Development of Metal-Resin Composite Restorative Material Part 2 Effects of acid and heat treatments of silver-tin filler particles on flexural properties of metal-resin composite

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The effects of acid and heat treatments of silver-tin filler particles on the flexural properties of metal-resin composite restorative materials were investigated. Five metal-resin composite restorative materials containing different silver-tin filler particles treated under different conditions were experimentally prepared. The conditions of the alloy particles were; 1) as atomized (NT), 2) 1.8% HCl acid-treated (AT), 3) heat-treated at 150°C for 5 min after AT (A15), 4) heat-treated at 200°C for 5 min after AT (A20) and 5) heat-treated at 250°C for 5 min after AT (A25). The flexural strength and the flexural modulus of elasticity were measured for the five metal-resin composites to evaluate the effects of the acid and heat treatments.

The flexural strength of the prepared composites was significantly influenced by the surface condition of the filler particles ($p < 0.01$), and increased significantly when the as atomized particles (NT) were acid-treated (AT) or acid- and heat-treated at 150°C (A15), but then significantly decreased as the heat treatment temperature increased (A20 and A25). The strength of the A15 composite was significantly higher than those of the other composites, and exceeded that (about 60 MPa) of the previous composite with no treatment. No significant difference was found in the flexural modulus of the composites.

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

INTRODUCTION

Metal-resin composite materials have been experimentally prepared by several researchers. Hirano *et al.*¹⁾ used stainless steel particles as a filler to prepare a composite for magnetic cores of fixed prostheses. Kakuta *et al.*²⁾ used amalgam alloy particles as a filler to prepare a composite for a direct posterior restorative material, aiming to improve the wear resistance and durability of the present posterior composite. The maximum strength of these experimental metal-resin composites was reported to be 76¹⁾ and 60²⁾ MPa, respectively which may need be further improved for posterior tooth application.

Kakuta *et al.*²⁾ used 4-META as a coupling agent for their experimental composite. They reported that the strength of the composite was dependent on the bond between filler particles and resin matrix, and 4-META took an essential role in the

bonding. It has been hypothesized that 4-META bonds with the alloy surface by hydrogen bonding between the carboxylic group or carboxylic anhydrous group of 4-META and metal oxide on the alloy surface³⁾. Therefore, the bond strength and durability of the 4-META can be improved by oxidation of the alloy surface. This has been reported by several researchers⁴⁻¹⁰⁾ using various techniques. Echizenya⁴⁾ used Fourier transform infrared reflection absorption spectroscopy (FT-IR-RAS) and X-ray photoelectron spectroscopy (XPS) to analyze the amount of resin adsorption by the alloy, and found that the adsorption was enhanced by increasing the hydroxyl groups on the alloy surface. Tanaka *et al.*⁵⁻¹⁰⁾ studied the effect of an alloy surface treatment on the adhesion of 4-META to the alloy. They found that conditioning of the alloy surface using either ion-coating⁵⁾, etching and immersion in an oxidizing agent⁶⁻⁸⁾ or heat treatment^{9,10)} can improve the adhesive strength and adhesive resistance to water penetration of the 4-META and alloy interface. Therefore, it should be possible to increase the strength of the metal-resin composite by conditioning the filler particles in order to improve the bond strength between 4-META and alloy fillers.

The purpose of this study was to investigate the effects of acid and heat treatments of the silver-tin filler particles on the flexural properties of a metal-resin composite restorative material.

MATERIALS AND METHODS

The materials used in this 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 μm , 38-45 μm and 45-53 μm were combined at the ratio of 3:1:1 by mass, respectively and utilized for the filler of a metal-resin composite.

Table 1 Materials used in this study

	Materials	Code	Batch No.
Metal filler	Ag-Sn alloy particle ¹	AS750	9608AS750
Coupling agent	4-(2-Methacryloyloxyethoxycarbonyl) phthalic anhydride ² (crystal form)	4-META	T1003
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	BPO	40618
	N, N-dimethyl-p-toluidine ⁶	DMPT	GA01

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4-(2-methacryloyloxyethoxycarbonyl) phthalic anhydride (4-META) was used as the coupling agent. A base monomer, consisting of 1,6-Bis (methacryloyloxy-2-ethoxycarbonyl-amino)-2,4,4 (2,2,4)-trimethylhexane (UDMA, 75 mass%) and tri-ethylene glycol dimethacrylate (TEGDMA, 25 mass%), was used as the resin matrix. Either benzoyl peroxide (BPO, 1.0 mass%) or N,N-dimethyl-p-toluidine (DMPT, 0.5 mass%) was added to the base monomer as a redox initiator.

