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Pultrusion techniques and evaluations of sandwich beam using phenolic foam composite

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Abstract—Phenolic resin has the excellent properties of fire resistance, low smoke production during burning, and a good balance between its cost and mechanical properties compared with other types of resin used in fire-resistant polymers (FRPs). If phenolic resin can be employed as a matrix of FRP, such FRP can have a higher fire safety factor which will be a desirable property in the structures of vessels and railway carriages. However, for the case of the resole type of phenolic resin, water formed from the condensation reaction remains in the matrix, and this water evaporates resulting in the formation of voids during the curing process. In order to develop a new type of phenolic composite that can overcome this weakness, we used a foam type of phenolic resin and glass fibers as the matrix and the reinforcement, respectively. We, then, developed a new pultrusion technique for the new phenolic foam composite and examined its mechanical properties and thermal conductivity.

In this paper, we report a new technique to mold not only a phenolic foam composite but also a sandwich beam in which the phenolic foam composite as a core and a thin phenolic FRP layer as a faceplate are used. We also investigated the compressive strength and elastic modulus under high temperatures and compared the result with that at room temperature. Finally, we show that the compressive properties of the phenolic foam composite and the sandwich beam are stable at higher temperatures.

Keywords: Phenolic resin; phenolic foam; glass roving; pultrusion; sandwich beam; compressive properties; high temperature.

1. INTRODUCTION

Phenolic resin has the excellent properties of fire resistance, low smoke formation during burning, and a good balance between its cost and mechanical properties compared with other types of resin used in FRPs. If phenolic resin can be employed as the matrix of FRP, such FRP can have a higher fire safety rate and this is a desirable property for the structures of vessels and railway carriages. Since the

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viscosity of the resole type of phenolic resin is higher than that of other types of resin, the diluted resole type of phenolic resin with water is used as the matrix. Moreover, water is also produced due to the condensation reaction of phenolic resin during the curing process. The matrix using this phenolic resin becomes inhomogeneous due to voids produced by the water that is evaporated after the curing process [1, 2]. In order to develop a new type of phenolic composite that can overcome these drawbacks, we fabricated a beam type of phenolic foam composite using phenolic foam as the matrix and glass fibers as the reinforcement and measured its mechanical and thermal properties. This new type of phenolic foam composite (PFC) has the advantages of light weight and high insulation and can be sawed and/or attached to other members with nails because the glass fibers are surrounded by the phenolic foam in the beam [3–5].

The result of flammability test of the PFC indicates that prevention of exhaust gas from the surface of the PFC is important in order to improve its fire resistant property. For this reason, we devised a method to cover the upper and the lower surfaces of the PFC with an FRP layer. This FRP consists of glass fibers with a higher volume fraction and usual phenolic resin. The glass yarn was impregnated with phenolic resin and was placed on the upper and lower surfaces of the PFC beam and they were pultruded together with the PFC. This method can mold the PFC covered with the FRP layer sequentially and unify them without any adhesive process. As a result, uncertain adhesive strength between the PFC and the covering FRP can be avoided. This composite looks like a sandwich beam and is denoted as a SWPFC in this paper. The method proposed in this paper can mold an arbitrary length of sandwich beam without an adhesive process and its core reinforced by glass fibers is stronger than a general foam core.

2. MOLDING METHOD

2.1. Outline of molding method

The SWPFC was also molded in the same way as the PFC by the pultrusion technique, which could manufacture the FRP layer having a uniform cross-section with an arbitrary length. Based on the molding method of the PFC, we devised a new system of pultrusion facilities of the SWPFC as shown in Fig. 1. A resin bath, yarn guides and a metallic die shown in Fig. 1 (highlighted in bold rectangles) were added to the PFC facilities in order to cover the upper and the lower surfaces of the PFC beam with the phenolic FRP layer. These added facilities were placed on the same line of molding as the PFC. Although a cross-section of the molding die for the PFC was 52 mm $\times$ 32 mm, the fabricated section of the PFC was about 51.4 mm $\times$ 31.4 mm. Since the thickness of the covering phenolic FRP layer was set as 0.5 mm as the design value, the section size of the metallic die for covering the PFC was set as 52 mm $\times$ 32.4 mm. There were some differences in the molding conditions between the PFC and the covering phenolic FRP layer. We used glass

