Condition

60 W of Input Power,

300 seconds of Operating Time

18 mL of Manufacturing Volume at one time

→ **700 °C Heat Treated HNTs, 1 wt.% HNTs**

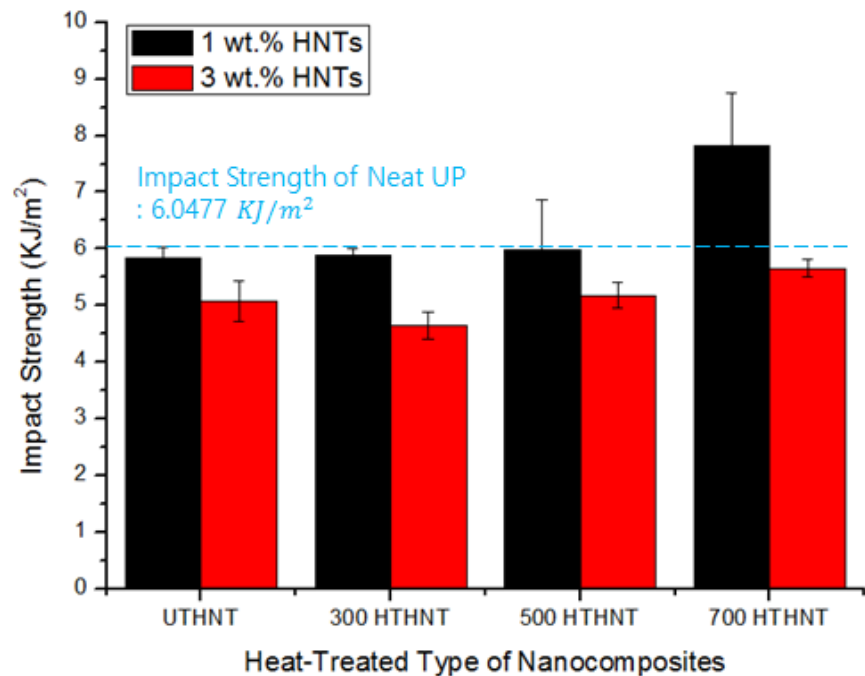


Fig. 9. Comparison of impact strength of neat UP and its nanocomposites

RESULTS AND DISCUSSION
IMPACT STRENGTH

This study was conducted by comparing HNTs contents by observing the reinforcement effect of heat treated HNTs and analyzing structural properties. **To sum up the results obtained as follows ;**

- (1) The HNTs heat treated up to 500 °C basically have a weaker structural change and dehydration between Al-OH(O) octahedral plates of clay mineral and all HNTs samples partially show rough surface but **nanocomposites heat treated at over around 500 °C presented the possibility of structural change.**
- (2) The toughening effect of HNTs was partly observed and, however, more important is the dispersion of HNTs. If the optimal nanoparticles limit, as a result it would backfire. Also we have **to consider the optimal dispersion process for preventing aggregations.**

04
CONCLUSION

A large container ship is shown at sea, with a crane on deck. The ship is blue and red, and the water is blue. The sky is blue with some clouds. The title of the paper is overlaid on the image in yellow text.

Absorption Behavior of HNT Reinforced GFRP under the Different Dispersion Ratio

Park, Soo-Jeong¹, Choi, Ji-Su², Kim, Yun-Hae^{2,†}

¹Department of Material Engineering, Korea Maritime and Ocean University, Busan, Republic of Korea

²Department of Mechanical Engineering, Korea Maritime and Ocean University, Busan, Republic of Korea

†Corresponding Author: yunheak@kmou.ac.kr

Autoclave Method、Oven Forming、Hot Press Forming

- 熱可塑性複合材料の成形は、加圧および温度調整が容易い
- Autoclave Method
- 長時間成形、高価の設備などの理由で現在は **Out-of-Autoclave** の必要性
- 単価が安い **Oven** 基盤真空成形法と短時間で製作する **Hot-press** 法の研究が行われている



Fig.4 Autoclave

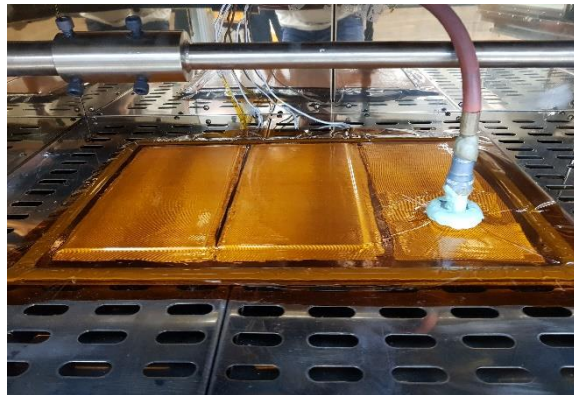


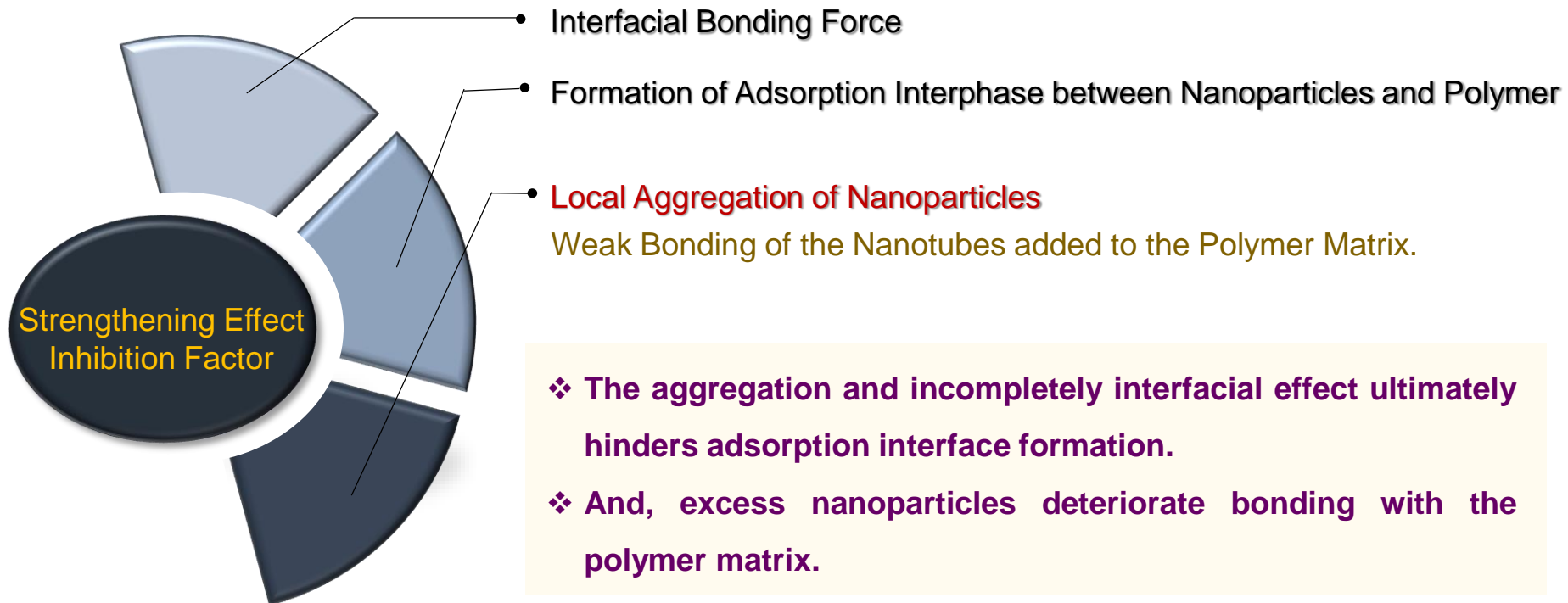
Fig.5 Oven forming



Fig.6 Hot-press forming

1 INTRODUCTION

In the Production of Nanocomposites



1 INTRODUCTION

Particle Aggregation Phenomenon

- Since the small particle size of the HNT causes a large surface area, it tends to aggregate due to the Van der Waals force generated by relatively large surface energy.

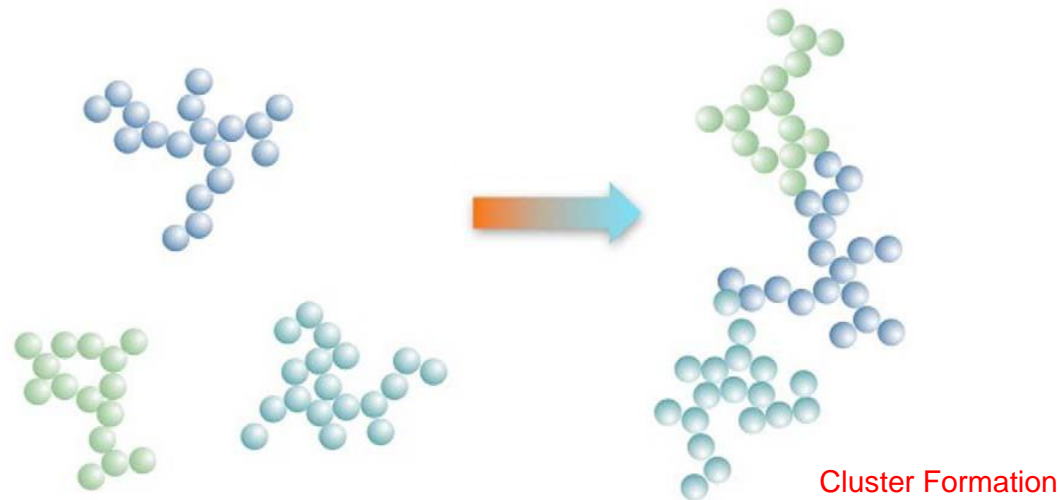


Fig. 1 Aggregation phenomenon of small particles

1 INTRODUCTION

Particle Aggregation Phenomenon

- Since the small particle size of the HNT causes a large surface area, it tends to aggregate due to the Van der Waals force generated by relatively large surface energy.