Alloy particle surface treatment

The alloy particles were immersed in 1.8% HCl at 80°C and slowly stirred with a magnetic stirrer for 20 min. After this acid treatment, the particles were thoroughly washed with distilled water until no residual acid remained on the surface. Washing was repeated until the removal of the acid was verified using AgNO₃ which showed the existence of HCl due to the milky color of AgCl. The particles were then filtered and dried at 50°C for 1 h. After drying, the particles were divided into four groups. One of the four groups was used as acid-treated without heat treatment (AT) to prepare a metal resin composite, and the other three groups were placed in an oven for heat treatment at three different temperatures, 150°C for 5 min (A15), 200°C for 5 min (A20), or 250°C for 5 min (A25). In addition to these four conditions, another condition of "as atomized without any treatment" (NT) was included, and thus five different surface conditions were investigated.

4-META treatment and specimen preparation

A 4-META acetone solution was prepared at a concentration of 2.5 mass%, based on the results of the previous study²⁾. The five different particle groups (NT, AT, A15, A20 and A25 particles) were immersed in this solution at 80°C and slowly stirred using a magnetic stirrer for 2 h. After this treatment, the particles were filtered and dried at 50°C for 1 h. Treated alloy particles were then mixed with the prepared base monomers to produce two metal-resin pastes containing either BPO or DMPT. Each paste contained 93 mass% alloy particles, also based on the previous study²⁾.

The specimens for the flexural test were prepared following ISO 4049 for Resin-based filling materials. Two metal-resin composite pastes were mixed at the ratio of 1:1 by mass for 1 min. The mixture was filled in a 25×2×2 mm PTFE-coated stainless steel mold on top of a glass plate, using a syringe (C-R Syringe, Centrix Inc., CT, USA). Another glass plate was applied on top of the mold to remove any excess material. The assembly was held together by a C-clamp and immersed in 37±1°C distilled water. Fifteen minutes after the start of mixing, the specimen was carefully removed from the mold and stored in distilled water at 37±1°C for 24 h. The specimen was polished using #1500 SiC paper, 3 μm diamond paste (Metadi, Buehler Co.Ltd., IL, USA) and 0.05 μm gamma alumina paste (Micropolish, Buehler Co.Ltd., IL, USA), and the dimensions measured before testing. Six specimens for each group were prepared. A three-point flexural test was carried out using a universal testing machine (Autograph DSS-5000, Shimadzu Co.Ltd., Kyoto, Japan) at a cross-head speed of 1 mm/min. The flexural strength (σ) and the modulus of elasticity under

flexural stress (flexural modulus, E) were calculated from formulae (1) and (2), respectively, as followed:

$$\sigma = \frac{3Fl}{2bh^2} \dots\dots(1)$$

where F is the maximum load (N),
 l is the distance between the supports (20 mm),
 b is the width of the specimen (mm),
 h is the height of the specimen (mm).

$$E = \frac{F_1 l^3}{4bh^3d} \dots\dots(2)$$

where F_1 is the load at a convenient point in the straight-line portion of the trace (N),
 l is the distance between the supports (20 mm),
 b is the width of the specimen (mm),
 h is the height of the specimen (mm).
 d is the deflection at load F_1 (mm),

The data of flexural strength and elastic modulus were analyzed by one-way ANOVA, and the means were compared using Duncan's multiple range test.

X-ray photoelectron spectroscopy (XPS) and Scanning electron microscope (SEM) observation

The five different particles were washed with acetone. After washing, the particles were dried in a desiccator under vacuum at room temperature for 12 h and then placed on a carbon tape. The surface of the particles was analyzed using an X-ray photoelectron spectroscope (ESCA-750, Shimadzu Co.Ltd., Kyoto, Japan) with Al K α radiation under a pressure of 1.33×10^{-5} Pa. The binding energy of the measured photoelectron peak was calibrated by the Cls peak at a binding energy of 285.0 eV.

The fractured surfaces of the prepared composites after the flexural test were observed under a scanning electron microscope (JSM-T20, JOEL Co.Ltd, Tokyo, Japan) at 19 kV of acceleration voltage at 350 and 2000 times magnification. In addition, the particle surfaces were observed at higher magnification ($\times 6000$) using another scanning electron microscope (S-800, Hitachi Ltd, Tokyo, Japan) at 15 kV of acceleration voltage.

