The purpose of the present investigation was to clarify the relationship between polymerization shrinkage of the matrix-monomers of the composite resins and marginal leakage. Eight matrix-monomers differing in polymerization shrinkage (2.7 to 11.4%) were experimentally prepared. Experimental composite resins were made from these monomers filling with 0.2 μm spherical silica particles with a constant volume of 54.5 percent. Standardized Class V cavities were prepared on the labial surface of freshly extracted bovine teeth. Before placement of each restoration, the cavities were conditioned and primed with an experimentally prepared bonding agent in which consist of the Bis-GMA-TGDMA system.

The marginal leakage was evaluated by the scores depending on the depth of the dye penetration. As a result, an S-shaped curve of correlation showed a clear transition at the point of 7 percent of the polymerization shrinkage of the matrix-monomer.

**Key words:** Polymerization shrinkage, Marginal leakage, Composite resin

### INTRODUCTION

The intimate marginal adaptation of composite resins is considered to be the most important requisite, and this is strongly influenced by polymerization shrinkage, thermal expansion or mechanical properties of the resins.

The highly loaded composite resins, developed recently have yielded good results on thermal expansion and mechanical properties. Consequently, little attention has been paid to the importance of the polymerization shrinkage.

Asmussen reported the relationship of wall-to-wall polymerization shrinkage of composites to their various components and the effects of diluent monomer on the contraction in composites based on Bis-GMA. Brauer et al. studied the marginal adaptation of Bis-GMA-based composites containing various diluents. Davidson et al. demonstrated the influence of contraction stresses, developed during the polymerization of composites, on adhesion to dentin.

The purpose of the present investigation was to clarify the relationship between polymerization shrinkage of the matrix-monomers of the composite resins and marginal leakage.

### MATERIALS AND METHODS

Eight matrix-monomers differing in polymerization shrinkage (2.7 to 11.4%) were experimentally prepared as listed in Table 1.

The rate of polymerization shrinkage (SV) was calculated by the specific gravities of
the monomer and the polymer using the following equation:

\[
S_v = \frac{1}{\frac{dm}{dp}} - 1 \times 100 \text{ (\%)}
\]

where \(dm\) is the specific gravity of the monomer, and \(dp\) is the specific gravity of the polymer.

The specific gravities of the monomers were determined using a pycnometer at a constant temperature room of 20°C, and those of the polymers were determined by measurement of the balancing point of a hydrometer in KCl solutions of varying concentrations.

### Table 1  Polymerization shrinkage of several monomer formulations

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Monomer</th>
<th>Wt %</th>
<th>Specific gravity</th>
<th>Polymerization shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-1</td>
<td>Bis-GMA</td>
<td>50.2</td>
<td>1.169</td>
<td>1.200</td>
</tr>
<tr>
<td></td>
<td>M-9G(^1)</td>
<td>49.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-2</td>
<td>Bis-GMA</td>
<td>51.0</td>
<td>1.170</td>
<td>1.218</td>
</tr>
<tr>
<td></td>
<td>9G(^2)</td>
<td>16.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>M-9G</td>
<td>33.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-3</td>
<td>Bis-GMA</td>
<td>51.1</td>
<td>1.163</td>
<td>1.225</td>
</tr>
<tr>
<td></td>
<td>9G</td>
<td>31.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>M-9G</td>
<td>17.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-4</td>
<td>Bis-GMA</td>
<td>50.3</td>
<td>1.156</td>
<td>1.227</td>
</tr>
<tr>
<td></td>
<td>9G</td>
<td>49.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-5</td>
<td>D-2.6E(^3)</td>
<td>77.7</td>
<td>1.101</td>
<td>1.192</td>
</tr>
<tr>
<td></td>
<td>NPG(^4)</td>
<td>22.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-6</td>
<td>D-2.6E</td>
<td>80.6</td>
<td>1.114</td>
<td>1.210</td>
</tr>
<tr>
<td></td>
<td>3G(^5)</td>
<td>19.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-7</td>
<td>Bis-GMA</td>
<td>55.5</td>
<td>1.133</td>
<td>1.235</td>
</tr>
<tr>
<td></td>
<td>3G</td>
<td>44.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-8</td>
<td>Bis-GMA</td>
<td>42.8</td>
<td>1.050</td>
<td>1.185</td>
</tr>
<tr>
<td></td>
<td>NPG</td>
<td>57.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) \(\text{CH}_3\text{CH}_2\text{CH}_2\text{O}n\text{C}=\text{C}=\text{CH}_2\)

