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Effect of Silane Coupling Agent Concentration on Interfacial Properties of Basalt Fiber Reinforced Composites

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Abstract: The purpose of this study is to investigate the effect of the concentration of silane coupling solution on the tensile strength of basalt fiber and the interfacial properties of basalt fiber reinforced polymer composites. The surface treatment of basalt fibers was carried out using an aqueous alcohol solution method. Basalt fibers were subjected to surface treatment with 3-Methacryloxypropyl trimethoxy silane at 0.5 wt.%, 1 wt.%, 2 wt.%, 4 wt.% and 10 wt.%. The basalt monofilament tensile tests were carried out to investigate the variation in strength with the concentration of the silane coupling agent. The microdroplet test was performed to examine the effect of the concentration of the silane coupling agent on interfacial strength of basalt reinforced polymer composites. The film was formed on the surface of the basalt fiber treated silane coupling agent solution. The tensile strength of basalt fiber increased because the damaged fiber surface was repaired by the firm of silane coupling agent. The firm was effective in not only the surface protection of basalt fiber but also the improvement on the interfacial strength of fiber-matrix interface. However, the surface treatment using the high concentration silane coupling agent solution has an adverse effect on the mechanical properties of the composite materials, because of causing the degradation of the interfacial strength of the composite materials.

Key words: Natural mineral fiber reinforced composites, basalt fiber, silane coupling agent, interface, fiber/matrix bond.

1. Introduction

Currently, efforts toward the realization of a sustainable society, which is the goal of the SDGs (Sustainable Development Goals), are gaining momentum around the world. Among them, the efforts toward carbon neutrality are one of the most important activities. A total of 127 countries, including Japan have pledged to achieve carbon neutrality [1].

Many car manufacturers have committed to increasing the uptake of electric vehicles. The entire automotive industry is moving towards electrification. Accordingly, there is an increasing demand for lightweighting. The use of CFRP (carbon fiber-reinforced composites) and GFRP (glass fiber-reinforced composites) with high specific strength and specific stiffness is being considered to reduce the weight of automobiles. Furthermore, the goal is not only to reduce carbon dioxide (CO_2) emissions from vehicles to zero, but also to reduce carbon dioxide emissions throughout their entire life cycle, from manufacture to disposal and recycling [2]. The use of fiber-reinforced composites of natural plant or natural mineral origin is an effective means of achieving them.

Annually renewable natural plant fibers such as hemp, jute, ramie, kenaf, bamboo and flax have attracted more interest as reinforcement for both thermosetting and thermoplastic polymer-based composites, because of lightweight, low cost and acceptable specific properties [3-11]. However, natural plant fibers are very sensitive to hygroscopic load and thermal load and have limited mechanical properties. The use of natural

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mineral fibers such as basalt fiber is represented as a possible solution to overcome the disadvantages of natural plant fibers.

Basalt fiber is an inorganic mineral fiber with extremely good modulus, high strength, high temperature resistance, excellent stability, good impact strength, chemical resistance, abrasion resistance though non-toxic, natural, and eco-friendly [12-15]. The production of basalt fibers is simple as basalt fibers are spun from molten basalt rock at high temperatures [16]. The cost of basalt fibers is lower than that of S-glass and carbon fibers [17]. Therefore, basalt fibers have received as a novel type of reinforcement material for thermosetting and thermoplastic polymer-based composites [18, 19].

Generally, the performance of composite materials depends on the type of fiber surface treatment and the processing conditions that affect the mechanical properties of fiber-matrix interface. The fiber-matrix interface plays an important role in load transfer between the fiber and the matrix. Sizing agents are coated on the fiber surface during manufacturing [20] and are made of water solution mainly composed of organic matter such as starch or oil. It is necessary to remove the sizing agent to improve the mechanical properties of fiber-matrix interface. Heat cleaning is the most effective as surface treatments to remove the sizing agents. However, this surface treatment reduces the mechanical properties of the fiber because the fiber exposes for long time at high temperature [21]. Bhat et al. [22] attributed this loss of strength to thermally activated growth of surface defects, probably resulting from a reaction process of the silicates in the basalt with water molecules in the air. The modification of silane coupling agents on the surface of basalt fibers to improve the interfacial adhesion of basalt fiber reinforced composites is also expected to improve the strength of the basalt fibers. Therefore, it is necessary to think about the new surface treatment method without reducing the tensile strength of the fiber. However, no other such reports have been published to the authors' knowledge.

