

# Influence of silanization and filler fraction on aged dental composites

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**SUMMARY** The effect of silanization and filler fraction on the mechanical properties of aged dental composites was investigated. Experimental composites (75/25 Bis-GMA/TEGDMA resin reinforced with 0, 12.6, 30.0, and 56.5 vol% 8 µm silanized/unsilanized BaSiO<sub>6</sub>) were fabricated into 4.7 mm diameter × 2.2 mm thick discs and 3.5 mm diameter × 7.3 mm thick discs for diametral tensile and compressive tests, respectively. The effect of immersion in 75% ethanol at 37 °C for 0–30 days on the diametral tensile strength (DTS) and compressive strength (CS) of the samples was evaluated and analysed by ANOVA and Tukey LSD test. The fracture interface between filler and resin matrix was then examined by scanning electron microscope. Results and subsequent statistical evidence from DTS (18.6 ± 7.6 MPa, silanized versus 11.7 ± 2.6 MPa, unsilanized) and CS (85.1 ± 29.7 MPa, silanized versus 56.0 ± 11.3 MPa, unsilanized) strongly implies

that silanization may greatly enhance the mechanical properties of the resin composites. Furthermore, it also shows that both DTS and CS increased proportionally as the filler fraction of the composites increased. However, in the unsilanized groups, DTS decreased (up to 40%) as the filler fraction increased, and CS showed no relevance to the filler fraction at all. As for the influence of aging, it was found that both DTS and CS showed a significant decrease after immersion in 75% ethanol, and silanization heavily correlated with the filler fraction of aged-resin composites. Microscopic examination of the fractured samples showed that failure primarily occurred within the resin matrix *per se* for silanized composites and adjacent to the filler particles for unsilanized composites. All the evidence points to the conclusion that mechanical properties of aged-resin composites can be greatly influenced by silanization and the filler fraction.

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## Introduction

Composites consist of two or more elemental materials with different properties which do not mutually dissolve. Researchers have adopted individual properties and merits of each material to create the new composites for various functional requirements. Dental composites nowadays play an increasingly important role in modern dentistry. Finding ways to improve their physical and mechanical properties fit into a more than complex oral environment has been the goal of dental research. Dental composites consist of matrix, filler, and coupling agent, and the properties are derived from the

respective properties of matrix and filler, and the connective status between matrix and filler.

In 1962, Bowen took advantages of the easily adaptable properties of methyl methacrylate, and the high intensity and low contraction properties of epoxy resin to synthesize bisphenol A and glycidyl dimethacrylate into 2,2-bis[4(2-hydroxy-3-methacryloxypropoxy)phenyl] propane (BisGMA), and later acquired a patent for it (Bowen, 1962). To this day, BisGMA is still the major choice for matrix of dental composites on the market.

Fillers, by modification of physical and chemical properties, can greatly improve the various properties

and broaden the applications of the dental composites. As early as 1951, Knock and Glenn had put inorganic filler into acrylic resin (Knock & Glenn, 1951). The main component of dental composite fillers is SiO<sub>2</sub>. The majority of SiO<sub>2</sub> particles have either irregular or round shapes, with a small percentage being fibre shapes. In the early days, E-glass fibre, soda lime glass, or synthesized calcium phosphate were used. By the 1970s, most products on the market consisted of 75–85 wt% quartz, but now are gradually replaced by glass-type fillers. The greatest merit of glass-type filler is that its properties are easily adjusted with the addition of modifiers. Nowadays, the most common glass-type fillers are silicate glass with barium and strontium, colloidal silica, and lithium aluminum silicate glass.

Dental composite contains at least two different phases, i.e. matrix and filler. Due to the polarity, glass filler surfaces can absorb a water layer by hydrogen bonds. Since resin matrix has no polarity and is hydrophobic, it has difficulty standing in solid compound status. When dental composites are under pressure, the stress of the composite is distributed from the matrix, through the interface between the matrix and the filler, then onto the filler itself. The interface, thus has definite effect on the behaviour of dental composites under stress and strain. An excellent interface not only increases the mechanical intensity of dental composites, but also prevents filler surface erosion. Presently, the most common coupling agent is silane, which provides covalent bonds between the filler and resin matrix.

