Energy dependent polymerization of resin-based composites
Halvorson, R.H.

Citation for published version (APA):
Halvorson, R. H. (2003). Energy dependent polymerization of resin-based composites
The effect of filler and silane content on conversion of resin-based composite.

Introduction

The extent of conversion of dental polymers based on methacrylate resins has been examined by a number of methods, including nuclear magnetic resonance spectroscopy [1,2], differential scanning calorimetry [3,4], Raman spectroscopy [5], conventional infrared [6,7,8,9,10], and Fourier transform infrared spectroscopy (FTIR) [11,12,13,14,15,16]. Of these methods, conventional infrared and FTIR spectroscopy have been used extensively, due in large part to the availability of equipment and numerous sampling techniques.

The vibrational mode typically analyzed in infrared characterization of methacrylate-based dental materials involves stretching of the carbon-carbon double bond of the methacrylate moiety centered around 1638 cm$^{-1}$ [6,7,9,11,16]. For photoactivated, resin-based composite, conversions ranging from 43-73 percent have been reported using this absorption [8,9,10,14]. Dissimilar monomer reactivities may account, in part, for differences noted among materials within a given study [10, 17,18,19]. Comparison of conversion values across studies may show additional deviations due to differences in the baseline parameters used to define the pertinent absorption bands needed to quantify conversion [16]. The term conversion, for resin-based composite, generally refers to the percentage of C=C bonds of the matrix monomers reacted. Additional C=C on, for example, silane molecules can lead to errors in determining the conversion. The magnitude of such error is expected to be related to the amount and reactivity of the silane on the filler.

Silane coupling agents are used to reinforce adhesion between filler and matrix polymer and also to increase hydrolytic stability [20]. In dental resin-based composite materials, the organofunctional silane, \( \gamma \)-methacryloxypropyltrimethoxysilane (\( \gamma \)-MPS), has been used extensively [21]. The enhanced stability of composites compounded with filler treated with \( \gamma \)-MPS or with other silane coupling agents, is attributed, in part, to formation of a siloxane bond between the filler and the coupling agent [22,23,24]. Additionally, covalent bonding may occur between the organofunctional group of the silane and reactive groups of the resin matrix [25,26]. The reactivity depends not only on the chemical nature of the reactants, but also on the spatial arrangement of silane on the filler.

The structural features of coupling agents processed on particulate fillers is dependent on a number of variables, with the concentration of the coupling agent having considerable impact. In dilute solution, \( \gamma \)-MPS has been shown to adsorb on clay and lead oxide particulates in monomolecular layers [27]. The arrangement of \( \gamma \)-MPS on the substrates was shown to be parallel to the surface with a calculated surface area per molecule of 0.60 nm\(^2\) and 0.59 nm\(^2\) on clay and lead oxide respectively. This coverage compared favorably to space filling projections for \( \gamma \)-MPS in a parallel orientation relative to the surface (0.55 nm\(^2\)). On colloidal silica, estimates of 0.43 to 1.04 nm\(^2\) per molecule have been reported [28,29]. Adsorption of \( \gamma \)-MPS in a parallel orientation approaching a monomolecular coverage, however, is not necessarily desirable for optimum reactivity with the resin matrix, or for physical/mechanical reasons. For these reasons, silanes are often processed at concentrations that yield structures that deviate considerably from the ordered molecular packing obtained from dilute solution. Disturbances in the molecular arrangement at the surface occur at increased concentration through association between silanols resulting in adsorption of higher molecular weight species [30,28]. Given sufficient time, intermolecular condensation forms a non-homogeneous polysiloxane interphase made up of a fraction covalently bonded to the substrate (chemisorbed) and a variable molecular weight fraction that is not chemically bonded (physisorbed). The composition and structural arrangement within this polysiloxane interphase impacts its interaction with the resin matrix, and hence, the chemical reactivity between the organofunctional group on silane with reactive groups of the resin matrix. This interaction forms the basis of the interpenetrating network (IPN) theory of silane reinforcement.
Studies with γ-aminopropyltriethoxysilane (γ-APS) and epoxy resin have shown that their reactivity with each other is dependant upon the extent of condensation of the silane interphase [32]. This result is due to decreased diffusion of resin into the polysiloxane network at increased condensation [32,33].

