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Degree of Remaining C=C Bonds, Polymerization Shrinkage and Stresses of Dual-cured Core Build-up Resin Composites

MM Stavridakis • AI Kakaboura • I Krejci

Clinical Relevance

The polymerization behavior of dual-cured core build-up resin composites is strongly material-related. None of the materials can be efficiently polymerized in terms of the remaining C=C bonds in regions of restorations with no direct light accessibility.

SUMMARY

This study measured the degree of remaining C=C bonds (RDB), linear polymerization shrinkage (LPS) and polymerization stresses (PS) of dual-cured resin composite build-up materials using a variety of light exposure scenarios.

Four commercially available materials were used: Bis-Core, FluoroCore, Build-it! and Permalute. The RDB was measured using FTIR spectroscopy, and custom-made devices were used to measure LPS and PS values. Data were obtained using three different modes of photo-activation: NLC (No Light-Curing); ILC (Immediate Light-Curing, where 60 second light-curing was applied at the start of the observation period); and DLC (Delayed Light-Curing, where 60-second light-curing was applied 10 minutes from the start of the observation period). Statistical evaluation of the data at the end of the 13-minute observation period was performed with two-way analysis of variance (ANOVA), Tukey's Studentized Range (HSD) Test (*p*=0.05) and simple linear regression. Differences in the development of LPS and PS during the 13 minutes were studied using mathematical calculus.

Bis-Core presented the highest RDB and Permalute the lowest when ILC was applied, while no differences were found between Build-it! and FluoroCore and NLC and DLC increased RDB for FluoroCore and Permalute compared to ILC; whereas, no differences were noted for Build-it! and Bis-Core. Using DLC, a decrease in RDB was found only for Build-it!

Permalute and Bis-Core presented the highest and lowest LPS and PS after ILC, accordingly. Higher LPS and PS were recorded for Build-it! compared to Fluorocore in the ILC group.

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FluoroCore and Permalute exhibited a reduction in LPS and PS using NLC relative to ILC. No differences in LPS and PS values were detected for the materials Bis-Core and Build-it! when subjected to NLC or DLC, compared to ILC.

Simple linear regression showed that only the two polymerization shrinkage properties studied were highly correlated (LPS-PS r^2=0.85). The RDB rate was not correlated with either polymerization shrinkage properties (RDB-LPS r^2=0.40; RDB-PS r^2=0.57). A study of the evolution of the real-time curves of percentage values of LPS and PS showed that these properties evolved in a similar exponential mode and that, most often, there was a delay in the development of PS.

INTRODUCTION

Foundation restorations are often required in order to build damaged teeth to ideal anatomic form prior to their preparation. Despite amalgam, resin composites from the early days of chemically cured materials have also been used for foundation restorations, even though poor adhesion to dentin was provided with previous generations of bonding systems (Bowen, 1985; Munksgaard & Asmussen, 1984; Asmussen & Munksgaard, 1983). Lately, light-cured resin composites, in combination with improved bonding agents, were recommended for core build-ups. These materials offer ample working time and present mechanical properties comparable to amalgam (Bonilla, Mardirossian & Caputo, 2000). Light-cured core build-up materials are more convenient to use than amalgam, when mechanical retention is difficult to achieve and when easy placement is required without the use of elaborate matrices. Additionally, these materials expedite the clinical process, as the restored tooth may be prepared in the same appointment. Thus, light-cured resin composites are often the material of choice.

Nevertheless, there are some concerns associated with resin composites: polymerization shrinkage (Stavridakis, Kakaboura & Krejci, 2000; Stavridakis & others, 2003), delayed expansion due to water sorption (Pearson, 1979; Chai & others, 2004) and the high coefficient of thermal expansion (Asmussen & Jorgensen, 1978). As a result, poor adaptation of the material to preparation is common (Dietschi & others, 2002). Many strategies have been used to overcome limitations caused by polymerization shrinkage. Various layering techniques are suggested in direct resin composite restorations. Nevertheless, time limitations, when placing core build-ups, do not usually allow the clinician to use elaborate multi-layering techniques, as the ideal restoration is not the final goal. The use of photo-activated materials often poses the problem wherein it is difficult for light to reach the deepest parts of a restoration in order to provide maximal resin composite polymerization.

Dual-cured core build-up resin materials have been designed to allow the clinician to build extended foundation restorations quickly, in bulk, as the chemical mode of the polymerization process can initiate resin polymerization in deep resin layers. However, the incorporation of chemical and light curing modes in the same material has not been shown to ensure maximal curing of the material, as the different curing modes may counteract one another. Additionally, polymerization shrinkage of dual-cured resin composite build-up materials has not been assessed.