RESULTS

The flexural strength of the experimental metal-resin composites ranged from 52.0 to 77.6 MPa and the flexural modulus from 12.2 to 14.5 GPa. Table 2 shows the results of the one-way ANOVA for the flexural strength and the flexural modulus. The flexural strength was significantly influenced by the different surface conditions of the alloy particles ($p < 0.01$). No significant difference among groups was found in the

Table 2 Result of one way ANOVA for flexural strength and flexural modulus

Source	df	Sum of Squares	Mean Squares	F value	P value
(Flexural strength)					
Treatment	4	2207.615	551.903	25.928	<0.001**
Error	25	532.151	21.286		
Total	29	2739.766			
(Flexural modulus)					
Treatment	4	24.278	6.069	1.689	0.184
Error	25	89.835	3.593		
Total	29	114.113

Fig. 1 The flexural strength of the experimental composite.
(comparison of the mean values by Duncan's multiple range test)

Fig. 2 The flexural modulus of the experimental composite.
(comparison of the mean values by Duncan's multiple range test)

flexural modulus. Figs. 1 and 2 show the flexural strength and the flexural modulus of each experimental composite respectively.

As shown in Fig. 1, the flexural strength increased when the as atomized particles (NT) were acid-treated (AT) or acid- and heat-treated at 150°C (A15), but then decreased as the heat treatment temperature increased (A20 and A25). The mean flexural strength of A15 composite was the highest and significantly different from the others ($p < 0.05$). A25 composite was the lowest and also significantly different from the others ($p < 0.05$).

Scanning electron photomicrographs of the surfaces of the alloy particles from groups NT, AT, A15, and A25 are shown in Fig. 3. On the surfaces of all treated par-

Fig. 3 SEM photograph of the NT particle surface (A), AT particle surface (B), A15 particle surface (C) and A25 particle surface (D) ($\times 6000$).

ticles, wider grooves at the grain boundaries than on NT particles were observed. No clear difference was found between the surfaces of the acid-treated particles and the acid- and heat-treated particles.

The fractured surfaces of A15 and A25 composites after the flexural test are shown in Figs. 4 and 5, respectively. A resin matrix was closely attached to the A15 particle surface, whereas it was separated from the surface of A25 in spite of the surface being similar to A15's.

The XPS spectra of Sn3d are shown in Fig. 6; the binding energy peak value of silver and tin, and element ratio on the metal surfaces are shown in Tables 3 and 4 respectively. Fig. 6 shows Sn 3d spectra obtained from AT and A25. In the dominant peak of Sn3d on AT, a shoulder was observed at the binding energy of 485 eV, which corresponds to the binding energy of tin in Table 3. The shoulder became less clear as the heat treatment temperature increased and finally disappeared on A25.

Fig. 4 SEM photograph of A15 fracture surface. Photograph B ($\times 2000$) is an enlargement of the circle area in photograph A ($\times 350$).

Fig. 5 SEM photograph of A25 fracture surface. Photograph B ($\times 2000$) is an enlargement of the circle area in photograph A ($\times 350$).

Fig. 6 Sn 3d spectra of AT and A25.

Table 3 Binding energy peaks (eV) of Ag and Sn on the metal surface

	Ag 3d	Sn 3d
NT	367.7	486.2
AT	368.3	486.7
A15	368.1	486.4
A20	368.1	486.5
A25	368.3	486.3
Ag	368.1-368.3 ¹	—
Ag ₂ O	367.8 ²	—
Sn	—	484.5-485.2 ¹
SnO, SnO ₂	—	486.0-489.0 ¹

¹(reference 21)

²(reference 22)

Table 4 Element ratio on the metal surface at Sn 3d=100 and Ag 3d=100

	Sn 3d=100		Ag 3d=100	
	Ag 3d	O 1s	Sn 3d	O 1s
NT	29	215	345	741
AT	77	219	130	284
A15	70	241	143	344
A20	49	234	204	478
A25	18	200	556	1111

Table 3 shows the binding energy peaks of Ag and Sn on the metal surface, indicating that the surfaces of all particle groups mainly consisted of Ag and SnO or SnO₂ except NT which had Ag₂O instead of Ag. Due to the function level of the XPS, SnO and SnO₂ could not be differentiated.

Table 4 shows the element ratio on the particle surface when either Sn or Ag is 100. When Sn was 100, the ratio of silver was much higher on AT and A15 surfaces than on the other NT, A20 and A25 surfaces, and that of oxygen was not much different among the five surfaces. When Ag was 100, the ratio of tin was lowest on the AT surface, and then increased with increasing heat treatment temperature, corresponding to the ratio of oxygen.

