How different curing methods affect the degree of conversion of resin-based inlay/onlay materials

Kjersti Karine Kildal and Ivar Eystein Ruyter
NIOM, Scandinavian Institute of Dental Materials, Haslum, Norway

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The purpose of this investigation was to measure the conversion of five inlay materials with different curing methods. In particular, the influence of secondary curing in light ovens—that is, additional curing with light and heat simultaneously—was evaluated. The conversion was determined by infrared multiple internal reflection spectroscopy. The inlays were cured with three curing methods (A, B, and C). The conversion was recorded immediately after ended curing and after an additional storage period (postcuring). The mean conversion with method A, using a handheld curing unit, was 42.1% and increased significantly to a mean of 55.4% during the storage period at (37 ± 1)°C. Both curing methods B and C, including the use of light ovens, gave a mean conversion of 65%, which did not increase significantly during the storage period. This investigation demonstrated that the degree of conversion depends on the curing method used. ☐ *Composite resin; conversion; curing methods; dimethacrylate polymers; inlay/onlay systems*

Kjersti Karine Kildal, Scandinavian Institute of Dental Materials (NIOM), Kirkeveien 71B, Postbox 70, 1344 Haslum, Norway

The composition of resin-based inlay/onlay materials is mainly the same as that of composite resin-based filling materials. With direct filling materials polymerization is done intraorally, whereas inlay materials often require an extraoral polymerization. Thus, inlays can be made either by an indirect or by a direct technique. With the indirect technique, the inlay is built up on a model and cured extraorally with light or heat. A combination of light and heat can also be used. With the direct technique, the inlay material is placed directly in the prepared tooth, and the primary polymerization is made by light activation with a handheld curing unit. Additional curing may take place extraorally with use of different curing ovens.

An advantage of the inlay technique is that the polymerization shrinkage of the materials occurs before bonding to the tooth structure. Polymerization contraction and insufficient adhesion to dentin have been cited as primary causes of microleakage with resin-based materials (1–3). Wear, hardness, creep, tensile strength (4, 5), and release of residual monomers are related to the degree of conversion (6). The degree of conversion depends on the monomer system used (7–9). The degree of conversion is also inversely correlated to curing depth (10, 11). With light-cured materials the highest conversion is at the surface of the material if oxygen inhibition is prevented (12). One investigation suggests that the light intensity of handheld light units varies and is greatly dependent on voltage (13, 14). Such variations result in variations in depth of cure and may have an effect on the degree of conversion. A possible effect of the extraoral or secondary curing is that it may improve the conversion (reduce the quantity of double bonds). Secondary curing can be performed in an oven using light and heat curing additional to and immediately after primary light curing with a handheld curing unit.

The purpose of the present investigation was to measure the degree of conversion of five different resin-based inlay materials as

Table 1. Investigated resin-based inlay materials

Name	Code	Lot no.	Shade	Manufacturer
Brilliant	BR	240991-60	U	Coltene
Charisma	CH	21	A20	Kulzer
Eos	ES	465701	LY	Vivadent
Estilux Posterior CV	EP	300692	A20	Kulzer
Prisma AP.H	PR	6130-1310	U	Dentsply Int.

a function of different curing methods. In particular, the influence of the secondary curing on conversion in light ovens—that is, additional curing with light and heat simultaneously—was to be evaluated. A secondary aim was to study how the degree of conversion changed after a primary light curing. The temperature change in the specimens during curing with the handheld curing unit and in the light oven was also investigated. The purpose of measuring the temperature increase was to evaluate the peak temperature of the specific systems investigated (sample size, light units, and light ovens) and to compare this temperature with the glass transition temperatures previously observed (15, 16).

Materials and methods

The five investigated inlay materials are listed in Table 1. The amount of unreacted methacrylate groups was determined with infrared spectroscopy (Model 683 with model 3600 data station, Perkin Elmer Corp., USA), using the multiple internal reflection (MIR) technique (7). The operating conditions of the spectrophotometer were slit program W and noise filter 4. The spectra of each material were recorded before and after curing. The different curing methods, A, B, and C, were in accordance with the manufacturers' instructions and are specified in Table 2.

Preparation of specimens

Specimens were prepared by compressing the uncured material into a thickness about 0.5 mm–1 mm between a 52-mm × 18-mm × 2-mm, 30° germanium crystal (Perkin Elmer Corp.) and a quartz glass cover. Sample preparation was carried out in a nitrogen atmosphere within a polyethylene glove bag (Model S-1, I2R, Instruments for Research and Industry, USA), to minimize the effect of oxygen inhibition (17). Before sample preparation was initiated the germanium plate was covered with a thin film of nitrogen-saturated hydrocarbon oil (Uvasol art.7161, Paraffin liquid for spectroscopy, Merck), which protects the plate and ensures good optical contact. Five specimens of each material were cured by methods A, B, and C at ambient conditions ((23 ± 1) °C).

