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**Evaluation of a newly developed polymethyl methacrylate powder for brush-dip
technique**

Abbreviated title: Evaluation of a PMMA powder

Keywords: bond strength, particle size distribution, polymethyl methacrylate

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Abstract

Purpose: The aim of this study is to evaluate a newly developed polymethyl methacrylate (PMMA) powder.

Methods: The particle size distribution, surface area, and particle shape of both new and traditional powders were compared. The shear bond strength of the resin cement with the new powder to a silver-palladium-copper-gold alloy was determined and compared to that for a cement with the traditional powder. Also, the weight of mixture held by the brush at one time of both powders was also calculated and compared as an index of mixability.

Results: The surface area of the new powder was smaller than that of the traditional powder, while the particles size distributions were similar. The new powder included various-sized spherical particles as well as irregular particles, while the traditional powder consisted of only irregular particles. The new powder showed significantly higher mixability, although its bond strength was not significantly different from that of traditional powder.

Conclusion: The results of this study show that the interminglement of spherical and irregular particles cannot influence the bond strength to the alloy but is helpful to improve the working properties.

1. Introduction

Resin bonded metal restoration offers a conservative or aesthetic treatment modality. Various bonding techniques have been reported in an attempt to increase and stabilize the mechanical and chemical bond between the luting agent and alloy [1-5]. The development and/or improvement of the luting agent itself is one approach to enhance bond strength.

The 4-methacryloyloxyethyl trimellitate anhydride/methyl methacrylate-tri-*n*-butylborane (4-META/MMA-TBB) chemical adhesive luting agent (Super-Bond C&B, Sun Medical Co. Ltd., Moriyama, Japan) is a self-curable resin cements employed for luting indirect restorations, because of its strong bond strength to enamel [6,7], dentin [8], metal alloy [7,9,10], porcelain [11], and composite materials [12]. 4-META/MMA-TBB has been used extensively for two decades in a wide range of dental applications.

4-META/MMA-TBB cement can be used with either the bulk-mix or the brush-dip technique. The bulk-mix technique involves the addition of the polymer powder directly to the activated liquid (mixture of 4 drops of monomer and 1 drop of TBB), and the brush-dip technique involves the formation of a powder/liquid ball at the tip of a brush by dipping the tip into the activated liquid and then touching it to the powder. According to the manufacturer, the bulk-mix technique is applicable to adhesion of a comparatively wide surface area, while the brush-dip technique is suitable for several small surface areas, although the technician can select the most familiar or favorite technique.

Recently, a new polymethyl methacrylate (PMMA) powder for the brush-dip technique (Super-Bond C&B Brush-dip Polymer, Sun Medical Co. Ltd.: BP) has been developed and marketed. The improvement involved only the polymer powder and not the monomer. The brush-dip technique requires a mastery of skills for its use, because the polymer/liquid ratio is higher and the progress of curing is faster than that of the bulk-mix technique. As stated by the manufacturer, this disadvantage could be overcome with the

new improved BP powder. However, little information is available concerning the performance of the powder.

The properties of 4-META/MMA-TBB cement are reported to be influenced by the molecular weight, molecular weight distribution, particle size, and shape of the powders [13]. Kim et al. stated that the size and molecular weight of PMMA powder in the resin seemed to influence the degree of conversion of the resin and its bond strength to metal [14].

The primary purpose of this study was to evaluate the performance of the resin cement using the newly developed BP powder. The bond strength of the cement to conventional dental metal alloy was examined, in addition to the particle size distribution, surface area of the powder, and mixability of the powder to the liquid monomer. The null hypothesis is that the difference of the PMMA powders has no effect on any experimental results of this study.

2. Materials and methods

2.1 PMMA particle characterization

A BP powder was selected and evaluated in this study. According to the manufacturer information, the powder consists of only PMMA, as with the traditional polymer powder (Super-Bond C&B Polymer, Sun Medical Co. Ltd.).

