Influence of Molecular Weight of PMMA in PMMA/MMA-TBB Resin on Durability of Adhesion to Titanium against Thermal Stress in Water

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The present study examined the effect of the molecular weight of poly(methyl methacrylate) (PMMA) used in PMMA/MMA-tributylborane (TBB) resin cement on the durability of adhesion to titanium against repeated thermal stress in water. PMMA beads with the same diameter and molecular weights of 1427, 239, 116, 78, and 66 ($\times 10^3$) were used. Titanium disks bonded to stainless steel or acrylic rods with the PMMA/MMA-TBB resin were subjected to a thermal cycling test (500 and 2,000 cycles) in water followed by tensile testing. Change in molecular weight of the resin cements collected after thermocycling and tensile testing was examined using size exclusion chromatography (SEC). The acrylic specimens exhibited a significant decrease in post-thermocycling bond strength as compared to the stainless steel specimens. It was also found that the molecular weight of PMMA powder in PMMA/MMA-TBB resin had little influence on adhesion durability to titanium. In terms of the molecular weight of resin cements, they decreased and then increased after 500 and 2,000 cycles respectively.

Key words : Metal bonding, Molecular weight of PMMA, Durability

INTRODUCTION

Recent advances in adhesive restorative dentistry have generated considerable interest in resin-bonded metal prostheses. However, since debonding is a frequently encountered problem[1,2], it is apparent that bonding between metals and resin cements needs further improvement.

The bond strength of a resin to a metal and its durability depend on factors such as type of metal, type of material to be bonded with metal, surface treatment of metal, and the luting resin cement. For the purpose of enhancing bond strength and durability, many researches[3−11] have embarked on a two-pronged approach: improve the metal surface properties by mechanical retention or surface preparation, as well as develop adhesion promoting monomers capable of bonding chemically to metals. Concerning chemical surface treatment agents for dental metals — especially with precious metals, its importance in metal-resin bonding has been revealed through the recent, extensive studies by Kadoma[6,7]. As for adhesion promoting monomers, they are also applied as a coupling agent between metal filler particles and the resin matrix in metal-resin composites[12,13].

On the other hand, little attention has been paid to the effect of luting resins on adhesion durability.

As a result, only limited information is available[14−21]. Based on the evaluation results[15−21] thus far, methyl methacrylate (MMA)-based resin cement was reported to exhibit superior durability as compared with the one that was based on dimethacrylate.

The durability of MMA-based cements has mostly been studied using a commercially available PMMA/MMA-tributylborane (TBB) resin (Super-Bond C&B). In experimental MMA/TBB-based resin cements, it was reported that the durability of adhesion to metals varied by the cement properties[16,22]. In the mean time, it was found that cement properties — such as setting time, working time, and film thickness — were influenced by molecular weight, molecular weight distribution, as well as particle size and shape of the PMMA powder used in PMMA/MMA-TBB resin cement[23,24]. However, to date, no study has been made regarding the effect of molecular weight of PMMA powder on the durability of adhesion to metals.

Therefore, the aims of this study were to examine: (1) the effect of molecular weight of PMMA in PMMA/MMA-TBB resin on the durability of adhesion to titanium against repeated thermal stress in water, and (2) the change in molecular weight of resin cement before and after the thermal stressing. The second objective was set because it was suggested

that the molecular weight of PMMA/MMA-TBB resin varied during the postpolymerization period[25−27]. For convenience reason, this experiment was conducted using materials employed in the previous studies of our research group[22,24].

MATERIALS AND METHODS

Materials

Titanium (JIS Class 2, Toho Titanium Co., Tokyo, Japan) was used as the metal in this study. Two kinds of rod, stainless steel rod (6 mm in diameter) and acrylic rod (8 mm in diameter) were employed as adherends. Both rods were 30 mm in length, with a hole at one end through which a metal pin could be inserted to attach it to a testing machine.

MMA (Mitsubishi Rayon Co., Tokyo, Japan), stabilized with 50 ppm of hydroquinone, was used without further purification. TBB, the catalyst used in a commercial MMA-TBB resin (Super-Bond C&B, Sun Medical Co., Shiga, Japan), was also employed. For the metal primer, an acetone solution of 0.5% 10-methacryloyloxydecyl dihydrogen phosphate (MDP) was used for surface treatment of titanium and stainless steel rod.

PMMA beads (MB-8C, Sekisui Co., Osaka, Japan), with a mean particle diameter of 7μm and with different molecular weights, were used after they were modified by γ-irradiation from ^{60}Co source at 30 kGy (dose rate of 10 kGy/hr) at 25℃. Details of the PMMA powders used were given in a previous report[24]. As for the codes and molecular weights of PMMA used in this study, they are listed in Table 1. The powder codes were likewise used for designating each resin in this paper.

