

## Bonding durability of custom-made mouthpiece for scuba diving after water storage under pressure

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The purpose of this study was to assess the behavior of laminated thermoforming materials in an underwater environment to understand the durability of mouthpieces for scuba diving. Two thermoforming materials, polyolefin (PO) and ethylene-vinyl acetate copolymer (EV), were laminated and stored in air, 37°C water, and 37°C water under 0.2-MPa pressure for 1 and 4 weeks. The load/bonding width (bonding strength: BS) and displacement at the start of delamination (SD) and fracture (FR) were analyzed with 3-way ANOVA. BS values at SD and FR in air were significantly greater than those under the other conditions, and the BS at SD of EV was significantly greater than that of PO, though the effects of materials, duration and their interactions were not significantly different. The displacements at SD and FR were significantly influenced by the material. These results suggest that both materials can be employed for making a diving custom mouthpiece.

**Keywords:** Bonding durability, Custom-made mouthpiece, Water storage under pressure

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### INTRODUCTION

Scuba diving is a popular sport that many people enjoy. In recent years, the number of scuba divers has been growing<sup>1</sup>. However, scuba diving may trigger problems in some parts of the body such as the nose, ear, lung, and temporomandibular joint<sup>2-6</sup>. Previous studies reported that the prevalence of temporomandibular disorders while scuba diving ranged from 24% to 68%<sup>7-10</sup>. The most common problems during or after the scuba diving are temporomandibular disorders (TMD)<sup>11</sup>. This type of TMD might be caused by not only environmental factors such as cold water<sup>8</sup>, but also the forward posturing of the mandible while holding and clenching a mouthpiece for a long time<sup>3,12</sup>. Therefore, beginner divers complain of TMD problems related to the mouthpiece more often than experts<sup>13</sup>. Thus, a well-designed custom mouthpiece is recommended for relieving and preventing TMD.

In our previous report, a new lamination forming technique using polyolefin thermoforming materials to fabricate a custom scuba-diving mouthpiece was introduced<sup>14</sup>. Both polyolefin and ethylene-vinyl acetate copolymer are commonly used sports mouthguard materials. The mouthpiece for scuba diving is exposed to water for a long time compared to mouthguards for other sports. Therefore, the mouthpiece for scuba diving is exposed to stress by biting and external force while the diver is underwater and surfacing. These stresses cause the mouthpiece to be damaged. A damaged mouthpiece is very dangerous, because the diver may not be able to breathe. However, the durability of custom scuba-diving mouthpiece materials under water has not been clarified. The purpose of the present study was to assess the bonding

behavior, tear strength and water absorption of laminated thermoforming materials in an underwater environment in an effort to understand the durability of the mouthpiece for scuba diving.

The null hypotheses of the present study were that the bonding and tear strengths of polyolefin and ethylene-vinyl acetate copolymer used as mouthpiece materials did not decrease after underwater storage.

### MATERIALS AND METHODS

#### Materials

Two types of commercial thermoforming-sheet materials for mouthguard, polyolefin clear and colored (PO: MG21, Molten Co., Hiroshima, Japan; Clear: Lot No. 1228004, Pink: 0330004) and ethylene-vinyl acetate copolymer clear and colored (EV: Mouthguard Sheet, Ultradent Co., Utah, USA; Clear: Lot No. B253H, Yellow: 59GC), were selected. Polyolefin is an ethylene propylene thermoplastic elastomer<sup>15</sup>.

#### Delamination test

A T-peel test was used as the delamination test<sup>16,17</sup>. Two sheets of the same mouthguard material in different colors were laminated together. Two film-shaped sheets for separation (Molteno Separate Film, Molten Co., Hiroshima, Japan) were placed on one mouthguard sheet to create an adhesive area so that the center of the sheet had a width of 15 mm. Then the other mouthguard sheet was heated and placed in a vacuum at 0.012 MPa when the sheet was hung 15 mm from the center using a vacuum thermoforming machine (Vacuum Forming Machine, Keystone Industries, Cherry Hill, NJ, USA)<sup>18</sup>. The laminated sheet was cut with a dumbbell-shaped cutter according

to JIS K6251:2004 so that the adhesive area was at the center of the isthmus, and sectioned at the center of the isthmus. The final specimens for delamination, with an adhesive area of 4.0 mm × 7.5 mm, are shown in Figs. 1 and 2. Thirty specimens of each material were prepared and assigned into the following three groups.

