Metal-resin Composite Restorative Material using Powder-liquid System

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In order to further improve the mechanical properties of a metal-resin composite and avoid the problems which were found in the previous metal-resin composite using a 2-paste system, another type of metal-resin composite using a powder-liquid system was developed. In the new system 4-META treatment was carried out at low temperature and DMPT was separated from the 4-META treated particles. The efficacy of this system as well as the effects of 4-META concentration, duration of 4-META treatment (immersion time) and filler content on the flexural properties, working time and setting time were investigated. The flexural strength of the powder-liquid composite was significantly affected by two main factors, immersion time and filler content, and the other properties (flexural modulus, working time and setting time) were by all three main factors. The highest flexural strength of the prepared composite was 91.8 MPa, which was higher than that of the 2-paste composite (64.0 MPa) by about 43%. This was achieved at a 0.1 ratio of 4-META concentration, 30 s immersion time and 94 mass% filler content. The working time and setting time ranged between 2.3–13.6 min and 4.2–20.1 min, respectively, and those of the highest strength composite were 3.0 and 5.2, respectively. The results of the present study indicate that the powder-liquid system is effective to improve the properties of the metal-resin composite.

Key words : Silver alloy, Dental composite, 4-META

INTRODUCTION

Direct restorative materials containing metal particles as the filler have been experimentally prepared by several researchers. Hirano *et al.*^{1,2)} used stainless steel particles as the filler to prepare a composite for magnetic cores of fixed prostheses. Kakuta *et al.*³⁾ used 70%Ag-27%Sn-3%Cu alloy particles as the filler to prepare a posterior composite, aiming to improve the wear resistance and durability. Following this study, Urapepon *et al.*⁴⁾ found that the flexural strength of this composite was improved by enhancing the bond between 4-(2-methacryloyloxyethoxycarbonyl) phthalic anhydride (4-META) and the filler particles using acid- and heat-treatments. Although the maximum flexural strength of these metal-resin composites was close to 80 MPa (76.0 MPa for stainless steel filled composite²⁾ and 77.6 MPa for Ag-Sn filled composite⁴⁾), this may not be sufficient for posterior tooth application⁵⁾, such as occlusal restorations and fixed prosthodontic cores.

In the previous study for Ag-Sn filled composite by Urapepon *et al.*⁴⁾, reactivity of the alloy particles was occasionally observed. Miyagawa *et al.*^{6,7)} further studied

this reactivity and reported that the polymerization of urethane dimethacrylate (UDMA) containing benzoyl peroxide (BPO) was induced by Ag-Sn particles treated with 4-META without tertiary amine. This result suggests that the UDMA in the previous metal-resin composite underwent some polymerization after the preparation of the paste, which may be related to the inadequate strength of the previously reported composite. This problem could be avoided by separation of the UDMA monomer from the 4-META treated particles and BPO. In addition to the reactivity of the alloy particles, another factor might have adversely affected the strength of the metal-resin composite. It has been reported that a chemical reaction can be induced between phthalic anhydride group and amine compounds⁸. Since 4-META has the phthalic anhydride group in its structure, it is likely that some part of N, N-dimethyl-p-toluidine (DMPT) in the catalyst paste dissolved in 4-META before mixing with the base paste containing BPO. This reaction may be avoided by the separation of 4-META from DMPT.

Based on the above points, a new system consisting of powder and liquid (powder-liquid system) is proposed to ameliorate the problems of the metal-resin composite containing of Ag-Sn particles as the filler, and to improve its mechanical properties. In the powder-liquid system, the powder component is Ag-Sn particles treated with 4-META and BPO. The temperature of 4-META treatment, in this system, is lower than that in the previous studies^{3,4} in order to prevent the decomposition of BPO. The liquid component is UDMA monomer containing DMPT. This system may be effective in minimizing both the early polymerization of UDMA and the reaction between 4-META and DMPT, and thus an improvement in the strength of the metal-resin composite can be expected.

The purpose of the present study was to experimentally prepare a metal-resin composite using the powder-liquid system (powder-liquid composite) under different conditions of 4-META concentration, treatment time and filler content, and to investigate the efficacy of this system as well as the effect of different conditions on some properties.

MATERIALS AND METHODS

Preparation of powder-liquid composite

The materials used in the present study are listed in Table 1.

