Reprinted from ORAL SURGERY, ORAL MEDICINE, ORAL PATHOLOGY, St. Louis
Vol. 59, No. 3, pp. 285-296, March, 1985 (Printed in the U.S.A.)

BOBGANNON
FAX
714 - 628 - 8503

The thermomechanical properties of gutta-percha. Part V. Volume changes in bulk gutta-percha as a function of temperature and its relationship to molecular phase tranformation

Herbert Schilder, D.D.S., Alvin Goodman, D.D.S., M.Sc.D.,** and Winthrop Aldrich, Ph.D.,*** Boston, Mass.*

GOLDMAN SCHOOL OF GRADUATE DENTISTRY, BOSTON UNIVERSITY

A variety of gutta-percha materials was subjected to dilatometric analysis to measure volume changes which take place with heating and cooling. The volume changes were found to be related directly to the molecular transformation kinetics of the polymer material and to the temperature ranges within which they take place. If the gutta-percha in the apical segment is not elevated above 45° C, molecular transformation is avoided and the ultimate volume changes which accompany temperature cycling are small, predictable, and controllable.
(ORAL SURG. ORAL MED. ORAL PATHOL. 59:285-296, 1985)

Little more than a century ago, man's knowledge of the properties of materials came only from his ability to detect gross qualities by visually examining and handling substances. Vastly improved technology now permits the investigation of characteristics of materials not readily apparent to the unaided senses. It is remarkable, therefore, that after one and a quarter centuries of using gutta-percha, dentistry has made only cursory observations concerning its physical behavior.

The popularity of gutta-percha techniques in endodontics represents an acknowledgment of the proven biologic and mechanical acceptability of this material. A better understanding of the mechanical and thermal properties of gutta-percha is required, however, if the benefits of its maximum potential are to be realized.

Dimensional stability has long been considered one of the most important characteristics of an acceptable root canal filling material. This concern with potential volume reduction, adversely affecting the seal at the dentin interface, has been pointed out repeatedly in the dental literature for almost 100 years. Evaporation, distortion, resorption, and corrosion have been implicated, as well as volume changes related to setting mechanisms and temperature variations.

The thermal-volumetric relationship of gutta-percha is one of the themes central to the current research effort at Boston University. Scientific

From a thesis submitted by Dr. Goodman in partial fulfillment of the requirements for the degree of Master of Science.
*Assistant Dean, Professor and Chairman, Department of Endodontics.
**Instructor, School of Graduate Dentistry.
***Assistant Professor, College of Engineering.

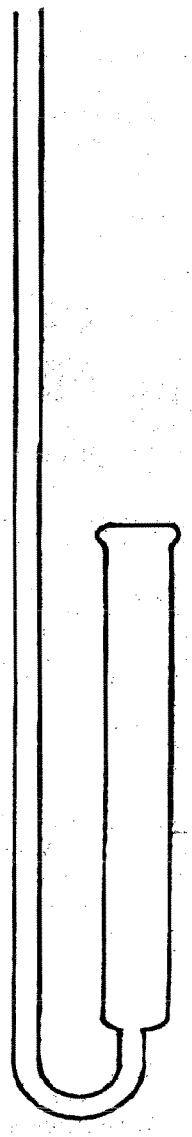

Fig. 1. U-shaped dilatometer with capillary tube and specimen chamber.

progress in the twentieth century has given us significant advantages over our predecessors and has supplied us with tools that were not available several decades ago. In addition, a comprehensive review of the molecular chemistry and engineering literature was necessary to correlate this information with our efforts.[1] Also, preliminary laboratory investigations were required in order to develop a realistic experiment.[2,3] To monitor precisely the volume changes that take place in gutta-percha as a function of temperature, a volume dilatometric technique was adopted. Although the concept is simple, extensive preparation was necessary to produce reliable results. Because determinations must be made on a material that changes from a solid to a fluid state* during the course of the experiment, traditionally applied methods, such as linear dilatometry,[4-6] were useless.

The technique employed involves the utilization of a glass capillary tube to which a specimen chamber is attached. A liquid of known thermal expansivity, such as mercury, can be introduced to surround the specimen and partially fill the capillary tube. When the assembly is then taken through an appropriate thermal cycle, the height of the mercury column in the tube can be monitored. As a function of temperature, this height represents the volume of liquid plus the volume of the specimen. Since both the volume-temperature relationship of the confining liquid and the expansivity of the glass are known, appropriate calculations with the available data make it possible to obtain the volume of the sample itself at any specific temperature.

