รายงานวิจัยฉบับสมบูรณ์

โครงการ
พัฒนาคุณภาพวัสดุอุดฟันทางทันตกรรมชนิดโลหะ-เรซินคอมโพสิต

โดย ผู้ช่วยศาสตราจารย์ ดร. สมชาย อุรพีพล และคณะ

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานฉบับนี้เป็นของผู้วิจัย สกว. ไม่จำเป็นต้องเห็นด้วยเสมอไป)

กิตติกรรมประกาศ

ขอขอบคุณ สำนักงานกองทุนสนับสนุนการวิจัย ที่กรุณาให้การสนับสนุนทุนวิจัย (สัญญาที่ PDF/34/2543), เจ้าหน้าที่หน่วยบริการวิชาการและวิจัย คณะทันตแพทยศาสตร์ มหาวิทยาลัยมหิดล ทุกท่าน ที่อำนวยความสะดวกในการใช้เครื่องมือและอุปกรณ์วิจัย และ Advanced Research Center, The Nippon Dental University at Niigata, Japan ที่อำนวยความสะดวกและให้การช่วยเหลือในการใช้เครื่อง X-ray Photoelectron spectroscopy.

Abstract (บทคัดย่อ)

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Abstract

The purpose of this project was to improve the mechanical properties of the Ag-Sn metal-resin composite to be a good posterior restorative material for amalgam alternation. The project was divided into two studies. First, improved the composite by acid and heat treatment of the filler particles. Secondly, changing the particle size. However, the second study was not possible due to the composite curing system that was not allow the material to cure properly. Therefore this study was modified to change the particle type to be Ag-In and investigated the bonding mechanism.

First project, the silver-tin alloy particles were treated the surface with HCl at 2%, 4% and water washing as a control in combination with heat treatment either at 150°C or 300°C, and no treatment as a control. The treated particles were used for preparation of the composite and done flexural test (ISO-4049) to evaluate the effect of acid and heat treatment on the flexural properties. The treated particle surface including standard sample of Sn, SnO, SnO_2, Ag, Ag_2O were analyzed using an X-ray photoelectron spectroscope (ESCA) to determine the most responsible substrate for the bonding mechanism. Second project, were also done the same as first project to the silver-indium alloy particles. The standard sample of In and the oxide form, InO_2 were used instead of Sn, SnO, SnO_2.

The composite showed the greatest strength when the silver-tin particles got the acid treated at 2% in combination with heat treated at 150°C. At that condition, the ESCA analysis showed the majority of the surface composed of SnO compound. Moreover, the correlation between flexural strength of the composite and their filler Sn3d binding energy was found significantly (R=0.90, P=0.02), which mean SnO might be the most responsible for the bond between the particle and coupling agent. While the silver-indium contained composite showed the greatest strength at 2-4% acid treated with heat treated at 350°C. At that condition, the ESCA analysis did not show any different in the surface composition, only some different in the thickness of the oxide film. However, the composite produced from these two filler particle show difference in flexural modulus with the same flexural strength. These mean we can control the flexural modulus of the composite by changing the particle without any effect on flexural strength.

บทคัดย่อ

โครงการนี้มีวัตถุประสงค์เพื่อพัฒนาคุณภาพวัสดุอุดฟันทางทันตกรรมชนิดโลหะ-เรซิน คอมโพสิต ให้เป็นวัสดุทางเลือกทดแทนวัสดุบูรณะฟันชนิดอมัลกัม เพื่อใช้ในการบูรณะฟันหลัง โครงการนี้แบ่งออกเป็นสองโครงการย่อย คือ โครงการย่อยที่หนึ่งปรับปรุงคุณภาพวัสดุอัดแทรกด้วยวิธีล้างผิวหน้าด้วยกรดและกรรมวิธีทางความร้อน และโครงการย่อยที่สอง โดยการเปลี่ยนขนาดของวัสดุอัดแทรกให้เล็กลง แต่โครงการย่อยที่สอง วิธีการที่นำเสนอไม่สามารถพัฒนาให้เป็นจริงได้เนื่องจากข้อจำกัดของระบบการแข็งตัวของเรซิน ดังนั้นจึงได้เสนอขอปรับปรุงโครงการย่อยที่สองไปเป็นการเปลี่ยนชนิดของวัสดุอัดแทรกเป็นผงเงิน-อินเดียมแทน พร้อมทั้งศึกษากลไกการยึดอยู่ของวัสดุอัดแทรกชนิดนี้ด้วย

นำวัสดุอัดแทรกชนิดผงเงิน-ดีบุก มาล้างผิวหน้าด้วยน้ำหรือกรดไฮโดรคลอริกที่มีความเข้มข้นที่ 2% หรือ 4% และนำไปผ่านกรรมวิธีทางความร้อนที่ 150หรือ 300 องศาเซลเซียส โดยมีผงที่ไม่ผ่านกรรมวิธีทางความร้อนเป็นตัวเปรียบเทียบ นำผงอัดแทรกที่ผ่านกรรมวิธีข้างต้นมาผลิตเป็นวัสดุบูรณะฟันคอมโพสิตและนำไปทดสอบการแตกหักตามวิธีที่แนะนำในมาตรฐานนานาชาติเลขที่ 4049 วัสดุบูรณะฟันทางทันตกรรม เพื่อศึกษาผลกระทบของการล้างผิวหน้าวัสดุอัดแทรกด้วยกรดและกรรมวิธีทางความร้อนต่อความต้านทานการแตกหักจากแรงดัดของวัสดุบูรณะฟัน นำวัสดุอัดแทรกที่ผ่านกรรมวิธีที่กล่าวมาข้างต้น รวมทั้งวัสดุมาตรฐาน ดีบุก, เงิน, ออกไซด์ของเงินชนิด Ag_2O, ออกไซด์ของดีบุกชนิด SnO และ SnO_2 มาวิเคราะห์ผิวหน้าด้วยเครื่อง X-ray photoelectron spectroscope (XPS) เพื่อหาส่วนประกอบบนผิวหน้า ที่รับผิดชอบต่อการยึดอยู่ระหว่างวัสดุอัดแทรกกับกาวซีเมนต์ที่เชื่อมกับเรซิน วิธีการทดลองของโครงการที่สองจะคล้ายกับโครงการที่หนึ่งเพียงแต่เปลี่ยนวัสดุอัดแทรกเป็นผง เงิน-อินเดียม และเปลี่ยนวัสดุมาตรฐานเป็น อินเดียมและออกไซด์ของอินเดียมชนิด In_2O_3

วัสดุบูรณะฟันคอมโพสิตแสดงความต้านการการแตกหักสูงที่สุดเมื่อผลิตโดยวัสดุอัดแทรกที่ได้รับการล้างผิวหน้าด้วยกรดที่ความเข้มข้น 2 เปอร์เซ็นต์ ร่วมกับทำกรรมวิธีทางความร้อนที่อุณหภูมิ 150 องศาเซลเซียส ซึ่งผิวหน้าของวัสดุอัดแทรกดังกล่าวประกอบด้วยสารประกอบดีบุกออกไซด์ชนิด SnO เป็นส่วนใหญ่ นอกจากนี้ ยังพบความสัมพันธ์ในระดับสูงระหว่างกำลังการต้านทานการแตกหักกับพลังงานการยึดอยู่ของสารประกอบที่ผิวหน้า ($R=0.90$, $P=0.02$) นั่นหมายถึง ดีบุกออกไซด์ชนิด SnO เป็นสารประกอบหลักที่รับผิดชอบต่อกำลังการยึดอยู่ระหว่างวัสดุอัดแทรกกับกาวซีเมนต์ที่เชื่อมกับเรซิน ส่งผลต่อกำลังความแข็งแรงของวัสดุบูรณะฟันที่สูงขึ้น ในขณะที่ วัสดุบูรณะฟันคอมโพสิตชนิดที่ใช้ ดีบุก-อินเดียมเป็นวัสดุอัดแทรกแสดงความต้านการการแตกหักสูงที่สุดเมื่อผลิตโดยวัสดุอัดแทรกที่ได้รับการล้างผิวหน้าด้วยกรดที่ความเข้มข้น 2-4 เปอร์เซ็นต์ ร่วมกับทำกรรมวิธีทางความร้อนที่อุณหภูมิ 350 องศาเซลเซียส ซึ่งผิวหน้าของวัสดุอัดแทรกดังกล่าวมิได้แสดงสารประกอบใดที่แตกต่างจากวัสดุอัดแทรกอื่นๆ นอกจากความหนาของออกไซด์ที่ต่างกันเพียงเล็กน้อย จากการทดลองทั้งสองโครงการพบว่า วัสดุบูรณะฟันคอมโพสิตที่ผลิตจากวัสดุอัดแทรกทั้งสองชนิดไม่มีความแตกต่างในแง่กำลังแรงดัด แต่มีความแตกต่างในค่ามอดูลัสของสภาพยืดหยุ่นจากแรงดัด ซึ่งหมายความว่าเราสามารถควบคุมค่ามอดูลัสของสภาพยืดหยุ่นจากแรงดัดได้ตามที่เราต้องการโดยไม่กระทบกับค่ากำลังแรงดัด โดยการเปลี่ยนวัสดุอัดแทรก

โครงการ (ภาษาไทย) **พัฒนาคุณภาพวัสดุอุดฟันทางทันตกรรมชนิดโลหะ-เรซินคอมโพสิต**

(ภาษาอังกฤษ) Improvement of metal-resin composite restorative material.

โครงการย่อยที่ 1 Improvement of metal-resin composite restorative material by acid and heat treatment.

INTRODUCTION

The metal-resin composite (MRC) using Ag-Sn alloy particles as filler, 4-META as a coupling agent and UDMA-TEGDMA as resin matrix, have been developed[1,2)]. The mechanical and physical properties of the composite showed the promising good posterior composite[1,2)]. The bonding between filler particle and coupling agent get through the resin matrix is the critical key point for the strength of the composite in this system, therefore the well understanding of the bonding mechanism would be necessary to improve this composite. It had been hypothesized and reported by several studies[3-9)] that adhesive resin form a chemical bond with metal oxide films especially of base metal (In, Cu, Zn and Sn). Although these oxide films are considered to play an important role in promoting the adhesive ability of adhesive resin to alloy, the detailed factors of these oxide films and adhesive resin has not been well understood. Ohno et al[3,4)] reported the base metal content and the area fraction of the oxide on the surface had great effect on the adhesive ability. Somchai et al[2)] reported the appropriate heat treatment for Ag-Sn particle is required to have good bond to 4-META resin. However the responsible oxide form could not be differentiated. Since the content of the metal element in the composite filler had fixed at the greatest mechanical and physical properties, the important point to clarified in this study is the detail oxide characteristics on the high temperature oxidation which play the important role on the adhesive ability to 4-META.

In the previous study (2), although the effect of the acid and heat treatment had been carried out, the detail information about the acid concentration and bonding mechanism was not well described. Therefore, The objective of this study was to investigate the detail oxide characteristics on the particle surface that modified by acid and heat to understand the bonding mechanism through the strength of the composite.

MATERIALS AND METHODS

Ag-Sn spherical alloy particles (73.2 mass% Ag, 26.8 mass% Sn, Lot no. 9804AS750) were produced by the research unit, Faculty of Dentistry, Mahidol University, Thailand, using an atomization method. The particle size bigger than 53 µm was crushed by a ball-milling machine

(Pulverisette, Fritsch, Germany) at the rate 8 (595 rpm) for 5 h to produce an irregular particle. After crushing, the particles were then sieved with 20 μm mesh size. The particles size less than 20 μm were utilized for the filler of MRC.

Alloy particle surface treatment

The alloy particles were immersed in either 2 or 4% HCl at 80°C and slowly stirred with a magnetic stirrer for 30 min. After this acid treatment, the particles were thoroughly washed with distilled water until no residual acid remained on the surface, verified using $AgNO_3$. The particles were filtered and dried at 40°C for 1 h. In addition to these treatments, water washing at the same condition as acid treatment was included. After drying, the particles were divided into three groups. One of the three groups was used as it is without any heat treatment and the other two groups were placed in an oven for heat treatment either at 150°C or 300°C for 5 min. Therefore, 9 different particles treated with different acid concentrations and heating temperatures were prepared.

The composite specimen preparation and flexural test

The preparation of the MRC specimen and the flexural test were carried out following the procedure reported in the previous study[3)]. The filler content was 93% by weight. Three replications were prepared for each of nine conditions for the flexural test. The data of flexural strength and flexural modulus were analyzed using two-way analysis of variance to analyze the effect of two factors, which were the acid concentration and the heating temperature. The iso-value curves for both of the flexural strength and flexural modulus were obtained using orthogonal polynomial.

Particle Surface analysis by XPS

9 different particles treated with different acid concentrations and heating temperatures including standard sample of Sn, SnO and SnO_2 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 (JPS-9000MC, JEOL Co.Ltd., Tokyo, Japan) with Al Kα radiation under a pressure of 2×10^{-5} Pa. The binding energy of the measured photoelectron peak was calibrated by the C 1s peak at a binding energy of 284.6 eV.

RESULTS

Flexural strength and flexural modulus of the composite

Table 1 shows the summaries of the flexural strength and flexural modulus of the experimental composite. The flexural strength ranged from 85.4 to 102.4 MPa and the flexural modulus from 9.1 to 11.8 GPa. Table 2 shows the result of ANOVA for the flexural strength and flexural modulus of the composite. The flexural strength was significantly influenced by all two main factors ($p<0.01$). The flexural modulus was significantly influenced only by acid concentration ($p<0.01$). Figs. 1 and 2 show the flexural strength and the flexural modulus of the experimental composite, which were drawn by the equation shown below the figure. The square root Ve seen in figure is the square root of mean square of error obtained from ANOVA. As shown in Fig. 1, the flexural strength increased either as the acid concentration increased up to 2.5-3 % or as the heating temperature increased up to 150°C. The highest flexural strength of the composite in this study (102.4 MPa) was obtained from the particle with 2% acid- and 150°C heat-treated. Fig.2 shows that the flexural modulus increased with the acid concentration increased.

Oxide analysis on particle surface

The Sn3d binding energy of the filler particle surface including as crushing particle as well as Sn, SnO and SnO_2 standard sample were shown in Table 1. Fig. 3 shows the Sn3d spectra obtained from as-crushed, 2% acid-treated, 2% acid- and 150°C heat-treated and 2% acid- and 300°C heat-treated particle. The spectra had a wide half width due to the mixture of metallic Sn and their oxidation states as SnO and SnO_2. The spectrum shifted to higher oxidation state as the heat-treated temperature increased. Fig.4 shows the Sn3d spectra obtained from the as-crushed, water waching, 2% acid-treated and 4% acid-treated particle. The spectrum shifted to higher oxidation state when the particle washed in water and to lower oxidation state or more metallic Sn when receive acid treating. The spectrum unclearly shows the different between 2% and 4% acid-treated.

The correlation between the flexural strength of the composite and its filler surface Sn3d binding energy was found and shows on Fig.5. The composite show the highest strength when its filler has Sn3d binding energy around 486.4 eV, which mean majority of its filler surface composed of SnO.

DISCUSSION

In the previous study[2)], although the effect of the acid and heat treatment had been carried out, the detail information about the acid concentration and bonding mechanism was not well described. The bonding between filler particle and coupling agent get through the resin matrix is the critical key point for the strength of the composite in this system, therefore the well understanding of the bonding mechanism would be necessary to improve this composite. In this study, the Ag3d binding energy of the filler particle surface including Ag and AgO_2 standard sample were also evaluated. However, there was not any relation or meaning to interpret and also half of the filler especially high oxidation condition, the Ag3d peak could not be detected, therefore the data of the Ag3d was not reported.

In this study, the acid and heat treatment was selected to modify the surface for analyzing the surface product, which was responsible for the bonding because the expectation that a contamination product would be removed and oxide product would be formed when a particle was acid and heat treated, respectively. The results in this study showed that the acid and heat treatment including their interaction affected the flexural strength of the composite while only acid treatment affected the flexural modulus. The past study[2,10-11)] clearly showed that the wider groove at the grain boundary was found and wider or became pitting on the grain surface with higher acid concentration. The wider grooves increase the bonding area and mechanical interlocking between the alloy particle and resin matrix. Increasing the bonding area will decrease the matrix mass regarding to increasing the flexural modulus. This might be the reason why acid concentration affected both flexural strength and flexural modulus. These results were conformed in vice versa to Kakuta et al's study[12)]. They study the acid and heat treatment on Ag-In, which require higher concentration to wider the groove of grain boundary. Therefore, they did not found any effect of acid treatment on both flexural strength and flexural modulus, only the trend to be higher to acid concentration.