Clinically, in the past, dental composites were used on anterior teeth only, however, their use on class I and class II cavities is becoming more and more popular. Nevertheless, long-term clinical studies have shown that the wear of restorative materials still presents the biggest problem. Several theories were set to explain the wear phenomenon. Microfracture theory (Bayne, Taylor & Heymann, 1992) proposes that, when suffering from occlusal stress, the harder filler will transfer impact to the softer resin matrix, causing microfractures. On the other hand, the protection theory proposes that food particles will easily wear off the inter-particle resin matrix. Therefore, matrices may not be protected by filler particles (Bayne *et al.*, 1992).

Soderholm (1981) proposed the hydrolysis theory, which suggests that silane coupling agent may degrade due to water dissolution, leading to loss of filler and

subsequent acceleration of wear. Wu *et al.* (1984) also observed obvious wear phenomenon on non-stress-bearing surfaces, as well as on occlusal surfaces. Therefore, the chemical degradation theory (Wu *et al.*, 1984) emphasizes that the chemical components of food and saliva may be absorbed by the resin matrix, causing resin softening and surface destruction. It is obvious that, in addition to occlusal stress and mechanical wear, the long-term high temperature, humidity, and complicated oral environments may cause aging of dental composites as well, a phenomenon which cannot be ignored. Hydrolytic degradation of filler particles could also be a potential problem regarding durability and recurrent caries, since it may cause debonding from the composite (Soderholm & Calvert, 1983). Such debonding can influence physical properties, such as strength and wear resistance (Craig & Powers, 1976; Soderholm, 1982). Degradation of these properties may not only increase the risk for percolation around unbonded composites, but can also be detrimental for the composite–enamel bond.

In 1976, the U.S. Food and Drug Administration (FDA) (Food and Drug Administration, 1976), in order to test the durability of food containers, chose organic solvents with solubility parameters from  $1.5$  to  $4.8 \times 10^4 \text{ J}^{1/2}/\text{m}^{3/2}$  for liquids to simulate foods. BisGMA has wide solubility parameters, from  $1.82$  to  $2.987 \times 10^4 \text{ J}^{1/2}/\text{m}^{3/2}$ . However, according to research by Wu & McKinney (1982) and McKinney & Wu (1985), the aging solution of 75 vol% alcohol (with a solubility parameter of approximately  $3.15 \times 10^4 \text{ J}^{1/2}/\text{m}^{3/2}$ ) has the greatest dissolving effect on dental composites. Several researchers' findings also indicate that soaking in 75 vol% alcohol would damage the resin surface and decrease the strength of the composites (Lee *et al.*, 1994; Lee, Greener & Mueller, 1995a). The soaking liquid also contains matrix-dissolving moieties (Pearson, 1979; Lee, Greener & Menis, 1995b; Lee *et al.*, 1998).

Due to the influence of oral environments on both percolation and bonding, the purpose of this investigation was to study how the filler fraction, as well as the quality of the filler–matrix bond, influences the mechanical strengths of experimental dental composites. Possible attributes of accelerated degradation by the aging solution (75% alcohol) in particle-reinforced dental composites were also evaluated.

**Table 1.** Effect of filler volume fraction, silanization, and immersion time on DTS (MPa)

Immersion time (days)	0%	12.6%		30.0%		56.5%	
		Silanized	Unsilanized	Silanized	Unsilanized	Silanized	Unsilanized
0	21.9 (0.6)	18.2 (0.7)	17.5 (0.8)	24.0 (0.8)	15.8 (0.5)	37.3 (5.5)	13.4 (0.3)
1	13.9 (2.3)	13.4 (0.6)	10.4 (2.2)	22.7 (0.9)	8.9 (0.5)	30.5 (4.7)	8.9 (1.0)
7	10.9 (0.6)	8.9 (0.8)	10.1 (1.0)	12.6 (0.5)	12.4 (0.4)	19.2 (3.6)	9.5 (0.4)
14	10.5 (1.8)	14.7 (1.8)	12.6 (0.6)	13.6 (2.0)	12.1 (0.7)	17.4 (2.3)	9.9 (0.5)
30	11.4 (0.5)	11.9 (2.3)	12.5 (0.6)	18.7 (1.9)	11.2 (0.8)	16.0 (1.1)	9.7 (0.7)

\* Standard deviations are given in parentheses.