2) \(\text{CH}_2=\text{C}-\text{C}=\text{C}=\text{CH}_2\)

3) \(n=3\ldots 36\)

4) \(n=9\ldots 96\)

5) \(\text{CH}_3\text{CH}_2\text{CH}_2\text{O}n\text{C}=\text{C}=\text{CH}_2\)

6) \(n=2.6\)

7) \(\text{CH}_3\text{CH}_2\text{CH}_2\text{O}n\text{C}=\text{C}=\text{CH}_2\)
the above temperature.

Experimental composite resins were made of these monomers by loading with 0.2 μm spherical silica particles at a constant volume of 54.5 percent.

Standardized Class V round cavities, 3 mm in diameter and 2 mm in depth, were prepared on the labial surface of freshly extracted bovine teeth. Each cavity was conditioned with 37% phosphoric acid solution for one minute. Before placement of the restoration, the cavities were primed with an experimentally prepared bonding agent consisting of the Bis-GMA-TGDMA system. Five teeth for each series were stored in water at 37°C for 24 hours. After careful finishing, the teeth were immersed in 0.1% aqueous solution of basic fuchsin under thermal cycling of sixty times between two water baths at 4°C and 60°C.

After removal from the dye, the restored teeth were cut longitudinally and observed under a stereomicroscope. The marginal leakage was evaluated by the scores depending on the depth of the dye penetration as shown in Figure 1.

![Diagram of marginal leakage](image)

**Table 2** Mean degree of marginal leakage of composites prepared with several monomer formulations

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Polymerization shrinkage (‰)</th>
<th>Mean degree of marginal leakage</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-1</td>
<td>2.7</td>
<td>0</td>
</tr>
<tr>
<td>M-2</td>
<td>3.9</td>
<td>0</td>
</tr>
<tr>
<td>M-3</td>
<td>5.1</td>
<td>0</td>
</tr>
<tr>
<td>M-4</td>
<td>5.8</td>
<td>0.2</td>
</tr>
<tr>
<td>M-5</td>
<td>7.7</td>
<td>2.8</td>
</tr>
<tr>
<td>M-6</td>
<td>7.9</td>
<td>3.0</td>
</tr>
<tr>
<td>M-7</td>
<td>8.2</td>
<td>3.2</td>
</tr>
<tr>
<td>M-8</td>
<td>11.4</td>
<td>3.0</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

The mean degree of marginal leakage of the composite resins prepared with several monomer formulations is shown in Table 2. The S-shaped curve of the correlation demonstrated a clear transition at the point of 7 percent of the polymerization shrinkage of the matrix-monomer. (Figure 2)

The relationship between polymerization shrinkage of matrix-monomer and marginal leakage affected by filler content is shown in Figure 3. Marginal adaptation improved
Table 3 Mean degree of marginal leakage of commercially available composite resins

<table>
<thead>
<tr>
<th>Material</th>
<th>Bonding agent</th>
<th>Mean degree of marginal leakage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adaptic Radiopaque</td>
<td>Bis-GMA-3G*</td>
<td>0.8</td>
</tr>
<tr>
<td>Clearfil F II</td>
<td>Bis-GMA-3G*</td>
<td>0.6</td>
</tr>
<tr>
<td>Superlux</td>
<td>Bis-GMA-3G*</td>
<td>1.2</td>
</tr>
<tr>
<td>Silar</td>
<td>Bis-GMA-3G*</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* Experimentally made liquid resin

by increasing filler content.