Ag-Sn spherical alloy particles (73.2 mass% Ag, 26.8 mass% Sn) were produced by the research unit, Faculty of Dentistry, Mahidol University, Thailand, using an atomization method. Three particle sizes of the alloy, under $38\mu\text{m}$, $38\text{--}45\mu\text{m}$ and $45\text{--}53\mu\text{m}$ were combined at the ratio of 3 : 1 : 1 by mass, respectively and utilized for the filler of a metal-resin composite. The powder part of the composite was prepared using these particles. The particles were treated with both 4-META and BPO. For this purpose, 4-META acetone solution was prepared at two different concentration ratios (1 : 10=0.1 and 2 : 10=0.2 by mass) of 4-META to acetone (JIS K 8034 S, Lot no. KCJ 7772, Wako pure chemical industrials Ltd. Osaka, Japan). BPO as an

Table 1 Materials used in this study

	Materials	Code	Batch No.
Metal filler	Ag-Sn alloy particle ¹	AS750	9801AS750
Coupling agent	4-(2-Methacryloyloxyethoxycarbonyl) phthalic anhydride ² (crystal form)	4-META	97001
Monomers	1,6-Bis(methacryloyloxy-2-ethoxycarbonyl-amino)-		
	2,4,4(2,2,4)-trimethylhexane ³	UDMA	050155
	Triethylene glycol dimethacrylate ⁴	TEGDMA	1104S
Redox initiator	Benzoyl peroxide ⁵ (crystal form)	BPO	M6K9289
	N, N-dimethyl-p-toluidine ⁶	DMPT	GA01
Inhibitor	Hydroquinone monoethyl ether ⁷	MEHQ	PAM0168

¹ Mahidol University, Bangkok, Thailand

² Sun Medical, Osaka, Japan

³ Negami Kogyo, Negami, Japan

⁴ Shin Nakamura Kagaku Kogyo, Osaka, Japan

⁵ Nacalai Tesque Inc, Kyoto, Japan

⁶ Tokyo Kasei Kogyo, Tokyo, Japan

⁷ Wako pure chemical industries, Osaka, Japan

initiator was then dissolved into the solution at 1 mass%. The alloy particles were immersed in the prepared solutions at $23 \pm 2^\circ\text{C}$ and stirred using a stainless steel spatula for 30 s. The particles were left in the solution for 30 s, 2 h or 4 h, and then dried in the oven at 40°C for 3 min. The liquid component of the system was prepared from a monomer consisting of urethane dimethacrylate (UDMA, 75 mass%) with triethylene glycol dimethacrylate (TEGDMA, 25 mass%) as the resin matrix. DMPT was added to the monomer at 0.25 mass%. Using the prepared powder and liquid, a flexural test and measurements of working time, setting time and temperature rise during the setting of the composite were carried out.

Flexural test

The specimens for the flexural test were prepared following the ISO 4049:1988 for resin-based filling materials. The treated particles were mixed with the resin monomer containing DMPT for 30 s, either at 93, 94 or 95 mass% of the filler content. The mixture was filled in a $25 \times 2 \times 2$ mm PTFE-coated stainless steel mold placed on a glass plate, using a syringe (C-R Syringe, Centrix Co. CT, USA). After the filling of the mixture, another glass plate was applied on top of the mold to remove excess material from the mold. The specimen assembly was held together by a C-clamp and immersed in $37 \pm 1^\circ\text{C}$ distilled water. The metal-resin composite specimen was carefully removed from the mold at 15 min after the start of mixing and then stored in distilled water at $37 \pm 1^\circ\text{C}$ for 24 h. After 24 h storage, the specimen was polished using #1500 SiC paper, and the dimensions were measured before testing. Four specimens were prepared for each of the 18 conditions which were the combinations of two concentration ratios of 4-META, three different immersion times and three contents of the filler particles. These experimental factors and levels are listed in Table 2. A

Table 2 The experimental factors and levels
For flexural strength, flexural modulus, working time, setting time and temperature rise

Factors	Level 1	Level 2	Level 3
A: 4-META concentration ratio	0.1	0.2	—
B: Immersion time	30 s	2 h	4 h
C: Filler content	93 mass%	94 mass%	95 mass%

For percent elution

Factors	Level 1	Level 2	Level 3
A: Immersion time	30 s	2 h	4 h
B: Filler content	94 mass%	95 mass%	—

three-point flexural test was carried out using a universal testing machine (Auto-graph DSS-5000, Shimadzu Ltd., Kyoto, Japan) at a cross-head speed of 1 mm/min. The flexural strength and the modulus of elasticity were calculated.