To characterize the BP, the particle size distribution and Brunauer-Emmett-Teller (BET) specific surface area (m^2/g) were primarily evaluated and compared to those for the traditional powder. The particle size distributions of the two powders were measured using a laser light scattering particle size analyzer (LS13 320, Beckman Coulter Inc., CA, USA). The BET specific surface area of the two powders was determined by the standard N_2 adsorption method at 77.3 K (Quadratorb SI, Quantachrome Instruments, FL, USA; three-point BET method, $0.05 < p/p_0 < 0.30$).

2.2 Scanning electron microscopy (SEM)

Both powders were dispersed on double-sided adhesive tape mounted on scanning electron microscope (SEM) specimen stubs. The powder specimens were then sputtered with osmium and the particles were observed using an SEM (TM-1000, Hitachi High Technologies Co., Tokyo, Japan) operated at 15 kV.

2.3 Shear bond strength

The materials used in this study are summarized in Table 1. An age-hardenable silver-palladium-copper-gold alloy (Castwell M.C.12, GC Corp., Tokyo, Japan) was selected as the substrate material.

A total of 64 disk-shaped specimens (10 mm diameter and 2.5 mm thick) were cast from the alloy according to the manufacturer specifications. All disks were ground flat with a series of silicon-carbide abrasive papers (up to #1000), followed by airborne-particle abrasion with 50 – 70 μm alumina particles (Hi-Aluminas, Shofu Inc., Kyoto, Japan) for 10 s. The supply-side air pressure was 0.3 MPa and the distance of the orifice from the metal surface was approximately 15 mm. The abraded surface was then air-blasted with compressed air. The bonding surface condition was set according to the previous study results [15].

The disks were divided into 2 sets of 32 disks each. Half (32 disks) was left unprimed, and remaining half (32 disks) was primed with a metal conditioner (V-Primer, Sun Medical Co. Ltd., Moriyama, Japan) containing 6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithiol, dithione tautomer (VTD) as a functional monomer. The primer, which was adopted for evaluation the influence of the powders on the bonding durability, was applied separately to the metal surfaces with a sponge pellet.

A piece of double-sided tape with a 5 mm diameter circular hole was positioned on

the surface of each metal specimen to define the bonding area. Both 32 disks were divided into the following two groups of 16 disks according to the cement type: 1) Super-Bond C&B (Sun Medical Co. Ltd.) and 2) a mixture of Super-Bond C&B liquid, Super-Bond C&B initiator, and BP. An acrylic rod (8 mm diameter and 5 mm high) was bonded to each disk specimen using the brush-dip technique. A new disposable brush (Brush Tips (S), Sun Medical Co. Ltd.) was prepared and used for each specimen.

Immediately after bonding procedure, a 5.0 N constant load was applied vertically to the specimens for 30 minutes. After bonding, all the specimens were immersed in water at 37 °C for 24 h; this state was defined as thermocycling 0. The 16 disks in one set were then divided into two groups of 8 specimens; half (8 specimens) were tested for 24 h shear bond strength at thermocycling 0. The remaining specimens (8 specimens) were placed in a thermocycling apparatus (Thermocycling Machine, RKC Instrument Inc., Tokyo, Japan) and cycled between 4 and 60 °C in a water bath with a 1 min dwell time for 10,000 cycles [16].

The specimens were positioned in steel molds, and seated in an ISO/TR 11405 shear testing jig. Shear bond strengths were determined by means of a mechanical testing device (AGS-10kNG, Shimadzu, Kyoto, Japan) at a crosshead speed of 0.5 mm/min. For each set of specimens, the mean shear bond strength and standard deviation (SD) of the 8 specimens were calculated.

The results of both powders for each status were statistically analyzed and compared using the Mann-Whitney's U tests with the value of statistical significance set at $\alpha = 0.05$. All statistical analyses including other experiments were carried out using SPSS[®] Statics 17.0 for Mac[®] OS X (SPSS Japan Inc., Tokyo, Japan).

