Development of Metal-resin Composite for Dental Magnet Keepers. Part 1: Effects of Filler and 4-META Contents on Setting and Flexural Properties

Hiroko SOMA[1] and Yukio MIYAGAWA[1,2]

[1]Division of Biomaterials, Advanced Research Center, School of Life Dentistry at Niigata, The Nippon Dental University, Niigata 951-8580, Japan
[2]Department of Dental Materials Science, School of Life Dentistry at Niigata, The Nippon Dental University, Niigata 951-8580, Japan
Corresponding author, Hiroko SOMA; E-mail: soma@ngt.ndu.ac.jp

Nine kinds of experimental soft magnetic resin composites containing SUS447J1 stainless steel particles as filler were prepared. A UDMA/MAA resin with an MAA mole fraction of 0.67 was used as a matrix resin. The effects of three levels of 4-META content and three levels of filler content on the setting and flexural properties were studied. Working time and setting time significantly increased with increase of 4-META and filler contents. Flexural strength significantly increased with increase of 4-META content but with decrease of filler content. Elastic modulus simply increased with increase of both 4-META and filler contents. Although the flexural strength obtained was low, results were considered promising being the first step of this novel development.

Keywords: Resin composite, Stainless steel filler, Magnet

INTRODUCTION

Dental magnetic attachments are used as excellent retainers for removable partial dentures because of two favorable reasons: they present a low risk factor for trauma to the supporting roots and they provide stable, unchanging retentive force. As Rutkunas et al.[1] reported, stud attachments are more susceptible to fatigue than magnets. Saygili and Sahmali[2] even reported that the retentive force of precision attachments decreased depending on the wear of female and male parts, while the magnetic retainers' retention increased over time and use according to the induction of magnetic fields. A dental magnetic attachment is usually composed of a magnet encapsulated in a cup yoke made of ferritic and austenitic stainless steels and a keeper made of ferritic stainless steel[3]. The magnet is normally embedded in a denture, and the keeper is fixed on a root cap made of noble metal alloy by cast bonding or cementation.

There are differences in electrode potential between keeper alloys and root cap alloys. Endo et al.[4] reported that the corrosion rate of ferric stainless steels increased two to six times when they were galvanically coupled with noble metal alloys. It is also very likely that a small gap exists between the keeper and root cap in a practical case, thereby leading to crevice corrosion. Pertaining to corrosion, Morito et al.[5] stated that magnetic keepers were liable to undergo corrosion. Moreover, Takada and Okuno[6] reported that heating the keepers at high temperature during the cast bonding procedure could deteriorate the corrosion resistance of ferritic stainless steels.

Apart from the corrosion liability drawback,

Hirano et al.[7] mentioned that incorporating the keeper in a root cap during casting is an intricate process too. Therefore, if strong and tough magnetic resin composite were to be developed, the root cap that can attract a magnet could be prepared in the oral cavity using the magnetic resin composite, thereby eliminating all the abovementioned disadvantages. In pursuit of this magnetic resin composite, Hirano et al. produced several valuable reports based on studies on resin composites that could attract magnets[7-9]. The properties of these experimental composites were fairly good. However, the mechanical strength was not as good as that of commercial composite resins used for cores or posterior restorations. As for the matrix resin of these experimental composites, it was composed of the traditional Bis-GMA (2,2 - bis [4 - (3-methacryloxy-2-hydroxypropoxyl) phenyl] propane) / TEGDMA (triethylene glycol dimethacrylate).

The chief aim of this research was to develop a soft magnetic resin composite that was not only strong and tough enough to be used for cores or posterior restorations, but also corrosion-resistant enough to be used even with Pt-Fe-Nb magnet alloy[10]. To achieve the above purpose, SUS447J1 stainless steel was selected for filler alloy and a UDMA (1,6-bis(methacryloxy - 2 - ethoxycarbonylamino) - 2,4,4 - trimethylhexane) /MAA (methacrylic acid) resin for the matrix resin. Being the first step in developing a soft magnetic resin composite for the keeper of magnetic attachment, the objectives of this study were to investigate the effects of filler and 4-META (4 - (2 - methacryloyloxyethoxycarbonyl) phthalic acid anhydride) contents on the setting and flexural properties of experimental metal-resin composites.

