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What is This?
Polymerization shrinkage of dental composite resins

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Abstract: Aesthetic materials have always been a priority for the restoration of anterior teeth; increasingly, they have also gained prominence in the restoration of posterior teeth. This has been due to their advantages as an alternative to amalgam. Their drawbacks however, can include poor marginal adaptation, postoperative sensitivity and cuspal movement. These are particularly associated with the polymerization shrinkage accompanying the placement of composite resins. Consequently, a variety of methods have been used for determining the polymerization shrinkage. These range from dilatometer methods, specific gravity methods and deflecting disc systems to optical methods. In this work a unique method for the qualitative analysis of polymerization shrinkage was undertaken. This method utilized a miniature transducer and provided details of the shrinkage from within the material. The results indicated movement of material towards the initiating light, followed by a return movement away from it. The study was expanded to incorporate clinical aspects, whereby the composite resin was in direct contact with dental tissue, as in a restoration. Tests were performed with surface-treated cavity moulds, as in restoration placement, and without surface treatment. Results indicated that the shrinkage was highly dependent upon the region under investigation, as well as on the state of the surface.

Keywords: polymerization shrinkage, dental composites, restorative resins

NOTATION

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>bis-GMA</td>
<td>2,2-bis[4-(2-methacryloyloxyethoxy)-phenyl]propane</td>
</tr>
<tr>
<td>DC</td>
<td>degree of conversion</td>
</tr>
<tr>
<td>DEGMA</td>
<td>diethylene glycol dimethacrylate</td>
</tr>
<tr>
<td>DVRT®</td>
<td>differential variable reluctance transducer</td>
</tr>
<tr>
<td>HEL</td>
<td>Heliomolar</td>
</tr>
<tr>
<td>/</td>
<td>contributing length</td>
</tr>
<tr>
<td>L</td>
<td>original length</td>
</tr>
<tr>
<td>MOD</td>
<td>mesial occlusal distal</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>triethylene glycol dimethacrylate</td>
</tr>
<tr>
<td>TET</td>
<td>Tetric</td>
</tr>
<tr>
<td>V</td>
<td>original volume</td>
</tr>
<tr>
<td>δL</td>
<td>change in length</td>
</tr>
<tr>
<td>δV</td>
<td>change in volume</td>
</tr>
<tr>
<td>Δl</td>
<td>DVRT® displacement</td>
</tr>
</tbody>
</table>

1 INTRODUCTION

The use of composite resins in dentistry and the interest in them have risen markedly in recent years. A wide variety of vastly improved composite materials have been and will continue to be used for the overall purpose of conservative restorative dentistry [1]. Dental composite resins are heterogeneous materials with two principal components, the resin matrix and the filler particles. The polymeric matrix in dental resins contains a variety of high molecular weight monomers, mainly based on bis-GMA, which is derived from bis-phenol A and glycidyl methacrylate [2–5]. The filler particles constitute up to 86 per cent weight, 71 per cent by volume of the material [6], and those used in commercial composites cover the whole range of quartz, borosilicate glass and aluminosilicate glass [6, 7]. The monomer matrix is very viscous and diluent monomers are added to improve workability. These are typically difunctional monomers, of lower mass than bis-GMA, such as DEGMA or TEGDMA [8]. Some composite resins also utilize alternative monomer systems in which bis-GMA is partly or wholly replaced by aliphatic or aromatic urethane dimethacrylates [5]. During setting, the resin typically undergoes free radical polymerization to...
harden with a consequent reduction in volume. The generally preferred mode of cure in dental composites is photopolymerization [9], whereby the polymerization is initiated by blue light acting on a photosensitive initiator, usually camphoroquinone, present in the monomer phase of the composite resin. These composite resins do not display complete polymerization, and there is considerable residual unsaturation in the final product [9], with a degree of conversion (DC) ranging from 55 to 75 per cent [10, 11]. Extensive accounts of the complex materials science associated with dental composite resins have been published [3–6, 12]. Composite resins have gained prominence in recognition of their superior aesthetic qualities along with their fulfillment of the basic requirements of restorative materials. Their drawbacks however, can include their relative cost and difficulty of placement as well as poor marginal adaptation, postoperative sensitivity and cuspal movement [13–18]. The latter features are particularly associated with the polymerization shrinkage that accompanies the placement of composite resins and, as would be expected, the increased use of these resins is accompanied by research into issues specific to them.