As for the resin, its formulation was as follows: powder was PMMA, liquid was MMA added with 8% TBB (which was added to MMA just before mixing), and a powder/liquid ratio of 1.6:1.

Specimen preparation

Titanium disk specimens (15 mm in diameter by 8 mm thick) were cut from a rod. They were then ground with 800-grit silicone carbide paper, and after which cleaned ultrasonically in acetone for five minutes. For both the titanium and stainless steel rod surfaces, MDP solution was brushed onto them. Then, the specimens were rinsed with acetone for five minutes and air-dried.

To define the resin adhesion area, a piece of 50-μm thick masking tape with a circular hole (3 mm diameter for the stainless steel rod and 5 mm diameter for the acrylic one) was placed on the bonding surface of each titanium disk. Finally, the mixed resin was applied to the bonding surface and affixed to either a stainless steel rod or an acrylic rod.

Tensile bond strength measurement

After bonding, test specimens were left undisturbed for one hour in air at room temperature. Then, the specimens were immersed in water at 37℃ for 24 hours. This state was defined as thermocycle 0. Following which, in a thermocycling machine (Rika Kogyo Co., Hachioji, Tokyo, Japan), the specimens were thermocycled 500 and 2,000 times between water baths held at 4 and 60℃ with a dwelling time of one minute per bath and an exchange time of three seconds between baths. Each specimen was then tested for tensile strength on a universal testing machine (Autograph AGS 1000A, Shimadzu Co., Kyoto, Japan) at a cross-head speed of 2 mm/min. Ten specimens for each resin were prepared and subjected to the same procedure described above. Means and standard deviations were calculated thereof.

Size exclusion chromatography (SEC)

Three specimens each from B0, B60, and B120 groups were randomly selected to be examined for change in molecular weight of the resin after thermocycling. After tensile testing, a resin sample that adhered to the adhesion area was scraped off the titanium and rod surfaces of the fractured specimens using a sharp blade. The retrieved resin sample (which was prefixed with R before each resin like RB0, RB60, and RB120) was then dissolved in tetrahydrofuran (THF) (Kanto Chemical Co., Tokyo, Japan). SEC analysis of the resin was performed on a GPC system (SC-8020, Tosoh, Tokyo, Japan) using two GPC columns (Asahipak GSM-700 7E, 7.6×250 mm, Showa Denko Co., Tokyo, Japan) at 40℃ and THF as the eluent at a flow rate of 0.8 ml/min. Weight average molecular weight (Mw) was calculated using the calibration data of polystyrene standards.

Statistical analysis

Data were subjected to analyses of variance. Depend-

Table 1 Molecular weight of PMMA powder used

Powder code	Molecular weight ($\times 10^3$)		Mw/Mn
	Weight average (Mw)	Number average (Mn)	
B0	1427	456	3.2
B30	239	108	2.2
B60	116	59	2.0
B90	78	38	2.0
B120	66	31	2.1

ing on the ANOVA results, the means were compared by post hoc Fisher's PLSD multiple comparison test at a significance level of 0.05 and grouped. These analyses were performed with a commercial software for statistics (StatView-J 5.0, SAS Institute Inc., Cary, NC, USA).

RESULTS

Table 2 shows the means and standard deviations of tensile bond strength calculated for each group of stainless steel (SS) rod and acrylic (AC) rod specimens before and after the thermal cycling. For SS group, the mean bond strengths ranged from 17.6 to 19.6 MPa, 15.3 to 17.4 MPa, and 14.4 to 17.5 MPa at 0, 500, and 2,000 cycles respectively. For AC group, the mean bond strengths ranged from 11.3 to 16.2 MPa, 7.5 to 9.8 MPa, and 4.9 to 7.6 MPa at 0, 500, and 2,000 cycles respectively.

In terms of failure mode, gross examination of the surface of debonded specimens yielded the following results. For SS specimens, the failure mode was either cohesive failure of the cement or a mixture of cohesive and adhesive failures. However, for AC specimens, failure mode was either mixed or adhesive failure. Furthermore, the frequency of adhesive failure increased with the number of thermocycles.

