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Effect of Binary and Ternary Filler Mixtures on the Mechanical Properties of Composite Resins

Taira MIYASAKA and Takaichi YOSHIDA

Department of Dental Materials Science, School of Dentistry at Tokyo, The Nippon Dental University
1-9-20 Fujimi, Chiyoda-ku, Tokyo 102-8159, Japan

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The mechanical strength of experimental light cure composites containing binary filler mixtures with various combinations of irregular and spherical macrofillers in various mixes, and the microfilled ternary system fillers were measured. The compressive strength of the binary mixtures between different shaped fillers was not related to mixing ratios, although it significantly increased as the filler size decreased. The mixing ratio was immaterial within the irregular filler mixture. The compressive strength of the binary mixtures within the spherical fillers increased as the mixing ratio increased while the filler size was relatively large, then the mixing ratio became insignificant as the filler size decreased under 1.4 μm. The compressive strength of the microfilled ternary fillers increased with the decrease in the macrofiller size and with the increase in the mixing ratio. A large diametrical tensile strength was found in several microfilled ternary mixtures containing different shaped macrofillers.

Key words : Filler, Light cure composite resin, Mechanical strength

INTRODUCTION

There has been a recent marked increase in the clinical use of dental composite resins, especially of hybrid filled composites, because of their superior mechanical properties[1]. According to a study on the filler systems of hybrid or semi-hybrid commercial composites[2], filler size and the contents of these composites were significantly different from each other. With regard to commercial products, the mean size of hybrid fillers ranged from the order of 1/100 μm to several μm, and the weight fractions were also widely distributed from more than 80% for highly compact-filled composites to under 75% for the traditional materials. The rapid increase in the clinical use of hybrid composites has preempted fundamental studies of these composites and basic understanding of the properties of composites, like the composition or the surface treatment of fillers, remains uncertain. Although there have been some studies on the classification of commercial hybrid composites[2−4], and several studies on microfilled or conventionally macrofilled composites correlated with filler shape and size[5−10], there have been few systematical studies on the hybrid filler system. Therefore, in the development of experimental hybrid composites, there is a lack of adequate information even about the size, composition and surface treatment of the hybrid fillers. To obtain proper information about hybrid fillers, we undertook systematic investigations on the filler compositions and the surface treatment of hybrid fillers[11-13]. In a previous study[13], we reported the composition of binary filler mixture systems, and that superior mechanical properties were found for mixtures of fillers under 5μm in mean diameter. In addition, when the microfiller was added to macrofillers, the strength of the composites increased as the size of the macrofiller became smaller[13]. However, because the previous study was limited to binary systems consisting of equal amounts of macrofillers, the effect of the mixing ratio of fillers remained unclassified. The addition of microfiller was also limited to individual macrofillers in the previous study[13], so no information of ternary or more complex filler systems was obtained.

In the present study, we aimed at further classification of the component ratios and the composition of hybrid filler mixtures. We focused on filler mixtures mainly composed of a similar binary system whose mechanical strength was found to be large in the previous study[13]. Namely, the effect of combinations and mixing ratios of binary filler mixtures of different shapes and sizes, and the effect of the addition of the microfiller as a tertiary component to binary filler mixtures on the mechanical strength of the experimental light cure composite resin were investigated.

MATERIALS AND METHODS

Fillers and their surface treatments

All types of macrofiller used in this study were fused quartz fine powder of irregular or spherical shapes. Two types of irregular fillers of 1.7 and 5.4μm in mean size, three types of spherical fillers of 0.5, 1.4 and 5.9μm, and a microfiller of 0.04μm were adopted. The characteristics and codes of fillers are presented in Table 1. The mixtures between different shape fillers, *i.e.* mixtures between irregular and spherical filler, and mixtures using the same shaped fillers, *i.e.* spherical-spherical or irregular-irregular mixtures, were made from the macrofillers listed in Table 1 as the binary system fillers. Three mixing ratio levels of 1 : 3, 1 : 1 and 3 : 1 were adopted. These ratios were converted to the percentage of the smaller filler component giving 25%, 50% and 75% in weight, respectively. Hereafter, the mixing ratio will be referred to

Table 1 Fused quartz fillers used in this study

Filler	Code	Shape	Mean size (μm)	Specific surface area (m^2/g)	Bulk density (g/cm^3)	lot.No.	Manufacturer
WX	I-1.7	Irregular	1.7	14.2	0.44 (0.006)	2G-3202	Tatsumori[1]
ZA-30	I-5.4	Irregular	5.4	4.7	0.96 (0.015)	0819-Q2	Tatsumori
ST-0.5	S-0.5	Spherical	0.46	7.5	0.62 (0.008)	DF17	Tatsumori
ST-1.5	S-1.4	Spherical	1.38	5.1	0.78 (0.029)	DD16	Tatsumori
ST-5	S-5.9	Spherical	5.9	3.7	0.91 (0.018)	31154	Tatsumori
OX50	MF	Spherical	0.04	50	0.14 (0.003)	1-13093	Nippon Aerosil[2]

The parenthesized numbers indicate the standard deviations.
[1]Tokyo, Japan, [2]Tokyo, Japan

as the mixing ratio in wt% of the smaller filler of the binary macrofiller mixture. In a previous study[13], the largest mechanical strength was identified for three kinds of binary macrofiller mixtures whose components were smaller than 1.7 μm in mean diameter, *i.e.* S-0.5+I-1.7, S-0.5+S-1.4 and S-1.4+I-1.7, therefore, the ternary hybrid systems were prepared by varying the mixing ratios of these three kinds of binary mixtures and admixing 30 wt% of the microfiller as the third component.