MATERIALS AND METHODS

Materials used in this study are listed in Table 1. Resin components of the base paste of the experimental metal-resin composite were UDMA, MAA, and 4-META with 1 mass BPO and a trace amount of inhibitor (hydroquinone). Mole ratio of UDMA and MAA was 1:4. The contents of 4-META used were 0, 0.5, and 1.0 mass. The resin monomer of catalyst paste was UDMA with 0.7 mass DMPT and a trace amount of inhibitor. SUS447J1 particles (45μ m) were used as filler. Table 2 shows the composition of SUS447J1 used. Filler contents of both pastes were 88.5, 90.0, and 91.5 mass.

The experiment was divided into two parts: (1) Measurement of working time and setting time; and (2) Measurement of flexural strength and elastic modulus.

Measurement of working time and setting time

Base paste and catalyst paste were mixed at a ratio of 1.75 : 1 for 20-30 seconds. After mixing, the working time and setting time were measured at 23$\pm$ 1 using the method described in ISO 4049 : 2000 for "Polymer-based filling, restorative and luting materials"[11]. Temperature change of each sample was recorded on a chart, and the working time was determined from the time at which mixing started until the time at which the temperature started to rise. Setting time was determined by extending the plateau backwards to meet an extension of the straight line of temperature increase. Nine kinds of composites were measured for five replications: the combination of three contents of 4-META and three contents of filler.

Measurement of flexural strength and elastic modulus

A three-point flexural test was carried out following ISO 4049 : 2000. The base paste and catalyst paste were mixed for 20-30 seconds at a mass ratio of 1.75 : 1 to make a matrix resin composed of the imino group of UDMA and carboxyl group of MAA at a 1 : 1 ratio. The mixture was filled into a 25$\times$ 2$\times$ 2 mm PTFE-coated stainless steel mold placed on a glass plate. Another glass plate was placed on the top of the mold to remove any excess material. The assembly was held together by a clamp and immersed in 37$\pm$ 1 distilled water. At one hour after the start of mixing, the specimen was carefully removed from the mold and stored in distilled water at 37$\pm$ 1 for 23 hours. The specimen was polished using SiC paper (#1000, Marumoto Struers K.K., Tokyo, Japan), and its dimensions were measured before testing. A universal testing machine (Autograph AG-I, Shimadzu Co. Ltd., Kyoto, Japan) was used for the flexural test at a crosshead speed of 1 mm/min. Flexural strength and elastic modulus under flexural stress were then calculated using the formulae described in ISO 4049 : 2000. Five replications were made for each of the nine experimental conditions.

The effects of three levels of 4-META content and three levels of filler content on the working and setting times as well as on flexural strength and elastic modulus were analyzed at 0.05 level of significance using two-way ANOVA and *post hoc* Tukey's multiple comparison test (Table 3). Then, orthogonal polynomials were calculated using the significant

Table 1 Materials used in this study

Material	Batch No.	Code
SUS447J1 stainless steel particles[1]	412341	SUS447J1
1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane[2]	050144	UDMA
4-(2-methacryloyloxyethoxycarbonyl)pthalic acid anhydride[2]	02001	4-META
Benzoyl peroxide[3]	FA011606	BPO
N,N-dimethyl-p-toluidine[4]	PKQ5663	DMPT
Methacrylic acid[4]	KLQ6716	MAA

[1]Fukuda Metal Foil & Power Co. Ltd., Kyoto Japan
[2]Sun Medical Co. Ltd., Osaka Japan
[3]Lancaster Synthesis, Morecambe, England
[4]Wako Pure Chemical Industries Ltd., Osaka, Japan

Table 2 Composition (mass) of SUS447J1 used

	C	Si	Mn	P	S	Cr	Cu	Ni	Mo	Fe
SUS447J1	0.006	0.08	0.05	0.006	0.004	30.0	0.01	0.11	2.0	Bal.

terms of factors obtained from the results of two-way ANOVA because the levels of each factor were equally spaced as in a previous paper[12]. These orthogonal polynomials were the response functions that described the relationship between the characteristics and their factors.

RESULTS

Setting time and working time

Table 4 shows the mean values and standard deviations of the working time and setting time of nine different experimental conditions. Working time ranged from 73.2 to 165.6 seconds, while setting time ranged from 157.8 to 299.4 seconds. Results of two-way ANOVA showed that both the setting time and working time were significantly influenced (p<0.01) by the two main factors (4-META content and filler content). However, the interaction between these two factors was not significant. There were significant differences among all the levels of the two main factors for both working time and setting time, except between 0.5 and 1.0 4-META contents and between 88.5 and 90.0 filler contents for working time. Using the statistically significant terms of each factor, *i.e.*, the linear effect of factor A (4-META content, p<0.01) and the quadratic effect of factor B (filler content, p<0.01), an orthogonal polynomial was obtained as follows:

$$t_w = 101.6 + 40.6(a\text{-}0.5) + 15.9(b\text{-}90) + 4.8(b\text{-}90)^2 \qquad (1)$$

where t_w is the working time (sec), a is the 4-META content ( ), and b is the filler content ( ).