Group 1. Storage in a container in the laboratory (23 ± 2°C) (hereafter referred to as in air)

Group 2. Storage in water in a glass beaker in a 37°C thermostatic chamber (Advantec CI-610, Toyo Seisakusho Co., Tokyo, Japan) (hereafter referred to as in water).

Group 3. Storage in water in a pressure pot (New Pressure Pot, Mokuda Shokai, Kobe, Japan) in a 37°C thermostatic chamber. The pressure was controlled to under 0.2 MPa (hereafter referred to as in 0.2 MPa water).

After 1 and 4 weeks in the above-mentioned storage conditions, the specimens were subjected to a delamination test. The size of the specimen was measured using a digital micrometer (Digimatic 293-421-20, Mitutoyo, Kanagawa, Japan. Minimum reading: 0.001 mm). The specimen was fixed to a universal test machine (1123, Instron, Canton, MI, USA) with a special jig to grip it firmly. The delamination test was carried out with the universal test machine at a cross-head speed of 50mm/min (Fig. 3). Changes of load and displacement until the specimen fractured were recorded with statistical software (Series IX, Instron).

A typical load-displacement curve is shown in Fig. 4. The load rapidly increased when delamination started. The bonding strength at the start of delamination (BS at SD) was calculated as the load at the start of delamination divided by the width of the specimen (approximately 4.0 mm). The load at the start of delamination was determined as the load of the cross point of the initial slope and the second slope of the load-placement curve (Fig. 4). The displacement at the start of delamination (displacement at SD) was also measured. The bonding strength at fracture (BS at FR) was calculated as the load at fracture divided by the width of the specimen. The displacement at fracture (displacement at FR) was also recorded.

#### Tear strength test

Unnicked angle-shaped specimens formed according to JIS K6252: 2004 were used for the tear strength test (Fig. 1). The specimens were cut from the original sheet using an angle-shape cutter. Thirty specimens of each material were prepared, and assigned into three groups in the same manner as for the delamination test. After storage, the thickness of the specimen was measured using a digital micrometer and it was subjected to the tear test using the universal test machine at a cross-head speed of 500 mm/min. Changes of load and displacement until the specimen fractured were recorded. The load/specimen thickness and displacement at the fracture were registered as the tear strength and tear displacement, respectively.

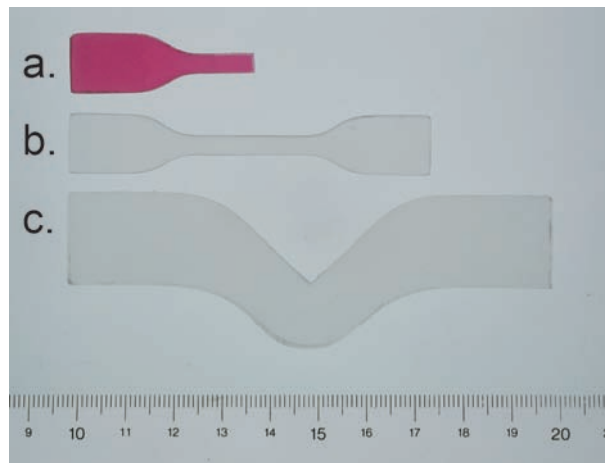


Fig. 1 Specimens used. a: delamination test, b: water sorption, c: tear strength test.

