

## Development of Pultrusion Techniques of Phenolic Foam Composites

Goichi Ben\* and Akiko Shoji\*\*

( Received March 3, 2003 )

### Abstract

Phenolic resin has the advantages of heat resistance, flame resistance and less smoke during burning which make phenolic resin a suitable material to be used in the construction area. This paper presents a method of molding phenolic foam composite materials by means of a pultrusion technique. Such phenolic foam composites are composed of phenolic resin of the foam type as the matrix and the glass fiber as the reinforcement. When molding phenolic foam composites, it is important to control the time until foaming and as well as during foaming and to control the temperature of a die for pultrusion to heat phenolic resin. Furthermore, it is also important to uniformly feed phenolic resin and a curing agent. A new feeder machine was developed by authors for this purpose.

This paper also presents the mechanical strengths of the phenolic foam composite in comparison with those of woods. It was found that the phenolic foam composite has a potential to be utilized in the construction area much same as natural woods.

Keyword: Phenolic foam, Pultrusion, Bulky roving glass fiber

### 1. Introduction

Since phenolic resin is inexpensive and has the advantages of superior mechanical strength and electric non-conductance among various kinds of resins, products made of phenolic resin by means of injection molding or lamination molding have been used as small parts in various engineering fields. Furthermore, the phenolic resin has additional advantages of heat resistance, flame resistance and less smoke during burning, and these advantages make the phenolic resin suitable materials in the field of construction. For these reasons, panels made of phenolic resin foam have been used as fire resistant and heat resistant materials. However, their me-

chanical strength is not strong enough as primary structural members, although their weight is very light.

In order to increase the mechanical strength of phenolic foam panels, we developed phenolic foam composites composed of phenolic resin of the foam type as the matrix and glass roving as the reinforcement. Such composites exhibited additional weight saving, shock absorption, high insulation and flame resistance. Furthermore, such composites have a potential to be applied to the fields of space structures because of their inflatable property.

---

\* Department of Mechanical Engineering, College of Industrial Technology, Nihon University

\*\* Graduate Department of Mechanical Engineering, Graduate School of Industrial Technology, Nihon University

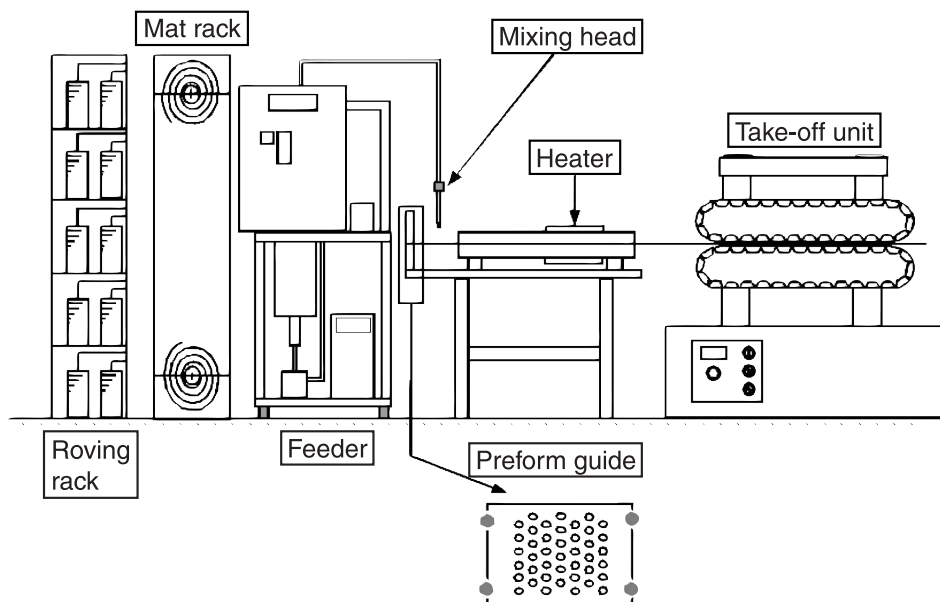
## 2. Molding method of phenolic foam composite