Figure 1 shows the iso-value curves of working time with the changes in 4-META and filler contents, which was drawn using the Equation (1). The square root of Ve in Fig. 1 shows the square root of the mean square of error obtained by two-way ANOVA.

As in the case of working time, an orthogonal polynomial for setting time was obtained as follows:

Table 3 Experiment factors and levels

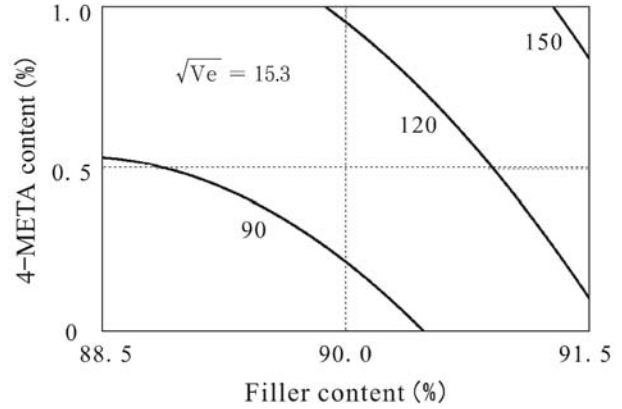| Factor	Level 1	Level 2	Level 3
A: 4-META content	0.0 mass	0.5 mass	1.0 mass
B: Filler content	88.5 mass	90.0 mass	91.5 mass

Fig. 1 Effect of 4-META and filler contents on working time.
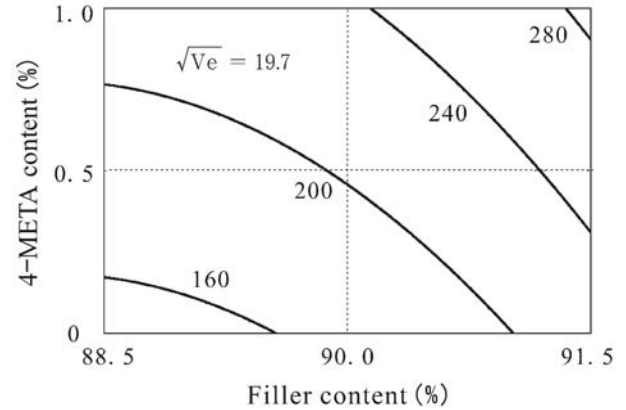

Fig. 2 Effect of 4-META and filler contents on setting time.

Table 4 Means and standard deviations of working time and setting time

4-META content	Filler content	Working time	(sec)	Setting time (sec)	
	88.5	75.0	(9.2)	157.8	(20.8)
0.0	90.0	73.2	(5.4)	164.4	(13.6)
	91.5	110.4	(9.3)	210.6	(18.7)
	88.5	94.2	(17.2)	185.4	(24.9)
0.5	90.0	113.4	(16.9)	211.2	(20.3)
	91.5	132.6	(24.4)	248.4	(22.7)
	88.5	96.6	(7.5)	202.8	(16.2)
1.0	90.0	118.2	(11.7)	232.8	(8.1)
	91.5	165.6	(23.0)	299.4	(25.8)

SD in parentheses

Table 5   Means and standard deviations of flexural strength and elastic modulus

4-META content	Filler content	Flexural strength (MPa)		Elastic modulus (GPa)	
	88.5%	51.7	(2.7)	14.0	(1.0)
0.0%	90.0%	45.0	(4.2)	16.4	(1.0)
	91.5%	42.2	(4.4)	17.2	(1.5)
	88.5%	55.8	(2.7)	16.0	(1.0)
0.5%	90.0%	53.6	(4.0)	18.2	(1.5)
	91.5%	49.2	(3.9)	18.5	(2.2)
	88.5%	58.8	(1.8)	16.7	(0.8)
1.0%	90.0%	56.6	(1.6)	18.0	(0.8)
	91.5%	54.1	(3.6)	20.2	(1.6)

SD in parentheses

$$t_s = 202.8 + 67.4(a\text{-}0.5) + 23.6(b\text{-}90) + 6.5(b\text{-}90)^2 \qquad (2)$$

where t_s is the setting time (sec), a is the 4-META content ( ), and b is the filler content ( ).