As mention above, we expected the oxide formation on the surface when the particle got the heat treatment. The results in this study suggested that there was a significant difference in the flexural strength of the composite among the temperature of heat treatment. This meant that the condition of the oxide, which was formed by heat, affected the flexural strength of the composite. Fig.1 shows that the flexural strength increased up to 150°C then decreased when the heating temperature increased. In this study, the highest flexural strength was obtained at condition 2% acid and 150°C heat-treated. Several study[3-9)] found that different metal oxide, thickness of the oxide layer or different metal oxide form affected the bonding strength. These founding can imply to explain the results of this study that the proper oxide layer or oxide form might be the main key of the bonding between particle surfaces and coupling agent regard to flexural strength of the composite. However, the specific metal oxide form cannot be distinguished.

From the particle surfaces analysis by XPS in Fig 4, The Sn3d spectra shifted to more metallic tin when received acid treated. This fulfills our expectation that acid treatment could remove any contaminated oxide on the surface. The unexpected data was found on water washing condition, the spectra shifted to higher oxidation state (SnO_2), which was different from the spectra of as-crushed particles. Ohno et al[4)] have been reported that H_2O molecule on the alloy surface exhibits the good adhesion of 4-META and alloy surface. This may be the reason why the flexural strength of the composite at condition at water washing without any heat treatment was different from as crushed composite in the past study$^{11)}$.

Fig 3 shows the Sn3d spectra shifted to oxidation state (SnO) when receive heat treated at 150°C and shift to higher oxidation state (SnO_2). This suggested that the oxide was formed on the particle surface by heat treatment and forming different oxide form up to the temperature of heat. These different oxide forms were expected to give the bond strength to coupling agent differently. As shown in fig 5, the high correlation (r=0.902, p=0.017) between the flexural strength of the composite and its filler surface Sn3d binding energy (eV) was found. The correlation was found in convex parabola shape. This could confirm the hypothesis that 4-META have adhesion ability differently to different oxide type and form. The highest strength of the composite was shown at the binding energy around 486.3-486.5 eV, which was SnO binding energy area. This result could comply that SnO might be the most responsible for the adhesive ability between 4-META and alloy surface.

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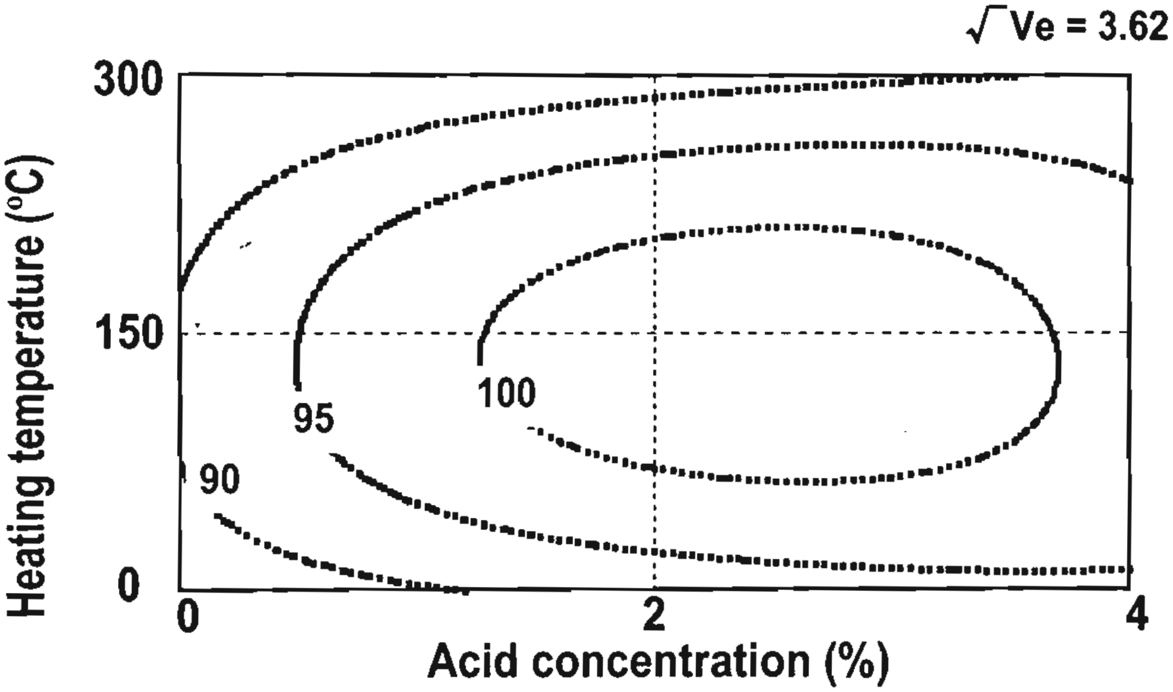
Table 1 The summary of the flexural strength, flexural modulus of the experimental composite and Sn3d binding energy of the filler particle surface including Sn, SnO, SnO_2 standard sample.

Metal-resin composite		Flexural strength: MPa (SD)	Flexural modulus: GPa (SD)	Sn3d binding energy: eV
Acid conc. (%)	Heat temp. (°C)			
0 (water)	Room temp	85.5 (5.2)	9.1 (0.9)	486.8
0 (water)	150	88.9 (1.8)	9.3 (0.5)	486.7
0 (water)	300	85.4 (0.9)	9.2 (0.5)	486.8
2	Room temp	93.9 (1.7)	10.6 (0.6)	486.2
2	150	102.4 (3.5)	10.3 (0.4)	486.4
2	300	85.8 (3.8)	10.8 (0.7)	486.8
4	Room temp	93.2 (4.2)	10.2 (0.6)	486.1
4	150	99.8 (4.7)	11.8 (1.1)	486.2
4	300	89.8 (4.2)	10.4 (1.6)	486.6
As crushing				486.3
Sn				484.9
SnO				486.5
SnO_2				486.7

Table 2 Results of ANOVA for the flexural strength and flexural modulus of the composite

Source	SS	df	MS	F	P
Flexural strength:					
A:Acid Conc.	343.73	2	171.87	3.16	0.00**
B: Heating T.	464.31	2	232.15	17.78	0.00**
AxB	130.16	4	32.54	2.49	0.00**
Error	235.05	18	13.06		
Total	1173.25	26			
Flexural modulus:					
A: Acid Conc.	12.47	2	6.24	8.96	0.00**
B: Heating T.	1.48	2	0.74	1.06	0.37
AxB	3.75	4	0.94	1.35	0.29
Error	12.53	18	0.70		
Total	30.23	26			

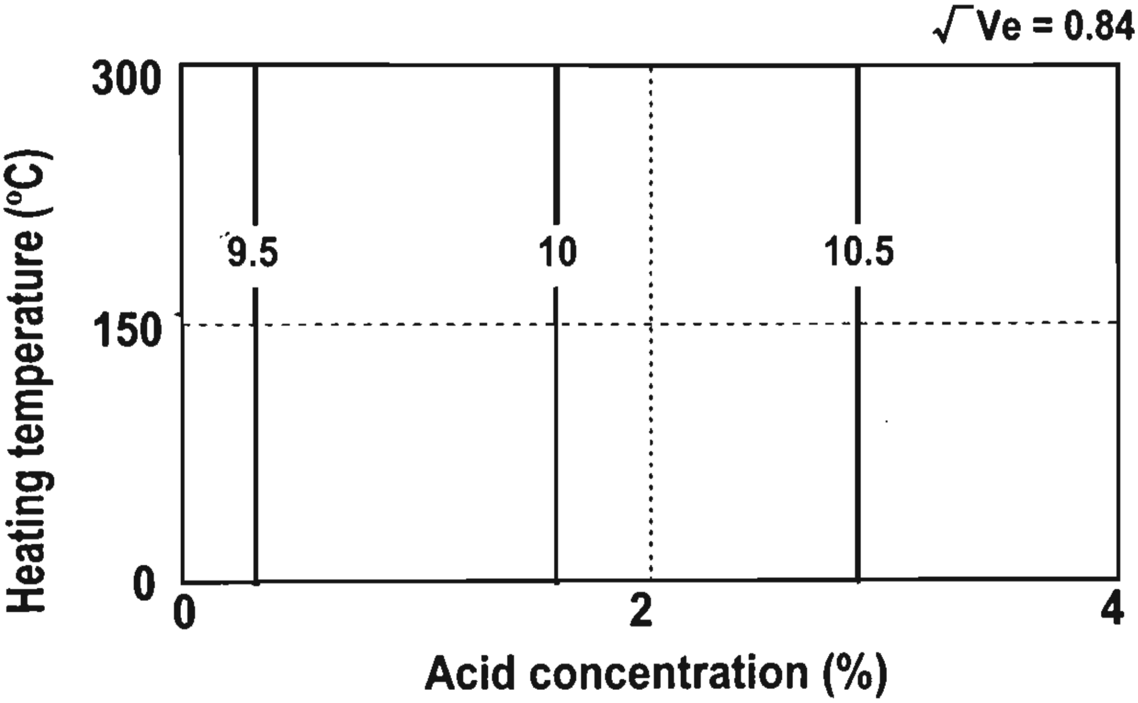
Fig. 1 The flexural strength of the experimental composite



$$Y = 102.43-0.013(a-150)-5.6\mathrm{E}{-04}(a-150)^2 +1.92(b-2)-2.01(b-2)^2+7.39\mathrm{E}{-05}(a-150)^2(b-2)^2$$

Y= Flexural strength (MPa)
a= Heating temperature (°C)
b= Acid concentration (%)

Fig. 2 The flexural modulus of the experimental composite



Y=10.16+0.39 (b-2) : Y= estimated flexural modulus (GPa)
b= acid concentration (%)

Fig. 3 shows the Sn3d spectra obtained from as-crushed, 2% acid-treated, 2% acid- and 150°C heat-treated and 2% acid- and 300°C heat-treated particle.

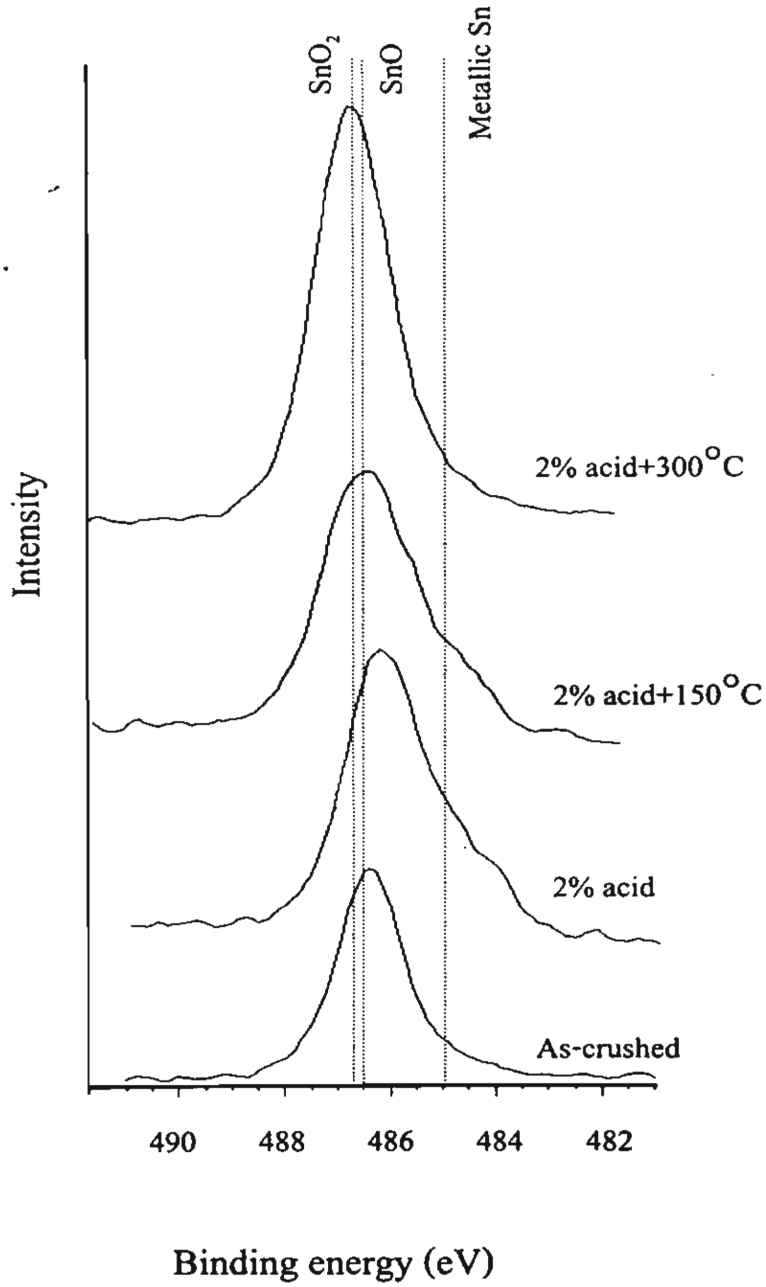


Fig.4 shows the Sn3d spectra obtained from the as-crushed, water waching, 2% acid-treated and 4% acid-treated particle.

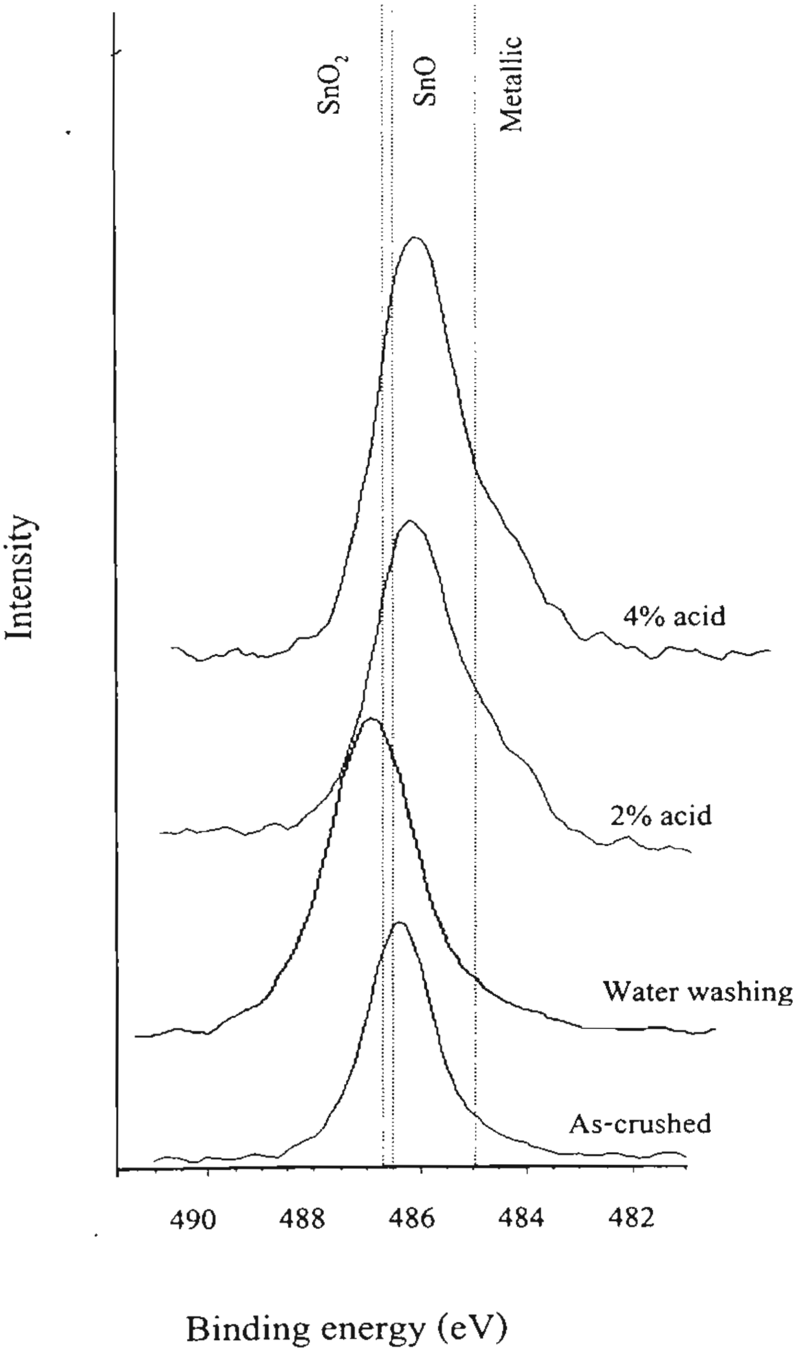
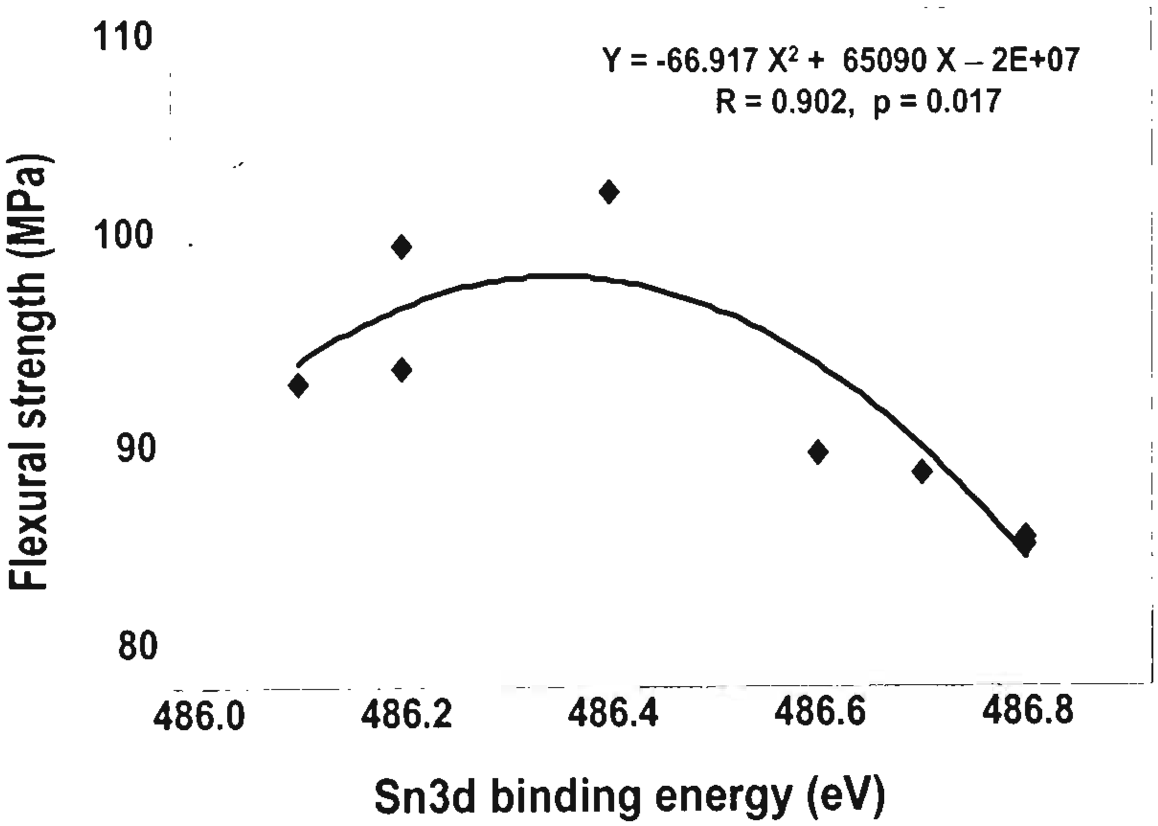


