Increased Water Resistance of Bamboo Flour/Polyethylene Composites

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Author, Affiliation

Akiko ISA, Faculty of Agriculture, Shizuoka University

Jun MINAMINO, Faculty of Agriculture, Shizuoka University

Haruna MIZUNO, Faculty of Agriculture, Shizuoka University

Shigehiko SUZUKI, Faculty of Agriculture, Shizuoka University

Yoichi KOJIMA, Faculty of Agriculture, Shizuoka University

Hirokazu ITO, Yamaha Livingtech Corporation

Rie MAKISE, Yamaha Livingtech Corporation

Masaki OKAMOTO, Yamaha Livingtech Corporation

Takamoto HASEGAWA, Yamaha Livingtech Corporation

Corresponding author

Name/ Affiliation/ Tel/ Fax/ E-mail

Yoichi KOJIMA

Faculty of Agriculture, Shizuoka University

054-238-4856 (Tel & Fax) aykojim@ipc.shizuoka.ac.jp

Abstract To improve the water resistance of bamboo flour/high-density polyethylene (HDPE) composites, the effects of "plastic content," "coupling agents," and the "addition of micro-fibrillated cellulose (MFC)" on formulations were studied, and their rheological and mechanical properties were evaluated. The composites were prepared by injecting molding with a basic composition of equivalent amounts of bamboo flour and HDPE, and the melting fluidity of the compounds, tensile strength, and tensile modulus of the composites were determined. An increase in water resistance was detected in all three tests. By increasing the "plastic content," negative effect such as a decreased tensile modulus was observed. When evaluating the compatibility between bamboo flour and plastic using "coupling agents" and "MFC addition," positive effects were noted for water resistance, melting fluidity, and tensile modulus. We also confirmed that the procedure used to increase the compatibility between bamboo flour and plastic could easily be used for industrial applications by changing the coupling agents. Overall, a novel positive property (increased tensile modulus) and an increased water resistance were observed after "MFC addition."

Key words

Bamboo, polypropylene, water resistance, wood plastic composites, micro-fibrillated cellulose.

Introduction

The demand for wood plastic composites (WPCs), which is made from wood flour and polyolefin resin and has the features of both wood and plastic, has been increasing due to its use for exterior applications such as decks.[1] Although WPCs have superior durability compared with traditional wooden construction materials, the requirement for increased durability has increased with the demand for enhanced housing lifestyles. Numerous studies on water resistance, which is one of the most important factors affecting durability, have been previously conducted.[2–4]

Bouafifet et al. reported that water absorption of wood-fiber/HDPE composites increased with increasing fiber content.[5] Dányádi et al. reported that the addition of a maleated polymer to wood-flour/PP composites improved interfacial adhesion and reinforcement, and does not influence water absorption.[6] Migneault et al. reported wood fiber length-to-diameter ratio had a beneficial effect on mechanical properties but the effect on water absorption characteristics was negative.[7] Minamino et al. investigated the effects of addition of the cellulose with the surface fibrillation on mechanical properties and water resistance for wooden board.[8] The results has suggested that addition of the fibrous wood filler, which was made by blending wood flour and the fibrous cellulose under wet condition, improved the mechanical and water resistant properties. [8]

WPCs have also attracted attention as a utilization procedure of an unused biomass resource because they can be used as wood materials by pulverizing the substance to a fine powder.[9–11] One of the unused biomass resources in Japan is bamboo from abandoned bamboo forests. WPCs made from bamboo flour/fiber have excellent mechanical properties.[12–14] In addition, bamboo is a useful material based on its effective utilization of biomass resources because it grows quickly and can be stably supplied. However, bamboo is rich in sugar and starch and has poor decay resistance,[15,16] and thus its use in WPCs for exterior applications remains difficult.

