Original Article

Changes in mechanical properties of seven light-cured composite resins after thermal cycling

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Abstract: Objective To examine the changes of the mechanical properties of 7 different light-cured composite resins after thermal cycling and the correlations between these properties. Methods Seven different light-cured composite resins, including 2 microfilled composites (A110:AH and ESTELITE: Σ:ET), 3 microhybrid composites (ELITE:AT, Z250:ZS, and CharmFil plus:CP), and 2 nanohybrid composites (Z350:ZH and Grandio:GD), were prepared into test specimens with a diameter of 12 mm and a thickness of 1.0 mm. The specimens were stored in distilled water at 37 ℃ for 24 h prior to 1 000 thermal cycles of 5 ℃ for 15 s and 55 ℃ for 15 s. The biaxial flexural strength (σf) was tested using the ball-on-three-ball method at a crosshead speed of 0.5 mm/min (ISO4049). The fracture surface was observed under scanning electron microscope (SEM), and the remaining specimens underwent Knoop hardness test with a 50-g loading for 10 s. Results The highest and lowest Weibull modulus was observed in AH (18.752) and AT (5.290) group, respectively. The highest and lowest biaxial flexural strength was observed in ZS (158.2 MPa) and ET (54.0 MPa) groups, respectively. The σf of the tested materials decreased in the order of microhybrid composite, nanohybrid composite, and microfiller composite, and the σf showed no significant difference between the composites with a similar filler (P>0.05). The fracture number was positively correlated to the strength of the material. The Knoop hardness numbers (H) was the highest in GD group (110.81±14.77 kg/mm²) and the lowest in AH group (42.81±1.91 kg/mm²). SEM showed that the interface region of the matrix and the filler was vulnerable to crack formation. Conclusion The nanohybrid composite resins better suit clinical applications than microhybrid composites. The applicability of Knoop hardness test in hardness measurement of the composite resins needs to be further demonstrated.

Key words: light-cured composite resins; thermal cycling; biaxial flexure strength; Knoop hardness

INTRODUCTION

Light-cured composite resins are widely used as dental restorative materials for their convenience of handling, good aesthetic effects, and good physical and mechanical properties. A range of factors may affect the performance of the resins, such as the types and relative content of the matrix resins and coupling between the fillers (organic or inorganic) and the matrix, among which the inorganic fillers is a key factor. The hardness and mechanical strength of the composite resins increase with the degree of polymerization [1,2]. The monomer viscosity and ratio, size of the fillers and the difference in the refractive index of the organic and inorganic constituents all contribute to a decreased degree of conversion [3].

Researchers have made considerable improvements in light-cured composite resins. The flexural strengths of such materials have been increased from 60 to 80 MPa (as of the microfilled composite resin systems) and to 120-160 MPa for the microhybrid composites [4], and nanofiller composite resins have been available. The partial replacement of Bis-GMA with UDMA and the increment of TEGDMA to 90% in Bis-GMA-based materials led to an increased conversion and flexural strength of the composites. Bis-EMA was developed as a substitute for Bis-GMA. There have also been improvements in the dental light curing units, such as quartz-tungsten-halogen lamps, plasma arc lamps, and light-emitting diodes.

Dislodgement of the filler particles was observed for resin composites after thermal cycling. It was concluded that thermal cycling affects the surface texture of the 7 resin composites examined [5].

The main disadvantages of the Knoop hardness test are the difficulty in microscopic measurement of the indentation (with an accuracy of 0.5 μm) and the time-consuming preparation of the sample and application of the indenter. The error increases with decreased indentation sizes. The Vickers and Knoop hardness test
procedure also has problems associated with the operator to affect the test results, even though automated units are available \(^a\). The use of the converted hardness values is limited to comparative purposes only. Conversion from the microhardness values to tensile strength and other hardness scales (e.g. Rockwell) is available for many metals and alloys. In addition, whether these values can be applied to composite resins needs to be considered.

In this study, we evaluated the mechanical properties of 7 different components of light-cured composite resins after immersion in water and thermal cycling and explored the relationship between these properties to provide an experimental basis for further modification of the materials to better suit clinical requirements.

MATERIALS AND METHODS

Specimen preparation

Ten specimens of each composite resin (Tab.1) were prepared according to the manufacturer’s instructions and the ISO. The composite resins were condensed into a mold inside a plastic steel mold, positioned on a glass slab, and covered with a polyethylene film. Another glass slab was pressed on the mold to obtain specimens with the required dimensions (12 mm in diameter and 1.0 mm in thickness). The dimensions of the specimens were confirmed using a digital caliper (Tokyo, Japan). Both surfaces of all the specimens were light-cured (VCL401, KERR SDS, USA) for 20 s, and polished with 1000 grit SiC paper to remove the excess material.

