Polymerization behavior of a light-cured resin using the laser speckle-correlation method

Tomomi Sato, DDS,[a] Masashi Miyazaki, DDS, PhD,[a,b] Akitomo Rikuta, DDS, PhD,[a,b] Hiroyasu Kurokawa, DDS, PhD,[a,b] and Toshiki Takamizawa, DDS, PhD[a]

[a]Department of Operative Dentistry, and [b]Division of Biomaterial Science, Dental Research Center, Nihon University School of Dentistry, Tokyo, Japan

Purpose: The aim of this study was to monitor the polymerization reaction of a light-cured resin using the laser speckle-correlation method.
Materials and Methods: The experimental apparatus comprised semiconductor lasers, a speckle analyzer and a computer-controlled data-acquisition system. The resin composite was condensed into a glass tube and irradiated using a curing unit with a light intensity of 100 or 600 mW/cm^2. The speckle patterns obtained from the lateral surfaces and the underside of the specimen were monitored using a CCD camera connected to a personal computer. A simplified correlation value was obtained for each pair of adjacent speckle patterns. The images of the speckle patterns were analyzed using the phase-only correlation method. The speckle contrast was then obtained as a function of the time that elapsed while measurements were made.
Results: The speckle contrast decreased soon after light exposure commenced, then gradually increased after irradiation. The changes in speckle contrast corresponded to changes in the polymerization reaction of the light-cured resin. The speckle-contrast data obtained from the underside were lower than those from the lateral surfaces. This tendency was more pronounced when the specimen was irradiated with lower intensity light.
Conclusion: This approach has the potential to record accurately the polymerization characteristics of light-cured resins. **(Int Chin J Dent 2004; 4: 45-50.)**

Clinical Significance: These data suggest that the shrinkage characteristics of a light-cured resin were influenced by the light intensity of the curing unit.
Key Words: laser speckle, light-cured resin, light irradiation, polymerization.

Introduction

The adhesive resin composites used in restorative dentistry undergo volumetric shrinkage during polymerization. This can create marginal gaps that negatively influence the bonding and longevity of a restoration. Proper infiltration of the resin on the surface of an etched primed tooth and retention within the tooth are both required to minimize shrinkage, which might disrupt bonding.[1] Various methods have been investigated for monitoring the polymerization shrinkage of restorative materials. For example, the specimen can be studied using changes in the height of the mercury within a capillary column.[2] Other methods have utilized changes in the level of water in a pycnometer containing the material of interest.[3-5] These systems have been modified in attempts to improve their accuracy, allowing them to monitor the polymerization of light-cured resin composites.[6-9] Dimensional strain in a material has also been measured using non-volumetric dilatometric methods employing either a deflecting disk[10-12] or the He-Ne laser-scanning method.[13]

As the superficial outer layer of a restoration shrinks more quickly than the deeper layers, it has been suggested that the shrinkage vector of light-cured resin is oriented towards the irradiated surface.[14] However, a finite elemental analysis has shown that the shrinkage vector is not significantly affected by the orientation of incoming light.[15] Asymmetric stress can build up inside the resin restoration, resulting in asymmetric three-dimensional shrinkage. Therefore, the shrinkage vectors within the light-cured resin might differ throughout the material. Conversely, the information provided by volumetric-shrinkage methods suggests that light-cured resin shrinks homogeneously. Hence, a new and independent method was required to confirm the nature of the shrinkage process.

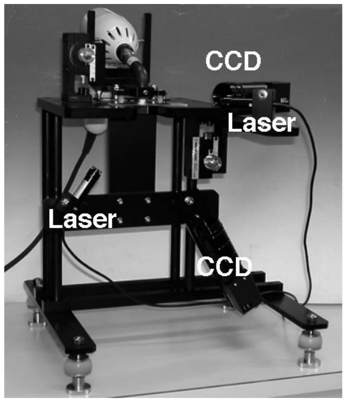
The laser speckle-correlation method is a simple non-contact non-destructive technique that does not require special treatment of the specimen surface.[15-18] The laser-speckle phenomenon occurs when an intense beam of coherent light is reflected on an object's surface. Speckles are formed by the random interference of coherent waves that are scattered from the rough surface. If the object has certain physical characteristics, a three-dimensional diffraction field is observed with random fluctuations in intensity. The relative intensity of bright and dark spots within the speckle pattern provides information about the material. The contrast between the bright and dark spots can be recorded using a digital image. This forms the basis of speckle interferometry, a technique in which the speckle patterns of an object at two different status points are compared in order to obtain the desired displacement information.[19-22] In the case of light-cured resins, the speckle patterns can reveal movement of the resin paste that has occurred during polymerization. The polymerization reaction causes small fillers within the resin composite to be in a state of motion, which increases as the reaction progresses.