In this study, the increased water resistance of WPCs for exterior applications was investigated to increase the utilization of bamboo materials. Three factors that influence the water resistance of bamboo flour/plastic composites were evaluated, i.e., the "plastic content," the change in the compatibility between bamboo flour and plastic due to "coupling agents," and "added micro-fibrillated cellulose (MFC)." The effects on water resistance were examined based on the composition of hybrid composites, i.e., wood flour with equivalent amounts of plastic. In this report, the possible applications of WPCs to bamboo flour/plastic composites are discussed while considering rheological and mechanical properties.

Materials and methods

Materials

Bamboo flour (Moso bamboo) used in this study was prepared after sieving with a 180-μm sieve. The flour was oven-dried at 105°C for 24 hours. High-density polyethylene (HDPE) [HDPE-870; Asahi Kasei Co., Tokyo, Japan, MI = 0.3 (g/10 min); JIS K7210] was used as the matrix plastic. Maleic anhydride grafted polyethylene (MAPE) (Fusabond; DuPont, Wilmington, DE, USA) was used as a coupling agent to improve the compatibility between the bamboo flour and the matrix. Two different kinds of MAPE (M603 and E265) were used in this study. M603 had MFR of 25 (g/10 min) at 190 °C /2.16kg and T_m of 108 °C. Density of M603 was unclear. E265 had MFR of 12 (g/10 min) at 190 °C /2.16kg, T_m of 131 °C, and density of 0.95 (g/cm^3).

Fibrillation of cellulose

Commercial cellulose powder (KC Flock W100GK; Nippon Paper Chemicals Co., Ltd., Tokyo, Japan) was fibrillated after adjusting the moisture concentration to 6% with distilled water and using a ball-mill (Pulverisette 6; Fritsch Japan Co., Ltd., Yokohama, Japan) at 250 rpm for 4 hours. MFC was prepared under the procedure of previous study.[8] The particle diameter of the MFC after ball-milling was measured using a laser-diffraction particle-size distribution analyzer (Partica LA-950; Horiba, Ltd., Kyoto, Japan). The average particle diameter of the MFC was 14 μm.

Compounding

Formulations of the compounds are shown in Table 1. The materials were premixed using a Labo-plastomill (30R150; Toyo Seiki Seisaku-sho, Ltd., Tokyo, Japan) at 190°C and 50 rpm for 2 minutes. The compounds were prepared by crushing the premixed mixtures to 1 mm or less using a Wonder Blender (WB-1; Osaka Chemical Co., Ltd. Osaka, Japan). Here, MFC was blended by replacing a part of the bamboo flour under wet condition. The amount of added water was controlled to adjust the moisture content upon compounding in the compounds of No.7-9. Blending of bamboo flour and MFC was performed using the Labo-plastomill at room temperature (50 rpm for 5 min), and the blends were vacuum-dried. The dried blends were crushed using a Wonder Blender and then compounded using the same procedure as described above. Although the formulation of compound No. 7 was equal to that of No. 2, it was repeated as a control because the procedure was different.

Injection molding

The crushed compounds were mixed using a micro compounder (Compounder 5; DSM

Xplore, Geleen, The Netherlands) at 190°C and 30 rpm for 2 minutes, and an injection molder (DSM Xplore) was used to mold the compounds into a dumbbell-shaped test piece at 190°C.

Melt flow rate (MFR)

MFR was measured with a melt indexer (LMI4000; Dynisco Polymer Test Systems, Morgantown, PA, USA) using a die with a diameter of 4 mm under a 10 kg load at 170°C. Measurement was started after loading the preheated (5 min) compounds.

Tensile test

The dumbbell-shaped test pieces after curing were measured using a universal precision test device (Autograph AG-IS; Shimadzu Co. Ltd., Kyoto, Japan) at 2 mm/min of load velocity after keeping at room temperature more than 2 hours.

Water absorption

Water absorption was tested in water at 60°C for 48 hours, and determined by measuring the change in weight of the test pieces before and after the water absorption test.

