Degree of Conversion of Dual-Cured Composite Luting Cements

Ikuro HARASHIMA, Takashi NOMATA and Tadashi HIRASAWA

Department of Dental Engineering, Tsurumi University School of Dental Medicine
2-1-3 Tsurumi, Tsurumi-ku, Yokohama 230, Japan

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The degree of conversion (DC) of dual-cured composite luting materials for composite inlay restoration was determined by Fourier transform infrared spectroscopy. Dual-cured composite cements showed a DC of 59.3-75.0% after self-cure and 66.6-81.4% after photo-cure. DC after photo-cure decreased with the increase in thickness of a restoring composite inlay between the composite cement and a light tip. A lower DC after photo-cure did not satisfactorily increase following subsequent self-cure. Sufficient light should be provided to the composite cement in photo-cure luting of composite inlays to achieve a high and uniform DC, as well as in filling restoration using photo-cured composites. Reirradiation, in which the tip of a light unit was brought close to the portion of the cement with a low DC, was very effective in increasing DC and making it more uniform.

Key words: Degree of conversion, Composite luting cement, Dual-cure

INTRODUCTION

Composite resins have been used for posterior restoration by improvements in the materials and in clinical techniques. A composite inlay technique is one of the choices for aesthetic posterior restorations. Many studies have been published regarding this indirect composite restoration1-6). In the composite inlay technique, the composite restoration is fabricated in the laboratory and then luted to the tooth with a composite resin cement. The benefits obtained from the composite inlay technique have been summarized as follows5): 1) improvements in the physical and mechanical properties of the composites fabricated as inlays; 2) accurate reconstruction of the contact points and anatomic form of the restoring proximal surfaces; and 3) a decrease in polymerization shrinkage when the cavity is restored using the composite material.

Most composite cements for luting a composite inlay are designed so that polymerization is activated both by photo-irradiation and by a redox reaction between organic peroxide and tertiary amine. This system of polymerization activation is known as "dual-cure". One reason for this design is that visible light must be irradiated to a part of the luting resin through a thick composite inlay at the cementation. The degree of conversion (DC) of the dual-cured luting composites may affect the quality of the composite inlay restoration.

The DC of dental resins has been studied by various methods including differential scanning calorimetry,7,8) densitometry,9) infrared spectroscopy10-16). Infrared spectroscopy allows for the rapid measurement of the DC of dental resins. However, Ruyter and Svendsen11) pointed out that the techniques of transmission infrared spectroscopy cannot be satisfactorily adapted to composite materials because of the inorganic filler. Fortunately,
considerable advances have been made in the resolution and sensitivity of infrared spectroscopy. A high-resolution, sensitive Fourier transform infrared spectrometer (FTIR) yields a spectrum of a composite material in its transmission mode sufficient to determine DC.

In this paper, we use the term "self-cure" with reference to curing at an environmental temperature below 50°C without any intentional photo-irradiation. This definition is based on the fact that benzoyl peroxide usefully decomposes in the temperature range of 60–90°C and that ordinary room light is too weak be used to cure dental photo-curable resins.

As mentioned above, dual-cured composite luting cements are both self- and photo-curable. We spectroscopically determined the DC of the materials after self- or photo-cure and examined the effect of the thickness of a restoring composite inlay on DC after the photo-cure luting. In addition, the effects of reirradiation were investigated to determine if it would increase and make more uniform the DC of the photo-polymerized cement.

MATERIALS AND METHODS

Composite luting materials

Five dual-cured composite luting cements for composite inlay restoration were used. They are abbreviated as ADH*, CRC#, DUAL$, DUO@, and RIC Yemen in this paper. The material RIC was not on the market in June, 1989 when the manufacturer provided us with the material. One self-cured composite luting cement (PAN$) was used as a control material. CRC and PAN are powder-liquid type materials, and each of the others includes two pastes. The constituents of the materials were mixed according to the manufacturer’s instructions.

The compositions of the composite luting cements are summarized in Table 1. The

<table>
<thead>
<tr>
<th>Material</th>
<th>Monomer identified</th>
<th>Filler content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dual-cured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ADH</td>
<td>BisGMA, UDMA, TEGDMA</td>
<td>74.7</td>
</tr>
<tr>
<td>CRC</td>
<td>BisMPEPP*</td>
<td>74.9</td>
</tr>
<tr>
<td>DUAL</td>
<td>UDMA, alkylene DMA</td>
<td>59.9</td>
</tr>
<tr>
<td>DUO</td>
<td>BisGMA, TEGDMA</td>
<td>67.7</td>
</tr>
<tr>
<td>RIC</td>
<td>BisGMA, TEGDMA</td>
<td>63.8</td>
</tr>
<tr>
<td>self-cured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN</td>
<td>BisMPEPP</td>
<td>75.6</td>
</tr>
</tbody>
</table>

a) A mixture of 2, 2-bis-4-(methacryloyloxypropoxy) phenyl propanes
b) An alkylene dimethacrylate