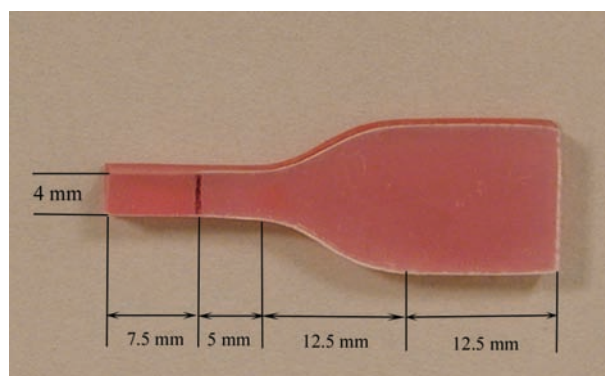


Fig. 2 Dimensions of the specimens for the delamination test (mm). The only left parallel portion of 7.5 mm was laminated.

#### Water sorption and solubility

Water sorption and solubility of the dumbbell-shaped specimens were measured (Fig. 1). Ten specimens were prepared for each material using the above-mentioned dumbbell-shaped cutter. The weight of each specimen after storage in a desiccator containing freshly dried silica gel was measured until the change of weight was less than 0.2 mg/day with a precise balance (Mettler Toledo AG245, Greifensee, Switzerland; minimum reading 0.1 mg), and recorded as a constant mass ( $m_0$ ). Then specimens were stored in the above-mentioned conditions in water or in 0.2 MPa water. After 4-week storage, specimens were removed from the water with a pair of polymer-coated tweezers, wiped with a clean dry paper towel until free from visible moisture, waved in the air for 15 s, and weighed at 60 s after removal from the water. Results were recorded as  $m_1$ . After

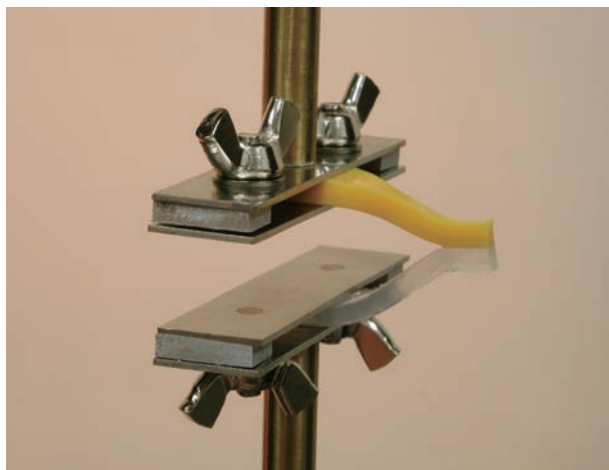


Fig. 3 Delamination test was carried out using a universal test machine with a special jig to grip the specimen.

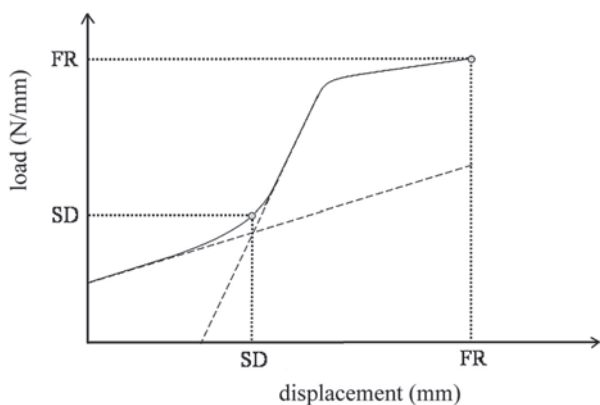


Fig. 4 Typical load-displacement curve of delamination. SD: the point at the start of delamination, FR: fracture point

$m_1$  measurement, the weight of each specimen was remeasured until it reached a constant mass in the desiccator. The weight of the reconditioned specimen was recorded as  $m_2$ .

Water sorption after 4-week storage (WS) was calculated in micrograms from the following equation:

$$WS = m_1 - m_2$$

Solubility,  $SB$ , leaching out during immersion, was expressed in micrograms and calculated for each specimen using the following equation:

$$SB = m_0 - m_2$$

#### Statistical analysis

The bonding strength and the displacement at SD and FR of the delamination test and the tear strength were statistically analyzed with 3-way analysis of variance (ANOVA) and Tukey's post-hoc test ( $p < 0.05$ ) using statistical software (JMP IN 5.1, SAS Japan, Tokyo). The water absorption and solubility were analyzed with 2-way ANOVA.