The filler mixtures were treated with γ-methacryloxypropyltrimethoxy-silane (γ-MPTS/LS-3380, lot. 512169, Shin-Etsu Chemicals Co., Ltd., Tokyo, Japan) as described previously[11,13]. Assuming the surface area of the filler mixture is S m^2/g, the amount of γ-MPTS corresponding to the filler surface being covered uniformly with γ-MPTS at 50 molecules/nm^2, was calculated to be 0.02062×S g per 1 g of filler[13]. The surface area of 10 g of filler mixture was calculated from the average surface area of component fillers and the mixing ratio, then the amount of γ-MPTS was calculated from the obtained surface area. The required amount of γ-MPTS was mixed with 95% ethanol containing 5% water, which gave 20 g of silane solution. Both the silane solution and 10 g of the filler mixture were transferred to a screw capped glass bottle, shaken for 2 hr at 50℃, then the solvent was removed by evaporation at 50℃ under reduced pressure. The filler was spread on a Petri dish, then heated at 90℃ in an oven for 2 hr, to obtain the experimental fillers.

Preparation of experimental light cure composite resin

As an organic matrix of the experimental composites, the monomer mixture was obtained by mixing 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane (D-GMA, lot. 1105K, Shin-Nakamura Chemical Co., Ltd., Tokyo, Japan) and triethyleneglycoldimethacrylate (NK-ester 3G, lot. 0305U, Shin-Nakamura Chemical Co., Ltd., Tokyo, Japan) with a 2 : 1 weight ratio. One percent of 2-(dimethylamino) ethylmethacrylate (lot. VIN9190, Nacalai Tesque, Inc., Kyoto, Japan) was added to the monomer as a reducing agent, and 200 ppm of 4-methoxyphenol (lot. FGA01, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) was also added as an inhibitor, then the organic mixture was stirred at 100 rpm. One gram of the monomer mixture was poured into the mortar and mixed with 1% of camphorquinone (lot. FIB03, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), then the silane treated filler was gradually added until the filler content reached 70%. The mixture was agitated for 20 min in an automatic mortar (ANM-150, Nitto Kagaku Co., Nagoya, Japan), then evacuated in a vacuum to give the experimental light cure composite resin. Preparations of each filler mixture, surface treatment and preparation of each experimental composite was repeated 3 times in a random sequence.

Preparation of test pieces and measurement of mechanical properties

The compressive strength and the diametrical tensile strength of the experimental composites were measured. A glass tube with a 4 mm inner diameter and 8 mm high, and one with 6 mm inner diameter and 3 mm high, were used as the moulds for preparation of the test specimens of compressive and diametrical tensile strength,

Table 2 The compressive strength and diametric tensile strength of experimental light cure composite resins in MPa

Mixing ratios		25%		50%		75%	
Filler 1	Filler 2	Compressive	Diametrical tensile	Compressive	Diametrical tensile	Compressive	Diametrical tensile
S-0.5	I-1.7	285 (37.8)	44.1 (6.94)	278 (19.7)	43.8 (5.26)	280 (34.2)	46.5 (3.48)
S-1.4	I-1.7	223 (73.9)	38.6 (5.10)	288 (29.9)	42.6 (4.74)	256 (63.2)	46.1 (3.74)
I-1.7	S-5.9	196 (24.0)	41.8 (10.19)	227 (20.8)	42.2 (5.06)	224 (26.3)	38.1 (2.14)
S-0.5	I-5.4	216 (16.5)	46.3 (1.97)	232 (19.7)	41.5 (1.42)	227 (14.9)	38.9 (3.27)
S-1.4	I-5.4	204 (16.6)	44.9 (4.50)	207 (18.6)	44.9 (0.85)	230 (3.5)	45.3 (5.06)
I-5.4	S-5.9	191 (3.6)	39.5 (2.06)	194 (8.9)	42.4 (2.42)	195 (6.1)	39.9 (2.41)
I-1.7	I-5.4	198 (17.0)	42.9 (2.01)	217 (5.7)	40.7 (4.92)	216 (9.0)	39.5 (3.92)
S-0.5	S-1.4	253 (6.7)	44.1 (0.67)	245 (9.9)	43.1 (2.81)	250 (4.6)	40.7 (3.35)
S-0.5	S-5.9	201 (11.3)	42.9 (2.62)	218 (9.9)	44.1 (2.30)	237 (11.1)	41.4 (1.76)
S-1.4	S-5.9	195 (7.6)	45.5 (1.10)	201 (3.0)	45.3 (5.33)	223 (7.6)	44.3 (2.29)
MF 30 wt% admixed							
S-0.5	I-1.7	279 (20.3)	45.2 (3.90)	280 (7.1)	45.6 (3.87)	295 (19.1)	47.2 (1.55)
S-0.5	S-1.4	293 (10.8)	48.5 (5.12)	302 (9.5)	47.2 (4.45)	311 (2.3)	44.1 (3.31)
S-1.4	I-1.7	281 (27.3)	41.1 (1.59)	281 (4.0)	45.0 (0.90)	311 (3.5)	55.2 (8.85)

The parenthesized numbers indicate the standard deviations.
The ternary systems shown in 3 rows from the bottom contained 30 wt% microfiller.

