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Mechanical behavior of bioactive composite cements consisting of resin and glass-ceramic powder in a simulated body fluid: Effect of silane coupling agent

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Time-dependent strength behavior was investigated for bisphenol-*a*-glycidyl methacrylate/triethylene glycol dimethacrylate (Bis-GMA/TEGDMA) resin cements combined with glass–ceramic A-W filler treated with various kinds of silane coupling agents. The fracture strength of the composite resin cements was measured by three-point bending as a function of stressing rate in a simulated body fluid (SBF), and thereby the stress-corrosion susceptibility constant was evaluated. The fracture strength was found to depend on the kind of coupling agent used. For the present Bis-GMA/TEGDMA resin, the silane coupling agents without hydrophilic amine groups can be used to obtain good adhesion between resin and A-W filler owing to their nature of co-polymerizing with the resin. On the other hand, all the composite resin cements showed nearly the same degree of stress-corrosion susceptibility whether the A-W fillers were treated or untreated with silane coupling agents. This means that the stress-corrosion susceptibility of the present composite cements is predominantly affected by that of the matrix resin. Thus, the microcrack formation and growth at the resin matrix near particle – resin interface were thought to determine overall time-dependent strength behavior of the composite cements.

1. Introduction

Polymethyl methacrylate (PMMA) has been widely used as a cement for fixing metallic and polymeric implants to the surrounding bones and for filling bone defects. However, this material does not bond to living bone, and hence its fixation is liable to degrade over a long period [1]. In addition, PMMA exhibits considerably low mechanical strength than bone cortex [2]. Recently, a number of studies have been made to develop inorganic filler-organic resin composite cements which can set in a few minutes and exhibit fairly high mechanical strength as well as high bioactivity. Raveh *et al.* [3] first reported that a composite cement of bisphenol-*a*-glycidyl methacrylate (Bis-GMA) resin with Bioglass® or tricalcium phosphate powder bonds directly to bone. Later, several investigations have been carried out for composite cements of $CaO–SiO_2–P_2O_5–CaF_2$ glass, $MgO–CaO–SiO_2–P_2O_5–CaF_2$ glass or glass–ceramic A-W combined with a liquid mixture of equal weights of Bis-GMA and triethylene glycol dimethacrylate (TEGDMA) [4–6]. These composite cements being superior in mechanical strength can directly bond to living bone by forming a biologically active bone-like apatite layer on their surfaces. It has also been reported that a composite cement consisting of sintered hydroxyapatite with a liquid mixture of Bis-GMA, TEGDMA and 2,2′-bis-(4-methacryloylethoxyphenyl)propane shows high mechanical strength and bioactivity [7].

In our previous study [8], strength behavior of Bis-GMA/TEGDMA-based composite cements containing bioactive $CaO–SiO_2–P_2O_5–CaF_2$ glass and glass–ceramic A-W powders was comparatively examined in a simulated body fluid (SBF). The fracture strength was examined for the composite cements having been soaked in SBF for a long time under unstressed conditions, and the stress-corrosion susceptibility of the cements in SBF environment was evaluated. From this study, it was concluded that glass–ceramic A-W, being chemically more durable than $CaO–SiO_2–P_2O_5–CaF_2$ glass, can be combined with Bis-GMA/ TEGDMA

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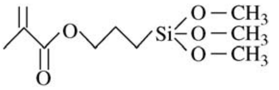
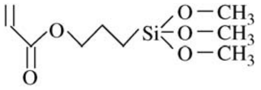
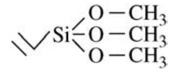
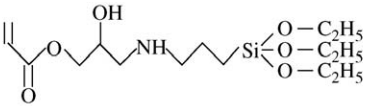
TABLE I Silane coupling agents used for study

Silane coupling agent	Structural formula	Product number*
[3-(methacryloxy)propyl]trimethoxysilane		M8550
[3-(acryloxy)propyl]trimethoxysilane		A0397
Vinyltrimethoxysilane		V4917
[*N*-(3-acryloxy-2-hydroxypropyl)-3-aminopropyl]triethoxysilane		A0380
[3-(2-aminoethyl)aminopropyl]trimethoxysilane		A0700

*Product code number put on the catalog issued by Chisso Corp./Azmax Co. Ltd.(Ref. 14). More systematic new code number is also assigned for each of the silane coupling agents; SIM6487.4 (M8550), SIA0200.0 (A0397), SIV9220.0 (V4917), SIA0180.0 (A0380), SIA0591.0 (A0700).

resin as a reliable filler for preparing bioactive composite cements.

In polymer composites reinforced with inorganic fillers, microcracks that may induce fracture are believed to occur during stressing at or near the filler-resin boundary. Coupling agents are generally applied to the fillers in order to improve strength properties of inorganic filler-resin composites [9–11]. It is thought that, in the case of silane coupling agents, a direct siloxane bridge is formed at the interphase, and this would result in the improvement of adhesive strength between filler and resin. Thus, the degree of interfacial bonding is one of the key factors which determine strength behavior of composite resin cements.