Fig. 5 The correlation between the flexural strength of the composite and its filler surface Sn3d binding energy



โครงการย่อยที่ 2 (โครงการทดแทน) Bonding mechanism of the Ag-In alloy and 4-META coupling agent

INTRODUCTION

A resin composite using inorganic filler has been commonly used for dental restorations. The mechanical properties of resin composites have been markedly improved compared with early composites 1-4). Those resin composites, however, retain some problems that require improvement. For example, their antagonistic wear is considerable for dental restorations, especially for posterior applications. Suzuki et al. 5) suggested that resin composite, which has hard filler particles, caused more antagonistic enamel wear than resin composite containing micro-filled or soft filler particles. Using micro-filler to improve the antagonistic wear, the plasticity of resin composite before setting may decrease 6). The decrease in the plasticity affects the handling of the resin composite.

We have been developing a metal-resin composite restorative material that used metal particles as filler and 4-META as the coupling agent7-10). If a metal particle can be used as the filler, which is more ductile than inorganic particles, the metal-resin composite restorative material would be tougher than the resin composite, which uses inorganic filler. In addition, ductile filler may improve antagonistic wear of the composite restorative material. Ag-Sn alloy particles were used as filler in previous studies 7-10), because Ag-Sn alloy was used as an amalgam powder for a long time, and the technology for making particles was established. In addition, it was expected that the Ag-Sn alloy particles adhered to the resin matrix through 4-META because Mogi reported Sn adhered to a resin using 4-META 11). The flexural strength of the metal-resin composite that used Ag-Sn alloy particles as the filler was 91.8 MPa 10), which matched ISO 4049:2000 "Dentistry - Polymer-based filling, restorative and luting materials" 12). The flexural modulus of the metal-resin composite that used Ag-Sn alloy as the filler was 16.6 GPa 10). This value is similar to other resin composites whose values are 2.3-17.8 GPa 13). Since the flexural modulus indicates the stiffness of materials, it is necessary to decrease the flexural modulus without decreasing the strength for developing tougher restorative materials.

In this study, Ag-In alloy was chosen for the filler particle because the elongation of Ag-In alloy is higher than Ag-Sn alloy 14). In addition, adding indium prevented tarnishing of the silver alloy. An adhesion between the filler and matrix resin is an important factor for the strength of composite materials. Ohno et al. 15) suggested that Ag-In alloy adhered to stainless steel with an adhesive dental resin containing 4-META. This suggests that 4-META is effective as a coupling agent between Ag-In alloy particles and the matrix resin. The purpose of the present study was to evaluate the effect of the acid treatment and the heat treatment of the Ag-In alloy filler particle on the flexural properties of the metal-resin composite that use Ag-In alloy as the filler and 4-META as the coupling agent.

Materials and Methods

Table 1 shows the Ag-In alloy used in this study. Spherical alloy particles of the Ag-In alloy (75 mass% Ag, 25 mass% In) were produced using the atomization method that was usually used for preparing amalgam alloy powder. The spherical alloy particles were sieved to divide them into three different particle sizes, which were less than 38 μm, 38-45 μm and 45-53 μm. These three particle sizes were mixed at the ratio of 3:1:1 by mass, respectively, for the metal filler of a metal-resin composite. The metal filler particles were acid-treated with HCl at 80°C at four different concentrations (0, 2, 4, 6 volume%) for 30 min. After the treatment, the metal filler was washed four times with distilled water and dried in a constant temperature oven (Model 2-2123, Isuzu, Japan) at 40°C. The acid-treated metal filler particle was then heat-treated at four different temperatures (50, 200, 350, 500°C) for 10 min. Sixteen metal filler particles were thus prepared under four concentrations of HCl and four temperatures of heat-treatment.

The prepared metal filler particles were then immersed in an acetone solution containing 4 mass% 4-(2-methacryloyloxy ethoxycarbonyl) phthalic anhydride (4-META) 0.4 mass% benzyl peroxide (BPO) at 40°C for 30 min. After the immersion, acetone was vaporized at 40°C for 10 min in the constant temperature oven. Table 2 shows the materials used for the aforementioned treatments.

The base resin monomer consisted of the mixture of 75 mass% 1,6-Bis(methacryloyloxy-2-ethoxycarbonyl-amino)-2,4,4,(2,4,4)-trimethylhexane (UDMA) and 25 mass% triethylene glycol dimethacrylate (TEGDMA). 0.25 mass% N,N - dimethyl - p - toluidine was added to the base resin monomer as an accelerator. Using the treated metal filler particles and the base resin monomer, flexural test specimens were prepared following the ISO 4049:2000 12). The treated particles were mixed with the resin monomer at 93 mass% of the filler content for 30 s. The mixture was filled in a polytetrafluoroethylene-coated stainless steel mold placed on a glass plate. After the filling of the mixture, another glass plate was applied on the top of the mold to remove excess material from the mold, and a clamp held the specimen assembly together. After 3 min from the start of mixing, the mold was immersed in 37°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°C for 24 h. After 24 h storage, the specimen was polished using #1000 SiC paper, and the dimensions were measured before testing. The specimen sizes were 25 ±0.1 x 2 ±0.1 x 2 ±0.1 mm. Two specimens were prepared for each of the 16 conditions, which were the combinations of the conditions of acid-treatment and the conditions of heart-treatment.

A three-point flexural test (cross-head speed: 1 mm/min, distance of support: 20 mm) was carried out using a universal testing machine (Autograph DSS-5000, Shimadzu Ltd., Kyoto, Japan), and the flexural strength (σ) and the modulus of elasticity under flexural stress (flexural modulus, E) were calculated from the following equations (1) and (2), respectively.

$$\sigma = 3Fl / 2bh^2 \qquad (1)$$

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

$$E = F_1 l^3 / 4bh^3 d \qquad (2)$$

F1 is the load at a convenient point in the straight-line portion of the trace (N),
l is the distance between the supports (mm),
b is the width (mm),
h is the height (mm) of the specimen,
d is the deflection at load F1 (mm),

Values for both the flexural strength and modulus were analyzed using two-way analysis of variance to analyze the effect of two factors that were the concentrations of HCl at acid-treatment and the temperature of heat-treatment.

Results

Table 3 shows the mean values of flexural strength of the experimental metal-resin composites, which used Ag-In alloy particles as the filler. The flexural strength of the metal-resin composite ranged from 65.5 MPa to 91.0 MPa under the different conditions of acid treatment and heat treatment. Results of ANOVA showed that the effects of the temperature of heat treatment and the interaction of two main factors, which were the acid concentration and the temperature of heat treatment, on the flexural strength were highly significant (temperature of heat treatment $p<0.01$, power >99.9%, interaction of two main factors $p<0.01$, power 98.2%). These results suggest that the temperature of the heat treatment influenced the flexural strength of the experimental metal-resin composite, which used Ag-In alloy particles as the filler, but its effect, varied with different acid concentrations of acid treatment. Fig. 1 shows the flexural strength of the metal-resin composite at each condition. The highest strength (91.0 MPa) was obtained at 350°C heat treatment except for the specimens which were treated with 0% HCl (distilled water). At 0% HCl, which was the immersion in distilled water without acid, there were no differences in the flexural strength among different temperatures of the heat treatment. Tukey's multiple comparison, as shown in Table 4, suggests that the flexural strength of the metal-resin composites, which used 350°C heat treatment, was higher than those of the other experimental metal-resin composites.

Table 5 shows the mean values of the flexural modulus of the experimental metal-resin composite. The mean values of the flexural modulus ranged from 8.4 GPa to 10.5 GPa at different treatments. Result of ANOVA showed that there were no significant effects of heat treatment and acid treatment on the flexural modulus of metal-resin composite. The total average of the flexural modulus was 9.1 GPa.

Discussion

ISO 4049: 2000 requires 80 MPa or greater flexural strength of polymer-based filling and restorative materials for restorations involving occlusal surfaces (Type 1, Class 1) 12). In this study, the metal-resin composite, which used acid-treated and 350°C heat-treated Ag-In alloy fillers, matched strength requirement. When a metal particle was acid-treated, it was expected that a product on the particle be removed, and when a metal particle was heat-treated, it was expected that an oxide on the particle be formed. The results in this study suggested that there was a significant difference in the flexural strength of the metal-resin composite among the temperatures of heat treatment. This meant that the condition of an oxide, which formed by heat treatment, affected the flexural strength of the metal-resin composite. The other result in this study showed the effect of heat-treatment on the flexural strength changed with the condition of acid treatment. Fig. 1 shows that there was a different tendency in the flexural strength clearly between not using acid-treated filler (0%) and using acid-treated filler (2%HCl, 4%HCl, 6%HCl). An original Ag-In alloy particle may have been covered with an oxide, which was formed during the atomizing process. It was suggested that the existence of an original oxide layer affected the form of the oxide on the Ag-In alloy particle by the heat treatment. In this study, the highest flexural strength was obtained using a 4% HCl acid-treated, 350°C heat-treated metal filler material, and the lowest strength was obtained with on acid-treated, 50°C heat-treated metal filler, which may have a little oxide layer. When the metal filler particle was not acid-treated, the flexural strength of the metal-resin composite was not changed with the temperature of the heat treatment.

To examine the surface condition of both the acid-treated and non-acid-treated metal filler particles, surface analysis by X-ray photoelectron spectroscopy (JPS-9010MC, JEOL, Japan) was performed with Mg Kα radiation on the typical metal particles in this study. The binding energy of elements were calibrated by C1s as 284.4 eV 16). Fig. 2 shows the wide spectrum of the X-ray photoelectron spectroscopy of the Ag-In alloy particle, which was treated with 0% HCl at 50°C. A high indium peak (3d5/2, 444.1 eV) and low silver peak (3d5/2, 367.8 eV) were found on the surfaces. Fig. 3 shows the wide spectrum of the Ag-In alloy particles, which were treated with 0% HCl at 350°C. There is a high indium peak (3d5/2, 444.2 eV) and a low silver peak (3d5/2, 368.1 eV) on the surface. There is a similar tendency of the spectrum between the 50°C heat-treated surface and 350°C heat-treated surface when the particle was not acid-treated. With referred to the NIST XPS Database 16), the peaks of indium in Figs. 2 and 3 are recognized as In or In2O3. It was difficult to identify In or In2O3 from the wide spectrums, but it was suggested to be In2O3 because the original Ag-In alloy particle was previously heated during the particle making process. Fig. 4 shows the wide spectrum of the X-ray photoelectron spectroscopy of the Ag-In alloy particle, which was treated with 4% HCl acid treatment and 350°C heat treatment. Two high peaks that are indium (3d5/2, 444.2 eV) and silver (3d5/2, 367.7 eV) were found clearly on the metal filler surface. The peak of indium was recognized as In or In2O3, but was suggested to be In2O3 because the Ag-In alloy filler was heat-treated at 350oC. The peak of silver was recognized as Ag, AgO or Ag2O. There was clearly silver or silver oxide on the acid-treated particle, while there was little silver or silver oxide on the non-acid-treated particle. This suggests that the existence of silver or silver oxide on the particle affects the adhesion between Ag-In alloy filler particle and matrix resin, and affects to the flexural strength of the metal-resin composite, which used Ag-In alloy particle as the filler. To clarify the mechanism of the bonding between the treated metal filler and matrix resin, it is necessary to use high resolving power equipment for analyzing the filler surfaces, and to identify the products on the metal filler. Further research is necessary to explain the relation between the surface condition and the mechanical properties of the metal-resin composites.

There was no significant difference in the flexural modulus among 16 metal-resin composites that were prepared under the different conditions of acid treatment and heat treatment in this study. This result suggested that the acid treatment and the heat treatment does not affect the flexural modulus of the metal-resin composite, which used Ag-In alloy particle as filler. Even if the treatments affected the flexural modulus, it would be only small effect. The average flexural modulus of the Ag-In alloy filler metal-resin composite was 9.1 GPa in a present study. This value was lower than that of the metal-resin composite, which used Ag-Sn alloy particles as the filler (16.6 GPa)10). The calculated volume percentage of the Ag-In alloy filler in the metal-resin composite was 59%, while the Ag-Sn alloy filler was 61% in the metal-resin composite10). A proportion of the matrix resin in a metal-resin composite was not so different between the Ag-In alloy filler metal-resin composite and the Ag-Sn alloy filler metal-resin composite. In addition the flexural strength of the Ag-In alloy filler metal-resin composite was 91.0 MPa, while that of the Ag-Sn alloy filler metal-resin composite was 91.8 MPa 10). When a comparison was made between the flexural properties of two metal-resin composites, only the flexural modulus decreased by approximately a half. As a result that surface treatments did not markedly affect the flexural modulus, and it was suggested that the flexural modulus of a metal-resin composite decreased by using Ag-In alloy particles as the filler. It is important to control the flexural modulus without decreasing the flexural strength using various filler materials. It was suggested that a restorative material, which is tough, could be developed using ductile filler materials.