A three-way ANOVA test was carried out to determine the effects of resin cement (or molecular weight of PMMA powder), thermal cycling, and adherend (SS and AC rods) on bond strength. The results showed that: (1) the influence of thermal cycling or adherend was significant ($p < 0.0001$ and $p < 0.0001$, respectively), but that of resin cement was insignificant ($p = 0.2721$); (2) interaction between the two factors of thermal cycling and adherend was significant ($p < 0.0001$), but interaction between the two factors of resin cement and thermal cycling

($p = 0.5571$) and that of resin cement and adherend ($p = 0.3028$) were insignificant. Likewise, interaction of these three factors was insignificant ($p = 0.9257$).

There was significant interaction between thermal cycling and adherend. On this note, it was difficult to directly compare the effect of thermal cycling exclusively on its own. Therefore, a two-way ANOVA test was carried out for each adherend to determine the effects of resin cement and thermal cycling. For SS group, the effect of thermal cycling was significant ($p = 0.0084$) but that of resin cement was insignificant ($p = 0.6520$). Likewise, interaction between the two factors was insignificant ($p = 0.9320$). Bond strength decreased significantly from 18.5 MPa at 0 cycle to 16.6 MPa after 500 cycles ($p = 0.0236$), but remained statistically unchanged between 500 and 2,000 cycles (15.9 MPa) ($p = 0.4140$).

For AC group, the effect of thermal cycling was significant ($p < 0.0001$). However, the effect of resin cement was insignificant ($p = 0.0701$), and likewise the interaction between the two factors ($p = 0.4469$). Bond strength decreased significantly from 14.0 MPa at 0 cycle to 8.5 MPa after 500 cycles ($p < 0.0001$), and decreased further with significant difference to 6.1 MPa after 2,000 cycles ($p = 0.0010$).

Fig. 1 presents the change of molecular weight distribution curve with thermal cycling for RB60 resin retrieved from the SS specimens. Fig. 1(a) shows that the curve was a two-peak pattern before thermocycling. The curve changed into a one-peak pattern at 500 thermal cycles (Fig. 1(b)) and returned to two-peak pattern again at 2,000 cycles (Fig. 1(c)). The changes in the curve for RB0 and RB120 resins collected from the SS specimens were as those described above. In contrast, for all samples collected from the AC specimens, two-peak pattern always appeared with little change in the molecular weight distribution curve before and after thermocycling. In

Table 2 Effect of resin and thermocycling on bond strength between titanium and stainless steel or acrylic rod (number of specimens: 10)

Resin	Bond strength, Mean (SD) in MPa					
	Stainless steel (SS) rod			Acrylic (AC) rod		
	Number of thermocycles			Number of thermocycles		
	0	500	2,000	0	500	2,000
B0	18.7 (4.1)	17.4 (5.0)	14.4 (5.4)	13.4 (3.4)	8.8 (4.0)	4.9 (1.4)
B30	18.8 (4.1)	16.8 (4.3)	16.4 (4.9)	14.8 (4.9)	7.5 (3.9)	5.1 (2.1)
B60	19.6 (4.0)	16.6 (4.3)	17.5 (3.5)	14.1 (3.5)	9.8 (4.3)	6.8 (3.9)
B90	18.0 (4.9)	15.3 (3.6)	15.7 (5.0)	16.2 (5.9)	8.7 (2.7)	7.7 (2.5)
B120	17.6 (3.8)	16.9 (4.4)	15.4 (3.7)	11.3 (3.9)	7.9 (2.5)	6.2 (1.3)

Statistical analysis results: (1) For SS group, resin type had no significant effect on bond strength. But, thermocycling had a significant effect on bond strength, where bond strength decreased significantly between 0 and 500 cycles, but not so between 500 and 2,000 cycles; (2) For AC group, resin type likewise had no significant effect on bond strength. But, thermocycling had a significant effect on bond strength, where bond strength decreased significantly between 0 and 500 cycles, as well as between 500 and 2,000 cycles.

addition, molecular weight distribution curves for the PMMA powders used were of a one-peak pattern similar to Fig. 1(b), as given in a previous paper[24].

Table 3 presents the comparison in weight average molecular weight among the collected RB0, RB60, and RB120 resins before and after thermocycling. A two-way ANOVA test was carried out to determine the effects of adherend and thermal cycling on the molecular weight for each resin. The results showed that the influences of adherend and thermal cycling were highly significant, and likewise the interaction between these two factors ($p \leq 0.0001-0.0067$). Due to the significant interaction, a one-way ANOVA test was carried out to compare: (1) the effect of thermal cycling on each resin and adherend; and (2) the effect of adherend on each resin and thermal cycling.

