Hardness of model dental composites – the effect of filler volume fraction and silanation

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The relationship between structure and mechanical properties for dental composites has often proved difficult to determine due to the use of commercially available materials having a number of differences in composition i.e. different type of resin, different type of filler, etc. This makes a scientific study of any one variable such as filler content difficult if not impossible. In the current study it was the aim to test the hypothesis that hardness measurements of dental composites could be used to monitor the status of the resin–filler interface and to determine the efficacy of any particle silanation process. Ten model composites formulated from a single batch of resin and containing a common type of glass filler were formulated to contain varying amounts of filler. Some materials contained silanated filler, others contained unsilanated filler. Specimens were prepared and stored in water and hardness (Vickers') was determined at 24 h using loads of 50, 100, 200 and 300 g.

Composites containing silanated fillers were significantly harder than materials containing unsilanated fillers. For unsilanated products hardness was independent of applied load and in this respect they behaved like homogeneous materials. For composites containing silanated fillers there was a marked increase in measured hardness as applied load was increased. This suggests that the hardness–load profile could be used to monitor the status of the resin–filler interface.

1. Introduction

Resin matrix composites have been used in dentistry for over 30 years and during that time measurement of hardness has been used routinely as a means of quality control and of predicting durability [1–2]. Other work has revealed that the zones of deformation produced in composites below Vickers' diamond indentations can be diagnostic of the wear behavior of these materials [3].

In much of this work, the measurement of hardness has not been used to directly elucidate any important material characteristic but more as a means of explaining a clinical observation. Furthermore, measurements have often been made on commercially available materials for which differences in the nature of the filler and the type of resin used make it difficult or impossible to draw any meaningful conclusions on the relationship between hardness and composition [4]. Hence, although hardness testing has proved useful, it is possible that some important materials characteristics could emerge by taking a closer and more analytical look at hardness measurements of a series of well characterized materials.

The properties of dental composites are related to the volume fraction of filler incorporated within the resin and with the efficacy of the silanation procedure used to link the filler and matrix phases [1, 5–7]. Since it would be expected that hardness would be related critically to both of the above factors it was considered that hardness measurements would be an obvious means of investigating resin–filler coupling.

Three hypotheses were tested: (a) that Vickers hardness is expected to increase monatonically as filler volume fraction increases; (b) that the Vickers' hardness of composites containing silanated fillers will be greater than those of equivalent products without silanation; (c) that Vickers' hardness measurements will be capable of detecting changes produced near the surface of a composite as a result of the breakdown of the silane coupling agent.

In order to test these hypotheses a series of model composites of varying filler volume fraction, (silanated or unsilanated) were used.

2. Materials and methods

2.1. Test materials

Ten model resin–matrix dental composites were used in the evaluation (Table I). They were manufactured by Shofu Inc., Kyoto, Japan. The resin matrix comprised a blend of urethane dimethacrylate (70%) and ethyleneglycol dimethacrylate (30%) along with small quantities of suitable activators/initiators. The filler consisted of a blend of a glass having a mean particle size of 3.1 μm and silica having a mean particle size of 0.04 μm. In some

TABLE I Composition of model composites

Material	Filler fraction (vol%)	Filler silanation
1	23.7	Yes
2	33.0	Yes
3	43.0	Yes
4	52.2	Yes
5	57.0	Yes
6	61.7	Yes
7	66.4	Yes
8	51.0	No
9	41.3	No
10	29.0	No

materials the glass had been silanated whilst in others it had not. The filler fraction varied from 23.7–66.4 vol%.

2.2. Test specimens

Disc specimens (10 mm diameter and 1.33 mm thick) of each material were prepared using metal molds backed with Melinex matrix (Dentsply, Weybridge, UK) and a sheet of polymethylmethacrylate (Perspex, ICI, UK). The mold was slightly over-filled and a second Melinex strip placed over the surface. Hand pressure was used to press down the strip using a Perspex sheet, expressing the excess material. After removing the top Perspex sheet, the materials were cured using a 60 s exposure to a curing light source (Visilux II, 3M Co., St Paul, MN). The whole curing procedure was then repeated on the second surface of the disc. The ''first-cured'' surface was used in all test procedures. This surface was ground and polished using 1200 grit carborundum paper followed by 0.5 μm alumina on a rotary pregrinder to produce a specimen in which the resin rich surface layer had been removed but which was still sufficiently glossy to enable measurements of hardness indentations to be made. The specimens were stored at 37 °C in distilled water prior to testing.

