ORIGINAL ARTICLE

Post-polymerization of dental resin composite evaluated with nanoindentation and micro-Raman spectroscopy

Mohamad Da*, Young RJb, Mann ABb, Watts DCc

a School of Dental Sciences, Universiti Sains Malaysia, 16150 Kubang Kerian, Kelantan, Malaysia.
b Manchester Materials Science Centre, School of Materials, University of Manchester, UK.
c Biomaterials Science Unit, School of Dentistry, University of Manchester, UK.

(Received 5 September 2006, revised manuscript accepted 1 October 2007)

KEYWORDS
Nanoindentation, dental composite, Young’s modulus, hardness, degree of conversion

Abstract The aim of the study was to evaluate post-polymerization of resin composite by measuring NanoHardness (H), Young’s Modulus (E) and Degree of Conversion (DC) using nanoindentation and Micro-Raman spectroscopy. For this purpose a computer-controlled NanoIndenter™ and a Renishaw 1000 Raman Spectrometer fitted with an Olympus microscope attachment, operated at 638 nm, were used. A light-activated resin composite was used in this study, (Z250, 3MESPE). Sub-groups (n=3) of specimens were irradiated for 20, 30, 40 s. All samples for nanoindentation were polished metallographically and typically 50 nano-indentations were performed per specimen. After curing and polishing, half of the samples were tested immediately (Group 1); the others after being stored dry at 37 °C for 7 days (Group 2) to allow scope for post-polymerization. H values ranged from 1.08 to 1.40 GPa for Group 1, and from 1.64 to 1.71 GPa for Group 2. E values in Group 1 ranged from 19.60 to 19.94 GPa and for Group 2, from 21.42 to 22.05 GPa. DC values ranged from 55 to 66.39%, and 60.90 to 66.47% for Group 1 and Group 2 respectively. All values obtained showed significant different between Groups 1 and 2 (p<0.05); ie as a result of any (further) monomer post-polymerization. The consistently greater H, E and DC values in Group 2 suggest that network stabilization may occur partly by mechanisms supplementary to monomer conversion per se. This could include annealing of the polymer chain segments.

Introduction

Nowadays, there is increasing use of polymer based composites in the restoration of cavities with the newly developed dimethacrylate monomers. These typically consist of resin that polymerized when exposed to light otherwise known as light-activated resin composites. A conversion of aliphatic carbon double bonds of the monomers to single bonds of polymer during polymerization is known as degree of conversion, DC. Ideally, the dental restorative resin would have all of its monomer converted to polymer. However all of the dimethacrylate monomers exhibit considerable residual unsaturation in the final product. The DC ranges from 55% to 75% under conventional irradiation conditions (Ferracane & Greener, 1986; Eliades et al., 1987; Ruyter & Oysaed, 1987). There are few factors which affected the DC namely, curing time, light irradiation, light curing unit, irradiation distances. It is also known that the polymerization reaction of light-activated composites continues even after the end of light irradiation (Leung et al., 1983; Tarumi et al., 1999). Hence, within this study it is part of the aim to know weather post-polymerization also affecting the DC. As for the curing time, it should be optimally used by the clinicians in order to obtain a high quality dental composite restoration. The quality of the restoration material can be quantified by measuring its physical properties, mechanical properties and efficiency of the polymerization during curing process. Most restorative materials must withstand high mechanical forces, during fabrication or mastication. Mechanical properties are therefore important in understanding and predicting a material’s behaviour under loading in the oral environment. Critical physical and mechanical properties of dental composites are influenced by the level of conversion attained during polymerisation. This involves isolated
methacrylate carbon-carbon double bonds being converted to an extended network of single bonds. Even relatively small changes in the extent of conversion near the end of the polymerisation reaction can cause variations in some polymer properties because these changes largely affect the density of cross-linking in the polymer network (Burtscher, 1993). Some investigators have shown a direct correlation between the DC of the resin and their bulk properties such as hardness, wear, tensile and compressive strength (de Lange et al., 1980; Cook, 1980; Tarumi et al., 1999).