The aim of this study is to investigate the effect of the concentration of silane coupling solution on the tensile strength of basalt fiber and the interfacial properties of basalt fiber/vinylester composites.

2. Experimental Procedure

2.1 Materials

The basalt fiber used in this study was monofilament extracted from the fiber bundle of plain woven basalt fabric (TBK400; Chubu-Kougyou Co. Ltd.). The heat cleaning was carried out at 350 °C for 48 h using a heating furnace in order to eliminate the organic material from the plain woven basalt fabrics. Vinylester resin (Diclite UE-3505; DIC Corporation), methylethylketoneperoxide (MEKPO) and cobalt napthenate (6% solution) (Co-Nap) were used as matrix, curing agent and room temperature catalyst, respectively. The silane coupling agent used in this study was 3-Methacryloxypropyl trimethoxysilane (LS-3380; Shin-Etsu Chemical Co. Ltd.) containing methacryl group.

2.2 Surface Treatment

The surface treatment of basalt fiber was carried out using an alcohol-water solution. Basalt fibers were surface treated with 3-methacryloxypropyltrimethoxysilane at five different concentrations of 0.5 wt.%, 1 wt.%, 2 wt.%, 4 wt.% and 10 wt.%. The silane coupling agent was prepared in water-ethanol mixed solution. To ensure complete hydrolysis of the silane, the solution was stirred with a magnetic stirrer for 2 h prior to use. Basalt fibers were immersed in a silane coupling agent solution for 2 min and the treated basalt fibers were dried in a convection oven at 80 °C for 1 h.

2.3 Monofilament Tensile Test

Monofilament tensile tests were carried out to determine the variation in strength with the concentration of the silane coupling agent. The basalt monofilament was stuck on a paper frame, as shown in Fig. 1. Twenty (20) fiber samples were tested for each surface treatment

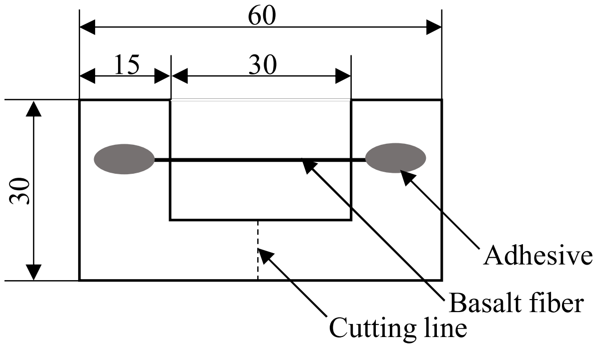

Fig. 1 Basalt monofilament tensile specimen.

condition. The fiber diameter was measured by using a digital microscope (BS-8000III, Sonic Co. Ltd.). The monofilament tensile test was conducted on a universal material testing machine (Ez-Graph; Shimadzu Co. Ltd.). The basalt monofilament was glued on a paper flame with 30 mm gauge length. The tensile tests were performed using a load cell of 40 N at a crosshead speed of 1.0 mm/min. After mounting both ends of the specimen shown in Fig. 1 in the chuck of the universal testing machine, the center portion of the specimen was cut with scissors. The tensile strength was obtained from the maximum stress of the stress-strain curve.