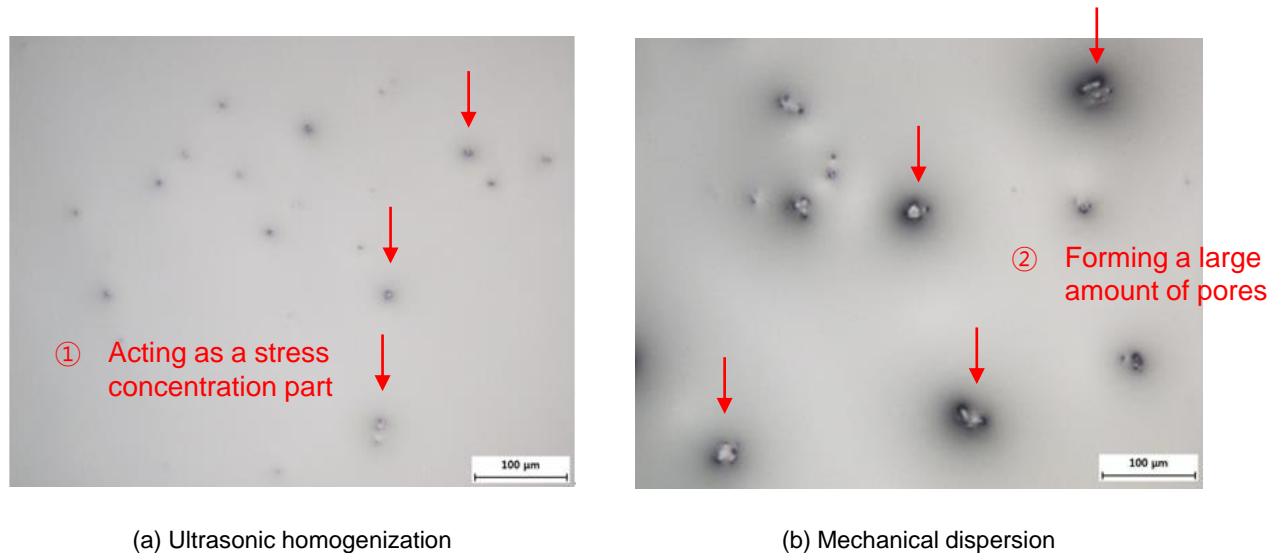
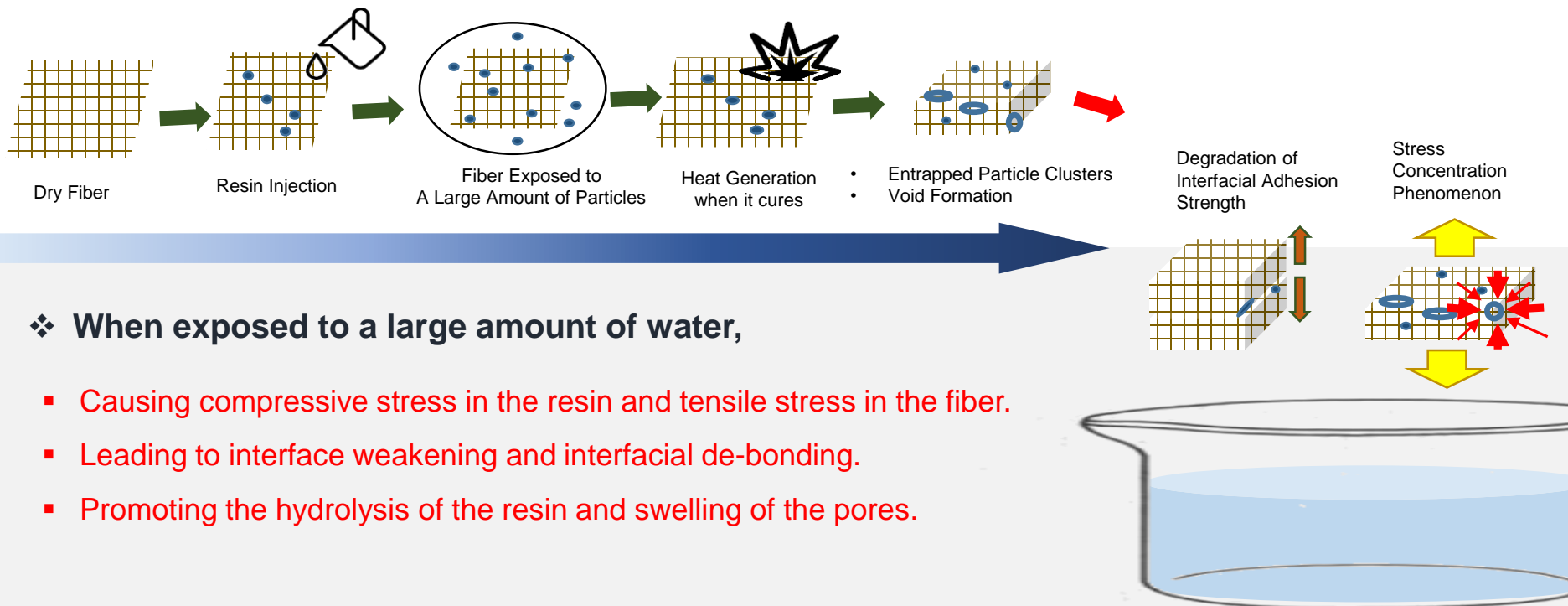


Fig. 2 Comparison of nanoparticle dispersion method as observed by optical microscope

1 INTRODUCTION

In Composites Containing a Large Amount of Pores



2 EXPERIMENTAL WORK

Main materials

- | | |
|----------------------|---|
| Matrix | • A Plain Woven Glass Fiber (Dry/Prepreg) (GM Composite Co. Ltd.) |
| Reinforcement | • Epoxy Resin (KFR-120V/KFH-141, Kukdo Chemical Co. Ltd.) |
| Additives | • Halloysite Nanotube (HNT) (Sigma-Aldrich Japan G.K. CAS-No. 1332-58-7) |



- Formula: $H_4Al_2O_9Si_2 \cdot 2H_2O$
- Molecular Weight: 294,19 g/mol
- Characteristic: Natural, Non toxic, Biocompatible, Retardancy
- Structure –
 Siloxane (Si-O-Si) groups
 Silanol (Si-OH) and Aluminum Hydroxide (Al-OH) groups
 Thin Layer of Water between Continuing Layers

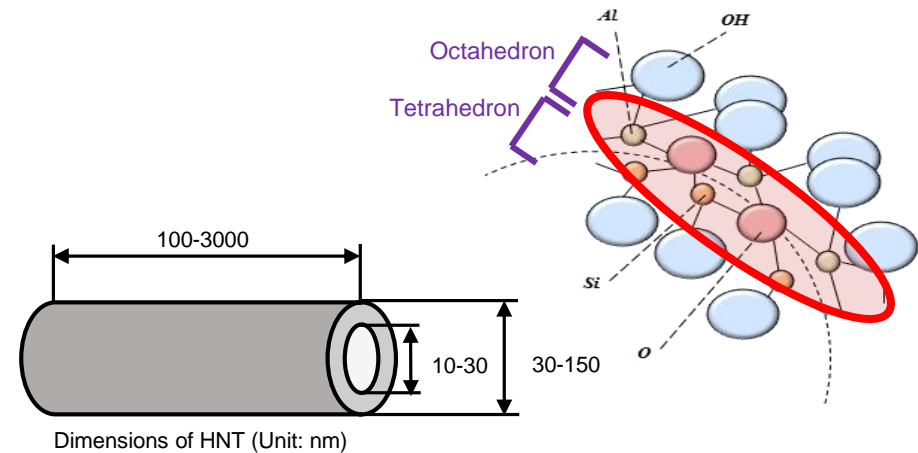


Fig. 3 Specification of the HNT

2 EXPERIMENTAL WORK

Manufacturing method for HNT reinforced GFRP

STEP 1

Heat-Treatment of HNTs

- Heat-treated at 700 °C and 1000 °C using PT-16EF030 electric furnace from PYRO TECH.

STEP 2

Ultrasonic Homogenization

- The production and disaggregation of nano-sized materials.
- Ultrasonic cavitation in liquids cause fast and complete degassing.

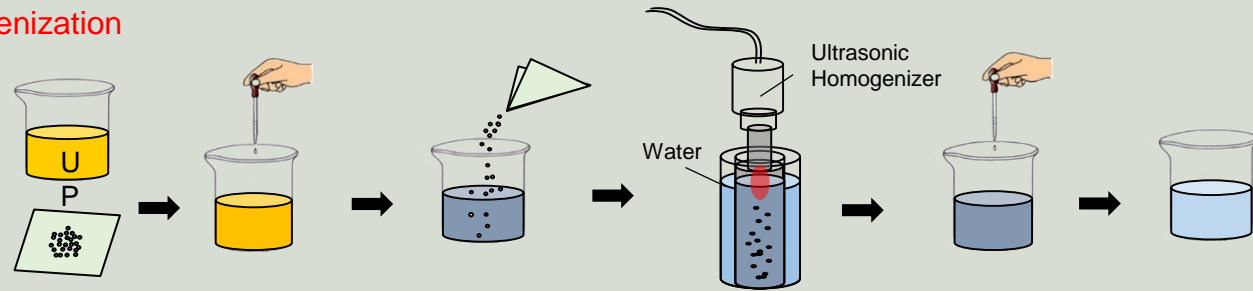


Fig. 4 Specification of the HNT

STEP 3

Semi-Autoclave Processing for Manufacturing GFRP

- Wet prepreg fabrication using hand lay up method.
- Removal of trapped moisture in the glass fiber.
- Uniform distribution and impregnation of the HNT between the fiber layers.
- Resin flow control for prevention of the HNT re-aggregation.

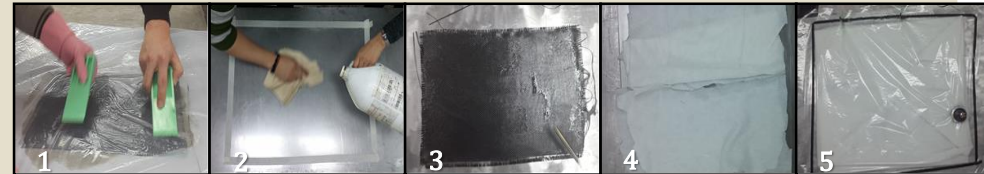


Fig. 5 GFRP manufacturing process

2 EXPERIMENTAL WORK

Structural change observation

❖ Heat Treatment of HNTs at Different Temperatures

- Preheating Time : 1 hour
- Processing Time : 4 hours
- Cooling Time : 1.5 hour

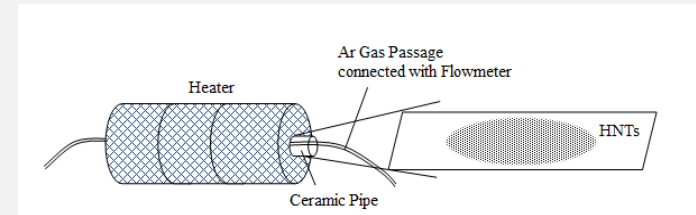


Fig. 6 Process diagram of heat treatment

X-ray Diffraction

- Rigaku Corporation
- $\text{CuK}\alpha$ radiation ($\lambda=0.154$) with Ni filter (40 kV, 40 mA)
- Scan Rate : $1^\circ/2\theta$ The range of X-ray Peak : $10^\circ 2\theta$ to $70^\circ 2\theta$
- Purpose of Use : By observing a **crystallographic change** and **chemical structure** of the heat-treated HNTs, structural changes of the HNTs in the actuality were demonstrated

TEM

- JEOL Ltd, model JEM-2100
- Application : To analyze the crystal structure of the material
- Purpose of Use : To investigate **the basic specification and structural changes of HNTs** due to heat treatment

2 EXPERIMENTAL WORK

Property evaluation

Moisture absorption test

- ASTM D5229
- In distilled water at 40 °C for up to 800 hours
- Measuring the Moisture Absorption Rate

$$M[\%] = \frac{W_l - W_f}{W_f} \times 100$$

W_l : Weight after Immersion in Water
 W_f : Weight before Immersion in Water



Fig. 7 Moisture testing equipment

**After water immersion,
 compared the change
 of the mechanical
 properties.**

Mechanical properties

- Tensile Test (ASTM D638)
- Interlaminar Shear Strength (ILSS) Test (ASTM D2344)

$$ILSS = \frac{3p}{4bh}$$

p : Load at Failure
 b : Width of Specimen
 h : Thickness of Specimen

- Calculating the Specific Strength

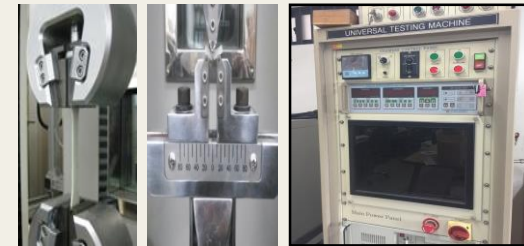


Fig. 8 Universal test machine

2 EXPERIMENTAL WORK

Manufacturing method for bonding test under laminating stepped patch



Step 1



Step 2

STEP 1

Add particles to resin

- The content of HNT / MC is changed and added to resin. (0.5 / 1.0 / 2.0 / 3.0 / 4.0 / 5.0wt%)

STEP 2

Stirred with ultrasonic waves

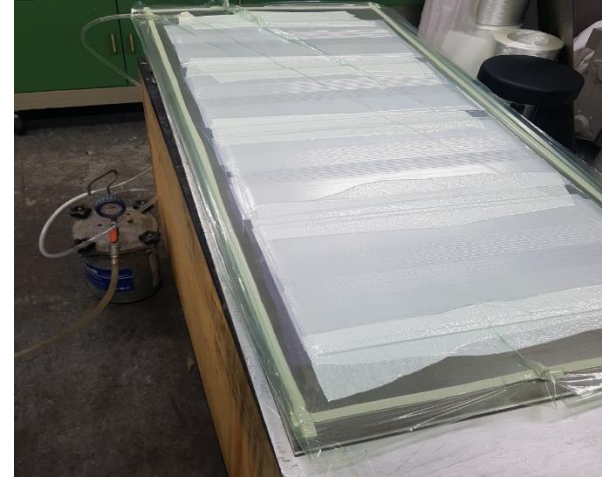
- Stirring for 30 minutes at a power of 500 Watt / 20 kHz at a specific cycle (5 sec dispersion, 2 sec stop)

2 EXPERIMENTAL WORK

Manufacturing method for bonding test under laminating stepped patch



Step 3



Step 4

STEP 3

Laminating glass fiber

- Using a glass fiber prepreg.
- Laminating Depth 4mm, Spacing between fibers 5mm(total 100mm)

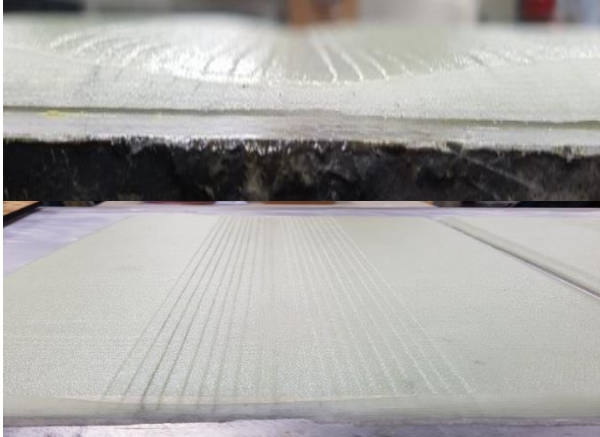
STEP 4

Vacuum molding

- A perforated film and a breather were laminated and then vacuum molding.