## Materials and methods

The experimental resin was made from 75 wt% Bis-GMA (Oligomer)\* and 25 wt% triethylene glycol dimethacrylate (TEGDMA, used as diluent)<sup>†</sup>. A total of 0.30 wt% of camphorquinone (CQ)<sup>‡</sup> and 0.15 wt% of 2-(dimethylamino) ethyl methacrylate (DMAEMA)<sup>§</sup> were added to make the resin photocurable. Quantities of the initiators, CQ and DMAEMA in this study, follow the formula cited by Ferracane (1983) in his study of experimental dental resins.

Six different types of experimental composites were made by mixing 25, 50, or 75 wt% of untreated or silane-treated barium borosilicate glass beads (average 8 µm in diameter)<sup>¶</sup> with the experimental resin mentioned above. Silanization of these glass beads was done with 2% γ-methacryloxypropyl trimethoxysilane\*\* solution in isopropyl alcohol in a Buchi Rotavapor R114 rotary evaporator<sup>††</sup> at 89 °C for 1 h. Because the density of the experimental resin is 1.18 g/cm<sup>3</sup> and the density of the filler is 2.73 g/cm<sup>3</sup>, the filler volume fractions were calculated as 12.6, 30, and 56.5 vol%, respectively.

Before polymerization, the experimental resin (0 vol%) and composites (silanized or unsilanized) were loaded into polyethylene tubes with inner diameters of 3.5 and 4.7 mm, respectively. These materials were cured for a total of 10 min in a Lab Lite oven<sup>‡‡</sup>. After being cold-cured for 24 h, they were removed from the tubes. Discs were cut off and ground flat at

both surfaces to give disc specimens with dimensions of 4.7 mm diameter × 2.2 mm thickness and 3.5 mm diameter × 7.3 mm thickness for diametral tensile and compressive tests, respectively. Specimens were stored at 37 °C, in 75% ethanol for 1, 7, 14, and 30 days. Specimens of corresponding control groups were stored in the dark without immersion at 37 °C for 1 day. The mechanical tests, diametral tensile test and compressive test, were performed after each immersion interval at room temperature with a universal testing machine (Autograph AGS-1000D)<sup>§§</sup>. The crosshead was driven at a speed of 2.5 mm/min until failure occurred.

For each group of six specimens, the mean and standard deviation of the diametral tensile strength (DTS) and compressive strength (CS) were calculated. A three-way ANOVA, using factors of filler fraction, silanization, and immersion time, was utilized to analyse DTS and CS. The Tukey LSD test ( $P < 0.05$ ) was employed for *post hoc* comparison among group means. To detect the differences in morphology between unsilanized and silanized samples, fractured surfaces caused by tensile stress were first sputter-coated with a gold-palladium film and then examined by scanning electron microscope (SEM) (Hitachi S-2400)<sup>¶¶</sup>.

## Results

### *Diametral tensile and compressive strengths*

DTS and CS of aged composite specimens as a function of filler fraction, silanization, and immersion time are presented in Tables 1 and 2, respectively. All three factors show significant effect on both DTS and CS statistically. Aging showed significant effect either by 1-day immersion for all unsilanized samples or by

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§§ Shimadzu Co., Tokyo, Japan.

¶¶ Hitachi Co., Tokyo, Japan.

**Table 2.** Effect of filler volume fraction, silanization, and immersion time on CS (MPa)

Immersion time (days)	0%	12.6%		30.0%		56.5%	
		Silanized	Unsilanized	Silanized	Unsilanized	Silanized	Unsilanized
0	63.4 (0.8)	92.7 (2.4)	75.5 (2.5)	95.3 (4.7)	76.7 (3.0)	140.8 (4.1)	78.7 (1.6)
1	50.0 (3.3)	83.2 (0.1)	42.8 (1.6)	83.9 (0.4)	44.5 (1.1)	138.7 (2.1)	48.5 (0.6)
7	37.3 (2.7)	49.4 (4.6)	52.6 (1.9)	59.7 (4.6)	51.8 (1.5)	108.2 (1.7)	48.6 (0.9)
14	40.0 (3.3)	50.9 (7.1)	52.2 (0.6)	61.4 (2.8)	56.8 (1.1)	106.3 (7.8)	50.8 (0.6)
30	41.6 (5.4)	52.3 (7.6)	52.3 (2.0)	56.2 (2.9)	56.9 (2.4)	97.0 (5.2)	49.4 (0.8)

\* Standard deviations are given in parentheses.