Material testing

After a 24-h storage at 37 °C in water, the samples were cycled thermally for 1 000 cycles (5 °C and 55 °C alternatively with a dwell time of 15 s). Ball-on-three-ball tests at a crosshead speed of 0.5 mm/min were performed (BINSTRON, UK/4301, 5KN). The largest fragment in each group was examined using scanning electron microscopy. The remaining fragments were stored in distilled water at 37 °C for 24 h, and highly polished with 1 200 to 2 000 grit SiC paper to allow accurate observations of the indent. A microhardness test (indentation load of 50 g and dwell time of 10 s) was performed for each specimen, and the diagonals were measured microscopically at a 400 × magnification (MHT-1, MATSUZAWA SEIKI CO. LTD, Tokyo, Japan).

Statistical analysis

The test results of the biaxial flexure strength were analyzed using Weibull statistics (Macintosh Computer Inc). All the results were analyzed statistically using analysis of variance (ANOVA) at a significance level of 5%. The relationship between the two properties was determined using Pearson’s correlation test.

<table>
<thead>
<tr>
<th>Material</th>
<th>Code</th>
<th>Composition</th>
<th>Filler loading (vol%/wt%)</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A110</td>
<td>AH</td>
<td>Silica, Bis-GMA, TEGDMA</td>
<td>40/56</td>
<td>3 M, USA</td>
</tr>
<tr>
<td>ESTELITEΣ</td>
<td>ET</td>
<td>Zirconia/silica, Bis-GMA, TEGDMA</td>
<td>71/82</td>
<td>Tokuyama Dental Corp., Japan</td>
</tr>
<tr>
<td>AELITE All-Purpose Body</td>
<td>AT</td>
<td>Amorphous Silica Glass Filler, TEGDMA</td>
<td>Ethoxylated Bis-GMA</td>
<td>Bisco, USA</td>
</tr>
<tr>
<td>Z250</td>
<td>ZS</td>
<td>Silica, Bis-GMA, Bis-EMA, UDMA</td>
<td>60/-</td>
<td>3 M, USA</td>
</tr>
<tr>
<td>CharmFil plus</td>
<td>CP</td>
<td>Silicon, Dioxide Bis-GMA, UDMA</td>
<td>_</td>
<td>Dentkist, Korea</td>
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<tr>
<td>Z350</td>
<td>ZH</td>
<td>Zirconia/silica, Bis-EMA, Bis-GMA, UDMA, TEGDMA</td>
<td>59.5/78.5</td>
<td>3 M, USA</td>
</tr>
<tr>
<td>Grandio</td>
<td>GD</td>
<td>Inorganic filler, Bis-GMA, TEGDMA</td>
<td>71.4/87</td>
<td>VOCO, Germany</td>
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</table>

RESULTS

The highest and lowest Weibull modulus was observed in AH (18.752) and AT (5.290) group, respectively (Tab.2). The highest and lowest biaxial flexural strength was observed in ZS (158.2 MPa) and ET (54.0 MPa) groups, respectively. Under the same press strength, the microfiller and microhybrid composite resins showed the highest and lowest failure probability, respectively (Fig.1). The order of the materials used in this study was as follows: microhybrid composite > nanohybrid composite > microfiller composite. There was no significant difference in the order between the composites with a similar filler (P>0.05, Fig.2). The fracture numbers showed a positive correlation to the material strength (Tab.3). The Knoop hardness numbers (H) was the highest in GD group (110.81 ± 14.77 kg/mm²) and the lowest in AH group (42.81 ± 1.91 kg/mm²) (Tab.4). The biaxial flexural strength of microhybrid composite resins was the highest among the specimens examined (Fig.3). Pearson correlation analysis indicated a positive correlation between the Knoop hardness and biaxial flexural strength (P<0.05). Fracture surface analysis of the specimens showed that the composite resin failure...
occurred along the matrix resin and resin/filler interface region, and the cracks spread in a conical shape from the maximum stress zone (Fig. 4, 5).