2 EXPERIMENTAL WORK

Manufacturing method for bonding test under laminating stepped patch



Step 5



Step 6

STEP 5

Removing from mold and surface treatment

- Removed from mold after hardening. Then, acetone is used to remove foreign substances on the surface

STEP 6

Making wet prepreg (stepped patch)

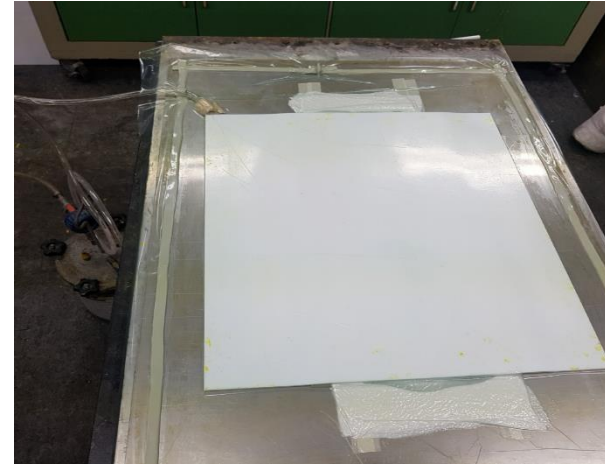
- After the particle and content are determined, wet prepreg is made. Altar to stair length

2 EXPERIMENTAL WORK

Manufacturing method for bonding test under laminating stepped patch



Step 7



Step 8

STEP 7

Laminating stepped patch

- Attach stepped patches to arbitrarily damaged specimens (glass fibers made in the form of wet prepreg)

STEP 8

Vacuum molding

- After lamination of Teflon plate and breather, vacuum molding.

2 EXPERIMENTAL WORK

Manufacturing method for bonding test under laminating stepped patch

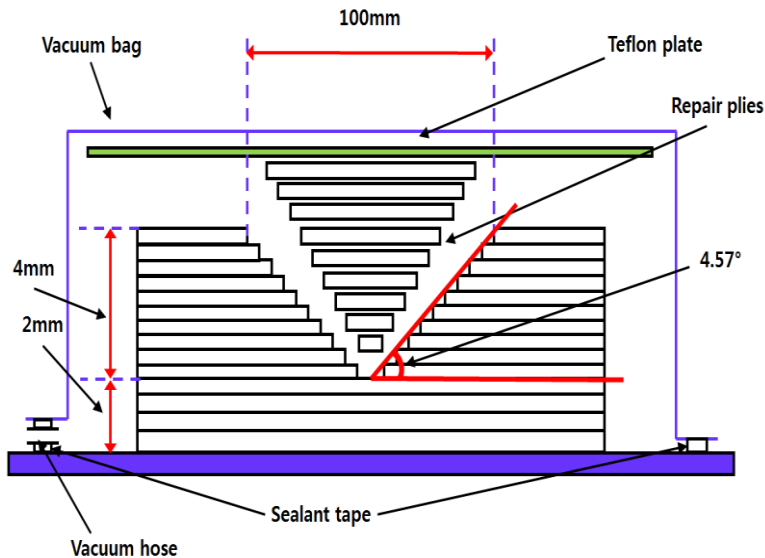


Fig. 9 Schematic of repair specimen

Table 1. Code of specimens

Name	Added particle	Content(wt. %)	Damage(O/X)
U.S (Undamaged specimen)	X	0	X
N.P (Non Particle)	X	0	O
MC0.5	Milled Carbon	0.5	O
MC1.0	Milled Carbon	1.0	O
MC2.0	Milled Carbon	2.0	O
MC3.0	Milled Carbon	3.0	O
MC4.0	Milled Carbon	4.0	O
MC5.0	Milled Carbon	5.0	O
HNT0.5	Halloysite Nano Tube	0.5	O
HNT1.0	Halloysite Nano Tube	1.0	O
HNT2.0	Halloysite Nano Tube	2.0	O
HNT3.0	Halloysite Nano Tube	3.0	O
HNT4.0	Halloysite Nano Tube	4.0	O
HNT5.0	Halloysite Nano Tube	5.0	O

2 EXPERIMENTAL WORK

Property evaluation



Fig. 10 Tensile test



Fig. 11 Bending test

Mechanical property test

- Kyung-Do Co. Ltd. Universal Test Machine KDMT-156
- Tensile Test (ASTM D3039)
- Bending Test (ASTM D790)
- 9 specimens per test

- Bending strength

$$\sigma_f = 3PL/2bd^2$$

P : Maximum load(N) L : Length of span
 b : Sample width d : Sample thickness

2 EXPERIMENTAL WORK

Property evaluation



Fig. 12 Moisture absorption test

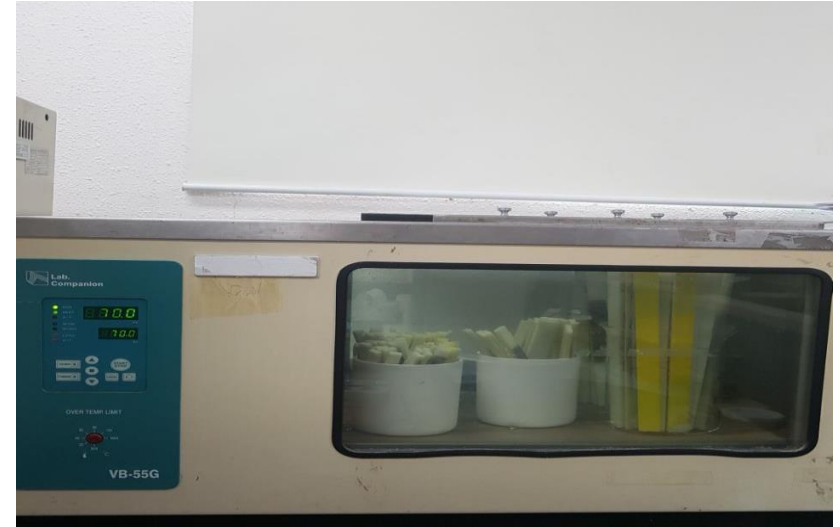


Fig. 13 Moisture absorption test machine

Moisture absorption test

- ASTM D5229
- In distilled water at 70 °C for up to 75 days
- Absorption and Tensile/Bending strength specimen (7 specimens per test)

• Measuring the Moisture Absorption Rate

$$M[\%] = \frac{W_i - W_f}{W_f} \times 100$$

W_i : Weight after Immersion in Water
 W_f : Weight before Immersion in Water

2 EXPERIMENTAL WORK

Property evaluation



Fig. 14 SEM apparatus



Fig. 15 PT Coating machine

Observation of lamination plane

1. The aggregation degree of the resin was observed at a magnification of 2K at the lamination surface
2. After Moisture absorption test, the bond between the fiber and the resin was observed at the magnification of 3.5K by using SEM

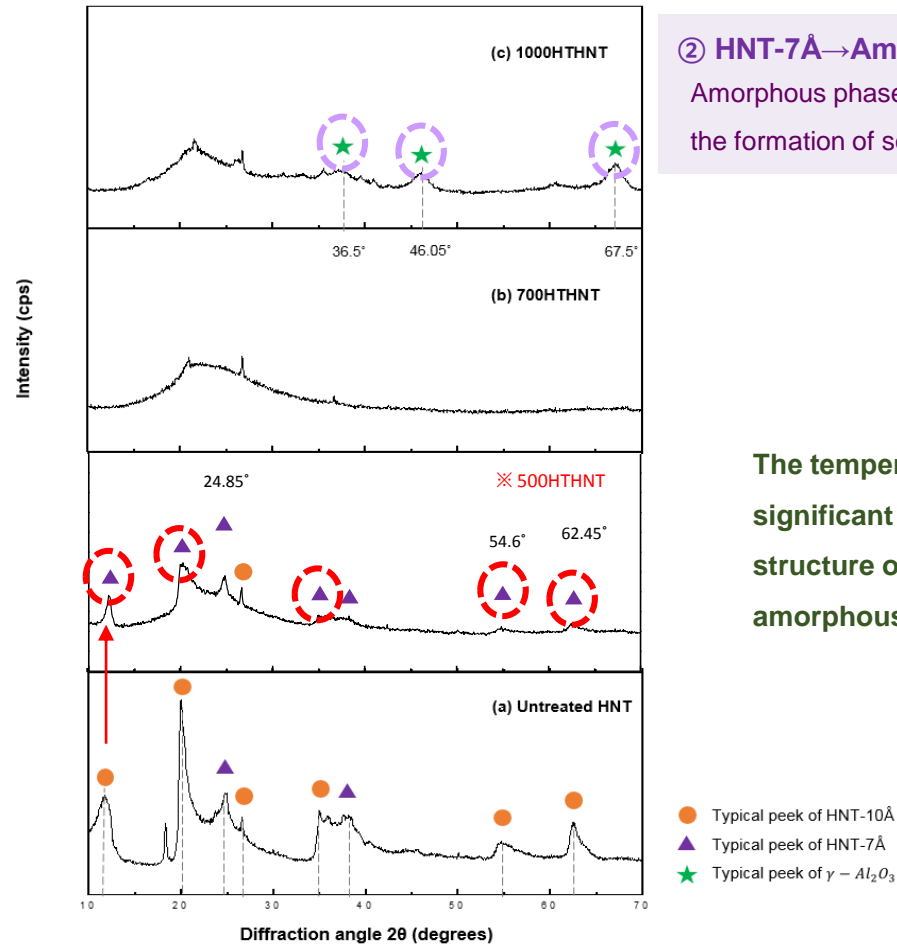
3 RESULTS AND DISCUSSIONS

X-ray diffraction

① HNT-10Å → HNT-7Å

001 diffraction at 12.30°
(By loss of interlayer water)

Mixture of HNT-10Å and HNT-7Å



② HNT-7Å → Amorphous

Amorphous phase and crystallinity HNT along the formation of some new broad peaks

The temperature of 500°C had a significant impact on the crystal structure of the HNT, that became amorphous above it.

Fig. 16 X-ray diffraction of HNTs at 700°C and 1000°C

3 RESULTS AND DISCUSSIONS

TEM imaging

- In common, HNT had a tubular structure and formed aggregates.
- For the case of heat-treated HNT, it showed broken or bent shapes and formed clusters.
- The surface was not smooth and had rough spots.