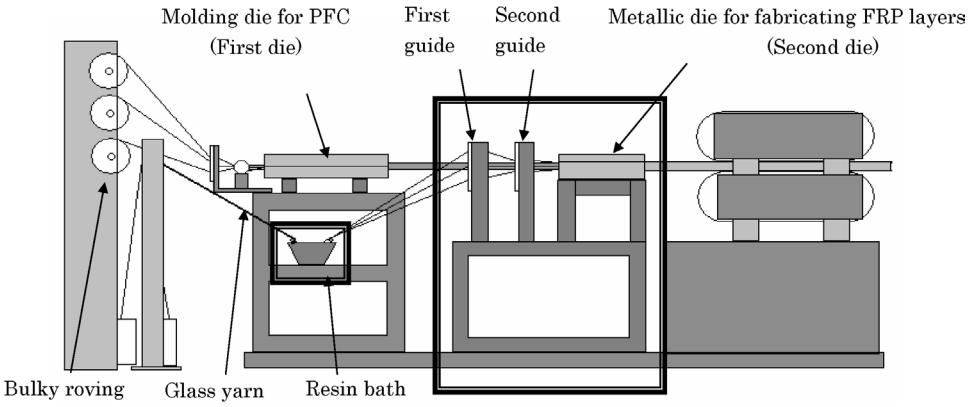

Figure 1. Pultrusion facility.

Table 1.
Molding conditions

	Molding method	Reinforcment	Matrix	Curing method	Curing temperature	Glass content
Covering FRP	Pultrusion	Glass fiber (Yam)	Phenolic resin	Heat cure	180°C (max.)	56 vol%
PFC	Pultrusion	Glass fiber (Bulky roving)	Phenolic resin (with foaming agent)	Acid cure	75°C (max.)	6 vol%

yarn as the reinforcement of the covering FRP layers against the bulky glass roving for the PFC. Next, the phenolic resin foam used as the matrix of the PFC was cured by acid reaction, while the covering FRP layers were molded by heat curing. In Table 1, the molding conditions for the PFC and the covering FRP layers are shown. Although the molding method of the covering FRP layers was the same as the general pultrusion, it was important that each fiber of the glass yarn was arranged accurately and was introduced into the metallic die to mold the covering FRP layers with uniform thickness. As a result, we were able to mold the PFC and sequentially the SWPFC beam by the same line.

2.2. Improvement of molding methods of PFC

In order to fabricate the SWPFC, we improved the conventional molding method [3] of the PFC. When the PFC was introduced to the second die, the PFC received pressure from the glass yarn placed on the upper and the lower surfaces of the PFC. For this reason, it was important for the PFC to have proper dimensional accuracy of its cross- section and a larger transverse compressive elastic modulus.

In the conventional method of molding PFC, Teflon tapes were placed on the four internal surfaces of the first die, and they were moved together with the PFC during molding in order to decrease the friction between the inside of die and the four

surface of the PFC. Since these tapes were easily warped during molding, it was not possible to obtain strict dimensional accuracy. In order to decrease the friction without using Teflon tapes, the inside surface of the die was coated with fluorine resin after polishing. The dimensional accuracy of the PFC was confirmed from the result of pultrusion molding.

Next, in order to increase the transverse compressive elastic modulus of PFC, the glass roving should be dispersed near the surface of PFC, so we changed the glass roving to a more bulky one. Figure 2 shows two kinds of the bulky glass roving. The upper one named Type I was used for the former PFC as the reinforcement, and the other one named Type II was bulkier. Table 2 shows the ratios of Type I mass and Type II mass to that of the direct glass roving. Both values are over 1 and Type I and Type II wind through along their length. From the results of the larger average values and the larger standard deviation as shown in Table 2, the dispersion rate of Type II is larger than that of Type I.