METHODS AND MATERIALS

Slow-cycle series

The method for construction of the apparatus used in this procedure was taken from ASTM Standard D 864-52[7] and from the work of Bekkedahl.[8] The dilatometers consisted of a 1 meter borosilicate (Pyrex) glass capillary tube with an outer diameter of 6 mm and an internal bore diameter of 0.7 mm. This was attached to a specimen chamber, also fashioned from borosilicate tubing but of different dimensions. The chamber was 20 cm long, with an internal bore diameter of 8 mm and an outer diameter of 10 mm. The chamber—capillary tube junction was modified from a straight line to a U shape so that, upon melting, the gutta-percha would rise to the top of the specimen chamber without clogging the capillary bore (Fig. 1).

Each capillary tube, with its specimen chamber, was weighed to the nearest ten thousandth of a gram. Sample materials, many of which were received in the form of slabs or sheets from the suppliers, were cut to fit conveniently within the chamber. The samples were weighed to the nearest ten thousandth of a gram and placed into each specimen chamber. A section of borosilicate glass rod was cut to proper size and inserted into the chamber over the specimen to act as a heat shield when the tube was sealed. This also increased the sensitivity of the test by increasing the volume ratio of specimen to confining liquid

*Viscosity studies relative to the flowability of gutta-percha at varying temperatures are currently under way at Boston University.

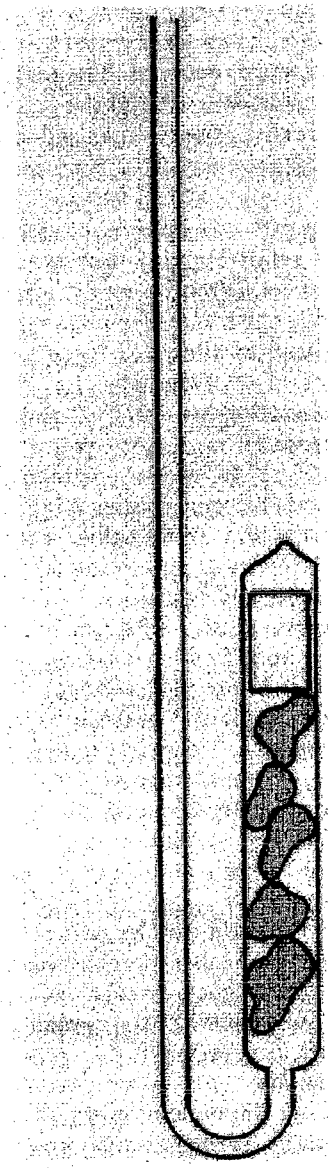

Fig. 2. Heat shield and specimen sealed into dilatometer chamber.

within the chamber. The orifice of the chamber was then heat-sealed, encapsulating the specimen and leaving the only atmospheric opening at the opposite end of the U-shaped capillary tube (Fig. 2). The dilatometer, with its encapsulated sample, was then reweighed.

The next step involved the introduction of the confining liquid. To overcome the difficulty of voids and entrapped air experienced by Price,[4] a two-way stopcock was connected to the open end of the capillary tube. In one position, the valve allowed a vacuum to be produced in the dilatometer by means

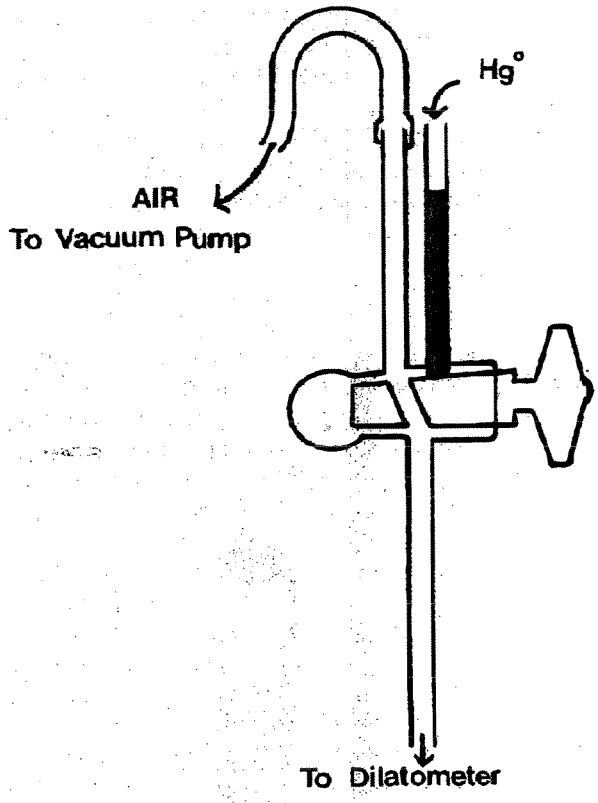

Fig. 3. Two-way stopcock for vacuum backfilling of mercury.