respectively. Avoiding air bubble contamination, the moulds were carefully filled with the experimental composite, sandwiched with polyester strips of 0.10 mm thickness, and then pressed against the glass plates. Every three specimens for the compressive and the diametrical tensile strength was cured using the light curing instrument (LV-Ⅰ, G.C. Co., Ltd., Tokyo, Japan) for 15 min, then turned over to cure from the other side for another 15 min. The light cure specimens were ground and polished with water proof silicone carbide paper of #800 grit under running water, then removed from the moulds and stored in water at 37℃. The compressive strength and the diametrical tensile strength were measured 24 hr after the preparation of specimens using a universal testing machine (DCS-10T, Shimadzu Co., Ltd., Kyoto, Japan) operated at 1 mm/min cross-head speed. The measured values of three specimens were averaged to represent the observed value of one repetition.

RESULTS

The averaged values and standard deviations of the compressive strength and the diametrical tensile strength of experimental composites with three repetitions are presented in Table 2.

Binary filler systems

1) Mixtures of irregular fillers and spherical fillers

The findings on the compressive strength of the experimental composites containing

Table 3 The result of three-way ANOVA of compressive strength of the composites consisting of filler mixtures with different shapes

Factor	s.s.	d.f.	m.s.	Fo	Fo'	Significance
A (Irregular)	21,881.0	1	21,881.0	23.62	25.52	**
B (Spherical)	21,554.0	2	10,777.0	11.63	12.57	**
C (Mixing ratio)	3,645.4	2	1,822.7	1.97	2.13	–
A×B	2,556.6	2	1,278.3	1.38	1.49	–
A×C	1,210.0	2	605.0	0.65	p	
B×C	1,642.4	4	410.6	0.44	p	
A×B×C	3,233.7	4	808.4	0.87	p	
e	33,355.0	36	926.5			
Total	89,078.1	53				
Pe	39,441.1	46	857.4	$Q_i=\pm11.34$, $Q_j=\pm13.89$		

The notes of – and ** respectively indicate the effect is not significant at the 95% confidence level and highly significant at 99%. The Q_i and Q_j denote a confidence interval of 95%, and the subscripts $_i$ and $_j$ denotes the factors A and B, respectively. The same expression will be used in the following tables.

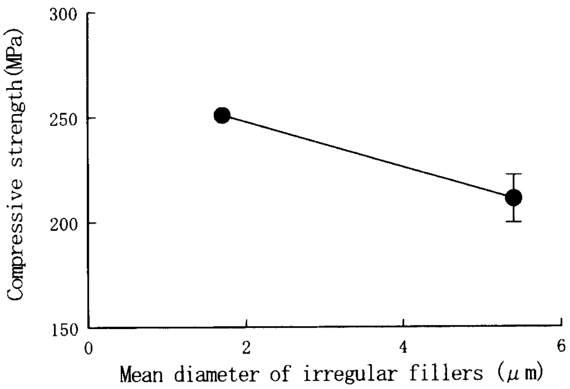

Fig. 1 The effect of mean size of irregular fillers on the compressive strength of the experimental composites consisting of mixtures of irregular fillers and spherical fillers. The longitudinal fine line represents the confidence interval of 95%.

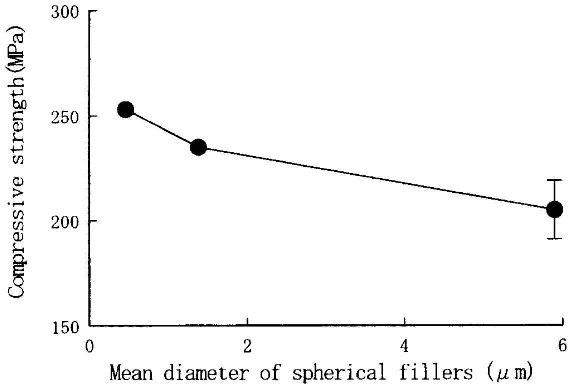

Fig. 2 The effect of mean size of spherical fillers on the compressive strength of the experimental composites consisting of the mixture of irregular fillers and spherical fillers. The longitudinal fine line represents the confidence interval of 95%.

filler mixtures of irregular and spherical fillers, were subjected to a three-way analysis of variance (ANOVA), whose three main factors were the mean size of irregular filler of 2 levels, the mean size of spherical filler of 3 levels and mixing ratio of 3 levels with 3 repetitions, the findings are presented in Table 3. A highly significant difference was found between the mean size of irregular fillers and among the mean size of spherical fillers, therefore, these findings are shown in Figs. 1 and 2. The averaged values of the compressive strength were plotted according to the respective main effect, *i.e.* the filler size of irregular fillers and spherical fillers. The longitudinal fine lines in the following figures represent the confidence interval of 95% significance of the averaged values. As can be seen in Fig. 1, with relation to the mean size of irregular fillers, the compressive strength increased with decreasing filler size, therefore, the composites containing I-1.7 were stronger than that of I-5.4. Similarly, Fig. 2 shows the tendency of an increase in strength with the decrease in the mean size of the spherical fillers from 6, 1.4 to 0.5μm, however, the effect of the mixing ratio was not significant as shown in Table 3. In the case of mixtures of different shaped fillers, because the compressive strength increased with the filler size as both shapes decreased, the filler mixtures of S-0.5+I-1.7 and S-1.4+I-1.7 yielded the strongest compressive strength and were not affected by their mixing ratios.