2.4 Microdroplet Test

Microdroplet test was used to study the effect of the concentration of the silane coupling agent on interfacial strength of vinylester/basalt composites. The basalt monofilament was glued on a paper frame, then a very small amount of vinylester resin was dropped on the monofilament using a thin needle, as shown in Fig. 2. The microdroplet test specimen was placed in a chamber at room temperature for 48 h, then, was placed in an oven at 80 °C for 8 h for post-curing. The microdroplet test was carried out on a universal material testing machine (Ez-Graph; Shimadzu Co. Ltd.). The jig with the microvise was attached to the lower chuck of the universal testing machine. The specimen was inserted into a small gap of a pair of microvises and the one end of microdroplet specimen was connected to the upper chuck of the universal testing machine. The basalt

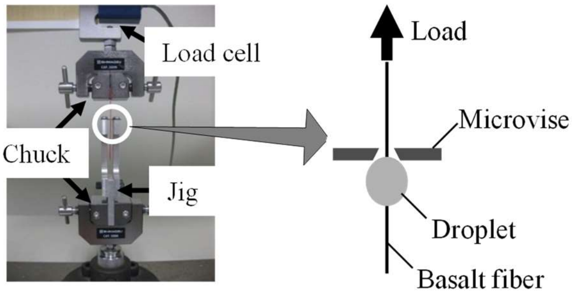

Fig. 2 Microdroplet specimen fixed to testing machine.

fibers were pulled out from the droplets constrained by microvices. The microdroplet tests were performed using a load cell of 40 N at a crosshead speed of 0.5 mm/min. The interfacial shear strength, τ, can be calculated as:

$$\tau = \frac{F_{\max}}{\pi d_f l} \quad (1)$$

where, $F_{\max}$ is the maximum pull-out load, d_f is the fiber diameter and l is the fiber embedded length, which was measured by using a digital microscope.

2.5 SEM (Scanning Electron Microscope)

Basalt fibers were observed using a SEM (NeoScope JCM-5000, JEOL Ltd.) to investigate the effect of silane coupling concentration. All microdroplet test specimens were observed by SEM after testing to observe the mechanisms of damage and delamination.

3. Results and Discussion

3.1 Surface of Basalt Fiber

Figs. 3a-3f show SEM micrographs of untreated and silane coupling agent-treated basalt fibers.

The surface of untreated basalt fiber is smooth. There was a significant difference in the surface morphology of the fiber after immersion treatment with silane coupling agent solution compared to the untreated one. Treatment with silane coupling agents at concentrations above 0.5 wt% caused a significant change in the surface morphology of the basalt fibers, as shown in Fig. 3b. It can be observed that a film is formed on the surface of all basalt fibers treated with silane coupling agent solution. There were some differences in the size of the

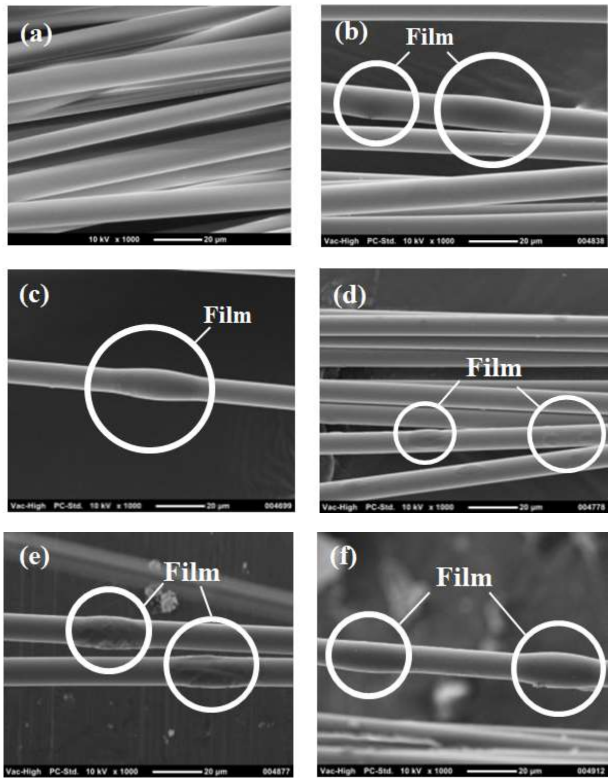

Fig. 3 SEM images of silane coupling treated basalt fibers, (a) untreated, (b) 0.5 wt.%, (c) 1.0 wt.%, (d) 2.0 wt.%, (e) 4.0 wt.%, (f) 10 wt.% .