In the present study, time-dependent strength behavior was investigated for glass–ceramic A-W–Bis-GMA/TEGDMA resin cements with different degrees of interfacial bonding. The degree of filler-resin bonding was varied by treating the filler particles with various kinds of silane coupling agents. The fracture strength of each of the composite resin cements in SBF was measured as a function of stressing rate, and stress-corrosion susceptibility was examined. Effect of different kinds of silane coupling agents on time-dependent strength behavior of the cements was discussed.

2. Experimental

2.1. Sample preparation

Glass–ceramic A-W (Nippon Electric Glass Co., Otsu, Japan) [12, 13] was crushed into fine powders with an average particle size of 5 μm. This powder was treated with five kinds of silane coupling agents (Chisso Corp., Tokyo, Japan) [14] listed in Table I. That is, 25 g of glass–ceramic A-W powder, 1.0 ml of each of the silane coupling agents and 0.5 ml of acetic acid were added to 100 ml of ion exchanged and distilled water and stirred with a magnetic stirrer for 1 h. If the coupling agent did contain an amine group, addition of acetic acid was omitted, since the hydrolysis should be autocatalyzed. The temperature of the suspension was maintained at 55 °C. After decantation, the silanized powders were dried and cured at 120 °C. Dibenzoyl peroxide was then added at 1.0% by volume as a polymerization initiator. For reference, untreated A-W powder was also used as filler.

As monomers from which a copolymer matrix is formed, a liquid mixture of equal weights of Bis-GMA and TEGDMA (Shin-Nakamura Chemical Industry, Wakayama, Japan) were used. To this liquid mixture, *N*, *N*′,-dimethyl-*p*-toluidine was added at 0.2% by volume as a polymerization accelerator. Each of the powders was then mixed with the liquid monomer mixture in a volume ratio of 50 : 50. The mixed paste thus obtained was cast in Teflon® molds into rectangular bars $3 \times 4 \times 30\,mm^3$. Solidification of the mixed paste was completed within about 5 min. At 5 min after mixing, the solidified specimen was taken out of the mold and then soaked in a simulated body fluid [13] (SBF: Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO^{3-} 4.2, HPO_4^{2-} 1.0, SO_4^{2-} 0.5 mM) which has nearly equal ion concentrations to those of human blood plasma [15]. This solution was buffered at pH 7.25 by trishydroxymethylaminomethane ($(CH_2OH)_3CNH_2$) and 1 M-HCl at 36.5 °C. After soaking in SBF at 36.5 °C for 28 d under unstressed conditions, the specimens were subjected to strength testing in SBF with varying stressing rate, the details of which will be described in the following section.

Hereinafter, the product code number (Table I) will be used to designate each of the coupling agents for convenience.

2.2. Evaluation of time-dependent strength characteristics

2.2.1. Background

A decrease in fracture strength with time is observed for many metallic and non-metallic materials in a corrosive environment [16]. This phenomenon is commonly referred to as delayed failure [17–19]. It is believed that such time-dependent strength degradation results from slow growth of preexisting flaws in the material, generally due to stress-assisted chemical reaction (stress-corrosion).

It has been well established that, crack velocity during subcritical flaw growth can be empirically expressed as a power function of the stress intensity factor [17–19].

$$V = AK_{\mathrm{I}}^{n} \tag{1}$$

where V is the crack velocity, K_{I} is the stress-intensity factor and A and n are empirical constants depending on the material and the environment. The constant n is a measure of the stress corrosion susceptibility of a material.

When Equation 1 is used for crack velocity, the fracture strength σ_f of a material tested with a constant loading rate can be predicted as follows [17, 18];

$$\sigma_f^{n+1} = 2\left(\frac{n+1}{n-2}\right)\frac{\sigma_{\mathrm{Ic}}^{n-2}}{AY^2K_{\mathrm{Ic}}^{n-2}}\dot{\sigma} \tag{2}$$

where $\dot{\sigma}$ is the loading rate (rate of stress application), K_{Ic} the critical stress-intensity factor, σ_{Ic} the strength in the absence of slow flaw growth and Y is a dimensionless factor which depends on crack configuration and the loading geometry. It follows from Equation 2 that, for a given material, the term in brackets is constant and that a logarithmic plot of fracture strength σ_f vs. loading rate $\dot{\sigma}$ should give a straight line with a slope $1/(n+1)$. The method to determine the parameters n and A on the basis of Equation 2 is termed stressing-rate technique [17, 18].