The former metal-resin composite using the 2-paste system (2-paste composite) was also prepared, following the previous study³⁾ at the highest strength condition (2.5% 4-META concentration and 93% filler contents), and its flexural properties were also measured for comparison with those of the powder-liquid composite.

The fractured surfaces of the prepared composites after the flexural test were observed under a scanning electron microscope (JSM-T20, JEOL Co.Ltd, Tokyo, Japan) at 19 kV of acceleration voltage.

Measurement of working time, setting time and temperature rise

The working time, setting time and temperature rise after mixing the powder and liquid were determined following the ISO 4049:1988 for resin-based filling materials using a thermocouple apparatus. The apparatus was placed in the closed polystyrene box for maximum temperature stability at $23 \pm 1^\circ\text{C}$, and connected to a chart recorder (LR4210, Yokogawa electric works Ltd., Tokyo, Japan). The treated particles were hand-mixed with the resin monomer containing DMPT for 30 s. The mixture was filled in a mold in the thermocouple apparatus and the temperature of the material was continuously recorded until the peak temperature was passed. The working time, setting time and temperature rise were determined from the recorded chart as described in ISO 4049:1988. Three replications were made for each of the 18 conditions which were the combinations of two concentration ratios of 4-META, three different immersion times and three contents of the filler particles (Table 2). As well as the flexural properties, the working time, setting time and temperature rise of the 2-paste composite were measured in order to compare with the powder-liquid composites.

Measurement of elution of leachable component

The specimens were prepared using the same procedure as described for the flexural

specimen preparation at 0.1 ratio of 4-META concentration, for 30 s, 2 h or 4 h of immersion time, and 94% or 95% filler content. Specimens of the 2-paste composite were also prepared, following the previous study³⁾. The flexural test was carried out for each specimen. After the flexural tests, all fractured specimens were ground with a pestle and mortar by hand. The ground composites were weighed on an analytical balance to the nearest 0.00002 g (CW).

After the mass measurement, the leachable component of the resin matrix in the ground composite was extracted using a Soxhlet extractor apparatus. The ground composite was put in a filter paper tube (Thimble filter advantec, Toyo Rocho Kaicha, Ltd., Tokyo, Japan), which was then placed in the lower part of the apparatus. A 100 ml volume of acetone was used as the solvent for the extraction. Hydroquinone monoethyl ether (MEHQ, 250 ppm) was added to the acetone to prevent polymerization of the extracted monomer in the solution. The extraction was carried out at 80°C for 20 cycles. After the extraction, the ground composites and filter paper were removed from the apparatus and dried in an oven at 40°C for 24 h, and the mass of the dried composite was measured (DW). The percentage of elution of leachable component from the composite (percent elution) was calculated using the following equation;

$$PE = \frac{CW - DW}{IW} \times 100 \dots\dots(1)$$

where PE: percent elution (%)

CW: total mass of the ground composite (g)

DW: total mass of the composite after extraction (g)

IW: calculated resin mass of the ground composite (g),
which was calculated from the following equation;

$$IW = \frac{CW \times (100 - FC)}{100} \dots\dots(2)$$

where FC: filler content (mass%)

The extraction and the mass measurement were carried out for three specimens in each condition (Table 2).

Statistical analysis of data

A one-way analysis of variance and a Tukey's multiple comparison test were used to statistically compare the evaluated properties between the powder-liquid composite and 2-paste composite. The effects of three factors, which were the 4-META concentration ratio, immersion time and the filler content, on the properties were analyzed using a three-way analysis of variance and Tukey's interval.

The data were analyzed using two-way ANOVA to determine the effect of the immersion time and filler contents on the percent elution, and one-way ANOVA with Tukey's multiple comparison test to compare the powder-liquid composite and 2-paste

composite.

Correlation among six properties, which were flexural strength, flexural modulus, working time, setting time, temperature rise and percent elution were statistically analyzed.

RESULTS

The results of ANOVA and the mean values for flexural strength, flexural modulus, working time, setting time and temperature rise are summarized in Tables 3 and 4, respectively. In Table 4, Tukey's intervals are included to compare the mean values.

