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Improvement of Water Resistance in Porous Carbon Material made from Rice Bran

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The rice-bran carbon-material (RB carbon) is developed for a useful utilization of the rice bran, which is one of the agricultural wastes in Japan. The RB carbon has some unique mechanical properties such as low Young's modulus, low friction coefficient and high abrasion resistance. Therefore, the RB carbon is expected to use as a sliding element in linear guides and linear sliders. The RB carbon is made from the defatted rice bran, which is impregnated with a resol-type phenol resin and then carbonized at high temperature under nitrogen gas atmosphere. However, since the defatted rice bran and the impregnated resol-type phenol resin include some inorganic components, it is anticipated that the water-soluble and absorbency inorganic compounds are produced during the carbonizing process. The inorganic components are considered to decrease the mechanical strength and hygroscopic expansion under the aqueous environments. In this study, the improvement of water resistance of the RB carbon was examined, especially some manufacturing processes were examined to reduce the amounts of inorganic components. The modified manufacturing processes sufficiently achieved the high water resistance in the RB carbon.

Key Words : Porous Carbon Material, Rice Bran, Material Testing, Water Resistance

1. INTRODUCTION

The rice bran is a residual product of rice, and the amount of it is about 0.9 million tons per year in Japan [1]. Rice-bran carbon-material (RB carbon) is developed in order to utilize the rice bran from the viewpoint of recycling by Sanwa Yushi Co. Ltd.. The RB carbon is a porous carbon material basing on the natural porous structure of rice bran [1]. Moreover, the refinement of the macrostructure and the inorganic components in the rice bran carbon is effectively used for the improvement of the mechanical strength [2]. Since the RB carbon has low friction and superior abrasion resistance under no lubrication, it has been used as a sliding material for linear guides and linear sliders.

However, since the inorganic components of P, K, Ca, and Mg are included in the rice bran, it is concerned about the production of water-soluble components during the carbonization. Moreover, the traditional RB carbon has been produced by mixing a resol-type phenol resin with the defatted rice bran and carbonized at 1173 K under nitrogen gas atmosphere. Recent study [3] reveals that the sodium in the resol-type phenol resin changes into the water-soluble inorganic compounds during the carbonization. The sodium component has the hygroscopicity and deliquescency. These properties cause the adverse effects under the aqueous environment. Therefore, the traditional RB carbon has low mechanical strength and high hygroscopic expansion under the aqueous environments. The traditional RB carbon has low mechanical strength and high hygroscopic expansion under the aqueous environments. The high water resistance is an important property to use it as a friction element in the industrial products. Therefore, the improvement of the water resistance is indispensable to expand the RB carbon into the industrial applications.

In this study, some manufacturing processes were proposed to inhibit the production of the water-soluble inorganic compounds. Especially, some clearing treatments were proposed to remove the water-soluble inorganic compounds. Moreover, the usage of a novolac-type phenol resin was examined to avoid the production of the water-soluble compounds.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Figure 1 shows the components of the rice bran. The rice bran consists of 86.5 mass% of organic component (Carbon, Hydrogen, etc.) and the rest of the inorganic components (Phosphorus, Potassium, Magnesium, etc.). The RB carbon is made from the defatted rice bran, which is mixed with about 25 mass% of phenol resin, and then carbonized at 1173 K under nitrogen gas atmosphere. Figure 2 shows the component of the traditional RB carbon, which consists of about 60 mass% of glassy carbon and 40 mass% of the inorganic components.

There are two types of phenol resin, i.e. resol-type and novolac-type phenol resins. The resol-type phenol resin has been used in manufacturing the traditional RB carbon, because of good flow property and the low production cost. Although the resol-type phenol resin contains sodium, the novolac-type phenol resin contains no sodium. Table 1 lists the water solubility of the

Table 1 Water solubility of inorganic component in traditional RB carbon

Inoganic compound	water-soluble
$Mg_3(PO_4)_2$	insoluble
K_3PO_4	104g/100ml (25°C)
K_2CO_3	deliquescent
Na_3PO_4	4.5g/100ml (0°C)
Na_2CO_3	deliquescent

inorganic components in the traditional RB carbon that is produced using a resol-type phenol resin. The sodium changes into a sodium carbonate or a sodium phosphate during the carbonization. These compounds are the water-soluble inorganic compounds.