The present study tested the hypothesis that the laser speckle-correlation method is a useful technique to study the reaction characteristics of light-cured resin polymerization. The main aim was to develop a laser speckle-correlation method to determine the polymerization characteristics of a light-cured resin.

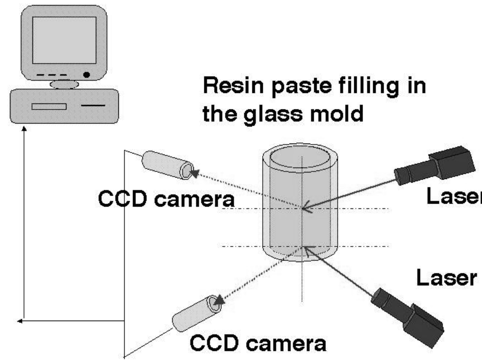
Materials and Methods

The resin composite Palfique Estelite (Shade A3, Lot No. J242, Tokuyama Dental, Tokyo, Japan) was used in this study. The Optilux 401 curing unit (Demetron/Kerr, Danbury, CT, USA) was employed, and the light intensity was adjusted to 100 or 600 mW/cm^2, as measured using a dental radiometer (Model 100, Demetron/Kerr).

The test apparatus, including the laser-speckle equipment (Toyo Seiki Seisaku-sho, Ltd., Tokyo, Japan), is shown in Fig. 1. The experimental set-up comprised coherent light sources (MLXS-D13, Kikoh Giken Co., Nishinomiya, Japan), charged couple device (CCD) cameras (CS8530-01, Tokyo Electronic Industry Co., Tokyo, Japan) and a personal computer. The resin composite was placed in a glass mold (4.0 mm in diameter and 4.0 or 6.0 mm in height) on a glass slide (No. 5116, Muto Pure Chemicals Co., Tokyo, Japan). The specimen was placed 20 cm from the laser source and the CCD cameras were placed 20 cm from the sample surface at an angle of 30° from each incident beam (Fig. 2). The spatial resolution of this system was determined as 5 μm. Vibration interference was minimized by fixing the lasers to a block, and the CCD cameras and a sample stage were placed in a darkened chamber.



1



2

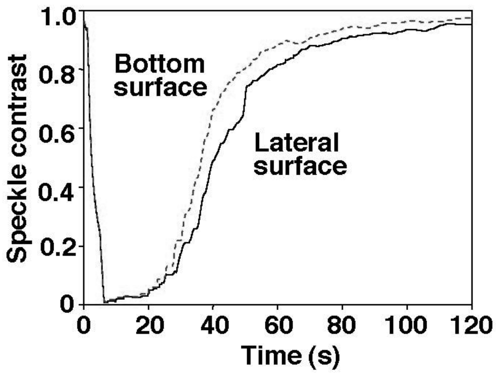
Fig. 1. Experimental equipment used in this study.
Fig. 2. Schematic diagram to show the laser speckle-contrast measurement system.

The wavelengths of the beams from the semiconductor lasers were tuned to 635 and 670 nm with a power of 4 mW, and focused on the lateral surfaces and underside of the specimen, respectively. Different wavelengths were used for the coherent light sources to avoid interference when detected by the CCD cameras. The CCD cameras were adjusted until sharply focused speckle patterns were observed on the video monitor. The resin paste underwent light irradiation for 30 s, and the data were collected for 120 s from the start of the irradiation. During the polymerization reaction, the movement of the resin paste produced dark and bright spots, which are referred to as speckle patterns. The speckle pattern recorded first was used as a reference, and was compared electronically with the speckle pattern obtained subsequently from the resin surface during polymerization. As the native speckle patterns had a poor signal-to-noise ratio, a Fourier phase-only correlation method[23] was adopted to improve and enhance the quality of the patterns. The images were then examined using an image analyzer connected to a personal computer. Measurements were recorded at a constant temperature of 23 ± 1°C, a relative humidity of 50 ± 5% and with illumination from only one small light source.