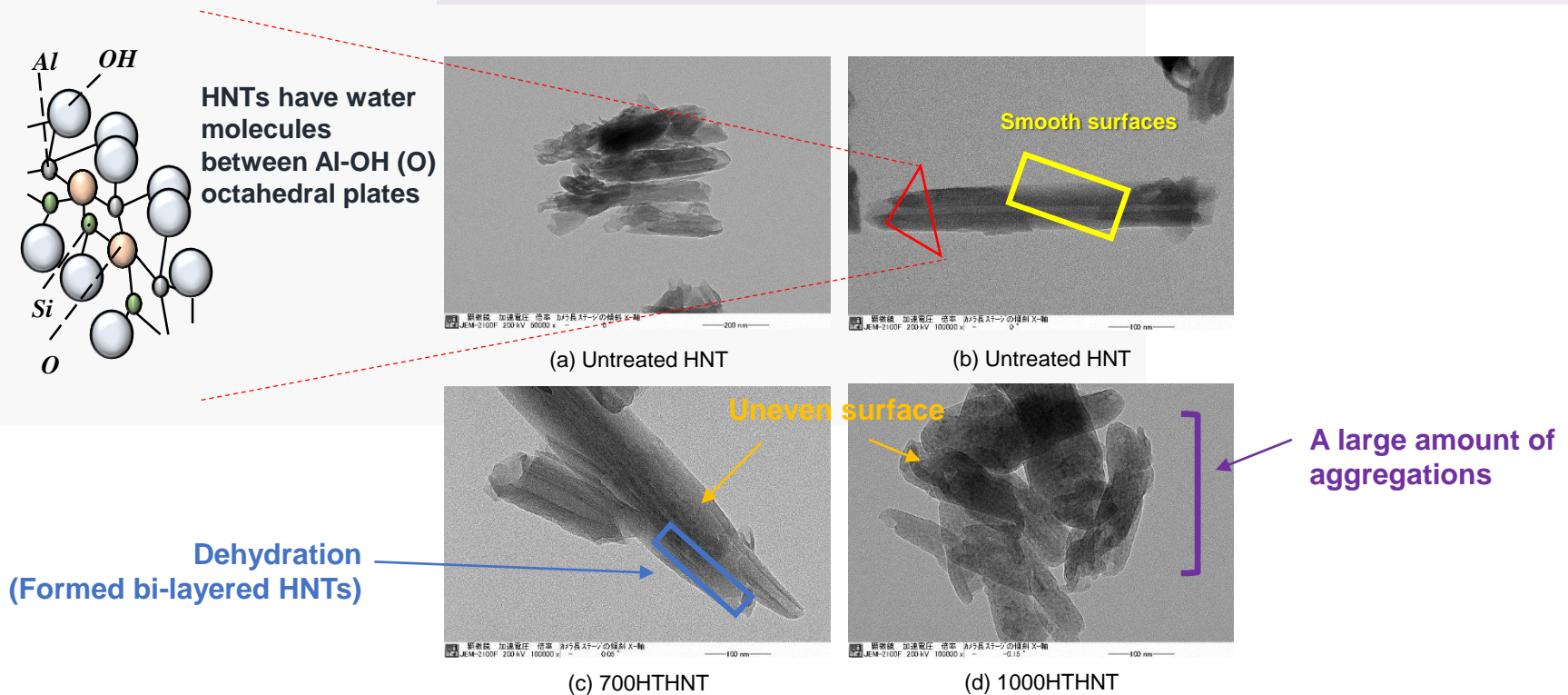


Fig. 17 TEM of HNTs at 700 °C and 1000 °C

3 RESULTS AND DISCUSSIONS

Moisture absorption rate

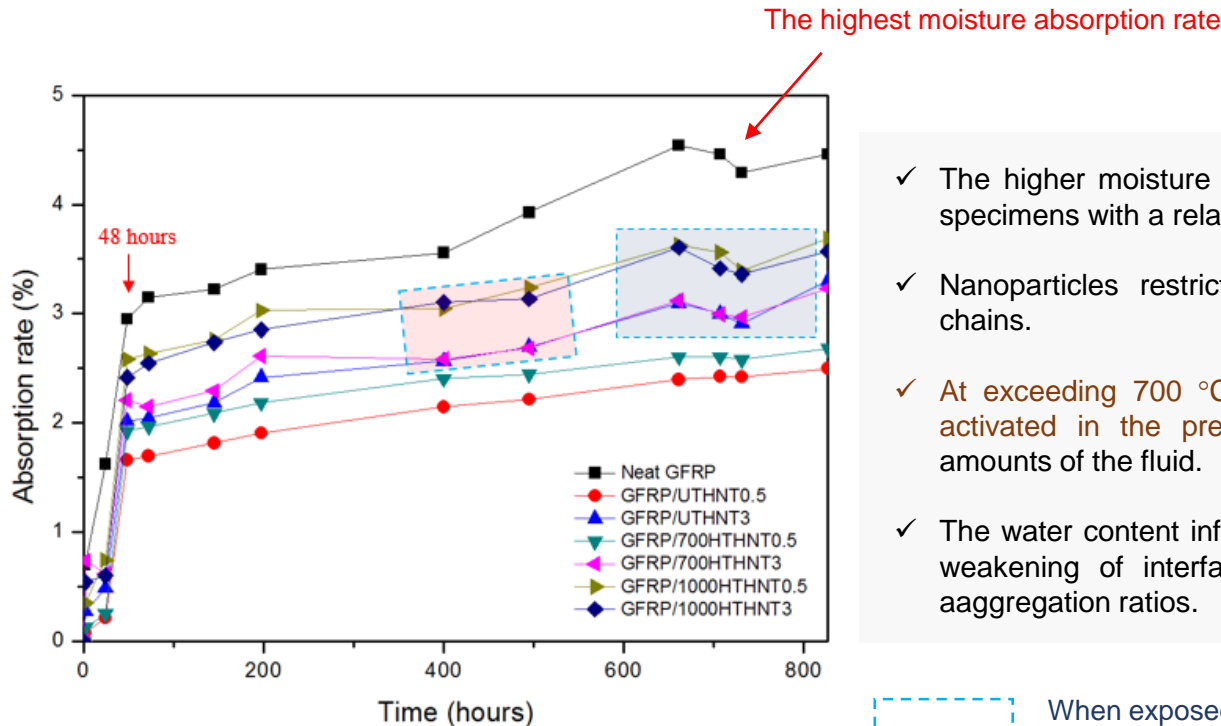


Fig. 18 Absorption rate of GFRP/HNTs nanocomposites

- ✓ The higher moisture absorption rate was calculated for the specimens with a relatively small amount of HNT.
- ✓ Nanoparticles restrict the movement of epoxy molecular chains.
- ✓ At exceeding 700 °C, the structure of the HNT is rapidly activated in the presence of water and takes up large amounts of the fluid.
- ✓ The water content influences the formation of pores and the weakening of interfacial bonding forces due to the high aggregation ratios.

When exposed to prolonged moisture, (UTHNT3, 700HTHNT3), (1000HTHNT0.5, 1000HTHNT3) show the same behavior.

3 RESULTS AND DISCUSSIONS

Moisture absorption rate of repair 700HTHNT/GFRP by stepped patch

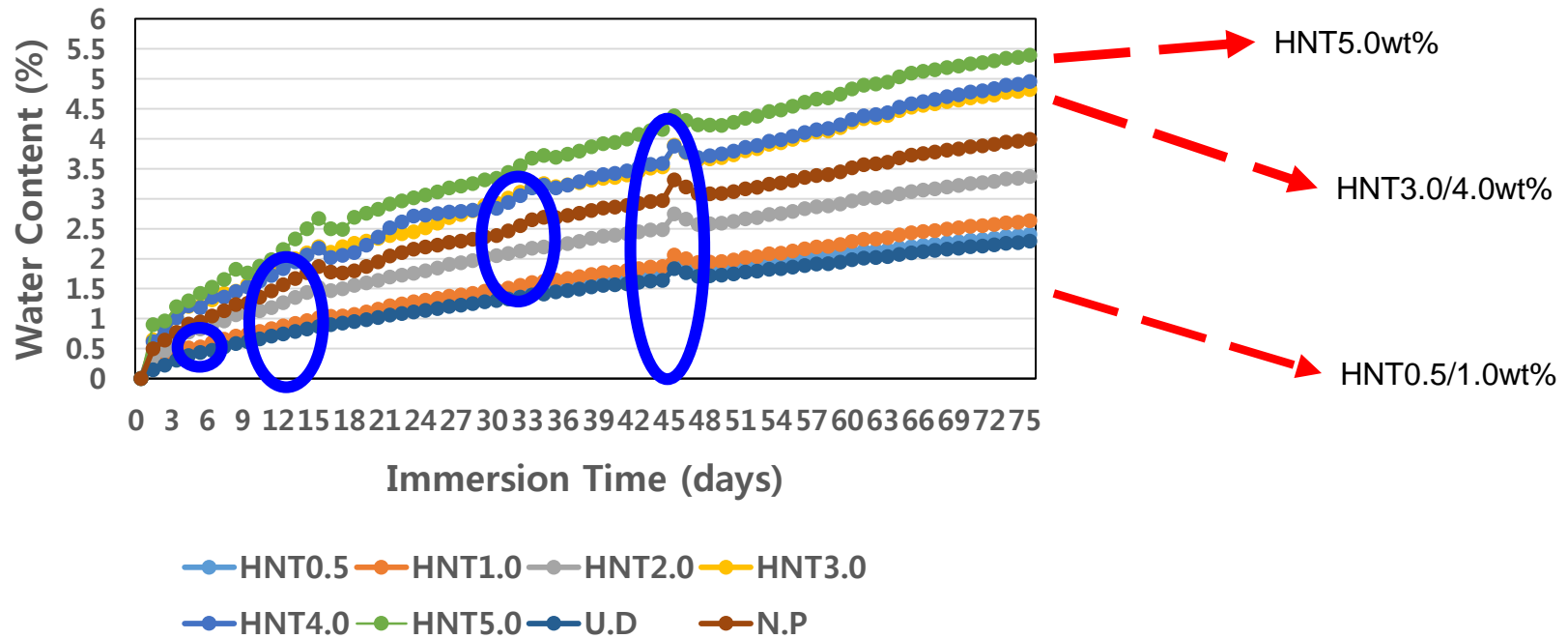


Fig. 19 Absorption behavior of specimens with Halloysite Nanotube

3 RESULTS AND DISCUSSIONS

Tensile property

- ✓ Before water immersion, the specimens with 700HTHNT and 1000HTHNT showed the reinforcing effect.
- ✓ All the specimens observed a decrease in strength, and GFRP/700HTHNT were much more hygroscopic than neat GFRP.
- ✓ In GFRP/700HTHNT, the specific strength was significantly lower than the tensile strength after water immersion; however, overall, there was no significant change.
- ✓ A large amount of water not only acts as an interfacial bonding force and strength inhibiting factor, but also increases resistance to tensile stress through bonding with 700HTHNT.