Figure 3 shows a manufacturing process of the modified RB carbon. It is necessary to use the novolac-type phenol resin to achieve the high water resistance. Moreover, the clearing treatment is also tried to remove the phosphate from the traditional RB carbon. The present authors examined four-types of clearing treatments, i.e. using water as treatment (A), citric acid (B, C), and oxalic acid as treatment (D). In the clearing treatment with the citric acid, the clearing was performed once as treatment (B) and twice as treatment (C).

Table 2 lists the test pieces, which were used for the strength and expansion tests. The novolac-type and resol-type phenol resins were used to make the test pieces. In the name of the test pieces,

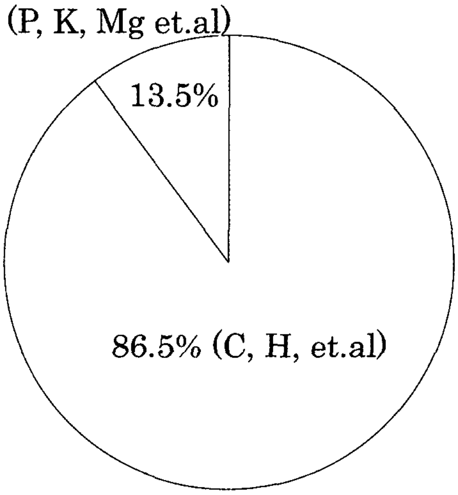


Figure 1 Chemical component of rice bran

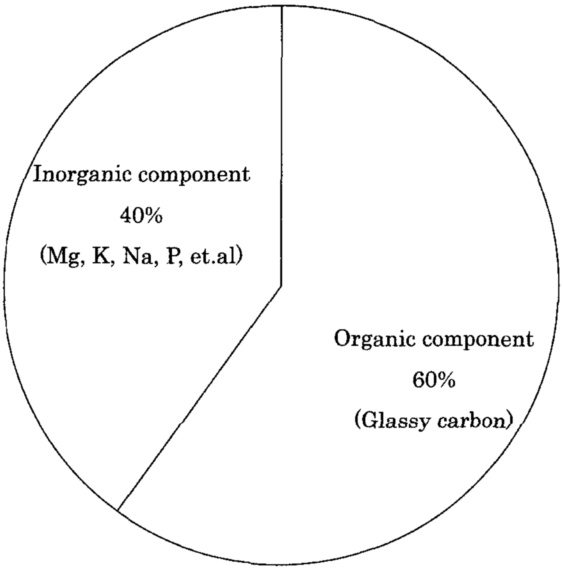


Figure 2 Chemical component of traditional RB carbon

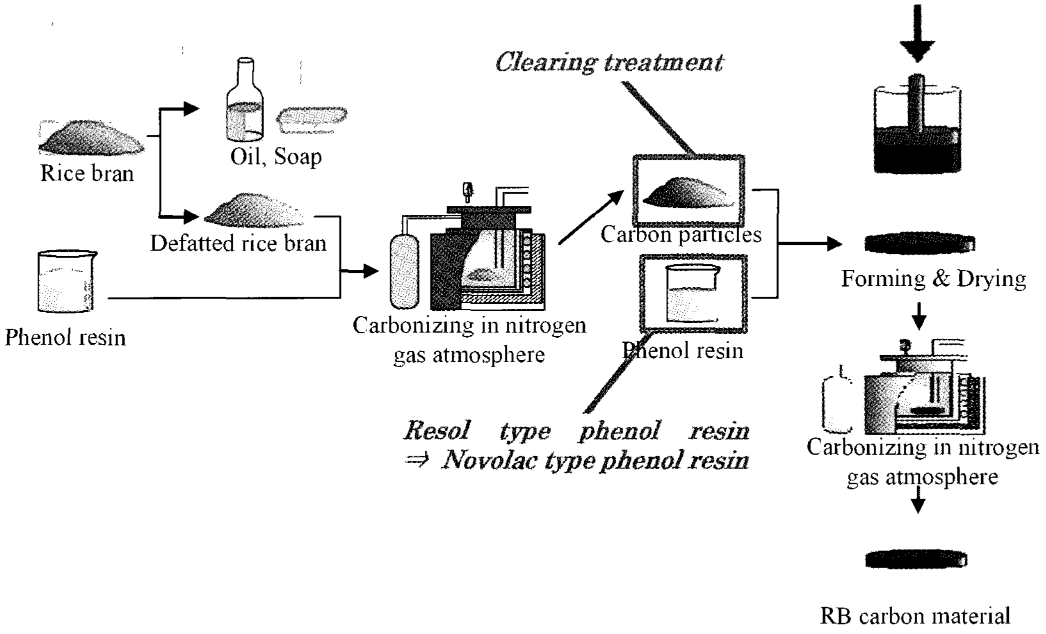


Figure 3 Manufacturing process of RB carbon

Table 2 Test-piece used in this study

	Phenol resin	
	resol-type	novolac-type
Untreated	U-TP-R	U-TP-N
Clearing treated	C-TP-R Citric acid	C-TP-N Citric acid

C shows clearing treated test piece and U shows untreated test pieces. Moreover, R shows the use of the resol-type phenol resin, and N shows the use of the novolac-type phenol resin.