of a vacuum pump. Mercury could be introduced through an adjacent tube by simply turning the valve (Fig. 3). For each specimen, the dilatometer was held at a partial vacuum continuously for 45 minutes to draw off moisture and absorbed and adsorbed gases. After evacuation, the stopcock position was changed to permit the introduction of mercury into the dilatometer system. This vacuum backfilling technique allowed for the elimination of unwanted gases and total confinement of the specimen, producing a completely filled system, free even of air entrapped in voids within the material (Fig. 4). With proper manipulation of the fill-evacuate cycle, the level of mercury was adjusted in the capillary tube to provide for expansion of the mercury column during the testing procedure.

The sealed and filled dilatometer was weighed to permit determination of the mass of mercury introduced into the system. This information, coupled with the known density of mercury at the weighing temperature, was later used to determine the volume of mercury introduced. Likewise, the measured weight of each gutta-percha specimen, with its experimentally determined density, allowed for vol-

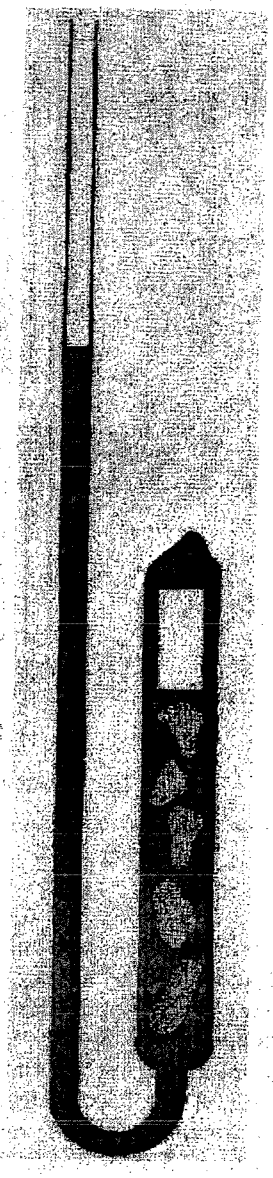

Fig. 4. Complete dilatometer system with confining liquid.

ume determinations in later calculations for each case.

A Cannon constant-temperature bath* was used to heat the dilatometer assemblies. This unit included an electric heating coil, an adjustable temperature control, and a motor-driven impeller to provide uniform water temperature. Rulers calibrated in millimeters were attached to the tubes, which were submerged in the water bath and clamped to ring stands for support.

*The Cannon Instrument Company, State College and Boalsburg, Pa.

The dilatometers were allowed to equilibrate i the water bath at room temperature and their initia mercury levels were recorded. The temperature con trol was then set at 80° C* and the bath was allowe to heat gradually. The height of each mercur column was read at every 2° C increment in temper ature.

The heating rate was approximately 1° C every minutes. This relatively slow rate was necessary i order to produce a definitive curve capable of reveal ing more clearly the molecular phase transformatio temperatures and to allow for the determination o cubical expansion coefficients.

After stabilization at 80° C, the temperature control was reset at body temperature and the bath was cooled to 37° C as readings were taken with each 2° C decrement. Upon reaching 37° C, readings of the mercury column were taken continually and recorded for 24 hours as a function of time, while the temperature remained constant.

A broad representation of gutta-percha materials was subjected to this dilatometric analysis. The following materials were selected for study:

1. Compounded dental gutta-percha and refined uncompounded dental-grade gutta-percha from the Mynol Company.
2. Compounded dental gutta-percha and refined uncompounded dental-grade gutta-percha from the Hygienic Dental Manufacturing Company.
3. Kerr dental gutta-percha points.
4. Premier dental gutta-percha points.
5. Starlite dental gutta-percha points.
6. L. D. Caulk dental gutta-percha points.
7. Pulpdent Corporation of America dental gutta-percha points.
8. Refined uncompounded gutta-percha imported by Hermann Weber and Company, Inc.
9. Precipitated gutta-percha and balata from the Acushnet Sales Company.
10. Trans-Pip (Synthetic transpolyisoprene) obtained from Polymer Corporation, Ltd., samples 2329, 52130, and 42317.