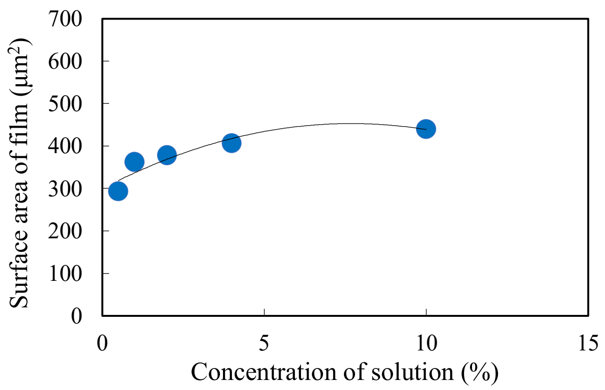

Fig. 4 Relationship between surface area of firm and concentration of silane coupling agent solution..

firm by increasing the concentration of silane coupling agent solution. The relationship between the surface area of the firm and the concentration of silane coupling solution was shown in Fig. 4. It was found that the size and surface area of the firms became larger as the concentrations of silane coupling agent solution became higher. It was considered that the methacryloxypropyl trimethoxysilane molecules, which were hydrolyzed, adhered to the basalt fiber surface and the firm was coated on the basalt fiber surface by causing dehydration condensation by hydroxyl groups of basalt fiber surface and reaction groups of silane coupling agent or intermolecular condensation. Therefore, the increased surface area of the film can be attributed to an increase in the area coated on the basalt fiber surface by increasing the silane coupling concentration.

3.2 Monofilament Tensile Test

Fig. 5 showed the variation of the tensile strength of basalt fiber by the surface treatment using silane coupling agent. A dotted line indicated the tensile strength of the basalt fiber without heat-cleaning treatment (non-cleaning). From this figure, it was found that the tensile strength of basalt fiber increased with increasing of the concentration of silane coupling agent solution. To clarify the relationship between the film formed by the silane coupling agent treatment and strength, Fig. 6 showed the relationship between the tensile strength of basalt fiber and the surface area of the film. The tensile strength increased with increasing of the surface area of the firm and indicated a peak tensile strength of 943 MPa at the surface area of the firm near 360 μm^2. Sizing agents applied to fibers during spinning have the role of protecting the fiber surface. However, the removal of the sizing agent causes damage to the fiber surface due to friction between the monofilaments as the monofilaments are

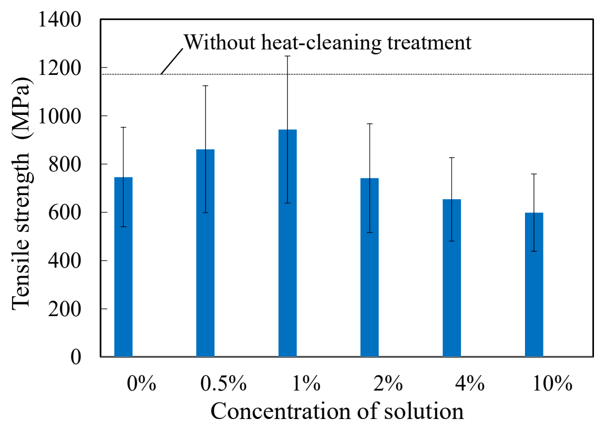

Fig. 5 Variation of tensile strength of basalt fiber by surface treatment using silane coupling agent solution.

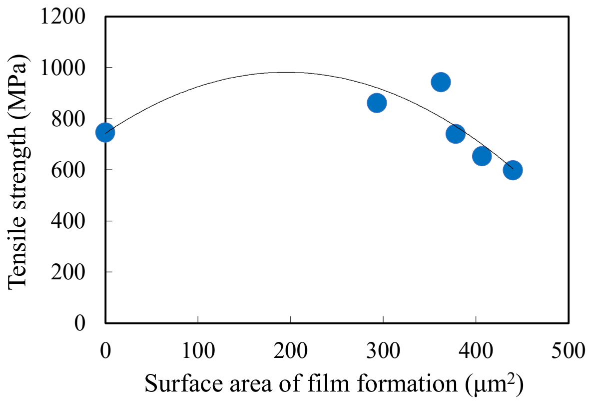

Fig. 6 Relationship between tensile strength of basalt fiber and surface area of film.

pulled from the fiber bundle. Therefore, it was assumed that the tensile strength of the basalt fiber was increased because the damaged fiber surface was repaired by the firm of silane coupling agent.