Hardness, H, is a function of the surface condition of a material as well as its intrinsic properties. By definition hardness is the resistance of a solid material to plastic deformation. Most of the definition hardness is the resistance of a solid material to plastic deformation. Most of the studies (Salako et al., 1979; de Lange et al., 1980; Cook, 1980; Tarumi et al., 1999) have shown a direct correlation between the DC of the resin and their bulk properties such as hardness, wear, tensile and compressive strength (de Lange et al., 1980; Cook, 1980; Tarumi et al., 1999).

Hardness, H, is a function of the surface condition of a material as well as its intrinsic properties. By definition hardness is the resistance of a solid material to plastic deformation. Most of the studies (Salako et al., 1979; de Lange et al., 1980; Cook, 1980; Tarumi et al., 1999) have shown a direct correlation between the DC of the resin and their bulk properties such as hardness, wear, tensile and compressive strength (de Lange et al., 1980; Cook, 1980; Tarumi et al., 1999). Hence it was the aim of the study to evaluate the effects of post-polymerization and different curing times on the H, E, and DC. Other objective of the study was to determine the validity and practicality of the Micro-Raman spectroscopic techniques for measuring the DC of the light-activated resin composite. The primary working hypothesis was that the values of H, E, and DC increases for post polymerization time and divided into two groups, group 1 and 2. All samples from group 1 were tested immediately; meanwhile samples from group 2 were tested after 7 days stored dry at 37°C. All samples were polished metallographically to produce the uniform baseline needed for nanoindentation testing. Waterproofed silicon carbide discs of decreasing abrasiveness (e.g. 400, 600, 800, 1200 grit) were used. For the final polishing, special soft discs with diamond suspensions of decreasing grit size (6µm, 3µm, and 1µm) were used combined with “Dp-Lubricant blue” cooling solution. The sample surfaces were cleaned using running water and a mild soap solution to remove polishing debris and paste. This cleaning procedure was repeated between each grit size and at the end of polishing.

### Materials and methods

The resin composite used for this study was Z250 of A3 shade (3M ESPE) as listed in Table 1. Z250 is an aesthetic, light-cured, radiopaque composite specifically designed for use in both anterior and posterior direct or indirect restorations. The Z250 universal restorative is packaged in bulk syringes.

<table>
<thead>
<tr>
<th>Material</th>
<th>Shade</th>
<th>Composition</th>
<th>Manufacturer</th>
<th>Batch No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z250</td>
<td>A3</td>
<td>Resin: Bis-GMA, TEGDMA, UDMA, Bis-EMA(6)</td>
<td>3M ESPE Dental Products, St. Paul, MN</td>
<td>19990225</td>
</tr>
</tbody>
</table>

The inorganic filler loading is 60% by volume with a particle size range from 0.01 to 3.5 µm. The light source used in this study was the ELIPAR Highlight lamp (ESPE GmbH, Seefeld, Germany) at light intensity of 800 mW/cm² with an irradiated diameter of 6 mm. For all measurements of H, E and DC, 2.5 mm thick teflon mould with a 6 mm diameter central opening was used.

The mould was placed on a microscope glass slide and slightly overfilled with the resin composite. The resin composite was covered with mylar in order to avoid contact with oxygen, which is an inhibitor of the polymerization. Immediately after collection of the uncured resin composite in the mould, the specimen was put under a cure treatment in open atmosphere, at 20 ± 2°C. Three different curing times were used which were 20 s, 30 s, and 40 s. Curing time recommendation from the manufacturer for this thickness and shade is 20 s. During the cure treatment, the mylar was removed. The tip of the light source was then placed against the resin composite and the light was activated for a predetermined time. The cure treatment was performed on the both sides of the samples, in order to make sure that the resin composite polymerized completely.

### Nanoindentation measurements

The operation principles of the computer-controlled Nano Indenter™ (Nano Instruments, Inc., Knoxville, TN) are schematically shown in Figure 1. The apparatus is enclosed in a heavy wooden cabinet and is installed in a small isothermal room to ensure thermal stability of the samples (21 ± 1°C). The system has load and displacement resolutions of 0.2 µN and 0.16 nm respectively. The instrument consists of three major components, the triangular pyramidal diamond indenter (called a Berkovich indenter),
Mohamad et al.