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Table 1 Ag-In alloy used in this study

Components of alloy	Ag 75 mass% In 25 mass%
Particle size	>45-53 μm 20 mass% >38-45 μm 20 mass% ≤38 μm 60 mass%
Lot No.	9808A1750

Prepared by The Research Unit, Faculty of Dentistry, Mahidol University, Thailand

Table 2 Materials used in this study

	Materials	Code	Batch No.
Coupling agent	4-Methacryloxyethyl trimellitate anhydride[1] (crystal form)	4-META	97001
Monomers	1,6-Bis(methacryloyloxy-2-ethoxycarbonyl-amino)-2,4,4(2,2,4)-trimethylhexane[2]	UDMA	050155
	Triethylene glycol dimethacrylate[3]	TEGDMA	1104S
polymerization initiator	Benzoyl peroxide[4]	BPO	M6K9289
	N, N-dimethyl-p-toluidine[5]	DMPT	GA01
inhibitor	Hydroquinone monoethyl ether[6]	MEHQ	PAM0168

[1] Sun Medical, Osaka, Japan

[2] Negami Kogyo, Negami, Japan

[3] Shin Nakamura Kagaku Kogyo, Osaka, Japan

[4] Nacalai Tesque Inc, Kyoto, Japan

[5] Tokyo Kasei Kogyo, Tokyo, Japan

[6] Wako pure chemical industries, Osaka, Japan

Table 3 Flexural strength of metal resin composite using Ag-In alloy as the filler, σ/MPa

Temperature of heat treatment	Concentration of HCl			
	0%	2%	4%	6%
50℃	78.0	65.5	69.5	68.5
200℃	73.5	68.5	71.0	71.0
350℃	73.0	82.0	91.0	85.0
500℃	80.0	69.5	71.0	75.5

$\sqrt{Ve}=3.5$

Table 4 Tukey's comparison of flexural strength by the temperature of the heat treatment (Probability of significance)

	50℃	200℃	350℃
200℃	0.983		
350℃	<0.001**	<0.001**	
500℃	0.196	0.339	0.001**

**Probability of significant difference is greater than 95%

Table 5 Flexural modulus of metal-resin composite using Ag-In alloy as filler, *E*/GPa

Temperature of heat treatment	Concentration of HCl			
	0%	2%	4%	6%
50℃	9.9	8.4	8.5	9.2
200℃	9.0	9.0	9.9	9.4
350℃	9.1	8.9	8.8	8.8
500℃	9.5	8.9	10.5	9.1

$\overline{Ve}=0.6$

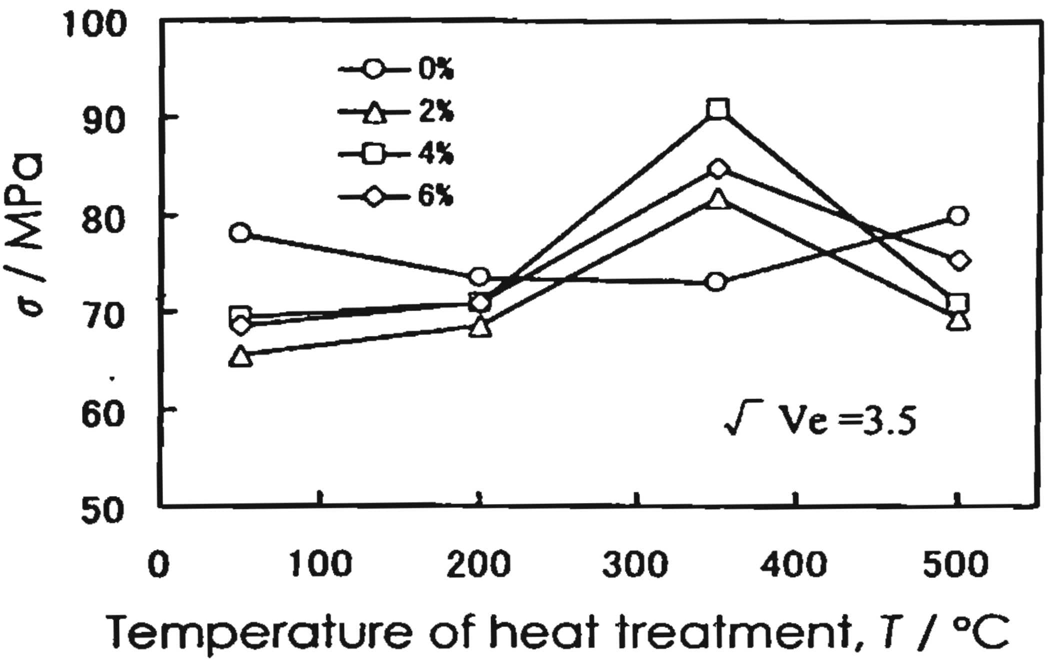

Fig. 1 Flexural strength of metal resin composite using Ag-In alloy filler.

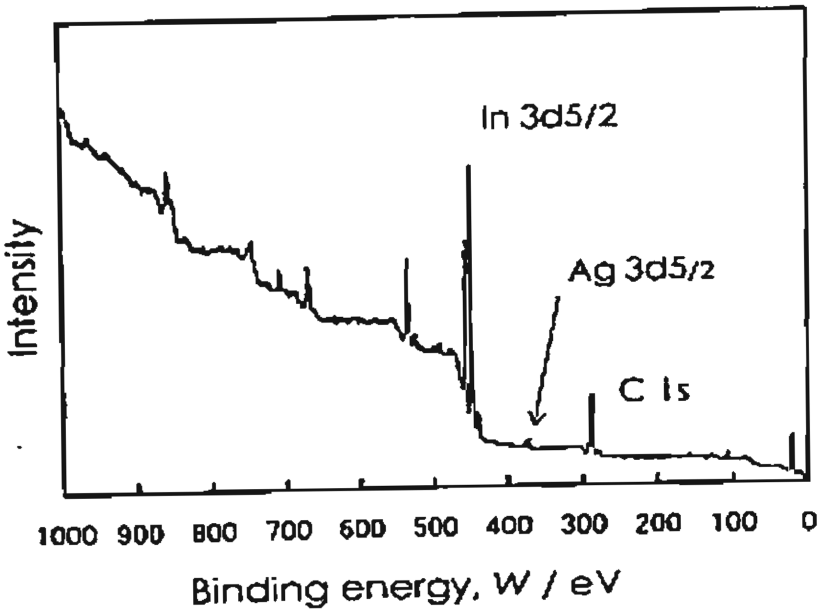

Fig. 2 Spectrum of X-ray photoelectron spectroscopy.
(0% HCl acid treatment and 50℃ heat treatment)

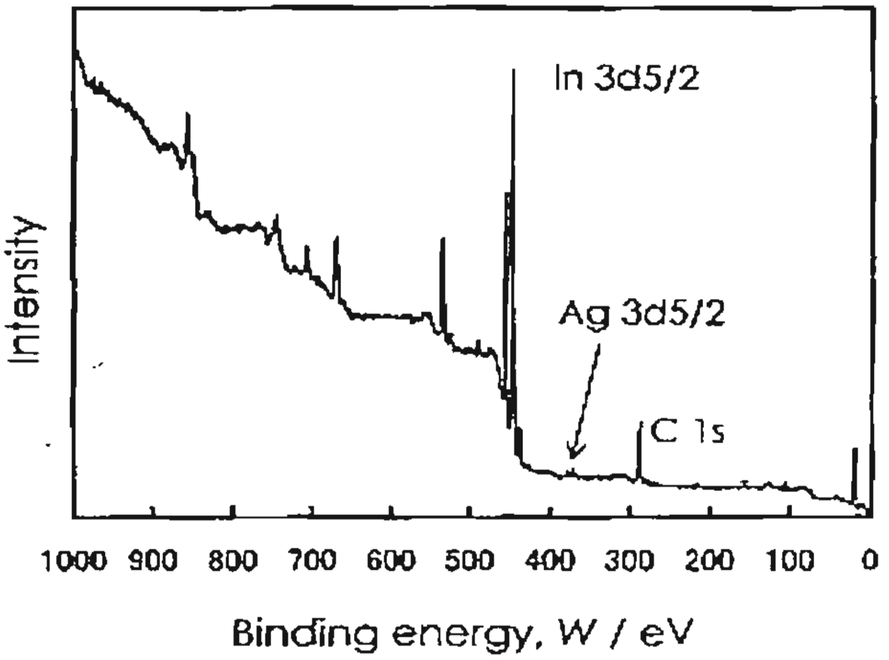

Fig. 3 Spectrum of X-ray photoelectron spectroscopy.
(0% HCl acid treatment and 350℃ heat treatment)

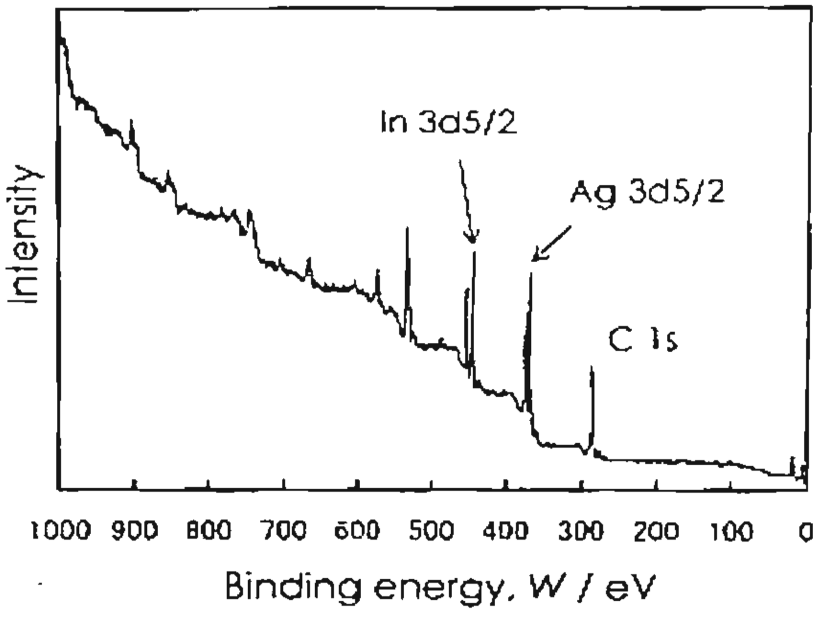

Fig. 4 Spectrum of X-ray photoelectron spectroscopy.
(4% HCl acid treatment and 350℃ heat treatment)

Output ที่ได้จากโครงการวิจัยที่ได้รับทุนจาก สกว

1. การเสนอผลงานในที่ประชุมวิชาการนานาชาติ ตามเอกสารในภาคผนวกที่ 1
2. การนำผลงานวิจัยที่ได้ไปใช้ประโยชน์
   - 2.1. เป็นการพัฒนา สร้างนักวิจัยใหม่ให้ได้เรียนรู้การทำงานร่วมกับนักวิจัยมืออาชีพในระดับนานาชาติ
   - 2.2. ความรู้ที่ได้เป็นองค์ความรู้พื้นฐานใหม่ที่สามารถปรับใช้กับการเรียนการสอน และเป็นพื้นฐานในการวิจัยเชิงลึกต่อไป
   - 2.3. เป็นการสร้างเครือข่ายความร่วมมือในระดับนานาชาติ ทั้งในระดับองค์กรวิชาการ และองค์กรเอกชน
   - 2.4. สร้างกระแสความสนใจในวงวิชาการอย่างกว้างขวาง เกี่ยวกับการยึดอยู่ของสารยึดติดทางทันตกรรม
3. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ
   - 3.1. Evaluation of the bonding between Ag-Sn particle and 4-META coupling agent of the metal resin composite (ตามเอกสารในภาคผนวกที่ 2)

     <u>หมายเหตุ</u> เอกสารที่ส่งมาเป็น manuscript ที่ส่งไปลงตีพิมพ์ในวารสาร Dental materials Journal แล้วอยู่ระหว่างการ Peer review โดยผู้เชี่ยวชาญ

   - 3.2. Development of Metal-resin Composite Restorative Material Part 4 Flexural Strength and Flexural Modulus of Metal-resin Composite using Ag-In alloy Particles as Filler, *Dent Mater J* 21 (2): 181-190, 2002. (ตามเอกสารในภาคผนวกที่ 3)

ภาคผนวก

เอกสารผลงานที่ได้จากการวิจัยครั้งนี้

1. บทคัดย่อ การเสนอผลงานวิจัยในการประชุม International Association in Dental Research, General Session. ณ.ประเทศญี่ปุ่น ระหว่างวันที่ 27-30 กรกฎาคม 2543 เรื่อง Effect of acid and heat treatment on the properties of metal-resin composite, Poster ที่ 1362

2. manuscript ที่ส่งไปลงตีพิมพ์ในวารสาร Dental materials Journal เรื่อง Evaluation of the bonding between Ag-Sn particle and 4-META coupling agent of the metal resin composite

3. Reprint เรื่อง Development of Metal-resin Composite Restorative Material Part 4 Flexural Strength and Flexural Modulus of Metal-resin Composite using Ag-In alloy Particles as Filler, *Dent Mater J* 21 (2): 181-190, 2002. (นักวิจัยร่วม)

เอกสารภาคผนวกที่ 1

บทคัดย่อ การเสนอผลงานวิจัยในการประชุม International Association in Dental Research, General Session. ณ.ประเทศญี่ปุ่น ระหว่างวันที่ 27-30 กรกฎาคม 2543 เรื่อง Effect of acid and heat treatment on the properties of metal-resin composite, Poster ที่ 1362

1321 Visco-Elasticity of Four Resilient Denture Liners as Determined by Relaxation Time

S DUSHYANTHRA, J KIM, L KNODLER, S SAADE, C THOMAS* (Faculty of Dentistry, University of Sydney, Australia)

The ideal semi-permanent resilient lining for dentures has been sought for many years and it is important for it to be either visco-elastic or elastic. Examples of an elastic material could be Molloplast B (Kulzer) and a visco-elastic a tissue conditioner such as Visco-Gel (Dentsply). Between these could be three recent introductions, Soft and Extra-soft (GC) and Permaquick (Kohler). A stress relaxation test was used to evaluate the visco-elasticity of the latter three and Molloplast B. Seven disc specimens from each material, 3 x 10 mm diameter, were made in a standardised mold stored in water at 37° and tested in a water bath at 37°. A testing sequence of cyclical loading was devised to simulate clinical function and establish relaxation time. A 200 gm load was applied and released through a transducer measuring device, at 5 sec intervals for 1 min and the dimensional change recorded by datalogger to a PC. All specimens were tested three times at weekly intervals. Relaxation time in secs (τ) was calculated by the formula

$$h(t) = h_\infty + (h_0 - h_\infty)(1 - e^{\frac{-(t-3)}{\tau}})$$

τ ranged from 0.77-1.12 (GC Soft), 0.90-1.66 (GC Extra Soft), 1.40-3.03 (Permaquick) and 0.62-1.13 (Molloplast B). Statistically there were no differences between the four materials although Permaquick came the closest in a one sample Kolmogorov-Smirnov Test ($p<0.068$). The material with longest relaxation (Permaquick) would be selected as the best for clinical purposes but clinical testing should be carried out, including longevity studies.

1322 Comparison of Retaining Properties of Impression Materials for Fixation Impressions.

B. REUSCH, E. WANEK, C. WILL, J. ZECH* (ESPE Dental AG, Seefeld, Germany)

In the making process of e.g. telescopic crowns or implants a fixation impression is necessary by which transfer caps are fixed in the impression. In the process of removing and pouring the impression the transfer caps have to be fixated precisely to achieve an accurate cast. The aim of this study was to compare the ability of three commercially available monophase impression materials to retain transfer caps in the set impression. Using metal pins as a model for those transfer caps placed on teeth, the force required to remove these pins out of the impression was measured. Four standardized hexagonally shaped metal pins were fixed in a silicone mold under different angles to the vertical (0.8°, 1°, 4°, 5°). Impregum Penta (IP, ESPE), Impregum Penta Soft (IPS, ESPE) and Monopren Transfer (MT, Kettenbach) were used to make six fixation impressions for each material transfering the metal specimens into the impression. The force required to pull the metal pins out of the set impression was determined using a Zwick universal testing machine. Mean values including the standard deviation (in brackets) are summarized in the following table. Mean values within one column marked by the same characters are not significantly different (ANOVA, $p \leq 0.05$)

Material	Force [MPa] 0.8°	Force [MPa] 1°	Force [MPa] 4°	Force [MPa] 5°
IP	42.1 (2.9)^a	45.6 (5.9)^a	35.2 (4.5)^a	28.6 (4.9)^a
IPS	41.1 (6.9)^a	40.8 (7.6)^a	29.6 (9.7)^a	30.0 (6.3)^a
MT	31.1 (1.2)^b	37.9 (5.4)^a	19.4 (4.2)^b	19.7 (3.5)^b

On the basis of this model it can be concluded that the ability to retain transfer caps in the set impression is not significantly different for IP and IPS whereas it is significantly lower for MT except for the 1° angle.

1323 Thickness and Stiffness Characteristics of Processed Customized Mouthguard Materials.

E.J. WAKED,* T.K. LEE, and A.A. CAPUTO (UCLA School of Dentistry).