At the time chosen for measuring hardness (24 h) the specimen was removed from the water bath and allowed to equilibrate at room temperature (23 ± 1 °C) for 5 min. Hardness was measured using a Miniload Hardness Tester (Leitz, Germany) utilizing a square based pyramidal Vickers' diamond indenter. A load of 50, 100, 200 or 300 g was applied for 20 s and measurements of the indentations were made 2 min after removing the load.

The volume fraction of filler in each material was given by the manufacturer. The weight fraction was determined gravimetrically by ashing samples of test material at 580 °C.

3. Results

Fig. 1 shows a plot of weight fraction, determined experimentally by ashing, against the volume fraction calculated from the known composition of the materials. This confirms that the materials used had been accurately formulated and that no separating out of components had occurred.

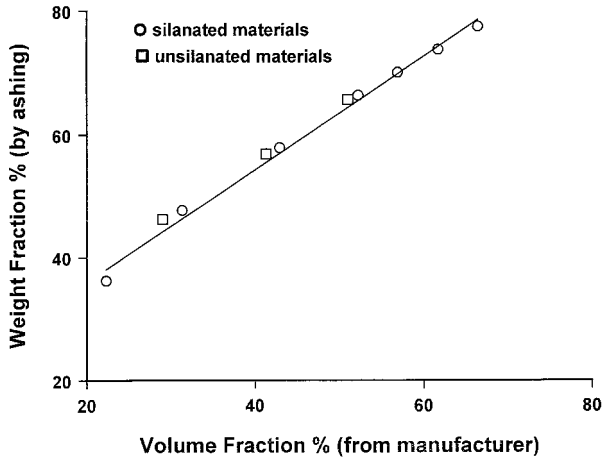

Figure 1 Weight fraction, determined by ashing plotted against volume fraction (manufacturers' information).

Figs 2–5 show hardness plotted as a function of filler volume fraction for composites having both silanated and unsilanated fillers as the test load is increased from 50 g through 100 g and 200 g to 300 g. In all cases the composites with silanated filler are significantly harder than those with unsilanated filler over a similar filler content range ($P < 0.05$ confidence interval analysis (CIA) [8]). The difference between the two increases as the test load increases.

Figs 6 and 7 show the hardness for the silanated and unsilanated composites as a function of filler volume fraction and test load in a manner which enables the effect of test load to be clearly seen. For silanated materials there is a tendency for hardness to increase with increasing test load ($P < 0.05$ CIA), whereas for unsilanated materials hardness is independent of test load ($P > 0.05$).

For both silanated and unsilanated materials hardness increases with increasing filler volume fraction though this is more noticeable with silanated materials than with unsilanated materials.

4. Discussion

Measurement of hardness requires attention to detail in both specimen preparation and methodology of testing. The pyramidal diamond methods (e.g. Vickers) have the

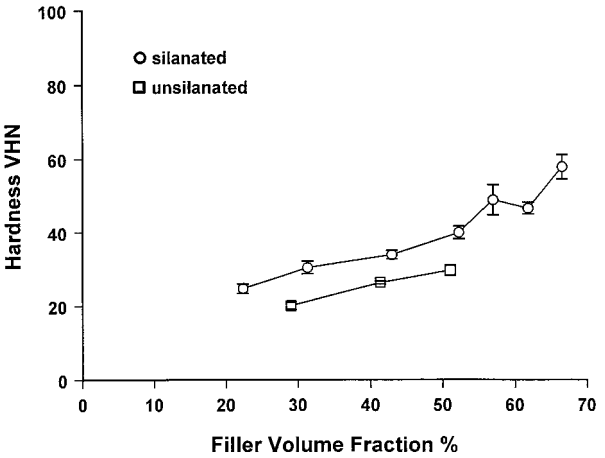

Figure 2 Hardness (determined using a 50 g load) plotted against filler volume fraction. Error bars indicate standard deviations.