2.4 Comparison of mixability

The mixability of the liquid (monomer and initiator) and two powders was compared. The disposable brush was first softened with fingers, and the weight of the brush was

measured. The whole of brush part was immersed into the liquid vertically for 1 s, and dipped into a respective powder for 2 s in the same way. After 5 min, the surplus powder around the mixture was removed using compressed air, and the weight of the brush including the mixture was re-measured, so that the weight of the mixture that the brush could hold at one time could be calculated from the difference. The schematic diagrams of the mixability test are shown as Fig. 1.

For each powder, the mean value and SD of 8 specimens were calculated, and the results were analyzed using Mann-Whitney's U tests with the value of statistical significance set at $\alpha = 0.05$.

3. Results

The results shown in Table 2 and Figs. 2 and 3 indicate the two powders had very similar particle size distributions. The mean particle diameters (d_{50}) were approximate, *i.e.*, 37.00 μm for the traditional powder and 39.31 μm for the BP powder. The shapes of the two particle distribution curves (Figs. 2 and 3) were also similar.

The BET surface area results for the two powders are given in Table 2. In contrast to the particle size distribution results, the surface area of the BP powder was significantly smaller (2.10 m^2/g) than that of the traditional powder (3.63 m^2/g).

Figs. 4 and 5 show SEM images of the two powders, with the difference of the PMMA particle composition apparent, although both powders consist of similar-sized PMMA particles. The BP powder included various-sized spherical particles as well as irregular particles, while the traditional powder consisted of only irregular particles.

Table 3 gives the shear bond strength results before and after 10,000 thermocycles. The strengths of the both powders were not statistically different, regardless of the priming and thermocycling status.

Table 4 gives a comparison of the mean weight of mixture that the brush can hold at one time. When compared to the traditional powder, the BP powder showed significantly higher mixability.

4. Discussion

The mechanical and clinical performance of 4-META/MMA-TBB adhesive is widely known, and it is employed for bonding by numerous dentists in daily clinical practice. Even then, the new powder evaluated in this experiment was developed to overcome the disadvantage of inoperability. Considering the mixability results of this study, the handling properties of the new BP powder seem to be an improvement.

The BP powder consists of only PMMA, just as the traditional powder, and the particle size distributions were also similar, as shown in Table 2 and Figs. 2 and 3. However, the SEM images in Figs. 4 and 5 show the difference in these powders. The presence of spherical particles was the most significant difference of the two polymer types. The BET surface area results indicated that the surface area of the BP powder was significantly smaller, because the spherical particles have a minimum surface area for a given volume.

With respect to the composite resin, several studies have been made on the influence of the filler shape. Generally, filler particle size and morphology affect the handling behavior of uncured composites [17]. The addition of spherical silica filler to resin-modified glass-ionomer cements has also been reported to lead to a significant decrease in the summed interfacial gap formation in a Class V cavity [18]. Therefore, it is quite likely that the addition of a spherical filler is related to the flow properties of the materials before curing. The same may be said of PMMA particles in 4-META/MMA-TBB resin. When dentists use the 4-META/MMA-TBB resin with the brush-dip technique, individual differences of the powder/liquid ratio would most likely occur and the ratio is often apt to be higher, because the brush-dip method is technique-sensitive. Therefore, the ratio should be preferably low,

because a higher ratio results in an increased vertical displacement of the cemented prosthesis [19]. The ratio has no effect on the post-curing properties [19], and a higher ratio only worsens the handling properties. Regarding BP powder, it was supposed that the powder-liquid mixture of lower ratio might have been easily provided, since the inclusion of spherical particles improves the flow properties because of their small surface area.

Kosuge [20] blended spherical PMMA particles with the traditional powder of 4-META/MMA-TBB resin and reported that the setting and working times were increased and that the film thickness remained thin over a long period. The results of this study indicated that the liquid (MMA monomer and TBB initiator) could be mixed with the BP powder including spherical PMMA particles more than the traditional powder consisting of irregular particles (Table 4). Accordingly, the combination of irregular and spherical particles is thought to improve the working properties.