Scanning electron microscopy (SEM)

SEM (Miniscope TM1000; Hitachi, Tokyo, Japan) was used to analyze the morphologies of samples at 15 kV.

Results and discussion

Effect of HDPE content on the properties of bamboo flour/HDPE composites

Figure 1 shows the relationship between the HDPE concentration and water absorption (composites No. 1–4). Water absorption decreased with increasing HDPE content. This result was consistent with the previous study.[5] The possibility exists that water absorption was induced by the presence of bamboo flour in the bamboo flour/HDPE composites. No extra void space existed based on the lack of significant differences between the observed density and theoretical density, which can be calculated from the densities of each component and their composition. Melt fluidity (MFR) of the compound increased with HDPE concentration (No. 2–4), as shown in Table 2. Although MFR is known to depend on the shape and size of cellulosic material as filler, MFR increases with the increase in plastic content.[17] Higher MFR makes it easy to mold injection since the pressure required at molding declined.[17]

Tensile strength was not affected by the HDPE concentration, as shown in Table 2. Figure 2 shows a SEM photograph of the fracture surface of composite No. 2 (49% HDPE content) after the tensile test. Based on Fig. 2, the interfacial bonding strength between bamboo flour and HDPE was strong because parts of HDPE extended to the fracture. Tensile strength of the bamboo flour/HDPE composites was dependent on HDPE; thus, the bamboo flour concentration did not affect the tensile strength.

In contrast, the tensile modulus decreased with the HDPE concentration. This result was consistent with the previous reports.[5] Composites for exterior applications (mainly deck materials) require a low flexibility volume (high tensile modulus). Thus, decreases in the tensile modulus are undesirable because some measures, such as increased cross-sectional area of molded composites or shortening of the span during construction, are required. Therefore, the strategy for increasing the water resistance of composites by increasing the HDPE content has some problems.

Effect of coupling agents on the properties of bamboo flour/HDPE composites

Figure 3 shows the water absorption of bamboo flour/HDPE composites prepared from equivalent amounts of HDPE and bamboo flour (No. 2, 5, and 6) using different coupling agents (MAPE). Based on differences between the theoretical and observed densities, the void spaces were approximately the same for three bamboo flour/HDPE composites. The water resistance of the composites with MAPE (No. 2 and 6) was higher than that without MAPE (No. 5). MAPE-modified polyethylene (PE) polymer resin was made using maleic acid or anhydride and had side chains containing carboxyl groups on PE polymer main chains. The surface of cellulose was modified and hydrophobized by an esterification reaction of hydroxyl groups in cellulose molecules with carboxyl groups in MAPE.[18,19] Therefore, moisture intrusion into the interfacial surface of the composite occurred easily without MAPE (No. 5) and resulted in decreased water resistance compared with the composites containing MAPE (No. 2 and 6). An increase in surface modification of the bamboo flour was also explained by increasing in MFR of the compounds with MAPE (No. 2 and 6) compared with that without MAPE (No. 5). An increase in MFR supports an increase in compatibility between the bamboo flour and HDPE. Figure 3 also shows that the water resistance of the composite with E265 (No. 6) was better than that with M603 (No. 2). Thus, the interfacial surface of the composite with E265 did not absorb moisture as efficiently as with M603. This result may be explained by differences in the PE polymer main chain of MAPE. Regarding differences in the average molecular weights of PE polymers, the M_w of M603 was small and the polymer showed high melting fluidity compared with E265 (MFR M603 =25 g/10 min, E265 = 12 g/10 min). The effect of the PE polymer main chain was also observed after compounding, reflecting the results of MFR (Table 2). The differences in water resistance may have occurred because of the increased dispersion and compatibility of bamboo flour in the E265 composite via increases in the shear stress on bamboo flour during the compounding stage due to the low melting fluidity of the compound and the higher M_w of the PE polymer. However, this consideration requires further validation.