The mean degree of marginal leakage of four commercially available composite resins is shown in Table 3. Clearfil F II, which contains the largest quantity of the inorganic filler among the four materials investigated, showed the least marginal leakage. In contrast, Superlux with the smallest quantity of the inorganic filler showed the greatest marginal leakage. From these data, it is considered that the increasing quantity of the filler compensated for the polymerization shrinkage of the matrix-monomer and improved the marginal adaptation of the composite resin.

CONCLUSION

1. An S-shaped curve of correlation showed a clear transition at the point of 7 percent of the polymerization shrinkage of the matrix-monomer.
2. It is considered that an increase in the filler content compensated for the polymerization shrinkage of the matrix-monomer and improved the marginal sealing property of the composite resin.

ACKNOWLEDGEMENT

This study was supported in part by a Grant-in-Aid for Special Project Research “Design of Multiphase Biomedical Materials” 1984, from the Ministry of Education, Science and Culture, Japan.

REFERENCES

ジウム含有量の低い金パラ合金についても測定した。接
着耐久性を評価するため4℃と60℃の水中熱サイクルを
最高2,000回まで行なってから引張り接着強さを測定し
た。その結果各表面処理のうち接着耐久性の向上に有
効であったのは加熱酸化処理、Sn 電析処理、シリー
ター処理などであった。また2種の接着材のうちでは
4-META-MMA-TBB 系レジンの方が接着耐久性がす
ぐれていた。電解エッチングは被着面の粗化化には有効
であったが接着強さにはほとんど効果がなかった。これ
は電解エッチングによって最表面に貴金属成分がより多
く残存したためであると考えられた。

純チタン・クラウンの臨床応用

井田一夫*、谷嘉明*、堤定美*、都置谷紀宏*、南部敏之*、
末澤一彦**、川添徳応**、中村雅彦**、和田弘毅****

*京都大学医学高分子研究センター歯科材料研究部門　**大阪歯科大学歯科工学部第二講座　***京都工芸繊維大学工芸学部無機材科学科　****和田精密歯科研究所

純チタンの機械的性質は貴金属合金に近く、耐蝕性や
生体安全性もすぐれているので、新たな機能開発された製
造方法により製作された純チタンのクラウン100本以上
を2年間に亘り臨床的に使用したところ、すぐれた結果が得
られた。

純チタン・クラウンの適合性は銀-パラジウム合金の

複合レジン修復材のマトリックスモノマーの
重合収縮率と辺縁封鎖性との関係

谷嘉明*、鈴木勝己**、浜田敏裕**、湯浅茂樹**

*京都大学医学高分子研究センター歯科材料研究部門　**德山曹達兵庫研究所

マトリックスモノマーの重合収縮率と辺縁封鎖性との
関係を定量的に明らかにすることを目的として、以下の
実験をおこなった。異なる重合収縮率のもつマトリックス
モノマーを5種類調製し、コンポジットレジンを試作
した。なお、フィラーとして0.2μmの球状シリカを用
い、充填率は54.5vol%に一定とした。固化前凝集面の円形
窓洞に試作コンポジットレジンを塗製した。97℃で水に
24時間浸漬保存後、辺縁部を仕上げ研磨し、0.1μm フラ
シン水溶液中でサマルサイクリング処理による色素浸
透試験をおこなった。修復歯の正中部を破断し、研磨し、
その断面における色素の浸透度から辺縁封鎖性を評価し
た。

その結果、マトリックスモノマーの重合収縮率が7%
付近に変曲点をもつS字形の相関曲線が得られ、重合
収縮率と辺縁封鎖性との間に明確な相関関係のあること
をあきらかにした。また、フィラー充填率の増大がマト
リックスモノマーの重合収縮を補償し、辺縁封鎖性が改
善されることも示唆された。

多官能性モノマーの合成と物性について
（第6報）分子内にスピロ環を有するジメタクリレートの合成と物性について

川口貞稀、福島忠男、宮崎光治、堀部隆

福井大、理工

歯科用レジン材料の物性を改良することを目的とし
て、分子内にスピロ環を有するジメタクリレート3.9-