2 POLYMERIZATION SHRINKAGE

The polymerization of dental composite resins is accompanied by shrinkage. This is a well known phenomenon and a comprehensive account can be found in many texts [12, 19–21]. The polymerization shrinkage is dependent on many factors, including the density of the double bonds, the average molecular weight and the degree of conversion. The polymerization shrinkage is defined as the ratio of the change in length or volume to the original length or volume respectively, i.e. \( \frac{\Delta L}{L} \) or \( \frac{\Delta V}{V} \).

2.1 Shrinkage vectors

The direction in which polymerization shrinkage takes place can be indicated by shrinkage vectors. In a free-standing block of material, the internal stresses and continuing reaction will tend to cause polymerization shrinkage to be manifested in compliance with the theory that composites shrink towards the light. In a tooth cavity, however, external constraints may operate, modifying the shrinkage vectors. These constraints are predominantly the cavity configuration and surface attraction between the cavity walls and the material. Initially, through the use of the acid etch technique and certain primers and bonding agents [6, 8], the resin attaches to the cavity wall, and shrinkage occurs exclusively from the free surface of the filling. Elastic yielding in the material in the region of the bond may alleviate some of the contraction forces. This degree of flow will depend on material supply from the free surfaces of the restoration and is thus highly dependent on the three-dimensional configuration of the restoration. However, if the net shrinkage forces are greater than those resisting it at the cavity walls, then the result will be interfacial bond failure [22]. A gap will be formed along the margin of the filling and contraction will continue relatively unrestricted. This will culminate in a filling with perfect adaptation for part of the margin and a gap for the remainder. Such marginal gaps are a direct consequence of the opposition by the shrinkage of the material to the bond between the composite and the tooth structure.

2.2 Problems associated with shrinkage

The shrinkage associated with the polymerization of dental composite resins acts in such a direction as to oppose the resin–tooth interface [23], and hinders good marginal adaptation. This may lead to microleakage [24], which entails the passage of fluids, bacteria, molecules, ions or even air along the restoration–tooth interface. Another major consequence of the polymerization shrinkage of composite restorations is cuspal movements of up to 46 \( \mu \text{m} \) [25]. The shrinkage generates considerable stresses on the surrounding tooth tissues [26]. Such stresses can have a detrimental effect on the longevity of the restoration and the dentine–restoration interface.

2.3 Methods used to measure polymerization shrinkage

A variety of methods have been used for determining the polymerization shrinkage. These range from dilatometer methods, specific gravity methods and deflecting disc systems, to optical methods. Table 1 lists some of the shrinkage values obtained by various researchers; it must be noted that the details of the method and materials are important and this provides an idea of the variability encountered.

<table>
<thead>
<tr>
<th>Method</th>
<th>Shrinkage values (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilatometer [27]</td>
<td>2.58–3.7*</td>
</tr>
<tr>
<td>Microscope [23]</td>
<td>0.168–0.81†</td>
</tr>
<tr>
<td>Denitrometer [28]</td>
<td>5–6.6*</td>
</tr>
<tr>
<td>Deflecting disc [29, 30]</td>
<td>0.65–7.9*</td>
</tr>
<tr>
<td>Microscope [31]</td>
<td>0.17–0.48‡</td>
</tr>
<tr>
<td>Laser interferometry [32]</td>
<td>0.4–9*</td>
</tr>
<tr>
<td>Specific gravity [33]</td>
<td>1.35–3.22*</td>
</tr>
<tr>
<td>Linometer [34]</td>
<td>0.06–0.14*</td>
</tr>
<tr>
<td>Laser beam scanning [35]</td>
<td>0.65–1†</td>
</tr>
</tbody>
</table>