Thus, this study investigated the polymerization reaction of dual-cured resin composite build-up materials in terms of the degree of carbon-carbon double bond (C=C) remaining, linear polymerization shrinkage (LPS) and polymerization stresses (PS) developed under various light exposure scenarios.

METHODS AND MATERIALS

The dual-cured resin composite core build-up materials tested are listed in Table 1. Three different experimental groups for each material were prepared, corresponding to three different light-curing modes: no light-curing (NLC), the materials were not light cured and kept under dark conditions; immediate light curing (ILC), immediate light exposure of the materials for 60 seconds (Translux EC, Kulzer & Co GmbH, Wehrheim, Germany) with a relative power density of 500 mW/cm^2 (Curing Radiometer, Demetron Research, Danbury, CT, USA) and delayed light curing (DLC), specimens were dark-stored for 10 minutes, then light cured for 60 seconds, as described above. Within each experimental grouping, three different parameters were measured: remaining C=C bonds (RDB), linear polymerization shrinkage (LPS) and polymerization stresses (PS).

For evaluation of RDB, five rectangular specimens (3x2x0.5 mm) per polymerization mode were prepared between two transparent glass slides covered with transparent polystyrene strips. An additional group sample per material, consisting of unset pastes, was performed for the RDB measurements. Spectra of the unset pastes and the directly irradiated surfaces were

Table 1: *Dual-cured Resin Composite Core Build-up Materials Used*

Material	Manufacturer	Color	Batch #
Bis-Core	BISCO, Inc, Schaumburg, IL, USA	Natural	109268
FluoroCore	Caulk/Dentsply, Milford, DE, USA	Tooth shade	990211
Build-it!	Jeneric/Pentron Inc, Wallingford, CT, USA	A2	17564
Permalute	Ultradent Products, Inc, South Jordan, UT, USA	A2	34F8

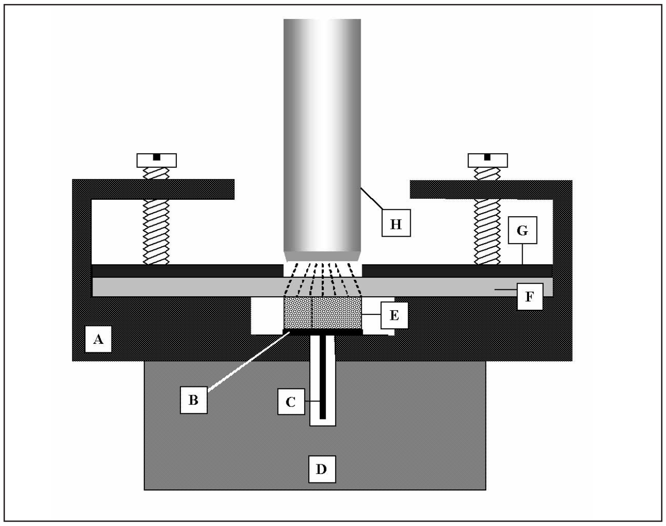

Figure 1: *Schematic presentation of the measuring device for linear polymerization shrinkage: (A) metal frame; (B) aluminum platelet; (C) diaphragm (8 x 8 mm); (D) infrared measuring sensor; (E) specimen; (F) glass plate (41 x 18 x 1 mm); (G) aluminum platen (13 x 20 mm); (H) light-curing tip.*

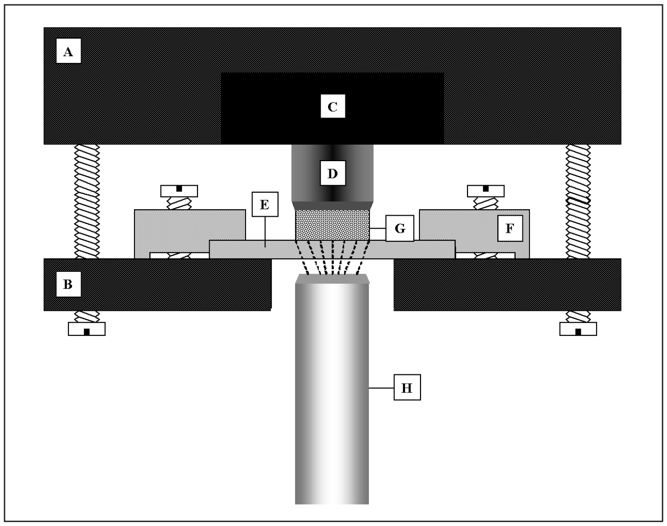

Figure 2: *Schematic presentation of the measuring device for polymerization stresses: (A) upper part of measuring device; (B) lower part of measuring device; (C) load cell; (D) metal cylinder; (E) glass plate; (F) holder of glass plate; (G) specimen; (H) light-curing tip.*