1-week immersion for all silanized samples. The 56.5 vol% silanized group showed the greatest DTS value ( $37.3 \pm 5.5$  MPa) and CS value ( $140.8 \pm 4.1$  MPa) of all control (non-immersion) specimens evaluated. However, the group also displayed the largest percentage DTS reduction from the control group of the 30-day immersion value (55%–60% deviation) compared to the other groups (25%–50%); whereas the overall CS was significantly different from the control group after 7-day immersion (25%–40%,  $P < 0.01$ ).

As a function of filler fraction, the DTS of 56.5 vol% ( $17.2 \pm 9.6$  MPa) and 30.0 vol% ( $19.9 \pm 4.3$  MPa) groups was higher ( $P < 0.01$ ) than that of the 0 vol% (control) ( $13.6 \pm 4.3$  MPa) or 12.6 vol% ( $13.0 \pm 3.2$  MPa) groups. Surprisingly, however, the overall DTS of the unsilanized groups was significantly less (20%–40%,  $P < 0.01$ ) as a function of filler fraction. It also showed that the DTS of the silanized group ( $18.6 \pm 7.6$  MPa) was statistically higher ( $P < 0.05$ ) than that of the unsilanized group ( $11.7 \pm 2.6$  MPa).

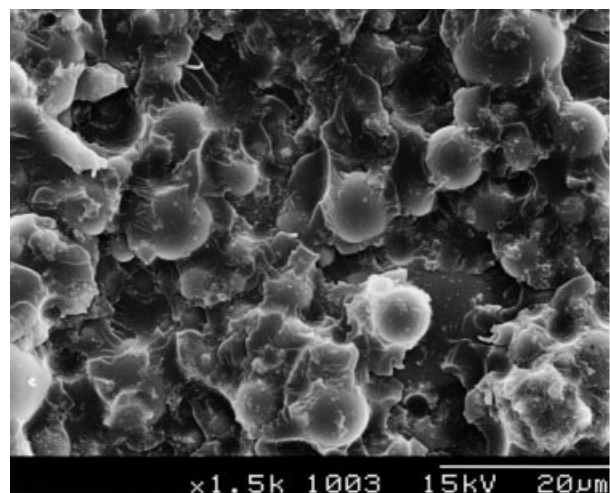
As a function of filler fraction, the CS of the 56.5 vol% group ( $86.7 \pm 35.3$  MPa) was statistically higher ( $P < 0.01$ ) than that of the 30.0 vol% ( $64.3 \pm 15.4$  MPa) and the 12.6 vol% ( $60.4 \pm 16.6$  MPa) group, which in turn, was higher than that of the 0 vol% (control) ( $46.4 \pm 10.1$  MPa) group. However, results for unsilanized groups showed no significant differences. Furthermore, it showed that the CS ( $85.1 \pm 29.7$  MPa) of the silanized group was significantly higher than that of the unsilanized group ( $56.0 \pm 11.3$  MPa).

#### Scanning electron microscopy examination

In the control (non-immersion) group, the fractured surface of the silanized specimens showed that the

resin matrix was still adherent to the filler and there was no filler exposed, nor was there any detachment of filler particles (Fig. 1). Under higher magnifications ( $\times 4000$ – $5000$ ), it is noted that appreciable amount of resin matrix has definite adhesion to the silanized filler (Figs 2 and 3), and fractures penetrated either the silane–resin interface or the resin matrix *per se* (Fig. 4). However, an obvious gap lay between the unsilanized filler and the resin matrix, and the fracture line extended through the resin–filler interface, resulting in a large exposure of filler particles (Figs 5 and 6).

Although fractures were observed on the surface of the specimens after 30 days immersion, it was also found that the silanized filler was still intact (Fig. 7); however, for the unsilanized group, fractured traces can be observed between the filler and resin matrix, probably due to the lack of protection between the coupling agent and unsilanized filler surface (Fig. 8).