### 2.1 Outline of pultrusion and foaming

For molding a phenolic foam composite, a pultrusion technique, which can produce FRP composites having uniform cross sections with an arbitrary length, is very useful because the volume and arrangement of fibers on the cross sections of FRP composites can be almost kept constant. We developed a new system of pultrusion facilities as shown in **Fig.1**. This system can mold composite having the same sectional area of 32mm×52mm. In the conventional method of pultrusion molding, glass roving pulled from a roving rack were impregnated with resin in a bath before being introduced to a steel die, or were impregnated with injected resin in the interior of a die<sup>1)</sup>. When phenolic resin containing di-chloromethane as a foaming agent was used as the matrix, we could not use both ways stated above because the phenolic resin containing the foaming agent in the bath started foaming in a few minutes. If the phenolic resin containing the foaming agent was mixed with a curing

agent, the temperature of the mixed resin increased due to a chemical reaction. When the temperature reached 39.8 °C, which is the boiling point of the foaming agent, the mixed phenolic resin started foaming and gradually became harder. In order to mold phenolic foam composites by the pultrusion method, the glass fibers must be sufficiently impregnated with the mixed phenolic resin before the start of foaming. For this reason, we developed a method in which the phenolic resin containing the foaming agent was mixed with the curing agent and this mixed phenolic resin was supplied uniformly and was impregnated to the glass fibers.

In order to control the successive start of foaming of the mixed resin in the die, the condition of forming process must be examined and a proper quantity ratio of the foaming agent to the curing agent must be decided. We decided the conditions to control the time until and during foaming and this time affected the pulling velocity in the pultrusion. Furthermore, a sufficient expansion ratio of the mixed phenolic resin before and after the foaming was obtained by controlling the environmental temperature<sup>2)</sup>.



**Fig.1 Pultrusion facilities**

2.2 Experimental results of foaming

Before applying the phenolic foam to the matrix of composite in the pultrusion method, behavior of foaming should be made clear. Furthermore, we need to extend the time until the foaming as longer as possible for ensuring sufficient immersion. The curing agent of 22g was added to the phenolic resin of 111g including the foaming agent of 11g in a beaker and the combination of this amount was finally obtained by a number of trial tests. Thereafter the time until and during the foaming was examined under three kinds of initial temperatures. The volume ratio of the mixed resin in a beaker was also measured before and after the expansion. **Table 1** shows the experimental results under three kinds of initial circumferential temperatures. The lower the initial temperature, the slower the starting time of the foaming. Furthermore, the lower the initial temperature, the smaller the volume expansion ratio. In par-

ticular, in the case of initial temperature of 15 °C, the expansion ratio decreased. This is because the temperature of mixed resin influenced the diffusion velocity of foaming gas and the lower initial temperature reduced the growth velocity of bubbles in the phenolic resin<sup>3)</sup>.

As a result, the lower initial temperature of mixed phenolic resin enabled to extend the time until the foaming but decreased the volume expansion ratio. In order to examine the effect of higher environmental temperature during the foaming on the volume expansion ratio, the mixed phenolic resin in the beaker was heated up immediately after this mixed resin started foaming. The beaker was soaked in hot water of 60 °C during the foaming. **Fig. 2** shows the temperature changes of the mixed phenolic resin. For the initial temperatures at 15 and 20 °C, the temperature of the mixed phenolic resin increased immediately after the start of the foaming and its expansion ratio also increased in spite of the lower initial temperature.