On the other hand, the tensile strength of basalt fibres treated with 2 wt%, 4 wt% and 10 wt% concentrations of silane coupling agent solutions was lower than that of basalt fibres treated with 1 wt% concentration of silane coupling agent solution. As the concentration of the silane coupling agent increases, aggregates tend to form in aqueous silane coupling agent solutions because the silane coupling agent is difficult to disperse in aqueous solutions and hydrolysis is insufficient. It is believed that the bond between the aggregate and the basalt fiber surface is weak. Therefore, it was considered that the reduction of the tensile strength was caused by forming the weak agglomerate on the fiber surface.

3.3 Microdroplet Test

The variation of the interfacial shear strength of basalt fiber reinforced polymer composites treated with silane coupling agent solution was shown in Fig. 7. The interfacial shear strength increased with increasing of the concentration of silane coupling agent solution. However, the interfacial shear strength of the composites treated with 2 wt.% and 4 wt.% silane coupling agent was almost same values as that of the composites treated with 1 wt.% silane coupling agent. The relationship between the interfacial shear strength of the composites and the surface area of the film was shown in Fig. 8.

The interfacial shear strength increased with increasing of the surface area of the firm and indicated a peak value of 18.9 MPa at the surface area of the firm 406 μm². However, the interfacial shear strength decreased above the surface area of the firm 406 μm², because of forming the weak agglomerate on the fiber surface.

Figs. 9a-9f show the SEM micrographs of the microdroplet specimens after debonding. It was observed that the sizes of the meniscus treated with 1 wt.%, 2 wt.% and 4 wt.% were larger than that of the meniscus treated with 0 wt.%. The relationship between the interfacial shear strength of the composites

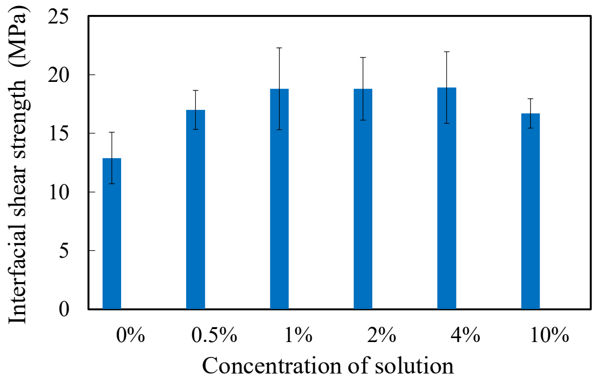

Fig. 7 Variation of interfacial shear strength of basalt fiber reinforced polymer composites treated with silane coupling agent solution.

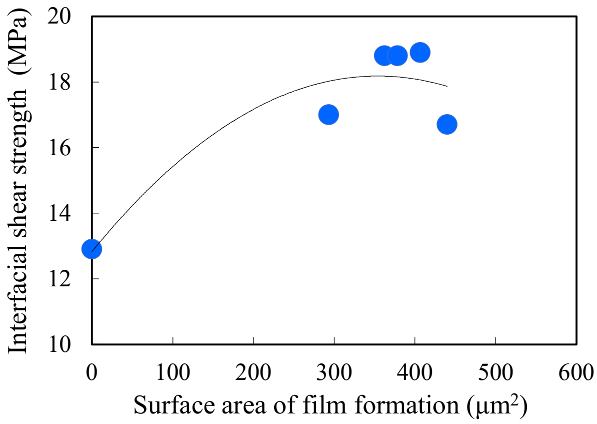

Fig. 8 Relationship between interfacial shear strength of basalt fiber polymer composites and surface area of film.