The tensile strength of the composite without MAPE (No. 5) was smaller than that of HDPE alone (No. 1), suggesting that the interfacial adhesion between the hydrophilic bamboo flour and the hydrophobic HDPE of the composite of No.5 was poor. In addition, the tensile strength of the composite of E265 (No. 6) was large compared with that of M603 (No. 2). This result also may be explained by the increased dispersion and compatibility of the bamboo flour in the composite of No.6 as previously stated. Good dispersion of the bamboo flour in the HDPE matrix may have improved nucleating activity of the bamboo flour for the HDPE[20], consequently increasing the crystallization in HDPE. It is known that increasing in crystalline of matrix polymer increase tensile strength.[20]

Little difference was observed in the tensile modulus among the composites of No. 2, 5, and 6, although the value of No. 6 was slightly higher. While modification of the crystallization state of HDPE was expected to affect the tensile modulus of the composite, differences in the tensile modulus of the HDPE was assumed to be minimal since the bamboo flour content (as fillers in the composites) was high. Thus, differences in the tensile modulus of the composites were likely minimal, as discussed in the preceding section, and the proportion of the bamboo flour in the composites were similar.

In conclusion, the strategy for improving water resistance of composites by increasing the compatibility using MAPE had little influence on the properties of the composite required for WPCs, such as the tensile modulus.

Effect of MFC addition on the properties of bamboo flour/HDPE composites

Figure 4 shows SEM photographs of the cellulose powder before and after boll milling. As shown in Fig.4 (b), the cellulose powder was fiberized and micro-fiber was formed on the surface. MFC may have tangled with bamboo flour by blending under wet condition, consequently bamboo flour with the micro-fibrous structure on the surface was made. This has been already suggested in the previous research.[8]

Figure 5 shows the relationship between the MFC content and water absorption of bamboo flour/HDPE composites (No. 7-9), which consist of equivalent amounts of HDPE and bamboo flour. As shown in Fig. 5, water resistance improved with increased MFC content. Since the void space based on observed and theoretical densities was similar, we concluded that water resistance was improved by MFC addition.

No difference existed in tensile strengths with changes in MFC content (composites of No.7-9), although the tensile strengths were larger than that in the composite with HDPE alone (No.1) and composite of No.2, which was made from equivalent amounts of bamboo flour and HDPE. Here, MFC was blended with the bamboo flour under wet condition in the compounds of No.7-9, therefore, the bamboo flour may be swelled and promoted fiberizing into fine particles. The increase in tensile strengths in the composites of No.7-9 may be explained by increasing the crystallization of HDPE due to good nucleating activity of the fine particles of the bamboo flour. An increase in the number of small bamboo particles was also observed based on MFR. The increase in MFR (No. 7-9) compared with No.2 supports an increase in the number of small particles. It remains to be seen if tensile strength was affected by addition of MFC. To further verify the result, modification of the crystallization state should be observed after the addition of MFC.

In contrast, the tensile modulus increased with increasing MFC content. The tensile modulus is known to increase by interacting with microfibrils in WPCs using fibrous wood filler.[9] The number of microfibrils on the surface of bamboo flour tended to increase with increasing MFC. Thus, the tensile modulus of composites would increase by interacting with microfibrils. The increase in water resistance by adding MFC was presumably due to the densification of bamboo flour/HDPE composites via interactions with microfibrils on the surface of bamboo flour, and contributed to the poor moisture intrusion.

Thus, the increased functionality could allow WPCs to be used for exterior applications since the properties of the composites such as water resistance and the tensile modulus were improved by adding MFC.

Conclusions

To allow WPCs to be used for exterior applications using bamboo flour, the effects of "plastic content," "improving compatibility between bamboo flour and plastic by coupling agents," and "MFC addition" on water resistance of the composites were evaluated to improve their decay resistance. By assuming that WPCs would be used in exterior applications for practical purposes, the rheological and mechanical properties of bamboo flour/HDPE composites were also evaluated.