Table 1 Experimental results of forming

Initial temperature [°C]	Time until start of foaming [s]	Time during foaming [s]	Volume expansion ratio
15	212.5	137.4	13.3
20	109.4	90.6	17.4
25	58.3	91.7	17.9

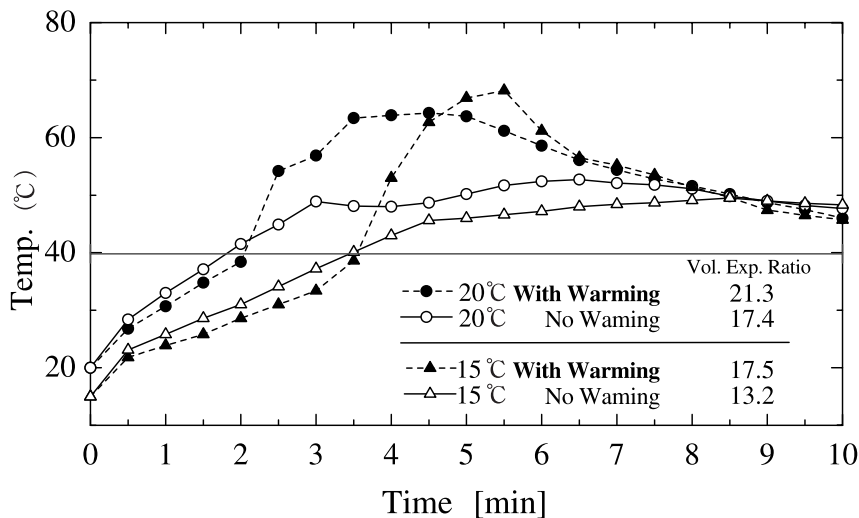


Fig.2 Relation between time and temperature during foaming (Initial temperatures of 15 and 20°C)

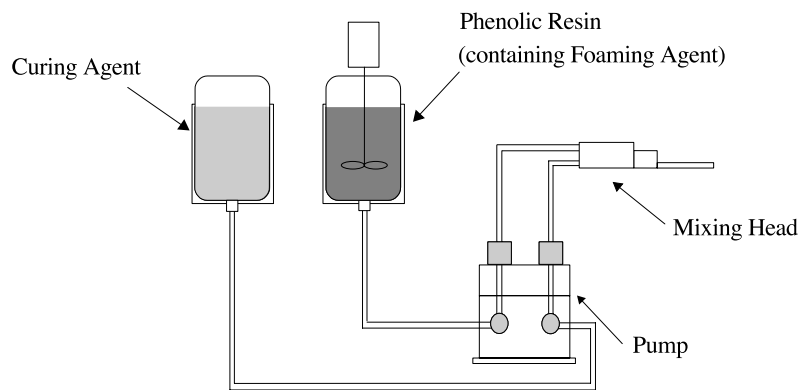
### 2.3 Feeder machine and mixing head

We developed an original and suitable feeder machine for molding the phenolic foam composite. This feeder machine was designed based on the RIM method as shown in **Fig.3**. This feeder machine can store and pump up phenolic resin containing a foaming agent and a curing agent separately. The resin and the curing agent can be warmed up to arbitrary temperature. This machine can supply the resin and the curing agent to a mixing head at a constant rate.

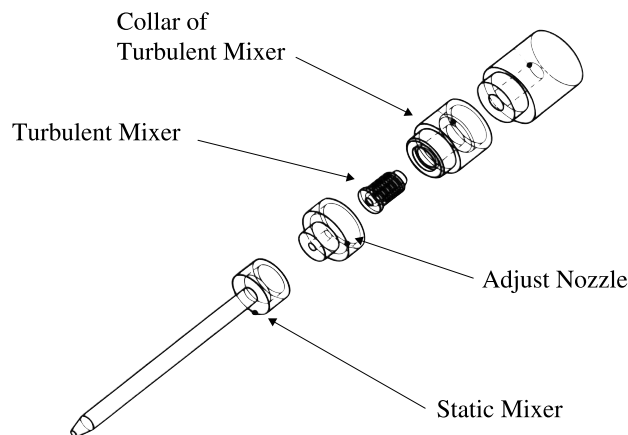
If the resin and the curing agent cannot be mixed sufficiently, the time and the process of foaming will become unstable. For this reason, the mixing process is very important. We used a turbulent mixer and a static mixer in the mixing head as shown in **Fig.4**. As a result homogeneously mixed phenolic resin was easily and securely obtained and it was supplied at the

rate of about 45g/min.