2.2 Material tests

The compressive strength of the RB carbon after water immersing was measured to estimate the water resistance of the RB carbons. The test pieces were immersed in the deionized water for 1, 5, 10, 50, 100, 500, and 1000 hours. After dried, the residual compressive strength was measured. The compression tests were carried out using a universal testing machine with 50 kN maximum load. The crosshead speed on the testing machine is 0.5 mm/min. The compressive strain was measured using a laser displacement measuring system. The geometry of the test piece was 5×5×10 mm^3.

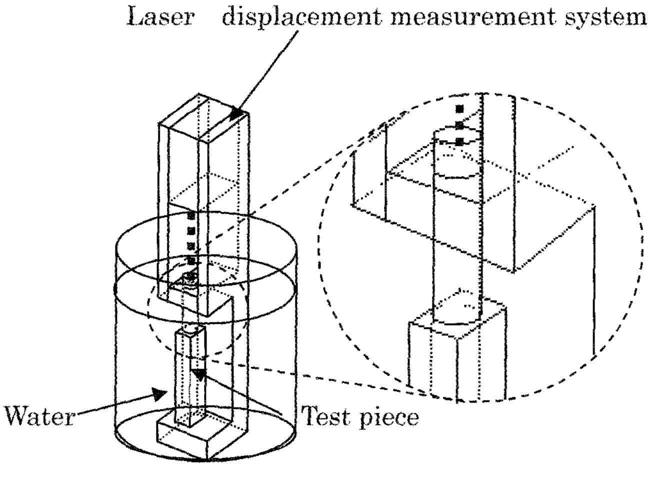


Figure 4 Test instrument for hygroscopic expansion

Table 3 Content of inorganic component after each treatment

Clearing treatment	Content of inorganic components (wt.%)
Untreated	37.8
(A) Water	37.8→32.6
(B) Citric acid	37.8→27.6
(C) Citric acid * twice	37.8→26.8
(D) Oxalic acid	37.8→28.8

The hygroscopic expansion was also measured to estimate the water resistance of the RB carbons. The expansion was measured using a laser-displacement measuring system, as shown in Figure 4. The test pieces were maintained in the deionized water at room temperature, and measured the expanded displacement. The geometry of the test piece was 5×5×50 mm^3.

