

Setting behaviour of luting cements monitored by an ultrasonic method

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Abstract: The purpose of this study was to monitor the setting behaviour and elastic modulus of luting cements using an ultrasonic device. The ultrasonic equipment comprised a pulser-receiver, transducers and an oscilloscope. The transit time through the cement disk was multiplied by the thickness of the specimen, and the sonic velocity within the material was then calculated. The sonic velocities of the longitudinal and shear waves were used to determine the elastic modulus. Analysis of variance and the Tukey HSD test were used to compare the elastic moduli of the set cements. In the earliest stages of the setting process, most of the ultrasound energy was absorbed by the cements and the sound waves were relatively weak. As the cements hardened, the sound velocities increased and this tendency differed among the luting cements used. The mean elastic moduli of the specimens ranged from 2.9 to 9.9 GPa after 15 min, from 14.4 to 20.3 GPa after 24 h and from 12.1 to 15.9 GPa after 1 month. The setting processes of the luting cements were thus clearly defined by using the present ultrasonic method. (*J. Oral Sci.* 50, 117-121, 2008)

Keywords: luting cement; ultrasonic sound velocity; elastic modulus.

Introduction

Many types of luting material are currently available for long-term cementation. Understanding this process can be difficult, as the setting reaction of luting cement is a time-dependent process, during which the properties of the material undergo rapid changes (1). For a glass-ionomer cement, an ion-leachable glass component and a polyalkenoic-acid component triggers acid-base reactions to produce cement mass (2). Resin-modified glass-ionomer cements have been developed by adding resin components to conventional glass ionomers, which can improve the mechanical properties (3). Many types of luting cements have been developed, and these have complex setting chemistry because of the variety of their components.

Ultrasonic imaging is used very frequently for characterizing the mechanical properties of materials as well as for diagnosis of diseases (4-6). Since the speed of sound is sensitive to the viscoelastic properties of materials (7), ultrasonic devices can be used to monitor the setting process of luting cements (8). Based on the international standard used to determine the net setting time of water-based cements (9), the surface of a luting cement can be examined visually to determine whether the material has reached its setting point; this is defined as the time point when no indent-marks can be seen on the surface of the cement. Unlike visual examination for monitoring the setting of luting cement, ultrasonic measurement facilitates observation of continuous changes in the setting process. The ultrasound approach can also provide more information about the elastic modulus (E) values of the materials (10-12). The E value is a good measure of the ability of a luting cement to transfer loads to the tooth, thus distributing

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stress (13). Although the ideal E value is not known, a suitable luting cement might have a value intermediate between that of the tooth and restoratives.

The purpose of the present study was to characterize the setting process of luting cements, and to determine the E values of the set cements using an ultrasonic device. The null hypothesis was that there were no differences in setting processes and E values among the luting cements tested in this study.

Materials and Methods

Three different types of luting cements, Fuji Lute BC (FB; GC Corp., Tokyo, Japan), Vitremer Luting Cement Fast Set (VF; 3M ESPE, St Paul, MN, USA), and Ionotite F (IF; Tokuyama Dental, Tokyo, Japan) were used (Table 1). All of the cements were hand-mixed in accordance with the instructions of each manufacturer, using the recommended powder/liquid ratio. Each mixed cement was condensed into a Teflon mold (2.0 mm in height and 4.0 mm in diameter), and then placed onto a sample stage. The ultrasound measurements were started soon after the cement mixing, and were repeated every 30 s for 15 min. Each specimen was then removed from the mold and placed in distilled water at 37°C in order to measure the elastic modulus; these measurements were carried out at 15 min (before immersion in distilled water), 24 h and 1 month after cement mixing. All the procedures including ultrasound measurements were performed under standard laboratory conditions in an atmosphere of 50 ± 5% at a relative humidity of 23 ± 1°C.

In this study, the pulse transmission method was used. The ultrasonic equipment employed comprised a pulser-receiver (5900PR; Panametrics, Waltham, MA, USA), transducers (V155 and V156; Panametrics) and an oscilloscope (Waverunner, LeCroy, Tokyo, Japan) (17).