Tab.2 Weibull analysis data of light-activated composite resins

<table>
<thead>
<tr>
<th>Parameter</th>
<th>AH</th>
<th>ET</th>
<th>AT</th>
<th>ZS</th>
<th>CP</th>
<th>ZH</th>
<th>GD</th>
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<tbody>
<tr>
<td>α₀(0.5)</td>
<td>56.4</td>
<td>54.5</td>
<td>150.2</td>
<td>160.2</td>
<td>128.1</td>
<td>128.5</td>
<td>125.1</td>
</tr>
<tr>
<td>m</td>
<td>18.752</td>
<td>12.055</td>
<td>5.290</td>
<td>7.297</td>
<td>9.121</td>
<td>7.146</td>
<td>8.220</td>
</tr>
<tr>
<td>σ₀</td>
<td>57.5</td>
<td>56.2</td>
<td>161.4</td>
<td>168.4</td>
<td>134.2</td>
<td>135.3</td>
<td>130.8</td>
</tr>
<tr>
<td>σ₀(avg)</td>
<td>56.0</td>
<td>54.0</td>
<td>148.9</td>
<td>158.2</td>
<td>127.6</td>
<td>127.0</td>
<td>123.7</td>
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<tr>
<td>CV</td>
<td>0.057</td>
<td>0.091</td>
<td>0.203</td>
<td>0.137</td>
<td>0.108</td>
<td>0.147</td>
<td>0.129</td>
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<tr>
<td>N</td>
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<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
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Tab.3 Fragment numbers of light-cured composite resins

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<th>3</th>
<th>4</th>
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<td>3</td>
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</tr>
<tr>
<td>ZS</td>
<td>3</td>
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<td>5</td>
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<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
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<td>4</td>
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<tr>
<td>CP</td>
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<td>2</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>3</td>
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<tr>
<td>ZH</td>
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<td>2</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>3</td>
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<tr>
<td>GD</td>
<td>2</td>
<td>2</td>
<td>2</td>
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<td>3</td>
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Tab.4 Knoop hardness test data of light-activated composite resins

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<th>Material</th>
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<th>5</th>
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<tr>
<td>AH</td>
<td>43.2</td>
<td>44.8</td>
<td>39.7</td>
<td>44.2</td>
<td>41.4</td>
<td>41.8</td>
<td>44.6</td>
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<tr>
<td>ET</td>
<td>46.1</td>
<td>52.4</td>
<td>44.7</td>
<td>47.9</td>
<td>51.2</td>
<td>50.9</td>
<td>53.4</td>
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<tr>
<td>AT</td>
<td>69.5</td>
<td>60.7</td>
<td>67.8</td>
<td>61.8</td>
<td>62.7</td>
<td>65.4</td>
<td>60.2</td>
</tr>
<tr>
<td>ZS</td>
<td>66.4</td>
<td>66.9</td>
<td>83.0</td>
<td>73.8</td>
<td>65.6</td>
<td>72.2</td>
<td>72.6</td>
</tr>
<tr>
<td>CP</td>
<td>55.4</td>
<td>49.2</td>
<td>56.0</td>
<td>54.6</td>
<td>53.8</td>
<td>52.7</td>
<td>52.8</td>
</tr>
<tr>
<td>ZH</td>
<td>78.8</td>
<td>82.6</td>
<td>74.7</td>
<td>87.8</td>
<td>80.0</td>
<td>73.0</td>
<td>82.4</td>
</tr>
<tr>
<td>GD</td>
<td>101.3</td>
<td>97.6</td>
<td>135.0</td>
<td>127.2</td>
<td>105.2</td>
<td>98.2</td>
<td>111.2</td>
</tr>
</tbody>
</table>

DISCUSSION

The deterioration of the composite resin, seen as cracks on the surface, occurs at the interface of the filler and matrix. Thermal cycling seriously decreased the performance of the light-cured composite resin, which is supported by the findings in previous studies. These mechanical properties of the materials were positively related. In this study, GD showed the highest hardness value after thermal cycling to simulate the oral environment, but this was still substantially lower than that of enamel (260-360 KHN). The deficiencies in the mechanical properties of the resins are affected by the types and relative content of the matrix resin, coupling between the inorganic or inorganic filler and the matrix, types of dental light curing units, curing tip distance or diameter, and temperature. In this study, we controlled all the compounding factors and only the component of the material differed. The differences in the monomer structure resulted in a

Fig.1 Weibull plots of the biaxial flexure strength of the light-cured composite resins.
significantly different morphology and physical properties
of the resulting polymer networks. The size and shape
of the heterogeneities affected the final mechanical
properties of the polymers, particularly the impact resistance [18].
Researchers have attempted to develop a monomer with
better performance than Bis-GMA. UDMAD has low
viscosity and good chain flexibility [19]. Bis-EMA is
characterized by a low water imbibition. TEGDMA
increases the level of double-bond conversion and forms
the most flexible polymer network structure [20–22], but
shows a high water imbibition. A combination of a larger
silica filler and microfiller would improve the properties
of the composite resin systems [23–24].