* Adhesive cement, Kulzer GmbH, Wehrheim, Germany
# Clearfil CR inlay cement, Kuraray Co. Ltd., Kurashiki, Japan
$ Dual-cement, Vivadent AG, Schaan, Lichtenstein
@ Duo cement, Coltène AG, Altstätten, Switzerland
Y Resin inlay cement-2, Tokuyama Soda Co. Ltd., Tokuyama, Japan
\ Panavia EX, Kuraray Co. Ltd., Kurashiki, Japan
monomers contained in the materials were identified by liquid chromatography, and the inorganic filler contents were determined by firing the materials at 575°C for 3 h.

Measurement of DC and effects of thickness of composite inlay

Figure 1 is an illustration of the specimen preparation of a composite cement for photo-irradiation. Mixed composite cement paste was interposed between two polyester strips together with a spacer which is 40 μm thick. These were then pressed between two glass plates. A disc of a composite inlay material**, which was fabricated according to the manufacturer’s instructions, was placed on the upper glass plate. The upper glass plate is necessary to prevent smearing the surface of the composite inlay disc with the excess of cement paste, and the polyester strips allows peeling off a thin film of the cured cement without breaking it. The thickness of the composite inlay discs used ranged between 1.16 and 5.42mm. The cement paste was irradiated through a composite inlay disc for 40 s with visible light from a dental visible light unit##. A composite luting cement film about 50 μm thick was produced in this manner. Composite cement films were prepared also when no composite inlay disc was placed on the upper glass plate.

The DC of the composite cement film was determined with an FTIR@@. The FTIR spectra were obtained from 50 scans over the 400-4000 cm⁻¹ range in the transmission mode. In the spectra of all the materials except DUAL, two absorbance bands appeared in the range from 1600 to 1650 cm⁻¹. The absorbance band centered at 1637 cm⁻¹ was assigned to C=C stretching vibrations of methacryloyl groups, and the other at 1608 cm⁻¹ to stretching vibrations of aromatic rings. The resolution and intensities of these bands were sufficient to

![Diagram of composite cement film preparation](image)

** Clearfil CR inlay (shade: UL), Kuraray Co. Ltd., Kurashiki, Japan
## Wite Lite, Tokuyama Soda Co. Ltd., Tokuyama, Japan
@@ JIR-100, JEOL Co. Ltd., Tokyo, Japan
allow quantitative determination of the DC of the composite cements. The ratio of the intensities of these absorbance bands indicated the fraction of unreacted methacryloyl double bonds remaining\(^{11}\). DC was obtained by subtracting the percentage of the remaining double bonds from 100\%. The material DUAL contains no aromatic monomers as shown in Table 1. The absorbance band at 1608 cm\(^{-1}\) did not appear in any IR spectrum of DUAL. The thickness of the DUAL film was measured with an electric micrometer after FTIR measurement. The intensity of the absorbance band at 1637 cm\(^{-1}\) was divided by the film thickness and then the corrected intensity determined as a fraction of the unreacted C=\(\text{C}\) bonds in the DUAL film. Spectrum acquisition was conducted immediately after photo-irradiation and after storage in the dark at 37°C for 1 and 7 d.

The films were prepared by storing the mixed paste in the dark at 37°C for 1 d without any photo-irradiation to determine the DC after self-cure.

**Effects of reirradiation**

Photo-irradiation of the CRC cement paste for 40 s was repeated up to 4 times through the composite inlay disc 5.42 mm thick. Identical reirradiation was conducted on the sample preparation setup without the inlay disc.

In reirradiation to the luting composite, dental practitioners will probably bring a light tip close to the part of the restoration which is presumed to have previously been insufficiently photo-irradiated. Experiments simulating this situation were conducted. First, the CRC luting composite was photo-irradiated through the composite inlay disc 5.42 mm thick. Next, the luting composite was reirradiated through discs of various thickness (0-5.42 mm). In these experiments, the action of a light tip brought close to the insufficiently irradiated part can be simulated by the use of a thinner disc during the second irradiation.

**RESULTS**

**DC after self- or photo-cure**

Table 2 shows the DC of dual-cured composite luting cements after self- or photo-cure.