We consider the case where the strength measurements are performed by use of a bending technique. Since maximum tensile stress σ in the surface of a bend specimen is directly proportional to the displacement δ of the loading point, the rate of stress application $\dot{\sigma}$ can be directly related to the displacement rate $\dot{\delta}$;

$$\dot{\sigma} = k\dot{\delta} \tag{3}$$

where k is a constant that depends on the elastic modulus of the specimen and the dimensions of the specimen and the test device. Let $\dot{\sigma}_0$ denote a base loading rate. Then the ratio of loading rates, $\dot{\sigma}$, $\dot{\sigma}_0$ at two displacement rates, $\dot{\delta}$, $\dot{\delta}_0$ is given by $(\dot{\sigma}/\dot{\sigma}_0) = (\dot{\delta}/\dot{\delta}_0)$ and hence we obtain from Equation 2:

$$\sigma_f^{n+1} = 2\left(\frac{n+1}{n-2}\right)\frac{\dot{\sigma}_0\sigma_{\mathrm{Ic}}^{n-2}}{AY^2K_{\mathrm{Ic}}^{n-2}}\left(\frac{\dot{\delta}}{\dot{\delta}_0}\right) \tag{4}$$

Equation 4 enables the parameter n to be evaluated by a simple logarithmic plot of bending strength σ_f vs. ratio of displacement rates (crosshead speed), $(\dot{\delta}/\dot{\delta}_0)$.

2.2.2. Measurement technique

Bending strength measurements were performed in SBF with an Instron-type testing machine (Model DSS500, Shimadzu Corp., Kyoto, Japan) using a three-point bending over a 20 mm span at five different crosshead speeds from 0.005 to 2.0 mm min^{-1}. During testing, the temperature of SBF was maintained at 36.5 °C. Ten specimens were fractured for obtaining the average strength value in each loading rate. After testing, the fracture surfaces were observed with a scanning electron microscope (Hitachi S-2500CX, Hitachi Ltd., Tokyo, Japan).

2.3. Water-resistance test of A-W powder–silane coupling agent bond

The glass–ceramic A-W powder was treated with various kinds of silane coupling agents and then soaked in 50 ml of SBF at 50 °C. The change in silicon concentration of SBF due to immersion of each of the treated A-W powders was measured as a function of soaking time by inductively-coupled plasma (ICP) atomic emission spectrometer (Model SPS1500, Seiko Instruments, Inc., Tokyo, Japan).

2.4. Water-resistance test of resin–silane coupling agent bond

An amount of 1.5 g of Bis-GMA/TEGDMA monomers was mixed with 0.5 mmol of each of the silane coupling agents. Dibenzoyl peroxide was added at 1.0% by volume to the monomers. The mixtures were then cast into $36 \times 36 \times 14\,\mathrm{mm}^3$ of polystyrene case. At 5 min after dibenzoyl peroxide was added, the case containing polymerized resin was soaked in 150 ml of SBF at 50 °C. The change in silicon concentration of SBF was measured for different combinations of resin and silane coupling agent as a function of soaking time by ICP atomic emission spectrometer.

3. Results

Fig. 1 shows the results of strength testing performed in SBF at 36.5 °C. For all composite cements containing glass–ceramic A-W powder untreated or treated with various kinds of silane coupling agents, bending strength is plotted as a function of ratio of crosshead speed, $\dot{\delta}/\dot{\delta}_0$. The middle of crosshead speed, 0.1 mm min^{-1} was taken as $\dot{\delta}_0$. The slope of this linear plot was determined for each of the materials by the least square method. The values for n obtained from the slope are given in Fig. 1. It can be seen that all the composite cements exhibit almost equal n values. However, from the viewpoint of the strength values, the composite cements may be divided into two groups: one is the cements containing A-W powder treated with M8550, A0397 or V4917, and the other is the cements containing A-W powder untreated, treated with A0380 or A0700. The former group exhibits higher strengths than the latter. By selecting two extreme