The shear bond strengths of both powders were not significantly different, irrespective of the thermocycling or priming status. As has been noted, the powder/liquid ratio of this cement has no effect on the post-curing properties [19]. Above all, in case of the experimenters who are familiar with the brush-dip technique using a traditional powder in routine clinical practice, the handling properties would have little influence on experimental measurements of the shear bond strength, even if the properties of the two powders were significantly different.

Within the limitations of this study, the new BP powder that includes spherical PMMA particles had better mixability than the powder consisting of only irregular particles, although both had very similar size distributions. Even then, it was also proved that the difference of two powders had no effect on the bond strength results to silver-palladium-copper-gold alloy. A further direction of continuing study will be to provide clinical evidence for the results.

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FIGURE LEGENDS

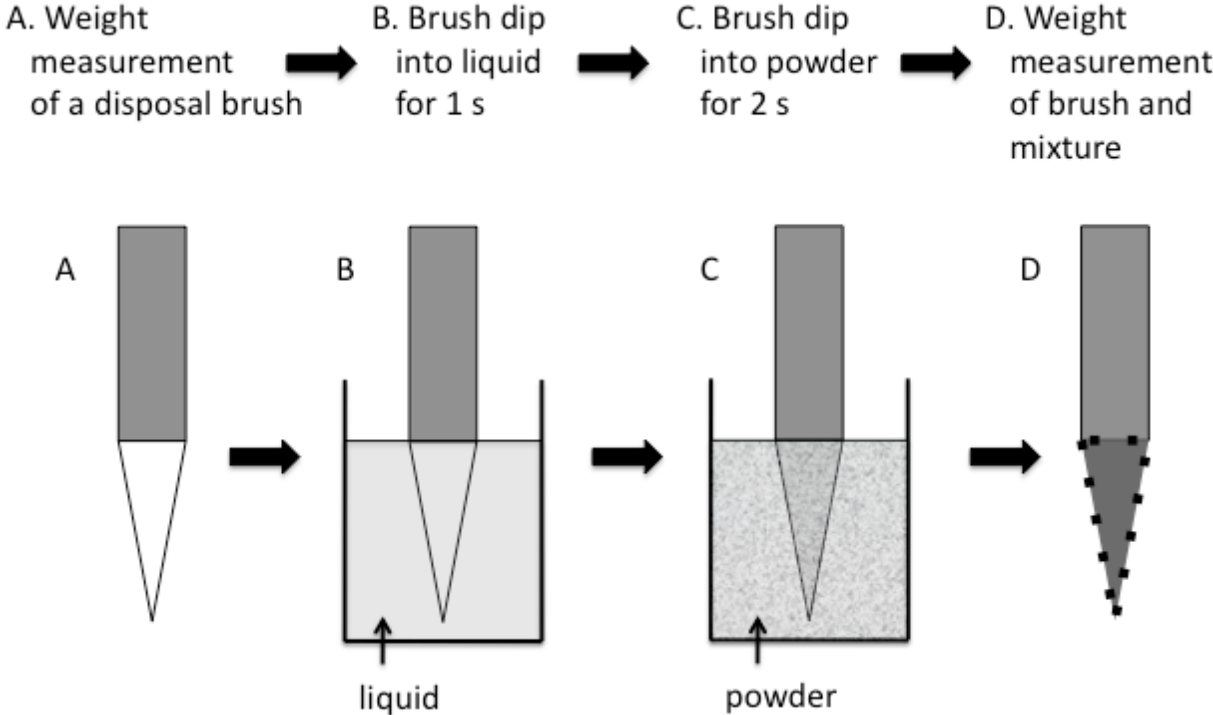


Fig. 1. Schematic diagrams of mixability test.