Mouthguard thickness and stiffness is important to provide proper support and protection for the orofacial structures. The purpose of this investigation was to determine the thickness after processing and the deformational changes after pressure loading of different types of customized mouthguards.

Two fabrication methods were used for the same dental arch, vacuum on a dental stone model and pressure lamination on a die stone model. Ten mouthguards were fabricated using the following materials and processing techniques: Group I-vacuumed (4 mm) Colored Mouthguard (National Keystone); Group II-vacuumed (4 mm) Proform (Dental Resources), Group III- pressure laminated (2 x 3 mm) Drufosoft (Westone Laboratories, Inc.). After processing, the thickness of the mouthguards was measured in 3 places: lingual cusps of first molar, distal marginal ridge of first premolar, facial of central incisor. The stiffness of each group was determined by applying a simulated grinding force to the first molar lingual cusp areas. A 10 lb force was applied on an Instron test machine with a blunt probe. The corresponding penetration was measured with a dial gage. Thicknesses and force-deflection measurements of different mouthguard groups were compared using ANOVA and post hoc tests.

The mean thickness at the molar for Groups I and II were 1.55 and 1.52 mm respectively and were significantly smaller than the corresponding thickness for Group III (3.48 mm). The mean thickness at the facial of the incisors for Groups I and II were similar (2.05 and 2.06 mm respctively) and were significantly smaller than the corresponding thickness for Group III (3.29 mm). Groups I and II demonstrated similar stiffness that was higher than for Group III. These results showed that only the pressure laminated mouthguards produced material thicknesses that have been previously shown to be adequate for protection from trauma to athletes.

1324 Bi-axial Flexural Strengths of Composites for Metal-free Crown and Bridge

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(1. University of Alabama, USA, 2. University of Kagoshima, Japan)

The purpose of this study is to evaluate the flexural strengths and effects of fiber reinforcement for indirect resin composites used for metal-free bridges. Composite disk specimens (16mm diameter, 2mm thick) were fabricatee with a low-temperature post-cure material, Cristobal (Densiply): and two high-temperature post-cure materials, Belleglass (Kerr) and Sculpture (Jeneric/Pentron). Fiber reinforced specimens were fabricated for Belleglass and Sculpture. The specimens were polished to #4000 grit and immersed in 37°C water for 24 hours. A bi-axial flexural test was employed by a ring-on-ring bending apparatus at 1.27 mm/min of crosshead speed, and failure modes were evaluated. Ten specimens were tested for each condition, and all data were statistically analyzed by ANOVA. The results (table below) demonstrated that flexural strengths were influenced by post-cure mode but not by fiber reinforcement. However, it is concluded that the fiber reinforcement is effective to prevent the catastrophic failure of composite bridge as the crack propagation can be stopped by fiber.

Table. Results of Flexual Strengths and Failure Mode (P: pulverized, C: cracked)

( ): failure mode	Cristobal	BelleGlass	Sculpture
Without fiber	138.9±16.4^a (P)	123.7±16.9^{ab} (P)	105.9±10.0^c (P)
Single fiber layer	N/A	120.2±19.2^d (C)	114.2±11.4^d (C)
Doublefiber layer	N/A	105.1±17.1^{bc} (C)	101.0±7.7^c (C)

N/A: No fiber system available. Groups with same alphabet present significance deference ($p<0.05$).

1325 Cross-Linked Dental Resin Reinforced with Noncovalent Bond.

J. TANAKA*[1], J.W. STANSBURY[2], J.M. ANTONUCCI[3], K. SUZUKI[1] ([1]Okayama Univ, Okayama, Japan, [2]Univ of Colorado, Aurora, CO, USA, [3]NIST, Gaithersburg, MD, USA

The purpose of this study was to improve the mechanical properties(MP) of dental resin from the viewpoint of the polymeric network structure. Acidic diluent monomers(ADM) were studied as potential alternatives to TEGDMA as a conventional diluent monomer. Photopolymerization kinetics were measured with near infrared spectroscopy. The effect of ADM on the MP was examined by three point flexural strength(FS) measurements on fully cured polymers. Resins based on UDMA with varying amounts of ADM as diluent monomers were evaluated in comparison with UDMA homopolymer. Each of the ADM(M_2) in this study resulted in accelerated copolymerization rates. Among the ADM used with UDMA(M_1), every ADM-modified resin was improved in MP($p<0.05$) and methacrylic acid(MAA) produced optimized improvement of MP. Moreover, the addition of Acrylic acid(AA) was also an effective way to improve the work of fracture(WF).

M_1(Mole ratio)	M_2(Mole ratio)	FS(MPa)	WF(kJ/m^2)
UDMA	————	169.1 ± 10.9	10.3 ± 2.9
UDMA(0.62)	Methacryloyl ethyl phthalate(0.38)	196.3 ± 1.8	14.4 ± 0.9
UDMA(0.33)	MAA(0.67)	250.1 ± 18.3	22.9 ± 3.6
UDMA(0.33)	AA(0.67)	205.2 ± 9.5	34.2 ± 13.5

Acidic monomers as diluent monomers had an excellent potential to improve the mechanical properties of resins based on UDMA. jiro_t@dent.okayama-u.ac.jp

1326 Effect of acid and heat treatments on the properties of metal-resin composite:

S. URAPEPON*, K. KAKUTA[1], H. OGURA[1] (Mahidol Univ., Bangkok, Thailand, [1]The Nippon Dental Univ. at Niigata, Japan)

The purpose of this study was to investigate the effects of the acid and heat treatments of the Ag-Sn filler particles on the flexural strength and flexural modulus of the metal-resin composite developed in our previous study. The filler particles were treated with HCl acid (2% and 4%) and heat (150°C, 300°C). In addition to these treatments water and 23°C were included in the test condition. The treated particles were coupled with 4-META. Flexural test specimens were prepared using the treated particles mixed with UDMA-based resin matrix at 93% filler content and tested following ISO 4049 for resin-based filling materials. Data for the flexural strength and flexural modulus were statistically analyzed using two-way ANOVA and Turkey's test. The surfaces of the treated filler particles as well as the standard sample of Sn, SnO and SnO_2 were investigated by X-ray photoelectron spectroscopy (XPS). The mean flexural strength and flexural modulus of the composites ranged from 85.0-102.4 MPa and 9.1-11.8 GPa, respectively. Both acid and heat treatments significantly influenced the flexural strength of the composite, whereas flexural modulus was significantly influenced only by acid treatment. The Sn3d spectra of the particles showed the peak shift to the lower binding energy side when the particles were treated with acid, and to the higher binding energy side when treated with water or the heating temperature increased. A significant correlation was found between the strength of the composite and the binding energy number. The highest strength was obtained from the metal-resin composite with 2% acid- and 150°C heat-treated filler particles. This filler particle had the Sn3d binding energy at 486.4 eV, which is SnO binding energy area. These results indicate that SnO is responsible for the good bond between Ag-Sn particle surface and 4-META coupling agent, regarding to the higher strength of the composite. This study was partially supported by Thailand Research Fund (PDF/34/2543)

1327 Di-methacrylate *versus* mono-methacrylate composites as temporary crown and bridge materials.

DC WATTS* and S-H KIM.
University Dental Hospital of Manchester, UK.

Polymer-based crown and bridge (TCB) materials must meet stringent design and performance requirements for effective clinical function. The aim was to investigate time-critical properties relating to network-formation of four materials: a mono-methacrylate based material, **TRM** (*Trim*, Boswoth, USA), & 3 di-methacrylate materials: **LXT** (*LuxaTemp*, DMG, D); **TMP** (*TempPhase*, Kerr, USA) and **PT3** (*ProTemp 3 Garant*, Espé Dental AG, D). All were fabricated *via* manufacturers' instructions & devices. The following properties were determined: Exotherm peak-temperatures (ΔT); Bonded-disk shrinkage-strain (ε) at 23 & 37 °C, (particularly at 5, 10, 120 min); Degree of conversion (DC) by FTIR at 24 h; Dynamic thermal strain; Diametral strength at 5 *min* & 1 h; Compressive creep; Strength (S_E) to resist chipping 0.5 mm from specimen-edges aged 1 mo. at 37°C and 80 % RH. The different chemistry of **TRM** resulted in slower setting, however the mean exotherm of 5 °C was not significantly lower ($p>0.05$, Scheffé) than that of **LXT** and **PT3**, but that for **TMP** was 12 °C. DC for dimethacrylates was *ca* 50 % for **LXT** and **PT3**, but 42 % for **TMP**. Shrinkage (ε) at 5 min & 23 °C was only 0.1 % for slow setting **TRM**. For the dimethacrylates, **LXT** and **PT3** were comparable (*ca* 2.3 %) and **TMP** was 3.3 %. Edge strength for **PT3** (2073 N) was a factor of 3 greater than that for either **TMP** or **LXT**. **PT3** and **LXT** had the better balance of properties, with **PT3** superior in Edge Strength.

1328 Histological Evaluation of PDL Cells 3D Cultured on Dental Implants

S. TSUTSUMI*, C. PENG, K. MATSUMURA, N. NAKAJIMA, S-H HYON.
(Institute for Frontier Medical Sciences, Kyoto University, Kyoto, Japan)

In order to require the functional recovery of dental implants, a trial of regenerating periodontal ligament (PDL) around dental implants was attempted using a hybrid dental implant of titanium coated with ethylene-co-vinyl-alcohol (EVA) on which collagen was immobilized. Our previous investigation on biocompatibility of this novel implant material has been reported in the last IADR meeting. It showed a good morphological behavior and physiological function of the PDL cells cultured around the implant in vitro. In this report, a 3D culture method and histological response around the hybrid implant were examined in dog experiments.

The PDL cells obtained from outgrowth of dog's periodontium. A titanium implant with EVA and collagen coating was rotated in the culture dishes so that the PDL cells can adhere over the cylindrical implant surface easily. Evaluation of adhesion and proliferation of the PDL cells around the implant surface was confirmed by Giemsa's staining and scanning electron microscope, and the living cells were observed under fluorescence microscope and phase contrast microscope. These images showed that our 3D culture method gained a satisfactory adhesion and proliferation of the PDL cells around the implants surfaces. Besides, We examined PDL regeneration in dog experiments. The histological tissue response showed that the synthesized fibers around implants which were similar to the periodontium were formed in vivo. These results suggest that the novel hybrid dental implants with PDL cells has potentiality to regenerate periodontal ligament which could mimic the behavious of the natural tooth root. Partially supported by Japan National Industrial Research Institute of Nagoya Grant H9-988.

Effect of acid and heat treatments on the properties of metal-resin composite:

S. URAPEPON*, K. KAKUTA[1], H. OGURA[1] (Mahidol Univ., Bangkok, Thailand, [1]The Nippon Dental Univ. at Niigata, Japan)

The purpose of this study was to investigate the effects of the acid and heat treatments of the Ag-Sn filler particles on the flexural strength and flexural modulus of the metal-resin composite developed in our previous study. The filler particles were treated with HCl acid (2% and 4%) and heat (150°C, 300°C). In addition to these treatments water and 23°C were included in the test condition. The treated particles were coupled with 4-META. Flexural test specimens were prepared using the treated particles mixed with UDMA-based resin matrix at 93% filler content and tested following ISO 4049 for resin-based filling materials. Data for the flexural strength and flexural modulus were statistically analyzed using two-way ANOVA and Turkey's test. The surfaces of the treated filler particles as well as the standard sample of Sn, SnO and SnO_2 were investigated by X-ray photoelectron spectroscopy (XPS). The mean flexural strength and flexural modulus of the composites ranged from 85.0-102.4 MPa and 9.1-11.8 GPa, respectively. Both acid and heat treatments significantly influenced the flexural strength of the composite, whereas flexural modulus was significantly influenced only by acid treatment. The Sn3d spectra of the particles showed the peak shift to the lower binding energy side when the particles were treated with acid, and to the higher binding energy side when treated with water or the heating temperature increased. A significant correlation was found between the strength of the composite and the binding energy number. The highest strength was obtained from the metal-resin composite with 2% acid- and 150°C heat-treated filler particles. This filler particle had the Sn3d binding energy at 486.4 eV, which is SnO binding energy area. These results indicate that SnO is responsible for the good bond between Ag-Sn particle surface and 4-META coupling agent, regarding to the higher strength of the composite. This study was partially supported by Thailand Research Fund (PDF/34/2543)

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ACCEPTANCE LETTER

February, 2001

Dear Presenter:

It is a pleasure to inform you that your abstract has been ACCEPTED as an ORAL PRESENTATION at the 79th General Session and Exhibition of the International Association for Dental Research. The meeting will take place at the Makuhari Center and the connecting Prince Hotel, June 27 – 30, 2001.

Enclosed is the notification of the session to which your paper has been assigned. DO NOT lose this notification because it is the only one you will receive. The mode of your presentation has been assigned by the Annual Session Committee and Group Program Chair and must be followed. Assignments were based on authors' requests as much as possible. It is your responsibility to check for conflicts between your assigned session and any other activities.

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Thank you for submitting your paper, and we look forward to your presentation at the meeting.

Sincerely,

G. Embery

Graham Embery
IADR President-elect
Annual Session Committee Chair

Enclosures

เอกสารภาคผนวกที่ 2

manuscript ที่ส่งไปลงตีพิมพ์ในวารสาร Dental materials Journal เรื่อง Evaluation of the bonding between Ag-Sn particle and 4-META coupling agent of the metal resin composite

Category of the manuscript: Original paper

Title: Evaluation of the bonding between Ag-Sn particle and 4-META coupling agent of the metal resin composite

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Running title: BONDING MECHANISM OF THE METAL RESIN COMPOSITE

Keyword: Silver alloy, Bonding, Dental composite

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SYNOPSIS

The objective of this study was to investigate the detail oxide characteristics on the particle surface that modified by acid and heat to understand the bonding mechanism through the strength of the composite.

Nine different composite produced from nine different conditions of Ag-Sn filler, which were acid and heat-treated. The flexural test was subjected to the composite following the ISO 4049. The filler surface of nine different acid and heat treated including standard Sn, SnO and SnO_2 were evaluated by X-ray Photoelectron Spectroscopy.

The flexural strength of the composite was significantly influenced by both acid- and heat-treated ($p<0.01$). Only acid treatment affected the flexural modulus of the composite. The highest flexural strength of the composite (102.4 MPa) was obtained at the condition 2% HCl and 150°C-treated. The flexural modulus increased as the acid concentration increased.

The XPS results showed more metallic tin (less oxide) on the surface when the acid treated was done. While heat treatment showed more oxide forming on the surface. The higher oxidation state oxide form (SnO_2) was more formed when the temperature of the heat-treated increased. The high correlation between flexural strength of the composite and Sn3d binding energy of their filler particles was found. The different oxide form (SnO and SnO_2) showed the different adhesive ability to 4-META regarding to different in flexural strength of the composite. The filler surface

of the highest flexural strength composite showed Sn3d binding energy at 486.4 eV that was the SnO binding area. This could comply that SnO was responsible for the good bond between particle surface and 4-META coupling agent regarded to high flexural strength of the composite.

INTRODUCTION

The metal-resin composite (MRC) using Ag-Sn alloy particles as filler, 4-META as a coupling agent and UDMA-TEGDMA as resin matrix, have been developed[1,2]. The mechanical and physical properties of the composite showed the promising good posterior composite[1,2]. The bonding between filler particle and coupling agent get through the resin matrix is the critical key point for the strength of the composite in this system, therefore the well understanding of the bonding mechanism would be necessary to improve this composite. It had been hypothesized and reported by several studies[3-9] that adhesive resin form a chemical bond with metal oxide films especially of base metal (In, Cu, Zn and Sn). Although these oxide films are considered to play an important role in promoting the adhesive ability of adhesive resin to alloy, the detailed factors of these oxide films and adhesive resin has not been well understood. Ohno et al[3,4] reported the base metal content and the area fraction of the oxide on the surface had great effect on the adhesive ability. Somchai et al[2] reported the appropriate heat treatment for Ag-Sn particle is required to have good bond to 4-META resin. However the responsible oxide form could not be differentiated. Since the content of the metal element in the composite filler had fixed at the greatest mechanical and physical properties, the important point to clarified in this study is the detail oxide characteristics on the high temperature oxidation which play the important role on the adhesive ability to 4-META.

In the previous study[2], although the effect of the acid and heat treatment had been carried out, the detail information about the acid concentration and bonding mechanism was not well described. Therefore, The objective of this study was to investigate the detail oxide characteristics on the particle surface that modified by acid and heat to understand the bonding mechanism through the strength of the composite.

