In vivo Wear Pattern of Experimental Composite Resins based on Different Resin Monomers

Kazuhito SEKIYA, Akira OKAMOTO, Masayoshi FUKUSHIMA and Masaaki IWAKU
Department of Operative Dentistry and Endodontics, Niigata University School of Dentistry, 5274, Gakkocho-dori 2-bancho, Niigata 951, Japan

Received July 26, 1993/Accepted October 15, 1993

This study investigated the effects of various monomer systems on composite resin wear in vivo. Experimental light-cured composite resins were prepared employing four different monomer systems: (1) Bis-GMA type, (2) D-2.6E type, (3) UDMA type, (4) UTMA type. The resin monomers consisted of 70wt% main monomer and 30wt% TEGDMA. These composites contained 80wt% fine quartz. The resins were placed in 2 mm diameter cylindrical cavities located in the occlusal contact area or the contact free area in cast crowns, temporarily set in a mouth. The crowns were removed at monthly intervals, for longitudinal SEM observation. Two months after setting, wear was analyzed, using an electron probe surface roughness analyzer. Microabrasion of the resin matrix and loss of filler particles were observed for all types of monomer systems. The effect of matrix resin systems on occlusal wear was smaller than that of filler systems.

Key words: Wear, Matrix monomers, ERA observation

INTRODUCTION

In recent decades, use of the synthetic composite resin introduced by Bowen\(^1\) has become popular in dental practice. This resin is adequate for use in Class I and Class II cavities in posterior teeth, because it possesses aesthetic and adhesive properties superior to those of the amalgam used in posterior teeth. The results of long-term evaluations of posterior composites in vivo\(^2,3\) showed that composite resins, though useful and effective for posterior restorations, are still subject to occlusal wear and marginal fractures. Therefore, the ingredients of composite resins, i.e., fillers, base resin monomers and coupling agents, have been changed to improve mechanical properties.

Although Bowen's Bis-GMA resin does have certain disadvantages as a binder for composite restorations, it has continued to enjoy the most extensive use. The disadvantages were a high viscosity that requires use of diluent monomers, difficulty in synthesizing a pure composition, strong air inhibition to polymerization, and high water absorption because of the diluents used and hydroxyl groups in the Bis-GMA molecule\(^4\). These problems have long been recognized and have led to the development of composite resins which employ various hydrophobic monomers or monomers which can form effective cross-linked polymers\(^5-9\). However, little is known about the structural effects of resin monomers on in vivo wear behavior. In a previous study\(^10\), the effects of a number of filler systems, regarding occlusal wear on composite resin was reported. Results showed that filler systems had considerable effect on occlusal wear. The findings also indicated that the dispersion of
colloidal silica among larger filler particles used in the hybrid type was most effective in enhancing the wear resistance of the resin matrix.

In this study, a method using temporary metal crowns\textsuperscript{11) was used to observe the in vivo wear pattern of composite resins by SEM (scanning electron microscope) and ERA (electron probe surface roughness analyzer), and the effect of matrix systems on occlusal wear was investigated.

MATERIALS AND METHODS

Experimental composite resins
Experimental light-cured composite resins with four different monomer systems\textsuperscript{*} were used; (1) Bis-GMA type (2, 2-Bis (p-2-hydroxy-3-methacryloxypropoxyphenyl) propane), (2) D-2.6E type (2, 2-Bis (4-methacryloxypropoxyphenyl) propane), (3) UDMA type (Urethane dimethacrylate), (4) UTMA type (Urethane tetramethacrylate) (Table 1). For chemical structures of the main monomers and diluent TEGDGA, see Fig. 1. Conventional filler\textsuperscript{11) was selected in the case of those composites, and fine quartz filler and colloidal silica filler without silane treatment were used (Table 2). In addition, unfilled resins, with the four different monomer systems described above, were prepared for measurement of microhardness.

Measurement of microhardness
Unfilled resins based on the Bis-GMA type, D-2.6E type, UDMA type, and the UTMA type were poured into a teflon mold (10 mm in diameter and 5 mm in depth) with the ends covered by glass plates. They were photopolymerized for 90 seconds on the top surface and for an additional 90 seconds on the bottom with a light-curing unit\textsuperscript{**}. After the cured resin was removed from the mold, the surface of the specimen was polished with silicon carbide paper #1500\textsuperscript{3} under running water and with 0.06\textmu m alumina paste\textsuperscript{##}. Knoop hardness was measured.