acquired employing a micro-MIR cell attached on a Fourier Transformation Infrared Spectroscopy (FTIR) spectrometer (Micro-MIR accessory and Spectrum GX FTIR spectrometer, Perkin-Elmer, Norwalk, CT, USA) under the following conditions: 4000-400 cm^{-1} range, 4 cm^{-1} resolution, 45° para edge KRS-5 mini-crystal of seven internal reflections and 40 co-added scans co-additions at 30 ± 1°C, which were kept constant with a temperature controller. The quantitative measurement of the % RDB was performed based on the two-frequency technique. The stretching vibrations of the methacrylate C=C bonds (1638 cm^{-1}) were used as an analytical frequency; whereas, the stretching vibrations of the aromatic bonds (1605 cm^{-1}) were used as a reference frequency for Bis-Core, Build-it! and Permalute, and the ester bonds (1712 cm^{-1}) for FluoroCore (Ruyter & Gyorosi, 1976; Rueggeberg, Hashinger & Fairhurst, 1990). The net peak absorbance areas of these peaks were used to quantify the extent of C=C remaining on the directly irradiated resin composite surfaces.

The measurement of LPS was performed with a custom-made measuring device (Figure 1) based on principles suggested by de Gee, Feilzer and Davidson (1993). A standardized amount of each dual-cured material was thoroughly mixed for 30 seconds, then placed on the aluminum platelet. The material was carefully flattened by means of a glass plate to a test height of 1.5 mm. Light-curing was performed from a distance of 1 mm through the glass plate. The vertical movement of the diaphragm caused by polymerization shrinkage of the tested material was detected by the infrared sensor for 13 minutes at a sampling frequency of 5 Hz to an accuracy of 100 nm. Using custom software, data were fed on-line by means of an A/D converter to a personal computer (Macintosh II fx, Apple Computer, Cupertino, CA, USA). Eight specimens for each material and polymerization mode were tested.

PS was measured using a custom-made device (Figure 2) developed following Feilzer, de Gee and Davidson (1987). The upper part consisted of a semi-rigid load cell (PM 11-K, Mettler, Greifensee, Switzerland) to which a metal cylinder was screwed, 8-mm in diameter. A standardized quantity of test material, the same as for the specimens used for measurement of the linear polymerization displacement, was placed on the cylinder and compressed onto a glass plate attached to the base of the device in order to produce a specimen 1.5-mm in height. To improve adhesion of the resinous core build-up material, the surfaces of the metal cylinder and glass plate were sandblasted with 50 mm Al_2O_3 (Microetcher, Danville Engineering, Danville, CA, USA) and silanized (Monobond S, Vivadent Ets, Schaan, Liechtenstein). Light curing was carried out via a recess in the lower frame, through the glass plate, at a distance 1-mm from the tested material. The polymerization stresses developed during the 13 minutes were measured with a load cell at a sampling frequency of 5 Hz. Using custom software, data were fed online by means of an A/D converter to a personal computer. Eight specimens for each material and polymerization mode were tested.

Statistical evaluation of the data at the end of the 13-minute observation period was performed by two-way analysis of variance (ANOVA). Following the ANOVA, Tukey's Studentized Range (HSD) Test (p=0.05) was used to identify pairwise differences. Simple linear regressions were also performed to determine correlations among all the characteristics measured.

The difference in evolution of LPS and PS over time was also measured using the following equations:

$$AD_{PS\text{-}LPS(13\ min)} = \frac{(sum\%PS - sum\%LPS)}{sum\%LPS} \times 100\% \quad (1)$$

$$sum\%\ LPS = \sum_{i=0}^{780} \frac{Y_{LPS_1}}{Y_{LPS_{13min}}} \quad (2)$$

$$sum\%\ PS = \sum_{i=0}^{780} \frac{Y_{PS_1}}{Y_{PS_{13min}}} \quad (3)$$

where

$AD_{PS\text{-}LPS(13min)}$ is the proportional difference between the percentage of polymerization stresses (PS) and linear polymerization shrinkage (LPS) with respect to the maximal value observed at 13 minutes (780 seconds), which numerically expresses the area difference between PS and LPS real-time curves after 13 minutes.

Y_{LPS_i} is the percentage of maximal value at any specific time (i) during the measurement of LPS.

$Y_{LPS_{13min}}$ is the maximum value of LPS recorded at 13 minutes (780 seconds) and taken as 100%.

Y_{PS_i} is the percentage of maximal value at any specific time (i) during measurement of PS.