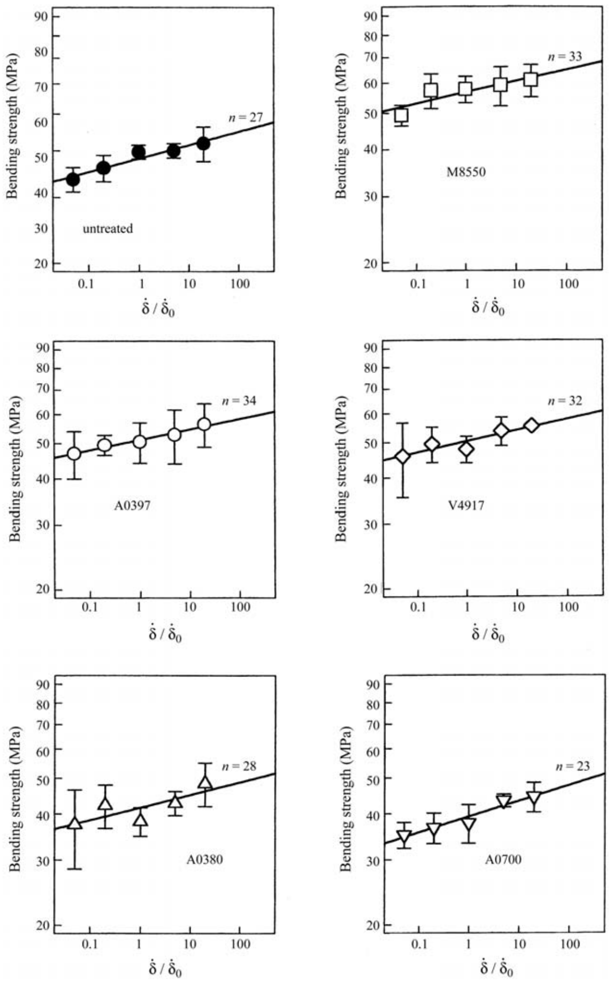


Figure 1 Bending strength measured in SBF at 36.5 °C as a function of relative crosshead speed for composite cement containing A-W powder. The silane coupling agent used is indicated in each of the drawings by its product code number (see Table I).

crosshead speeds, the representative stress–strain curves are shown in Fig. 2 for the cements containing untreated, M8550-treated and A0380-treated filler particles. It should be noted that the cements containing untreated and A0380-treated filler fail at lower strains than that containing M8550-treated filler if tests are conducted at the same crosshead speed. Fig. 3 shows the fracture surfaces of the composite cements subjected to strength testing in SBF at 36.5 °C. For each of the cements, fracture surfaces of the specimens broken at a high crosshead speed $(2.0\,\mathrm{mm\,min^{-1}})$ and at a low crosshead speed $(0.005\,\mathrm{mm\,min^{-1}})$ are shown. Voids were observed in the filler particle–resin interface in the composite cements containing untreated, A0380-treated and A0700-treated filler. However, as for the composite cements containing M8550-, A0397- and V4917-treated filler, voids were not formed around filler particles even if they were fractured at low stressing rate.

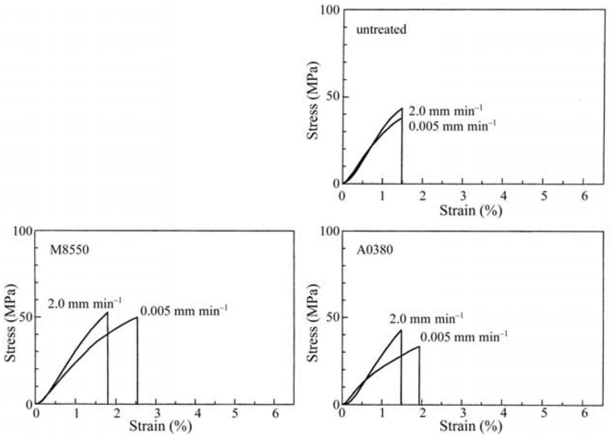


Figure 2 Stress–strain curves obtained from three-point bending tests in SBF at 36.5 °C for composite cements containing A-W powder. Three cases are shown: resin filled with untreated A-W powder, resin filled with A-W powder pretreated with the coupling agent M8550 and resin filled with A-W powder pretreated with the agent A0380. For each material, two curves representatively obtained under low and high crosshead speeds, 0.005 and $2.0\,\mathrm{mm\,min^{-1}}$, respectively, are shown.

Fig. 4 shows the change in concentration of the silicon of SBF with the soaking of glass–ceramic A-W powder treated with various silane coupling agents as a function of soaking time. All the powders are found to release almost equal silicon into SBF.

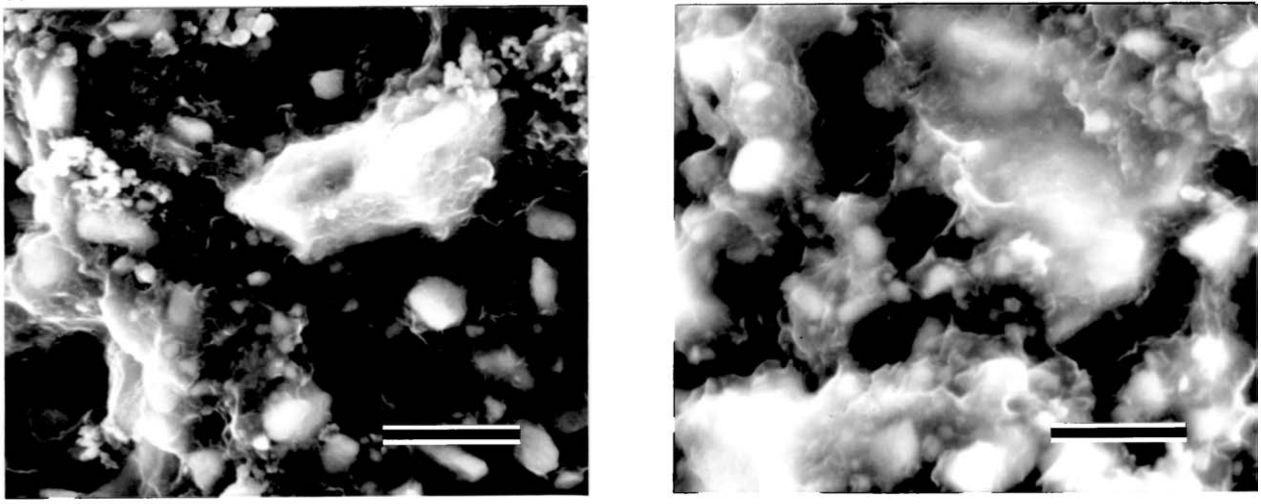
Fig. 5 shows the change in concentration of the silicon of SBF with the soaking of resin mixed with various silane coupling agents as a function of soaking time. Resins mixed with A0380 and A0700 release much more silicon into SBF at the initial stage of soaking than those treated with M8550, A0397 and V4917.