Since ANOVA of the diametrical tensile strength demonstrated no significant difference in all factors, the diametrical tensile strength of the binary system of different shaped fillers were not influenced by the compositions of this binary system.

2) Mixtures using only the irregular fillers

Using the irregular fillers, only one combination of fillers as a binary system, *i.e.* I-1.7+I-5.4, was possible. The compressive strength and diametrical tensile strength for the mixtures of irregular fillers with different mixing ratios was subjected to a one-way ANOVA regarding the mixing ratios as a factor. Neither compressive strength nor diametrical tensile strength were significantly different.

3) Mixtures using only the spherical fillers

A two-way ANOVA on the compressive strength for binary filler mixtures within the spherical fillers was performed with regard to the combinations of spherical fillers and the mixing ratios as the main factors, and the findings are presented in Table 4. From Table 4, it can be seen that the effect of the combinations of spherical fillers, that of the mixing ratios and their interactions were highly significant, which are illustrated in Fig. 3. With regard to the filler combinations and mixing ratios, the compressive strength tended to increase as the averaged filler size of the two components decreased, and as the mixing ratios increased. As can be seen in Fig. 3, S-0.5+S-5.9 was slightly stronger than S-1.4+S-5.9 as a whole, and the compressive strength of both mixtures tended to increase with the increase in the mixing ratios. Although

Table 4 The result of two-way ANOVA of compressive strength of the composites consisting of filler mixtures using only spherical fillers

Factor	s.s.	d.f.	m.s.	Fo	Significance
A (Combination)	8,960.3	2	4,480.2	63.40	**
B (Mixing ratio)	2,034.7	2	1,017.4	14.40	**
A×B	1,322.6	4	330.7	4.68	**
e	1,272.0	18	70.7		
Total	13,589.6	26	$Q_i=\pm5.89$,	$Q_j=\pm5.89$,	$Q_{ij}=\pm10.20$

The Q_{ij} denotes the confidence interval of A×B at 95%. The same expression will be used in the following tables.

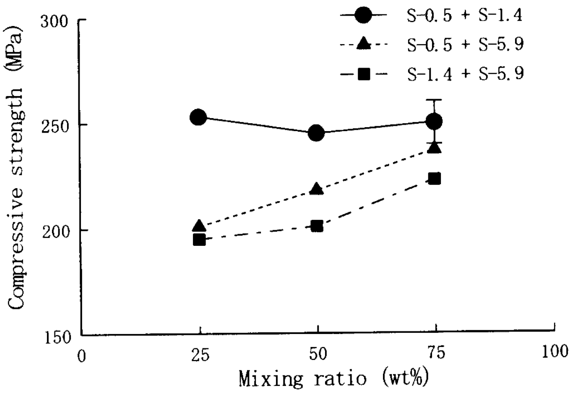

Fig. 3 The interaction effect between the combination and mixing ratios of fillers on the compressive strength of the experimental composites containing filler mixtures of only spherical fillers. The longitudinal fine line represents the confidence interval of 95%.

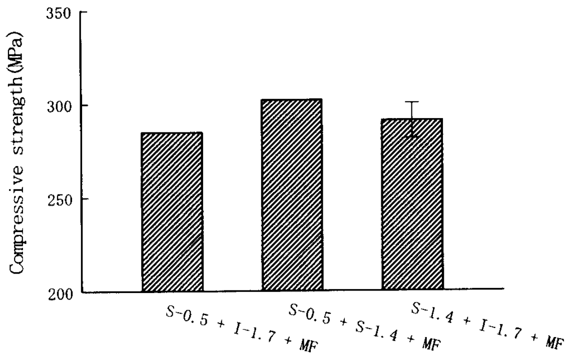

Fig. 4 The effect of combinations of macrofillers on the compressive strength of the experimental composites consisting of microfiller admixed ternary system fillers. The longitudinal fine line represents the confidence interval of 95%.

Table 5 The result of two-way ANOVA of compressive strength of the composites consisting of microfiller admixed ternary fillers

Factor	s.s.	d.f.	m.s.	Fo	Fo'	Significance
A (Combination)	1,369.0	2	684.5	3.40	3.78	*
B (Mixing ratio)	2,411.2	2	1,205.6	5.99	6.66	**
A×B	357.3	4	89.3	0.44	p	
e	3,623.3	18	201.3			
Total	7,760.8	26				
Pe	3,980.6	22	180.9	$Q_i = \pm 9.30$, $Q_j = \pm 9.30$		

The note of * indicates the effect is significant at the 95% confidence level. The same expression will be used in the following table.

the compressive strength of S-0.5+S-1.4 was relatively high, no significant differences were found between the different mixing ratios.

A two-way ANOVA on the diametrical tensile strength was performed, which showed no significant differences between any effect or their interactions.