Table 3 Summary of the results of one-way and three-way ANOVA for flexural strength, flexural modulus, working time, setting time and temperature rise of the experimental composite

Factors	Flexural strength	Flexural modulus	Working time	Setting time	Temperature rise
One-Way ANOVA Different composites	4.50 (<0.01)**	5.54 (<0.01)**	49.43 (<0.01)**	59.06 (<0.01)**	13.32 (<0.01)**
Three-Way ANOVA					
A (4-META conc.)	1.09 (0.30)	29.17 (<0.01)**	527.19 (<0.01)**	646.78 (<0.01)**	101.28 (<0.01)**
B (Immersion time)	6.88 (<0.01)**	10.39 (<0.01)**	12.23 (<0.01)**	8.11 (<0.01)**	2.47 (0.10)
C (Filler content)	7.73 (<0.01)**	6.45 (<0.01)**	106.45 (<0.01)**	135.13 (<0.01)**	48.75 (<0.01)**
A×B	2.20 (0.12)	0.56 (0.58)	5.15 (0.01)*	3.33 (0.047)*	1.10 (0.34)
A×C	2.15 (0.13)	0.23 (0.79)	18.84 (<0.01)**	19.90 (<0.01)**	2.42 (0.10)
B×C	0.39 (0.82)	2.34 (0.07)	0.52 (0.72)	0.35 (0.84)	0.36 (0.83)
A×B×C	0.35 (0.84)	2.33 (0.07)	0.46 (0.76)	0.49 (0.74)	0.71 (0.59)

The numbers are F value, and P value in parenthesis

Fig.1 Flexural strength of the powder-liquid composite, at different immersion times (A) and by different filler contents (B).

Fig.2 Fractured surface of the powder-liquid composite specimen.

Table 4 The flexural strength, flexural modulus, working time, setting time and temperature rise of the powder-liquid composite and former 2-paste composite

Condition			Mean									
			Flexural strength (MPa)		Flexural modulus (GPa)		Working Time (min)		Setting Time (min)		Temperature rise (℃)	
2-paste composite			64.00* (2.68)		11.90* (0.74)		9.30* (0.26)		13.43* (0.06)		1.00* (0.10)	
Powder-liquid composite												
4-META conc.	Immersion time	Filler content										
0.1	30 s	93%	87.59	(3.48)	16.10	(1.38)	2.33	(0.43)	4.23	(0.14)	2.35	(0.15)
		94%	91.83	(4.66)	16.61	(0.88)	3.03	(0.26)	5.22	(0.45)	2.13	(0.20)
		95%	83.09	(4.97)	17.63	(2.05)	4.50	(0.72)	7.85	(1.40)	1.33*	(0.49)
	2 h	93%	79.54	(5.77)	13.93*	(1.34)	2.60	(0.17)	4.42	(0.16)	2.28	(0.20)
		94%	85.83	(2.40)	15.60	(1.14)	3.48	(0.23)	5.63	(0.32)	1.90	(0.09)
		95%	74.69*	(9.88)	15.13*	(0.22)	5.65	(0.61)	8.97	(0.59)	1.27*	(0.40)
	4 h	93%	79.91	(3.10)	13.84*	(0.72)	2.45	(0.13)	4.25	(0.05)	2.68	(0.24)
		94%	83.62	(5.43)	14.94*	(1.30)	3.08	(0.28)	4.95	(0.38)	2.15	(0.09)
		95%	74.74*	(5.06)	15.55*	(1.55)	4.70	(0.92)	7.60	(1.15)	1.60*	(0.26)
0.2	30 s	93%	80.94	(9.69)	12.88*	(2.32)	5.40	(1.06)	8.90	(1.56)	1.65*	(0.36)
		94%	84.11	(4.93)	14.17*	(1.25)	7.07*	(1.00)	11.23*	(1.50)	1.03*	(0.51)
		95%	82.96	(5.13)	16.54	(0.90)	10.93*	(1.10)	18.30	(2.00)	0.99*	(0.14)
	2 h	93%	79.44	(9.80)	12.71*	(1.78)	7.87*	(0.65)	12.03*	(0.06)	1.48*	(0.28)
		94%	81.33	(6.14)	13.02*	(0.94)	8.83*	(1.52)	13.97*	(2.31)	1.28*	(0.23)
		95%	74.83*	(3.04)	13.19*	(0.38)	13.60	(1.22)	20.07	(0.12)	0.82*	(0.03)
	4 h	93%	78.19*	(4.22)	12.70*	(2.22)	7.30*	(1.61)	11.17*	(2.10)	1.73*	(0.25)
		94%	84.10	(4.09)	15.31*	(2.17)	7.90*	(0.95)	11.90*	(1.22)	1.20*	(0.18)
		95%	80.74	(2.20)	12.20*	(1.25)	13.53	(1.17)	19.07	(1.01)	0.85*	(0.13)
Tukey's Interval for one-way ANOVA			14.64		3.70		2.70		3.54		0.81	