$Y_{PS_{13min}}$ is the maximum value of LPS recorded is the maximum value of PS recorded at 13 minutes (780 seconds) and taken as 100%.

This effort depicted the area difference derived between two curves: the real-time curve of percentage values of LPS and the real-time curve of percentage values of PS over time. Therefore, equation 1 was able to show the area that expresses the result of the deduction of the areas below the two aforementioned curves and expressed it in percentage points in relation to the larger curve (LPS)

RESULTS

The RDB values measured at the end of the observation period are reported in Table 2. Bis-Core presented statistically significant higher and Permalute statistically significant lower RDB when ILC was applied (Bis-Core: DLC=NLC<ILC, Permalute: ILC<DLC=NLC). FluoroCore and Build-it! exhibited statistically significant differences among all the different curing modes (FluoroCore: ILC<DLC<NLC, Build-it!: DLC<NLC<ILC). Statistically significant differences were observed among all the materials when DLC and NLC were applied (Build-it!<Permalute<Bis-Core<Fluorocore). Statistically significant differences were also detected among all the materials, except FluoroCore and Build-it!, in the ILC group (Permalute<Fluorocore=Build-it!<Bis-Core).

LPS values measured at the end of the observation period are reported in microns in Table 3. Bis-Core presented statistically significant lower LPS when NLC was applied (DLC=ILC>NLC). FluoroCore and Permalute exhibited statistically significant differences among all the different curing modes (FluoroCore: ILC>DLC>NLC, Permalute: DLC>ILC>NLC), while Build-it! demonstrated no differences (ILC=DLC=NLC). Statistically significant differences were found among all the materials, except Bis-Core and FluoroCore when DLC and NLC were applied (Permalute>Build-it!>Bis-Core=Fluorocore). ILC resulted in statistically significant differences among all the materials (Permalute>Build-it!>Fluorocore>Bis-Core).

PS values measured at the end of the observation period are reported in kilograms in Table 4. Bis-Core exhibited statistically significant differences among all the different curing modes (DLC>ILC>NLC). FluoroCore and Permalute presented statistically significant lower PS when NLC was applied

Table 2: *Remaining C=C Double Bonds (%) at 13 Minute Post-mix (mean±SD)*

	Method of Light-curing Application											
Material	**NLC**				**ILC**				**DLC**			
Bis-Core	48.6	±	1.4	C a	53.6	±	1.5	C b	45.7	±	1.7	C a
FluoroCore	78.7	±	2.3	D c	29.1	±	1.6	B a	68.5	±	2.6	D b
Build-it!	26.1	±	1.8	A b	31.3	±	2.8	B c	20.1	±	1.8	A a
Permalute	30.0	±	1.9	B b	21.5	±	0.5	A a	29.4	±	2.7	B b

NLC: No Light-Curing; ILC: Immediate Light-Curing; DLC: Delayed Light-Curing.

Within a column, values having similar upper case letters did not exhibit statistical difference (p>0.05); comparison of materials within the same method of light-curing application. Within a row, values having similar lower case letters did not exhibit statistical difference (p>0.05); comparison of methods of light-curing application within the same material.

Table 3: *Linear Polymerization Shrinkage (in microns) at 13 Minute Post-mix (mean±SD)*

	Method of Light-curing Application											
Material	**NLC**				**ILC**				**DLC**			
Bis-Core	24.3	±	1.3	A a	27.8	±	1.2	A b	28.9	±	0.8	A b
FluoroCore	21.6	±	1.8	A a	32.5	±	2.4	B c	29.7	±	0.9	A b
Build-it!	36.0	±	2.6	B a	38.6	±	2.8	C a	36.4	±	1.7	B a
Permalute	48.0	±	4.9	C a	62.4	±	4.4	D b	68.9	±	3.9	C b

NLC: No Light-Curing; ILC: Immediate Light-Curing; DLC: Delayed Light-Curing.

Within a column, values having similar upper case letters did not exhibit statistical difference (p>0.05); comparison of materials within the same method of light-curing application. Within a row, values having similar lower case letters did not exhibit statistical difference (p>0.05); comparison of methods of light-curing application within the same material.

Table 4: *Polymerization Stress (in kilograms) at 13 Minute Post-mix (mean±SD)*

	Method of Light-curing Application											
Material	**NLC**				**ILC**				**DLC**			
Bis-Core	2.36	±	0.12	B a	2.60	±	0.13	A b	2.77	±	0.09	A c
FluoroCore	1.26	±	0.13	A a	3.14	±	0.16	B b	3.09	±	0.17	A b
Build-it!	4.08	±	0.12	D a	4.29	±	0.21	C a	4.09	±	0.19	B a
Permalute	3.49	±	0.35	C a	6.08	±	0.47	D b	5.95	±	0.42	C b

NLC: No Light-Curing; ILC: Immediate Light-Curing; DLC: Delayed Light-Curing.