Figure 1 A schematic representation of the experimental apparatus of the Nanoindenter: A, sample; B, indenter; C, load application; D, indentation column guide springs; E, capacitive displacement sensor (Oliver and Pharr, 1992)

an optical microscope with a maximum magnification of 5000x, and an X-Y table that transports the specimen between the microscope and the indenter with a high lateral precision of 3-5 µm. The complete device is installed on a pneumatic anti-vibration table to exclude transmission of building vibrations. A load controlled test mode was used for examining hardness at shallow indentation depths. The instrument monitors the load as well as the loading rate continuously during the loading and unloading segments of the indentation procedure. By means of the computer controlled X-Y table, the specimen can be transferred to the indenter. An accurate calibration of the distance between the microscope and the indenter was made before testing to ensure a precise transfer of the pre-programmed positions to the indenter.

The Young’s modulus, E was calculated as described in Oliver and Pharr (1992). Effects of non-rigid indenters on the load-displacement behaviour can be effectively accounted for by defining a reduced modulus $E_r$, through the following Equation 1;

$$\frac{1}{E_r} = \left(1 - \nu_i^2\right) \frac{E}{E_i} + \left(1 - \nu^2\right)$$

where $E$ and $\nu$ are Young’s modulus and Poisson’s ratio for the specimen and $E_i$ and $\nu_i$ are the parameters for the indenter. Indentation load-depth data obtain, shown schematically in Figure 2, (Oliver and Pharr 1992) is then analyzed according to the Equation 2 below;

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A}$$

Here, $S = dP/dh$ is the experimentally measured stiffness of the upper portion of the unloading data, and A is the projected area of the elastic contact. By measuring the initial unloading stiffness and assuming that the contact area is equal to the optically measured area of the hardness impression, the modulus, E can thus be derived. $H$ was calculated using the maximum load and the contact area at maximum load.

Indents were typically made to 200 nm as a minimum depth limit and a maximum depth limit of 1900 nm. Poisson’s ratio used was 0.3. For each location on the sample, values of E and $H$ were determined using 10 closely spaced indentations. The spacing between indentations was typically 10-15µm. There were approximately 3 to 5 locations of indentation on the sample surface. In total about 50 indentations were performed across the entire surface of each sample using the same experimental parameters.

Micro-Raman spectroscopy measurement

The polymerized resin composite samples were examined using a Renishaw 1000 Raman spectrometer fitted with an Olympus optical microscope attachment. A He-Ne laser which
emits radiation at 632.8 nm was used as the excitation source. The laser power at the sample position is of the order of 25mW which was focused through a x 50 objective lens. Raman spectra were obtained in the region of 1500 cm$^{-1}$ to 1800 cm$^{-1}$ at 2 cm$^{-1}$ resolution. For each sample 3 scans were made with number of accumulations for every scan is 10. The irradiation time was 10 s. The spectra in the region of interest between 1500 and 1800 cm$^{-1}$ were analyzed using a curve fitting program which allowed each vibration to be a mixture of a Lorentzian and Gaussian peak shape. The program was run to optimize the Lorentzian and Gaussian combination which gave the best fit between the calculated curve and the real data because the vibrational modes for these condensed phase systems do not have a particular peak shape. Since the samples used are systems containing aromatic vibrations, two peaks were always observed at 1583 cm$^{-1}$ (weak) and at 1616 cm$^{-1}$ (strong). The C=C vibration was always observed as a singlet at a frequency of 1650 cm$^{-1}$. The C=O vibration was observed as a poorly resolved doublet in the calibration mixtures because the frequency of the C=O is affected by intra and intermolecular bonding. The degree of conversion (DC) was calculated by the following Equation 3;

$$DC(\%) = 100 \times \left[1 - \left( \frac{R_{\text{polymerized}}}{R_{\text{unpolymerized}}} \right) \right]$$

where \( R \) = band height at 1650 cm$^{-1}$/band height at 1616 cm$^{-1}$.