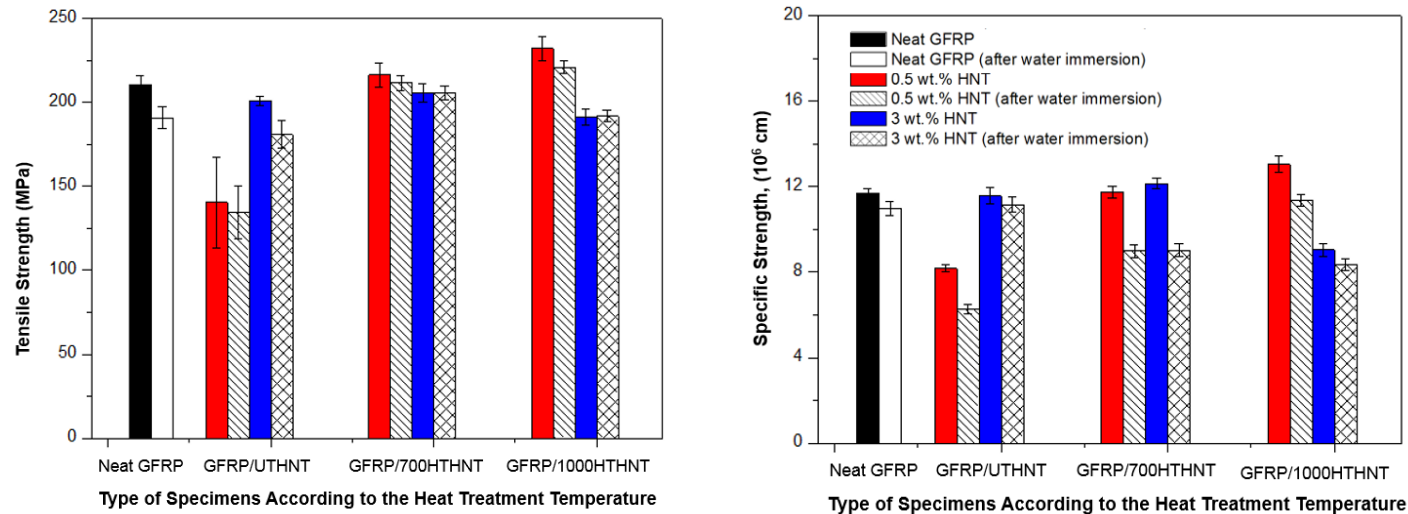


Fig. 20 Comparison of tensile properties of GFRP/HNTs before and after water

3 RESULTS AND DISCUSSIONS

Interlaminar shear strength

- ✓ UTHNT maintains strong interfacial bonding force by preventing the swelling of epoxy through the combination of UTHNT and a small amount of water while lowering the moisture absorption rate.
- ✓ In GFRP/1000HTHNT, relatively low ILSS was observed compared with high tensile strength, which resulted in **increased fracture toughness by aggregation of HNT with cracks perpendicular to the tensile direction**.
- ✓ This aggregation seems to be due to the decrease of the ILSS as a main factor which interferes with the interfacial bonding force.

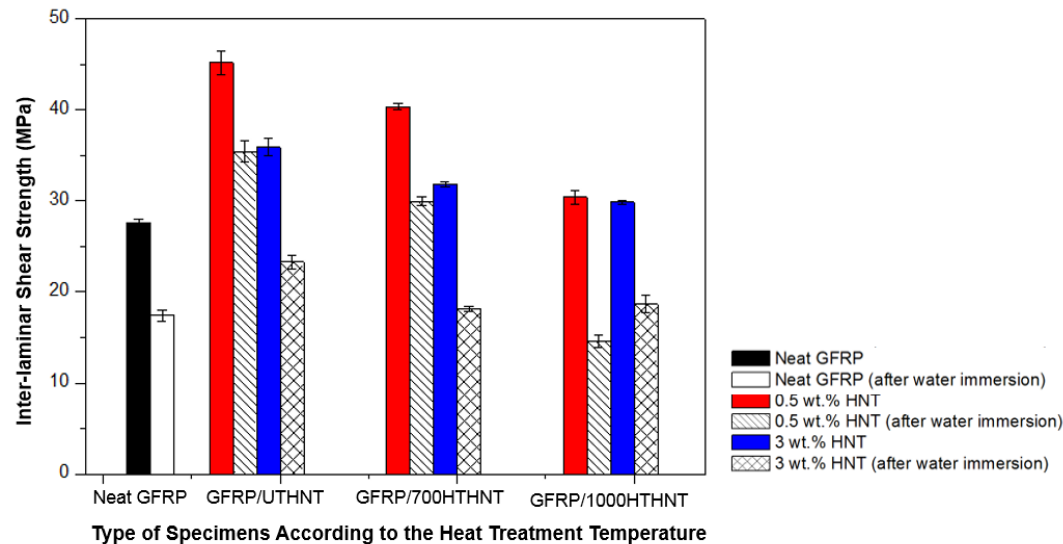


Fig. 21 Results of ILSS of GFRP/HNTs before and after water immersion

3 RESULTS AND DISCUSSIONS

Mechanical properties of repair 700HTHNT/GFRP by stepped patch

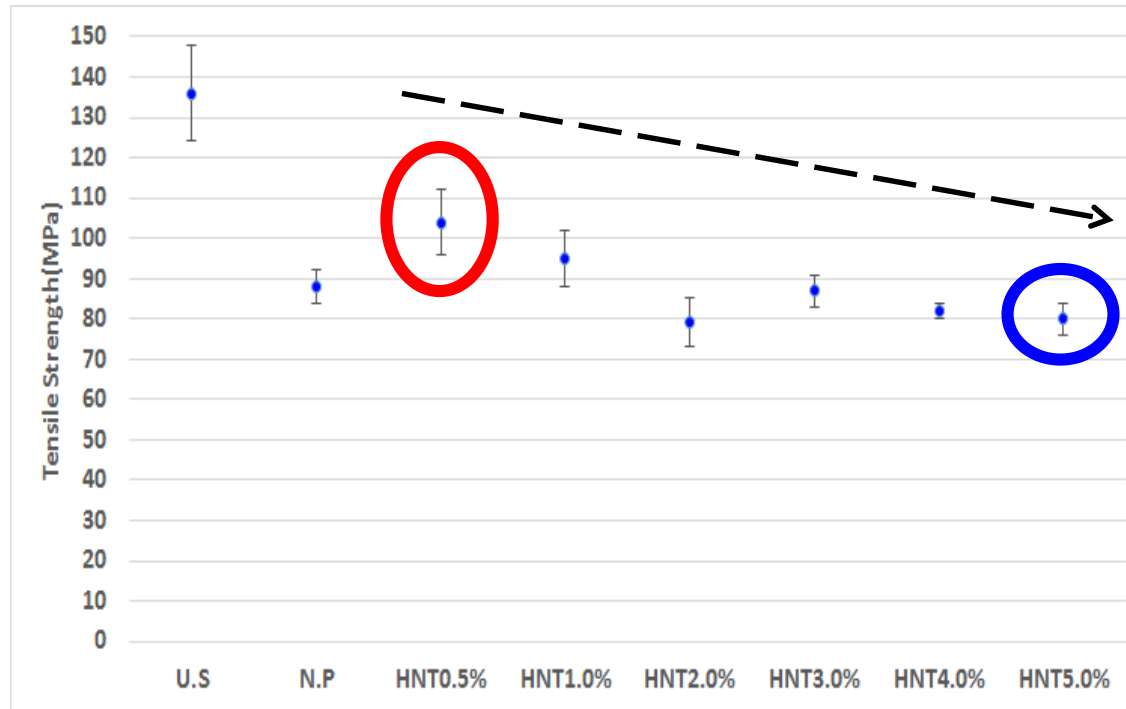


Fig. 22 Tensile strength of repaired specimens with Halloysite Nanotube

3 RESULTS AND DISCUSSIONS

Mechanical properties of repair 700HTHNT/GFRP by stepped patch

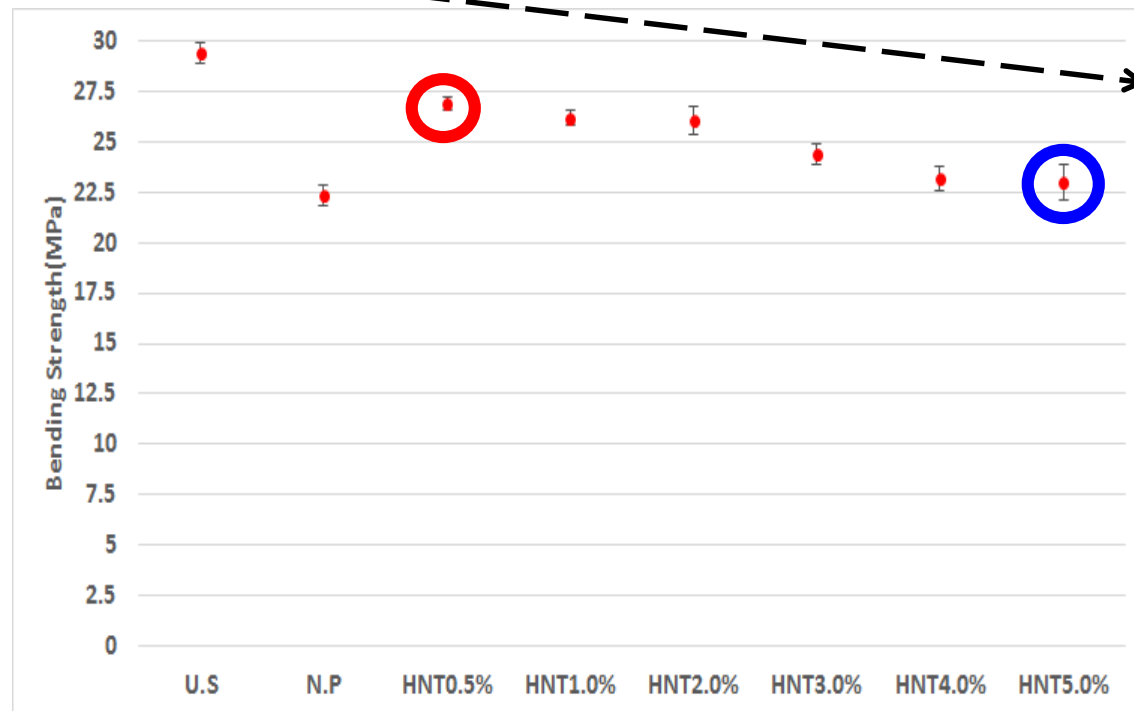


Fig. 23 Bending strength of repaired specimens with Halloysite Nanotube

3 RESULTS AND DISCUSSIONS

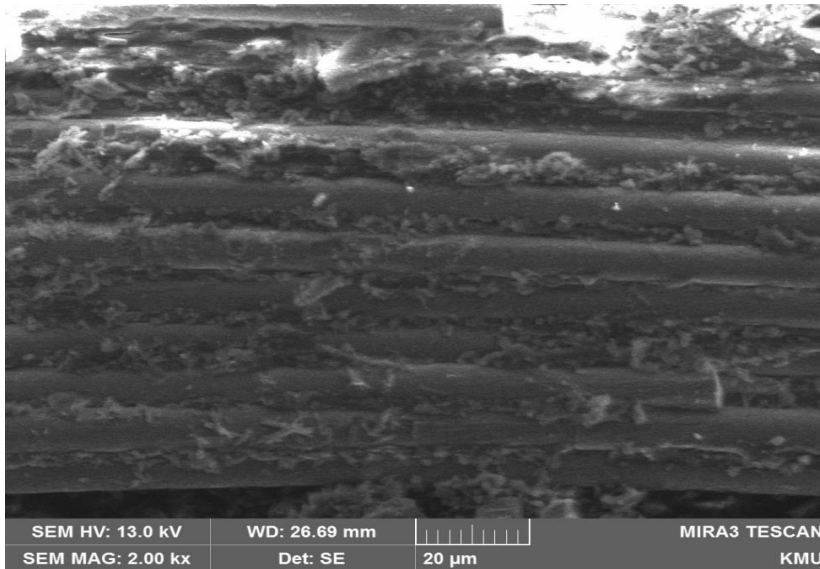
Mechanical properties of repair 700HTHNT/GFRP by stepped patch