4. Discussion

All coupling agents used in this study have the characteristic of containing an organo-functional group and methoxy or ethoxy groups. It is expected that the alkoxy groups react with OH groups in the glass–ceramic surface to form a direct siloxane bridge and the organic group of the coupling agent molecule takes part in the polymerization of the resin phase and thereby provide a direct covalent link between coupling agent and polymerized resin.

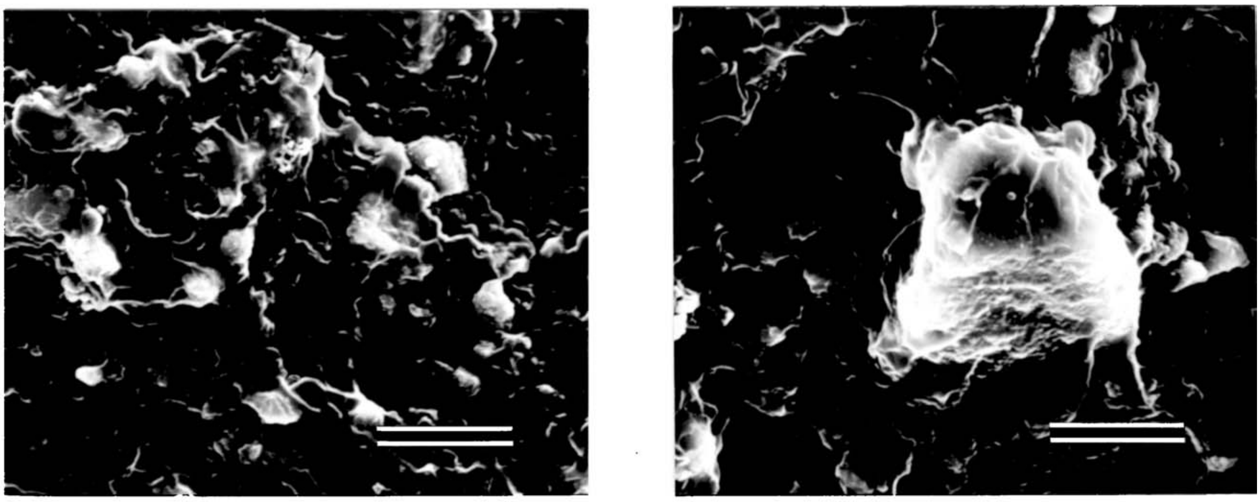
Fig. 1 shows that the fracture strength depends upon the kind of coupling agent used, although the stress-corrosion susceptibility constant n is similar for all the composite resin cements whether the A-W fillers were treated or untreated with the coupling agents. Fig. 1 suggests that the silane coupling agents M8550, A0397 and V4917 contribute to the improvement in fracture strength, whereas the use of coupling agents A0380 and A0700 is not of benefit. In fact, taking into account the amount of scatter in measured values, we can consider that the composite cements containing A-W filler treated with either A0380 or A0700 have almost the same fracture strength as the cement containing untreated A-W filler. Such dependence of fracture strength on coupling agent may be well interpreted in terms of the resin A-W filler adhesion, the degree of which is strongly affected by the coupling agent–resin bond. Fig. 4 indicates that some amounts of silane coupling agent deposited on the surface of glass–ceramic A-W filler are removed from the surface and then they dissolve into SBF. It is found in Fig. 4 that the amount and rate of dissolution of the silicon ion from the surface of A-W particle are similar for all the coupling agents. This means that the degree of coupling agent–filler adhesion is similar for all the coupling agents used, when they are applied to the glass–ceramic A-W. On the other hand, Fig. 5 clearly indicates that, when the coupling agent is mixed with Bis-GMA/TEGDMA resin and then soaked in SBF, the amount of