Figure 2 shows the iso-value curves of setting time with the changes in 4-META and filler contents, which was drawn using the Equation (2). As shown in Figs. 1 and 2, working time and setting time significantly increased with the increase of 4-META and filler contents.

Flexural strength and elastic modulus
Table 5 shows the mean values and standard deviations of flexural strength and elastic modulus. Flexural strength ranged from 42.2 to 58.8 MPa, while elastic modulus ranged from 14.0 to 20.2 GPa. Results of two-way ANOVA showed that both main factors significantly ($p<0.01$) influenced flexural strength and elastic modulus. However, the interaction effect was not significant. There were significant differences among all the levels of the two main factors for both flexural strength and elastic modulus, except between 0.5 and 1.0 4-META contents and between 90.0 and 91.5 filler contents for elastic modulus. Figures 3 and 4 were drawn using orthogonal polynomials like Figs. 1 and 2. As shown in Fig. 3, flexural strength significantly increased with increase of 4-META content and with decrease of filler content. As shown in Fig. 4, elastic modulus simply increased with the increase of both 4-META and filler contents.
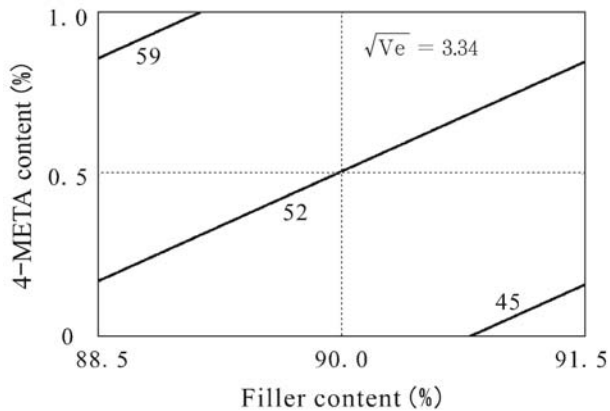

Fig. 3   Effect of 4-META and filler contents on flexural strength.
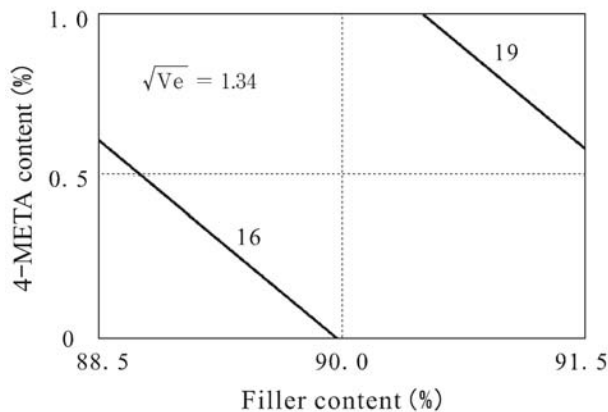
Fig. 4   Effect of 4-META and filler contents on elastic modulus.

DISCUSSION

Among soft magnetic alloys, SUS447J1 was chosen for filler alloy because of its superior corrosion resistance. In commercial dental magnetic attachment systems, ferritic stainless steels are used as a material for keepers. Chromium and molybdenum in ferritic stainless steels are known to improve the resistance to pit formation and crevice corrosion.

Okuno et al.[13] reported that SUS447J1 showed better corrosion resistance than SUS444 (18.6 Cr, 2 Mo) for keepers and SUS316L (17.7 Cr, 2 Mo) for surgical implants. Endo et al.[4] also reported that the breakdown potential of ferric stainless steels increased and the total amount of released metal ions decreased linearly with increase in the sum of Cr and Mo contents. As for experimental magnetic resin composites, immersion tests have been conducted by Hirano et al. using SUS444 (18 Cr, 2 Mo)[7] and SUS446 (26.7 Cr, 0 Mo)[9] fillers. The sums of the Cr and Mo contents of SUS444 and SUS446 were 20 and 26.7, respectively, and the amount of eluted metals from the resin composite containing SUS446 was reported to be less than that from the resin composite containing SUS444[9]. The sum of the Cr and Mo contents of SUS447J1 was 32. Therefore, the resin composite containing SUS447J1 probably had better corrosion resistance than the former experimental magnetic resin composites.