Table 2. Recovery rate of Bending strength

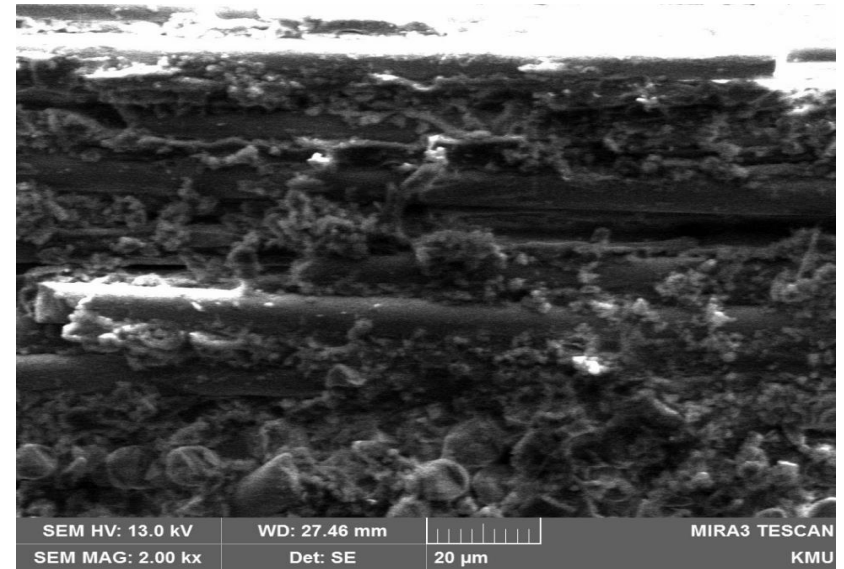
Name	Recovery rate of Tensile strength(%)	Recovery rate of Bending strength(%)
U.S	100	100
N.P	64.7	75.8
HNT0.5%	76.4	91.3
HNT1.0%	69.8	89.0
HNT2.0%	58.0	88.5
HNT3.0%	63.9	82.9
HNT4.0%	60.2	78.9
HNT5.0%	58.8	78.1

3 RESULTS AND DISCUSSIONS

fracture surface and interface of repair 700HTHNT/GFRP by stepped patch



(a) HNT 0.5



(b) HNT 5.0

Fig. 24 HNT laminate plane

3 RESULTS AND DISCUSSIONS

fracture surface and interface of repair 700HTHNT/GFRP by stepped patch

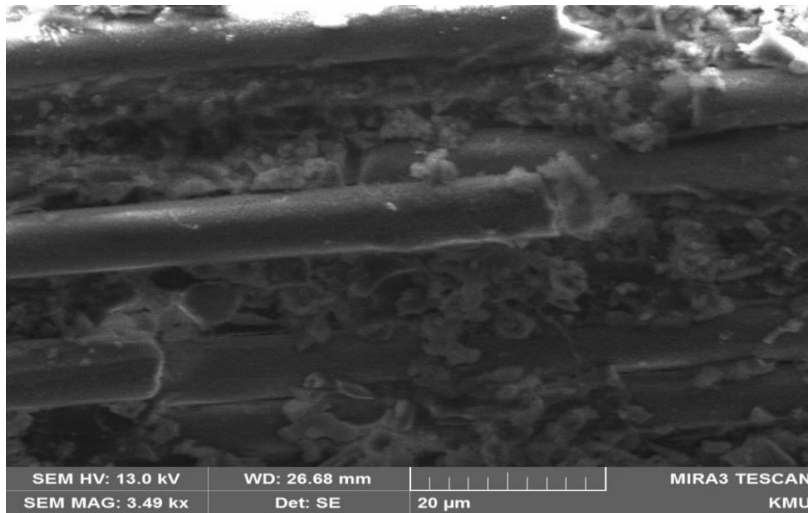


Fig. 25 After moisture absorption, N.P laminate plane

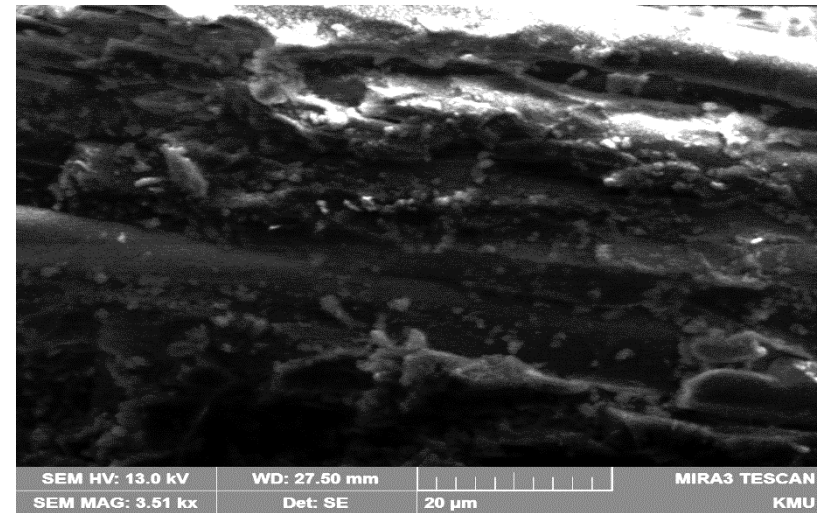


Fig. 26 After moisture absorption, 0.5% HNT laminate plane

4 CONCLUSIONS

- 1) The HNT, which contains a thin layer of water, is easily transformed from a two-layered hollow tubular to a bi-layered structure by high temperatures such as 700 °C and 1000 °C (because it is vulnerable to heat). At that time, the HNT involves changes such as uneven surfaces, particle shrinkage, low crystallinity and an amorphous structure.
- 2) The HNT particles suppress the expansion of epoxy by moisture and control moisture absorption. The specimens with 0.5 wt.% HNT were highly hygroscopic, and when the heat treatment temperature exceeded 700 °C, the specimens were activated by a large amount of water. In this case, the addition amount of HNTs has little effect on the moisture absorption rate.

4 CONCLUSIONS

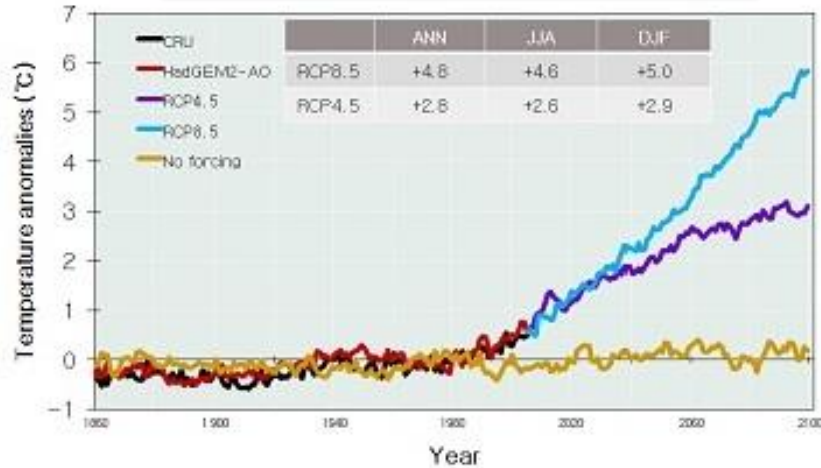
- 3) GFRP/UTHNT0.5 showed higher hygroscopicity and ILSS, while the tensile strength was significantly lower. However, GFRP/700HNT0.5 exhibited a low moisture absorption rate, high tensile strength and ILSS. It is considered that 700HTHNT prevents the swelling of the epoxy through chemical bonding with a small amount of water and increases the interfacial bonding force.
- 4) The cohesive 1000HTHNT increased the fracture toughness by resisting crack propagation when subjected to a tensile load, but decreased the durability by acting as a stress concentration part rather than the interfacial bond force directly connected to ILSS.

4 CONCLUSIONS

- 5) Through the analysis of the laminate surface, it was confirmed that the agglomeration of the resin became worse as the particle amount increased. After the hygroscopicity test, the HNT particles added on the lamination surface prevented the penetration of moisture, which is considered to prevent the deterioration of interfacial bonding force.
- 6) The effect of the content on the deterioration of the properties of the HNT added specimen showed no specific trend, and HNT showed a similar hygroscopic rate to that of the undamaged specimen, and the hygroscopic rate increased sharply as the particles agglomerated over a certain amount.

Application of Composite Materials to Green Ship and Ocean Plant

Global warming



International standard Greenhouse gas emission scenario (RCP)

RCP4.5(530ppm) → 2.8°C

RCP8.5(940ppm) → 4.8°C

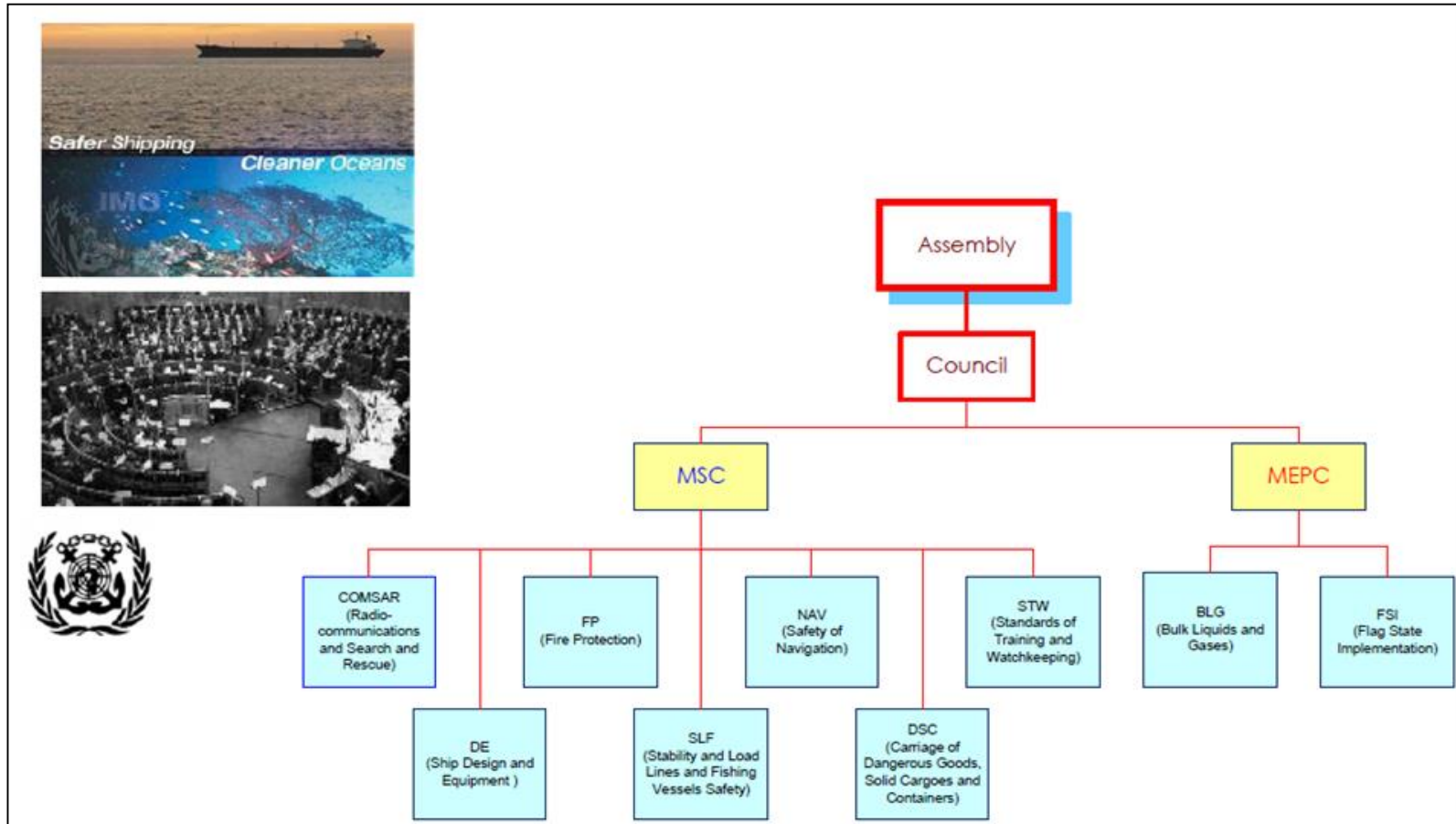
RCP8.5 → In the end of 21C

The Artic iceberg will be decreased more than 70%



船舶への応用

IMO's Regulation for Global Warming, CO₂



Application of Composite Materials to Green Ship and Ocean Plant

■ IMO regulates air pollutants reduction from ship

● Nitrogen oxides

- Tier II and III
- Formation of various kinds of SCR
- Cheap and long-lasting Catalyst