The chemical similarity between the silane methacrylate functional group and that of the matrix methacrylates yields a virtually identical infrared signature. It is possible that this similarity will confound resin matrix conversion analysis if the silane-based methacrylate is present at measurable amounts and structural variables (e.g. steric limitations) within the interphase leave silane methacrylate unreacted. Such conditions would lead to underestimating the actual resin matrix conversion when calculated in the conventional manner. Preliminary investigation by the authors suggested that silane content on the filler could cause a measurable decrease in the conversion for model resin-based composite and that most of the silane C=C bonds appeared to remain unreacted. Similar observations were made in a study of microfilled composites where the silica filler was treated with either a methacrylate functionalized silane or a non-functionalized silane [34]. The composite containing non-functionalized silane filler had the same conversion as the unfilled resin while the composite formed from the methacrylate functionalized silane had reduced conversion. In the above mentioned preliminary studies it was also observed that reduction in conversion occurred for increasing filler loadings that could not be accounted for by silane unsaturation.

The objective of this investigation was to examine the effect silane may have in underestimating the conversion of resin based composite via FTIR, and to determine a silane-adjusted resin matrix conversion. A related objective was to determine the effect of filler loading on resin matrix conversion.

Materials and Methods

Filler preparation and characterization

Silane-treated, zirconia/silica fillers (average particle size 0.6 microns; nominal surface area 60 m²/gm) were prepared with 4, 8, 12, 16 and 20
weight percent methacrylate functionalized silane (γ-methacryloxypropyltrimethoxysilane) (Aldrich, Milwaukee, WI). Silane was added, under constant stirring, to aqueous solutions of the filler adjusted to a pH of 3.5 with acetic acid [24]. The slurries were stirred constantly for one hour followed by tray drying at 70°C for 12 hours. The processed fillers were analyzed by diffuse reflectance (DRIFT) using a Fourier transform infrared spectrometer (IR44, Nicolet, Madison, WI) and a diffuse reflectance accessory (Spectra-Tech, Shelton, CT). Spectra were obtained from the coaddition of 200 scans at a resolution of 4 cm⁻¹ using a KBr background. To more closely approximate the packing density in the compounded paste, spectra were obtained on the neat fillers rather than diluting with KBr. Sampling neat via DRIFT also limited water interference, which can be problematic with a pressed halide disk. The methacrylate unsaturation centered at 1638 cm⁻¹ was measured by integration using the baseline parameters indicated in Table 1 and referencing this absorption to the absorption centered at 1880 cm⁻¹ attributed to overtones of the silica network [35] (identified as –Si-O-Si– in this paper). Three separate samplings of filler were measured by DRIFT and mean values for Si-O-Si and C=C absorption were determined.

<table>
<thead>
<tr>
<th>Table 1. Baseline parameters (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
</tr>
<tr>
<td>C=\text{C(methacrylate)}</td>
</tr>
<tr>
<td>Si-O-Si</td>
</tr>
<tr>
<td>C=\text{C(aromatic)}</td>
</tr>
</tbody>
</table>

Composite formulation and characterization

Since preliminary investigation suggested that conversion was affected by filler loading, the pastes were compounded to an approximate equivalent inorganic content (72 weight percent total solids) with a 50/50 (wt%) BisGMA/TEGDMA resin. A photoinitiating system, comprised of ethyl 4-dimethylaminobenzoate and camphorquinone at an approximate proportion of 2.5:1 weight percent, was incorporated into the resin prior to compounding. Total percent solids in each filler formulation was determined by mass loss after burn-off at 600°C for thirty minutes. After determining the percent solids in the various fillers, the appropriate filler content was hand-mixed with sufficient resin to obtain approximately 72 weight percent total solids in all pastes. Transmission spectra of uncured and cured paste was obtained by compressing pastes between two KBr plates (Optovac, North Brookfield, MA) and measuring in transmission at
32 scans and 4 cm\(^{-1}\) resolution. After obtaining the spectrum of the uncured paste, the specimen was irradiated for 30 seconds (3M™ Visilux 2™ Visible light Curing Unit, 3M Dental Products, St.Paul, MN) and stored at 37°C. Spectra were obtained on the cured paste 72 hours after irradiation. The material was left between the KBr plates throughout this procedure. The same baseline parameters as for diffuse reflectance were used to calculate the integrated absorbance areas (Table 1). Using this information, conversions of the polymerized pastes were calculated using the following equation:

\[
\% \text{ Conversion} = 1 - \frac{\text{Abs}(C=\text{C}/\text{Si}-\text{O}-\text{Si})_{\text{cured}}}{\text{Abs}(C=\text{C}/\text{Si}-\text{O}-\text{Si})_{\text{uncured}}} \times 100\% \quad (1)
\]

To validate the use of the Si-O-Si absorption as an internal reference, the conversion was also calculated by equation (1) using the aromatic skeletal absorption at 1584 cm\(^{-1}\) as a reference.