**Fig. 1.** Representative fractured surface of the silanized specimen in the control (non-immersion) group.

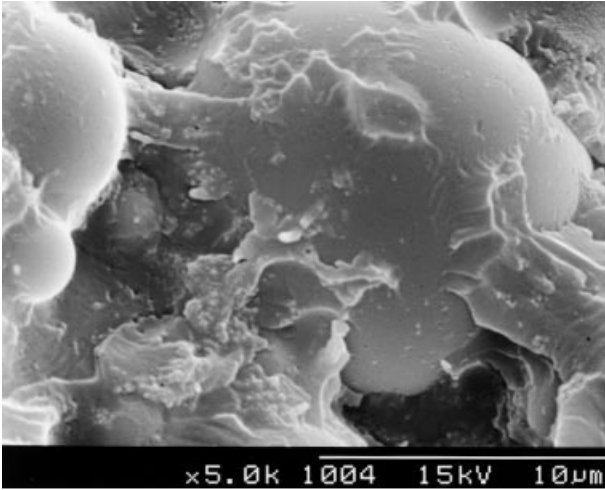


Fig. 2. Definite adhesion between resin matrix and silanized filler under higher magnification ( $\times 5000$ ).

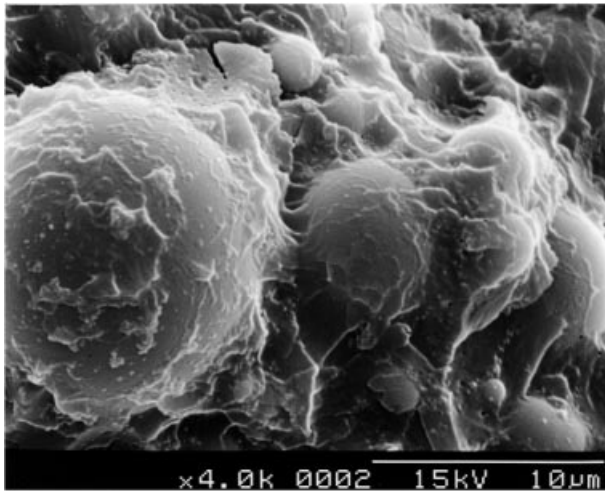


Fig. 3. Appreciable amount of resin matrix was adhesively left on the silanized fillers.

**Discussion**

For some time now, conventional mechanical tests have been used to evaluate the effects of filler silanization or filler volume fraction on mechanical properties of the commercial dental composites. However, the composites on the market differ greatly in their composition of polymer matrix, filler type, filler volume percentage, particle size and shape, particle distribution, and the inclusion of prepolymerized fillers. This wide variety of products makes analysis difficult if not impossible. Therefore, this study adopted the same matrix and filler to fabricate experimental composites, and

used silanized and unsilanized treatments on the fillers and different volume percentage values to conduct a more thoughtful examination of the properties of dental composites.

In the diametral tensile test, the tensile stress was developed along the diameter on the cross section of the specimen. The tensile strength can then be interpreted as being derived from the cohesive force of resin and the bonding between resin and filler. When the amount of filler in composites increases, the quantity of resin in the cross section shows a relative decrease. In this study, a decrease in DTS in the unsilanized composites can be attributed to an increase in the

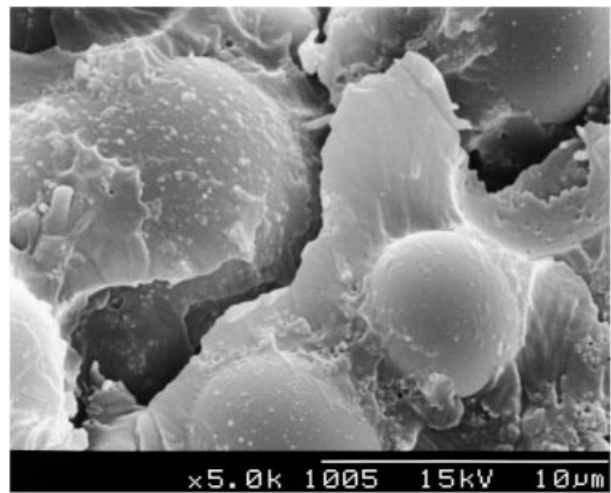


Fig. 4. Representative crack within the silanized specimen.