<table>
<thead>
<tr>
<th>Material</th>
<th>Degree of conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Self-cure(^a)</td>
</tr>
<tr>
<td>dual-cured</td>
<td></td>
</tr>
<tr>
<td>ADH</td>
<td>67.4 ± 0.4</td>
</tr>
<tr>
<td>CRC</td>
<td>75.0 ± 0.5</td>
</tr>
<tr>
<td>DUAL</td>
<td>59.3 ± 2.1</td>
</tr>
<tr>
<td>DUO</td>
<td>61.6 ± 0.4</td>
</tr>
<tr>
<td>RIC</td>
<td>71.4 ± 0.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>self-cured</th>
<th>Degree of conversion (%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN</td>
<td>76.1 ± 1.4</td>
</tr>
</tbody>
</table>

Curing conditions:
- a) storage in the dark at 37°C for 1 d after mixing
- b) direct photo-irradiation for 40 s plus storage in the dark at 37°C for 1 d
The data for photo-cure listed in the table were obtained from samples that were prepared by photo-irradiation for 40 s, without the interposition of the composite inlay disc, and then stored in the dark at 37°C for 1 d. The storage of the photo-cured samples was conducted to make the DC data comparable to that of the self-cured samples with regard to the elapsed time.

Fig. 2 Relationships between DC after photo-cure and thickness of a restoring composite inlay. DC measurements were conducted immediately after photo-irradiation (open circles) and after storage of the cured film in the dark at 37°C for 7 d (closed circles).
time.

DC varied between 59.3 and 76.1 percent for the materials undergoing self-cure and between 66.6 and 81.4 percent for photo-cure. DC for photo-cure was higher than that for self-cure for four of the five dual-cured materials, although one material (CRC) showed comparable DC values for self- and photo-cure (75.0% and 74.5%, respectively).

*Effects of the thickness of the restoring composite inlay*

Figure 2 displays the relationships between DC after photo-cure and the thickness of a restoring composite inlay for the five dual-cured luting compolites. DC was measured immediately after photo-irradiation. The measurement was repeated on the same sample after storage in the dark at 37°C for 7 d to determine the subsequent change in DC.

DC after photo-cure decreased with the increase in thickness of the composite inlay. This tendency was more clearly observed in the materials CRC and DUO. The material DUAL, for which the DC values listed in Table 2 were low, showed a slight decrease.

DC after photo-cure increased very slight for four of the five dual-cured composite luting cements during storage. The DC curve of the material CRC became flatter after storage for seven days than it was previously, increasing the DC values. However, horizontal curve, which would be expected for self-curred luting composites, was not observed.

*Effects of reirradiation*

Figure 3 is a plot of DC after photo-cure vs. the accumulative length of photo-irradiation. The forty-second photo-irradiation was repeated up to 4 times with or without the interposition of a composite inlay disc 5.42 mm thick between the light tip and the luting material.

![Fig. 3](image_url)  
*Fig. 3*  
Effects of accumulative time of photo-irradiation on DC.  
Light irradiation was repeated in the absence (open circles) and presence (closed circles) of a composite inlay disc 5.42mm thick. Measurements were conducted immediately after photo-irradiation.
DC gradually increased with the increase in photo-irradiation time when the cement was irradiated through the disc of the inlay material. In the absence of the composite inlay disc during irradiation, saturation of the DC increase occurred at 80 s of accumulative irradiation time. Consequently, the difference in DC in the presence and absence of the composite inlay disc became smaller with the increase in photo-irradiation time.

In the experiments summarized in Fig. 4, the material CRC had been irradiated once for 40 s through the composite inlay disc 5.42 mm thick. In the second photo-irradiation, the thickness of the inlay disc interposed between the light tip and the luting composite was made to vary between 0 and 5.42 mm. The thickness of the composite inlay disc used in the second irradiation is plotted as the abscissa in Fig. 4. The DC of the material CRC was 21.0% when it was irradiated for 40 s through the composite inlay disc 5.42 mm thick (the lowest horizontal line in Fig. 4). The width of the shaded band in Fig. 4 shows the change in DC after increasing the photo-irradiation time from 40 to 80 s in the absence of the composite inlay disc. The initial low DC clearly increased when the composite inlay disc used in the second

![Fig. 4 Effects on DC of reirradiation of poorly cured luting composites.](image-url)
DISCUSSION

The dual-cured composite luting cements showed 59.3-75.0% of DC after self-cure and 66.6-81.4% after photo-cure (Table 2). The values for DC obtained after self-cure were comparable to the reported values for other self-cured dental resins\textsuperscript{8,10-14}. Fifty-five to seventy-five percent DC has been reported for photo-cured composite filling restorative materials\textsuperscript{17}. The DC summarized in Table 2 varied from material to material because the luting composites used have different compositions (Table 1). The materials CRC and PAN have a similar composition except for their polymerization activation system. The former is dual-curable and the latter is only self-curable. They showed practically the same DC after self-cure, 75.0% for CRC and 76.1% for PAN (Table 2).