3. EXPERIMENTAL RESULTS AND DISCUSSION

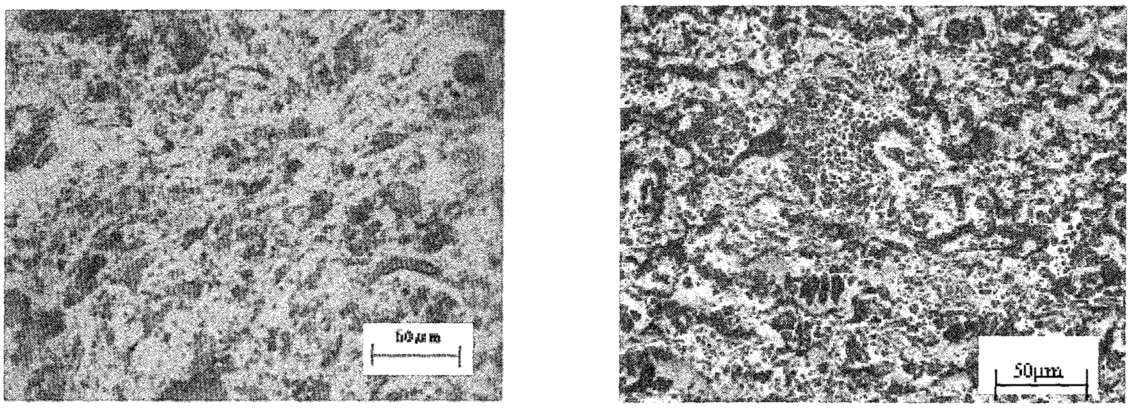
3.1 Effect of clearing treatment

Photo 1 (a) and (b) show the macrostructures of the traditional and modified RB carbon. The dark areas in the photograph are pores, and white regions are the inorganic and organic components. The pore is uniformly distributed in the both materials. The small voids were derived from the natural porous structure of the rice bran, and the big pores were opened at the interface between the RB particles. The number of small voids slightly increases in the clearing treated material, although the measured area fraction of the pores is not changed.

The content of inorganic component after each clearing treatment is listed in Table 3. The inorganic components are removed about from 10 to 11 mass% by (B), (C), and (D) clearing treatments.

3.2 Compressive strength

The relationship between water immersing time and compressive strength in the each clearing treated materials are shown in Figure 5. The compressive strength in the clearing treated materials (A), (B) and (C) are higher than that in the untreated material. The results show that the strength of the water-soluble components is low. Since the water-soluble inorganic compounds were removed by the clearing treatment, the strength



(a) Traditional RB carbon

(b) Modified RB carbon using clearing treatment (B)

Photo 1 Microstructure of RB carbon

in these materials became high comparing to the original RB carbon. The reduction of compressive strength in the untreated material after 1000 hours was about 60% of that in the virgin one. The compressive strength after the clearing treatment is not much decreased.

The relationship between water immersing and relative compressive strength in the U-TP-R and the U-TP-N are shown in Figure 6. The compressive strength in the U-TP-N was about 80% of the strength in the U-TP-R. The compressive strength in the U-TP-R gradually decreased with the immersing time. On the other hand, the compressive strength in the U-TP-N did not much decrease, and was about 90% of that in the virgin one.

The relationship between water immersing time and relative compressive strength in the U-TP-R and the C-TP-R are shown in Figure 7. The compressive strength in the C-TP-R was about 120% of the strength in the U-TP-R. By contrast, the compressive strength in the C-TP-R is not much decreased, and was about 80% of that in the virgin one.

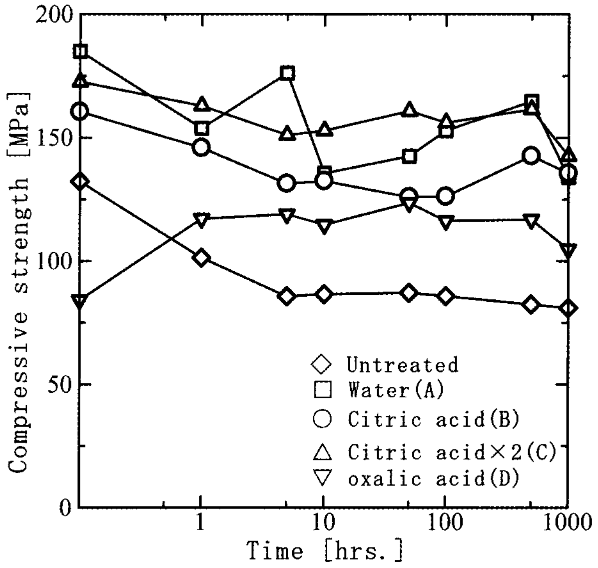


Figure 5 Effect of immersing time on compressive strength in each clearing treatment