Method A (primary cure)

Method A consisted of light curing with a handheld curing unit. Relative radiant exitance of the handheld light sources was 384.3 mW/cm^2 for Coltolux II, 241.1 mW/cm^2 for Translux CL, and 226.6 mW/cm^2 for the Heliolux II (13, 18). These relative radiant exitances were of the same magnitude as the radiant exitances normalized to 1 cm^2 area of the fiberoptic tip reported by Fan et al. (19).

The tip of the handheld light source was placed against the quartz glass (Fig. 1), and that section of the specimen was irradiated for the exposure time specified in Table 2. The light tip was then moved, and a section overlapping the previous section was irradiated. This procedure was continued until the whole specimen was irradiated (18–20 exposures per specimen). This method was in accordance with the method described in the international standard for resin-based filling materials (20).

Table 2. The curing methods for the different materials

	Method			
Code	A	B	C	Postcuring*
BR	Coltolux II, 40 sec	Coltolux II, 40 sec DI-500, 410 sec	DI-500, 410 sec	24 h at 37°C
PR	Prismetics lite II, 40 sec	Prismetics lite II, 40 sec DI-500, 410 sec	DI-500, 410 sec	24 h at 37°C
CH	Translux CL, 20 sec	Translux CL, 20 sec Dentacolor, 360 sec	Dentacolor, 360 sec	24 h at 37°C
EP	Translux CL, 20 sec	Translux CL, 20 sec Dentacolor, 360 sec	Dentacolor, 360 sec	24 h at 37°C
ES	Heliolux II, 60 sec	Heliolux II, 60 sec Dentacolor, 360 sec	Dentacolor, 360 sec	24 h at 37°C

* Immediately after methods A, B, and C, respectively.

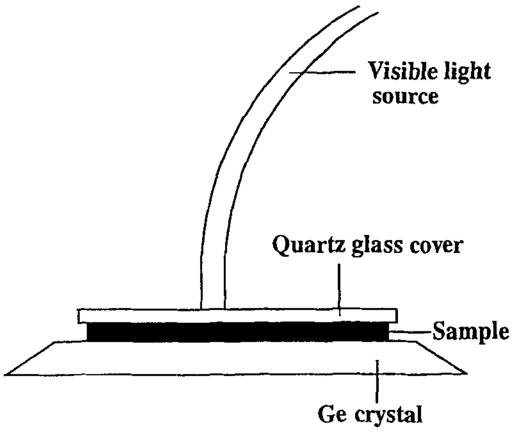

Fig. 1. Schematic presentation of the curing procedure with a handheld curing unit.

Method B (primary and secondary cure)

In method B, the specimens were primary-cured with a handheld curing unit and secondary-cured in a curing oven for the exposure times specified in Table 2. The secondary curing followed immediately after the primary curing.

Method C

In method C the specimens were cured in a curing oven as specified in Table 2. The Dentacolor oven is a light curing oven. The DI-500 is a light and heat curing oven, in which the temperature is preprogrammed by the manufacturer. All curing times were in accordance with the manufacturers' instructions.

Postcuring

The specimens were stored under dry conditions for 24 h at (37 ± 1)°C after being cured with either of the three methods.

Analysis

The monomers in these products show absorption bands in the infrared region that can be used to determine the degree of conversion. The base-line method for determining peak absorbances was used (21). The degree of conversion was determined in percentage of the methacrylate groups originally present in the unpolymerized composite. The quantitative measurements were made on a relative basis (22), in which the peak absorbances of the methacrylate C=C bond at 1638 cm^{-1} and the aromatic $C\overset{\cdots}{=}C$ stretching vibrations at 1608 cm^{-1} were used to calculate the degree of conversion (7, 17).