<table>
<thead>
<tr>
<th>Table 1 Monomer composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Bis-GMA</td>
</tr>
<tr>
<td>D-2.6E</td>
</tr>
<tr>
<td>UDMA</td>
</tr>
<tr>
<td>UTMA</td>
</tr>
<tr>
<td>TEGDMA</td>
</tr>
<tr>
<td>Camphoroquinone</td>
</tr>
<tr>
<td>Dimethylaminoethylmethacrylate</td>
</tr>
<tr>
<td>Inhibitor</td>
</tr>
<tr>
<td>Pigments</td>
</tr>
</tbody>
</table>

\* Experimental materials, Kuraray Co., Ltd., Osaka, Japan
\** Suncure light, Sankin Industry Co. Ltd., Tokyo, Japan
\# Waterproof paper, Marumoto kogyo Co. Ltd., Tokyo, Japan
\## Alumina polishing powder, Marumoto kogyo Co. Ltd., Tokyo, Japan
Fig. 1  Structural formulas of matrix resin monomers.
Table 2  Filler Composition (wt%)

<table>
<thead>
<tr>
<th>Filler</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine quartz filler*</td>
<td>82</td>
</tr>
<tr>
<td>Untreated colloidal silica filler</td>
<td>(80)</td>
</tr>
<tr>
<td>Monomer</td>
<td>18</td>
</tr>
</tbody>
</table>

* The mean particle-size is 4 micron meters diameter.
Coupling agent: \( \gamma \)-methacryloxypropyltrimethoxy silane

...sured, both immediately after polishing, and after storage in distilled water, at 37°C for 2 months, using hardness tester\(^\circ\). Microhardness was measured with a 50g load, for 30 seconds. Five measurements were performed on each of five specimens within each unfilled resin monomer and their mean values were assessed. The data were analyzed by oneway analysis of variance for detection of significant differences at a level of 0.05.

**Observation of occlusal wear by SEM and ERA**

Young adult volunteers (24-26 years old), needing full-crown molar restorations that would be in contact with enamel antagonists were selected for this study. First, the cast gold-silver-palladium alloy\(\text{\textregistered}\) full coverage crowns were formed for these molars, and three or four small cylindrical cavities (2 mm in diameter \(\times\) 1 mm in depth) limited to the occlusal contact area (OCA) or contact free area (CFA) were prepared on each occlusal surface of the crowns. Composite resins were then placed in the prepared cavities. After occlusal adjustments were made to assure proper fit, these resin fillings were polished using silicon polishing points\(\text{§}\) and 0.06\(\mu\)m alumina paste\(\text{\##}\). Before placement in patients' mouths, the fillings were gold-ion coated\(\text{\$}\), and observed at the baseline, by SEM\(\text{\textasteriskcentered}\). These micrographs were taken at magnifications of 50 \(\times\), 200 \(\times\), 1000 \(\times\) and 3000 \(\times\). The crowns were subsequently removed after one and two months, and the microstructures of worn surfaces of each material were longitudinally compared with the baseline features. Three fillings were studied in each group. In the CFA after 2 months, topographic contrast secondary electron photographs of worn surfaces were taken, and three-dimensional profiles were analyzed using ERA\(\text{\textasteriskcentered\textdagger}\). ERA consists of a scanning electron microscope, with two pairs of secondary electron detectors and a computer system, which are capable of measuring microtopography three-dimensionally. The principle of surface profile measurement is as follows: the electron probe incident angle is found through processing data derived from the intensity of the output-signal generated by each detector, and the three-dimensional profile is found by integration of each incident angle.

\(\circ\) MVK-E, Akashi Co. Ltd., Tokyo, Japan
\(\text{\textregistered}\) Pallatop 12, Sankin Industry Co. Ltd., Tokyo, Japan
\(\text{\textsection}\) Silicone point M-2 & M-3, Shofu Co. Ltd., Kyoto, Japan
\(\text{\$\$}\) Ion Coater IB 3, Eiko Engineering, Co. Ltd., Ibaragi, Japan
\(\text{\textdagger}\) S-430, Hitachi Co. Ltd., Tokyo, Japan
\(\text{\textdagger\textdagger}\) ERA8000, Elionix Co. Ltd., Tokyo, Japan
RESULTS

Microhardness values of unfilled resins

Microhardness values of unfilled resins are shown in Table 3. Immediately after polishing, the microhardness value of the UTMA-based resin was the highest of the four. Microhardness values of all types decreased after storage in water for 2 months. In particular, the degree of decrease in resins based on Bis-GMA, UDMA and UTMA were significant. The D-2.6E type maintained a relatively higher microhardness value, and, after storage in water for 2 months, was the highest among the four.