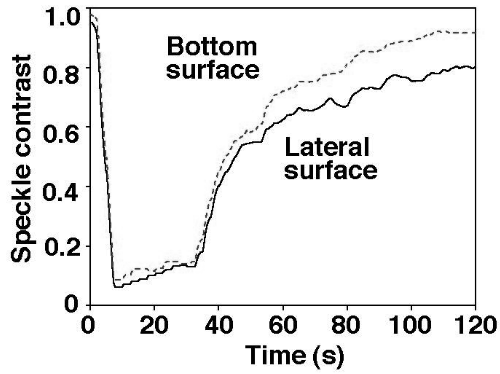
Results

The speckle contrasts for two light-cured resin samples of different thickness, which were polymerized using the light intensities indicated, are shown in Figs. 3-6 as a function of time. The overall magnitude of the speckle contrasts decreased soon after light exposure commenced and remained at a low level during irradiation. After irradiation, the speckle contrasts gradually increased, particularly for the specimen irradiated at a higher light intensity. Differences between the speckle contrasts obtained from the lateral surfaces and underside of each specimen were observed for all specimens tested. A higher level of speckle contrast was detected for the underside than for the lateral surfaces.

The differences in the speckle contrast obtained from the lateral surfaces and underside were more pronounced when a lower light intensity was used. The speckle contrast decreased when light irradiation commenced and remained at lower levels. After irradiation, the speckle contrast increased relatively slowly for both lateral surfaces and undersides.

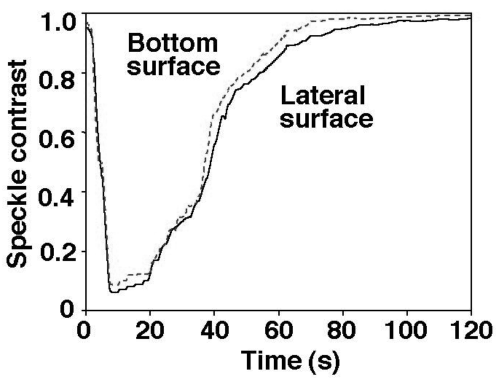


Light intensity, 600 mW/cm^2 3

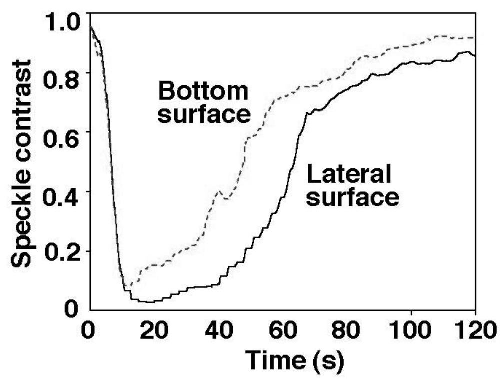


Light intensity, 100 mW/cm^2 4

Figs. 3, 4. Speckle-contrast measurements of the lateral surfaces and underside as a function of time (mold diameter, 4 mm; mold height, 4mm).



Light intensity, 600 mW/cm^2 5



Light intensity, 100 mW/cm^2 6

Figs. 5, 6. Speckle-contrast measurements of the lateral surfaces and underside as a function of time (mold diameter, 4mm; mold height, 6mm).