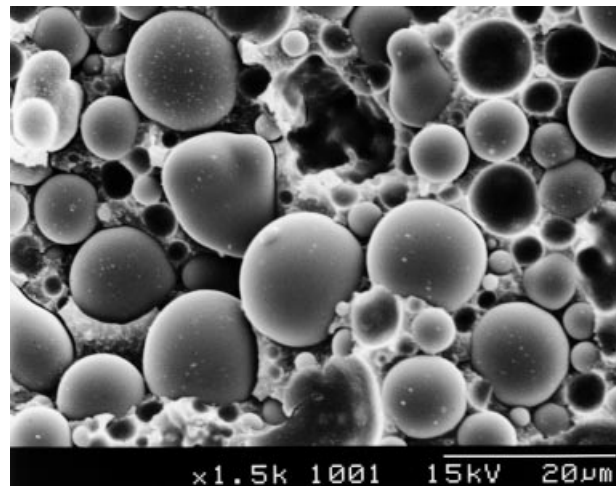
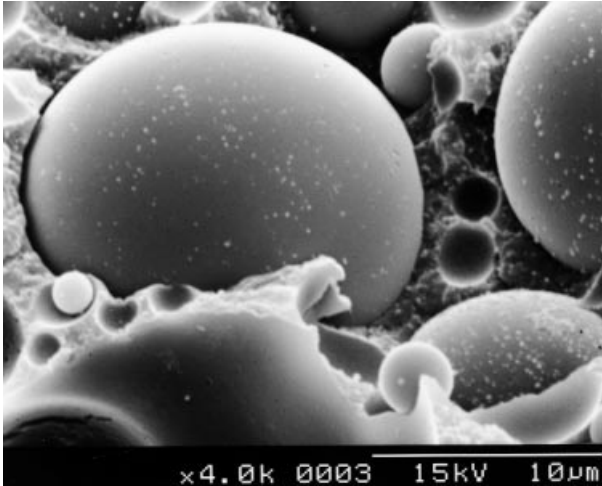
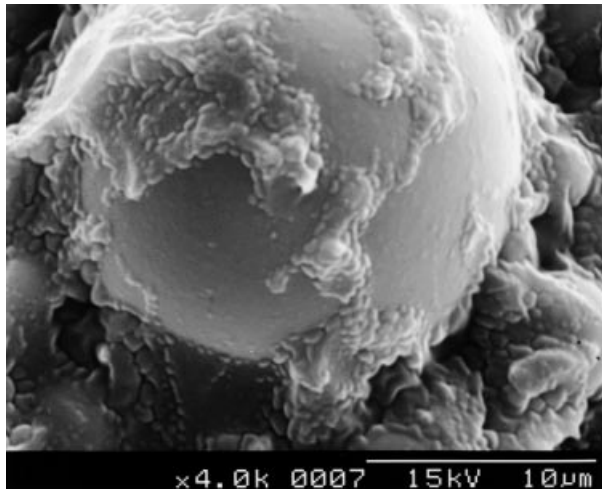


Fig. 5. Representative fractured surface of the unsilanized specimen in the control (non-immersion) group.