● Sulphur oxides

- Low sulphur fuel oil
- DeSOx system – Scrubber, Cyclone and etc

● Carbon dioxide

- Energy saving device
- New generation model

● PM

- PM reduction devices
- High quality bunker and/or better maintenance

● VOC

- Onboard VOC control system
- Shore VOC control system

Application of Composite Materials to Green Ship and Ocean Plant

$$EEDI = \frac{\text{CO}_2 \text{ emission (g)}}{\text{transport work (tonne}\cdot\text{nm)}} \cdot$$



MAIN ENGINES
EMISSIONS

AUXILIARY ENGINES
EMISSIONS

SHAFT GENERATORS/MOTORS
EMISSIONS

EFFICIENCY
TECHNOLOGIES

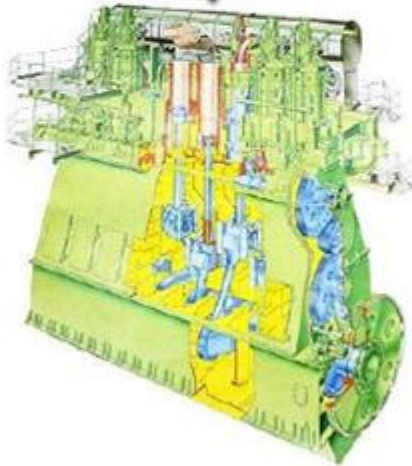
$$\left(\prod_{j=1}^M f_j \right) \left(\sum_{i=1}^{nME} P_{ME(i)} \cdot C_{FME(i)} \cdot SFC_{ME(i)} \right) + (P_{AE} \cdot C_{FAE} \cdot SFC_{AE}^*) + \left(\left(\prod_{j=1}^M f_j \cdot \sum_{i=1}^{nPTI} P_{PTI(i)} - \sum_{i=1}^{neff} f_{eff(i)} \cdot P_{AE_{eff(i)}} \right) C_{FAE} \cdot SFC_{AE} \right) - \left(\sum_{i=1}^{neff} f_{eff(i)} \cdot P_{eff(i)} \cdot C_{FME} \cdot SFC_{ME} \right)$$

$$f_i \cdot \text{Capacity} \cdot V_{ref} \cdot f_w$$

TRANSPORT WORK

Application of Composite Materials to Green Ship and Ocean Plant

$$\frac{\left(\prod_{j=1}^M f_j \right) \sum_{i=1}^{n_{ME}} P_{ME(i)} C_{FME(i)} SFC_{ME(i)} + P_{AE} C_{FAE} SFC_{AE} + \left(\prod_{j=1}^M f_j \sum_{i=1}^{n_{PTI}} P_{PTI(i)} - \sum_{i=1}^{n_{eff}} f_{eff(i)} P_{AE_{eff}(i)} \right) C_{FAE} SFC_{AE}}{f_i \text{ Capacity } V_{req} f_w} - \left(\sum_{i=1}^{n_{eff}} f_{eff(i)} P_{eff(i)} C_{FME} SFC_{ME} \right)$$

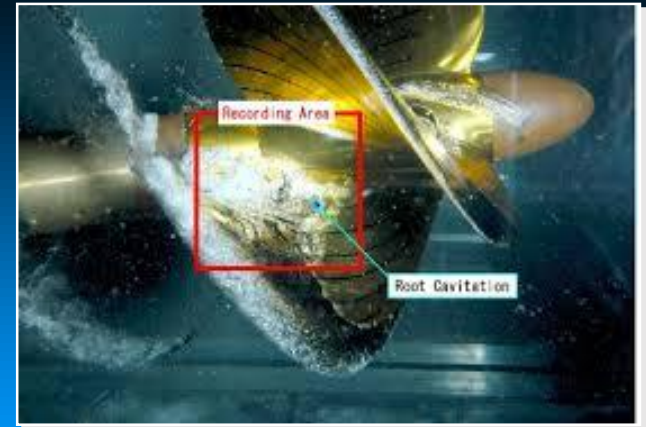
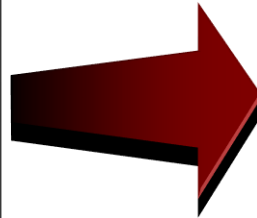
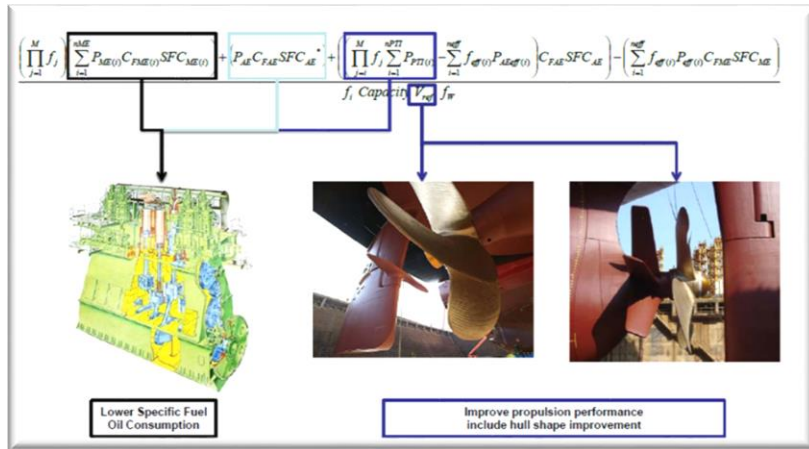