The transducer equipment was calibrated each time it was used by employing a standard calibration procedure on calibration blocks. The transducer was oriented perpendicular to the contact surface of each specimen in order to detect the echo signal. The ultrasonic waves with a center frequency of 10 MHz were propagated from the transducer to the specimen. The other transducer was then used as a receiver to record the reflected echos. The first echo was from the transducer/cement interface and the second echo came from the interface between the cement/transducer interface (Fig. 1). The transmission time (Δt) of the second echo and the thickness (T) of the cement sample gave the sound velocity (C), as shown in the following equation:

$$C = 2T / \Delta t$$

To measure the elastic modulus, the thickness and the size of each set cement were measured using a dial gauge micrometer (CPM15-25DM; Mitsutoyo, Tokyo, Japan). The weight of each specimen was also measured (AE

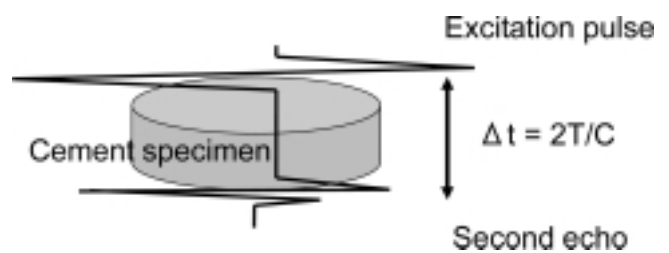


Fig. 1 Cement mix was placed between the transducers, and a reflected echo from cement specimen was obtained. The round-trip transit time (Δt) between the excitation pulse and the back wall echo was measured. Since the propagation thickness (T) of the specimen was known, the sound velocity (C) was calculated as $C = 2T / \Delta t$.

Table 1 Luting cements used in this study

Material (code, manufacturer)	Lot no.	P/L ratio (g)	Main component
Fuji Lute BC (FB, GC)	P: 308231 L: 308021	2.0/1.0	P: fluoroaluminosilicate glass, amine L: water, polycarboxylic acid, methacrylate, HEMA
Ionotite F (IF, Tokuyama Dental)	P: 20134 L: 20231	2.8/1.0	P: Calciumaluminosilicate glass silicate, BPO L: BPO amine, HEMA, UDMA, MTU-6, phosphoric monomer
Vitremer Luting Cement Fast Set (VF, 3M ESPE)	P: 3WG L: 3JU	1.6/1.0	P: fluoroaluminosilicate glass, initiator L: polycarboxylic acid modified with pendant methacrylate, water, HEMA, tartaric acid

HEMA: 2-hydroxyethyl methacrylate, BPO: benzoyl peroxide, UDMA: urethane dimethacrylate, MTU-6: 6-methacryloyloxyl-2-triouracil-5-carboxylate

163; Mettler, Greifensee, Switzerland), and its density (ρ) was calculated. We recorded the transit time through an area of known thickness with both longitudinal-wave and shear-wave transducers, and then used the following equation to calculate the Poisson ratio (ν):

$$\nu = 1 - 2(V_S / V_L)^2 \div 2 - 2(V_S / V_L)^2$$

Here, V_S represents the shear (transverse) sound velocity and V_L represents the longitudinal sound velocity.

$$E = V_L^2 \rho (1 + \nu) (1 - 2\nu) \div (1 - \nu)$$

Six samples were tested for each type of cement. The data were subjected to one-way analysis of variance (ANOVA) followed by the Tukey HSD test at a significance level of 0.05. All of the statistical analysis was carried out with the Sigma Stat 3.1 program (SPSS Inc., Chicago, IL, USA).

Results

The measured ultrasound longitudinal velocities determined for the luting cements as a function of time are shown in Fig. 2. In the earliest stages of the setting process, the ultrasound energy was absorbed by the cement mix and the second echo was very weak. As the cements hardened, the sound velocities increased differentially among the luting cements. For FB, ultrasound velocities increased rapidly 150 s after the start of measurement and then reached a plateau. A gradual increase in sonic velocities was observed for IF. Although the second echoes were detectable from the beginning of sonic-velocity measurements, the rates of sonic velocity increase were relatively slow for VF. The sound velocity at 15 min differed significantly among the luting cements tested.

The E values obtained from the hardened cement specimens using the ultrasonic device are listed in Table 2. The mean E values of the specimens ranged from 2.9 to 9.9 GPa after 15 min, from 14.4 to 20.3 GPa after 24 h, and from 12.1 to 15.9 GPa after 1 month. During 24 h storage in distilled water, the E values increased significantly for all of the materials tested. After 1 month,

all the luting cements tested showed significant decreases compared with the E values at 24 h.