Within a column, values having similar upper case letters did not exhibit statistical difference (p>0.05); comparison of materials within the same method of light-curing application. Within a row, values having similar lower case letters did not exhibit statistical difference (p>0.05); comparison of methods of light-curing application within the same material.

(ILC=DLC>NLC). Build-it! exhibited no statistically significant differences among all the different curing modes (ILC=DLC=NLC). Statistically significant differences were observed among all the materials when ILC and NLC were applied (NLC: Build-it!>Permalute>Bis-Core>Fluorocore, ILC: Permalute>Build-it!>Fluorocore>Bis-Core). Finally, statistically significant differences were determined among all the materials except FluoroCore and Bis-Core in the DLC group (Permalute>Build-it!>Fluorocore=Bis-Core).

Linear regression proved high correlation between LPS and PS for all light-curing modes evaluated (r^2=0.85). RDB was not correlated with either LPS or PS (RDB-LPS r^2=0.40; RDB-PS r^2=0.57).

Table 5: *Results of Equation 1* That Numerically Express the Area Difference Between PS and LPS Real-time Curves After 13 Minutes*

Material	Light-curing Application	Equation 1
Bis-Core	NLC	-15.5%
Bis-Core	ILC	-3.4%
Bis-Core	DLC	-4.6%
FluoroCore	NLC	-29.4%
FluoroCore	ILC	-5.7%
FluoroCore	DLC	-27.1%
Build-it!	NLC	-3.9%
Build-it!	ILC	0.4%
Build-it!	DLC	3.1%
Permalute	NLC	-28.8%
Permalute	ILC	-2.9%
Permalute	DLC	-22.4%

NLC: No Light-Curing; ILC: Immediate Light-Curing; DLC: Delayed Light-Curing.

** The smaller the value of Equation 1 in absolute numbers, the more PS and LPD develop at similar rates.*

Table 5 shows the results of Equation 1. Figures 3 through 5 show representative curves of Permalute depicting the evolution of LPS and PS in different light-curing modes. The smaller negative values in Equation 1 indicate that LPS and PS develop in a more similar fashion, as there is less delay in the development of PS with respect to LPS. The results from Table 5 clearly show that ILC demonstrated the lowest negative values in all materials. On the other hand, NLC exhibited the highest negative values. DLC presented values which indicate that, in some materials (FluoroCore and Permalute), LPS and PS evolved in a similar fashion when ILC was applied, while in other materials (Bis-Core and Build-it!), the behavior resembled that of NLC.

DISCUSSION

The degree of remaining C=C bonds has been proven to influence several properties in resin composite materials (Peutzfeldt & Asmussen, 2000). Infrared spectroscopy is a well-established method for evaluating the conversion of methacrylate groups in light-cured resin composites (Silikas, Eliades & Watts, 2000; Park & Lee, 1996; Park, 1996; Chung & Greener, 1990; Papagiannoulis & Eliades, 1989; Eliades, Vougiouklakis & Caputo, 1987; Ferracane, 1985). This method has also been applied to study dual-cured resin cements (Braga, Cesar & Gonzaga, 2002a; Eliades & others, 2000) and resin-modified glass-ionomer materials (Braga, Condon & Ferracane, 2002b; Kakaboura, Eliades & Palaghias, 1996a,b).

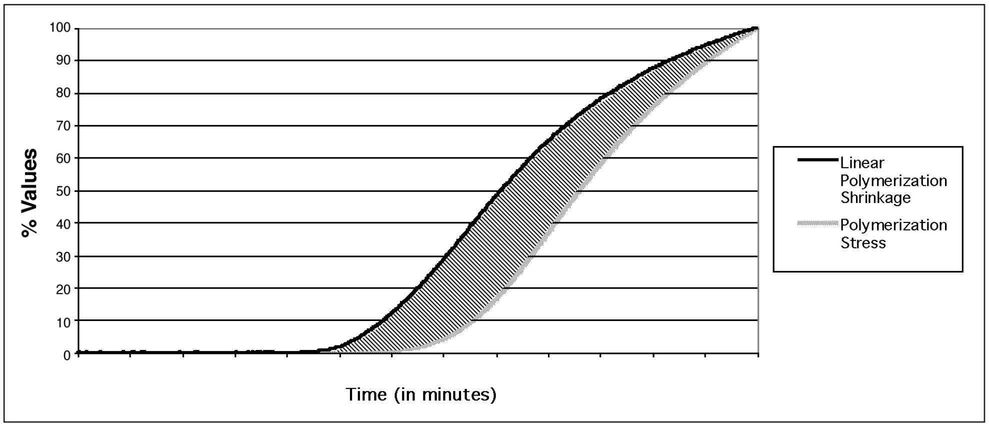

Figure 3: *Real-time curves of percentage values (13-minute value taken as 100%) of LPS and PS development using NLC for Permalute. The result of Equation 1, which numerically expresses the area difference (downward diagonal marked area) between PS and LPS real-time curves, was -28.8%.*