SEM observation of occlusal wear in vivo

Low magnifications of each experimental composite resin tested in the OCA are shown, in sequence, in Figs. 2-5. All types of the monomer system exhibited distinct wear facets, after one month. The wear facets of the Bis-GMA, UDMA and UTMA-based resins remained pronounced, even after 2 months. Within the same period, wear facets in the D-2.6E type, became obscure, due to increasing roughness over the entire surface of the specimen. Under high magnification, differences between types became less pronounced, because surface areas were filed away and quartz filler-particles were broken.

Sequential photographs of each experimental composite resin in the CFA under high magnification are shown in Figs. 6-9, respectively. The resin matrices of the Bis-GMA, D

<table>
<thead>
<tr>
<th>Monomer Type</th>
<th>At the baseline</th>
<th>Stored in water for 2 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-GMA Type</td>
<td>20.51(0.43)</td>
<td>15.64(0.48)*</td>
</tr>
<tr>
<td>D-2.6E Type</td>
<td>19.33(0.19)</td>
<td>18.82(0.30)</td>
</tr>
<tr>
<td>UDMA Type</td>
<td>18.92(0.60)</td>
<td>12.86(0.19)*</td>
</tr>
<tr>
<td>UTMA Type</td>
<td>21.51(0.11)</td>
<td>16.80(0.17)*</td>
</tr>
</tbody>
</table>

* 1% significantly different

Table 3  Microhardness of unfilled resin monomers (K H N)

Fig. 2  Serial SEM pictures of the wear process in Bis-GMA based resin, in OCA. Original magnification 50×.
(a: base-line b: 1 month c: 2 months)
White arrows indicate wear facets.
Fig. 3 Serial SEM pictures of the wear process in D-2.6E based resin, in OCA. Original magnification 50×.
(a: base-line b: 1 month c: 2 months)
White arrows indicate wear facets.

Fig. 4 Serial SEM pictures of the wear process in UDMA based resin, in OCA. Original magnification 50×.
(a: base-line b: 1 month c: 2 months)
White arrows indicate wear facets.

Fig. 5 Serial SEM pictures of the wear process in UTMA based resin, in OCA. Original magnification 50×.
(a: base-line b: 1 month c: 2 months)
White arrows indicate wear facets.
-2.6E and UDMA types have eroded, and a crevice was observed along the filler-matrix interface with the passage of time. By the second month, it could be clearly seen that the protruding filler particles lacked any support from the resin matrix. In addition, the surface of these composites became slightly roughened with the passage of time, even under low magnification. However, the resin matrix of the UTMA type showed inconsiderable microabrasion, maintaining a relatively smooth surface.

ERA observation of the surface of the composites in the CFA

Contrast secondary electron images and isometric views (Fig. 10, 11) demonstrated worn surfaces in the CFA after 2 months. The isometric view was rotated 15° and tilted 60°, and contour lines were represented by color chart. Contrast secondary electron images revealed

Fig. 6 Serial SEM pictures of the wear process in Bis-GMA based resin, in CFA. Original magnification 1000 x.
(a: base-line b: 1 month c: 2 months)

Fig. 7 Serial SEM pictures of the wear process in D-2.6E based resin, in CFA. Original magnification 1000 x.
(a: base-line b: 1 month c: 2 months)
that those composites based on the Bis-GMA, the UDMA, and the UTMA types showed distinct abrasion of the matrix resin and protrusion of filler compared with ordinary SEM observation. Those isometric views showed that the degree of protrusion was 2-4 micron meters. Analysis of three dimensional profiles showed that the UTMA type had the lowest values of surface roughness, in those observation areas. The composites based on D-2.6E showed a loss of filler particles due to abrasion of the matrix in contrast secondary electron image, and the surface roughness values of composites based on D-2.6E were the highest among the four.

Fig. 8 Serial SEM pictures of the wear process in UDMA based resin, in CFA. Original magnification 1000 x.
(a: base-line b: 1 month c: 2 months)

Fig. 9 Serial SEM pictures of the wear process in UTMA based resin, in CFA. Original magnification 1000 x.
(a: base-line b: 1 month c: 2 months)
DISCUSSION