Plunge-cycle series

A second series of volume dilatometric tests was run in an effort to parallel more closely thermal cycles to which the material is subjected clinically. These were termed "plunge tests." They were designed to study volumetric changes which take place with more rapid heating and cooling of the

*The representative maximum regional temperature to which bulk gutta-percha is subjected in the body of the root canal during the warm gutta-percha packing procedure.[3]

gutta-percha. In the plunge tests, the samples and dilatometers were prepared as previously described but were plunged into fixed-temperature baths, which introduced more clinically realistic temperature changes. Two temperatures were chosen: the representative maximum temperature determined for bulk gutta-percha in the body of the root canal during the warm gutta-percha packing procedure (80° C) and the highest temperature ever recorded for the material in the apical region 2 mm from the apex (45° C).[3]

In the plunge-test series the prepared dilatometers were allowed to equilibrate at room temperature, and an initial mercury column height was recorded. They were then plunged into a 37° C constant-temperature water bath. The height of the mercury column was observed, and successive readings were recorded as a function of time until the volume stabilized. Two identical groups of samples were held in this fashion at 37° C. One group was removed and plunged into a water bath at 45° C, and the other was plunged into a water bath at 80° C. Readings of the mercury column were taken until all of the systems stabilized again. Both groups were plunged directly back into the 37° C bath and allowed to restabilize, plunged again into their respective elevated temperature baths, and again back to 37° C. This alternate plunging was performed in an effort to simulate the thermal cycle experienced by gutta-percha at various locations within the root canal during clinical usage.

Samples for this test were chosen to represent naturally occurring uncompounded dental-grade gutta-percha, synthetic transpolyisoprene, balata, and a compounded dental gutta-percha. The following materials were selected as representative of each of the above categories:

1. Uncompounded dental-grade gutta-percha from the Hygienic Dental Manufacturing Company.
2. "Trans-Pip," synthetic transpolyisoprene from Polymer Corporation, Ltd., sample 52130.
3. Precipated balata from the Acushnet Sales Company.
4. Compounded dental gutta-percha from the Hygienic Manufacturing Company.

Two dilatometric samples were prepared for each of the above materials for use in the two respective plunge tests. In each case the volume changes that occurred as a result of cyclical variations were monitored as a function of time.

The graphs themselves represent the combined volumetric reactions of the samples, plus the mercury and the glass dilatometer. It was therefore necessary to extract the two latter effects quantitatively in order that the volume-temperature relationship of the gutta-percha itself be analyzed. The calculations were based on the ASTM Standard Designation D 864-52.[7]

The volume of mercury introduced into each tube was determined by dividing the weight by the density. The volume of the specimen specific to each test was also required. To calculate this, it was necessary to determine the specific density of each of the sample materials using the displacement method as outlined in ASTM Standard D 792-66.[9]

After physically installing each dilatometer it was necessary to determine, for the correction of glass and mercury expansion, what part of the total dilatometer-mercury system was below the water level, actually in contact with the water bath, and therefore directly affected by the elevated temperature.

Graphic analysis of the raw data produced by slow-cycle and plunge-cycle dilatometry made it possible to calculate cubical expansion coefficients and percent volume changes for the gutta-percha samples. The cubical thermal expansion coefficient is the normalized volume change per initial unit volume of specimen per degree of change in temperature.

Voluminous mathematical calculations were necessary in order to apply the working equation for gutta-percha expansion to cubical thermal expansion coefficients for the beta, alpha, and amorphous phases which occurred in the various polymer samples during the slow thermal cycle. These calculations were performed and are available to us. Volume changes, however, are more clearly envisioned in terms of percent change by volume as a function of temperature. For this reason, only data stated in terms of percent volume change are reported in this article.

RESULTS

Slow-cycle series

An example of the curves produced by the slow-cycle series is presented in Fig. 5. Here the height of the mercury column in the dilatometer is plotted as a function of the slowly increasing and decreasing temperature of the water bath. Although there were minor differences in the temperature—volume relationship between individual samples, the stages produced during the thermal cycle followed the same general pattern in each case.