SD in parentheses

Data with superscript* are not statistically different from 2-paste composite at $p=0.05$ using Tukey's test □ : 95% confident interval, * : Significantly different at $P < 0.05$

Tukey's interval : 0.69 for 4-META concentration, 1.01 for immersion time and filler content

Fig. 3 Flexural modulus of the powder-liquid composite, at different 4-META concentrations (A), different immersion times (B) and different filler contents (C).

The flexural strength of the experimental metal-resin composites using the powder-liquid system ranged from 74.7 to 91.8 MPa, whereas that of the 2-paste composite was 64.0 MPa. 14 of the 18 powder-liquid composites had significantly higher flexural strength than the 2-paste composite, and the highest strength was obtained at the 0.1 ratio of 4-META concentration, with 30 s immersion time and 94% filler content. This was greater than that of the 2-paste composite by about 43%. The immersion time and filler content significantly influenced the flexural strength of the powder-liquid composite ($p < 0.01$). Fig. 1 shows the flexural strength of the composite at different immersion times and with different filler contents. The strength decreased as the immersion time increased, and a significant difference was found between 30 s and the other two times, 2 h and 4 h ($p < 0.05$). The 94% filler composite had significantly higher strength than the 93% and 95% filler composites ($p < 0.05$). Fig. 2 shows the fractured surfaces of the powder-liquid composite specimens. The resin matrix was found closely attached to the particle surfaces and covered the small particles.

The flexural modulus of the powder-liquid composite ranged from 12.2 to 17.6 GPa, whereas that of the 2-paste composite was 11.9 GPa. Five of the 18 powder-liquid composites had a significantly higher modulus than the 2-paste composite ($p < 0.05$). Three main factors, 4-META concentration, filler content and immersion time, significantly influenced the flexural modulus of the powder-liquid composite ($p < 0.01$). Fig. 3 shows the flexural modulus at different 4-META concentrations, immersion times and filler contents. The modulus significantly increased as the 4-META concentration decreased from 0.2 to 0.1, as the immersion time decreased from 2 h to 30 s, and as the filler content increased from 93% to 94%.

The working time and setting time of the powder-liquid composite ranged from 2.3 to 13.6 min, and from 4.2 to 20.1 min, respectively. All of the powder-liquid composites fulfilled the requirement of ISO 4049 for resin-based filling materials⁵⁾ for working time (not less than 90 s). Four composites complied with the standard requirement for setting time (not more than 5 min). For the 2-paste composite, these times were 9.3 and 13.4 min, respectively. 10 of the 18 powder-liquid composites showed a significantly shorter working time whereas two of them had a significantly longer working time than the 2-paste composite. Both the working time and setting time of the powder-liquid composite were significantly influenced by all main factors ($p < 0.01$) and two interactions; that between 4-META concentration and immersion time ($p < 0.05$) and that between 4-META concentration and filler content ($p < 0.01$). Fig. 4 shows the working time and setting time for different 4-META concentrations, immersion times and filler contents. Both the working time and setting time significantly increased as 4-META concentration increased from 0.1 to 0.2, as filler content increased from 94% to 95%, and as immersion time increased from 30 s to 2 h at 0.2 ratio of 4-META concentration ($p < 0.05$). A significant correlation was found between the working time and the setting time ($r = 0.994$) and the regression equation was as follows.

Fig. 4 Working time and setting time of the powder-liquid composite, at different filler contents and 4-META concentrations (A) and different immersion times and 4-META concentrations (B).