Based on a report by Tanaka et al.[14], a UDMA/MAA resin with an MAA mole fraction of 0.67 was selected as the matrix resin. This was because some interaction between the matrix resin and SUS447J1 filler particles as well as a strong and tough matrix resin were expected. A complex composed of UDMA and MAA based on noncovalent bonds such as hydrogen bonds or an electrostatic interaction between the imino group of UDMA and the carboxyl group of MAA might be formed, such that the resultant matrix resin might become strong and tough[14]. It is well known that zinc polyacrylate cements or glass polyalkenoate cements bond well to stainless steel because of the carboxyl group of polyalkenoic acid. Therefore, it is reasonable to expect some interaction between the stainless steel filler particles and the carboxyl group of MAA.

In the present study, both working time and setting time significantly increased with increase of both 4-META and filler contents. This effect of 4-META was not in agreement with those of previous studies[12,15] that used Cu or Ag-Cu particles as filler in metal-resin composites. In those previous studies, 4-META was considered to be an important factor in promoting polymerization. However, 4-META was not related to the initiation reaction of polymerization in this study. It was reasonable that the inclusion of a material independent of the setting reaction retarded the setting reaction. The increase of filler content meant the decrease of BPO and DMPT amounts in the mixing paste in the tube of the apparatus that determined working and setting times. The presence of filler particles might decrease the amount of heat liberated during the polymerization reaction, thereby retarding setting. This then led to the extension of working and setting times.

The shortest working and setting times were 73.2

seconds and 157.8 seconds, and the longest were 165.6 seconds and 299.4 seconds, respectively. Most of the samples prepared from the nine experimental conditions met the requirements for working time (not less than 90 seconds) and setting time (not more than five minutes) specified in ISO 4049 : 2000, except for two conditions (0 4-META with 88.5 filler and 0 4-META with 90.0 filler).

Flexural strength significantly increased with the increase of 4-META content in this study. This result was in accordance with previous results by Kakuta et al.[16] and Soma et al.[12]. This was because 4-META was considered to improve the bond between metal particles and resin matrix. Elastic modulus also increased as the 4-META content increased. This result agreed well with the previous result by Soma et al.[12], but was not consistent with those of Kakuta et al.[16] and Urapepon and Ogura[17]. The latter studies used 4-META only as a coupling agent between the surface of filler particles and resin matrix by immersing the filler particles in 4-META/acetone solutions, while the former study as well as this study used 4-META as a component of the matrix resin. Therefore, a complex composed of UDMA and 4-META based on noncovalent bonds could be formed like in the case of UDMA and MAA, and might have increased the elastic modulus of the metal-resin composites in the former study as well as in this study.

Flexural strength significantly decreased with the increase of filler content in this study. As clearly shown by Braem et al.[18], the flexural strength of dental composite resins usually increases with the increase of filler content. The opposite tendency observed in this study might be due to the lack of good bond between filler particles and resin matrix. On the other hand, Hirano and Hirasawa[8] reported the same tendency observed in this study using experimental magnetic resin composites. The elastic modulus significantly increased with the increase of filler content. As the elastic modulus of filler was much higher than that of resin matrix, this result was therefore quite reasonable. Similarly, the same tendency has been reported not only by Braem et al.[18], but also by Kakuta et al.[16] and Soma et al.[12].

The highest flexural strength was 58.8 MPa in this study. This value fulfilled the requirement for Type 2 polymer-based filling and restorative materials, but was much less than 80 MPa, the minimum value for Type 1 materials claimed by the manufacturer as suitable for restorations involving an occlusal surface[11]. Therefore, the mechanical strength of the experimental magnetic composites would not be good enough for practical use. However, this was our first step in developing magnetic resin composites for this system. In their initial attempts at developing metal-resin composites,

Hirano et al.[8] and Kakuta et al.[16] reported that the highest flexural strengths were 55.9 MPa and 61.3 MPa, respectively which were almost the same as that obtained in the present study. Subsequently, they reported much better values by modifying the methods in later papers[9,19]. As suggested in Fig. 3, the mechanical strength of this experimental magnetic composite could probably be improved by increasing the 4-META content. In addition, an adequate surface treatment of filler particles should also help to increase the flexural strength significantly by improving the bond between filler particles and resin matrix. As for the obtained elastic moduli, they were equal to or higher than those of commercial hybrid composite resins[20].