Ternary filler system

The compressive strength for the ternary filler mixtures whose two components were chosen from three kinds of macrofillers under 1.7μm in mean diameter, *i.e.* S-0.5, S-1.4 and I-1.7, and whose remaining component was the microfiller MF, was measured. Assigning the combinations of macrofillers and the mixing ratios as two main factors, a two-way ANOVA on the compressive strength was performed, and the findings are shown in Table 5. Since significant differences between filler combinations and highly significant differences between mixing ratios were found, these findings

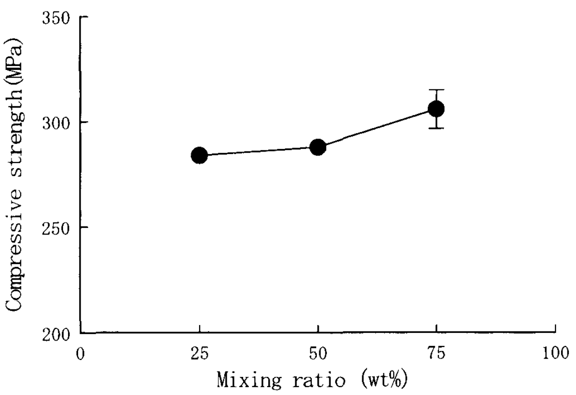

Fig. 5 The effect of the mixing ratio of macrofillers on the compressive strength of the experimental composites consisting of microfiller admixed ternary system fillers. The longitudinal fine line represents the confidence interval of 95%.

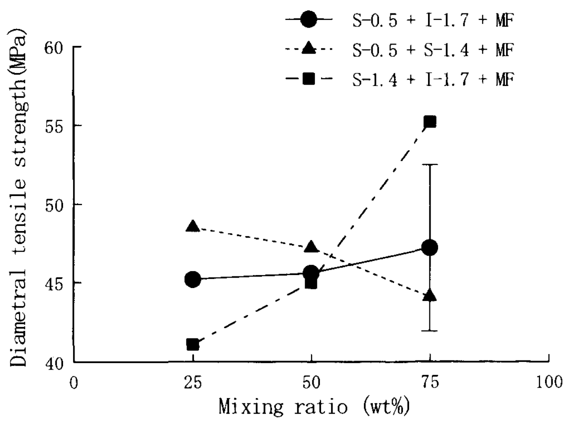

Fig. 6 The interaction effect between combinations and mixing ratios of macrofillers on the diametrical tensile strength of the experimental composites consisting of microfiller admixed ternary system fillers. The longitudinal fine line represents the confidence interval of 95%.

Table 6 The result of two-way ANOVA of diametrical tensile strength of the composites consisting of microfiller admixed ternary fillers

Factor	s.s.	d.f.	m.s.	Fo	Significance
A (Combination)	5.57	2	2.79	0.15	–
B (Mixing ratio)	72.83	2	36.42	1.91	–
A×B	283.20	4	70.80	3.72	*
e	342.41	18	19.02		
Total	704.01	26		$Q_{ij}=\pm 5.29$	

are illustrated in Figs. 4 and 5. With regard to the combination of macrofillers, Fig. 4 shows that the combination of the smallest fillers, *i.e.* S-0.5+S-1.4+MF, was stronger than the mixtures including I-1.7. It is also apparent from Table 2 that the composites made of ternary mixtures were stronger than those of binary mixtures. Fig. 5 shows the tendency of the increase in compressive strength with the increase of mixing ratios, therefore, in the case of the ternary system, it was clear that the strength increased as the quantities of smaller filler increased.

The findings of analogous two-way ANOVA on the diametrical tensile strength are presented in Table 6. Significant differences were found in the interactions between the combination of fillers and the mixing ratios, and the findings are shown in Fig. 6. Although the diametrical tensile strength tended to increase as the content of S-1.4 increased in the combination of S-1.4+I-1.7+MF, the mixing ratios scarcely influenced other combinations.

DISCUSSION

The binary or ternary mixtures of fillers, whose shape, specific surface area and mean particle size are shown in Table 1, were prepared to obtain the experimental light cure composite resins in the present study. Since a previous study[13] indicated that the filler mixtures whose components were greater than 10μm in mean diameter tended to decrease in mechanical strength, macrofillers under 5.9μm in mean diameter were adopted in this study.

With regard to the characteristics of the fillers in Table 1, although it was clear that the decrease in mean size caused a significant increase in the specific surface area in irregular fillers, the specific surface area of spherical fillers increased less than in irregular fillers.

Since the quantity of the silane treatment agent was estimated from the surface area of the filler, the properties of the composite resins were also affected by the surface area of the filler. Therefore, the relationship between the mean filler size and the specific surface area of the filler was discussed theoretically as follows. Generally, a filler is regarded as a rigid sphere and the densest packing of the spheres based on the face center cubic lattice structure is assumed for the condensed state of the fillers. Considering the spheres of d in diameter are packed in the cubic of $\sqrt{2}\,d$ in length of one side, *i.e.* corresponding to a unit cell of the face center cubic lattice composed of 4 spheres of d in diameter, the sum of the surface areas of spheres included in the cubic is calculated as $4\times4\pi(d/2)^2=4\pi d^2$. However, when the spheres of d/n in diameter, where n is an arbitrary real number, are packed in the same

Table 7 The sum of the surface areas and volumes of fillers calculated for packing structure examples

Diameter	Number of particles	Surface area of one particle	Sum of surface areas	Volume of one particle	Sum of volumes
d	4	πd^2	$4\pi d^2$	$\pi d^3/6$	$2\pi d^3/3$
$d/3$	$4\cdot3^3=108$	$\pi d^2/9$	$12\pi d^2$	$\pi d^3/(6\cdot3^3)$	$2\pi d^3/3$
d/n	$4n^3$	$\pi d^2/n^2$	$4\pi d^2 n$	$\pi d^3/(6n^3)$	$2\pi d^3/3$