By using the Type II bulky roving as the reinforcement, a more stable and harder surface of the PFC was obtained. In Table 3, the results of transverse compression test of PFC using Type I and Type II are shown. The transverse compressive elastic

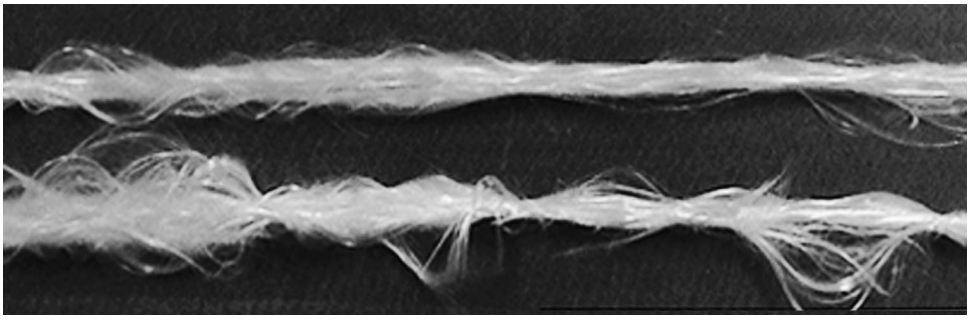

Figure 2. Bulky glass roving.

Table 2.
Mass ratio of bulky roving

	Direct	Type I	Type II
Average	1	1.037	1.089
Standard deviation	—	0.010	0.016

Table 3.
Results of transverse compression test

	Compressive modulus (MPa)	Compressive strength (MPa)
PFC (Type I)	31.5	0.48
PFC (Type II)	40.7	1.22

modulus of the PFC using Type II as the reinforcement increased, which is an improvement over the one using Type I and we could fabricate the PFC covered with the phenolic FRP layer.

2.3. Resin compound of covering FRP layer

Pultrusion trials were carried out to determine the ratio of additive agent for the phenolic resin of the FRP layer as shown in Table 4. We prepared two types of resin compounds, A and B. The symbol, '-C' indicates post-cure in Table 4. $Al(OH)_3$ was added to improve the fire-resistant properties and INT1850 and carnauba wax were the agents for releasing from the die. MgO was added to decrease the generated water due to condensation reaction. Although Type A was recommended as a fire resistance compound by the manufacturer of phenolic resin, we prepared Type B because the viscosity of Type A increased with time and this made pultrusion more difficult. The compound ratio of Type B was the same as that of Type A except for MgO. The rates of increase for the viscosity of Types A and B along with time are shown in Fig. 3. The viscosity of Type A is over 1.5 times that of Type B after 4 hours.

We tried to pultrude the FRP layer with both compounds. The color of the FRP layer with Type A was reddish-brown, and that with Type B was ivory. There was no crack or void on the surfaces of both of FRP layer. The gelation point of FRP layer with Type A was 100–150 mm from the entrance of the die and that with Type B was 200–250 mm. As a result, we expected that MgO in the phenolic resin accelerated the hardening reaction. To verify this, we measured the gelation rate of the FRP layer as shown in Table 5. Small pieces of FRP layers were dipped in

Table 4.
Resin compounds

	Compound ratio (matrix) (g)						Thickness	Post cure
	Phenolic resin	H_2O	$Al(OH)_3$	INT1850HT	Carnauba wax	MgO	(mm)	
Type A	100	5	20	1	1.5	0.5	0.515	non cure
Type A-C	100	5	20	1	1.5	0.5	0.515	150°C × 3 h
Type B	100	5	20	1	1.5	0	0.514	non cure
Type B-C	100	5	20	1	1.5	0	0.514	150°C × 3 h

Table 5.
Results of gelation test

	Post cure	Resin content (%)	Gelation rate (%)
Type A	non cure	23.1	1.14
Type A-C	150°C × 3 h	21.2	0.47
Type B	non cure	19.0	8.05
Type B-C	150°C × 3 h	18.3	0.49