Discussion

In the present study, non-destructive ultrasonic testing was applied to monitor the setting processes of luting cements, based on the relationship between the ultrasonic velocities and the elastic constants described by a micromechanical model (8,14). From the results of this study, the initial hardening process of the luting cements was detectable based on changes in ultrasonic velocities. Since sound velocity is determined by a material's density and elastic stiffness, it provides a more direct measure of the mechanical properties. It has also been reported that ultrasound velocity is a very sensitive tool for monitoring the setting reaction of a cement (15). Unlike measurement of surface hardness (16), the ultrasound approach does not define the setting reaction as the time point when the cement reaches a specific strength; rather, it monitors the viscoelastic properties of the materials. Furthermore, the setting behaviour of a luting cement under standard

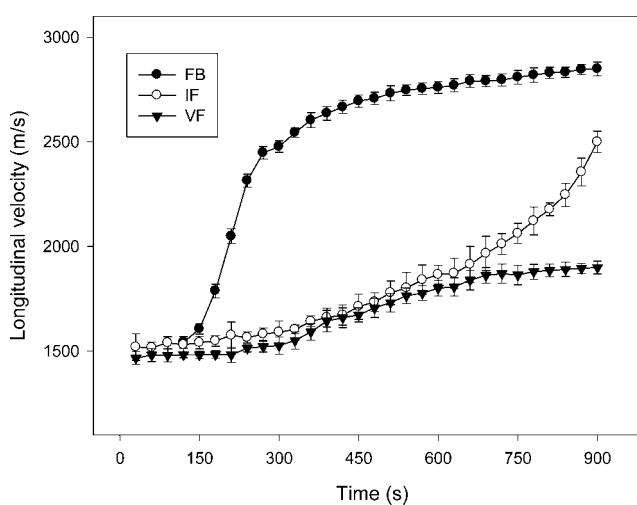


Fig. 2 Changes in ultrasound velocities in glass-ionomer cements as a function of time. As the glass-ionomer cements hardened, the sound velocities increased.

Table 2 Influence of storage period on the elastic modulus (GPa) of luting cements

	Storage time		
	15 min	24 h	1 month
FB	7.8 (0.5)	20.3 (1.3)	15.9 (1.1)
IF	9.9 (0.2)	19.1 (0.8)	15.2 (0.7)
VF	2.9 (0.4)	14.4 (0.6)	12.1 (1.1)

$N = 6$. Values in parenthesis indicate standard deviations.

laboratory conditions may be significantly different from those characterized by conditions in the mouth. The temperature, relative humidity, mixing techniques, and sample thickness are quite different than those used *in vivo*, and all of these factors need to be considered in further research.

Since the cement mix attenuated most of the ultrasound energy, minimal second echo was obtained at the beginning of ultrasonic measurement. When the attenuation of the cement was sufficiently low to obtain a second echo, the sonic velocity increased differentially among the various luting cements tested, a rapid increase in sonic velocity being found for FB, whereas a gradual increase in velocities was observed for IF and VF.

The early setting reaction of luting cements is principally affected by their chemical composition and powder/liquid ratio. These factors might be responsible for the present variations observed in the ultrasonic velocities. Although the chemical reactions of the setting process are not yet well understood, strength appears to improve with higher sonic velocities. The present results showed that luting cement FB had a rapid increase of ultrasonic velocities after the initial setting period, which was explainable by the first setting reaction of the material. It has been reported that the changes in mechanical properties of luting cements are caused by a further setting reaction of their components. The changes in mechanical properties in a short period of time might reflect the extent of the continuous setting reaction.

In the case of VF, the sonic velocity increased gradually, and neither a significant nor rapid increase was observed. This cement has two different kinds of setting reactions: an acid-base reaction between the fluoroaluminosilicate glass and the polycarboxylic acid, and a free-radical polymerization of the pendant methacrylate groups of the polymer and 2-hydroxyethyl methacrylate (HEMA) (17). Low-phase separation during the setting reaction between the glass-ionomer matrix and the polymerizable methacrylate groups on the polycarboxylic acid chain might account for the differences in the setting reaction among the luting cements.

Ultrasonic examination is an efficient tool for characterizing the mechanical properties of materials, and the E value can be obtained by measuring both the longitudinal and the shear sonic velocities. In the present study, the E values of all of the materials increased significantly after 1 d of storage in water. After 1 month, a significant decrease in the E value was observed compared with the values at 24 h. The mechanical properties of the luting cements continued to increase during the early stages of the setting reaction, and therefore an increase in the E values was

observed for the luting cements tested. Differences in the water sorption of luting cements have been reported (18). Luting cements that contain polyHEMA and unconverted monomers in the set cements have been shown to exhibit high water sorption. All the luting cements tested in this study contain polyHEMA, and a high proportion of hydrophilic functional groups within a cross-linked matrix. The cross-linked matrix in the set-cement structure can be likened to the structure of a synthetic hydrogel (19). Hydrogels have been designed to take up large amounts of water, leading to softening of luting cements through swelling and weakening of the physical and mechanical properties of the material.

In this study, we have used an ultrasound device to evaluate the setting processes and E values of three different kinds of luting cements. The method is easy to use and the testing can be performed throughout the entire setting process without having to move the cement sample. The results obtained with this ultrasound technique are reproducible and objective, which may make it possible to compare results between different researchers.

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