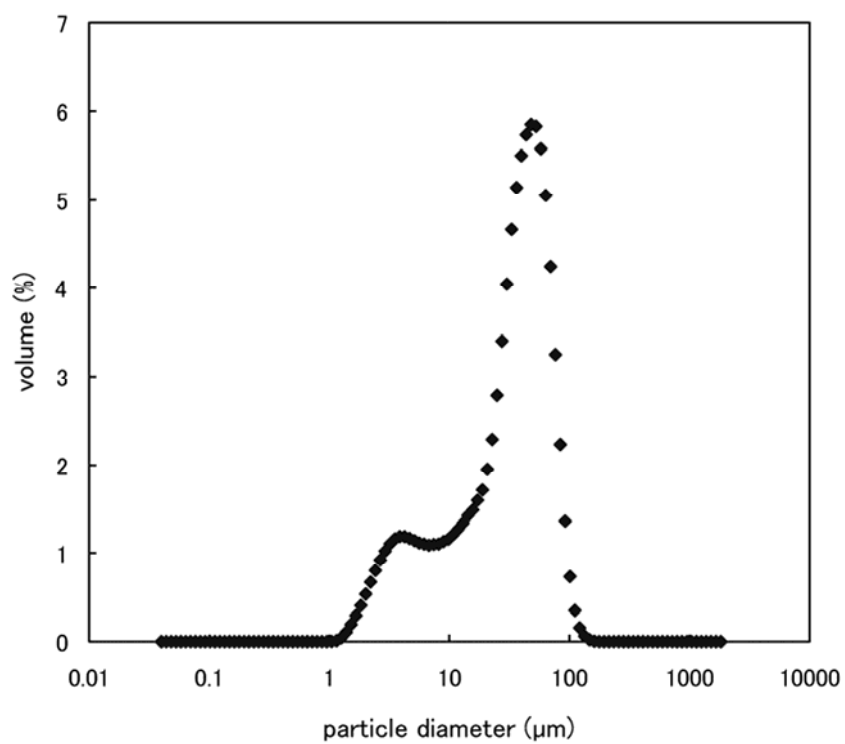


Fig. 2. Particle size distribution of the traditional Super-Bond C&B Polymer.

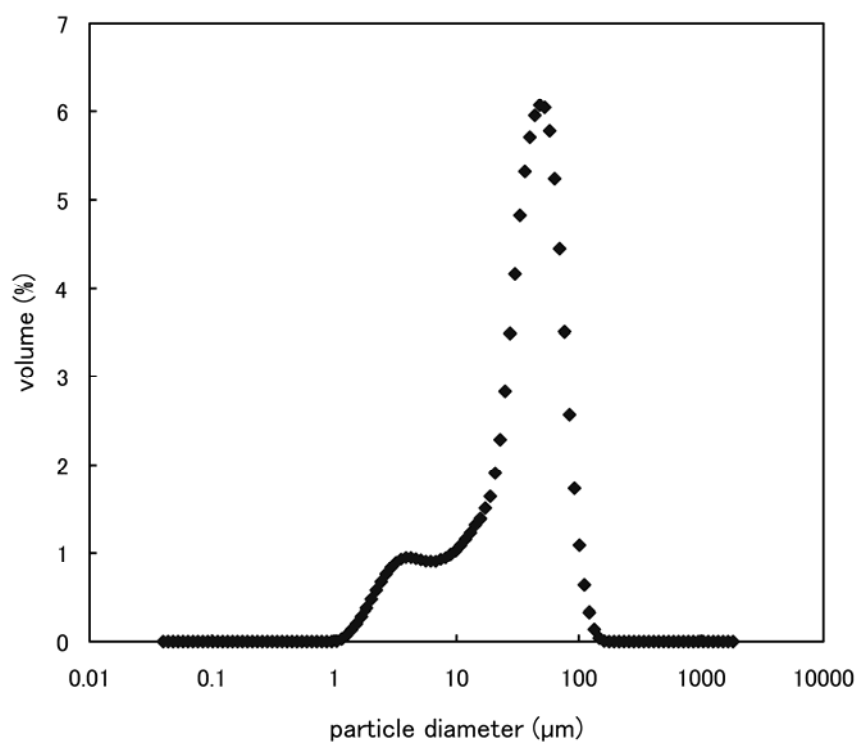


Fig. 3. Particle size distribution of the new Super-Bond C&B Brush-dip Polymer.