Calculations and statistics

The degree of conversion (%) was calculated with the formula

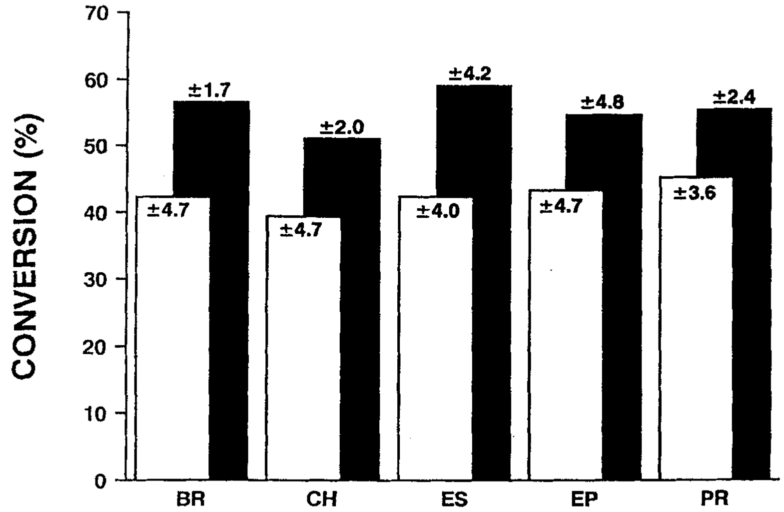

Fig. 2. The degree of conversion in five inlay materials after curing with method A. The open bars represent the conversion immediately after curing by the handheld units. The closed bars represent the conversion after the storage period of 24 h at (37 ± 1)°C. The numbers at the top of the bars indicate standard deviation.

$$[(A_{\text{cured}}(1638/1608)\text{cm}^{-1}/A_{\text{uncured}}(1638/1608)\text{cm}^{-1}) - 1] \times 100,$$

where A is the absorbance.

Student's paired two-tailed t test with $p = 0.05$ was used to determine whether significant differences existed between the curing methods (23).

Temperature measurements

The temperature increase inside the materials during curing was recorded. The registration was done with a copper/constantan thermoelement coupled to a digital multimeter (Model 160B, Keithley Instruments Inc., USA). The thermoelement was placed inside a 2-mm-thick specimen. Readings were recorded every 30 sec during curing inside ovens and every 10 sec when the handheld curing units were used. Temperature registrations without the material were performed and used as a reference. Three registrations of each specimen and the reference were carried out.

Results

The degree of conversion for the different curing methods is presented in Figs. 2–4.

Method A

Immediately after the primary light curing the mean conversion was 42.5% for the five materials (Fig. 2). After postcuring (storage at (37 ± 1)°C for 24 h) the mean conversion showed a significant ($p < 0.05$) increase to 55.4%.

Method B

Additional light curing in an oven, immediately after the primary light curing, resulted in a mean conversion of 64.2% (Fig. 3), whereas the mean conversion measured after postcuring was 64.3%. The latter increase was not significant.

Method C

Light curing by method C resulted in a mean conversion of 66.3% (Fig. 4). After postcuring the mean conversion was 67.3%, which was not significantly different from the initial values.

Methods B and C gave significantly higher conversion ($p < 0.05$) than method A. The degree of conversion obtained by method C was not significantly different from that obtained by method B.

Postcuring

Fig. 5 shows the increase in the degree

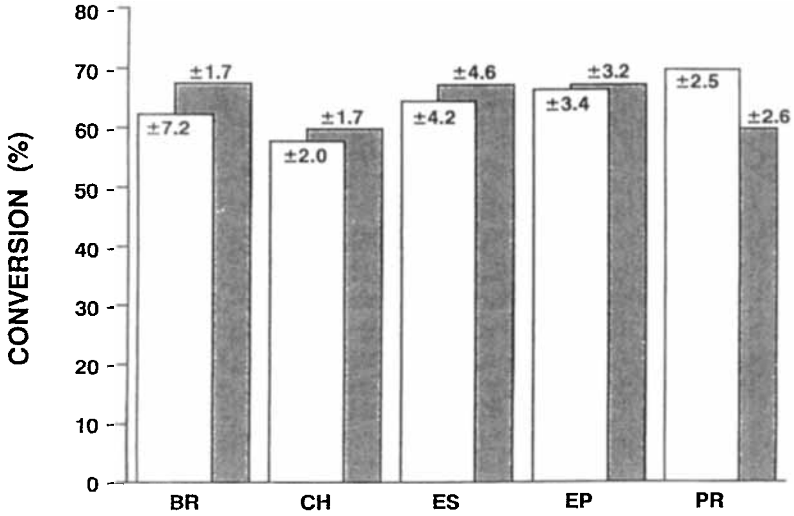

Fig. 3. The degree of conversion in five inlay materials after curing with method B. The open bars represent the conversion immediately after curing in the ovens. The hatched bars represent the conversion after the storage period of 24 h at (37 ± 1)°C. The number at the top of the bars indicate standard deviation.