Table 4 Saturated hygroscopic expansion

	Phenol resin	
	resol	novolac
Untreated	0.20%	0.15%
Clearing treated*	0.14%	0.07%

* ; using clearing treatment (B)

3.3 Improvement in hygroscopic expansion

Figure 8 (a) and (b) show the hygroscopic expansion in the U-TP-R and the C-TP-R. The strain largely increased during the first three hours after water immersing for the both materials. The saturated expansion in the U-TP-R was about 0.2%, and about 0.13% in the C-TP-R. The clearing treatment improves the hygroscopic expansion.

Figure 9 (a) and (b) show the hygroscopic expansion in the U-TP-N and the C-TP-N. The strain in the U-TP-N was increased by the water immersing and then saturated. The saturated expansion in the C-TP-N was about 0.07%. The hygroscopic expansion is improved in the test pieces using the novolac-type phenol resin. Table 4 lists the saturated hygroscopic expanded strain. The hygroscopic expansion was most improved in the C-TP-N. This high improvement is considered to be explained by the clearing of the potassium phosphate, which is made from the phosphorous in the rice bran.

4. CONCLUSIONS

High water resistant RB carbon was produced by using some clearing treatments and the novolac type phenol resin. The results

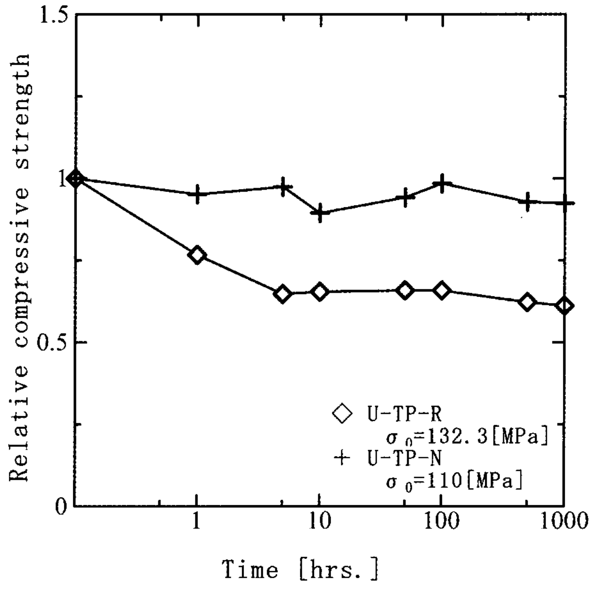


Figure 6 Effect of immersing time on relative compressive strength in U-TP-R and U-TP-N

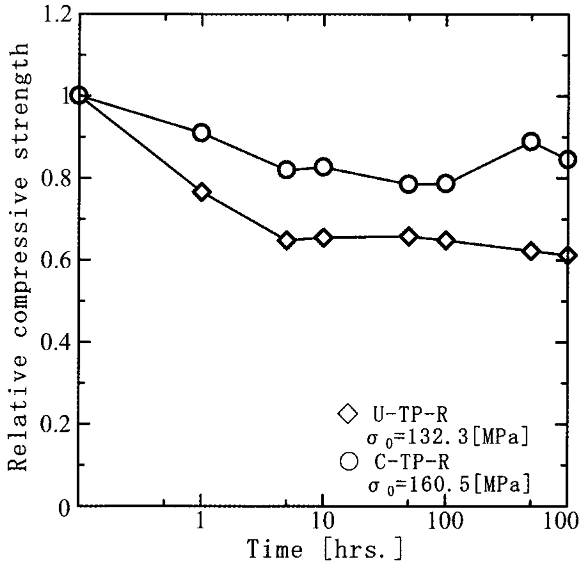


Figure 7 Effect of immersing time on relative compressive strength in U-TP-R and C-TP-R using (B) clearing treatment

obtained in this study are summarized as follows:

1) The reduction of compressive strength after water immersing is inhibited by the clearing treatment and the use of novolac-type phenol resin.