It is well known that curing of photo-activated composite filling materials is generally dependent on the thickness of the restoration. A lower DC is obtained in the inner part of the restoration. As represented in Fig. 2, the dual-cured composite luting cements generally decreased DC after photo-cure with the increase in thickness of the restoring composite inlay. A more important result shown in Fig. 2 is that a lower DC after photo-cure was not satisfactorily increased by the following self-cure. Consequently, dependence of DC on the thickness of the inlay restoration was observed even after storage of the cured cements in the dark at 37°C for 7 d. The working time of 4-4.5 min for the dual-cured luting composites is noted in the manufacturer's instructions. The dual-cured cements are set to highly cross-link by photo-irradiation before their self-cure systems initiate polymerization. The reaction of the remaining C=C bonds is restricted in the cross-linked media. In addition, polymerization induced by the redox reaction between benzoyl peroxide and tertiary amine has a 2.5-10 times greater activation energy than does photo-polymerization\textsuperscript{18}.

Incomplete polymerization of dual-cured luting composites may lead to adverse pulp tissue reactions and to retention failures. When a composite inlay is luted with a dual-cured luting composite using photo-irradiation, sufficient light should be provided to polymerize the luting material as completely and uniformly as possible.

DC increased and became more uniform following repeated photo-irradiation (Fig. 3). However, when the thickness of the composite inlay between the light tip and the luting composite was 5.42 mm, the forty-second photo-irradiation needed to be repeated 4 times to obtain ca. 45% DC. The accumulative irradiation time of 160 s is scarcely practical. When dental practitioners presume that they have insufficiently irradiated the luting composite, it is reasonable that they should bring a light tip closer to the incompletely cured part of the cement for reirradiation. The smaller numbers on the abscissa in Fig. 4 mean that the tip of a light unit used for reirradiation is brought closer to the portion of the luting composite with a low DC of ca. 20%. This reirradiation technique was very effective in increasing DC and making it more uniform.
CONCLUSIONS

Composite luting cements for composite inlay restoration were curable both by photol-irradiation and by the redox reaction between organic peroxide and tertiary amine, yielding DC values of 66.6–81.4% and 59.3–75.0%, respectively. These values were comparable to those obtained from other photo- or self-cured dental resins. DC after photo-cure decreased according the increase in thickness of a restoring composite inlay between a light tip and the luting cement. A lower DC obtained after photo-cure did not satisfactorily increase following subsequent self-cure. Sufficient light should be provided to polymerize the luting composites as completely and uniformly as possible. Reirradiation, in which the tip of a light unit was brought close to the portion of the materials with a low DC, was very effective in increasing the DC and making it more uniform.

ACKNOWLEDGEMENT

The authors wish to thank Ms. Rie Nomoto, Tsurumi University School of Dental Medicine, for her helpful advice on the FTIR measurements.

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本号掲載論文の和文抄録

デュアルキュアーレ型
コンポジットレジンセメントの反応率

原島郁郎，野侯尚，平澤忠
鶴見大学歯学部歯科理工学教室

デュアルキュアーレ型コンポジットレジンセメントの硬化反応率をフーリエ変換赤外吸収分光法で測定した。デュアルキュアーレ型レジンセメントの反応率は、レドックス反応による常温硬化では59.3~75.0％、光硬化では66.6~81.4％を示した。光硬化時の反応率は、セメントと照射器照射口の間に介在するコンポジットレジンインレーブの厚さが増加するにつれて減少した。また、光硬化時の低反応率は、経時的に十分には向上しなかった。したがって、デュアルキュアーレ型のレジンセメントを光硬化させる場合、充填用光重合型コンポジットレジンの場合と同様十分光照射しなければならない。反応率を向上させ、均一化するためには、低反応率になったと思われる部位に照射口を近づけて再照射する方法が非常に有効であった。

歯髄側象牙質とコンポジットレジンセメントとの接着に及ぼす

MTYA・G・H処理の効果

村上芳弘*，塚田典功*，和田守康*，山崎宗与*
早川徹**，遠藤浩**，堀江港三**

*日本大学松戸歯学部保存学第Ⅲ教室
**日本大学松戸歯学部理工学教室

本研究では、歯髄側象牙質をMTYA・G・Hで処理したときの接着強さを、唇側象牙質と比較しながら調べた。新鮮牛抜去歯の唇側、あるいは歯髄側象牙質表面を被着体として用い、40％リン酸、10％ウメ酸、または0.5MのEDTA水溶液でエッチングし、37℃水中に1日浸漬後の引張接着強さを測定した。

各エッチング剤間で、唇側象牙質と歯髄側象牙質とに

歯科用接着性モノマー(4-methacryloyloxyethoxycarbonylphthalic Anhydride, 4-META)の溶血性とNMR,DSCによる4-META/リン脂質リポソームの相互作用

藤沢盛一郎*，門脇義則**，志田泰夫**

*東京医科歯科大学歯学部付属病院総合診断部
**東京医科歯科大学医科附属病院研究所