All the available data were entered into a database utilizing SPSS statistical software (SPSS 12.0). One-way ANOVA followed by Scheffe’s post hoc was evaluated for all parameters when subjected to curing time. Paired t-test used to analyze H and E between group 1 and 2, also for DC in both groups.

**Results**

The nanoindentation mean values for H and E can be seen in Table 2. Generally both values of H and E in group 2 were higher than group 1. H values ranged from 1.08 to 1.40 GPa for group 1 and from 1.64 to 1.71 GPa for group 2 (Table 2). While E in group 1 ranged from 19.60 to 19.94 GPa (Table 2). In group 2 the values of the E were 21.42 to 22.05 GPa. Statistical analysis of paired t-test between group 1 and group 2 of H has shown significant different (p<0.05). The same test also revealed significant different (p<0.05) for E between both groups. Within group 1 and 2, H and E has no significant different (p>0.05) at different curing times except for 40 s curing time in group 1 showed higher value of H.

For the DC evaluated by Micro-Raman spectroscopy, two peaks were clearly observed in the spectral region between 1500 cm$^{-1}$ and 1800 cm$^{-1}$ (Figure 3). The highest peak was the residual unpolymerized methacrylate C=C stretching mode at 1650 cm$^{-1}$. While the second peak at 1616 cm$^{-1}$ was the aromatic C=C stretching mode.

DC values ranged from 55.00% to 66.39% and 60.90% to 66.47% for group 1 and group 2 respectively. From the result, it has found that for both groups, at 40 s curing time the highest DC, were obtained (Table 2). Statistical analysis of paired t-test shown the DC of group 2 has significant different (p<0.05) values of DC compared with the DC in group 1.

**Discussion**

Post-polymerization of group 2 exhibited greater values for both H and E. It can be suggested that the higher H and E values are associated with higher molecular weights as a result of more extensive polymerization. Polymerization of the composite still continued at a slow rate after the curing.

It has been reported (Salako et al., 1979; de Lange et al., 1980; Cook, 1980) that the results of hardness on light-activated composite resin are varied. Post-irradiation or post-polymerization increases in hardness by visible light exposures between one hour and 24 hour have been reported (de Lange et al., 1980). Moreover, de Lange et al. (1980) indicated that there was some increase in hardness from one to three days. Hence, the results of these studies are consistent with their studies. Nevertheless, Cook (1980) found no significant changes in hardness values for light-activated resin composites between one and 12 days. Salako et al. (1979) reported that there was no increase in hardness for light-activated composites resin measured immediately and up to three weeks after irradiation. All those discrepancies may be due to differences in the composition of the materials and storage conditions, such as lighting, temperature and humidity. It is suggested that at certain period

---

**Table 2** NanoHardness, Young’s Modulus and Degree of Conversion % (DC) mean values for Group 1 and 2

<table>
<thead>
<tr>
<th>Curing Time (s)</th>
<th>Group 1 NanoHardness, H (GPa)</th>
<th>Young’s Modulus, E (GPa)</th>
<th>DC (%)</th>
<th>Group 2 NanoHardness, H (GPa)</th>
<th>Young’s Modulus, E (GPa)</th>
<th>DC(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.08 (0.03)$^a$</td>
<td>19.60 (1.00)$^c$</td>
<td>56.77 (1.21)$^b$</td>
<td>1.71 (0.31)$^a$</td>
<td>21.73 (1.68)$^c$</td>
<td>60.90 (3.18)$^a$</td>
</tr>
<tr>
<td>30</td>
<td>1.12 (0.03)$^b$</td>
<td>19.90 (1.00)$^c$</td>
<td>56.00 (2.15)$^b$</td>
<td>1.76 (0.42)$^a$</td>
<td>22.05 (3.12)$^c$</td>
<td>63.38 (2.62)$^b$</td>
</tr>
<tr>
<td>40</td>
<td>1.40 (0.22)$^b$</td>
<td>19.94 (1.62)$^c$</td>
<td>66.39 (0.89)$^b$</td>
<td>1.64 (0.26)$^a$</td>
<td>21.42 (1.07)$^c$</td>
<td>66.47 (1.11)$^a$</td>
</tr>
</tbody>
</table>