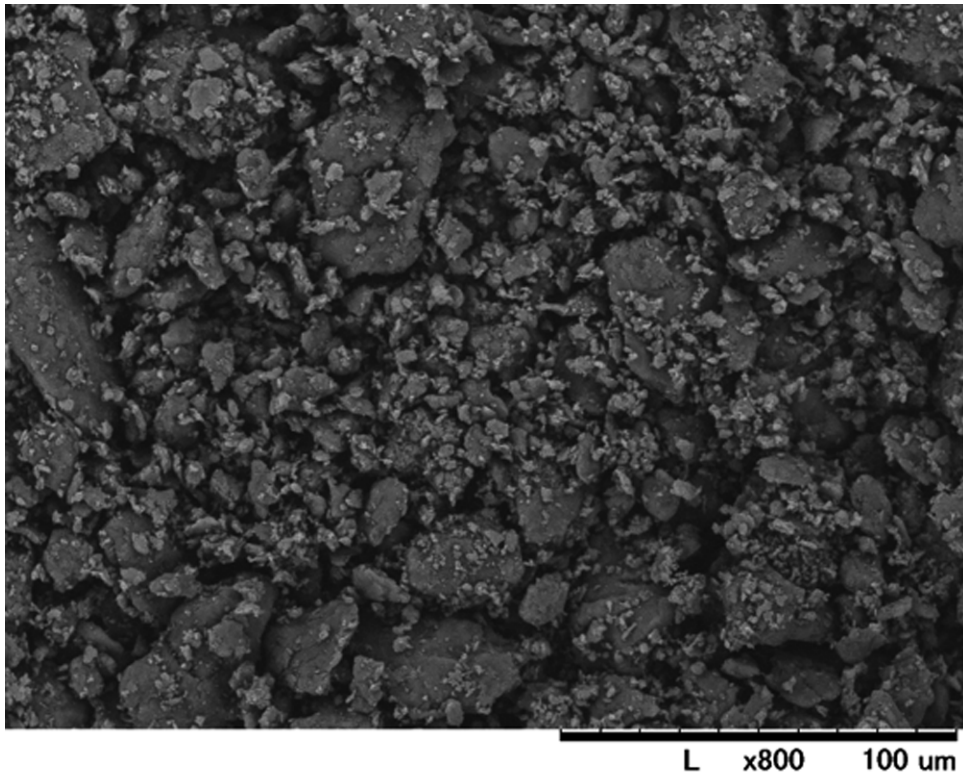


Fig. 4. SEM image of the traditional Super-Bond C&B Polymer. All particles are irregular and spherical particles are not included.