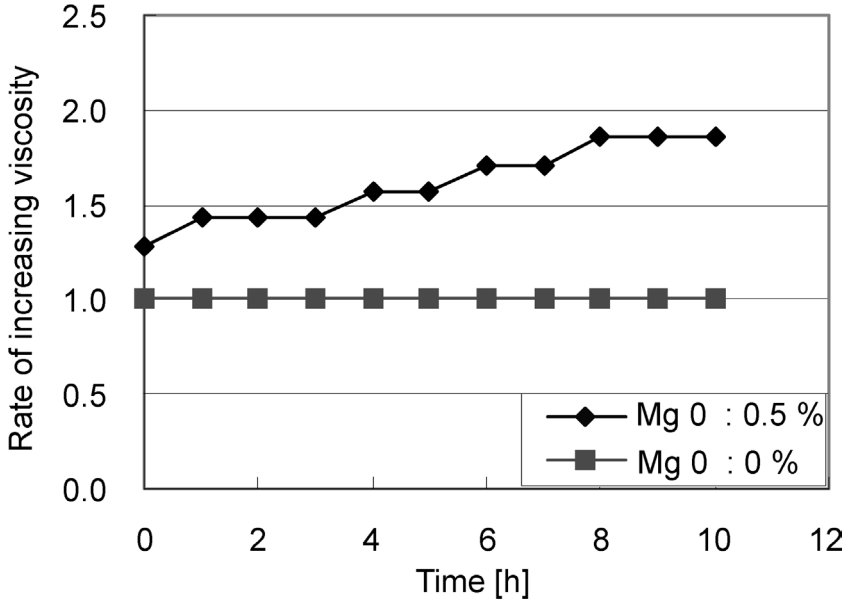

Figure 3. Changes of viscosity.

THF (tetrahydrofuran) for 2 days, and the remains of the phenolic resin in uncured state after pultrusion were dissolved in THF. The gelation rate was defined as the rate of the dissolved mass of the phenolic resin in THF to that of the phenolic resin in the FRP layer. The larger value of gelation rate means that FRP layer was not sufficiently cured by pultrusion.

The gelation rate of Type B was higher than that of Type A and it was confirmed that MgO contributed to the cure of the phenolic resin. However, the gelation rates for Type A-C and Type B-C were almost the same and it was proven that Type B was sufficiently cured at 150°C for 3 hours. As a result, we selected Type B-C as the matrix of the FRP layer from the viewpoint of the viscosity and the gelation rate.

2.4. Experiments of molding SWPFC

Since the pultrusion facilities for molding PFC were placed in the front part of the system as shown in Fig. 1, the positions of the resin bath and the second die for covering the FRP layer should be limited so as not to prevent the PFC from being molded, and the paths of glass yarn for covering the surface of PFC had to be set properly. For the regular intervals of glass yarn on the upper and the lower surfaces of PFC, the paths of glass yarn were fixed by the two yarn guides. In addition, arrangement and the size of holes in the guides are important in order to place glass yarn for molding the covering FRP layer with uniform thickness so that no cracks are formed. The holes with a diameter of 2.5 mm could squeeze out the phenolic resin properly, keeping a uniform volume fraction. In order to determine the arrangement of holes, we prepared two types of guides, (a) and (b), as shown in

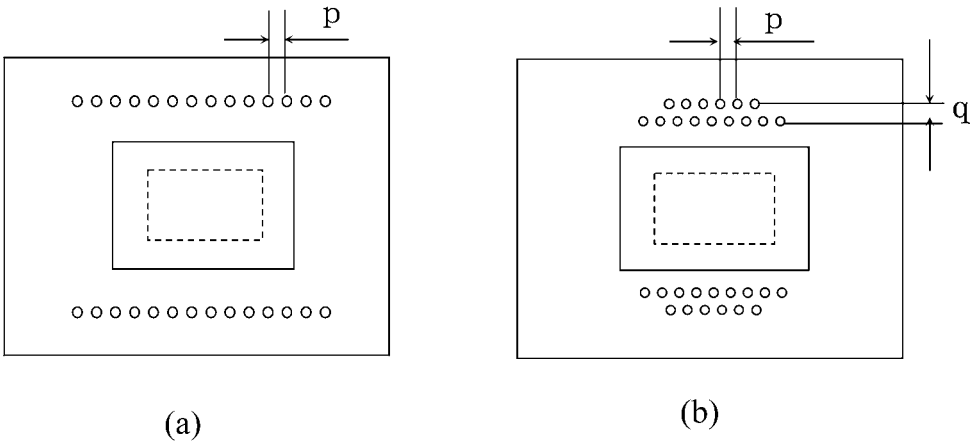

Figure 4. Yarn guides.