A previous study\textsuperscript{11)} showed that the wear patterns in the OCA and the CFA were quite different. Especially, in the CFA, conventional resin showed the microabrasion of the matrix resin, protrusion of filler particles and the dislocation of filler particles due to its failure to bond to the matrix. Furthermore, the wear resistance of resin matrix was distinctly improved by the dispersion of colloidal silica among larger filler particles\textsuperscript{10}). As would be expected from the reports, if the resin monomer was more wear resistant, composites based of that monomer would show improved wear resistance. The most commonly used components in the resin matrix of commercial composite resins are Bis-GMA, modified Bis-GMAs, urethane diacrylates, TEGDMA, and a number of diluents\textsuperscript{12–16). However, the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10}
\caption{A: A contrast secondary electron image of the wear process in Bis-GMA based resin, after 2 months in the CFA.
Original magnification 1000×
(a: Topographic contrast secondary electron image)
(b: Isometric view)
B: A contrast secondary electron image of the wear process in D-2.6E based resin, after 2 months in the CFA.
Original magnification 1000×.
(a: Topographic contrast secondary electron image)
(b: Isometric view)
}\end{figure}
components in the resin matrix of commercial composites are not presented in detail. Therefore, to investigate the effect of matrix systems on occlusal wear, experimental composite resins based on different resin monomers were prepared, and wear patterns of those experimental composite resins were observed by SEM and ERA.

The results of this study revealed that the effect of matrix resin systems on occlusal wear was less than that of filler systems. In a previous study\(^{17}\), it was shown that ERA was useful for highlighting local differences in wear patterns of composite restorations. In this study, ERA also revealed the microstructure of the wear surfaces in detail, so that differences in wear patterns of experimental composite resin monomers became clear. Particularly, the matrix resin based on D-2.6E was the most abraded, among the four experimental resins, and consequently, protruding filler particles, lacking the support of the resin matrix, loosened

---

**Fig. 11 C:** A contrast secondary electron image of the wear process in UDMA based resin, after 2 months in the CFA.
Original magnification 1000×.
(a: Topographic contrast secondary electron image)
(b: Isometric view)

**Fig. 11 D:** A contrast secondary electron image of the wear process in UTMA based resin, after 2 months in the CFA.
Original magnification 1000×.
(a: Topographic contrast secondary electron image)
(b: Isometric view)
themselves from the surface. However, matrix resin based on UTMA showed better wear resistance than the other composites. This result might be explained by the fact that UTMA could form a more rigid polymer, due to its four methacrylate groups in monomer structure.

Wear resistance is commonly regarded as correlated with surface hardness, so, the hardness test is applied to evaluate the mechanical properties of restorative materials. In this study, the relationship between wear resistance and hardness was investigated. Unfilled resins based on Bis-GMA, UDMA, and UTMA showed significant decreases in microhardness, after storage in water for 2 months. This might be explained by relatively higher water sorption due to their monomer structures. Bis-GMA monomer has hydroxy groups, and UDMA and UTMA monomers have higher polar urethane bonds in their monomer structures. In addition, diluent TEDGMA itself also increased the water sorption due to its ether bond, while at the same time, decreasing microhardness. However, the D-2.6E based unfilled resin showed a negligible decrease in microhardness. The D-2.6E monomer is a kind of 2, 2’-bis (4-methacryloxy polyethoxyphenyl) propane (Bis-MPEPP) monomer, and is a mixture of a dimethacrylates with side chains of various lengths. The D-2.6E monomer does not have hydroxy group in the monomer structure, which could explain why it maintains a relatively higher microhardness value, after storage in water. Furthermore, the mechanical properties of the D-2.6E based resin, such as compressive strength, indirect tensile strength and transverse strength, were superior to those of the Bis-GMA based resin examined in the previous study. However, it was difficult to clarify the relationship between those mechanical properties and in vivo wear patterns. Loss of material from surfaces of composite resins was difficult to explain by mechanical wear mechanisms alone. In the oral environment, it is necessary to consider degradation of the mechanical properties by water. However, Murakami et al. reported that the mechanical properties of experimental composites based on Bis-GMA, TMM-3M, EO modified bisphenol A dimethacrylate and UDMA were almost unaffected by long-term (1 year) storage in water. To clarify the degradation of the mechanical properties of these experimental composites by water, further sophisticated water immersion tests are necessary.