The mixed phenolic resin supplied from the feeder machine must be immersed to glass fibers before foaming. We selected bulky roving glass fibers because the bulky roving can be impregnated with the mixed resin more quickly than other types of glass fibers. Next, the amount of resin was smaller than general pultrusion composite because of using foam type resin and the volume of glass fiber is reduced corresponding to the amount of resin. As a result, the volume fraction of the glass fibers reached about 6%. Additionally we used a sizing mold instead of a resin bath for the immersion. The sizing mold was placed before the die and it was devised to impregnate the mixed phenolic resin with the glass fibers along the ditch of the inside of the sizing mold. Consequently, it was possible to impregnate the bulky roving sufficiently with the mixed phenolic resin.



**Fig.3 Feeding system**



**Fig.4 Mixing head**

### 2.4 Temperature control of die

If the temperature variation obtained from the experimental result in the beaker (Fig.2) can be realized in the interior of die, a sufficient time for impregnating the mixed resin with the glass fibers and a temperature causing a proper expansion ratio can be obtained in the pultrusion forming. For realizing this temperature variation, four heaters were installed at the back part of the die to warm the die up to 60 °C and the front part of die was cooled with four water pipes. As a result, the temperature of the front part of die was set at 20 °C and the back part of die was set at 60 °C as shown in Fig.5 and it was possible to divide the die into the two parts of the immersion and of the foaming in our pultrusion method.

If we know the temperature of the mixed resin inside the die during the pultrusion molding, it is easy to find whether the mixed resin starts foaming or not. In order to measure the temperature of the mixed resin, two thermo couples were inserted at the center and near the surface of glass fibers passing through the die, respectively. The temperature of mixed resin near the surface increased suddenly and surface resin started foaming at 40 °C in the back part of die (Fig. 6). However the temperature of resin at the center of the cross section increased gradually. It meant that the start of foaming was different between the center and the surface of mixed resin. In order to produce a composite having a homogenous and higher density, the temperatures of inside and on the surface should be controlled properly.