Fig. 5 Temperature rise of the powder-liquid composite, at different 4-META concentrations (A) and different filler contents (B).

$$ts = 1.4tw + 0.90 \dots\dots(3)$$

where ts : Setting time of the powder-liquid composite (min)

tw : Working time of the powder-liquid composite (min)

The temperature rise of the powder-liquid composite ranged from 0.8 to 2.7°C and that of the 2-paste composite was 1.0°C. Six of the 9 powder-liquid composites treated at 0.1 ratio of 4-META concentration showed a significantly higher temperature rise, but no significant difference was found between the 2-paste composite and

any of the powder-liquid composites treated at 0.2 concentration. The temperature rise of the powder-liquid composite was significantly influenced by the 4-META concentration and the filler contents ($p < 0.01$). As shown in Fig. 5, the temperature rise increased significantly with the decreases of 4-META concentration and filler content ($p < 0.05$). The temperature rise had a significantly negative correlation with working time ($r = -0.863$) and setting time ($r = -0.874$), and the regression equations were as follows.

$$tw = -5.6Tr + 15.30 \dots\dots(4)$$

$$ts = -8.2Tr + 23.04 \dots\dots(5)$$

where Tr: Temperature rise of the powder-liquid composite ($^{\circ}\text{C}$)

tw and ts: as above defined

The percent elution of leachable components from the powder-liquid composites ranged from 23.2 to 33.7% and that from the 2-paste composite was 22.6% (Table 5). No significant difference in the percent elution was found between the 2-paste and

Table 5 The percent elution of leachable components from the powder-liquid composite and former 2-paste system

Condition		Percent elution (%)
2-paste composite		22.63 (2.22)
Powder-liquid composite		
Immersion time	Filler content	
30 s	94%	
	95%	
2 h	94%	
	95%	
4 h	94%	
	95%	
Tukey's Interval for one-way ANOVA		12.33

SD in parentheses

No significant difference was found among all means

Table 6 The results of two-way ANOVA for the percent elution of leachable components from the powder-liquid composite

Factors	df	Sum of Squares	Mean Squares	F value	P value
A (Immersion time)	2	19.445	9.723	0.442	0.653
B (Filler content)	1	293.546	293.546	13.347	0.003**
A×B	2	30.710	15.355	0.698	0.517
Residual	12	263.913	21.993		
Total	17	607.614

Fig. 6 Percent elution of the powder-liquid composite.

powder-liquid composites. Table 6 shows the result of two-way ANOVA for the percent of elution from the powder-liquid composite. The percent elution was significantly influenced by filler content ($p < 0.01$). As shown in Fig. 6, the percent elution significantly increased as filler content increased. A significant correlation was found between the percent elution and the flexural strength of the powder-liquid composite ($r = -0.851$). The percent elution also had a significant correlation with working time ($r = 0.908$), setting time ($r = 0.951$) and temperature rise ($r = -0.957$). The regression equations between the percent elution and three properties, the flexural strength, working time and setting time, were as follows.

$$FS = -0.7PE + 96.04 \quad \text{.....(6)}$$

$$PE = 4.2tw + 10.73 \quad \text{.....(7)}$$

$$PE = 2.8ts + 9.20 \quad \text{.....(8)}$$

$$PE = -11.8Tr + 48.05 \quad \text{.....(9)}$$

where FS: Flexural strength of the powder-liquid composite (MPa)

PE: Percent elution of the powder-liquid composite (%)

Tr, tw and ts: as above defined

DISCUSSION

In the previous study^{3,4)}, the metal-resin composites were experimentally prepared in 2-paste form. As mentioned in the introduction, several problems might have been generated in the 2-paste system due to the reactivity of the alloy particles and the reaction between 4-META and DMPT, which may have resulted in the low strength of these composites. To minimize these problems and to further improve the strength of the composite, a powder-liquid system was developed in the present study. The 4-META-treated particles were separated from the UDMA monomer containing DMPT in order to prevent the early polymerization of UDMA and the reaction between DMPT and 4-META. The results of the flexural tests showed that many of the

prepared powder-liquid composites had significantly higher strength than the 2-paste composite, and the highest value was about 43% more. This result indicates that the powder-liquid system is effective for improving the mechanical properties of the metal-resin composite consisting of Ag-Sn filler particles and 4-META coupling agent. Generally, the flexural strength of a composite depends upon the filler content^{9,10)}, the rate of conversion¹¹⁾, the degree of polymerization¹²⁾ and the bond between the filler particles and the resin matrix^{3,4,10)}. The increase in flexural strength of the powder-liquid composite may be related to these factors.