Results for (1) were as follows. For SS group, the p values for RB0, RB60, and RB120 were 0.0033, 0.0003, and 0.0001 respectively. For AC group, the p values were 0.4981, 0.1313, and 0.0018 respectively. In SS group, the molecular weight of the three resins decreased significantly at 500 cycles, but was statistically unchanged between 0 and 2,000 cycles. In contrast, in AC group, there were no significant differences in molecular weight for the three resins before and after thermal cycling, except for one case for RB120 resin at 2,000 cycles — at which the molecular weight increased significantly.

Results for (2) were as follows. Difference between SS and AC groups was insignificant before thermal cycling for the three resins ($p=0.6668-$ 0.9654) and at 2,000 cycles for two resins ($p=0.1207$ and 0.5148). However, difference between SS and AC groups was significant at 500 cycles for the three resins ($p=0.0003-0.0100$) and at 2,000 cycles for B120 ($p=0.0072$).

DISCUSSION

In this study, the effect of molecular weight of PMMA powder used in PMMA/MMA-TBB resin cement on the durability of adhesion to titanium was examined using two adherends (SS and AC). This was because adherend was reported to have a significant effect on the durability of adhesion to metals[15,22].

It was found that the molecular weight of PMMA powder had no significant influence on durability irrespective of the adherend. The reason for this finding was that the molecular weight of cured resin for all the powders was high enough to guarantee mechanical strength, based on a published report[28] that molecular weight of PMMA exceeding 10^5 had little influence on mechanical properties. In addition, a similar finding has been reported previously that bond strength of MMA-TBB resin to dentin was independent of the molecular weight of PMMA powders used for the resin[24].

The adherend, however, had significant effect on durability, as described previously. Compared to SS group, AC group demonstrated a more significant decrease in post-thermocycling bond strength. The decrease in bond strength after thermal cycling was most probably associated with the stress induced at

Table 3 Comparison of the molecular weight of resin retrieved from bonded specimens before and after thermocycling (number of samples: 3)

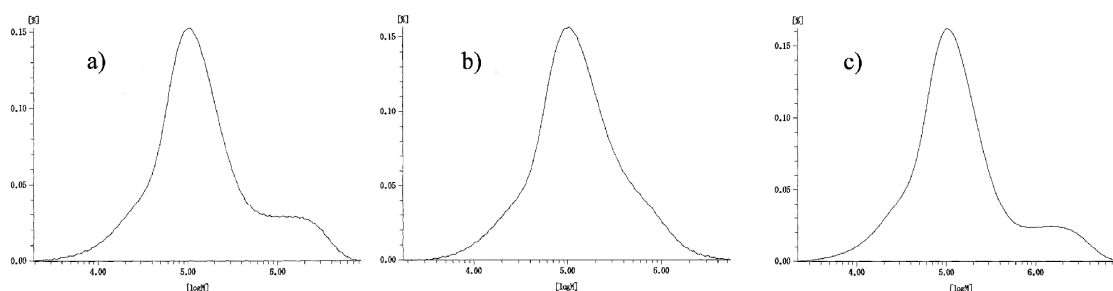| Retrieved Resin	Weight average molecular weight (Mw) ($\times 10^3$), Mean (SD)					
	Stainless steel (SS) rod			Acrylic (AC) rod		
	Number of thermocycles			Number of thermocycles		
	0	500	2,000	0	500	2,000
RB0	1922 (64)	1451 (128)	1843 (113)	1919 (108)	1838 (69)	1896 (60)
RB60	406 (15)	224 (23)	396 (37)	413 (20)	410 (15)	461 (44)
RB120	348 (17)	213 (10)	329 (22)	355 (17)	317 (23)	487 (50)

Fig. 1 Change of molecular weight distribution curve for RB60 resins retrieved from stainless steel rod specimens: (a) before thermal cycling; (b) after 500 cycles; and (c) after 2,000 cycles.

the metal-resin interface. A thermal stress induced at a metal-PMMA adhesion interface was reported to depend on the PMMA resin layer thickness, where the stress increased with increase in thickness such that total interfacial failure occurred when the resin was thicker than 0.55 mm[29]. By considering these findings, it could be said that the stress imposed by thermal cycling on the metal-resin interface was more severe for the AC group than for the SS group. This was most probably because the effective cement thickness was considerably thicker in AC group. For SS group, it could be assumed that the thickness was about 50 μm (i.e., thickness of the masking tape used). However, for AC group, the effective resin thickness should be assumed to be far beyond 50 μm. This was because the cement was actually integrated into the acrylic rod. These speculations were further reinforced by the obtained failure mode results: predominantly cohesive failure for SS group, but adhesive for AC group.

Bond strength for AC group was significantly lower than that of SS group even before thermocycling. The reason for this could not be well explained at this juncture, but we believed that it could be due to the partial absorption of MMA monomer into the acrylic rod, thus affecting cement curing and thereby the bond strength too.