Lower Specific Fuel
Oil Consumption



Improve propulsion performance
include hull shape improvement

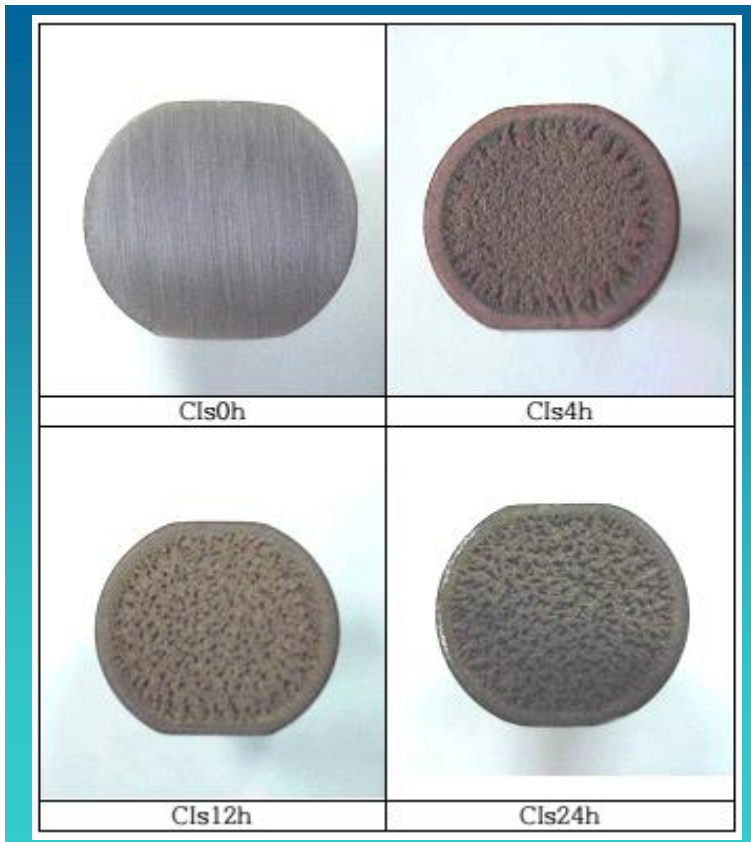
複合材料の応用



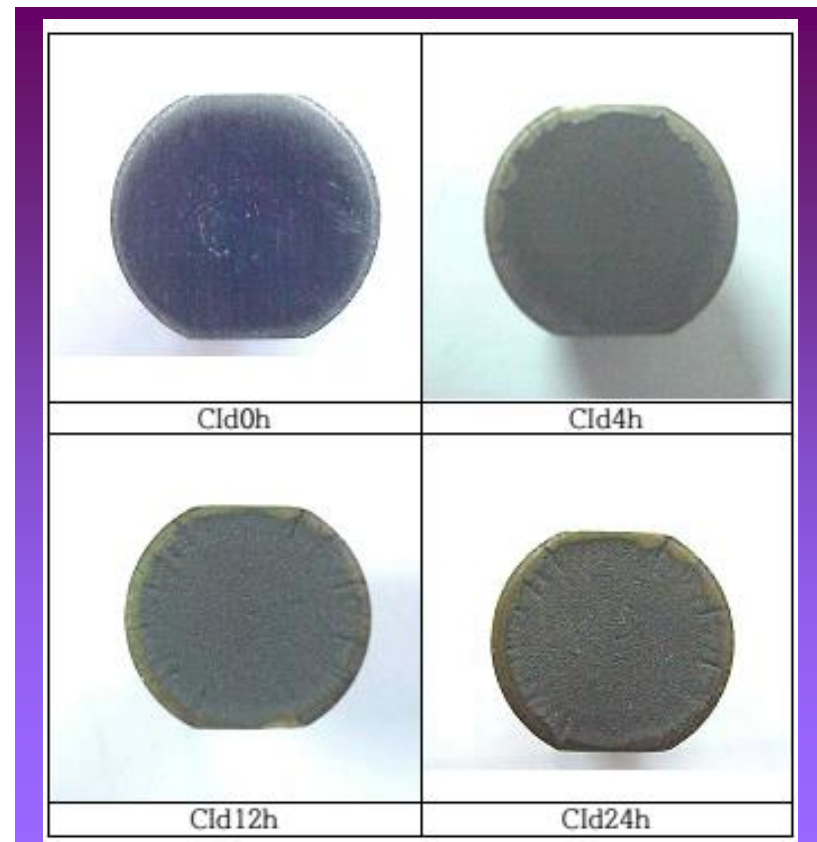
Cavitation Erosion



Application of Composite Materials to Green Ship and Ocean Plant

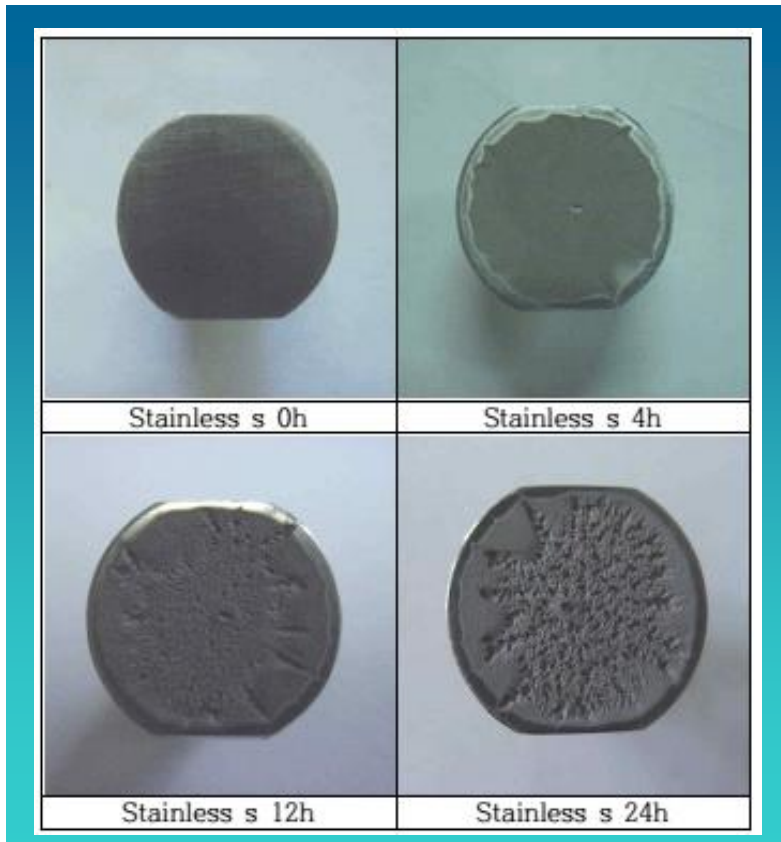


**Progressive change of damaged surface
According to testing time (0, 4, 12, 24 hr)
In sea water for cast iron**

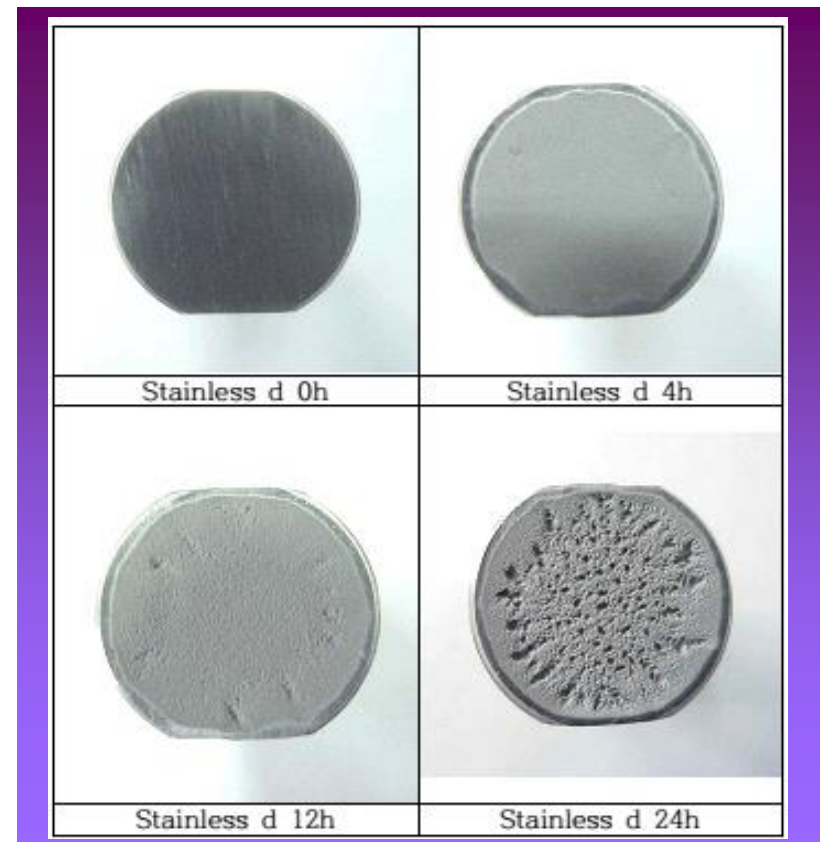


**Progressive change of damaged surface
According to testing time (0, 4, 12, 24 hr)
In distilled water for cast iron**

Application of Composite Materials to Green Ship and Ocean Plant



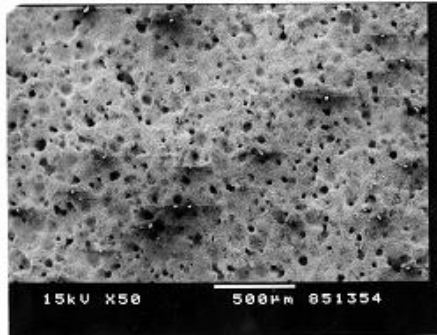
**Progressive change of damaged surface
According to testing time (0, 4, 12, 24 Hrs)
In sea water for stainless**



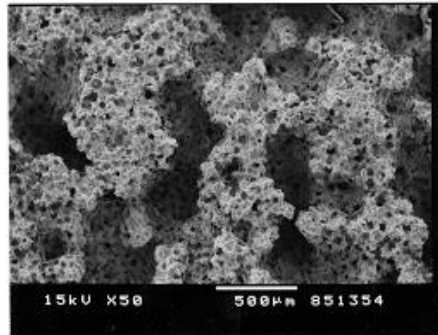
**Progressive change of damaged surface
According to testing time (0, 4, 12, 24 Hrs)
In distilled water for brass**

Application of Composite Materials to Green Ship and Ocean Plant

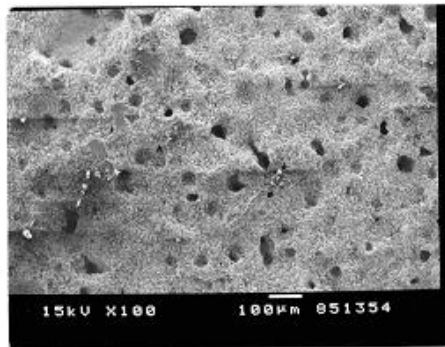
- SEM for cavitation-erosion of cast iron



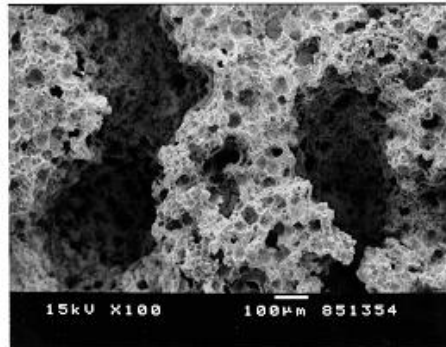
(a) Cast iron, ×50



(a) Cast iron, ×50



(b) Cast iron, ×100

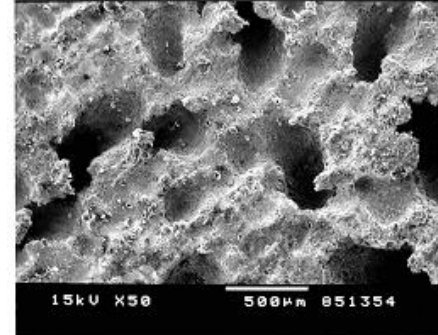


(b) Cast iron, ×100

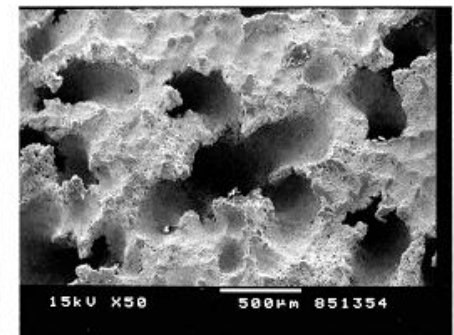
- In distilled water

- In sea water

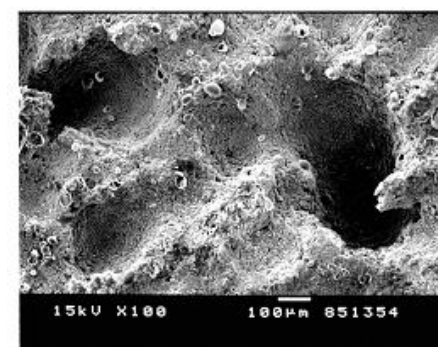
- SEM for cavitation-erosion of brass



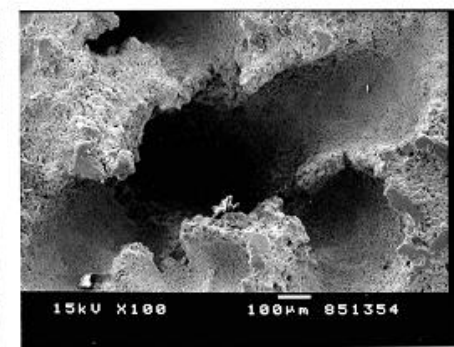
(a) Brass, ×50



(a) Brass ×50



(b) Brass, ×100



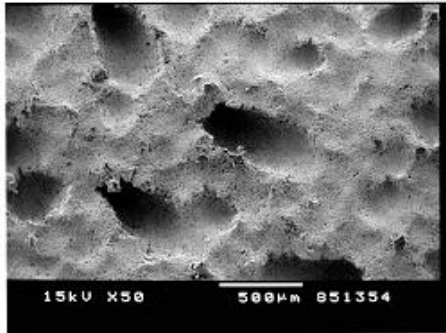
(b) Brass, ×100

- In distilled water

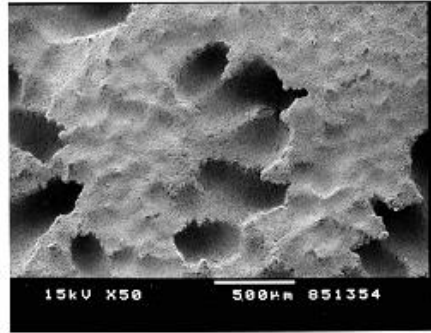
- In sea water

Application of Composite Materials to Green Ship and Ocean Plant

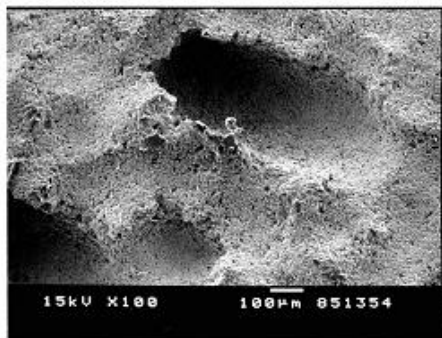
- SEM for cavitation-erosion of stainless



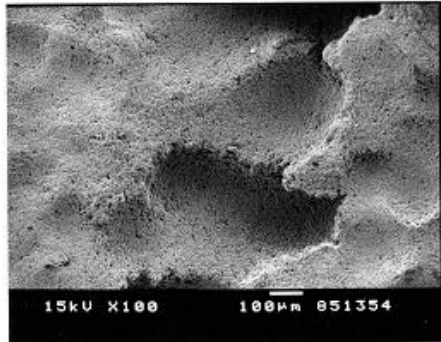
(a) Stainless, ×50



(a) Stainless, ×50



(b) Stainless, ×100

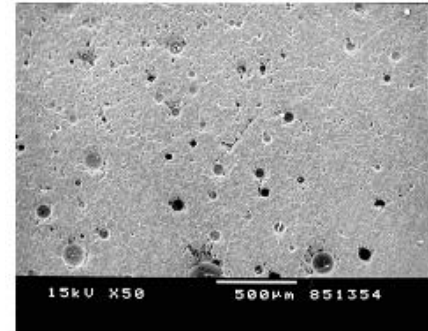


(b) Stainless, ×100

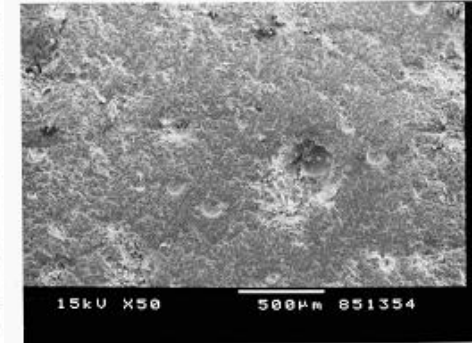
- In distilled water

- In sea water

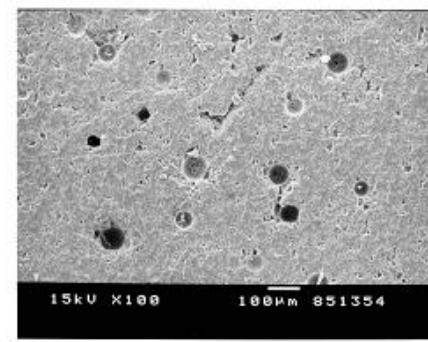
- SEM for cavitation-erosion of composite



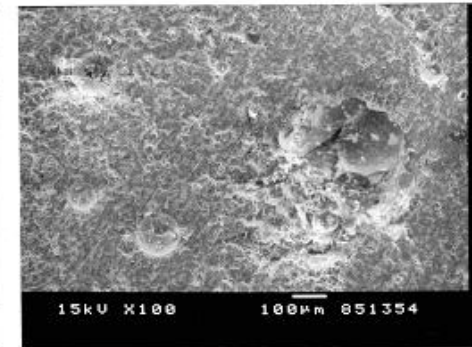
(a) Composites ×50



(a) Composites ×50



(b) Composites ×100



(b) Composites ×100

- In distilled water

- In sea water

Thank you!
有難うございます！
謝謝！
감사합니다!