Five of the six powder-liquid composites containing 93% filler showed significantly higher strength than the 2-paste composite which also contained 93% filler (Table 4). This result may indicate that the filler content may not have been the reason for the increase in flexural strength of the powder-liquid composite. Although we expected a higher rate of conversion in the powder-liquid system than in the 2-paste system, no significant difference was found in the percent elution between powder-liquid and 2-paste composites, which indicates no difference in the rate of conversion between these two types of composite. This result suggests that the increase in the flexural strength of the powder-liquid composite was not related to the rate of conversion of the resin matrix. Therefore, the other two factors, the degree of polymerization and the bond between filler particles and resin matrix, could be responsible for the increase in the flexural strength. One of the main differences between the previous 2-paste system and the present powder-liquid system is the distribution of BPO. The BPO in the powder-liquid system is only available on the surface on the filler particles whereas that in the 2-paste paste system is distributed in the monomer of one paste. This difference may be related to the propagation of polymer chains and consequently to the degree of polymerization in the powder-liquid system, resulting in the increase in the flexural strength. This should be further investigated in a future study. With respect to the bond between filler particles and resin matrix, Fig. 2 showed a similar attachment of the resin matrix to the metal particles to that previously reported⁴⁾, indicating that the bond between the filler particles and the resin matrix is different between the two systems. A further study, however, is necessary to prove the absence of differences in the bond between these two systems since SEM photographs cannot show differences in the structure.

For the powder-liquid composite, the flexural strength was significantly influenced by two factors, immersion time and filler content. It decreased as the immersion time increased (Fig. 1A). According to the studies by Miyagawa *et al.*^{6,7)}, UDMA polymerizes under the existence of Ag-Sn particles, 4-META and BPO. This result suggests that not only UDMA but also 4-META has polymerized. Polymerization of the 4-META might not have been induced at 30 s immersion but induced at longer immersion such as 2 h and 4 h. And thus the co-polymerization between 4-META and UDMA was not well achieved at longer immersion time, resulting in the lower strength of the composite. As shown in Fig. 1B, a higher flexural strength was obtained at 94% filler content regardless of 4-META concentration and immersion time. Several studies^{9,10)} have shown that the strength of composites increases with the

increase of the filler content. This was also found in the present study up to 94%. The strength, however, significantly decreased at 95%. This may be related to the lower rate of conversion of the 95% composite. As shown in Fig. 6, the percent elution at 95% filler content was significantly higher than that at 94%, which indicates lower rate of conversion, resulting in the lower strength of 95% composite. As well as the result of the temperature rise in Fig. 5B, 95% filler content clearly showed the significantly lower temperature rise than that at 94%, which may be related to the lower rate of conversion^{13,14}. Ferracane *et al.*⁹) found that the rate of conversion increases with the increase of filler content up to certain filler content and then decrease as the filler content increases. This result is in agreement with that of the present study. The reason for the decrease in the rate of conversion should be further investigated.

As discussed before, percent elution was not the reason for the increase in the flexural strength of the powder-liquid composites when compared with the 2-paste composites. Among powder-liquid composites, however, a significant correlation was found between flexural strength and percent elution. This indicates that the strength of the powder-liquid composite was influenced by the rate of conversion, which is in agreement with the previous studies^{11,12}.

The flexural modulus of the powder-liquid composites was significantly influenced by three main factors; 4-META concentration, immersion time and filler content. In composite materials, the filler particles are distributed in the matrix and work to restrict the deformation of the matrix. Thus, the modulus of the composite is dependent on that of the filler and its content^{10,15,16}. The results of this study also show these roles of the filler for the flexural modulus. The higher concentration of 4-META and longer immersion time significantly decreased the flexural modulus of the composite. This can be explained by the increase of 4-META layer at the higher 4-META concentration and the longer immersion time in the set composite. If the whole amount of 4-META was consumed to cover the filler particles, the average percentage of total resin matrix including 4-META was calculated to be 5.89 mass% (4-META: 0.93 mass%) and 6.77 mass% (4-META: 1.84 mass%) at 0.1 and 0.2 ratio of 4-META concentrations, respectively. It is very probable that the composite treated at the higher concentration and for a longer immersion time contains more resin matrix, including 4-META, resulting in the lower flexural modulus.

Not only the mechanical properties but also the working and setting time were improved by the powder-liquid system. The working time and setting time of the 2-paste composite were 9.3 and 13.4 min, respectively. These may be too long for clinical use. On the other hand, some of the powder-liquid composites fulfilled the requirements for working time (not less than 90 s) and setting time (not more than 5 min) specified in ISO 4049⁵). These composites appear to have appropriate working and setting times for practical use. It should be noted that the working time and setting time of one composite which had the highest flexural strength (91.8 MPa) were 3.0 min and 5.2 min, respectively. Although this setting time was slightly longer than the ISO requirement, this composite can be applied for posterior restorations.