(a) M8550-treated A-W filler



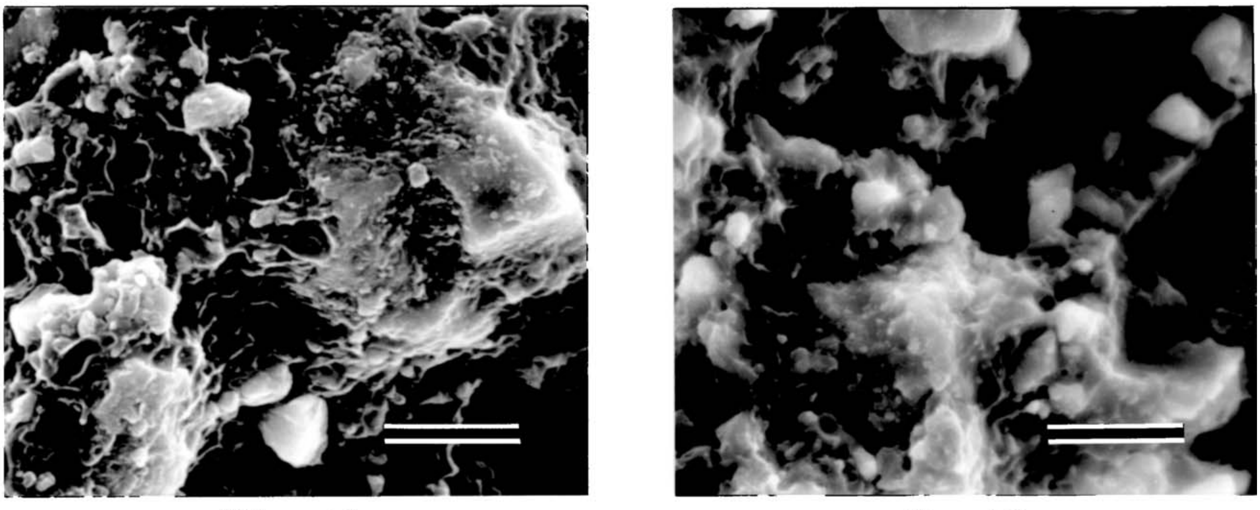
0.005 mm min^{-1} 2.0 mm min^{-1}

(b) A0397-treated A-W filler



0.005 mm min^{-1} 2.0 mm min^{-1}

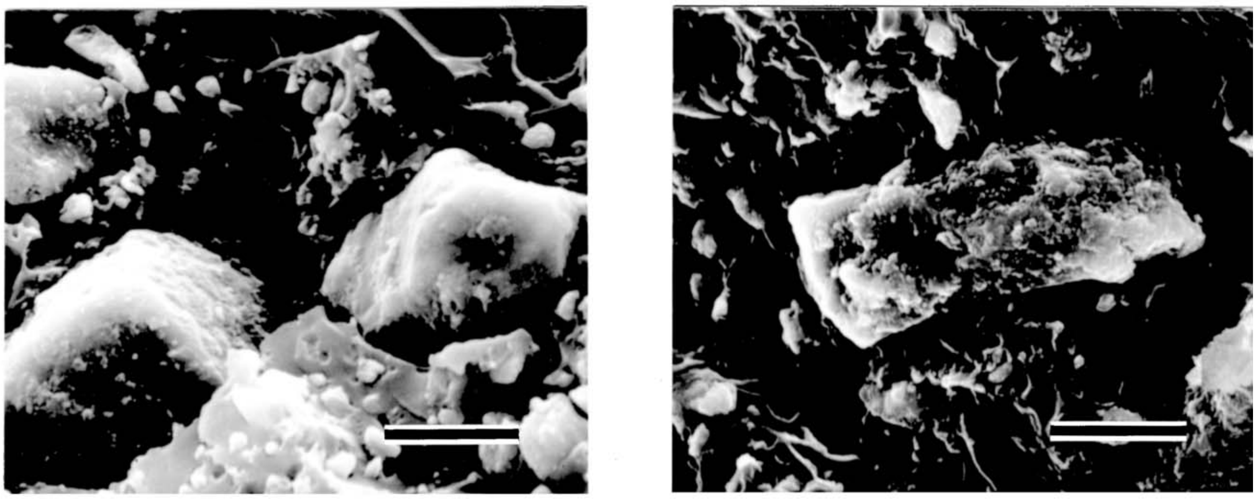
(c) V4917-treated A-W filler



0.005 mm min^{-1} 2.0 mm min^{-1}

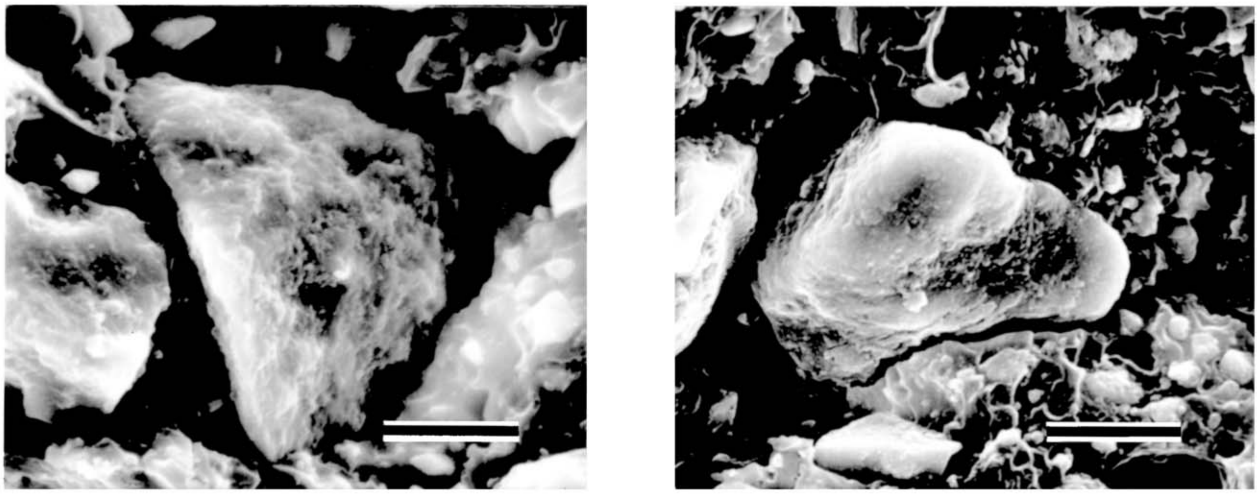
Figure 3 SEM photographs of fracture surfaces of composite cements containing A-W powder untreated or treated with various kinds of silane coupling agents. The fracture surfaces obtained by the bending tests in SBF at low and high crosshead speeds, 0.005 and 2.0 mm min^{-1}, respectively, are shown. Scale bar = 5 μm.