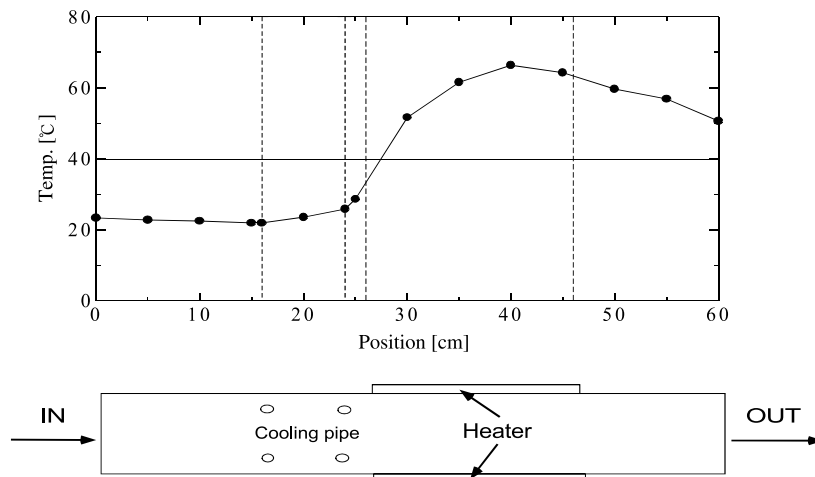


Fig.5 Temperature distribution of the die

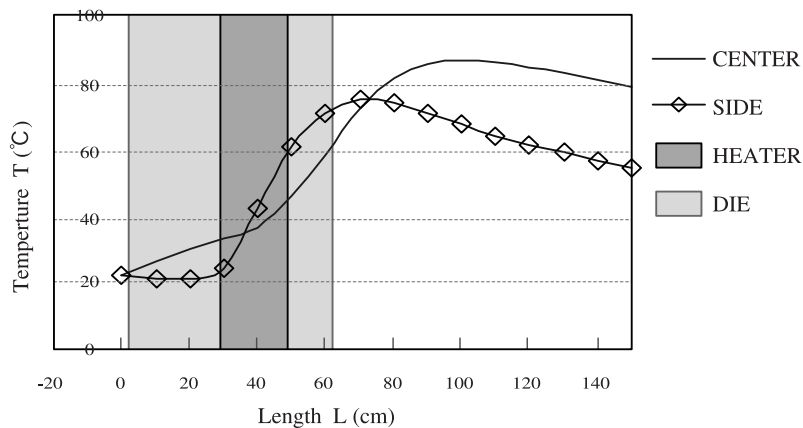


Fig.6 Thermal shift in the die during molding

### 3. Results of molding phenolic foam composite

#### 3.1 Observation of cross section

From the observation on the cross section of composite, the bundles of bulky roving were spread all over the composite and sufficient expansion of foaming resin was observed. However some centers of bundles of fibers were not impregnated with the mixed resin and

the non-uniform size of foam cells were also observed. Fig.7 shows two typical states of sectional area of the phenolic foam composite. The left one shows high density inside the bundle of fibers and the right one shows some air void areas indicated by the darker color owing to the arrangement of fibers. The proper type of glass fibers, their arrangement and the efficient impregnation method should be made clear to obtain uniform density of composites.

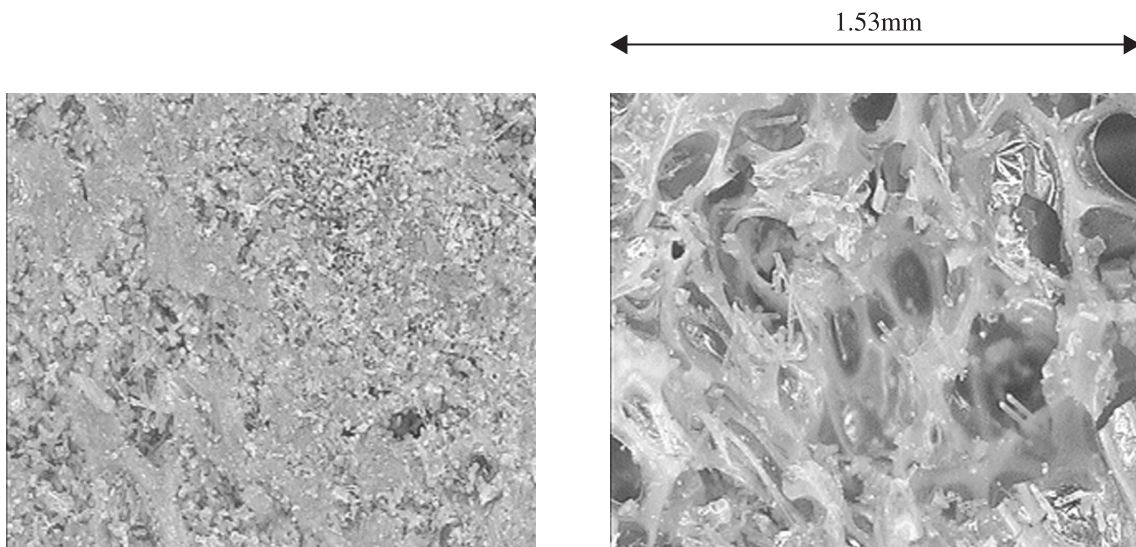


Fig.7 Observation of a cross section( $\times 200$ )

#### 3.2 Mechanical strengths

The width, height and length of the composite specimen were 52 mm, 32 mm, and 100 mm for the compression test and 52 mm, 32 mm, and 512 mm for the bending test, respectively and the distance of two supports was 448 mm in the bending test.