MATERIALS AND METHODS

Ag-Sn spherical alloy particles (73.2 mass% Ag, 26.8 mass% Sn, Lot no. 9804AS750) were produced by the research unit, Faculty of Dentistry, Mahidol University, Thailand, using an atomization method. The particle size bigger than 53 µm was crushed by a ball-milling machine (Pulverisette, Fritsch, Germany) at the rate 8 (595 rpm) for 5 h to produce an irregular particle. After crushing, the particles were then sieved with 20 µm mesh size. The particles size less than 20 µm were utilized for the filler of MRC.

Alloy particle surface treatment

The alloy particles were immersed in either 2 or 4% HCl at 80°C and slowly stirred with a magnetic stirrer for 30 min. After this acid treatment, the particles were thoroughly washed with distilled water until no residual acid remained on the surface, verified using $AgNO_3$. The particles were filtered and dried at 40°C for 1 h. In addition to these treatments, water washing at the same condition as acid treatment was included. After drying, the particles were divided into three groups. One of the three groups was used as it is without any heat treatment and the other two groups were placed in an oven for heat treatment either at 150°C or 300°C for 5 min. Therefore, 9 different particles treated with different acid concentrations and heating temperatures were prepared.

The composite specimen preparation and flexural test

The preparation of the MRC specimen and the flexural test were carried out following the procedure reported in the previous study[3)]. The filler content was 93% by weight. Three replications were prepared for each of nine conditions for the flexural test. The data of flexural strength and flexural modulus were analyzed using two-way analysis of variance to analyze the effect of two factors, which were the acid concentration and the heating temperature. The iso-value curves for both of the flexural strength and flexural modulus were obtained using orthogonal polynomial.

Particle Surface analysis by XPS

9 different particles treated with different acid concentrations and heating temperatures including standard sample of Sn, SnO and SnO_2 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 (JPS-9000MC, JEOL Co.Ltd., Tokyo, Japan) with Al Kα radiation under a pressure of 2×10^{-5} Pa. The binding energy of the measured photoelectron peak was calibrated by the C 1s peak at a binding energy of 284.6 eV.

RESULTS

Flexural strength and flexural modulus of the composite

Table 1 shows the summaries of the flexural strength and flexural modulus of the experimental composite. The flexural strength ranged from 85.4 to 102.4 MPa and the flexural modulus from 9.1 to 11.8 GPa. Table 2 shows the result of ANOVA for the flexural strength and flexural modulus of the composite. The flexural strength was significantly influenced by all two main factors ($p<0.01$). The flexural modulus was significantly influenced only by acid concentration ($p<0.01$). Figs. 1 and 2 show the flexural strength and the flexural modulus of the experimental composite, which were drawn by the equation shown below the figure. The square root Ve seen in figure is the square root of mean square of error obtained from ANOVA. As shown in Fig. 1, the flexural strength increased either as the acid concentration increased up to 2.5-3 % or as the heating temperature increased up to 150°C. The highest flexural strength of the composite in this study (102.4 MPa) was obtained from the particle with 2% acid- and 150°C heat-treated. Fig.2 shows that the flexural modulus increased with the acid concentration increased.

Oxide analysis on particle surface

The Sn3d binding energy of the filler particle surface including as crushing particle as well as Sn, SnO and SnO_2 standard sample were shown in Table 1. Fig. 3 shows the Sn3d spectra obtained from as-crushed, 2% acid-treated, 2% acid- and 150°C heat-treated and 2% acid- and 300°C heat-treated particle. The spectra had a wide half width due to the mixture of metallic Sn and their oxidation states as SnO and SnO_2. The spectrum shifted to higher oxidation state as the heat-treated temperature increased. Fig.4 shows the Sn3d spectra obtained from the as-crushed, water waching, 2% acid-treated and 4% acid-treated particle. The spectrum shifted to higher oxidation state when the particle washed in water and to lower oxidation state or more metallic Sn when receive acid treating. The spectrum unclearly shows the different between 2% and 4% acid-treated.

The correlation between the flexural strength of the composite and its filler surface Sn3d binding energy was found and shows on Fig.5. The composite show the highest strength when its filler has Sn3d binding energy around 486.4 eV, which mean majority of its filler surface composed of SnO.

DISCUSSION

In the previous study$^{2)}$, although the effect of the acid and heat treatment had been carried out, the detail information about the acid concentration and bonding mechanism was not well described. The bonding between filler particle and coupling agent get through the resin matrix is the critical key point for the strength of the composite in this system, therefore the well understanding of the bonding mechanism would be necessary to improve this composite. In this study, the Ag3d binding energy of the filler particle surface including Ag and AgO_2 standard sample were also evaluated. However, there was not any relation or meaning to interpret and also half of the filler especially high oxidation condition, the Ag3d peak could not be detected, therefore the data of the Ag3d was not reported.

In this study, the acid and heat treatment was selected to modify the surface for analyzing the surface product, which was responsible for the bonding because the expectation that a contamination product would be removed and oxide product would be formed when a particle was acid and heat treated, respectively. The results in this study showed that the acid and heat treatment including their interaction affected the flexural strength of the composite while only acid treatment affected the flexural modulus. The past study[2,10-11)] clearly showed that the wider groove at the grain boundary was found and wider or became pitting on the grain surface with higher acid concentration. The wider grooves increase the bonding area and mechanical interlocking between the alloy particle and resin matrix. Increasing the bonding area will decrease the matrix mass regarding to increasing the flexural modulus. This might be the reason why acid concentration affected both flexural strength and flexural modulus. These results were conformed in vice versa to Kakuta et al's study[12)]. They study the acid and heat treatment on Ag-In, which require higher concentration to wider the groove of grain boundary. Therefore, they did not found any effect of acid treatment on both flexural strength and flexural modulus, only the trend to be higher to acid concentration.

As mention above, we expected the oxide formation on the surface when the particle got the heat treatment. The results in this study suggested that there was a significant difference in the flexural strength of the composite among the temperature of heat treatment. This meant that the condition of the oxide, which was formed by heat, affected the flexural strength of the composite. Fig.1 shows that the flexural strength increased up to 150°C then decreased when the heating temperature increased. In this study, the highest flexural strength was obtained at condition 2% acid and 150°C heat-treated. Several study[3-9)] found that different metal oxide, thickness of the oxide layer or different metal oxide form affected the bonding strength. These founding can imply to explain the results of this study that the proper oxide layer or oxide form might be the main key of the bonding between particle surfaces and coupling agent regard to flexural strength of the composite. However, the specific metal oxide form cannot be distinguished.

From the particle surfaces analysis by XPS in Fig 4, The Sn3d spectra shifted to more metallic tin when received acid treated. This fulfills our expectation that acid treatment could remove any contaminated oxide on the surface. The unexpected data was found on water washing condition, the spectra shifted to higher oxidation state (SnO_2), which was different from the spectra of as-crushed particles. Ohno et al[4)] have been reported that H_2O molecule on the alloy surface exhibits the good adhesion of 4-META and alloy surface. This may be the reason why the flexural strength of the composite at condition at water washing without any heat treatment was different from as crushed composite in the past study[11)].

Fig 3 shows the Sn3d spectra shifted to oxidation state (SnO) when receive heat treated at 150°C and shift to higher oxidation state (SnO_2). This suggested that the oxide was formed on the particle surface by heat treatment and forming different oxide form up to the temperature of heat. These different oxide forms were expected to give the bond strength to coupling agent differently. As shown in fig 5, the high correlation ($r=0.902$, $p=0.017$) between the flexural strength of the composite and its filler surface Sn3d binding energy (eV) was found. The correlation was found in convex parabola shape. This could confirm the hypothesis that 4-META have adhesion ability differently to different oxide type and form. The highest strength of the composite was shown at the binding energy around 486.3-486.5 eV, which was SnO binding energy area. This result could comply that SnO might be the most responsible for the adhesive ability between 4-META and alloy surface.

CONCLUSION

The effect of acid and heat treatment on the Ag-Sn alloy particles and its particles surface oxide characteristics were evaluated. Both acid and heat treatment affected the flexural strength, while only acid treatment affected the flexural modulus of the composite. The highest flexural strength of the composite (102.4 MPa) was obtained at the condition 2% HCl and 150°C-treated. The flexural moduli were ranged from 9.1-11.8 GPa.

When acid treated was done, The XPS result showed more metallic tin (less oxide) on the surface. While heat treatment showed more oxide forming on the surface. The higher oxidation state oxide form (SnO_2) was more formed when the temperature of the heat-treated increased. The different oxide form (SnO and SnO_2) showed the different adhesive ability to 4-META regarding to different in strength of the composite. The high correlation between flexural strength of the composite and Sn3d binding energy of their filler particles was found. The filler surface of the highest flexural strength composite showed Sn3d binding energy at 486.4 eV that was the SnO binding area. This could comply that SnO was responsible for the good bond between particle surface and 4-META coupling agent regarded to high flexural strength of the composite.

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Tables and figures

Table 1 The summaries of the flexural strength and flexural modulus of the irregular particle MRC.

Table 2 Results of ANOVA for the flexural strength, the flexural modulus and condensability

Table 3 The resistance force at 2 mm penetration depth.

Fig. 1 Schematic of the penetration test apparatus

Fig. 2 The flexural strength of the experimental composite

Fig. 3 The flexural modulus of the experimental composite

Fig. 4 SEM photographs of polished surface of MRC;
20-53μm MRC (A) and <20μm MRC (B)

Fig. 5 SEM photographs of fractured surface of MRC;
irregular particle MRC (A) and spherical particle MRC (B)

Fig. 6 The resistance to condensation of the materials.

Fig. 7 SEM photographs of cross-sectional surface of MRC before and after condensation; irregular particle MRC (A) and spherical particle MRC (B)

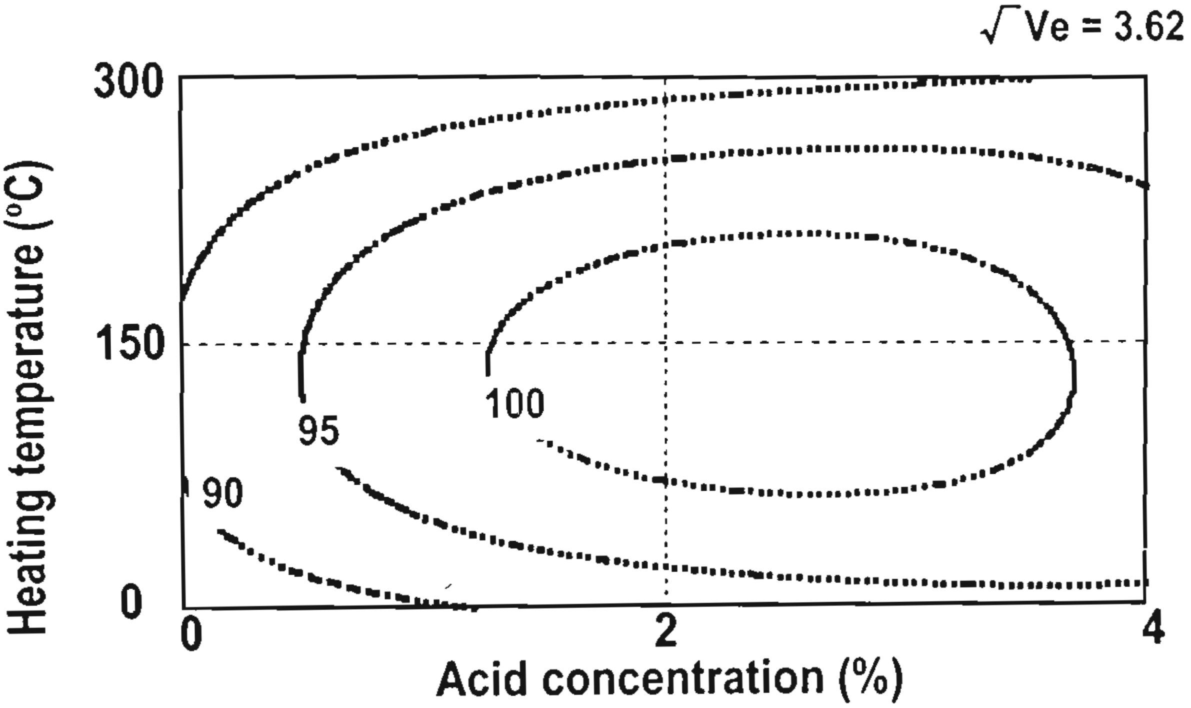
Table 1 The summary of the flexural strength, flexural modulus of the experimental composite and Sn3d binding energy of the filler particle surface including Sn, SnO, SnO_2 standard sample.

Metal-resin composite		Flexural strength: MPa (SD)	Flexural modulus: GPa (SD)	Sn3d binding energy: eV
Acid conc. (%)	Heat temp. (°C)			
0 (water)	Room temp	85.5 (5.2)	9.1 (0.9)	486.8
0 (water)	150	88.9 (1.8)	9.3 (0.5)	486.7
0 (water)	300	85.4 (0.9)	9.2 (0.5)	486.8
2	Room temp	93.9 (1.7)	10.6 (0.6)	486.2
2	150	102.4 (3.5)	10.3 (0.4)	486.4
2	300	85.8 (3.8)	10.8 (0.7)	486.8
4	Room temp	93.2 (4.2)	10.2 (0.6)	486.1
4	150	99.8 (4.7)	11.8 (1.1)	486.2
4	300	89.8 (4.2)	10.4 (1.6)	486.6
As crushing				486.3
Sn				484.9
SnO				486.5
SnO_2				486.7

Table 2 Results of ANOVA for the flexural strength and flexural modulus of the composite

Source	SS	df	MS	F	P
Flexural strength:					
A:Acid Conc.	343.73	2	171.87	3.16	0.00**
B: Heating T.	464.31	2	232.15	17.78	0.00**
AxB	130.16	4	32.54	2.49	0.00**
Error	235.05	18	13.06		
Total	1173.25	26			
Flexural modulus:					
A: Acid Conc.	12.47	2	6.24	8.96	0.00**
B: Heating T.	1.48	2	0.74	1.06	0.37
AxB	3.75	4	0.94	1.35	0.29
Error	12.53	18	0.70		
Total	30.23	26			

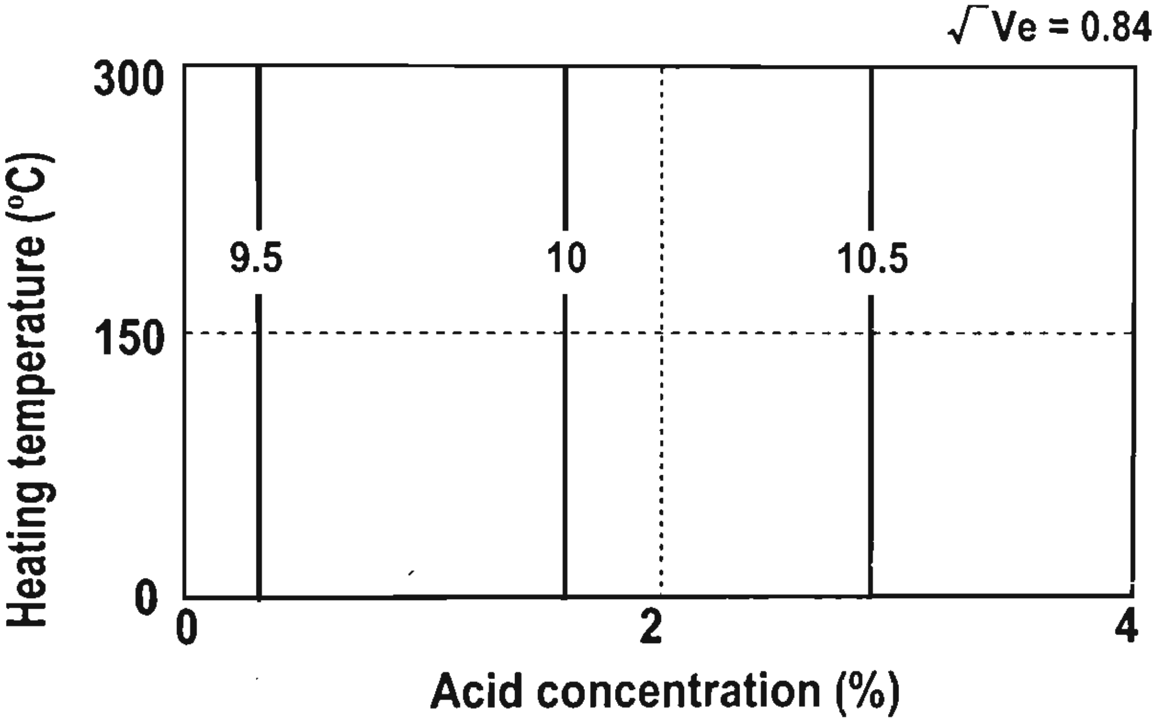
Fig. 1 The flexural strength of the experimental composite



$$Y = 102.43-0.013(a-150)-5.6E\text{-}04(a-150)^2 +1.92(b-2)-2.01(b-2)^2+7.39E\text{-}05(a-150)^2(b-2)^2$$