(d) A0380-treated A-W filler



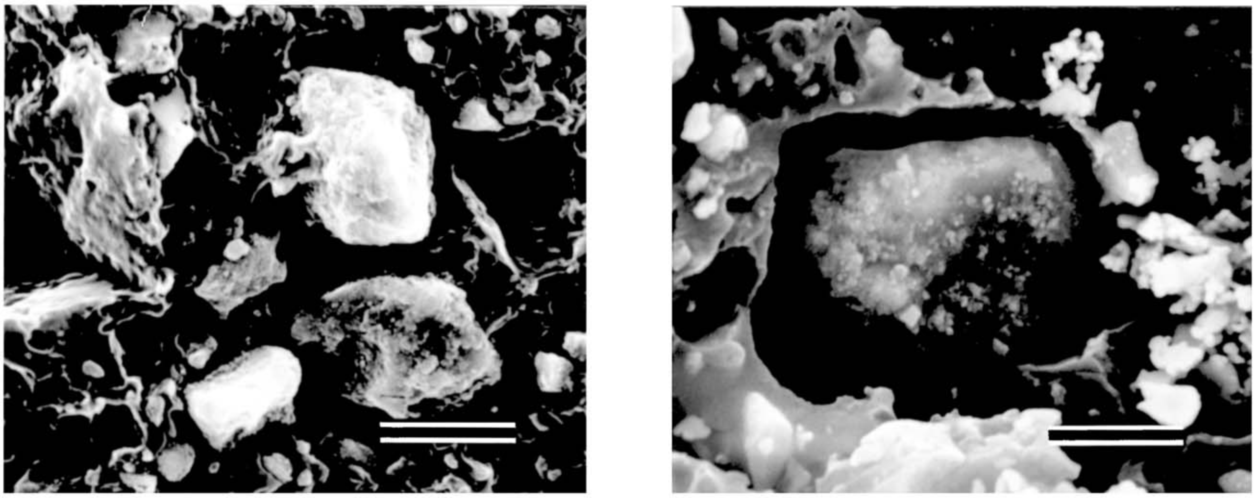
0.005 mm min^{-1} 2.0 mm min^{-1}

(e) A0700-treated A-W filler



0.005 mm min^{-1} 2.0 mm min^{-1}

(f) Untreated A-W filler



0.005 mm min^{-1} 2.0 mm min^{-1}

Figure 3 (Continued)

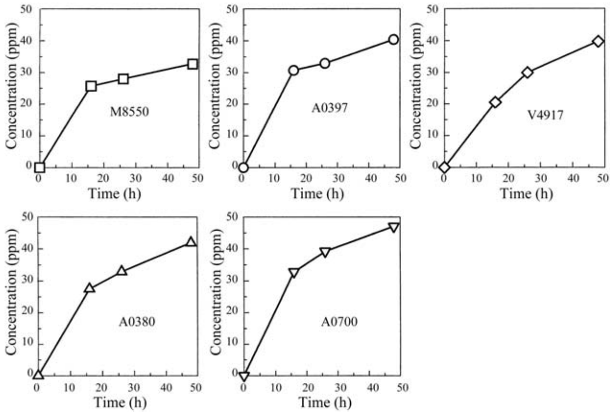


Figure 4 Changes in Si concentration of SBF due to immersion of A-W powder treated with various kinds of silane coupling agents. The coupling agent used is indicated in each of the drawings by its product code number.