The results of compression test and bending test were compared with those of cedar and they are shown in **Tables 2** and **3**. From the **Table 2**, the longitudinal compressive strength,  $F_L$ , of the phenolic foam composite was five times that of the pure phenolic foam but its density was almost the same. This result shows the effectiveness of reinforcement to phenolic foam by the glass fibers. Although the strengths,  $F_L$  and  $F_T$ , of

the composite were lower than those of cedar, these data were not discouraging either considering that it was the first trial production and their strengths will be improved by revising arrangement and/or increase of glass fibers and by controlling the size of foaming cells. The relations of these parameters to the strengths of the phenolic foam composites should be further investigated.

Next, the nail drawing resistance was also considered as an important property for the materials used in the field of construction and the result is shown in **Table 4**. The nail drawing resistance of the phenolic foam composites using bulky type glass fibers showed a value very closed to that of cedar. The nail drawing resistance will be also improved by dispersion and/or increase of glass fibers and by controlling the size of foaming cells.

**Table 2 Results of compression tests**

	Density [g/cm <sup>3</sup> ]	Compressive strength [MPa]		L direction		
				Specific strength [m]	Compressive modulus [MPa]	Specific modulus [m]
Phenolic foam	0.4	3.89		992	138	$3.5 \times 10^4$
Phenolic foam FRP	0.42	FL	FT	3484	1362	$3.3 \times 10^5$
		14.34	0.67			
<i>Cedar</i>	0.33	27.44	0.68	8485	7355	$2.2 \times 10^6$

**Table 3 Results of bending test**

	Density [g/cm <sup>3</sup> ]	Bending strength [MPa]	Specific strength [m]	Bending modulus [MPa]	Specific modulus [m]
Phenolic foam FRP	0.42	18.95	4405	2015	$4.7 \times 10^5$
<i>Cedar</i>	0.33	63.74	19709	7355	$2.3 \times 10^6$

**Table 4 Results of nail drawing resistances**

		Phenol foam FRP [Vf=6%]	<i>Cedar</i>
Density [g/cm <sup>3</sup> ]		0.42	0.33
Nail drawing resistance [N/mm]	T <sub>L</sub>	2.31	4.76
	T <sub>T</sub>	4.89	5.86

### 3.3 Thermal conductivity

In order to evaluate the thermal insulation performance of phenolic foam composite materials, we measured the thermal conductivity of the phenolic foam composite. In the thermal conductivity test, a specimen must be plate-shaped. Four specimens of phenolic foam composites stated above were bonded by phenolic resin along their axial direction each other. The test specimens were 200×200mm<sup>2</sup> and were placed under 150 for 2 hours for post curing. The experimental result is shown in **Table 5** and the value of density of the test plate was somewhat larger than one of the phenolic foam composite shown in the parenthesis owing to the pure phenolic resin used for adhesion. In **Table 5**, the thermal conductivities of pure phenolic foam and poly-

urethane foam are listed and these values are referred as a heat insulating material in JIS A 9511. The density values of two foams are very small and they are changed by the foaming expansion ratio. Although their foaming expansion ratios were not listed, they were estimated as about 30. Generally speaking, the smaller the thermal conductivity, the higher the thermal insulation performance. In the foam type of materials, the larger the foaming expansion ratio (the lower the density), the higher the thermal insulation performance. In **Table 5**, though the density of the phenolic foam composite was about 10 times that of the two pure foams, the thermal conductivity was merely about 2~3 times. As a result, it was clarified that the thermal insulation performance of phenolic foam composite was sufficiently high.

**Table 5 Results of Thermal conductivity test**

	Density [g/cm <sup>3</sup> ]	Expansion ratio	Thermal Conductivity [W/mK]
Phenolic Foam Composite	0.476 (0.437)	4.4	0.0668
Phenolic foam	0.045	30?	0.032
Urethane foam	0.045	30?	0.024

### 3.4 Flammability test

In order to obtain burning-resistant phenolic foam composites, a combustion test by heat was carried out. An outline of this test was that radiant heat of 50kW/m<sup>2</sup> was irradiated on the surface of the test specimen by a radiation electricity heater and that electricity spark was simultaneously operated. Exhaust gas from the test specimens was collected and its temperatures, heat value and heat released rate were measured. The test specimens were wrapped by aluminum foils except the front surface of test specimens. After the wrapped specimens were stacked on ceramic wool and a back holder, they were enclosed with a holder as shown in **Fig.8**. Two kinds of phenolic foam composite specimens were tested. The first one was the same as the one used for the thermal conductivity test

and the second was the first one bonded with a steel plate (thickness of 0.4 mm) to the surface not wrapped with an aluminum foil. The former was tested for 10 minutes combustion and the latter was tested for 20 minutes because no burning was observed for the first 10 minutes.