## RESULTS

There were no obvious changes of the specimens after storage that could be recognized by the naked eye.

#### Delamination test

Bonding strengths (BS) and displacements are summarized in Table 1.

Regarding BS at the start of delamination (SD), the storage condition and material had significant effects, but the other factors did not. BS at SD stored in air, 5.27 N/mm, was significantly greater than that in water, 4.50 N/mm, and in 0.2 MPa water, 4.36 N/mm. The BS at SD of EV, 5.46 N/mm, was significantly greater than that of PO, 3.96 N/mm.

Regarding displacement at SD, there was a significant difference between the materials. The value

Table 1 Results of the delamination test

		in air		in water		in 0.2MPa water	
		PO	EV	PO	EV	PO	EV
BS at SD/ N/mm	1 week	4.50 (0.48)	6.35 (1.20)	4.12 (0.25)	5.21 (0.79)	3.79 (0.43)	5.25 (1.22)
	4 weeks	4.21 (0.28)	6.03 (0.68)	3.64 (0.57)	5.04 (0.81)	3.53 (1.05)	4.87 (0.38)
Displacement at SD / mm	1 week	19.1 (0.5)	18.4 (1.3)	19.2 (0.5)	17.9 (0.9)	18.5 (1.1)	17.4 (1.3)
	4 weeks	19.7 (1.1)	18.3 (1.2)	18.8 (1.4)	18.4 (1.1)	19.6 (1.8)	18.1 (1.8)
BS at FR/ N/mm	1 week	8.33 (1.47)	8.47 (0.70)	6.78 (0.10)	7.36 (1.50)	7.65 (0.61)	6.11 (1.90)
	4 weeks	7.29 (0.84)	7.36 (0.46)	7.34 (0.54)	6.73 (1.77)	7.14 (0.50)	6.37 (1.66)
Displacement at FR / mm	1 week	142.0 (22.9)	65.7 (9.9)	100.4 (14.6)	61.4 (7.0)	131.3 (12.6)	49.2 (7.7)
	4 weeks	138.5 (33.8)	58.0 (3.4)	133.2 (32.4)	60.2 (20.1)	124.6 (21.9)	56.3 (10.6)

mean (s.d),  $n=5$

BS: Bond strength, SD: the point at the start of delamination, FR: fracture point

Table 2 Results for the fracture pattern of the delamination test (interfacial fracture/cohesive fracture)

	PO			EV		
	in air	in water	in 0.2 MPa water	in air	in water	in 0.2 MPa water
1 week	3/2	5/0	4/1	5/0	5/0	5/0
4 weeks	3/2	2/3	4/1	5/0	5/0	5/0

n=5

Table 3 Results of the tear test

		in air		in water		in 0.2 MPa water	
		PO	EV	PO	EV	PO	EV
Tear strength N/mm	1 week	53.0 (2.0)	58.9 (1.3)	49.0 (1.0)	52.3 (1.8)	48.7 (0.4)	51.7 (3.0)
	4 weeks	52.1 (0.4)	55.8 (1.0)	49.8 (0.5)	55.7 (0.7)	50.5 (0.7)	53.7 (3.0)
Displacement mm	1 week	152.7 (11.0)	128.2 (22.0)	149.7 (5.6)	127.8 (22.8)	147.0 (4.3)	125.0 (18.4)
	4 weeks	151.0 (4.8)	124.8 (18.7)	154.2 (9.4)	135.2 (8.1)	162.8 (7.1)	128.5 (12.6)

mean (s.d), n=5

Table 4 Results for water sorption and solubility

	in water				in 0.2 MPa water			
	PO		EV		PO		EV	
WS (mg)	0.1	(0.2)	3.9	(0.6)	0.2	(0.2)	6.0	(2.1)
SB (mg)	0.1	(0.2)	0.2	(0.1)	-0.1	(0.1)	-0.1	(0.2)

mean (s.d), n=5

WS: water sorption after 4 weeks, SB: water solubility

for PO, 19.2 mm, was significantly greater than that for EV, 18.6 mm. The other factors and their interactions were not significantly different.