Table 6.
Specifications of yarn guides

	First guide			Second guide		
	Interval p (mm)	Gap q (mm)	Hole Diameter (mm)	Interval p (mm)	Gap q (mm)	Hole Diameter (mm)
Type-a	8	—	2.5	6	—	2.5
Type-b	6	10	2.5	4	10	2.5

Table 7.
Size of SWPFC

	Thickness	Width	Thickness of the covering FRP layer
Average (mm)	32.4	51.6	0.514
Standard deviation	0.06	0.06	0.084

Fig. 4. The holes of Type (a) were arranged in one line and the angles of glass yarn being introduced to the die were the same. On the other hand, the holes of Type (b) were arranged in two lines and the angles from two lines were different and the intervals of holes were smaller than in Type (a). Table 6 shows the specification of these yarn guides and Fig. 5 shows the photographs of the surface in the trial products by using Type (a) or (b). The glass fibers were concentrated on the edges in Type (a) and the covering FRP layer was not fabricated uniformly. On the other hand, a uniform FRP layer was obtained in the case of Type (b).

A trial product of the SWPFC by using guide (b) is shown in Fig. 6. The FRP layers were uniformly smooth and the appearance of the surfaces was improved. The measurement results of the section of SWPFC and the thickness of the covering FRP layer are shown in Table 7.

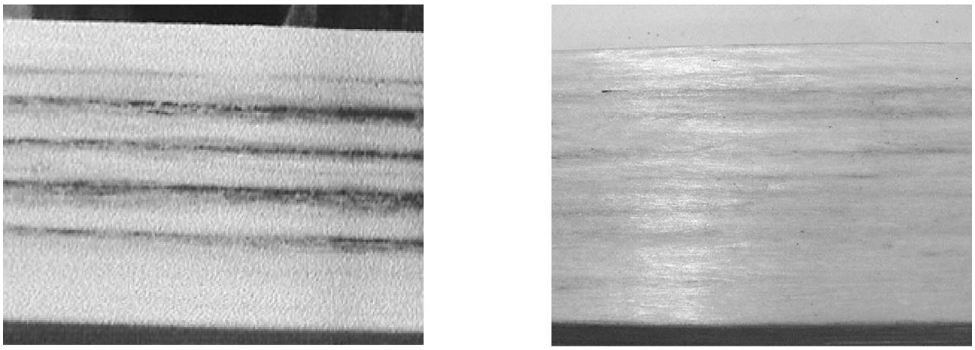

Figure 5. Surface of the FRP layer.

Figure 6. Photograph of SWPFC.

3. MECHANICAL PROPERTIES OF SWPFC

3.1. Flexural elastic modulus

We evaluated the flexural elastic modulus of SWPFC by a three point bending test and the result is shown in Table 8. Although the thickness of the FRP layer was only 0.5 mm, the flexural elastic modulus of SWPFC was 1.5 times that of PFC and was close to that of cedar.

Table 8.
Flexural elastic modulus

	Modulis of elasticity (GPa)
PFC	4.00
SWPFC	5.91
Cedar	7.36

Table 9.
Specifications of test specimens

	Width (mm)	Thickness (mm)	Height (mm)	Density (g/cm^3)	Number of specimens
PFC	31.9	31.8	100.4	0.41	4
SWPFC	25.7	32.4	100.9	0.43	4
Cedar	25.8	33.2	100.0	0.43	3

3.2. Testing method of compression under high temperatures

We executed the compression test for specimens of the PFC and the SWPFC. We also tested natural wood, cedar, in order to compare the result with those of the PFC and the SWPFC, because they had some similar properties of being able to be cut and joined as woods. Both ends of the test specimen were wound up with a heat-proof aluminum tape (9 mm wide) as the tab reinforcement. The specifications of the test specimens are shown in Table 9. In this table, the width of SWPFC was shared due to the limitation of the compressing jig.

The compression test was carried out under three kinds of temperatures — room temperature, 100°C and 200°C — by using a constant thermostat chamber and a compressive jig of cage type. The test specimens were set in the thermostat chamber and the compression test was carried out with a loading speed at 1.0 mm/min after the circumferential temperature became stable within ±0.2°C of the target temperature. The test equipment is shown in Fig. 7.

3.3. Results of compression test

The results of the compression test are shown in Table 10 under the three kinds of temperatures. Under the room temperature, the compressive elastic modulus of SWPFC was about 4 times that of the PFC. Although the compressive strengths of PFC and SWPFC were not so strong compared with that of cedar, the compressive elastic modulus of SWPFC was almost the same as that of cedar. However at 200°C, the compressive strength of SWPFC became almost the same as cedar and the compressive elastic modulus of SWPFC was larger than that of cedar.