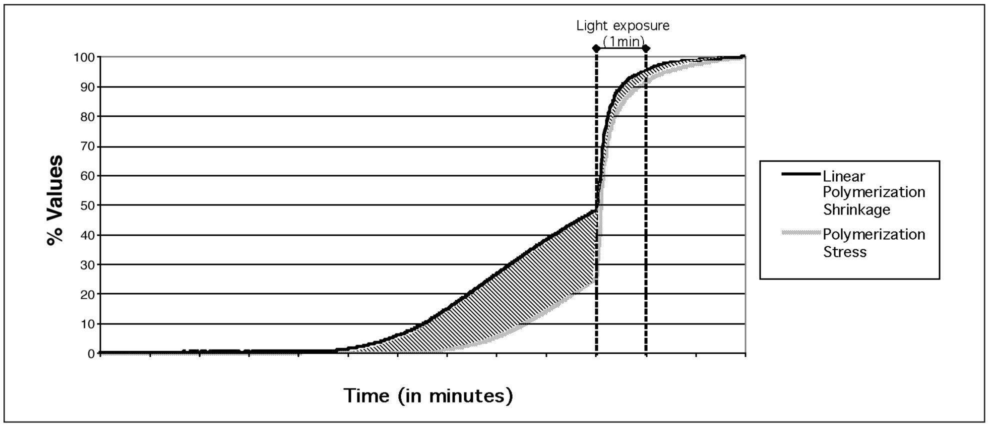

Figure 4: *Real-time curves of percentage values (13-minute value taken as 100%) of LPS and PS development using DLC for Permalute. The result of Equation 1, which numerically expresses the area difference (downward diagonal marked area) between PS and LPS real-time curves, was -22.4%.*

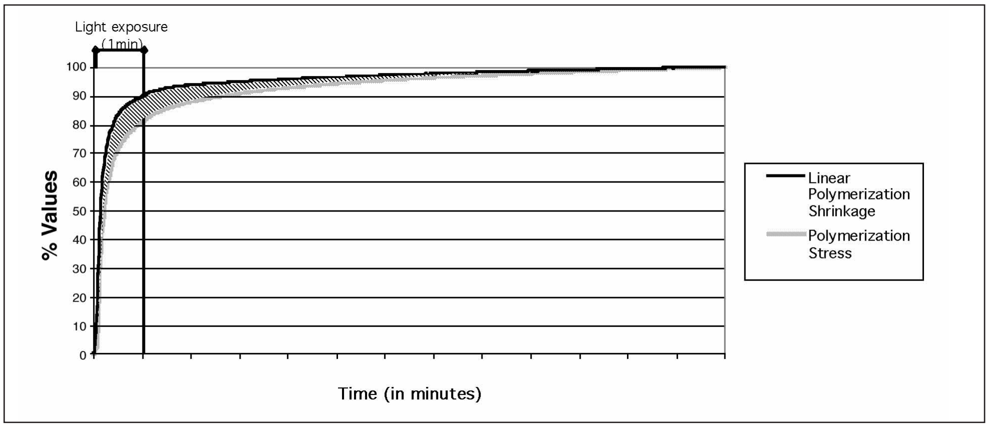

Figure 5: *Real-time curves of percentage values (13-minute value taken as 100%) of LPS and PS development using ILC for Permalute. The result of Equation 1, which numerically expresses the area difference (downward diagonal marked area) between PS and LPS real-time curves, was -2.9%.*

The RDB levels obtained after ILC simulate the values reached under common clinical practice. Also, as both mechanisms of polymerization, chemical and light, are induced within 13 minutes after ILC, it can be hypothesized that each material reached nearly its minimum RDB value. The wide range of RDB values observed under the ILC scenario (21.5% to 53.6%) were consistent with those reported for restorative resin composites (Chung & Greener, 1990; Park, 1996; Peutzfeldt & Asmussen, 2000; Silikas & others, 2000). The differences found in RDB values of the materials investigated may be attributed either to differences in monomer composition or to variations in catalyst systems. The results of this study suggest that ILC provides low levels of RDB on the direct irradiated surface of all materials except Bis-Core. However, an even lower RDB value was achieved in Build-it! when DLC was applied. This finding indicates that the immediate light curing of Build-it! may lead to increased steric hindrance, which decreases the segmental mobility of methacrylate groups and reduces reactivity of the chemical polymerization reaction.