DISCUSSION

In the previous study²⁾, a metal-resin composite was experimentally prepared using silver-tin amalgam particles as filler and 4-META as coupling agent, but its strength was not sufficient enough for posterior tooth restoration. In order to improve the strength, the effects of acid and heat treatments on the flexural properties were investigated in the present study. The alloy particles were self-produced with an exact ratio of silver and tin. This binary alloy system was chosen to simply analyze the effect of the treatments, since the silver-tin alloy particles used in the previous study²⁾ were an amalgam alloy containing small amount of copper.

The flexural strength of the experimental composite in this study significantly increased with acid treatment (AT) and heat treatment at 150°C (A15). The highest flexural strength obtained from A15 composite (77.6 MPa) was higher than NT by about 22%. These results indicate that the bond between 4-META and the alloy particle surface could be improved by the aforementioned treatments of the alloy particles. As shown in Fig. 3, the grooves at the grain boundaries of AT, A15, and A25 were wider than those of NT. The wider grooves promote the adhesive property due to an increase of the bonding area and also higher mechanical interlocking between the alloy particle and resin matrix⁶⁾. However, the flexural strength decreased when the heat treatment temperature was higher than 200°C. As shown in Figs. 4 and 5, the fractured surface of A15 showed resin attached to the alloy surface, whereas the resin was found to be detached from the surface of A25. This indicates that the bond between the resin matrix and the A25 particles was not successful, which resulted in the lower strength of A25 composite. A question arises why this difference is induced in spite of the similar surfaces of A25 and A15. This could be explained by the increase of the elemental ratios for both tin and oxygen on the surface of A25 (Table 4), which would result a thicker oxide layer compared with A15. Previous studies⁸⁻¹¹⁾ have shown that the amount and thickness of metal oxides on the surface largely influence the adhesive properties of 4-META to the alloy surface. Therefore, the result of the present study may be due to the negative or adverse effect of a thick oxide layer on the adhesive properties of 4-META to the alloy particle surface.

The higher strength of AT and A15 could be explained by the previous studies^{5,12-15)}. Some of these studies^{5,12,13)} reported that an appropriate amount and thickness (very thin layer) of tin oxide played a positive role in adhesion between 4-META and tin-coated or -containing alloys. On AT and A15 surfaces, lower ratios of Sn and O were found (Table 4) which might indicate that these surfaces had an appropriate oxide layer for good adhesion. In addition, the other studies^{14,15)} indicated that SnO had better adhesion than SnO₂. It is probable that SnO is mainly formed on AT and A15 surfaces, although SnO and SnO₂ could not be differentiated in this study. A further study may be required to differentiate the quality and quantity of SnO and SnO₂ on metal surfaces, using standard specimens of SnO and SnO₂ as described by Ohno *et al.*¹⁴⁾

Another point of view could be related to tin and silver. Mogi¹⁶⁾ reported that

4-META strongly adhered to the polished surfaces of Ag and Sn in dry conditions. In the present study, tin was detected on both AT and A15 and silver was also found on these surfaces, which may be the cause of the improved adhesion.

As discussed above, there are many factors influencing the adhesion between 4-META and metal surfaces. Further studies are necessary to determine the individual effects of these factors.

The flexural moduli of the five groups were not significantly different from each other. This result suggests that the elastic modulus of metal-resin composites is independent of the bond between the resin matrix and the filler, as was found on the other composite materials¹⁷⁾.

During the experiment, we occasionally found the reactivity of the alloy particles, which could activate the polymerization of resin matrix and also 4-META itself. This reactivity has been further studied and reported by Miyagawa *et al.*^{18,19)} The alloy reactivity could be enhanced by the type of metal element in the alloy¹⁸⁾, small amounts of water¹⁹⁾ and also high temperature²⁰⁾. Since the 4-META treatment is carried out at 80°C for 2 h, it is probable that the alloy reactivity promoted the polymerization of 4-META to some extent before the alloy was mixed with the resin matrix, and thus the bond between 4-META might not have bonded well with the resin matrix. In order to further improve the mechanical properties of the metal-resin composite, another coupling procedure which does not induce adverse effects of alloy particles should be developed.

CONCLUSION

The flexural strength of the prepared composites was significantly influenced by the surface condition of the filler particles ($p < 0.01$), and significantly increased when the atomized particles (NT) were acid-treated (AT) or acid- and heat-treated at 150°C (A15), but then significantly decreased as the heat treatment temperature increased (A20 and A25). The strength of the A15 composite was significantly higher than those of the other composites, and exceeded that (about 60 MPa) of the previous composite with no treatment. No significant difference were found in the flexural moduli of the composites.

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