Same lowercase letters and numbers in superscript indicates no significant differences within column at the p>0.05

(One way ANOVA, Scheffe’s post hoc)
of time the exhausting of the initiator occurred which then terminates the polymerization. Furthermore, all the studies stated were not using the same hardness testing as used in this study. However, Drummond (2006) used nanoindentation technique and obtained the nanoHardness of 1.3-1.6 GPa for Renew composite (Bisco, Schaumburg, IL). The result of his finding was consistent with this study.

For DC, the study of the light-cured resin composite polymerization with a vibrational technique is made on a relative basis by comparing the C=C vinyl stretching mode at 1640 cm$^{-1}$ to a reference band which is the aromatic band at 1610 cm$^{-1}$ before and after the photopolymerization (Planelli et al., 1999). From the results obtained, the C=C vinyl stretching mode found at 1650 cm$^{-1}$ and the aromatic band at 1616 cm$^{-1}$. This difference may be due to the difference of the chemical surrounding arises from a different monomer resin. Planelli et al., (1999) used sample Z100 while this study was based on the Z250 sample. From this study it is also revealed that the improvement of new composite Z250 from the manufacturer by replacing TEGDMA with UDMA, BisEMA, resulted in higher DC, 66.5% compared to Z100 the DC is about 50% (Planelli et al., 1999). The results also showed the DC of both groups 1 and 2 reach a plateau value at about 66.5% for 40 s curing.

The extent of polymerization of a photo-activated composite, was influenced by the exposure time to the photo-activating radiation, as the curing time increased from 20s to 40 s, the polymerization also increases resulting in higher values of the DC. High DC is also associated with light intensity (Silikas et al., 2000; Emami and Soderholm, 2003). However, during this study the H and E did not show any significant result as the curing time increased in post-polymerization. Nevertheless, only H of immediate polymerization increases as the curing time increases but the trend is not significant for E of the resin composite tested.

According to Tarumi et al. (1999) the relationship is possibly attributable to the mobility of reactive molecules in the polymer network. During polymerization, the free radicals located at functional groups of unreacted molecules are trapped within the polymer network due to the rapid increase in viscosity. For post-polymerization, unreacted species with free radicals need to be sufficiently mobile to make contact with other reactive species in the polymer network. The composites with a greater DC are considered to form more rigid networks than specimens with lower conversion. In the initially highly polymerized composites, therefore, it is more difficult for the residual unpolymerized species to be involved in further reaction. The above results also suggest that the timing of testing is very critical when studying properties of composite resin.

**Conclusions**

All values obtained shown significant different between Groups 1 and 2 ($p<0.05$), as a result of any (further) monomer post-polymerization. The consistently greater H, E and DC values in Group 2 suggest that network stabilization may occur partly by mechanisms supplementary to monomer
conversion per se. This could include annealing of the polymer chain segments. The extent of polymerization of a photo-activated composite, was influenced by the exposure time to the photo-activating radiation, as the curing time increased from 20 s to 40 s, the polymerization also increases resulting in higher values of the DC. However, for post-polymerization, H and E did not show any significant result as the curing time increased. The findings from this study suggested the optimum exposure time is 40 s, whereas the manufacturer recommendation is 20 s. Also the micro-Raman spectroscopy is proved to be an easy and useful technique to follow the DC without tedious sample preparations. From the results obtained, it is considered that the timing of testing is very critical when studying properties of resin composite. Hence, for a further work, sample preparation of polishing, time of curing and polymerization should be taken very precisely. Further evaluation of the post-polymerization has to be demonstrated.

Acknowledgement

This article is based on a dissertation submitted to the Manchester Materials Science Centre, UMIST, in partial requirements for the MSc degree.

References