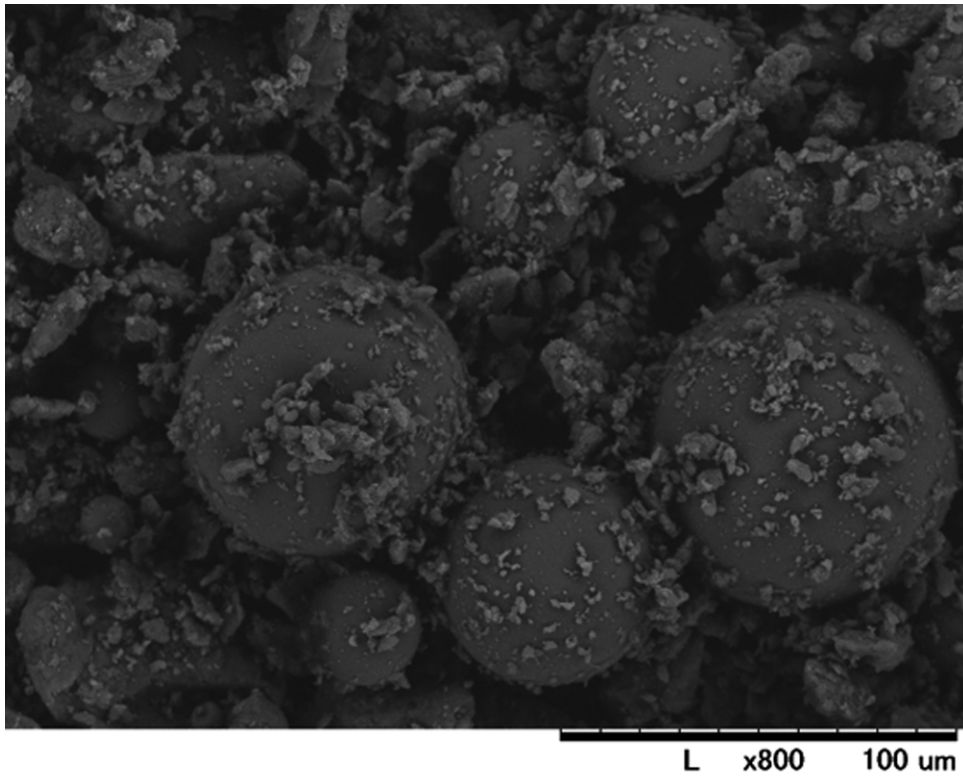


Fig. 5. SEM image of the new Super-Bond C&B Brush-dip Polymer. Various-sized spherical particles are included with the irregular particles.

Table 1. Materials assessed for shear bond strength testing.

Trade Name	Manufacturer	Lot No.	Component/Information
<i>Casting alloy</i>			
Castwell M.C. 12	GC Corp., Tokyo, Japan	9907271	Ag 46, Cu 20, Pd 20, Au 12, Others 2 mass %
<i>Adhesive resin material</i>			
Super-Bond C&B	Sun Medical Co. Ltd.	RX11	Initiator: TBB ^f
	Moriyama, Japan	RK2	Liquid: MMA, 4-META ^g
		SF12	Polymer: PMMA
Super-Bond C&B (Brush-dip Polymer)	Sun Medical Co. Ltd.	RX11	Initiator: TBB*
		RK2	Liquid: MMA, 4-META*
		081014	Polymer: PMMA
<i>Primer</i>			
V-Primer	Sun Medical Co. Ltd.	RX1	VTD ^h in acetone

^amethyl methacrylate, ^bdimethacryloyloxyethyl 2,2,4-(or 2,4,4-)trimethylhexamethylene diurethane, ^c2-hydroxyethyl methacrylate, ^d6-methacryloyloxyhexyl 2-thiouracil-5-carboxylate, ^epolymethyl methacrylate, ^ftri-*n*-butylborane, ^g4-methacryloyloxyethyl trimellitate anhydride, ^h6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithiol, dithione tautomer.

*Super-Bond C&B product.

Table 2. PMMA particle characterization.

Powder	Particle size [μm] ($d_{10}/d_{25}/d_{50}/d_{75}/d_{90}$)	BET surface area [m^2/g]
Super-Bond C&B Polymer	4.80/15.69/37.00/56.04/73.48	3.63
Super-Bond C&B Brush-dip Polymer	5.64/19.73/39.31/58.27/76.50	2.10

Table 3. Shear bond strength results in MPa.

Method		Super-Bond C&B		Super-Bond C&B Brush-dip Polymer		<i>p</i> -value
		Mean	SD	Mean	SD	
Thermocycling 0	Air-abrasion	36.50	1.32	37.27	0.64	0.18
	Air-abrasion + priming	38.91	4.05	38.41	0.57	0.70
Thermocycling 10,000	Air-abrasion	8.04	1.51	7.53	1.31	0.49
	Air-abrasion + priming	37.44	4.61	37.94	4.34	0.10

SD: Standard deviation, Statistical methods are the Mann-Whitney's U tests.

Table 4. Mean weight of mixture held by the brush at one time.

Powder	Mixture weight [mg] (SD)
Super-Bond C&B Polymer	7.75 (1.43)
Super-Bond C&B Brush-dip Polymer	11.40 (2.83)

SD: standard deviation, alpha = 0.05, the values are significantly different ($p < 0.05$, Mann-Whitney's U tests).