Increases in water resistance were observed using three methods; however, negative effect was also observed such as a decreased tensile modulus with increasing "plastic content." In contrast, positive effects were observed for all properties by "increasing compatibility between bamboo flour and plastic" and "MFC addition." The strategy of "increasing compatibility between bamboo flour and plastic" can easily be used for industrial applications by changing the type of added coupling agent. The increased tensile modulus by "MFC addition" is as valuable as an increase in water resistance.

In conclusion, expansion of the WPC market to exterior applications using bamboo materials could allow for practical use of WPCs due to the increased water resistance.

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Table 1. Formulation of compounds (by weight)

Table 2. Mechanical and rheological properties. The standard deviation is shown in parentheses

Fig. 1. Effect of HDPE content on water absorption

Fig. 2. SEM photograph of the fracture surface of the No. 2 composite (49% of HDPE content) after the tensile test

Fig. 3. Effect of a coupling agent (MAPE) on water absorption

No add, M603 (2%), and E265 (2%) represent the composite without MAPE and that with 2% M603 and 2% E265, respectively. M603 and E265 were different types of MAPE

Fig. 4. SEM photograph of the cellulose powder before and after boll milling

Fig. 5. Effect of MFC content on water resistance of the mold

Table1 Formulation of compounds (by weight)

No.	Bamboo	MFC	HDPE	MAPE	
				M603	E265
1	-	-	100	-	-
2	49	-	49	2	-
3	39	-	59	2	-
4	29	-	69	2	-
5	50	-	50	-	-
6	49	-	49	-	2
7	49	-	49	2	-
8	48	1	49	2	-
9	44	5	49	2	-

Table2 Mechanical and rheological properties. The standard deviation is shown in parentheses

No.	Bamboo content (%)	HDPE content (%)	MaPE		MFC content (%)	MFR (g/10min)	Tensile strength (MPa)	Tensile modulus (MPa)
			M603	E265				
1	-	100	-	-	-	40.4 (1.1)	32.0 (0.5)	322.6 (45.7)
2	49	49	2	-	-	5.8 (0.2)	32.9 (0.7)	735.3 (10.9)
3	39	59	2	-	-	8.7 (0.2)	35.3 (0.4)	617.3 (52.2)
4	29	69	2	-	-	13.6 (0.1)	34.0 (0.7)	560.7 (75.0)
5	50	50	-	-	-	2.8 (0.1)	25.0 (2.2)	740.3 (64.8)
6	49	49	-	2	-	4.0 (0.1)	44.7 (1.7)	773.7 (81.4)
7	49	49	2	-	-	6.5 (0.5)	38.6 (2.2)	771.9 (97.0)
8	48	49	2	-	1	6.3 (0.2)	38.3 (0.8)	850.7 (86.4)
9	44	49	2	-	5	7.1 (0.6)	38.2 (1.4)	867.8 (84.7)