Although the results of the present study have indicated the efficacy of the powder-liquid system, it seems that the rate of the polymerization is still the same as the 2-paste system. Therefore, a further study is necessary to improve the rate of conversion of the metal-resin composite. In addition, the other properties such as wear resistance, dimensional change and biocompatibility should be further investigated before clinical use of this material.

A significant correlation was found among the percent elution, working time, setting time and temperature rise. These correlations indicate that a shorter working time and/or setting time results in a higher temperature rise and a lower rate of conversion of the composite. Fundamentally, the working time and setting time can be prolonged or shortened by the temperature¹⁷⁾, the ratio of the redox initiator¹⁸⁾ and addition of an accelerator or retarder¹⁸⁾. Therefore, it should be noted that the correlations related to working time and setting time can stand when these conditions are fixed as in the present study.

In a preliminary experiment, the residual monomer content in a set composite was measured using gas chromatography to investigate the rate of conversion of the powder-liquid composite in relation to its properties. The measured amount, however, was only 0.2-0.3% which was far below the eluted amount (about 20-30%) using a Soxhlet extraction device. It was noted in this experiment that the difference between amounts of the measured monomer and the eluted component might have been due to polymerization of the extracted monomer. This was suggested by the production of a film-like substance in the extracted liquid. It is very probable that the surfaces of the metal particles are exposed by crushing of the composite specimen and are activated at high temperature for extraction, resulting in polymerization of the extracted monomer. For this reason, gas chromatography measurement of the residual monomer was not adopted but the eluted component was measured to investigate the effect of the rate of conversion on the properties of the powder-liquid composite.

The residual monomer in this study was evaluated by extraction of the components eluted from the whole composite mass. The Soxhlet extraction procedure was adopted to produce an aggressive environment for extraction. Acetone was selected as the solvent for extraction based on two reasons. First, acetone has a solubility parameter of $1.9 \times 10^4 \text{ (J/m}^3\text{)}^{1/2}$ ¹⁹⁾ which is suitable to dissolve base polymers of dental composites²⁰⁾. Second, acetone itself has a high ability to soften and swell the polymer network to easily release the residual monomer which is entrapped in the network. This ability is higher than water, methanol, ethanol or their combination¹⁹⁾, which were used in the past studies²⁰⁻²⁸⁾. The percent elution ranged from 23.2 to 33.7% of the initial monomer. These values were slightly lower than those of previous studies^{9,29-31)}. Tanaka *et al.*²⁴⁾ studied the elutable components of conventional dental composites in water and concluded that the minor component, mainly TEGDMA, dissolved into water, but most residual monomers remained in the set composite. Another study by Ferracane *et al.*²⁸⁾ has shown that most of the minor component of the composite can dissolve into water within 24 h. In this study, the composite was immersed for 24 h before the flexural test and thus some of the elutable component

could have dissolved into the water, resulting in the lower value of the percent elution.

CONCLUSION

The highest flexural strength of the powder-liquid composite was 91.8 Mpa, which was higher than the 2-paste composite (64.0 MPa) by about 43%. This was achieved at a 0.1 ratio of 4-META concentration, 30 s immersion time and 94% filler content. The working time and setting time ranged between 2.3-13.6 min and 4.2-20.1 min, respectively and those of the highest strength composite were 3.0 and 5.2, respectively. These results indicate that the powder-liquid system is effective for improving the properties of the metal-resin composite.

The flexural strength of the powder-liquid composite increased significantly as the filler content increased from 93 to 94% and as the immersion time decreased from 2 h to 30 s. A significant correlation was found between the flexural strength and percent elution of leachable components from the powder-liquid composite, indicating that the rate of conversion is one of the factors responsible for the strength of the powder-liquid composite but not the reason for the improvement of this composite. The flexural modulus increased significantly as the filler content increased from 93 to 94%, as the immersion time decreased from 2 h to 30 s, and as the 4-META concentration decreased from 0.2 to 0.1.

The working time and setting time significantly increased as the filler content increased from 93 to 95%, as the immersion time increased from 30 s to 2 h, and as the 4-META concentration increased from 0.1 to 0.2. The temperature rise during setting ranged between 0.8 and 2.4°C. It decreased significantly as the 4-META concentration increased from 0.1 to 0.2 and as the filler content increased from 93 to 95%. A significant correlation was found among these three parameters as well as between the three parameters and percent elution of leachable components from the powder-liquid composite under the test conditions of this study.

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