Although the attraction force between the experimental soft magnetic resin composites and a commercial hard magnet was not measured because of the difficulty in applying the method described in a report[7], specimens for the flexural test were attracted very well by a commercial hard magnet. Based on this observation, it could be said that this soft magnetic resin composite was thought to be promising in terms of magnetic attractive force. In the next experiment, the chief focus would be on seeking the optimum 4-META content. Our first priority is to develop a magnetic resin composite that has a good flexural property with an appropriate setting property. After which, further studies will be conducted to confirm whether other properties including magnetic, chemical, and biological properties would render the soft magnetic resin composite suitable for practical use.

ACKNOWLEDGEMENTS

REFERENCES

1) Rutkunas V, Mizutani H, Takahashi H. Evaluation of stable retentive properties of overdenture attachments. Stomatologija 2005; 7:115-120.
2) Saygili G, Sahmali S. Retentive forces of two magnetic systems compared with two precision attachments. J Oral Sci 1998; 40:61-64.
3) Okuno O, Ishikawa S, Imuro FT, Kinouchi Y, Yamada H, Nakano T, Hamanaka H, Ishihata N, Mizutani H, Ai M. Development of sealed cup yoke type dental magnetic attachment. Dent Mater J 1991; 10:172-184.
4) Endo K, Suzuki M, Ohno H. Corrosion characteristics of ferric and austenitic stainless steels for dental magnetic attachment. Dent Mater J 2000; 19:34-49.
5) Morito M, Hasegawa K, Hirano S, Yamada K, Mizuno Y, Hosoi T, Hirasawa T. Clinical observation on magnetic keepers. J J Mag Den 1996; 5:45-50.
6) Takada Y, Okuno O. Effect of heat history on the corrosion of ferritic stainless steels used for dental magnetic attachments. Dent Mater J 2005; 24:39-397.
7) Hirano S, Yasukawa H, Nomoto R, Moriyama K, Hirasawa T. Properties of magnetically attractive experimental resin composites. Dent Mater J 1996; 15:91-97.
8) Hirano S, Hirasawa T. Soft magnetic stainless steel powder filled composites. J J Mag Dent 1994; 3:9-13.
9) Hirano S, Oyama T, Matsumoto K, Morito M. Magnetically attractive composites containing SUS446 stainless steel filler. J J Dent Mater 2000; 19:533-537.
10) Haoka K, Kanno T, Takada Y, Kimura K, Okuno O. Corrosion resistance of the Pt-Fe-Nb magnets for dental-casting. Dent Mater J 2000; 19:270-282.
11) International Organization for Standardization. ISO 4049:2000. Dentistry Polymer-based filling, restorative and luting materials; 2000.
12) Soma H, Miyagawa Y, Ogura H. Setting and flexural properties of metal-resin composite using Ag-Cu particles as filler and chemical accelerator. Dent Mater J 2003; 22:543-555.
13) Okuno O, Takada Y, Kikuchi M, Kimura K. Corrosion resistance of magnetic stainless steel keeper for dental magnetic attachment. J J Mag Den 2002; 11:100-104.
14) Tanaka J, Hashimoto T, Stansbury JW, Antonucci JM, Suzuki K. Polymer properties on resins composed of UDMA and methacrylates with the carboxyl group. Dent Mater J 2001; 20:206-215.
15) Miyagawa Y, Urapepon S, Ogura H, Honda N. New initiation system for resin polymerization using metal particles and 4-META. Dent Mater J 2000; 19:164-172.
16) Kakuta K, Urapepon S, Miyagawa Y, Ogura H, Suchatlampong C, Rittapai A. Development of metal-resin composite restorative material. Part 1: Experimental composite using silver-tin alloy as filler and 4-META as coupling agent. Dent Mater J 1999; 18:1-10.
17) Urapepon S, Ogura H. Metal-resin composite restorative material using powder-liquid system. Dent Mater J 1999; 18:278-294.
18) Braem M, Finger W, Van Doren VE, Lambrechts P, Vanherle G. Mechanical properties and filler fraction of dental composites. Dent Mater 1989; 5:346-349.
19) Urapepon S, Kakuta K, Ogura H. Development of metal-resin composite restorative material. Part 5: Evaluation of the bonding between Ag-Sn particle and 4-META coupling agent of the metal-resin composite. Dent Mater J 2003; 22:137-145.
20) Ersoy M, Civelek A, L'Hotelier E, Say EC, Soyman M. Physical properties of different composites. Dent Mater J 2004; 23:278-283.