To compensate for silane and obtain the resin matrix conversion, the ratio of C=\text{C}/\text{Si}-\text{O}-\text{Si} absorbance areas obtained by diffuse reflectance for the silane-treated fillers was subtracted from the absorbance ratio of their respective uncured and cured pastes. As a first approximation, the full silane contribution was subtracted based on preliminary experiments that suggested little conversion in the silane layer. To eliminate absorbance other than that contributed by silane C=\text{C}, the spectrum of the non-silane treated filler was subtracted from the spectra of the silane-treated fillers. The integrated C=\text{C}/\text{Si}-\text{O}-\text{Si} values were then substituted into the above equation to calculate a silane adjusted conversion. For this correction to be valid, it was assumed that the absorption ratio of C=\text{C} to Si-O-Si does not change upon compounding resin with the filler. Duplicate specimens were prepared from each paste and the mean values for the pertinent absorptions were used in the calculations.

To determine the impact of filler content on matrix conversion, two series of pastes were compounded with variable weight percent total solids (20, 40, 60, 70 and 75). One series was formulated with non-silane treated zirconia/silica filler, while the other was formulated with eight weight percent silane-treated filler. Specimens were prepared between KBr plates and spectra were obtained for the uncured and cured paste after storage at 37°C as described earlier. Conversions were calculated using equation (1).
Results

Transmission spectra of the uncured pastes formulated with the various fillers are shown in Figure 1. An increase in methacrylate unsaturation with increasing silane concentration is observed by scaling the spectra to the Si-O-Si absorption. Because the pastes were compounded to maintain a constant weight percent solids, the resin concentration decreased proportionally with increasing silane concentration (as shown for the aromatic peak at 1610 cm\(^{-1}\)). Thus, the differences observed for the C=C absorption do not correspond solely to changing silane concentration.

DRIFT spectra of silane treated fillers are shown in Figure 2. The absorbance due to methacrylate unsaturation (1638 cm\(^{-1}\)) is observed to increase with increasing silane concentration. A relatively broad peak at

\[ \text{Absorbance} \]
\[ \text{Wavenumber (cm}^{-1}\text{)} \]

**Figure 1.** Transmission spectra of pastes compounded to 72 weight percent total solids with \(\gamma\)-MPS silane treated fillers at the designated weight percent. Spectra shown were scaled to the Si-O-Si absorption.

**Figure 2.** DRIFT spectra of treated zirconia/silica filler processed with 4, 8, 12, 16, and 20 weight percent \(\gamma\)-MPS.
1630 cm\(^{-1}\) is also observed with the non-silane treated filler and is attributed, in part, to the bending vibration of water adsorbed on filler. Absorption ratios of filler C=C/Si-O-Si were determined by subtracting this non-silane treated absorbance from those of the spectrum for silane-treated filler. Table 2 lists these ratios as well as those for the pastes and resin matrix. These latter values were obtained by subtracting the filler ratios from the paste ratios. Graphical comparison of the C=C/Si-O-Si ratio for the various fillers versus the percent solids after burn-off (Figure 3) yields a linear correlation, suggesting that the amount of adsorbed water is similar among the five silane-treated fillers. The percent deviation of the mean for the C=C/Si-O-Si ratios ranged from 1 to 4 percent for the silane-treated fillers. Conventionally calculated paste

### Table 2. C=C/Si-O-Si absorbance ratios.

<table>
<thead>
<tr>
<th>Weight % Silane</th>
<th>Cure State</th>
<th>Paste</th>
<th>Corrected Filler</th>
<th>Resin Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Uncured</td>
<td>3.344</td>
<td>0</td>
<td>3.344</td>
</tr>
<tr>
<td>0</td>
<td>Cured</td>
<td>1.181</td>
<td>0</td>
<td>1.181</td>
</tr>
<tr>
<td>4</td>
<td>Uncured</td>
<td>3.567</td>
<td>0.173</td>
<td>3.37</td>
</tr>
<tr>
<td>4</td>
<td>Cured</td>
<td>1.326</td>
<td>0.173</td>
<td>1.129</td>
</tr>
<tr>
<td>8</td>
<td>Uncured</td>
<td>3.689</td>
<td>0.293</td>
<td>3.396</td>
</tr>
<tr>
<td>8</td>
<td>Cured</td>
<td>1.516</td>
<td>0.293</td>
<td>1.223</td>
</tr>
<tr>
<td>12</td>
<td>Uncured</td>
<td>3.907</td>
<td>0.486</td>
<td>3.421</td>
</tr>
<tr>
<td>12</td>
<td>Cured</td>
<td>1.667</td>
<td>0.486</td>
<td>1.181</td>
</tr>
<tr>
<td>16</td>
<td>Uncured</td>
<td>4.019</td>
<td>0.656</td>
<td>3.363</td>
</tr>
<tr>
<td>16</td>
<td>Cured</td>
<td>1.821</td>
<td>0.656</td>
<td>1.165</td>
</tr>
<tr>
<td>20</td>
<td>Uncured</td>
<td>4.325</td>
<td>0.808</td>
<td>3.544</td>
</tr>
<tr>
<td>20</td>
<td>Cured</td>
<td>2.057</td>
<td>0.808</td>
<td>1.249</td>
</tr>
</tbody>
</table>