According to Kim et al, round particles had the
highest filler content. Composites with the highest filler
by volume showed the highest flexural strength and
hardness [25]. The filler concentration plays a prominent
role in determining the properties of posterior composite
resins [26]. In this study, AH and ET had the same matrix,
and ET contained 100% spherical filled composite with
a higher volume than AH. The of and H were similar
between AH and ET. Therefore, the filler volume is not
the only factor responsible for the differences in the
performance between the two materials, but rather, the
filler species, particle size, particle distribution, chemical
constituents, refractive index, and surface treatment all
play a role. Another possible reason for the result is
water absorption that caused hydrolysis of the silane
coupling agent to give rise to micro-cracks, which
damaged the bonding between the matrix and the filler.
Increasing the filler volume should reduce water
absorption, but the increase in water uptake is due
directly to the presence of porosity and the filler particle
aggregates in the microstructure [27]. According to Bea et
al [7], immersion in water and thermal cycling significantly
decreased the mechanical properties of light-cured
composite resins.

The accuracy of the Knoop hardness needs to be
considered. The main drawback of the Knoop test is the
need to optically measure the indent size. This requires
the test point to be highly polished in order to observe
the indent well enough to allow an accurate measurement.
Polishing may alter the thickness of the specimen, thus
leading potentially to a difference in the measurement
results from those for an unpolished specimen. In
addition, a resin composite has the capacity to reduce
light penetration, and consequently decrease the polymerization effectiveness of the bottom surface of the sample. The top surface of the increments showed a greater microhardness than the bottom surface (0.5 mm in height)\(^{20}\). In some studies of the Knoop hardness of composite resins, the specimens prepared often can be slightly greater than 1.0 mm in height. Therefore, even if 1.0 mm height specimens were prepared and both surfaces were light cured, there would be significant differences in the hardness between the surface and the center of the specimens. Because of the different performance of the materials, some of the specimens are liable to produce bubbles, which can be observed by optical microscopy. Some other factors, such as refraction and reflection of light, surface roughness\(^{20}\) and diameter of the light guide tip\(^{18}\), can also affect the results. GD is the least transparent specimen. However, further research is needed to determine if it is suitable for composite resins.

**CONCLUSION**

Thermal cycling seriously decreases the performance of light-cured composite resin. After thermal cycling, the of the materials decreases in the order of microhybrid composite, nanohybrid composite, and microfiller composite, and the H value decreases in the order of nanohybrid composite, microhybrid composite, and microfiller composite. Under clinical conditions, GD has the highest H value. ZS shows the highest biaxial flexural strength. The nanohybrid composites may perform better than microhybrid composites. After thermal cycling, the microfiller composite resins containing a similar matrix, filler volume and resin properties show no absolute positive relationship. Further study will be needed to examine the factors that affect the measurement of the Knoop hardness, and to determine if it is suitable for composite resins. The properties of H and of are positively related.

**ACKNOWLEDGEMENT**

We thank Dr. Lee Min-ho for kindly providing the compound dental material.

**References**


七种光固化复合树脂冷热循环后机械性能评价

姜玲, 陈从容, 金东春, 李敏镐, 贾春圣, 周聪, 张晓燕, 孙永智, 金光春

摘要: 目的 研究7种不同类型的光固化复合树脂在冷热循环试验后的机械性能, 探讨其性能之间的关系。方法 将每种树脂(A110:AH, ESTELITE Sigma; ET, Aelite; AT, Z250; ZS, CharmFil plus; CP, Z250; ZH, Grandio; GD,其中 AH, ET为微充填复合树脂, AT, ZS, CP为混合型复合树脂, ZH, GD为纳米型复合树脂)制成直径为12 mm, 厚度为1.0 mm的实验样本。所得样本在37 ℃的蒸馏水中浸泡24 h, 然后在5 ℃和55 ℃下间隔30 min冷热循环1 000次。应用尖端速率为0.5 mm/min的双轴挠曲强度试验测量材料的强度值(ISO4049), 所得数据采用Weibull和ANOVA统计学分析。样本断面经扫描电镜观察, 剩余样本碎片经Knoop硬度测试试验(负载50 g, 时间10 s)。结果 最高和最低的Weibull系数值分别为出现在AH (18.752) 和AT (5.290)组, 最高和最低的双轴挠曲强度试验值分别出现在ZS (158.2 MPa) 和ET (54.0 MPa)组。不同填料的强度大小依次为混合型复合树脂>纳米型复合树脂>微充填复合树脂, 具有相同类型填料的复合树脂之间的强度值差异没有统计学意义(P>0.05), 且强度试验所得碎片的数量与材料强度大小成正相关。GD组的硬度值最大(100.81±14.77) kg/mm2, AH组平均硬度值最小(42.81±1.91) kg/mm2, 复合树脂的强度值与硬度值成正相关。扫描电子显微镜观察显示树脂基质和填料之间的裂纹形成的薄弱部位。结论 纳米型复合树脂比混合型复合树脂更适于临床应用。Knoop硬度试验是否适用于复合树脂材料的硬度测量还需要进一步证实。

关键词: 光固化复合树脂; 冷热循环试验; 双轴挠曲强度; Knoop硬度

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