The compositions of the test specimens and the combustion test results are shown in **Table 6**, in which the heat release rate means the change of heat value in a unit time. If the heat release rate of some material increases continuously, this material is in danger of a big fire. In the case of phenolic foam composite, its exhaust gas was ignited at 40 seconds after the start of test and therefore, the heat release rate and smoke density rapidly increased. Though the heat release rate rapidly increased, no crack that reached the back surface was observed. The test specimen was continuously kept burning and the total amount of heat re-

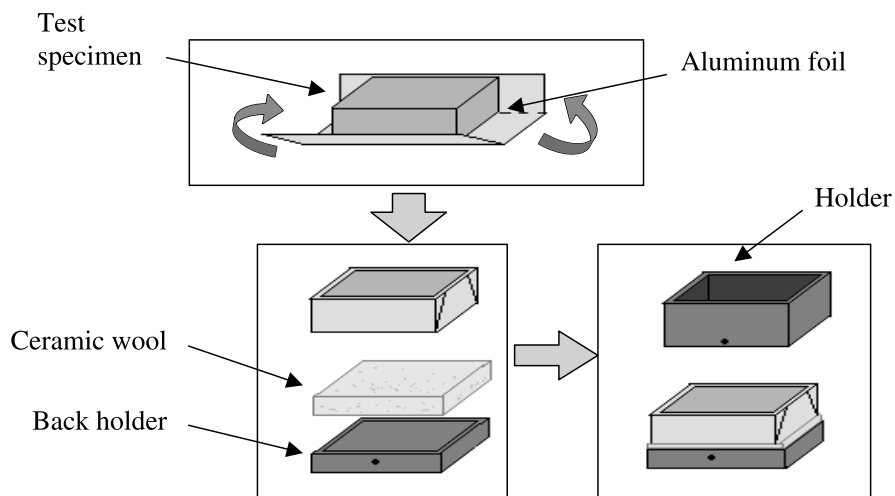
**Fig.8 Test specimen**



Table 6 Results of flammability

		Phenolic Foam Composite	Steel Surface+ Composite Core
Size	[mm]	100 100	100 100
Thickness	[mm]	31.5	0.4+31.6
Mass	[g]	132.48	157.3
Vf	[%]	6	6 (core)
Total heat released	[MJ/m <sup>2</sup> ]	20.56	0.89 (20min)
Rate of heat release(av.)	[kW/m <sup>2</sup> ]	76.22	6.05 (20min)
Rate of heat release(max)	[kW/m <sup>2</sup> ]	35.01	0.77 (20min)
Mass loss rate	[g/s • m <sup>2</sup> ]	2.581	1.023 (20min)
Crack (penetration)		nothing	nothing (20min)

lease and the average heat release rate increased. In the case of the test specimen with a steel plate on the surface, the steel plate prevented exhaust gas from being generated from the surface. The steel plate functioned as a cover and very little combustion of this specimen was observed. As a result, the total amount of heat release was 0.89MJ/m<sup>2</sup> which is a very low value. From the combustion test, it is important to find how to prevent the generation of exhaust gas from the surface of phenolic foam composite in order to improve the fire resistance.

#### 4. Conclusion

Pultrusion techniques to mold phenolic foam composites were demonstrated by taking account a proper control of the temperature distribution in the interior of die into account. This temperature distribution meant the division of the die into the two parts, namely the first part of the impregnation of mixed phenolic resin with a sufficient amount of glass fibers and the second part of the foaming and solidifying of the mixed phenolic resin.