Y= Flexural strength (MPa)
a= Heating temperature (°C)
b= Acid concentration (%)

Fig. 2 The flexural modulus of the experimental composite



Y=10.16+0.39 (b-2) : Y= estimated flexural modulus (GPa)
b= acid concentration (%)

Fig. 5 The correlation between the flexural strength of the composite and its filler surface Sn3d binding energy

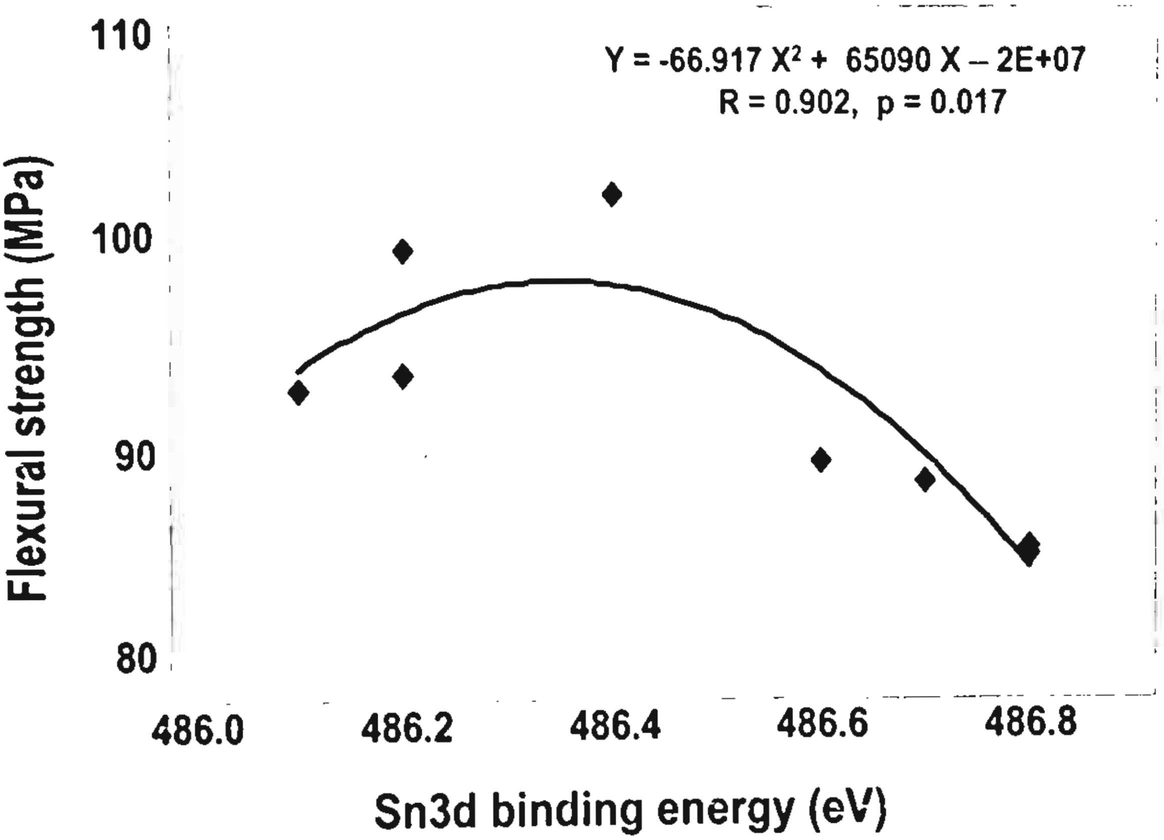


Fig. 3 shows the Sn3d spectra obtained from as-crushed, 2% acid-treated, 2% acid- and 150°C heat-treated and 2% acid- and 300°C heat-treated particle.

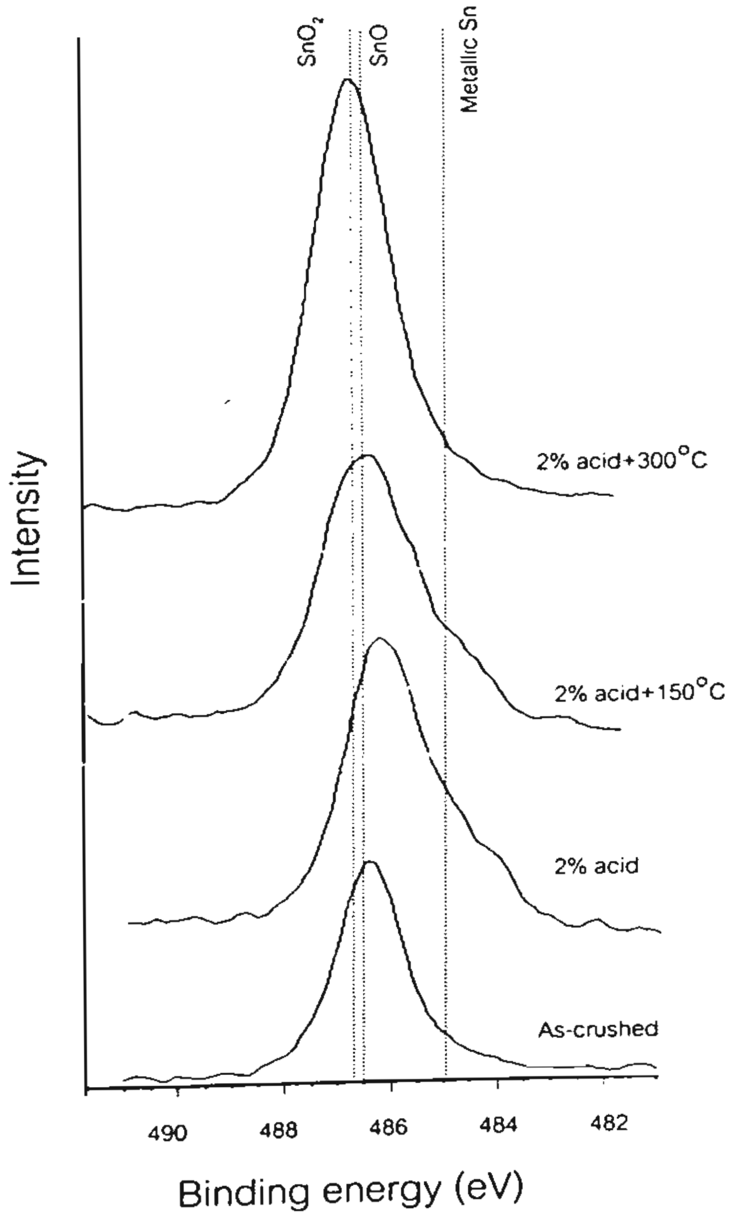
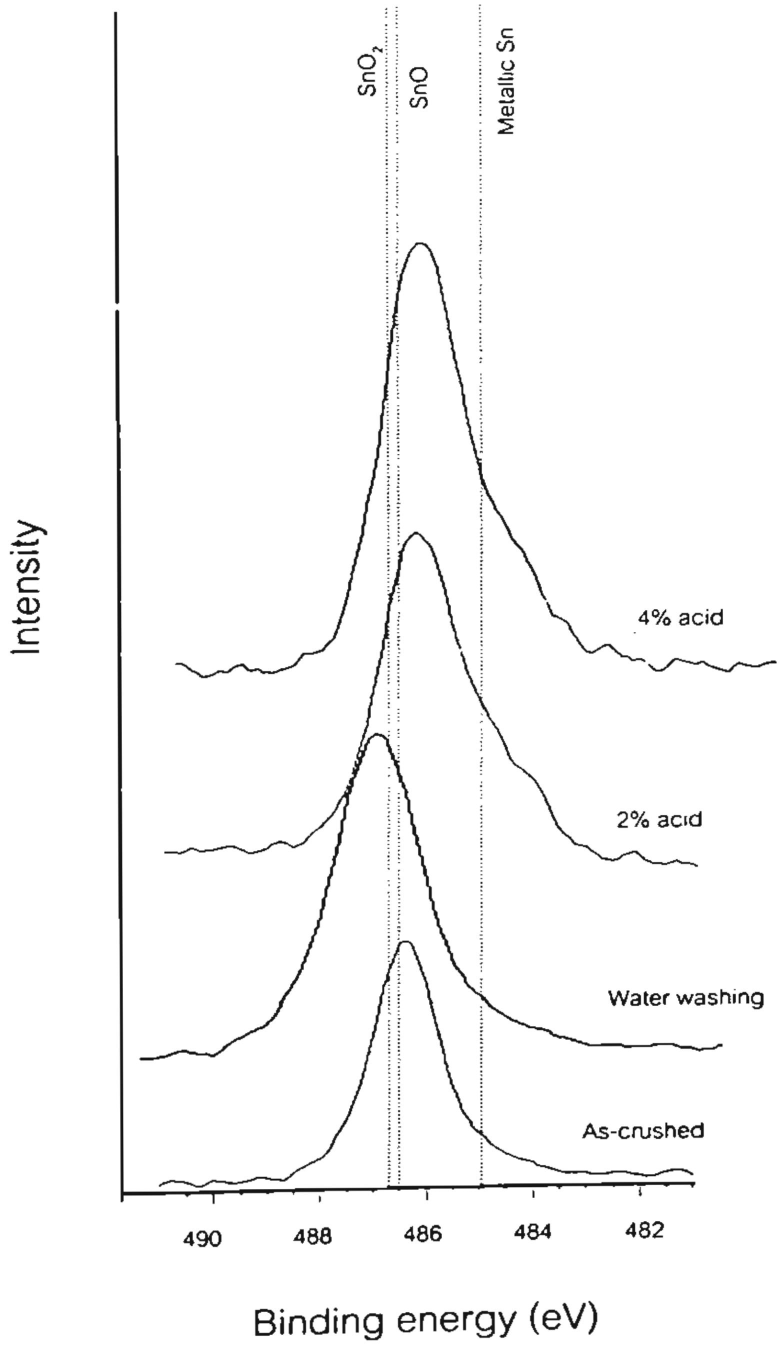


Fig.4 shows the Sn3d spectra obtained from the as-crushed, water waching, 2% acid-treated and 4% acid-treated particle.



เอกสารภาคผนวกที่ 3

Reprint เรื่อง Development of Metal-resin Composite Restorative Material Part 4 Flexural Strength and Flexural Modulus of Metal-resin Composite using Ag-In alloy Particles as Filler, *Dent Mater J* 21 (2): 181-190, 2002. (นักวิจัยร่วม)

Development of Metal-resin Composite Restorative Material Part 4 Flexural Strength and Flexural Modulus of Metal-resin Composite using Ag-In Alloy Particles as Filler

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Development of Metal-resin Composite Restorative Material Part 4 Flexural Strength and Flexural Modulus of Metal-resin Composite using Ag-In Alloy Particles as Filler

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The flexural strength and flexural modulus of an experimental metal-resin composite, which used Ag-In alloy particle as the filler, were evaluated. The effect of acid treatment and heat treatment on the Ag-In alloy particle was investigated.

The flexural strength of the experimental metal-resin composites ranged from 65.5 MPa to 91.0 MPa. The flexural strength of the metal-resin composite increased with the temperature of the heat treatment until 350℃, but its effect varied with the concentrations of HCl of the acid treatment. A metal-resin composite, which used acid-treated and 350℃ heat-treated Ag-In alloy fillers, matched the requirement of strength of ISO 4049.

The average of flexural modulus of the experimental metal-resin composite was 9.1 GPa. The flexural modulus of the metal-resin composite did not vary with the treatment conditions of the metal filler. The flexural modulus of a metal-resin composite, which used Ag-In alloy particle as the filler, was lower than that of Ag-Sn alloy metal-resin composite, which was reported previously. However, the flexural strength of the Ag-In alloy metal-resin composite was similar to that of Ag-Sn alloy metal-resin composite. We can control a flexural modulus of a metal-resin composite without decreasing flexural strength by choosing filler materials.

Key words : Dental composite, Ag-In alloy, 4-META

INTRODUCTION

A resin composite using inorganic filler has been commonly used for dental restorations. The mechanical properties of resin composites have been markedly improved compared with early composites[1-4]. Those resin composites, however, retain some problems that require improvement. For example, their antagonistic wear is considerable for dental restorations, especially for posterior applications. Suzuki *et al.*[5] suggested that resin composite, which has hard filler particles, caused more antagonistic enamel wear than resin composite containing micro-filled or soft filler particles. Using micro-filler to improve the antagonistic wear, the plasticity of resin composite before setting may decrease[6]. The decrease in the plasticity affects the handling of the resin composite.

We have been developing a metal-resin composite restorative material that used metal particles as filler and 4-META as the coupling agent[7-10]. If a metal particle can be used as the filler, which is more ductile than inorganic particles, the metal-resin composite restorative material would be tougher than the resin composite, which uses inorganic filler. In addition, ductile filler may improve antagonistic wear of the composite restorative material. Ag-Sn alloy particles were used as filler in previous studies[7-10], because Ag-Sn alloy was used as an amalgam powder for a long time, and the technology for making particles was established. In addition, it was expected that the Ag-Sn alloy particles adhered to the resin matrix through 4-META because Mogi reported Sn adhered to a resin using 4-META[11]. The flexural strength of the metal-resin composite that used Ag-Sn alloy particles as the filler was 91.8 MPa[10], which matched ISO 4049 : 2000 "Dentistry-Polymer-based filling, restorative and luting materials"[12]. The flexural modulus of the metal-resin composite that used Ag-Sn alloy as the filler was 16.6 GPa[10]. This value is similar to other resin composites whose values are 2.3-17.8 GPa[13]. Since the flexural modulus indicates the stiffness of materials, it is necessary to decrease the flexural modulus without decreasing the strength for developing tougher restorative materials.

In this study, Ag-In alloy was chosen for the filler particle because the elongation of Ag-In alloy is higher than Ag-Sn alloy[14]. In addition, adding indium prevented tarnishing of the silver alloy. An adhesion between the filler and matrix resin is an important factor for the strength of composite materials. Ohno *et al.*[15] suggested that Ag-In alloy adhered to stainless steel with an adhesive dental resin containing 4-META. This suggests that 4-META is effective as a coupling agent between Ag-In alloy particles and the matrix resin. The purpose of the present study was to evaluate the effect of the acid treatment and the heat treatment of the Ag-In alloy filler particle on the flexural properties of the metal-resin composite that use Ag-In alloy as the filler and 4-META as the coupling agent.

MATERIALS AND METHODS

Table 1 shows the Ag-In alloy used in this study. Spherical alloy particles of the Ag-In alloy (75 mass% Ag, 25 mass% In) were produced using the atomization method that was usually used for preparing amalgam alloy powder. The spherical alloy particles were sieved to divide them into three different particle sizes, which were less

Table 1 Ag-In alloy used in this study

Components of alloy	Ag 75 mass% In 25 mass%
Particle size	>45-53 μm 20 mass% >38-45 μm 20 mass% ≤38 μm 60 mass%
Lot No.	9808A1750

Prepared by The Research Unit, Faculty of Dentistry, Mahidol University, Thailand

Table 2 Materials used in this study

	Materials	Code	Batch No.
Coupling agent	4-Methacryloxyethyl trimellitate anhydride[1] (crystal form)	4-META	97001
Monomers	1,6-Bis(methacryloyloxy-2-ethoxycarbonyl-amino)-2,4,4(2,2,4)-trimethylhexane[2] Triethylene glycol dimethacrylate[3]	UDMA TEGDMA	050155 1104S
polymerization initiator	Benzoyl peroxide[4] N, N-dimethyl-p-toluidine[5]	BPO DMPT	M6K9289 GA01
inhibitor	Hydroquinone monoethyl ether[6]	MEHQ	PAM0168

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[4] Nacalai Tesque Inc, Kyoto, Japan
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than 38μm, 38-45μm and 45-53μm. These three particle sizes were mixed at the ratio of 3 : 1 : 1 by mass, respectively, for the metal filler of a metal-resin composite. The metal filler particles were acid-treated with HCl at 80℃ at four different concentrations (0, 2, 4, 6 volume%) for 30 min. After the treatment, the metal filler was washed four times with distilled water and dried in a constant temperature oven (Model 2-2123, Isuzu, Japan) at 40℃. The acid-treated metal filler particle was then heat-treated at four different temperatures (50, 200, 350, 500℃) for 10 min. Sixteen metal filler particles were thus prepared under four concentrations of HCl and four temperatures of heat-treatment.