* Volume shrinkage.  † Linear shrinkage.
3 THE DVRT® METHOD

This method was based around a differential variable reluctance transducer (DVRT®) (MicroStrain Inc., Vermont, USA). The sensor was positioned by its barbs, with one or both being inserted into the unpolymerized material. The polymerization shrinkage of the material necessarily causes the movement of the barbs and these dimensional changes are then monitored by the transducer. Consequently, as the material polymerizes, the shrinkage can be recorded continuously with time. A schematic representation of the transducer is given in Fig. 1 along with the electrical and mechanical specifications in Table 2. The DVRT®, developed in the early 1990s, is capable of measuring linear displacements with a high degree of accuracy. Its overall length of 10 mm makes it suitable for inaccessible sites. The device consists of two coils and a free sliding core. The position of the core is detected by measuring the coils’ differential reluctance, using a sine wave excitation and a synchronous demodulator [36].

4 MATERIALS AND METHODS

The materials used in this study are given in Table 3 and the experimental setup used is given in Fig. 2. Auxiliary apparatus included a curing unit, with an 8 mm light

Table 3 Composite resins investigated in the DVRT method

<table>
<thead>
<tr>
<th>Code</th>
<th>Material</th>
<th>Manufacturer</th>
<th>Batch number</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEL</td>
<td>Heliomolar</td>
<td>Vivadent, Liechtenstein</td>
<td>460203</td>
</tr>
<tr>
<td>TET</td>
<td>Tetric</td>
<td>Vivadent, Liechtenstein</td>
<td>700204</td>
</tr>
</tbody>
</table>

Fig. 1 Schematic diagram of the DVRT®

Fig. 2 Schematic diagram of the experimental setup used in the DVRT method
guide (Lamp Heliolux GT PM2706, 12V, 75W, Vivadent) to irradiate the composite resin and initiate the polymerization, and a data logger capable of recording at a frequency of 1 Hz, to monitor the DVRT output. In all, three moulds, ‘mould A’, ‘mould B’ and ‘mould C’, were designed and made; these are shown in Fig. 3. Mould A, comprising Delrin parts, enabled the DVRT to be positioned parallel or perpendicular to the irradiation. One barb of the DVRT was within the material sample, 2.5 mm × 3 mm × 8 mm, while the other barb was placed outside the material. Mould B, similar to mould A, held both barbs within the material sample, 2.5 mm × 3 mm × 15 mm, and perpendicular to the irradiation. Mould C incorporated tooth sections and the DVRT was positioned parallel to the irradiation and only one barb was placed within the material.

The various experimental series undertaken are listed in Table 4. Series V consisted of tests using mould A, with the back face lubricated using a highly refined mineral oil. This was to hinder any bonding between the material and the back face and to further investigate the effects of the bond between the material and the mould and any influence this may have had on the polymerization shrinkage. The tooth sections used in mould C were human lower third molars with MOD (mesial occlusal distal) cavities prepared in them such that the resulting cavity was a channel from end to end. The material could then be placed into a well, bounded by enamel at the periphery and dentine around the rest. Tests were undertaken with untreated cavities, series VII and cavities with surface preparation, series VI, according to the manufacturer’s instructions.

A standard method of experimentation was adopted for all of the series. The mould was assembled and the material was placed in the mould recess or the tooth cavity (in the case of mould C) and levelled out. Lengths of Teflon tubing (CP Instrument Company Limited, Hertfordshire, UK) were used to cover the barbs of the DVRT, to facilitate easy removal. The barbs were inserted with one barb placed in the material and the other in the main body of the mould. An alternative arrangement was used with mould B in series IV when both barbs were inserted in the material. The system was allowed to stabilize and data logging was started. This was followed 60 s later by the onset of irradiation. Using the 8 mm light guide, the material was irradiated from a position immediately adjacent to the microscope slide. Irradiation was for 60 s and overall logging of data for 60 min. After completion, the DVRT was removed by simply lifting the barbs from the Teflon tubing, now set in the polymerized material. The diameter of the Teflon tubing and the dimensions of the cured material were measured using a micrometer.