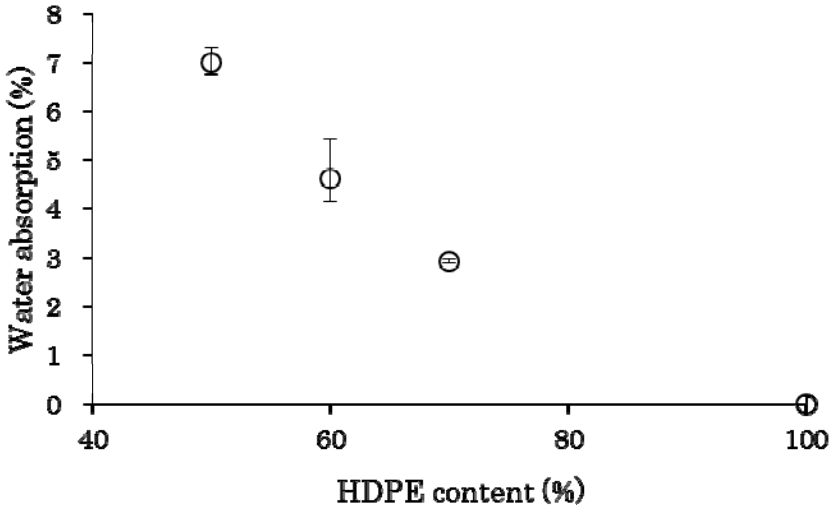

Fig.1 Effect of HDPE content on water absorption

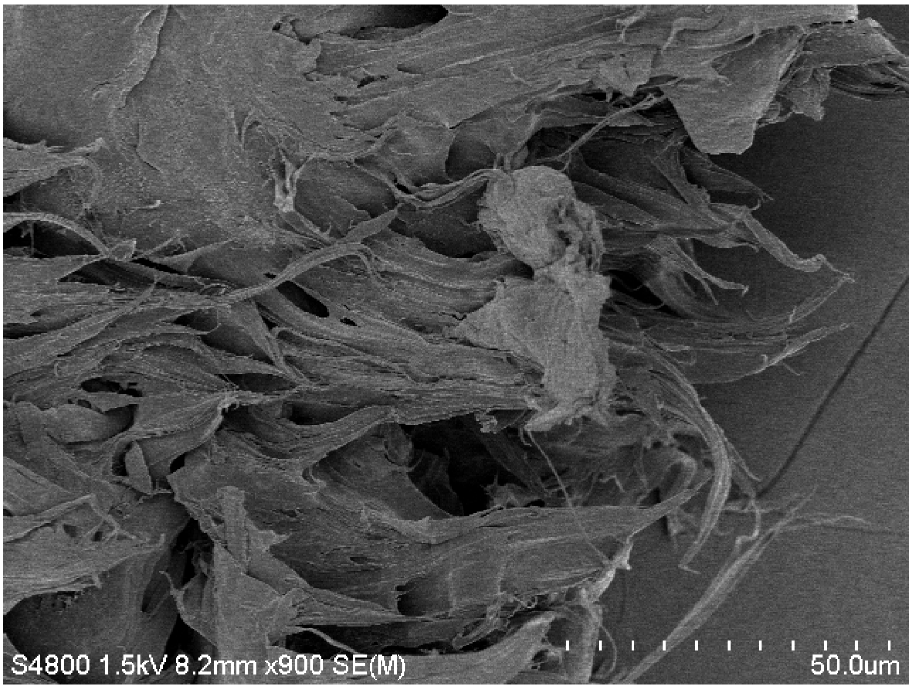

Fig.2　SEM photograph of the fracture surface of the No.2 composite (49% of HDPE content) after the tensile test