The changes of compressive strength and compressive elastic modulus under the three circumferential temperatures are shown in Fig. 8. As is seen in the figure, the compressive strength and elastic modulus of cedar were decreased with a higher

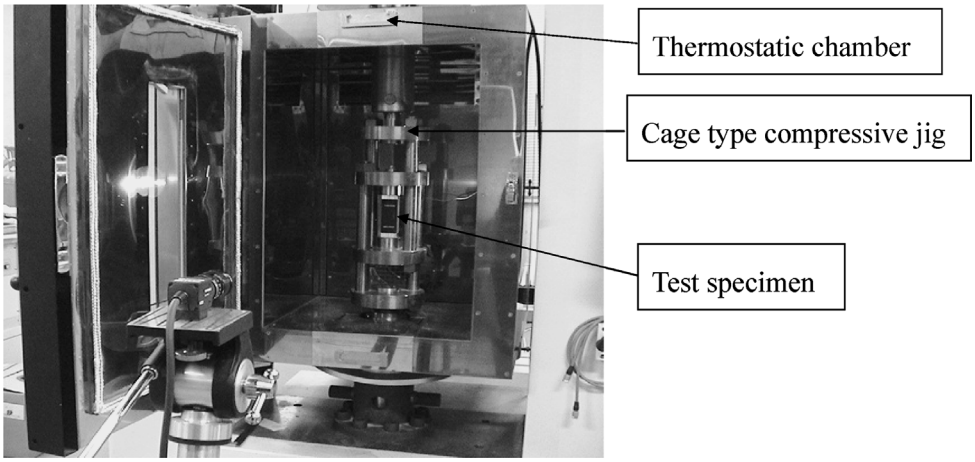

Figure 7. Compression test equipment.

Table 10.
Results of compression test under three temperatures

	R.T.		100°C		200°C	
	Compressive Modulus (GPa)	Compressive Strength (MPa)	Compressive Modulus (GPa)	Compressive Strength (MPa)	Compressive Modulus (GPa)	Compressive Strength (MPa)
PFC	1.28	17.10	1.30	13.31	1.04	12.98
SWPFC	5.01	20.28	4.39	19.50	4.46	19.08
Cedar	5.71	44.45	4.60	27.50	3.17	19.35

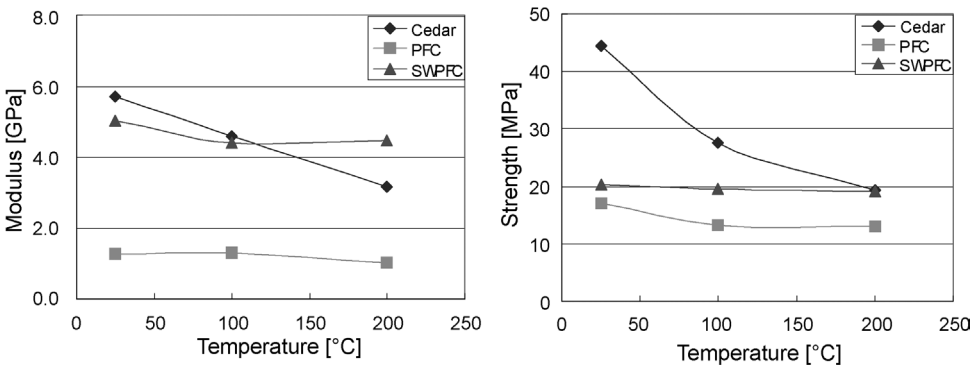

Figure 8. Compressive elastic modulus and strength at three temperatures.

circumferential temperature. In particular, these values at 200°C dropped to 50% of those at room temperature. On the other hand, the compressive strength and elastic modulus of the PFC and SWPFC at higher temperature were stable compared with those of cedar. In Fig. 9, the load-stroke curves of SWPFC under RT and 100°C