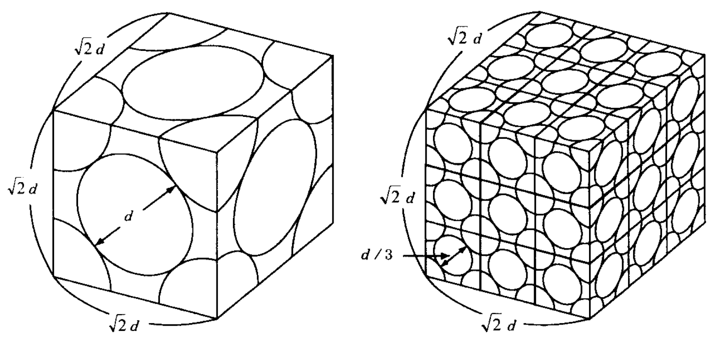

Fig. 7 Particles of d and $d/3$ in diameter packed in the cubic of $\sqrt{2}\,d$ in the length of one side to form the face center cubic closest packing.

cubic, the corresponding sum of surface areas is calculated as $4\pi d^2 n$. The packing structure examples of $n=1$ and $n=3$ are illustrated in Fig. 7 and the sum of surface areas and volumes of fillers are listed in Table 7. The respective volumes of the spheres of different diameters included in the cubic of $\sqrt{2}\,d$ in length of one side remain at the constant value of $2\pi d^3/3$ when the most dense packing is assumed, in other words, the volumes included in the cubic are not affected by their diameters. The correlation between the diameters and surface areas and volumes for the examples of $n=1$ and $n=3$ and the generalized case are also listed in the caption of Fig. 7. Therefore, if the diameter of fillers decreases $1/n$ from the original value, and assuming that the densities of the fillers are the same, the sum of surface area of the filler of the same weight is predicted to be n times as large as its original area. The same relationship between the diameters and the surface areas of the rigid spheres packed in the same space could be drawn from other lattice systems, such as a simple cubic lattice. The tendency observed in the irregular fillers in Table 1 was found to be in good agreement with the calculated results. Namely, the surface area of I-1.7 (14.2 m^2/g), whose mean filler size was approximately 1/3 of I-5.4, was approximately 3-fold larger than that of I-5.4 (4.7 m^2/g). Although the relationship between filler size and surface area was well correlated in the irregular fillers, Table 1 shows the absence of such a relationship in the spherical fillers contrary to the expectation that the adoption of the rigid sphere models appeared to be more suitable for the spherical fillers.

Due to the disagreement between the theoretical consideration and the experiments in the spherical fillers, further discussion about the packing volume fraction of fillers was made. The packing volume fraction was introduced as the ratio of the real volume of constituent particles to the apparent bulk volume, where the real vol-

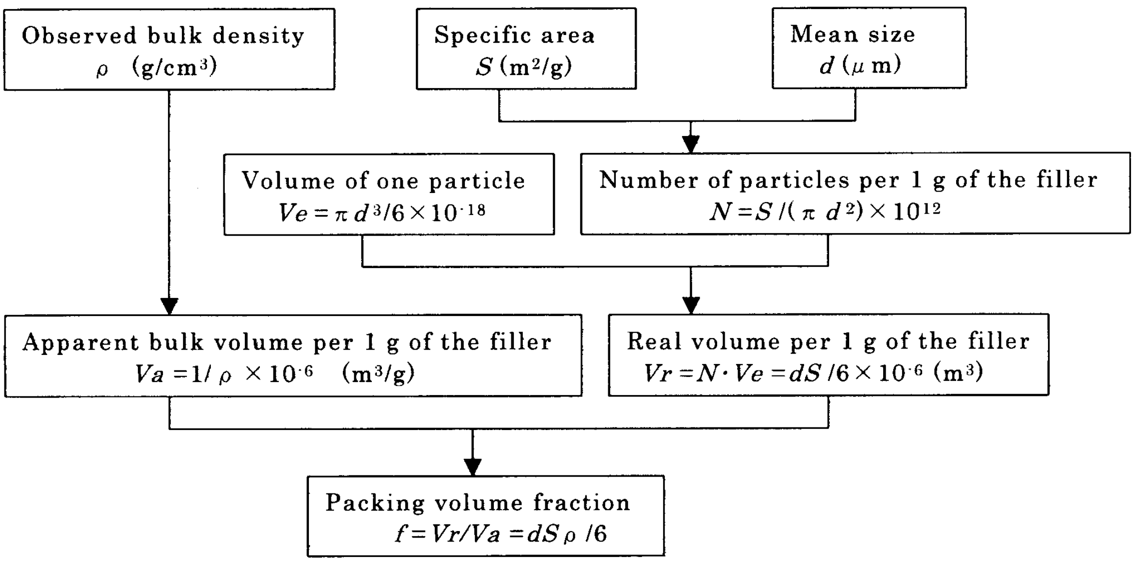

Fig. 8 The schematic diagram of the calculations of the packing volume fraction f of the filler.