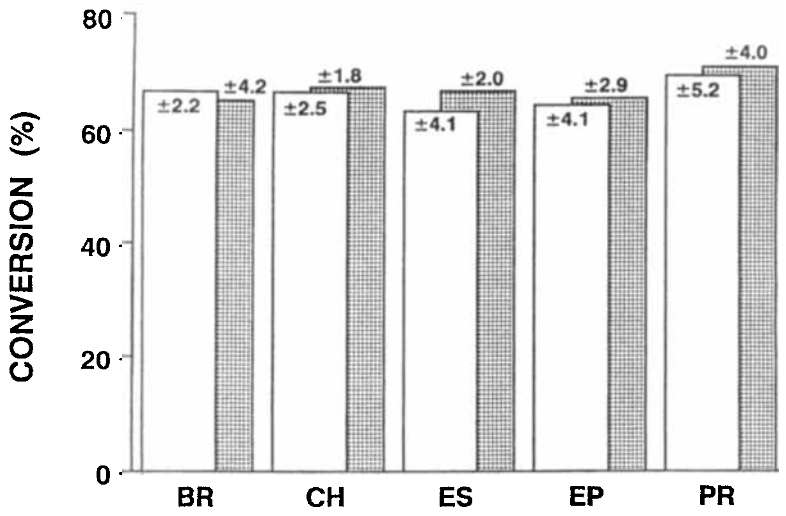

Fig. 4. The degree of conversion in five inlay materials after curing with method C. The open bars represent the conversion immediately after curing with the handheld units and in the ovens. The dotted bars represent the conversion after the storage period of 24 h at (37 ± 1)°C. The number at the top of the bars indicate standard deviation.

of conversion during the postcuring period after the primary light activation of product CH. Immediately after ended curing the conversion was 44.9%. After 5–6 h a conversion value of about 60% was obtained. Thereafter the increase was below the limit of quantification for the IR method used.

Temperature measurements

Fig. 6 shows the mean temperature increase inside the materials ES and BR during exposure to light and heat in the curing oven. During the first 3 min of curing the temperature increased from 28°C to 77.5°C in the Dentacolor oven and to 100.5°C in the DI-500 oven. During the rest of the curing period the temperature rose to 91°C in the Dentacolor oven and to 141°C in the DI-500 oven. There was no significant difference between the reference and the material ES.

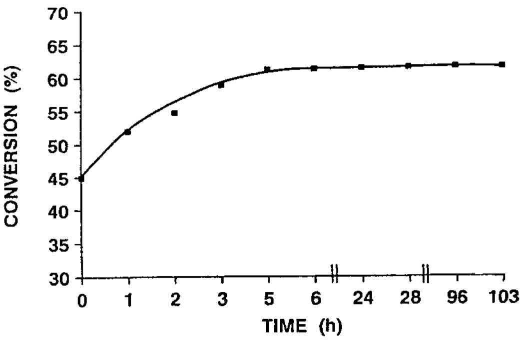

Fig. 5. The degree of conversion, for the material ES, during the postcuring period after the end of light curing by method A. The standard deviation was between ±1.5% and ±3.4%.

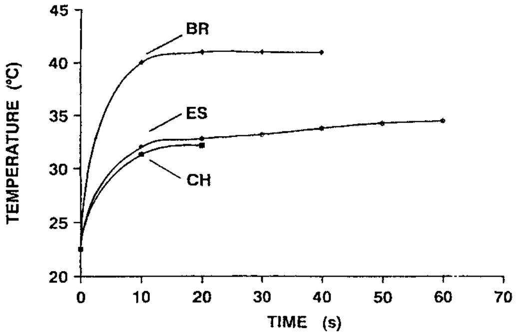

Fig. 7. The mean temperature increase inside the materials BR, ES, and CH during curing with the handheld curing units Coltolux II, Heliolux II, and Translux CL, respectively. The standard deviation was between ±0.2°C and ±1.2°C.

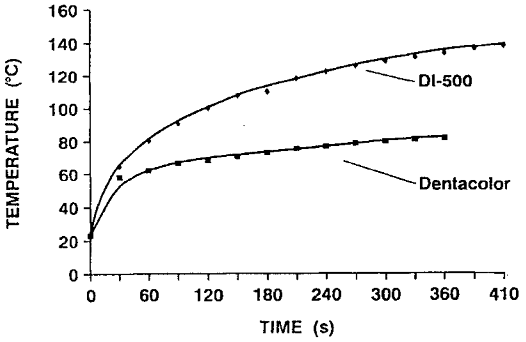

Fig. 6. The mean temperature increase inside materials ES and BR during curing in the Dentacolor and DI-500 ovens, respectively. The standard deviation was between ±1.7°C and ±8.5°C.