**Figure 3.** Percent by weight organics determined from pyrolysis of silane-treated fillers versus ratio of integrated areas of carbon-carbon double bond and Si-O-Si internal reference.
Conversions are shown in Table 3 together with silane adjusted resin matrix conversion. With regard to the paste conversion, the data show very similar values irrespective of the internal reference used. This similarity supports the use of the 1880 cm⁻¹ Si-O-Si absorption as an internal reference. The data also reveal a progressive decrease in paste conversion with increasing silane levels (Figure 4). The difference from the mean conversion for the two replicates measured for each paste was less than one percent. The resin matrix conversions after correcting for silane are virtually the same for each of the paste formulations with an average conversion of 65.1±0.8 percent (Table 3).

**Table 3. Conversion for pastes compounded to 72% total solids with indicated weight % silane-treated filler together with their respective adjusted resin matrix conversion.**

<table>
<thead>
<tr>
<th>Weight % Silane</th>
<th>Aromatic Ring</th>
<th>Si-O-Si</th>
<th>Resin Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>64.5</td>
<td>64.7</td>
<td>64.7</td>
</tr>
<tr>
<td>4</td>
<td>62.6</td>
<td>62.8</td>
<td>66.0</td>
</tr>
<tr>
<td>8</td>
<td>59.2</td>
<td>58.9</td>
<td>64.0</td>
</tr>
<tr>
<td>12</td>
<td>57.3</td>
<td>57.3</td>
<td>65.5</td>
</tr>
<tr>
<td>16</td>
<td>55.3</td>
<td>54.7</td>
<td>65.4</td>
</tr>
<tr>
<td>20</td>
<td>53.7</td>
<td>52.7</td>
<td>64.8</td>
</tr>
</tbody>
</table>

65.1 (0.8)

Conversions for the pastes containing varying weight percent of untreated and treated filler are shown in Figure 5. The aromatic skeletal vibration was used as an internal reference for both series of pastes due to the diminishing intensity of the Si-O-Si absorption as filler content increases.

**Figure 4.** Conversion of pastes compounded to 72 weight percent total solids with γ-MPS treated fillers versus weight percent silane processed on filler.
decreased. A progressive conversion decrease is noted with increase in filler content. This trend is true for pastes compounded with both types of filler. At higher filler levels, the two series diverge, with the silane-treated series showing an apparent greater decrease. This seeming difference can be compensated through subtraction of the silane component, as indicated in the figure for the 72 percent filled paste (Table 3) with eight percent silane.

**Figure 5.** Conversion of pastes compounded with non-treated and γ-MPS treated filler to 20,40,60,70 and 75 percent solids by weight. The silane treated pastes were compounded using the filler processed with 8% by weight γ-MPS. The conversion value from Table 3 for the paste formulated with 8% silane-treated filler and its adjusted resin matrix conversion are also shown.