ume was obtained from the sum of the volumes of the constituent particles. The packing volume fractions were calculated using the specific surface areas, mean particle sizes and bulk densities. The bulk densities obtained through the measurements of apparent bulk volumes and weights of the fillers are presented in Table 1. A schematic diagram of the calculations of the packing volume fraction f of the filler is shown in Fig. 8. The real volume was theoretically calculated from the specific surface area and the mean particle size as follows. Assuming the filler consisted of only one kind of sphere of similar size, the number of particles N included in 1 gram of the filler with a specific area S (m^2/g) and mean size d (μm), was calculated to be $N = S/\{4\pi(d/2)^2 \times 10^{-12}\} = S/(\pi d^2) \times 10^{12}$ (particles/g). The real volume was calculated as the sum of the volumes of every particle, where the volume of one particle with a mean size d (μm) was $4/3 \times \pi(d/2)^3 \times 10^{-18} = \pi d^3/6 \times 10^{-18}$ (m^3), hence the real volume V_r per 1 g was obtained from the product of the number of particles N and the volume of one particle as $V_r = N \times \pi d^3/6 \times 10^{-18} = Sd/6 \times 10^{-6}$ (m^3/g). However, if the observed bulk density is denoted by ρ (g/cm^3), the apparent bulk volume per 1 g is denoted by $V_a = 1/\rho \times 10^{-6}$ (m^3/g). Therefore, the packing volume fraction f of the spheres was calculated as $f = V_r/V_a = Sd\rho/6$. The f values of I-1.7 and I-5.4 calculated from the findings listed in Table 1 were 1.76 and 4.05, respectively. The respective f values of S-0.5, S-1.5 and S-5.9 were 0.35, 0.91 and 3.33, and that of the microfiller was 0.05. Since the f value of 0.74 was calculated to the closest packing of a face center cubic lattice, the fillers with larger f values than this were inconsistent with the assumption of these arguments.

One of the most important factors we had not taken into account in the above discussion and appeared to be significantly different from the real state, was the distribution of the particle size. An assumption of one kind of particle constitution was adopted to calculate the number of particles, however, the real filler was composed of widely distributed particles in size. When the distribution in size was taken into account, the kind of mean values that represented the distribution characteristics became very important. For this purpose, the number averaged mean values would be preferable to the weight averaged mean value usually used as a general mean value for the fillers. Since the weight averaged mean value is generally much larger than the number averaged ones[14], this may have led to the extraordinary f value. Conversely, the ordinary f values as seen in S-0.5 or MF, meant the ratio of the number averaged mean values to the weight averaged one was near unity, so these fillers had relatively narrow dispersion widths and appeared to be almost mono-dispersed. In fact, S-0.5 had a mean size of 0.46μm and a standard deviation of 0.17μm, so the dispersion of the filler was suggested to be very narrow. Although S-1.4 was the second narrowest in the order of the dispersion sequence and had a 1.38μm mean diameter, it showed a much larger standard deviation of 1.02μm. In comparison, S-0.5 was considerably smaller in the width of the dispersion than any other fillers used in the present study.

Considering the above discussion about the filler size and specific surface area, the effects of the binary or ternary filler systems on the mechanical properties of experimental light cure composites were investigated. The mixtures of macrofillers with different shapes tended to show increased compressive strength with a decrease in filler size, but there was no significant difference between the mixing ratios. The largest compressive strength within the combinations of the different shaped fillers was obtained from S-0.5+I-1.7 and S-1.4+I-1.7, and this finding was in agreement with a previous study[13]. The most dense packing in large volumes of powder has not yet been produced, so generally speaking, the highest dense packing achieved by filling the space of large particles with smaller particles, occurred when the volume ratio of the small particle to large particle was 0.23 : 0.63, where the packing ratio was calculated as $0.63+(1-0.63)\times0.63=0.86$. The ratio of 1 : 20 in the diameters of small particles to large particles was required to achieve such a highly dense packing[15]. Since the ratios in diameter of the binary filler mixtures adopted in this study ranged from 1 : 3 to 1 : 13, these ratios could only contribute to reduce the overall mean particle size by mixing with the smaller fillers. The highly dense packing achieved by filling the space of the large fillers with the smaller ones appeared to be not so prominent in this case. The absence of the effect of the dense packing appeared to be insignificant on the effect of the mixing ratios. In relation to the increase in strength with the decrease in filler size, it was reported that compressive failure of composites occurred mainly by slippage along a plane inside the material[16]. In the fracture plane of the composite resin, the increase in the number of filler particles increased the internal friction with a plane, but reduced the cohesive area of the matrix at the same time. If the reduction in cohesive force of the matrix was smaller than the increase in friction force by the filler, the strength of the composite increased[16]. Regarding the increase of friction against fracture sliding, the smaller fillers strongly bonding to the matrix were more effective than the larger ones. Consequently, the decrease in the size of fillers brought an increase in compressive strength.

With regard to the binary mixture between the same shaped fillers, although the effect of the mixing ratio was not significant within combinations of irregular fillers, the effects of the mixing ratio on the compressive strength of the binary mixtures within spherical fillers were significantly different. In the composites containing S-5.9, an increase in the mixing ratio of the smaller filler caused a decrease in the overall mean size of the filler mixture, and hence tended to increase the compressive strength. Although the combination of S-0.5+S-1.4, whose overall mean size was the smallest, showed the largest compressive strength, the effect of the mixing ratio was not significant. In such a combination, the increase in the mixing ratio could decrease the mean size minimally so the increase in the strength with the decrease in filler size would scarcely be expected.

With respect to the binary fillers made of the macrofillers listed in Table 1, it was suggested from the above discussions that the composites consisting of S-0.5+I-1.7, S-1.4+I-1.7 or S-0.5+S-1.4 with an arbitrary mixing ratio would be the strongest in compression. In other words, the fillers up to 2 μm in mean diameter should be used and mixed so that the mean size of fillers were as small as possible, then the strongest composite would be obtained.