Discussion

When the resin paste underwent light polymerization, the test area moved and the coherent wave fronts were scattered, resulting in changes in the speckle patterns. Images of the speckle patterns were recorded on the CCD camera and stored in its memory. The digital absolute-value subtraction between the initial image of the object and those taken during polymerization resulted in an image with speckle-pattern displacement (Δd) that can be expressed as follows:

$$\Delta d = n\ \lambda/2\sin\ \alpha$$

Where, λ is the wavelength of the laser light, n is the number of fringes forming the interferogram and α is the angle of inclination of the coherent wave front to the surface. The speckle patterns have a similar appearance to moire fringes and represent contours of equal displacement, with each fringe resulting from a displacement in the order of one-half of the wavelength of the laser light source used.[19-22]

The laser speckle-contrast measurement has the advantage that a small amount of sample can be analyzed with great accuracy.[16] The spatial resolution of the equipment employed in this study was estimated as 5 μm, and this precision allows any movement of the resin composite during polymerization to be monitored. During this experiment, measurements were recorded 120 s from the start of light irradiation; however, it is also possible to examine the polymerization reaction in greater detail over a longer period of time. A lower number for the speckle contrast indicates that the movement of the resin composite occurred rapidly during polymerization. The majority of the polymerization shrinkage occurred during and immediately after irradiation, which is reflected in the speckle contrasts measured during light irradiation.

Since this method was first used to observe the polymerization reaction of light-cured materials, a commercially available resin known as Palfique Estelite has been introduced. The base resin of the paste is Bis-GMA with an inorganic-filler content of 62 wt%. Comparisons among light-cured materials are generally inaccurate, even when the resin composites are produced by the same manufacturer. This is because their volumetric changes depend on many factors, including the loading, type and size of the filler. Other factors that contribute to the volumetric changes are the monomer and initiating systems that determine the structure of the hardened material. As most light-cured materials employ camphorquinone as a photoinitiator,[24] an adequate intensity of visible light around the 470 nm wavelength is required to activate polymerization. An appropriate wavelength is absorbed by the photosensitizer, which enters an excited state and reacts with an amine-reducing agent to produce reactive free radicals.[25] The transmission of light through the material and the composition of the photoinitiator is known to influence the mechanical properties of light-cured materials.[26] The intensity of light passing through a material is controlled by its absorption and scattering properties.[27] If a lower energy light is used, it could be difficult for the photoinitiators to be excited in the deeper areas of the material. The data from this study show that the rate of speckle contrasts was slightly reduced at the underside of the specimen compared to that at the lateral surface. This phenomenon was more pronounced when the specimens were irradiated with lower intensity light.

The detailed behavior of samples with different measurement spots is shown graphically. The changes in speckle contrasts obtained at the underside of the specimen were weaker than those from the lateral surfaces located closer to the light source. The information provided by studies using volumetric-shrinkage measurement is only equivalent in the case of homogenous shrinkage. Our data indicate that a symmetric movement of the resin paste can be detected using the laser speckle-contrast approach.

Conclusion

We investigated the laser speckle-correlation method for characterizing the polymerization reaction of a light-cured resin. Changes in speckle patterns were converted into an intensity correlation, which provided information on the status of the polymerization reaction. The method described here might offer an alternative approach to determine the polymerization-shrinkage characteristics of light-cured resins with greater accuracy and precision.

Acknowledgments

This work was supported in part by Grant from the Dental Research Center, Nihon University School of Dentistry, Japan, 2003, Grant from the Ministry of Education, Culture, Sports, Science, and Technology of Japan to promote multi-disciplinary research project, and Grant-in Aid for Encouragement of Young Scientists (B) 40287660 from the Japan Society for the Promotion of Science. The authors would like to thank Mr. Kouichi Kobayashi, Dr. Toshiki Ooguro and Ms. Naoko Noguchi for their contributions to the experiments.