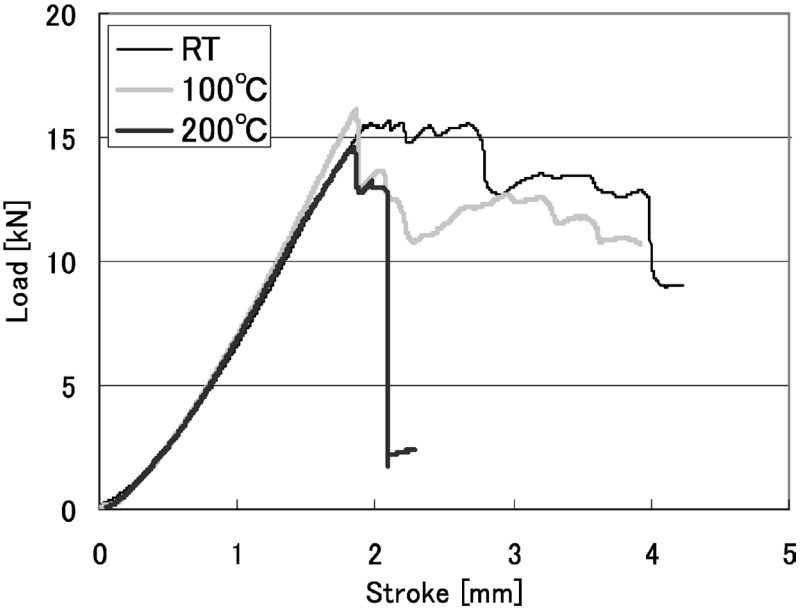

Figure 9. Relation of compressive load to stroke in SWPFC.

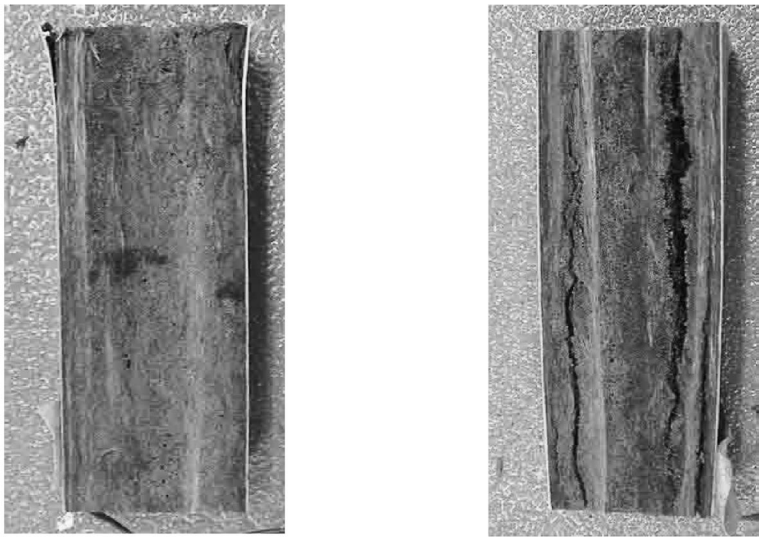

Figure 10. Fracture modes of SWPFC.

did not drop after their initial failure and they gradually reached the final failure through peeling the surface layer and/or through collapsing of the PFC as shown in Fig. 10a. On the other hand, the specimen at 200°C was suddenly broken as is

shown in Fig. 10b. The reason for this was that the foam of phenolic resin hardened and became brittle at high temperature. The effect of temperature on the foam of phenolic resin will be investigated for further study.

4. CONCLUSION

A pultrusion technique to mold a new type of sandwich beam is demonstrated. In this method, after the phenolic foam composite (PFC) is pultruded through the first die, the phenolic FRP layers are placed to cover on the upper and lower surfaces of the PFC and they are pultruded through the second die together with PFC in order to fabricate the sandwich beam of the phenolic foam composite (SWPFC).

As a result, our method can fabricate sandwich beams more effectively without a secondary adhesive process. Furthermore, this SWPFC has higher shear rigidity compared with the conventional foam sandwich and it can be connected to other members with nails or screws because it contains glass fibers in the foamed core.

Because the SWPFC was covered with the thin phenolic FRP layer having a higher glass content, the flexural elastic modulus was about 1.5 times that of PFC.

The compressive elastic modulus of SWPFC is almost the same as that of cedar. The compressive strength and elastic modulus of cedar decreased with elevation of the circumferential temperature. On the other hand, the compressive strength and the elastic modulus of PFC and SWPFC were stable. These properties are suitable for the structures that require safety under higher temperatures.

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