The ternary system fillers consisted of the strongest combinations of the binary system macrofillers, and 30 wt% of the microfiller were prepared to investigate the mechanical properties of the experimental composites. Regarding the effect of the combinations of fillers on the compressive strength, the composites containing S-0.5+S-1.4+MF showed the largest compressive strength. This finding showed that the combination of macrofillers possessing the smallest over all mean size, gave the strongest composites of microfiller admixed ternary systems or binary systems. However, it was different from the binary systems that the effects of the mixing ratios were found to be significant in the ternary systems. The compressive strength tended to increase as the mixing ratio of the smaller fillers increased. This finding was because of the increase in the packing volume fraction with the decrease in the overall mean size of macrofiller portion and with the admixing of the microfiller. In the admixture of the microfiller, since the space among the macrofillers was filled with the microfiller, the packing fraction was increased, as a result, the strength was increased. To induce such a reinforcement effectively, the ratio of the diameter of smaller filler to the larger one should be 1 : 20[13,15] as mentioned above. The theoretically suitable diameter of the macrofiller against the microfiller of 0.04 μm should be 0.8 μm. For the strongest combination of fillers of S-0.5+S-1.4+MF, with the mixing ratio of S-0.5 increased from 25% to 75%, the arithmetic means of the macrofiller portion decreased from 1.18 μm to 0.73 μm. Admixing a microfiller of 0.04 μm to these binary mixtures approached the ideal value of 0.8 μm in the mean size of the macrofiller portion resulting in an increase in the compressive strength. The compressive strength of the ternary fillers was not markedly greater than that of the binary fillers containing microfiller in a previous study[13]. This similarity in strength might be caused by the packing state of the fillers. From the viewpoint of reinforcement due to filler packing, which was most effectively shown in the ratio of the diameter of fillers at 1 : 20, the theoretically predicted combinations of filler diameters were 20 μm+1 μm+50nm, 1 μm+50 nm+2.5 nm, etc. There would be little importance to investigate such combinations of fillers. For example, a problem would arise as to how to secure the smooth surface from the former combination of fillers, and for the latter, the production of the smallest filler of 2.5 nm in diameter and the treatment of such small fillers appears to be very difficult. Therefore, it appears there is little use in adopting the ternary filler systems.

With respect to the finding of the diametrical tensile strength in the ternary systems, the mixture containing S-0.5 was affected little by the mixing ratio, although the diametrical tensile strength of the mixture of S-1.4+I-1.7+MF tended to increase with the increase in the S-1.4 content, and the largest diametrical tensile strength was obtained from the mixture of S-1.4+I-1.7+MF with 75% of S-1.4 in the macrofiller portion. Therefore, with respect to the diametrical tensile strength, the microfiller admixed mixture between different shaped macrofillers was stronger than the mixtures of spherical macrofillers alone. This finding may be caused by the difference between the fracture mechanism of compressive and diametrical tensile strength. The internal friction and the cohesive force in the fracture plane of the composite played important roles in resisting compressive fractures, as mentioned above. Although the compressive strength was affected more by the frictional force than by the cohesive force, from the viewpoint of the propagation of the crack by tensile stress, the filler-matrix bonding strength appeared to be more important for the tensile strength. If the interface between the filler and matrix was strongly bonded, an increase in the surface area of the filler at unit volume increased the debonding force to fracture such an interface. This effect preferred the irregular filler to the spherical filler, although the spherical filler appeared to be preferable from the viewpoint of the filler packing fraction. The mixture of irregular and spherical fillers fulfilled both requirements of the increase in debonding force and the increase in the packing fraction, therefore, the tensile strength of the composite using these mixtures was significantly increased.

CONCLUSION

The binary system fillers obtained by varying the combinations and mixing ratio of the fused quartz macrofillers differing in shape (irregular or spherical) and mean size ($0.5\sim5.9\mu m$) were prepared. The ternary system fillers, with two components chosen from the same binary mixtures, up to $1.7\mu m$ in individual mean diameter, and with 30 wt% microfiller as the third component, were also prepared. The light cure experimental composite resins were made from the binary or ternary system filler mixtures, then the compressive strength and the diametrical tensile strengths were investigated. The following findings were obtained.

1) In the binary system consisting of combinations of different shaped fillers, although the effect of the mixing ratio on the compressive strength was not significant, the compressive strength was significantly increased with decreasing mean size of the filler mixtures.

2) In the binary system consisting of combinations of the same shaped fillers, the influence of the mixing ratio was insignificant in combinations of irregular fillers alone. With combinations of only spherical fillers, although the compressive strength of the composites containing relatively large filler ($5.9\mu m$ of mean particle size) increased as the mixing ratio of smaller fillers increased, the effect of the mixing ratio was not significant when combinations of fillers under $1.4\mu m$ in mean diameter were used.

3) With respect to the binary fillers made of the macrofillers used in this study, the strongest composite was obtained when fillers up to $2\mu m$ in mean diameter were used and mixed so that the mean size of the fillers were as small as possible.

4) In the microfiller admixed ternary system, the compressive strength increased as the mean size of the macrofiller portion of the filler mixture decreased, however, the strength of the ternary system was not markedly greater than the microfilled binary systems. Large diametrical tensile strength was found in mixtures of irregular filler and spherical fillers.

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