4.1 Theory and data processing

For each of these runs, the data had to be converted to shrinkage values and then, for each material, plots of shrinkage against time were produced. The demodulator output was correlated with displacement using the following rationale:

\[
DVRT \text{ barb separation} = \text{transducer output} \times \text{calibration factor} \quad (1)
\]

\[
DVRT \text{ displacement } \Delta l = DVRT \text{ separation} - \text{initial separation} \quad (2)
\]

\[
\text{Original sample length} = \text{final sample length} + \text{final displacement} \quad (3)
\]
Table 4  Experimental series undertaken using the DVRT

<table>
<thead>
<tr>
<th>Series</th>
<th>Mould</th>
<th>DVRT alignment</th>
<th>Material</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A</td>
<td>Parallel to irradiation</td>
<td>TET</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>A</td>
<td>Perpendicular to irradiation</td>
<td>TET</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>A</td>
<td>Parallel to irradiation</td>
<td>HEL</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>B</td>
<td>Perpendicular to irradiation</td>
<td>HEL</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>A</td>
<td>Parallel to irradiation</td>
<td>HEL</td>
<td>Greased mould</td>
</tr>
<tr>
<td>VI</td>
<td>C</td>
<td>Parallel to irradiation</td>
<td>HEL</td>
<td>Surface treatment</td>
</tr>
<tr>
<td>VII</td>
<td>C</td>
<td>Parallel to irradiation</td>
<td>HEL</td>
<td>No surface treatment</td>
</tr>
</tbody>
</table>

Contributing length $l$

$= \text{original sample length} - \text{Teflon diameter}$  \hspace{1cm} (4)

Percentage linear shrinkage

$= \frac{\Delta l}{l \times 100\%}$  \hspace{1cm} (5)

5 RESULTS

The shrinkage plots obtained are given in Figs 4 to 10. Smoothing was applied to all of the DVRT plots, in order to provide a better overview of the data series. All samples can be seen to begin shrinking just after 60 s. The series conducted with the DVRT aligned parallel to the irradiation (series I and III in Figs 4 and 6 respectively) showed the shrinkage starting at 2.5 to 3 s after the onset of irradiation. Series II and IV (Figs 5 and 7) showed the shrinkage starting at a slightly later time of 5–7 s after the onset of irradiation. Series V conducted using greased mould A produced strikingly different results from its ungreased counterpart in series III and the results are shown in Fig. 8. The shrinkage is apparently directed towards the irradiation but is not followed with a return movement, as seen in Fig. 6 of Series III. The shrinkage profiles obtained while using mould C with the tooth sections, i.e. series VI and VII, are given in Figs 9 and 10. For all profiles the predominant shrinkage occurred within the first 300 s. As is evident from the figures, a mean plot was inappropriate, as was the determination of standard deviation values. The use of statistical analysis was thus rendered inconsequential by the nature of the results.
6 DISCUSSION

The series conducted with the DVRT aligned parallel to the irradiation (series I and III in Figs 4 and 6, respectively) showed the shrinkage starting at 2.5–3 s after the onset of irradiation. Series II and IV (Figs 5 and 7), where the DVRT was aligned perpendicular to the irradiation, showed the shrinkage starting at a slightly later time of 5–7 s after the onset of irradiation. This can be explained in terms of the causative factors of the shrinkage in each of the cases. Figure 11 is a schematic representation of the alternative alignments of the DVRT. The shaded regions depict the material considered to contribute to the shrinkage as measured by the DVRT in each of the alignments. It is apparent that the contributory material in (a) will begin shrinking before the equivalent contributory material in both cases of (b), simply because of the relative orientation to the irradiation source. This accounts for the difference in the timing of the onset of shrinkage between the two cases.