BS at FR showed significant differences among the storage conditions as for BS at SD. BS at FR for materials stored in air, 7.86 N/mm, was significantly greater than that for those stored in water, 7.05 N/mm and in 0.2 MPa water, 6.82 N/mm. The other factors and their interactions were not significantly different.

Statistical analysis of the displacement at FR showed the same results as that at SD. Displacement at FR of PO, 128.3 mm, was significantly greater than that of EV, 58.4 mm. The other factors and their interactions were not significantly different.

The delaminated surfaces are classified in Table 2. All delaminated EV surfaces showed interfacial fracture, and one-third of delaminated surfaces of PO exhibited cohesive failure.

#### Tear strength test

All specimens after the tear strength test were broken at the center portion. Tear strength and tear displacement are presented in Table 3. Regarding tear strength, 3-way ANOVA revealed that the storage condition, material, and the interaction of the storage condition and storage period significantly affected the results of the test. The estimated tear strength in air,

54.9 N/mm, was significantly greater than that in water, 51.7 N/mm, and that in 0.2 MPa water, 51.2 N/mm. The estimated tear strength of EV, 54.7 N/mm, was significantly greater than that of PO, 50.5 N/mm. The estimated tear strength in air after 1 week was significantly greater than that after 4 weeks; however, the estimated tear strength in 0.2 MPa water after 1 week was significantly smaller than that after 4 weeks.

As for tear displacement, only the material significantly influenced the results. The tear displacement of PO, 152.9 mm, was significantly greater than that of EV, 128.3 mm.

#### Water sorption and solubility

The results for water sorption (WS) and solubility (SB) are shown in Table 4. Two-way ANOVA of WS revealed that the storage condition and material were significant factors affecting water sorption but that their interaction was not. The estimated WS in 0.2 MPa water, 3.1 mg, was significantly greater than that in water, 2.0 mg; the estimated WS of EV, 5.0 mg, was greater than that of PO, 0.1 mg.

With respect to the SB, only the storage condition was a significant factor according to 2-way ANOVA. The estimated values of SB in water, 0.15 mg, was significantly greater than that in 0.2 MPa water, -0.06 mg.

## DISCUSSION

The TMD problem related to the mouthpiece for divers has been reported more often for beginners than for experts<sup>13</sup>. Moreover, these TMD problems of the beginner diver have been reported to be improved when a custom-made mouthpiece for scuba diving is used<sup>19</sup>. Therefore, the present study was conducted for diving conditions of beginner divers. According to the recommendations of organizations such as PADI and SSI, which issue certification cards for the Japanese association of scuba divers, the maximum depth of recreation for entry-level scuba divers should be less than 18m. Specimens were stored in 37°C water and in 37°C water under 0.2 MPa pressure to simulate the oral cavity situation and underwater situation (approximately 20 m from the sea surface), respectively. The storage periods selected were 1 week and 4 weeks. If a recreation diver dives 20 m deep twice a week for 1 hour each time, 1-week and 4-week storage could be considered to be 1.6- and 5.4-year usage of a mouthpiece for diving, respectively. However, actual mouthpieces are subjected to repeated pressure changes and repeated dry and wet stresses. These factors may reduce the durability of lamination and further research will be required to clarify them.