A comparison of the three light-curing modes revealed interesting observations with respect to the dominant curing mode in each material. That was the reason why a clinically unacceptable 10-minute delay was chosen as a curing mode in this study. DLC provides ample time for the chemical curing mechanism to progress prior to light application. The dominant curing mode is a point of outmost clinical importance in order to differentiate which materials' chemical curing plays a substantial role compared to light polymerization. Thus, these materials may be used in areas where negligible light is applicable.

Differences in RDB between the surface layer of a restoration, expressed in this study using ILC, and the deep aspects, represented by the NLC group, may develop anisotropic properties in the core material under load. This difference, in turn, may stress the tooth-material interface and may cause a non-uniform distribution of stress within the material. According to the results of this study, such differences were found only for FluoroCore. This material's dominant curing mode was as a light-cured resin composite, because a very high RDB level (78.7%) was measured when NLC was applied. Even more, DLC resulted in high RDB, as well (68.5%). On the contrary, when this material underwent ILC, low RDB was recorded (29.1%). This result could be attributed to the fact that 60-second light-curing could not substantially increase the restricted mobility of the monomer chains embedded into the "poorly developed" polymer network, which resulted in a chemical cure within the first 10 minutes. Materials like Build-it! and Permalute exhibited high levels of chemical curing, as low RDB was found even when NLC was used. Nevertheless, when these materials were subjected to DLC, only Build-it! presented a decrease in RDB. This result could be due to the fact that the polymer network developed in Permalute by chemical cure did not allow any additional mobility of the polymer chains in order to improve the C=C conversion. Even though Build-it! and Permalute can be polymerized under dark conditions, the degree of C=C conversion under ILC surpassed that of NLC and light curing acted as the dominant mechanism. The curing mode had no impact on the RDB of Bis-Core, since high values were measured under the three curing modes applied. The latter finding may highlight the monomer type(s) and concentration as the main contributor factors for the insufficient polymerization of this material and not the curing mechanism.

Various experimental methods have been used to determine shrinkage and stress of resin composites during polymerization. Dilatometric methods are commonly used to measure polymerization shrinkage of chemically cured materials (Iga & others, 1991; Rees & Jacobsen, 1989; Hay & Shortall, 1988; Feilzer, de Gee & Davidson, 1988; Bullard, Leinfelder & Russell, 1988; Patel, Braden & Davy, 1987; Penn, 1986; Bandyopadhyay, 1982; de Gee, Davidson & Smith, 1981; Jacobsen, Whiting & Richardson, 1977; Hegdahl & Gjerdet, 1977; Jacobsen, 1975; Dennison & Craig, 1972; Lee, Swartz & Smith, 1969). These techniques present a significant number of problems related to the access of light to the light-cured material tested. Furthermore, when water is used, temperature changes occur due to thermal expansion/contraction of the surrounding fluid. Non-volume dilatometric methods have been used lately for measurement of polymerization shrinkage in light-cured resin-based restorative materials (Feilzer, de Gee & Davidson, 1993; de Gee, Feilzer & Davidson, 1993; Watts & Cash, 1991; Feilzer, de Gee & Davidson, 1989; Walls, McCabe & Murray, 1988; Bausch & others, 1982). The materials tested in this study were dual-cured, and both chemical and light-curing polymerization processes were assessed. Therefore, a non-volume dilatometric measurement technique, as described in the materials and methods section, was used to measure linear polymerization displacement. The LPS values of this study are reported in microns, as these were the recording units of the infrared sensor used for measuring the vertical movement of the diaphragm, which was caused by polymerization shrinkage of the test material. The technique used in this study permitted measurement of the evolution of linear polymerization displacement through time.

Methods commonly used for polymerization stress measurement differ in the configuration by which specimens are connected to the load cell (Feilzer & others, 1993; Bullard & others, 1988; Feilzer & others, 1987; Hegdahl & Gjerdet, 1977). Various techniques have been used to maintain the distance between the load-cell and the testing machine crosshead stable. The latter permits for the measurement of stress developing when shrinkage is restrained, simulating clinical conditions where resin composite is bonded to non-flexible preparation walls. The PS values of this study are reported in kilograms (actual measurements of load cell) and were not transformed in Megapascals (MPa) to avoid confusion with literature data with completely rigid experimental set-ups. In the experimental design of this study, axial specimen deformation was partially restricted, since the load cell was axially displaced 4 mm for each kilogram of measured force, resulting in a maximum of 28 mm deformation of the specimen. In this way, a semi-rigid configuration of a preparation having a C-factor of 2.67 was simulated. Several studies have demonstrated that cusps of molars and premolars deflect inward after placement of Class II resin composite restorations, with the amount of the reported contraction ranging from 18 to 45 µm (Smith & Caughman, 1989; Causton, Miller & Sefton, 1985; Lutz, Krejci & Barbakow, 1991), thus justifying the experimental set-up used in this research.