Next, by introducing the original feeder machine and the sizing mold, it was possible to supply the resin containing the foaming agent and curing agent and impregnate the mixed resin with the glass fibers. Thereafter, a type of bulky roving among various types of glass rov-

ing was employed because it was easily impregnated with the mixed phenolic resin.

Furthermore, the experimental results of the phenolic foam composite strength showed a possibility of utilization in the field of construction. In order to increase the compressive strength and the bending strength of the phenolic foam composite, the volume fraction of fibers should be increased and then the relations of the strength to the fiber volume and to the expansion ratio must be investigated in the future.

Finally, the thermal conductivity of phenolic foam composite material was 0.0668W/mK which implies that the thermal insulation performance was high enough. From the flammability test of the phenolic foam composite, the cause of combustion was due to the exhaust gas which was generated from the surface of the specimen and was ignited. Prevention of gas from the surface seems to be a conclusive factor in order to improve the fire resistance of phenolic foam composite.

#### Acknowledgement

This study was supported by a special research grant for the development of characteristic education, Ministry of education culture, sports, science and technology of Japan.

**References**

- 1) Nobuyuki Ozawa, "Pultrusion Techniques" (in Japanese), Advanced Techniques of Molding, Sigma Publication. pp.345~352(1999).
- 2) Akiko Shoji and Goichi Ben, "Development of Pultrusion Techniques of Phenolic Foam Composite", The Proceedings of The Seventh Japan International SAMPE Symposium, pp.979~982(2001).
- 3) Hiroshi Abe, "Happouseikei" (in Japanese), Advanced Techniques of Molding, Sigma Publication. pp.213~264(1999).

# フェノールフォーム複合材料引抜成形技術の開発

邊 吾一，莊司 明子

## 概 要

フェノール樹脂は、耐熱性、難燃性、低発煙性といった特性を持ち、これらの利点は建築用構造材料として最適である。本研究は、母材としてフェノール樹脂を採用し、これを発泡させ、ガラス繊維によって強化したフェノールフォーム複合材料を引抜成形によって成形する技術を開発する。このフェノールフォーム複合材料の成形においては、引抜金型を適切な温度に設定することで、フェノール樹脂の発泡開始時間と発泡硬化時間を制御することが重要である。また、フェノール樹脂と硬化剤を連続的に混合し供給する必要があり、樹脂の連続吐出装置の設計試作をおこなった。さらに、フェノールフォーム複合材料の機械的特性について天然木材との比較を示し、建築構造材料としての可能性を示す。

## Biographical Sketches of the Authors



Goichi Ben (O-II Byon) is a professor of College of Industrial Technology, Nihon University.

He was born in Akita, Japan on November 29, 1945. He received his B.S. from Nihon University, Japan in 1969, M.S. from the University of Tokyo, Japan in 1971 and Ph.D. in Engineering from the University of Tokyo in 1974. He joined College of Industrial Technology, Nihon University in 1974.

He has been engaged in the study of strength and optimum design of light weight structures.

The present research is focused on composite engineering, namely mechanics and strengths of composites, evaluation of mechanical properties in composites, optimal design of composite structures fabrications of composites and so on.

Dr. Ben had stayed each one year at the University of Delaware from 1988 to 1989 and at the University of Colorado from 1996 to 1997 in the U.S.A. as a visiting associate and full professor, respectively.

He is now a member of board directors of the Japan Society for Composite Materials and the Association of Reinforced Plastics in Japan. He is a member of council of the Japan Society for Computational Engineering and Science and a member of the Japan Society of Mechanical Engineers, the Japan Society for Aeronautical and Space Sciences, the Society of Material Science, Japan, Dr. Ben is also a member of AIAA in the U.S.A. and American Society for Composite Materials.



Akiko Shoji was born in January 14, 1977 in Saitama prefecture, Japan.

She received her Bachelor of Engineering Degree from Nihon University in 2000, her Master of Engineering Degree from Nihon University in 2002.

She is a student of Doctoral course of department of mechanical engineering, college of industrial technology, Nihon University.