### Discussion

The results of the present investigation suggests that most of the methacrylate functionality within the silane layer is in a non-reactive environment. This is supported from the data represented in Figure 4, which reveals that the reduction in paste conversion relates directly to the amount of silane on the filler. A highly condensed silane interphase that limits mobility of the silane methacrylate, and hence its reactivity, would account for the progressive conversion decrease among the pastes. In addition, Table 3 shows that correcting for the full methacrylate component of silane on the filler for the respective pastes yielded very similar percent conversion for the resin matrix (mean conversion 65.1±0.8%) and is comparable to the conversion for paste formulated with filler not treated with silane. Thus, the same structural features that limit mobility of silane methacrylate within the interphase presumably limits penetration of resin methacrylate into the interphase. Similar conclusions have been made from studies involving epoxy resin and epoxy functional silane[32]. Under conditions that restrict mobility of the silane interphase and resin penetration, polymerization will be limited
primarily to methacrylate of the resin matrix. Preliminary experiments suggested that surface interactions between filler and resin may affect conversion. For this phase of the investigation, these possible interactions were minimized among the pastes by formulating to an equivalent inorganic content. Provided such interactions are minimized, it is reasonable to expect similar resin matrix conversion among the pastes after adjusting for silane unsaturation. Intrinsic inhibition by silane is not expected to contribute to reduced conversion as shown through experiments with composites formulated from microfiller processed with either 15 weight percent methacrylate-functional silane or non-functional silane [34]. Similar conversion was found for the composite formulated with non-functional silane and the unfilled resin while the composite formulated with methacrylate-functional silane showed reduced conversion. This result supports the observations found in the present investigation.

The similarity of the resin matrix conversions after correcting for the full amount of silane may suggest that the silane interphase is unreactive. However, it is expected that a small portion of the methacrylate functional silane does react with matrix methacrylate by virtue of the heterogeneity of the silane layer. From extraction studies, a graded interphase [36] forms on particulate fillers at increased silane concentrations with the chemisorbed layer forming predominately the base while the periphery is composed primarily of physisorbed structures. Provided that the matrix monomers are compatible with the organofunctional silane it is expected that some localized mixing and subsequent cross-linking is possible with the outer physisorbed layers. Such mixing has been demonstrated with γ-MPS treated silica with 75/25% BisGMA/TEGDMA resin by measuring the viscoelastic properties of the cured composite [37]. In the present investigation, at the 4 percent silane level, the number of silane molecules per gram of filler exceeds 1 x 10^{20}. A small fraction of this value would yield considerable cross-linking yet not be resolvable under the experimental conditions.

The influence of filler content on conversion is shown in Figure 5 for non-silane treated filler. A progressively lower conversion is noted with increasing percentage filler in the paste. This decrease is mostly observable at higher filler loadings. While various fillers have been shown to inhibit free radical polymerization through electron transfer from constituent oxides [38,39], silane treatment of the fillers generally
reverses this effect with γ-MPS being particularly effective. From examination of Figure 5, an inhibition mechanism does not appear to be contributing to any significant extent since the trend towards lower conversion was not reversed by silane treatment. When the data from Table 3 are plotted on Figure 5 it appears that correcting for silane unsaturation equalizes the effect for silane treated and non-treated fillers. Alternatively, the conversion decrease can be considered from factors that impair the mobility of the reactants. The limited conversion found in many network polymers is due to restricted mobility of radical chain ends, pendant methacrylate and monomer imposed at high crosslink density. This limitation is true whether the system is filled or unfilled and is especially true for dental restorative materials based on dimethacrylates. The impact can be seen for the unfilled resin in this experiment (50/50 wt % Bis-GMA/TEGDMA), which has approximately 20 percent unreacted methacrylate remaining (Figure 5). Incorporation of filler into polymerizable resins has also been shown to impact molecular mobility within boundary regions extending from the interface of the filler [40]. Further, this impact was independent of whether or not the filler was unmodified or treated with an organofunctional silane to affect the surface energy. From those results, the authors concluded that the filler surface places conformational restrictions on the molecules within a boundary region that are greater than those of the bulk matrix and are independent of the chemical nature of the filler. In the present investigation, the progressive decrease in conversion of the silane treated pastes appears to be identical to that of the pastes with untreated filler after correcting for silane unsaturation. This similarity in the curves suggests a similar mechanism is prevailing for both series of pastes based exclusively upon the relative amounts of resin and filler and is consistent with a mechanism of restricted mobility of the reactants. The results of the present investigation are based on model composites and other composites processed differently may show more or less effect from silane depending on amount placed on filler and filler loading.

**Conclusions**

Within the parameters of this investigation of model resin composites, the measured conversions were underestimated due to methacrylate unsaturation associated with the silane. Further, for these formulations, the results suggest very little reaction of the C=C bonds of the silane methacrylate.
It was also found that conversion progressively decreased with increasing filler loading and this effect was independent of whether the filler was silane treated or not.
References


[26] Ishida H, Koenig JL. An investigation of the coupling agent/matrix


[37] Nishiyama N, Horie K, Shick R, Ishida H. Influence of adsorption...
behavior of a silane coupling agent onto silica on visco-elastic properties. Polymer Communications 1990;31:380-383.