Fig. 8 Polymerization shrinkage results of series V

Fig. 9 Polymerization shrinkage results of series VI
It is apparent in Fig. 6 that there is a movement of material towards the initiating light, followed by a return movement away from the irradiation towards the distant corners of the mould. The initial movement towards the irradiation is to be expected as the material adjacent to the initiating light begins to polymerize and shrink. This sequence is propagated through the width of the sample. The far side of the sample, however, is in direct contact with the back face of the mould. As a consequence, an adhesive bond is created, and this is in direct opposition to the shrinkage movement of the material towards the irradiation. It is a combination of this bond and the advancing shrinkage that results in the movement of material away from the irradiation.

Figure 5 represents the shrinkage occurring in the plane perpendicular to the irradiation. The plots show a wide variety of responses. There was no method of ensuring the precise positioning of the barb within each sample, and this varied. This in part is considered to account for the wide variation in resultant plots, which would have been influenced by the barb's original position.

Series IV was the only series conducted using mould B, with which both barbs were inserted in the material. There was a notable difference in the results obtained. Series IV, with both barbs in the material, produced an overall picture of the shrinkage within the material. Series II, on the other hand, provided a more intrinsic picture of the movement of material within the mould. Such a distinct difference, as apparent in Figs 5 and 7, can be attributed to the presence of the second barb within the material. While a single barb in the material monitors the movement of the material in its vicinity, the use of both barbs gives an overall shrinkage value for that dimension. This accounts for the difference observed in the respective profiles.
Series V was conducted to examine the influence of the macromolecular bond between the material and the back face of the mould. This bond was prevented from forming by the introduction of grease to the face, and the results are shown in Fig. 8. Unlike the case for the ungreased counterpart (Fig. 6), the shrinkage is towards the irradiation, with no return movement. This endorses the rationale put forward for the return movement away from the irradiation, i.e. that it is due to the formation of a bond with the mould. This indicates that the shrinkage behaviour of a dental composite material is strongly influenced by the bonding to its surroundings. On the whole, the shrinkage values are higher for the greased mould than for the ungreased mould, with maximum linear shrinkages of 0.7 per cent and 0.4 per cent, respectively. This is as would be expected, with higher shrinkages in the unrestrained environment. The material in the ungreased mould does, however, shrink away from the irradiation later in the series. It is difficult to form a comparison between any values as the final state of stress of the material is unknown.

The profiles obtained for series VI and VII show much variation and this can be attributed to the variation in the position of the barb within the composite material. When the barb was placed in the lowest regions of the cavity, there was a movement towards the irradiation. This is a result of the material adjacent to the irradiation pulling the barb towards the irradiation and the lack of material between the barb and the tooth wall to pull back. As the original position of the barb in separate samples is nearer to the irradiation, this movement was reduced until a second movement came into play: the return movement away from the irradiation. This second movement is a direct result of the interfacial bond formed.

Figure 10 of series VII entailing no surface treatment shows the movement of the barb in each sample towards the irradiation. The extent of the return movement seen in series VI is not apparent in this series, although some samples show a slight return movement away from the irradiation. This difference between series can be attributed to the weaker bond between the material and the tooth boundary as a result of the lack of surface treatment, which would have promoted stronger adhesion. Furthermore, it was found that the position of the barb had an influence on the extent of the movement experienced. As the amount of material between the barb and the irradiation source increased, the initial movement increased, as did the initial rate of movement. Both Figs 9 and 10 show the initial movement of the barb just after the time of starting irradiation, at 60 s from the start of the data logging. The range of the movement varies between the two series and within them. Series VI with surface treatment exhibited a range of percentage movement of approximately 0.2–0.7 per cent, while series VII showed a range of 0.03–0.5 per cent. In both series, the barb movement settled within two minutes of the start of irradiation.

7 CONCLUSIONS

The DVRT method provided details of the shrinkage vectors within the material and provided valuable results indicating that polymerization shrinkage was highly dependent upon the region under investigation, as well as on the state of the surface. Such qualitative details provided by the DVRT method are relevant, as shrinkage is a vector quantity. The overall configuration in dental restorations is often anisotropic, depending on the degree of nonuniformity. The DVRT provided details of such shrinkage vectors within the material.

ACKNOWLEDGEMENTS

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