Bonding behavior of laminated thermoforming materials has been evaluated using several test methods such as the T-peel, 180° peel, 90° peel, and floating-roller methods. However, the T-shape shear test has been one of the most popular test methods and the bond strength at the fracture has been discussed<sup>16,17</sup>. The load-displacement curve during the delamination test showed an S-shape (Fig. 4). The delamination started when the load rapidly increased. The load at the start of delamination is more important than the load at the final fracture. Consequently, not only the load at the final fracture but also that at the start of delamination were analyzed in the present study. These loads were designated 'BS at SD' and 'BS at FR', respectively. BS at SD of EV was significantly greater than that of PO, which suggests that the EV mouthpiece was more resistant to delamination than that made from PO. However, BS at FR was not significantly different regardless of the material used. Previous studies reported that BSs at FR were 12.7-14.4 N/mm<sup>16</sup> for PO, and 7.4 N/mm<sup>16</sup> and 1.46-5.4 N<sup>17</sup> for ethylene-vinyl acetate copolymer materials. Regarding the BS at FR of PO, the previously reported values were different from the values obtained in the present study<sup>17</sup>. This was due to the different specimen preparation. The fracture pattern after the delamination test of EV was interfacial fracture; therefore, the bonding strength of EV could be improved if the laminate conditions were changed. One-third of the PO fracture pattern was cohesive fracture, which suggested sufficient adhesion of the two sheets. The ratios of BS at SD to BS at FR for PO were from 49 to 61%, and smaller than those for EV. Moreover, the displacements at both SD and FR of PO

were greater than those of EV. These results suggested that, compared with EV, PO could be easily deformed and elongated before and after the start of delamination.

Mechanical properties of mouth guard materials were evaluated by a tensile test and tear test. When the tensile test of a dumbbell-shaped mouth guard specimen material without a notch is performed, the specimen is sometimes pulled out of the grips due to great deformation during the test. Therefore, the tear test was used in the present study. With regard to storage conditions, the tear strength and BS at SD and FR in air were greater than those in water and 0.2 MPa water. Moreover, water sorption, even though slight, was observed after storage in water and 0.2 MPa water regardless of the material. This is why the BS and tear strength in water and 0.2 MPa water were significantly smaller than that in air.

The water storage period did not significantly influence the material properties examined in the present study. Regarding the effect of water immersion, the bonding strength of the EV material was not influenced by 23 or 37°C water immersion for 1 month<sup>17</sup>. The ratios of the BS at SD of PO in 0.2 MPa water to that in air were 84.2% for 1w and 83.9% for 4w; those of EV were 82.7% for 1w and 80.7% for 4w. These ratios showed a tendency to decrease with longer storage; however, the decreases were not large. These results suggest that BS might not decrease greatly after a longer period of storage.

The main constituents of mouthpieces for scuba diving are silicone-rubber materials according to the manufacturers. However, physical and mechanical properties of these materials have not been widely reported. The tear strength of polyolefin for mouthguard materials have been reported 27.6-65.5 N/mm (28.2-66.8 kgf/cm)<sup>15</sup> and that of ethylene-vinyl acetate copolymer has been reported to be 47.1 N/mm (48 kgf/cm)<sup>15</sup>. The tear strength of silicone-rubber materials for maxillofacial prostheses has been reported to be 4.0-35.5 N/mm (4.1-36.2 kgf/cm)<sup>20</sup>, and those for impression materials to be 1.6-5.4 N/mm (1.6-5.5 kgf/cm). The tear strengths of PO and EV in 0.2 MPa water were 48.7-53.7 N/mm, which were greater than those above<sup>15</sup>. Though there is no clear required value for bonding strength for the scuba-diving mouthpiece, the custom diving mouthpiece fabricated using the same method as in the present study shows adequate bonding behavior. Therefore, the obtained BS at SD and FR of EV and PO might be sufficient to withstand deformation during usage if an adequate area is laminated. Thus, both PO and EV can be employed for a custom diving mouthpiece.

In summary, the null hypothesis that the bonding strengths of PO and EV did not decrease after underwater condition storage was rejected. However, the bonding strength at the start of delamination after underwater storage ranged from 3.5 to 5.2 N/mm, which was more than 4/5 of that in air. Further research is necessary to determine whether these

values are sufficient for durability of the scuba-diving mouthpiece. Moreover, the test storage conditions in the vitro present study were only static. More dynamic storage conditions simulating occlusal force, the stress of waves, pressure changes or repeated dry and wet stresses should be considered for the actual usage of the scuba diving mouthpiece. These tests should be conducted in the future.

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