The prepared metal filler particles were then immersed in an acetone solution containing 4 mass% 4-(2-methacryloyloxy ethoxycarbonyl) phthalic anhydride (4-META) 0.4 mass% benzyl peroxide (BPO) at 40℃ for 30 min. After the immersion, acetone was vaporized at 40℃ for 10 min in the constant temperature oven. Table 2 shows the materials used for the aforementioned treatments.

The base resin monomer consisted of the mixture of 75 mass% 1,6-Bis(methacryloyloxy-2-ethoxycarbonyl-amino)-2,4,4,(2,4,4)-trimethylhexane (UDMA) and 25 mass% triethylene glycol dimethacrylate (TEGDMA). 0.25 mass% N,N-dimethyl-p-toluidine was added to the base resin monomer as an accelerator. Using the treated metal filler particles and the base resin monomer, flexural test specimens were prepared following the ISO 4049 : 2000[12)]. The treated particles were mixed with the resin monomer at 93 mass% of the filler content for 30 s. The mixture was filled in a polytetrafluoroethylene-coated stainless steel mold placed on a glass plate. After the filling of the mixture, another glass plate was applied on the top of the mold to remove excess material from the mold, and a clamp held the specimen assembly together. After 3 min from the start of mixing, the mold was immersed in 37±1℃ 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±1℃ for 24 h. After 24 h storage, the specimen was polished using #1000 SiC paper, and the dimensions were measured before testing. The specimen sizes were

25±0.1×2±0.1×2±0.1 mm. Two specimens were prepared for each of the 16 conditions, which were the combinations of the conditions of acid-treatment and the conditions of heart-treatment.

A three-point flexural test (cross-head speed: 1 mm/min, distance of support: 20 mm) was carried out using a universal testing machine (Autograph DSS-5000, Shimadzu Ltd., Kyoto, Japan), and the flexural strength (σ) and the modulus of elasticity under flexural stress (flexural modulus, E) were calculated from the following equations (1) and (2), respectively.

$$\sigma = \frac{3Fl}{2bh^2} \tag{1}$$

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

$$E = \frac{F_1 l^3}{4bh^3 d} \tag{2}$$

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 (mm),
b is the width (mm),
h is the height (mm) of the specimen,
d is the deflection at load F_1 (mm),

Values for both the flexural strength and modulus were analyzed using two-way analysis of variance to analyze the effect of two factors that were the concentrations of HCl at acid-treatment and the temperature of heat-treatment.

RESULTS

Table 3 shows the mean values of flexural strength of the experimental metal-resin composites, which used Ag-In alloy particles as the filler. The flexural strength of the metal-resin composite ranged from 65.5 MPa to 91.0 MPa under the different conditions of acid treatment and heat treatment. Results of ANOVA showed that

Table 3 Flexural strength of metal resin composite using Ag-In alloy as the filler, σ/MPa

Temperature of heat treatment	Concentration of HCl			
	0%	2%	4%	6%
50℃	78.0	65.5	69.5	68.5
200℃	73.5	68.5	71.0	71.0
350℃	73.0	82.0	91.0	85.0
500℃	80.0	69.5	71.0	75.5

$\sqrt{Ve}=3.5$

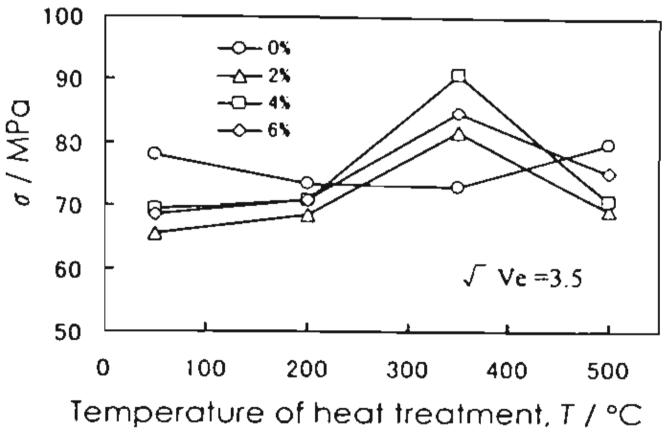

Fig. 1 Flexural strength of metal resin composite using Ag-In alloy filler.

Table 4 Tukey's comparison of flexural strength by the temperature of the heat treatment (Probability of significance)

	50℃	200℃	350℃
200℃	0.983		
350℃	<0.001**	<0.001**	
500℃	0.196	0.339	0.001**

**Probability of significant difference is greater than 95%

Table 5 Flexural modulus of metal-resin composite using Ag-In alloy as filler, *E*/GPa

Temperature of heat treatment	Concentration of HCl			
	0%	2%	4%	6%
50℃	9.9	8.4	8.5	9.2
200℃	9.0	9.0	9.9	9.4
350℃	9.1	8.9	8.8	8.8
500℃	9.5	8.9	10.5	9.1

$\sqrt{Ve}=0.6$

the effects of the temperature of heat treatment and the interaction of two main factors, which were the acid concentration and the temperature of heat treatment, on the flexural strength were highly significant (temperature of heat treatment $p<0.01$, power>99.9%, interaction of two main factors $p<0.01$, power 98.2%). These results suggest that the temperature of the heat treatment influenced the flexural strength of the experimental metal-resin composite, which used Ag-In alloy particles as the filler, but its effect, varied with different acid concentrations of acid treatment. Fig. 1 shows the flexural strength of the metal-resin composite at each condition. The highest strength (91.0 MPa) was obtained at 350℃ heat treatment except for the specimens which were treated with 0% HCl (distilled water). At 0% HCl, which was the immersion in distilled water without acid, there were no differences in the flexural strength among different temperatures of the heat treatment. Tukey's multiple comparison, as shown in Table 4, suggests that the flexural strength of the metal-resin composites, which used 350℃ heat treatment, was higher than those of the other experimental metal-resin composites.

Table 5 shows the mean values of the flexural modulus of the experimental metal-resin composite. The mean values of the flexural modulus ranged from 8.4 GPa to 10.5 GPa at different treatments. Result of ANOVA showed that there were no significant effects of heat treatment and acid treatment on the flexural modulus of metal-resin composite. The total average of the flexural modulus was 9.1 GPa.

DISCUSSION

ISO 4049: 2000 requires 80 MPa or greater flexural strength of polymer-based filling and restorative materials for restorations involving occlusal surfaces (Type 1, Class 1)[12]. In this study, the metal-resin composite, which used acid-treated and 350℃ heat-treated Ag-In alloy fillers, matched strength requirement. When a metal particle was acid-treated, it was expected that a product on the particle be removed, and when a metal particle was heat-treated, it was expected that an oxide on the particle be formed. The results in this study suggested that there was a significant difference in the flexural strength of the metal-resin composite among the temperatures of heat treatment. This meant that the condition of an oxide, which formed by heat treatment, affected the flexural strength of the metal-resin composite. The other result in this study showed the effect of heat-treatment on the flexural strength changed with the condition of acid treatment. Fig. 1 shows that there was a different tendency in the flexural strength clearly between not using acid-treated filler (0%) and using acid-treated filler (2%HCl, 4%HCl, 6%HCl). An original Ag-In alloy particle may have been covered with an oxide, which was formed during the atomizing process. It was suggested that the existence of an original oxide layer affected the form of the oxide on the Ag-In alloy particle by the heat treatment. In this study, the highest flexural strength was obtained using a 4% HCl acid-treated, 350 ℃ heat-treated metal filler material, and the lowest strength was obtained with on acid-treated, 50℃ heat-treated metal filler, which may have a little oxide layer. When the metal filler particle was not acid-treated, the flexural strength of the metal-resin composite was not changed with the temperature of the heat treatment.

To examine the surface condition of both the acid-treated and non-acid-treated metal filler particles, surface analysis by X-ray photoelectron spectroscopy (JPS-9010MC, JEOL, Japan) was performed with Mg Kα radiation on the typical metal particles in this study. The binding energy of elements were calibrated by C1s as 284.4 eV[16]. Fig. 2 shows the wide spectrum of the X-ray photoelectron spectroscopy of the Ag-In alloy particle, which was treated with 0% HCl at 50℃. A high indium peak (3d5/2, 444.1 eV) and low silver peak (3d5/2, 367.8 eV) were found on the surfaces. Fig. 3 shows the wide spectrum of the Ag-In alloy particles, which were treated with 0% HCl at 350℃. There is a high indium peak (3d5/2, 444.2 eV) and a low silver peak (3d5/2, 368.1 eV) on the surface. There is a similar tendency of the

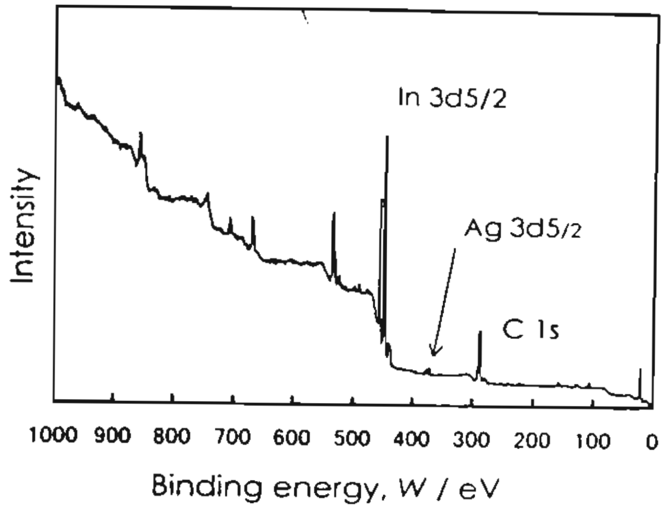

Fig. 2 Spectrum of X-ray photoelectron spectroscopy.
(0% HCl acid treatment and 50℃ heat treatment)

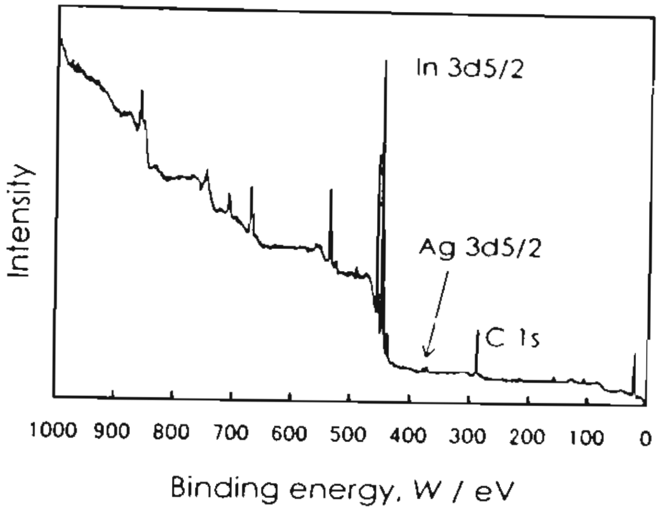

Fig. 3 Spectrum of X-ray photoelectron spectroscopy.
(0% HCl acid treatment and 350℃ heat treatment)

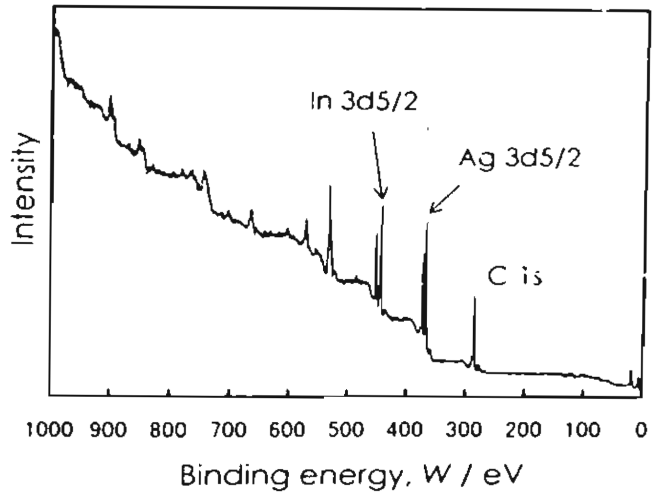

Fig. 4 Spectrum of X-ray photoelectron spectroscopy.
(4% HCl acid treatment and 350℃ heat treatment)

spectrum between the 50℃ heat-treated surface and 350℃ heat-treated surface when the particle was not acid-treated. With referred to the NIST XPS Database[16], the peaks of indium in Figs. 2 and 3 are recognized as In or In_2O_3. It was difficult to identify In or In_2O_3 from the wide spectrums, but it was suggested to be In_2O_3 because the original Ag-In alloy particle was previously heated during the particle making process. Fig. 4 shows the wide spectrum of the X-ray photoelectron spectroscopy of the Ag-In alloy particle, which was treated with 4% HCl acid treatment and 350 ℃ heat treatment. Two high peaks that are indium (3d5/2, 444.2 eV) and silver (3d5/2, 367.7 eV) were found clearly on the metal filler surface. The peak of indium was recognized as In or In_2O_3, but was suggested to be In_2O_3 because the Ag-In alloy filler was heat-treated at 350℃. The peak of silver was recognized as Ag, AgO or Ag_2O. There was clearly silver or silver oxide on the acid-treated particle, while there was little silver or silver oxide on the non-acid-treated particle. This suggests that the existence of silver or silver oxide on the particle affects the adhesion between Ag-In alloy filler particle and matrix resin, and affects to the flexural strength of the metal-resin composite, which used Ag-In alloy particle as the filler. To clarify the mechanism of the bonding between the treated metal filler and matrix resin, it is necessary to use high resolving power equipment for analyzing the filler surfaces, and to identify the products on the metal filler. Further research is necessary to explain the relation between the surface condition and the mechanical properties of the metal-resin composites.

There was no significant difference in the flexural modulus among 16 metal-resin composites that were prepared under the different conditions of acid treatment and heat treatment in this study. This result suggested that the acid treatment and the heat treatment does not affect the flexural modulus of the metal-resin composite, which used Ag-In alloy particle as filler. Even if the treatments affected the flexural modulus, it would be only small effect. The average flexural modulus of the Ag-In alloy filler metal-resin composite was 9.1 GPa in a present study. This value was lower than that of the metal-resin composite, which used Ag-Sn alloy particles as the filler (16.6 GPa)[10]. The calculated volume percentage of the Ag-In alloy filler in the metal-resin composite was 59%, while the Ag-Sn alloy filler was 61% in the metal-resin composite[10]. A proportion of the matrix resin in a metal-resin composite was not so different between the Ag-In alloy filler metal-resin composite and the Ag-Sn alloy filler metal-resin composite. In addition the flexural strength of the Ag-In alloy filler metal-resin composite was 91.0 MPa, while that of the Ag-Sn alloy filler metal-resin composite was 91.8 MPa[10]. When a comparison was made between the flexural properties of two metal-resin composites, only the flexural modulus decreased by approximately a half. As a result that surface treatments did not markedly affect the flexural modulus, and it was suggested that the flexural modulus of a metal-resin composite decreased by using Ag-In alloy particles as the filler. It is important to control the flexural modulus without decreasing the flexural strength using various filler materials. It was suggested that a restorative material, which is tough, could be developed using ductile filler materials.

CONCLUSIONS

The flexural strength and flexural modulus of the experimental metal-resin composite, which used Ag-In alloy particles as the filler, were evaluated. The effect of acid treatment and heat treatment on the Ag-In alloy particles was investigated.

The flexural strength of the metal-resin composite increased with the temperature of the heat treatment until 350℃, but its effect was varied with the concentrations of HCl of the acid treatment. A metal-resin composite, which used acid-treated and 350℃ heat-treated metal fillers, matched the strength requirement of ISO 4049: 2000 "Dentistry-Polymer-based filling, restorative and luting materials (Type 1, Class 1) as suitable for restorations involving occlusal surfaces".

The flexural modulus of the metal-resin composite was not varied with the conditions of treatments on the metal filler. The flexural modulus of a metal-resin composite, which used Ag-In alloy particles as the filler was lower than that of Ag-Sn alloy metal-resin composite, reported previously10). However, the flexural strength of Ag-In alloy metal-resin composite was similar to that of Ag-Sn alloy metal-resin composite10). The flexural modulus of a metal-resin composite can be controlled without decreasing the flexural strength by choosing appropriate filler materials.

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