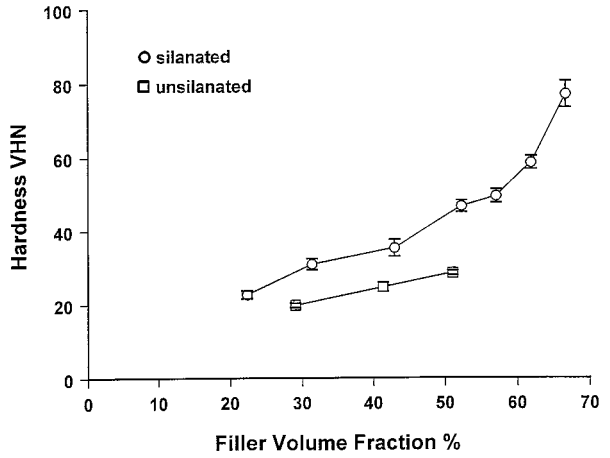

Figure 3 Hardness (determined using a 100 g load) plotted against filler volume fraction. Error bars indicate standard deviations.

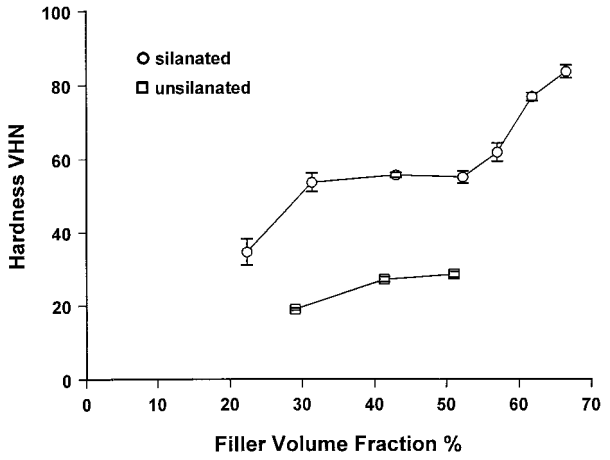

Figure 5 Hardness (determined using a 300 g load) plotted against filler volume fraction. Error bars indicate standard deviations.

advantage that for homogeneous materials the hardness is theoretically independent of the size of the indentation produced [9] although this argument can break down when the test material has a surface coating or when elastic recovery occurs slowly after load [9–10]. In practice, hardness measurements tend to be greater when smaller indentations are used. The most obvious method used for producing smaller indentations is to work at lower loads. In the current work increasing the test load (and therefore the size of indentation) has no effect for unsilanated composites and carries a marked increase in measured hardness for silanated composites. These results suggest that with regard to resistance to surface penetration the unsilanated materials behave like homogeneous materials. For the silanated products penetration causes closer packing of filler beneath the indenter and flow of filler away from the loading area is prevented by the silane coupling. These results suggest that the efficacy and durability of silane coupling can possibly be monitored by evaluating the relationship between surface hardness and test load. As the silane coupling of a composite material breaks down it will begin to behave like an unsilanated product and the load dependency of the hardness would reduce. As it would not always be possible to compare the results of a silanated product with an equivalent unsilanated product, the hardness test load profile may prove an invaluable means of monitoring changes in the surface characteristics of these materials. One complication which may arise is that caused by the change in hardness caused by water absorption or continued conversion of monomer. Both of these changes may cause a change in the hardness but providing no change in the filler–resin interface occurs neither should produce a change in the hardness–load profile. The latter should therefore act specifically as a diagnostic aid to the state of the resin–filler interface.

Attempts have often been made to relate hardness to other mechanical properties such as yield stress, but Tabor has shown [10] that hardness is such a complex surface property that no matter how accurately we determine it we cannot expect it to provide a simple correlation with any other yield property. It is unlikely therefore that hardness measurements taken in isolation will ever provide a direct indication of materials performance or durability. An example of this complexity can be seen when considering the surface contact fatigue characteristics of the same group of resin – matrix model composites as used in this study [7]. Here there was a tendency for the fatigue life to increase between 23–33% volume fraction but to decrease again beyond 43% volume fraction. Clearly, surface contact fatigue life cannot be predicted from hardness even though surface deformation is the first stage involved in contact fatigue.