Molecular weight of the resin cements retrieved from the debonded specimens after thermal cycling varied in an unexpected manner. In all the six resins shown in Fig. 2, molecular weight tended to decrease after 500 cycles and then increased after 2,000 cycles. This change was significant for SS group but insignificant for AC group, although the molecular weight of the cements was the same for both SS and AC groups before thermal cycling. These changes in the molecular weight of the cements, however, had little direct correlation with the decrease in bond strength.

These unexpected findings could partly be explained based on our previous findings and discussion regarding PMMA/MMA-TBB resin[25,27]:

(1) High molecular weight PMMA was formed first, and then decreased rapidly with time during the course of postpolymerization under a sealed condition;

(2) While stored in water at 37℃ or 90℃ during postpolymerization, the decrease in molecular weight of resin was reduced — suggesting that the presence of water containing oxygen suppressed the decrease in molecular weight of resin, possibly due to oxygen interfering with the action of free radicals; and

(3) Concerning the decrease in molecular weight of resin, it was hypothesized that polymer radicals entrapped within the resin attacked — by chain transfer mechanism — the high molecular weight polymer chains containing TBB moiety, which were already formed by then, thus resulting in reduced molecular weight[27].

Based on (1) above, the decrease in molecular weight of MMA-TBB resin after 500 cycles would neither seem strange nor unusual. However, the re-increase in molecular weight during 500-2,000 cycles was indeed strange and unexpected. As for the significant difference in the extent of molecular weight reduction at 500 cycles between SS and AC groups, it could be explained by (2) above concerning the influence of water containing oxygen. For SS group, the penetration of water into the resin cement and the intake of water by the latter were limited and small. But for AC group, it was a generous intake of water since the predominant failure mode was cohesive and adhesive in nature for SS and AC groups, respectively.

As for the re-increase in molecular weight after 2,000 cycles, the reason still remained unknown at present. Fig. 1 shows clearly that high molecular weight fraction was produced after 2,000 cycles. The thermal cycling process appeared to play an important role in this phenomenon. Although recombination of polymer radicals might have contributed to this change, the involvement of this mechanism remains to be investigated in future.

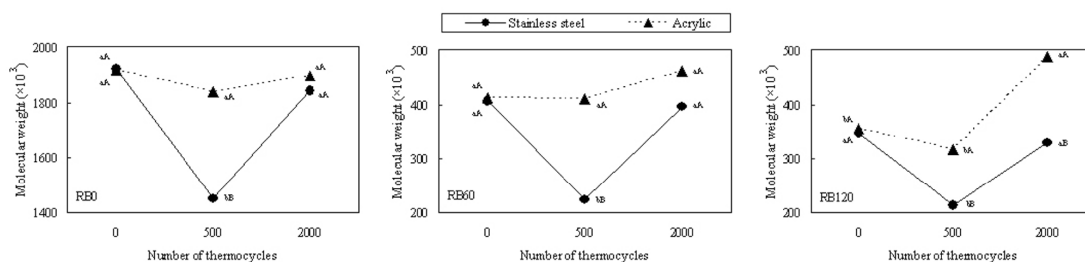This study witnessed the first incidence of a

Fig. 2 Change in molecular weight of resin cements retrieved from bonded specimens after thermal cycling and tensile tests for three resins. Different lower-case letters for stainless steel or acrylic and the upper-case letters for each number of thermocycles near the marks indicate that the mean values are significantly different between the numbers of thermocycles and the adherends, respectively.

strange and unusual molecular weight change during thermal cycling. One could argue, therefore, that this study revealed another interesting new aspect of MMA-TBB resin in addition to its unique characteristics noticed previously[25-28], where residual MMA monomer content in the resin decreased with time at 37℃ to the level in a heat-cured resin and that the molecular weight of resin also decreased with time during the course of postpolymerization.

CONCLUSIONS

Within the limitations of the current study, the following conclusions were drawn:

1. Molecular weight of PMMA powder used in the PMMA/MMA-TBB resin cement had little influence on the durability of adhesion to titanium against thermal stressing in water within the range of molecular weights studied.

2. Bond strength to titanium decreased as the frequency of thermal cycling increased, and the decrease was more significant in the acrylic rod than in the stainless steel rod — where both were used as adherends to titanium.

3. Molecular weight of the cements retrieved from debonded specimens decreased after 500 cycles and then increased after 2,000 cycles.

4. There was little direct correlation between decrease in bond strength and change in the molecular weight of the retrieved cements.

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