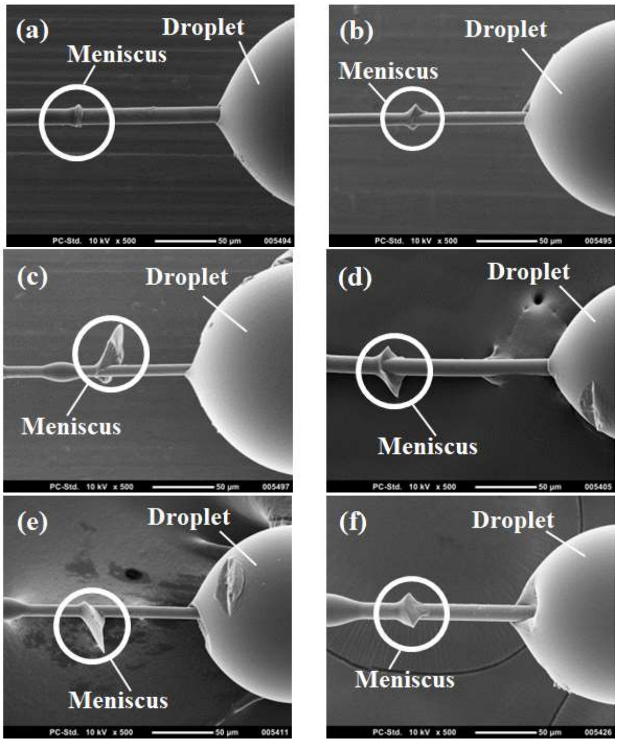

Fig. 9 SEM images of microdroplet specimens after debonding, (a) untreated, (b) 0.5 wt.%, (c) 1.0 wt.%, (d) 2.0 wt.%, (e) 4.0 wt.%, (f) 10 wt.%.

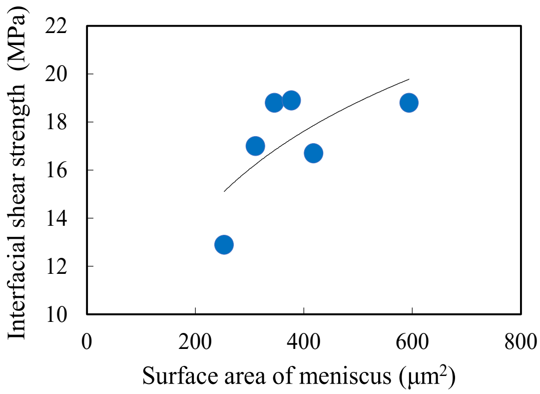

Fig. 10 Relationship between interfacial shear strength of basalt fiber polymer composites and surface area of meniscus.

and the surface area of the meniscus was shown in Fig. 10. It was found that the interfacial shear strength increased with increasing of the surface area of meniscus. The results indicated that it is not only effective in protecting the surface of the basalt fibers, but also in improving the interfacial strength of the fiber-matrix interface by reducing the delamination of the fiber-matrix interface. However, the interfacial strength of the composites did not change even though the firm on the fiber surface grew up with increasing of the concentration of silane coupling agent solution. On the contrary, the surface treatment using the high concentration silane coupling agent solution such as 10 wt.% silane coupling agent has an adverse effect on the mechanical properties of the composite materials, because of causing the degradation of the interfacial strength of the composites. Therefore, it was considered that there was an optimum value of the concentration on silane coupling agent solution.

4. Conclusions

The effects of concentration of silane coupling solution on the tensile strength of basalt fiber and the interfacial properties of basalt fiber reinforced polymer composites were investigated. Some conclusions could be obtained as follows.

(1) The film was formed on the surface of the basalt fiber treated silane coupling agent solution. The size and surface area of the firms became larger with increasing of the concentrations of silane coupling agent solution.

(2) The tensile strength of basalt fiber increased because the damaged fiber surface was repaired by the firm of silane coupling agent.

(3) The tensile strengths of the basalt fibers treated with 2 wt.%, 4 wt.% and 10 wt.% silane coupling agent decreased as compared with that of the basalt fiber treated with 1 wt.% silane coupling agent.

(4) The firm was effective in not only the surface protection of basalt fiber but also the improvement on the interfacial strength of fiber-matrix interface.

(5) There was an optimum value of the concentration on silane coupling agent solution.

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