dissolved agent from the resin–coupling agent mixture is larger for the mixtures, resin–A0380 and resin–A0700 than for the mixtures, resin–M8550, resin–A0397 and resin–V4917. That is, the coupling agent–resin bond is weaker for the former than latter mixtures. This may suggest that the organic end groups in the silanes are specific in relation to the resin with which they are used. It is thought that the organo-functional groups in M8550, A0397 and V4917 can be linked to Bis-GMA/TEGDMA resin by radical co-polymerization. However, A0380 and A0700 which contain hydrophilic amino groups are considered not to provide an effective link between coupling agent and polymerized resin. The presence of the hydrophilic amino groups is assumed to result in a low wettability of the A0380- or A0700-treated filler powder by the Bis-GMA/TEGDMA resin.

Fig. 2 also indicates that, when the composite cements were fractured at high stressing rate, failure strains of the composite cements containing untreated and A0380-treated filler are smaller than the cement containing M8550-treated filler, although the slope of stress–strain curve is similar for these cements. Voids around filler particles were observed in fracture surfaces of the cements containing untreated, A0380- or A0700-treated filler, when they were fractured at the high stressing rate, and no voids were observed in the cements containing M8550-, A0397- or V4917-treated filler, even when they were fractured at the low stressing rate (Fig. 3). These facts can be explained in terms of different degrees of filler–resin interfacial bonding. In the composite cements containing A0380- or A0700-treated filler, a weaker coupling agent–resin bond results in a weaker filler–resin bonding. In these composite cements, microcracks may form easily at the resin matrix near filler–resin interface at lower stress levels. During stressing of the Bis-GMA/TEGDMA cement containing A-W particles with such weak interfacial bonding, the resin surface normal to the applied tensile force will easily separate from the A-W surface to form a ''pseudovoid'' at low stress levels due to the stress concentration occurring at the resin–particle interface. The pseudovoids may act as stress-concentrators as well as crack precursors, and hence they cause the strength degradation of the cements. This may lead to lower strengths and failure strains. In fact, the strengths observed in the composite cements containing A0380- or A0700-treated filler are similar to that observed for the cement containing untreated filler (Fig. 1).

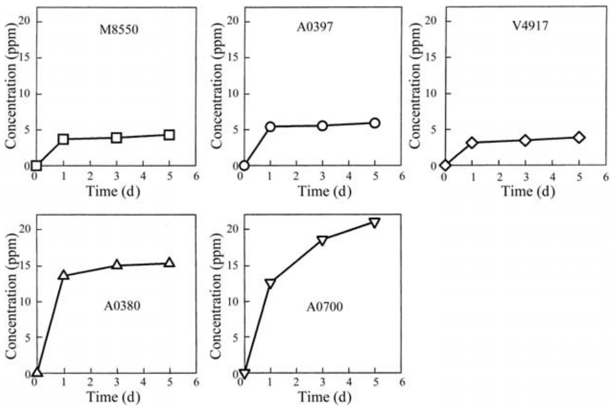


Figure 5 Changes in Si concentration of SBF due to immersion of resin mixed with various kinds of silane coupling agents. The coupling agent used is indicated in each of the drawings by its product code number.

Strength measurements performed in SBF with varying stressing-rates gave almost equal n values from 23 to 34, regardless of the kinds of silane coupling agent, and even for the cement consisting of the resin with untreated glass–ceramic A-W, the value of n similar to those described above was obtained. In other words, each of cement materials studied shows almost equal susceptibility to time-dependent strength degradation in SBF. Thus, it may be concluded that the microcrack formation and growth at the resin matrix near particles–resin interface determine overall strength behavior.

5. Summary

The time-dependent strength degradation behavior of Bis-GMA/TEGDMA resin cements combined with glass–ceramic A-W filler treated with various kinds of silane coupling agent was investigated by evaluating stress-corrosion susceptibility constant n by stressing-rate technique.

The cements containing filler powder treated with M8550, A0397 or V4917 showed higher bending strengths than those containing filler powder untreated and treated with A0380 or A0700. It is suggested that the use of M8550, A0397 and V4917 give higher degrees of interfacial bond than that of A0380 and A0700, although each of silane coupling agents exhibits nearly equal degree of adhesion to glass–ceramic A-W. These results indicate that the use of silane coupling agents containing hydrophilic amino groups are not effective for Bis-GMA/TEGDMA resin. For this resin, M8550, A0397 or V4917 can be used as reliable silane coupling agents because of its nature of co-polymerizing with the resin.

Acknowledgment

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