The first stage is an essentially linear increase in volume as the beta crystalline gutta-percha rises in temperature to approximately 46° C. There is then a nonlinear increase (between 46° C and 52° C) during which the beta transforms to the alpha structure. This is followed by a second linear region

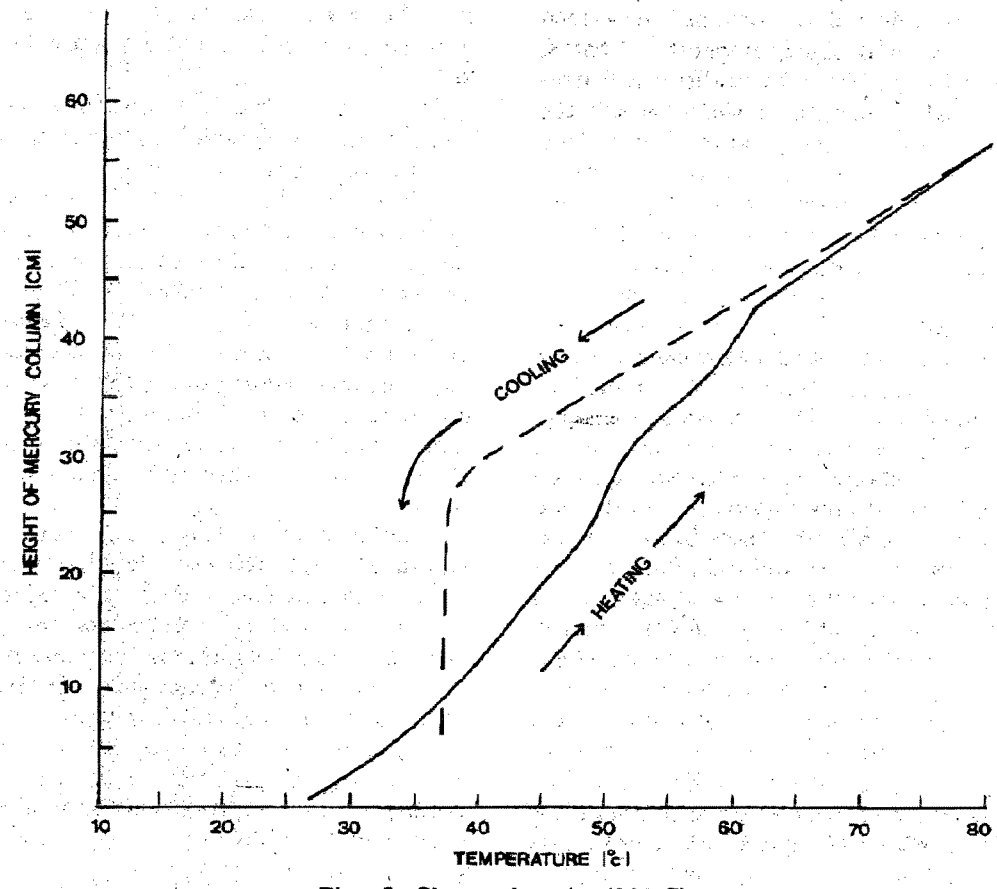

Fig. 5. Slow cycle series (80° C).

as the alpha crystalline form increases in temperature to approximately 56° C. A second nonlinear region occurs (between 56° C and 62° C) representing the transition of the alpha crystalline structure to the amorphous melt. The amorphous melt behaves linearly up to 80° C.

The cooling curve for these materials did not replicate the heating curve. With cooling, the materials characteristically acted as supercooled amorphous liquids until 42° C to 40° C was approached. In this range the melt began to crystallize, producing a semicrystalline solid of beta structure, with rapid decrease in volume.

Table I lists the percent volume changes that took place as the result of each step in the slow-cycle series, as well as the net final percent change. When the water bath temperature was raised to 80° C, the dental compounds of gutta-percha experienced an increase in volume from just under 3% to just over 5% of their original volume at room temperature, depending upon the specific compound tested. The uncompounded materials experienced essentially one and one- half times greater increases in volume with the same rise in temperature. It becomes apparent that dental compounding reduces thermal expansion.

In spite of volume reductions on cooling from 80° C to 37° C, it can be extrapolated in Table I that volumes upon cooling were still 0.01% to 0.72% greater than the original volumes prior to temperature cycling. After the samples had been held at 37° C for 24 hours, additional crystallization resulted in an overall decrease in volume for several dental compounds of 0.03% to 1.1% relative to original volume at room temperature. Two dental compounds were exceptions and maintained overall increases after the 24-hour holding period. Likewise, the majority of the nondental, uncompounded gutta-percha demonstrated overall volume increases.

Plunge-cycle series

Examples of the curves produced by the plunge-cycle series are represented in Figs. 6 and 7. Figs. 6 represents the 80° C plunge-cycle series, and Fig. 7