Fig. 7 shows mean temperature increase inside materials CH, ES, and BR when cured with the handheld curing units Translux EC, Heliolux II, and Coltolux II, respectively. After 10 sec of curing the temperature inside the materials rose from 22°C to (31.3 ± 0.5)°C for CH, to (32.3 ± 0.6)°C for ES, and to (38.8 ± 1.04)°C for BR. No further increases in temperature were recorded at the end of curing. With material BR, a significantly higher temperature ($p < 0.05$) was obtained after only 10 sec. With CH and ES almost the same temperature was obtained during curing.

Discussion

To ensure quantitative conditions for the infrared spectroscopic procedure, the absorbance measurements must follow Beer's law, and no interfering bands should be present (24). The validity is based on the fact that there should be similar absorptivity values at 1638 cm^{-1} for all monomers included in the inlay composites. A previous study (17) showed transmission infrared absorptivity values at 1639 cm^{-1} of the same magnitude for the monomers in question.

The base-line method used for peak absorbance permits accuracies of ±3% in concentration determinations by the MIR technique (22). The investigated inlay materials contain two or more monomers. Various dimethacrylate monomers show different reactivities (25). At a given time this may lead to different degrees of conversion for the various inlay materials.

The present data suggested that different curing methods result in different degrees of conversion. The quality of the network structure formed during polymerization depends on the quantity of unreacted pendant methacrylate groups and residual monomers (7, 26). There will always be some unreacted pendant methacrylate groups locked up inside the three-dimensional network after the end of curing (7). Low concentrations of residual monomers are observed after ended exposure to heat during secondary curing in an oven (15).

An increase in conversion was observed during postcuring when curing had been done with a handheld unit (method A). This occurs only when reactive radicals are present in the polymer matrix. The presence of such radicals in the polymer matrix of dental composite restorative materials has recently been established with electron spin resonance spectroscopy (27). The dimethacrylate molecules are probably able to diffuse and react with reactive ends even after the viscosity has increased (28). The mobility of the dimethacrylate monomers at 37°C is apparently too restricted to improve the conversion further after more than 6 h (Fig. 5).

The system had probably reached a maximum conversion of 71% when cured by methods B and C, since the conversion did not increase during the following postcuring. Consequently, the polymer shrinkage was also completed. The extraoral curing of inlay materials reduces the effects of microleakage (2) because the polymer shinkage is completed before placing the inlay in the cavity. A relatively thin layer of resin-based cement is used to fill the gap between the inlay and the cavity.

The reactivity of the radicals is affected by the viscosity of the matrix, which determines the mobility of the polymer radicals. The high temperature in the curing ovens may lead to an enhanced mobility of dimethacrylate monomers and a greater flexibility of the chains in the network. The temperature inside the inlays during curing with handheld units increased about 15°C to 20°C (29). This was about 100°C lower than the temperature observed in the inlays when cured in the ovens by methods B and C. This might explain the higher conversion obtained with the curing ovens compared with curing with the handheld units.

The DI-500 curing oven had a higher maximum temperature than the Dentacolor. Products PR and BR were therefore exposed to higher temperature than products CH, ES, and EP. This was not reflected in a significantly higher degree of conversion. The temperatures in both ovens were above the lower glass transition temperature (T_g) of (60–80)°C for primary light-cured dimethacrylates (15, 16). Therefore, no significant differences in the degree of conversion were observed.

Previous studies of polymerized dimethacrylate monomers by dynamic mechanical analysis demonstrated that a secondary cure due to heat exposure is accompanied by a considerable change in the material. The dynamic analyses indicate that the materials cured only with a handheld unit have two transition peaks (representing glass transitions of two phases), whereas the material with additional curing in an oven has one peak (15). The heat treatment reduces the quantity of residual monomers that are concentrated in the matrix phase, resulting in a T_g of the matrix of the same magnitude as that of the so-called microgels (30). The exposure time in light ovens with an elevated temperature should give a homogeneous polymer matrix with a minimum of pendant methacrylate groups (30). These studies support the results obtained in the present work, indicating that curing in a light oven contributes to a higher conversion and to a more homogeneous polymer matrix.

Results of the present investigation showed that the conversion obtained after curing in a light oven (methods B and C)—that is, simultaneous exposure to light and heat—was significant but not substantially greater than that achieved after only light curing (method A) followed by postcuring. These results are in agreement with investigations showing that secondary curing of resin-based inlay materials will not result in significant improvements in the mechanical properties (31–33).

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