2) Hygroscopic expansion could be decreased by the clearing treatment and the use of novolac-type phenol resin.

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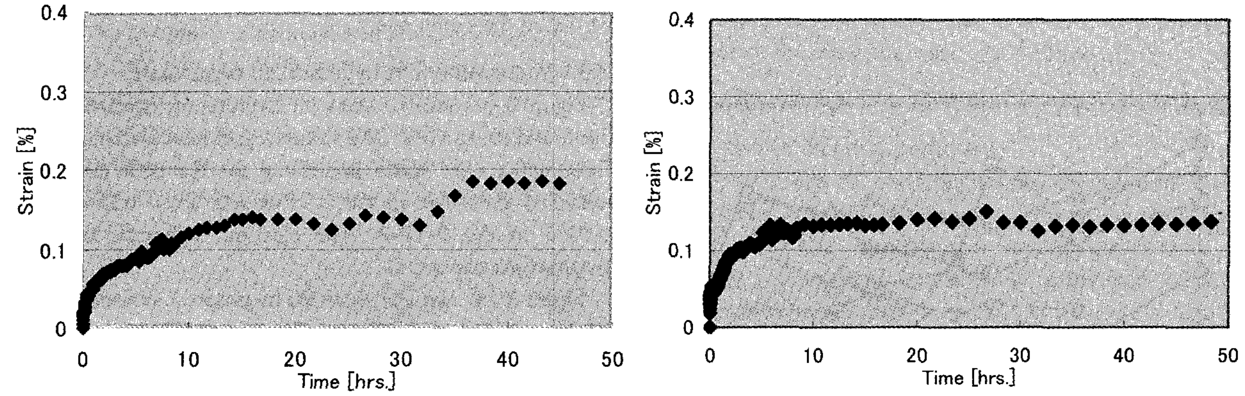
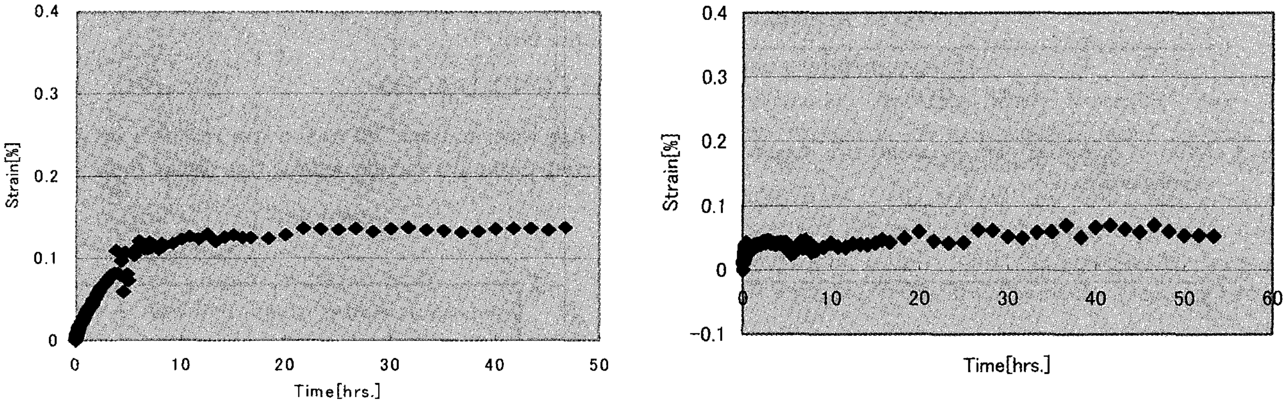


(a) U-TP-R

(b) C-TP-R

Figure 8 Effect of immersing time on expansion in U-T P-R and C-TP-R using (B) clearing treatment



(a) U-TP-N

(b) C-TP-N

Figure 9 Effect of immersing time on expansion in U-T P-N and C-TP-N using (B) clearing treatment