In the oral environment, the wear mechanisms of composites are partially associated with chemical degradation of the surface. Chemical degradation in vivo might be caused, not only by water sorption, but also, by enzymes present in saliva, thermal stress, and chemical agents in food. The wear facets of the D-2.6E based resin in the OCA were clearly discernible after only one month, but were then obscured after 2 months, due to increasing the roughness of the whole surface of the specimen. These findings suggested that the matrix of the D-2.6E based resin might be affected by chemicals from food or saliva. Roulet reported that chemical degradation in vivo increased surface roughness of the composites, under test conditions which excluded mechanical wear. Those chemicals may cause a softening of the outermost layers of matrix resin, so that mechanical attack will more easily remove the softened layer and then expose a new surface layer to enzymatic attack. Powers et al. showed that in vitro wear characteristics of the composites exposed to accelerated aging in a weathering chamber were different from those of unaged composites, and accelerated aging was used as a model to simulate the erosive wear of composites. However, in vivo wear characteristics of the composites might be altered more gradually,
and it is difficult to simulate in vitro the softening of matrix resin caused by chemical degradation. Consequently, in vivo examination is necessary to study the influence of chemical degradation. Observation of in vivo wear patterns of composite resins using temporary metal crowns and ERA are useful in developing resin matrices with high wear resistance, and selecting suitable filler systems.

CONCLUSION

Recently, the electron probe surface roughness analyzer was developed, allowing three-dimensional measurement of microtopography by secondary electron signals. In this study, occlusal wear patterns of experimental light-cured conventional composites with four different monomer systems were observed by SEM and ERA. The following results were obtained:

(1) Microhardness values of all types of monomer systems decreased after storage in water for 2 months. Particularly, the unfilled resins based on Bis-GMA, UDMA, and the UTMA showed a significant decrease in microhardness after storage.

(2) All types of monomer systems showed distinct wear facets in the OCA after one month, with wear facets of Bis-GMA, UDMA and the UTMA remaining distinct after 2 months. In contrast, the wear facets of D-2.6E based resins in the OCA became obscured after 2 months due to increasing roughness of the whole specimen surface.

(3) In the CFA, the microabrasion of resin matrix and the loss of filler particles were observed in all types of monomer systems. UTMA based resin showed the greatest wear resistance among the four.

(4) The effect of matrix resin systems on the occlusal wear was less than that of filler systems.

(5) ERA was more effective for observing and analyzing the surface morphology of composite resins, compared with ordinary SEM.

ACKNOWLEDGMENT

We gratefully acknowledge the expert technical assistance of Kuraray Co. Ltd., who made the experimental composite resins. Thanks are also given to Elionix Inc. for the use of the ERA.

REFERENCES


29) Asmussen, E.: Softening of BisGMA-based polymers by ethanol and by organic acids of plaque,


モノマー組成の異なる試作コンポジットレジンの口腔内摩耗像

関矢一仁，岡本 明，福島正義，岩久正明
新潟大学歯学部歯科保存学第一教室

本研究の目的は、in vivoにおける試験により、コンポジットレジンの耐摩耗性に及ぼすマトリックスレジンの影響を評価することである。4種類のマトリックスレジンシステム、すなわち、Bis-GMA, D-26E, UDMA, UTMAをそれぞれ主成分（70 wt%）とし、希釈材としてTEGMDA (30 wt%)を用いた光重合型レジンが試作された。なお、試作レジンには、粉末石英フィラー（81 wt%）を含有する従来型フィラーシステムを用いた。
従来より当教室において行ってきた仮着クラウンを応用した観察法により、試作レジンの口腔内摩耗像をSEMにより連続的に観察した。また2ヶ月経過後の試片については、ERAにより摩耗像の分析を行った。
試作レジンのすべてにおいて、マトリックスレジンの摩耗及びフィラーの脱落が観察された。4種の試作レジンの内では、UTMAを主成分とするレジンが最も高い耐摩耗性を示したが、マトリックスレジンが耐摩耗性に及ぼす影響は、フィラーシステムのそれに比して小さかった。

II級光重合コンポジットレジン修復物の重合性
積層充填法，照射時間，レジンインレーにおける加熱の影響

平林 茂，James A. A. HOOD1，平澤 忠
金沢大学歯学部歯科理工学教室

1Department of Oral Biology and Oral Pathology, University of Otago Faculty of Dentistry

比較的大きなII級窪洞に修復された光重合コンポジットレジンの重合の程度を修復物断面のヌープ硬さの測定により評価した。光療法，照射時間，レジンインレーにおける加熱処理の重合性に及ぼす影響を，MFR型のHEおよびハイブリッド型のP50を使用して検討した。
いずれの材料もほぼ同じ傾向が得られた。すなわち，直接充填法により修復する場合，3回積層充填法が推奨された。レジンインレー使用時における加熱後の最終重合率は，光重合段階のレジンの重合率に影響を受けた。その結果，光重合段階で，2回積層法が推奨された，照射時間に関しては，使用する材料の光透過性や光照射器の強度により影響されることから，メーカーの指示に従い適宜選択すべきと思われる。