Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.intl.elsevierhealth.com/journals/dema

Nanoindentation tests to assess polymerization of resin-based luting cement

Mitsuha Sato[a], Akihiro Fujishima[b], Yo Shibata[b,*], Takashi Miyazaki[b], Mitsuko Inoue[a]

[a] Department of Pediatric Dentistry, Showa University School of Dentistry, 2-1-1 Kitasenzoku, Ohta-ku, 145-8515 Tokyo, Japan

[b] Department of Conservative Dentistry, Division of Biomaterials & Engineering, Showa University School of Dentistry, 1-5-8 Hatanodai, Shinagawa-ku, 142-8555 Tokyo, Japan

ARTICLE INFO

Article history:
Received 6 November 2013
Received in revised form
16 April 2014
Accepted 29 May 2014

Keywords:
Dimethacrylate
10-Methacryloxydecyl dihydrogen phosphate
FTIR
Nanoindentation
Polymerization

ABSTRACT

Objective. The optimal polymerization of resin-based luting cements plays a critical role in the long-term clinical success of dental prostheses and indirect restorations. This study investigated a mutual action between the conformational changes and mechanical properties of a dimethacrylate resin-based luting cement with and without pre-application of the acidic functional monomer 10-methacryloxydecyl dihydrogen phosphate.

Methods. Degree of conversion in the luting cement was measured using conventional infrared spectrophotometry. Mechanical properties of the luting cements were also evaluated by quasi-static and dynamic nanoindentation tests.

Results. The results of infrared spectrophotometry and nanoindentation testing were proportional in samples without functional monomer pretreatment. When considerable residual monomer remains within the final products, the mechanical properties of the resin-based luting cements could possibly be impaired. Although the apparent degree of conversion increased with a mixture of functional monomer, a reduction in the cross-linking polymer network may have resulted in the highest viscoelastic creep behavior of the luting cement. The time-dependent behaviors found in the nanoindentation tests likely resulted from linear polymerization chains of the functional monomer.

Significance. The application of an acidic functional monomer may affect the viscosity of resin-based luting cements. Quasi-static or dynamic nanoindentation is a useful tool for assessing the polymerization qualities of resin composites.

1. Introduction

The integrity of luting cements is an important determinant of the long-term success of dental prostheses and indirect restorations [1,2]. With increasing demand for esthetic properties and adequate marginal seal, the use of resin-based luting cement has become dominant.

Despite their superior esthetic and mechanical properties, conventional resin-based cements require pre-application of

* *Corresponding author.* Tel.: +81 3 3784 8178; fax: +81 3 3784 8179.
E-mail address: yookun@dent.showa-u.ac.jp (Y. Shibata).

http://dx.doi.org/10.1016/j.dental.2014.05.034

Table 1 – Sample preparation protocol.

Sample group	Treatment
Control	Mixed resin-based luting cement (Rely-X_{TM} ARC, 3M ESPE).
LC	Mixed resin-based luting cement was photo-irradiated for 30 s with a light cure unit.
MDP-pretreated	Mixed resin-based luting cement was placed on a CaF_2 disc pretreated with MDP monomer (Epricode, Kuraray).
MDP-mixed	MDP monomer and resin-based luting cement were mixed and then immediately placed on a CaF_2 disc.

total etch adhesives or a self-etching primer containing an acid-functionalized monomer such as 10-methacryloxydecyl dihydrogen phosphate (MDP), because the resin substrate lacks chemical adhesive properties [3,4]. Acidic monomers may compromise the curing mechanism of resin-based cements [5,6] and hence optimal polymerization of the cements with MDP application is uncertain. Inferior polymerization of resin-based materials may negatively affect their mechanical properties, causing significant deterioration of clinical performance [7,8].

Infrared (IR) spectrophotometry has been used to evaluate the polymerization of dental composites [9,10]. In this technique, the relative intensities of the C=C double bond peak at 1637 cm^{-1} and of the phenyl group peak at 1608 cm^{-1} indicate the degree of conversion. However, IR spectrophotometry also detects MDP vibration modes, which theoretically overlap with the cement spectra, so that isolation of polymerization is unlikely [11]. Thus, an evaluation technique that combines IR spectrophotometry and direct mechanical characterization is needed.

IR spectrophotometry using two-beam transmission devices allows visualization of conformational changes over time in thin film preparations of luting cements. Concurrent microscale mechanical testing on the thin film is desirable. Nanoindentation is depth-sensing mechanical testing that continuously measures hardness and elastic modulus by quasi-static load displacement in the thin film preparation [12]. A drawback in mechanical testing of resin-based luting cements is the unavoidable viscoelastic response, which increases with decreased polymerization because of delayed fluid movement of the residual monomer [13,14]. However, nanoindentation systems currently have high placement precision and can capture a material's responses over a range of imposed frequencies using dynamic force and displacement amplitudes [15,16], enabling measurement of the viscoelastic properties of resin-based materials.

This study evaluates the polymerization of dimethacrylate resin-based luting cement with and without MDP pre-application by measuring conformational changes over time with quasi-static and dynamic nanomechanical testing.

2. Materials and methods

2.1. Materials

This study used dual-polymerizing resin-based luting cement (Rely-X_{TM} ARC, 3M ESPE, Tokyo, Japan) and MDP monomer (Epricode, Kuraray, Tokyo, Japan).

2.2. Sample preparation

Table 1 shows sample preparation protocols. Mixed resin-based luting cement was placed directly between CaF_2 discs (control) or was photo-irradiated for 30 s with a light cure unit (LC) (DP-075, Morita, Tokyo, Japan). The intensity of the halogen lamp was assessed (470 nm and >500 mW/cm^2) with a photoelectric sensor before testing and its intensity was maintained throughout the study. In the MDP-pretreated samples, CaF_2 discs were pretreated with MDP monomer, and then resin-based luting cement was pressed between a pretreated and an untreated disc (MDP-pretreated). Pretreatment was performed according to manufacturer's instructions. For the mixed samples, the same volume of MDP monomer and resin-based luting cement were mixed and then immediately placed between CaF_2 discs (MDP-mixed). CaF_2 discs were used because of their IR translucency and their distinctive mechanical properties compared with the samples.

2.3. IR spectrophotometry

The samples were subjected to a Fourier Transform Infrared (FTIR) analyzer (FT/IR-660, JASCO, Tokyo, Japan). Conformational changes of each composite over time were monitored for 24 h. At a resolution of 4 cm^{-1}, we performed 200 iterations within the range from 400 to 4000 cm^{-1} to characterize the various functional groups. The degree of conversion was measured by the intensities of the C=C peak at 1638 cm^{-1} and the C- - -C reference peak at 1608 cm^{-1}, using a standard baseline technique [9,17]. The peak at 1608 cm^{-1} originated from aromatic rings, whose intensity remains unchanged during polymerization. Therefore, the ratio of the absorbance intensities of C=C/C- - -C reveals the polymerization ratio of the samples using following formula:

$$\text{Degree of conversion (\%)} = 100 - \left(\frac{\text{cured peak intensities of C} = \text{C/C} - - - \text{C}}{\text{uncured peak intensities of C} = \text{C/C} - - - \text{C}} \times 100 \right)$$

2.4. Phase detection by scanning probe microscope

One CaF_2 disc was removed to expose a bare LC sample surface, which was subjected to phase detection. Scanning probe microscopy (SPM) (SPM-9700; Shimadzu, Kyoto, Japan) was performed in the phase mode using rectangular silicon cantilevers with a spring constant of ~40 Nm^{-1} and typical resonance frequencies between 250 and 300 kHz. Imaging was accomplished in the attractive tip-sample interaction regime,