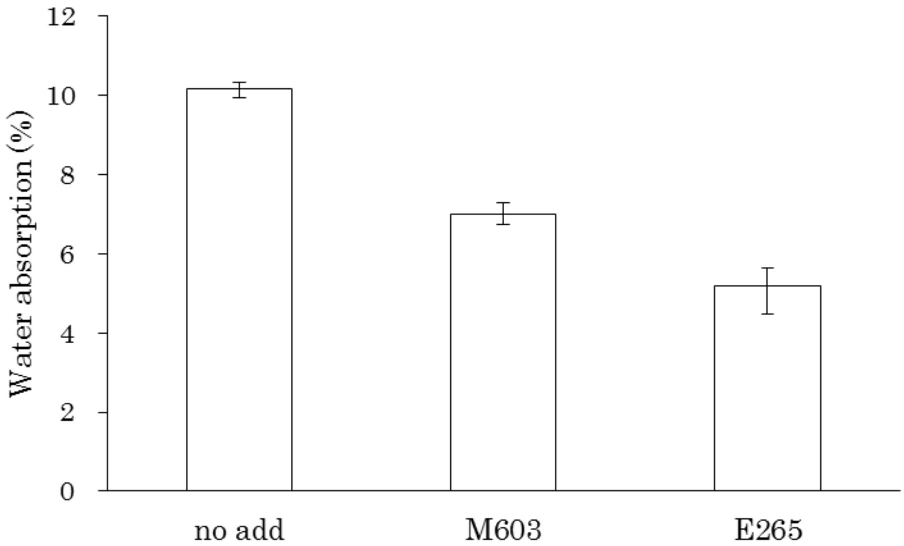

Fig.3 Effect of a coupling agent (MAPE) on water absorption

No add, M603 (2%), and E265 (2%) represent the composite without MAPE and that with 2% M603 and 2% E265, respectively. M603 and E265 were different types of MAPE

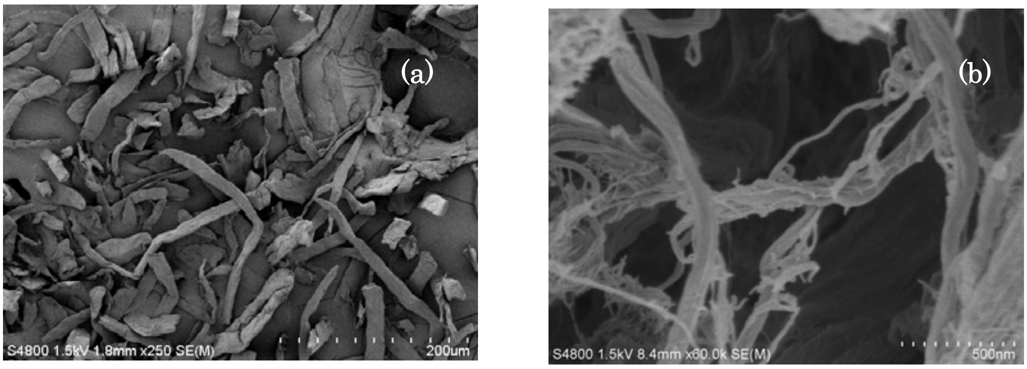

Fig.4 SEM photograph of the cellulose powder: (a) before boll milling and (b) after boll milling at 250rpm for 4 hours.

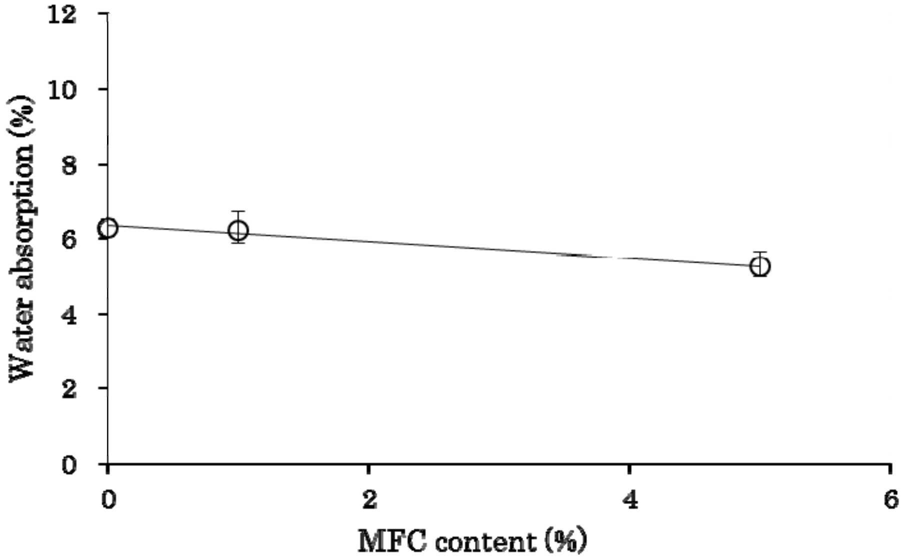

Fig.5　Effect of MFC content on water resistance of the mold