Most of the LPS and PS values encountered in this research, when ILC was applied, were consistent with those reported for restorative resin composites (Stavridakis & others, 2000; Stavridakis & others, 2003). However, in the case of Permalute, higher values were measured. Nevertheless, this result was expected, as Permalute is characterized by the manufacturer as a low-viscosity composite luting/restorative resin. The small filler fraction and high portion of monomer caused increased LPS and PS (Stavridakis & others, 2000). On the other hand, the high flow capacity of Permalute should compensate for the shrinkage effect during the pre-gelation phase. However, using ILC, the material reaches the gel point rapidly. Therefore, viscous flow cannot reduce the shrinkage stress developed in Permalute. The low LPS and PS exhibited by Bis-Core cannot be characterized as an advantage, because they are attributed to the high RDB of the material.

The high correlation of LPS and PS noted in this study is in accordance with results from similar studies (Davidson & Feilzer, 1997; Stavridakis & others, 2000; Stavridakis & others, 2003). Generally, although the amount of shrinkage is related to the extent of C=C remaining, no high correlation was found between RDB and either LPS or PS. Thus, when ILC was applied, high RDB was associated with low values in LPS and PS. On the contrary, using NLC or DLC, neither LPS nor PS was related to RDB. For example, after DLC of FluoroCore, very high RDB resulted in unexpectedly high values of PS. This result may be explained by the kinetics of the polymerization process. It is likely that after 10 minutes of chemical cure, the material has reached a state where restricted mobility of free radicals in the polymer network resulted in the development of the polymer network. As a consequence, there was an increase in the modulus of elasticity that restricts the material's capacity for viscous flow and decreases its compliance, thus causing a dramatic increase in PS (Braga & Ferracane, 2002). One should always keep in mind that low polymerization stresses alone are not the only quest, as adequate C=C conversion is also a prerequisite that was not obtained in some dual-cured materials. The evolution of PS was both material- and curing-mode dependent.

The inconsistencies noted between the development of LPS and PS may be more easily understood by observing the kinetics of the properties that were studied. In the chemical curing mode of Permalute (Figure 3), the delay in PS development is easily observed. Equation 1 expresses the differences in evolution of the two properties over time in a numerical manner. The application of Equation 1 in some cases resulted in high negative values, indicating that larger delays in development of PS, with respect to LPS, were evident due to the slow development of polymerization stresses. In other cases, the results of Equation 1 were again negative values but of a lower magnitude (Figures 4 and 5). In those cases, there was again a delay in the development of PS with respect to LPS, but of a lower magnitude, meaning that the two properties developed more at the same rate and at the same proportional level. In two instances, Equation 1 resulted in positive values, demonstrating that PS evolved faster than LPS.

From a clinical standpoint, materials with a low RDB, LPS and PS are preferable. Low RDB is necessary in order for the material to obtain maximal mechanical properties. This is why ILC is the polymerization mode of choice for FluoroCore, as the other two curing modes produce a low degree of RDB. The second aim is to use materials that produce low polymerization stresses. For this reason materials with low LPS are preferred, as this property is highly correlated with PS. Nevertheless, this research showed that there are other options available as a means of lowering PS, depending on the behavior of the dual-cured materials. In some situations, obtaining low polymerization stresses was acquired by using NLC when this curing mode provided low RDB (Bis-Core). In other cases, using DLC resulted in lower PS (Permalute and Build-it!).

CONCLUSIONS

1. Significant differences were manifested among the materials tested in terms of the remaining C=C bonds (RDB), linear polymerization shrinkage (LPS) and polymerization stresses (PS) under all different modes of photo-activation studied.
2. Bis-Core provided the highest percentage of RDB with the lowest LPS and PS; whereas, Permalute presented the lowest RDB along with the highest LPS and PS, irrespective of curing mode.
3. The RDB in Build-it! was equal, using either ILC or NLC conditions with no significant changes in either LPS and PS; DLC reduced RDB.
4. The polymerization of FluoroCore using NLC or DLC modes caused a dramatic increase in RDB.
5. No correlation was found between RDB and LPS or PS. On the contrary, a strong correlation was evident between LPS and PS.

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