References

1. Miyazaki M, Hinoura K, Onose H, Moore BK. Effect of filler content of light-cured composites on bond strength to bovine dentine. J Dent 1991; 19: 301-3.
2. Smith DL, Schoonver IC. Direct filling resins: dimensional changes resulting from polymerization shrinkage and water sorption. J Am Dent Assoc 1953; 46: 540-4.
3. de Gee AJ, Davidson CL, Smith A. A modified dilatometer for continuous recording of volumetric polymerization shrinkage of composite restorative materials. J Dent 1981; 9: 36-42.
4. Bandyopadhyay S. A study of the volumetric setting shrinkage of some dental materials. J Biomed Mater Res 1982; 16: 135-44.
5. Goldman M. Polymerization shrinkage of resin-based restorative materials. Aust Dent J 1983; 28: 156-61.
6. Penn RW. A recording dilatometer for measuring polymerization shrinkage. Dent Mater 1986; 2: 78-9.
7. Rees JS, Jacobsen PH. The polymerization shrinkage of composite resins. Dent Mater 1989; 5: 41-4.
8. Lai JH, Johnson AE. Measuring polymerization shrinkage of photo-activated restorative materials by a water-filled dilatometer. Dent Mater 1993; 9: 139-43.
9. Walls AF, McCabe JF, Murray JJ. The polymerization contraction of visible-light activated composite resins. J Dent 1988; 16: 177-81.
10. Watts DC, Cash AJ. Determination of polymerization shrinkage kinetics in visible-light-cured materials: methods development. Dent Mater 1991; 7: 281-7.
11. de Gee AJ, Feilzer AJ, Davidson CL. True linear polymerization shrinkage of unfilled resins and composites determined with a linometer. Dent Mater 1993; 9: 11-4.
12. Fano V, Ortalli I, Pizzi S, Bonanini M. Polymerization shrinkage of microfilled composites determined by laser beam scanning. Biomaterials 1997; 18: 467-70.
13. Hansen EK. Visible light-cured composite resins: polymerization contraction, contraction pattern and hygroscopic expansion. Scand J Dent Res 1982; 90: 329-35.
14. Versluis A, Tantbirojn D, Douglas WH. Do dental composites always shrink toward the light? J Dent Res 1998; 77: 1435-45.
15. Brillaud J, Lagattu F. Limits and possibilities of laser speckle and white-light image-correlation methods: theory and experiments. Appl Opt 2002; 41: 6603-13.
16. Yamaguchi I. Holography, speckle, and computers Opt Lasers Eng 2003; 39: 411-29.
17. Mohan NK, Rastogi P. Recent developments in digital speckle pattern interferometry Opt Lasers Eng 2003; 40: 439-45.
18. Jones J, Tyrer J. An introduction to laser speckle strain imaging as a quantitative tool for structural NDT and lifetime prediction. Insight 2003; 45: 272-5.
19. Román JF, Fernández P, Moreno V, Abeleira M, Gallas M, Suárez D. The mechanical behaviour of human mandibles studied by electronic speckle pattern interferometry. Eur J Orthod 1999; 21: 413-21.
20. Fukuoka S, Hotokebuchi T, Jingushi S, Fujii H, Sugioka Y, Iwamoto Y. Evaluation of blood flow within the subchondral bone of the femoral head: use of the laser speckle method at surgery for osteonecrosis. J Orthop Res 1999; 17: 80-7.
21. Kishen A, Murukeshan VM, Krishnakumar V, Asundi A. Analysis on the nature of thermally induced deformation in human dentine by electronic speckle pattern interferometry (ESPI). J Dent 2001; 29: 531-7.
22. Ayers MR, Hunt AJ. Observation of the aggregation behavior of silica sols using laser speckle contrast measurements. J Non-Cryst Solids 2001; 290: 122-8.
23. Kobayashi K, Nakajima H, Aoki T, Kawamata M, Higuchi T. Principles of phase only correlation and its applications. ITE Technical Report 1996; 20: 1-6.
24. Taira M, Urabe H, Hirose T, Wakasa K, Yamaki M. Analysis of photo-initiators in visible-light-cured dental composite resins. J Dent Res 1988; 67: 24-8.
25. Watts DC, Amer O, Combe EC. Characteristics of visible-light-activated composite systems. Br Dent J 1984; 156: 209-15.
26. Cook WD. Photopolymerization kinetics of dimethylacrylates using the camphorquinone/ amine initiator system. Polymer 1992; 33: 600-9.
27. Arikawa H, Fujii K, Kanie T, Inoue K. Light transmittance characteristics of light-cured composite resins. Dent Mater 1998; 14: 405-11.

Reprint request to:

Dr. Masashi Miyazaki
Department of Operative Dentistry, Nihon University School of Dentistry
1-8-13, Kanda-Surugadai, Chiyoda-ku, Tokyo 101-8310, Japan
Fax: +81-3-3219-8347 E-mail: miyazaki-m@dent.nihon-u.ac.jp

Received March 4, 2004. Revised April 23, 2004. Accepted April 30, 2004.