**Fig. 6.** No resin matrix was left on the unsilanized fillers under higher magnification ( $\times 4000$ ).

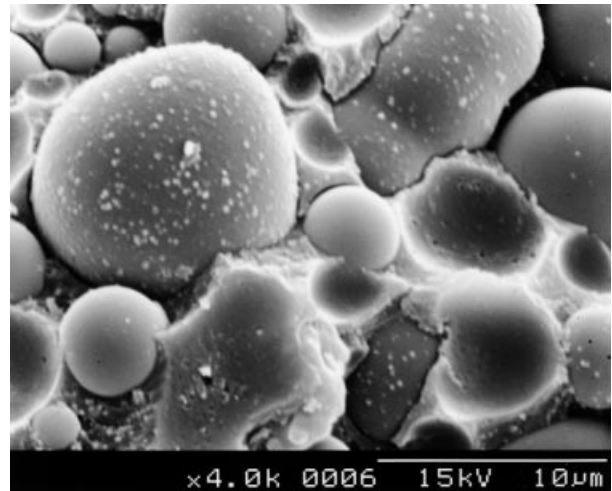


**Fig. 7.** Silanized filler is still intact after 30-day immersion in the 75% ethanol.

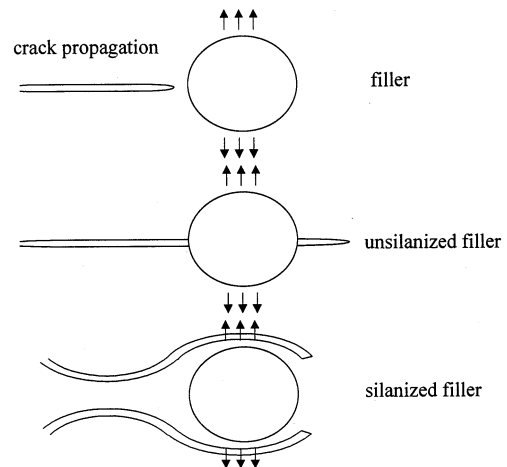
loading percentage of filler volume ( $r = -0.89$ ,  $P < 0.01$ ). However, in the silanized composites, a positive correlation ( $r = 0.83$ ,  $P < 0.01$ ) between DTS and filler fraction was found. The inference based on these results is that the effect of the connectivity of the resin–filler interface is more important than the resin cohesive force along the diameter on the cross section under diametral tensile stress. That is, a good connectivity may halt displacement or crack propagation in the matrix surrounding the filler. When the fractured surface of the unsilanized composite was observed under SEM (Figs 5 and 6), it is found that half the filler particles are exposed. This may imply that the stress

distribution mostly occurs around the equator of the filler particle, and that with silanization, the filler is more able to impede such a crack process (Fig. 9).

The compressive test, however, yielded different results. The increase of filler volume percentage did not reduce the CS of the unsilanized composite at all, even though its strength is still less than that of the silanized group (Table 2). By observing the fractured surface of the compressive specimens, it is found that fractures mainly passed through the diagonal inclined plane of the specimen (Fig. 10). Soderholm (1982) had proposed the internal friction theory to explain a similar



**Fig. 8.** Fractured traces were noted between filler and resin matrix after 30-day immersion in the 75% ethanol.



**Fig. 9.** Diagram for the crack propagation passing around the equator of the unsilanized filler compared with the crack process for the silanized specimen.

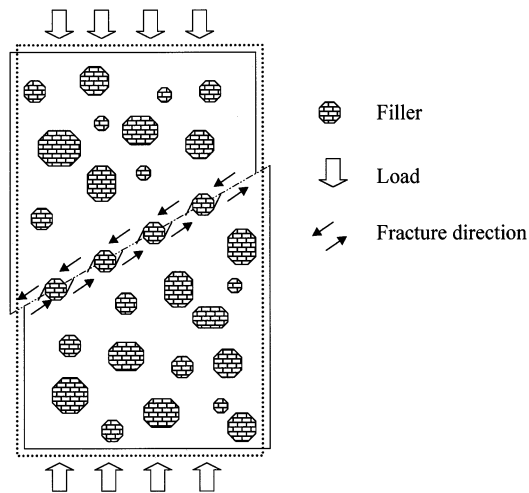


Fig. 10. Diagram for the fracture lines passing through the diagonal inclined plane of the compressive specimen.

phenomenon. He proposed that the increase of fillers may play two important roles in the diagonal inclined plane: (1) it increases the friction between resin and fillers to continue strengthening the inhibiting effect on the movement of resin matrix under stress; and (2) at the same time, this increase of fillers also decreases the cohesive force of the resin *per se*. In the compressive test, factors 1 and 2 mentioned above inherited from the unsilanized fillers might compensate for each other such that compressive strength does not decrease with an increase in the amount of filler.

Due to the addition of filler, it may, for the most time, form obstacles to matrix transformation. Thus, no matter whether the filler is silanized or unsilanized, the tensile and compressive moduli of the composite sample were noted to have increased as a function of filler volume fraction with no exception.

Based on the above conventional mechanical parameters, the diametral tensile test seems to be the more reasonable method for evaluating the connective status of the resin–filler interface. However, by comparing the experimental resin (0 vol% control) with the 56.5 vol% silanized and unsilanized experimental composites after 30-day aging, it is found that DTS and/or tensile modulus of all the three materials have the same inclination. Therefore, when relying

on conventional mechanical tests alone, it is indeed difficult to distinguish whether respective effects on composite degradation was from the resin *per se* or the resin–filler interface.

## Acknowledgments

This investigation was supported by a grant (NSC 84-2331-B-038-036) from the National Science Council, Taipei, Taiwan, R.O.C.

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