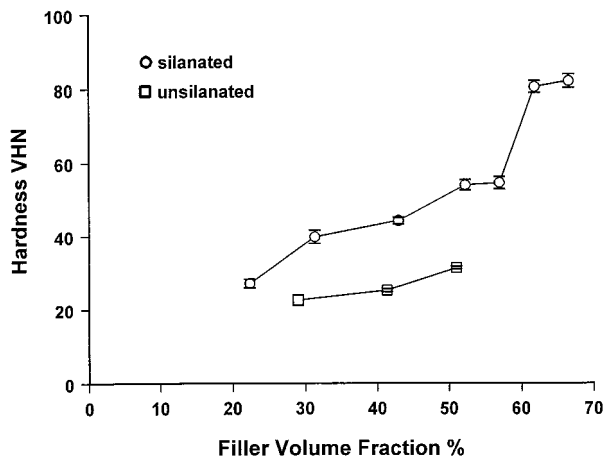

Figure 4 Hardness (determined using a 200 g load) plotted against filler volume fraction. Error bars indicate standard deviations.

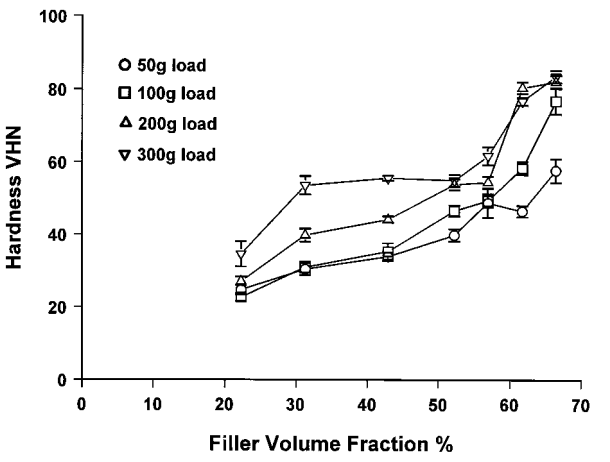

Figure 6 Hardness of composites (at various test loads) plotted against filler volume fraction for silanated fillers.

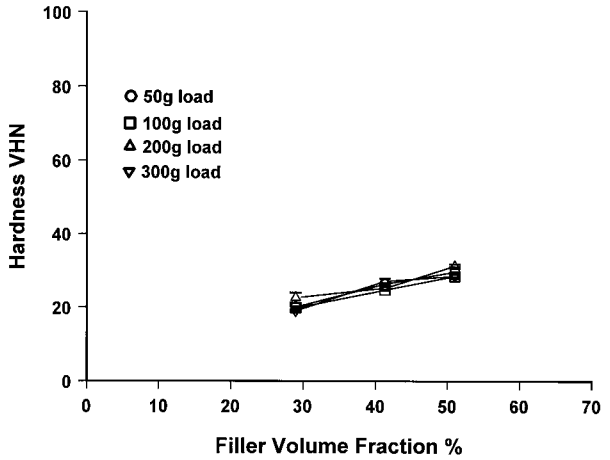

Figure 7 Hardness of composites (at various test loads) plotted against filler volume fraction for unsilanated fillers.

However, the type of measurement reported here may offer a useful means of monitoring the state of the filler–matrix interface which itself may be a major factor in controlling durability since the fatigue life of composites is markedly dependent on effective resin–filler coupling [7].

When the findings are related to the original test hypotheses it can be reported that:

1. Hardness increases almost monatonically with filler volume fraction for silanated fillers but there is no such clear relationship when fillers are unsilanated.
2. Hardness of composites with silanated fillers is significantly greater than equivalent products with unsilanated filler.
3. Measurement of Vickers' hardness may potentially be used to detect differences in filler silanation status through a consideration of the hardness–load profile.

It remains to be seen whether measurements of hardness can detect changes in the status of the resin–filler interface during long-term storage under conditions which would be expected to compromise the interfacial bond.

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