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The Chemical Composition and Mechanical Properties of Gutta Percha Endodontic Filling Materials

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THE CHEMICAL COMPOSITION AND MECHANICAL PROPERTIES
OF GUTTA PERCHA ENDODONTIC FILLING MATERIALS

by
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A Thesis Submitted to the Faculty of the Graduate School
of Loyola University in Partial Fulfillment of
the Requirement for the Degree of
Master of Science

June
1973

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CURRICULUM VITAE

Charles E. Friedman was born on November 25, 1944, in Little Rock, Arkansas.

He graduated from Hall High School in Little Rock in 1962, and attended the University of Oklahoma from 1962 to 1967, where he received a Bachelor of Arts degree in political science.

He began his dental studies at the University of Tennessee College of Dentistry in 1967, and graduated in 1970 with the degree of Doctor of Dental Surgery.

From July 1970 to July 1971, he interned at Michael Reese Hospital in Chicago, Illinois, in the rotating dental internship program.

His graduate studies began in the Department of Oral Biology of Loyola University in September 1971. Specialty training was in the Department of Endodontics under the Director of Graduate Endodontics, Dr. Franklin S. Weine.
DEDICATION

To my mother and father, Sylvia and Maury, for the many years of their guidance, encouragement, and support.
ACKNOWLEDGEMENTS

I wish to thank Dr. Gustav W. Rapp, for his constant encouragement and advice during the preparation of this thesis.

I am especially grateful to Dr. James L. Sandrik, whose continual guidance and enthusiasm have provided me with a sincere appreciation of investigative principles.

I gratefully acknowledge the assistance and advice of Dr. Michael A. Heuer, under whose suggestion this study was undertaken.

In addition, I extend my gratitude to Dr. Hunter L. Mermall, for his valuable assistance with the chemical assay used in this investigation.
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CHAPTER 1
INTRODUCTION

For over 100 years, dental practitioners have used gutta percha as a root canal filling material with only scant knowledge of its chemical and mechanical properties. Its use has been based totally upon clinical results and impressions. Dentists have empirically modified it in a multitude of ways according to their own desires (1-3), while research on the material has been either too limited or too irrelevant in relation to its use in endodontic therapy. It was not until 1918 that the first scientific study on the physical properties of gutta percha in relation to its use in dentistry was reported (4). Since then, investigations of dental gutta percha have been directed primarily toward its compatibility with living tissues and sealing properties (5-9). Recently, workers (10,11) have attempted to define further the physical parameters of gutta percha endodontic filling material, but it has yet to be methodically analyzed in accordance with valid investigation.

In the health fields currently, there is an emphasis toward a need for thorough knowledge of materials and medicaments intended for application to the human body. Use of this knowledge enables standards to be established which not only serve to protect the patient, but also contribute to the future development of better materials. The purpose
of the present investigation, therefore, is to bring our knowledge of gutta percha endodontic filling material closer to this goal. An attempt will be made to determine whether a correlation exists between the composition and mechanical properties of commercially available gutta percha endodontic filling materials.

Considering the lack of investigation in this area, this report must be regarded as the first of a series. It is intended as a starting point from which our knowledge can be accrued.
CHAPTER 2
REVIEW OF THE LITERATURE

Throughout most of the history of dentistry, there have been attempts by many dentists to preserve, rather than condemn, nonvital teeth. Historically, the dental literature speaks of the methods used by dentists in preserving teeth endodontically. The root canals were debrided by several methods, but of importance to this paper, they were filled with many interesting materials.

Grossman (12) reports the use of the following root filling materials in the past: amalgam, asbestos, balsam, bamboo, copper, cotton, gold, indium, ivory, lead, paper, paraffin, pitch, rosin, rubber, spunk, thistles, wax, and wood. McElroy (13) described the use of "gold foil, gold foil with a shellacked surface, tricalcium phosphate with eugenol, zinc oxide and hydrochloric acid, pulverized animal charcoal with iodoform, orange wood points dipped in Black's 1-2-3, iodoform and phenol paste, oxychloride of zinc and mineral wool, tin foil, lead foil covered with a paste of phenol and iodol, wood points soaked in bichloride or mercury 1:200, red cedar dipped in paraffin, cotton points saturated with cinnamon oil, dog dentin, human dentin, and ivory dust." Adams (14) further reported that salol, beeswax, and paraffin were recommended by men who afterwards "were sorry". So many substances have been used in attempting to fill the root canal
space, that Grossman aptly termed the root canal as "the attic of the dental household" (15). However, gutta percha has predominated as the root canal filling material of choice. Swain in 1890 (16), Puterbaugh in 1928 (2), and Adams in 1941 (14), all noted that gutta percha had best withstood the test of time.

Gutta percha was modified in many ways. In the early 1900's, the most popular method was by dissolution of the gutta percha in either chloroform (chloropercha), eucalyptol (eucapercha), or chloroform with rosin added. These techniques were introduced by Johnston, Buckley, and Callahan, respectively (1, 2, 4). The resultant paste was vertically forced throughout the root canal system.

Grossman (12) proposes that the objective "of obturating the root canal, is the substitution of an inert, hermetic sealing agent for the destroyed or extirpated pulp, in order to prevent subsequent infection by way of the blood stream or crown of the tooth." He further defines the purpose of a combination filling, as the filling of the "bulk of the canal with a solid core and the remainder of the canal, including irregularities and crevices, with a more adaptable substance cement."

Adams (14) placed endodontic objectives in perspective when he stated that the material used in filling a canal was not of paramount importance. Instead, he noted that it would probably be better to have an imperfect material tightly packed in an empty and sterile canal, than
a perfect material indifferently placed in an unclean, infected canal.

In 1927, Fisher (17) devised a seemingly valid investigation regarding the choice of the correct root canal filling material. He proposed that the rationale for choice of a root canal filling material should be physiologically based. The deciding factor in successful treatment is the attachment of the tooth. He postulated that since the normal sequence of pulpal age is a closing off of the pulp canal space, the dentist should therefore try to copy as nearly as possible this closure and hermetically seal the apex. Fisher added that the root filling should seal the pulp canal so that it is obliterated from the apex to the floor of the chamber, while the relationship between the tooth and its environment remains normal and healthy.

In addition, Fisher noted various conditions which influence or limit the choice of a root canal filling material. Environmental conditions such as the physical characteristics of the canals should be considered. The canals are never the same size, length, or shape. They may be straight, curved, round, ribbon-shaped, spindle-shaped, or stellate, and these variations may occur within the same canal. Even though these irregularities may be modified by canal preparation, the modifications are relatively slight. Fisher states that these variations demand a filling material that is readily adaptable to fill all irregularities. The filling material must also be able to seal the apical foramen
in the presence of moisture, but be impervious to it.

Operative conditions are also a limiting factor in the choice of the proper root filling material. Endodontic procedures should be able to be performed simply by general practitioners as well as specialists. Difficult areas of access and total manipulation by feel alone, require skill and a material that is easy to handle and place. Fisher advises the use of a material that is semifluid in nature, or one that can be placed simply and then packed.

An ideal root canal filling material, as proposed by Grossman (12), should have the following characteristics: (1) it should be easily introduced into a root canal; (2) it should be preferably a semisolid upon insertion and become solid afterwards; (3) it should seal the canal laterally as well as apically; (4) it should not shrink after being inserted; (5) it should be impervious to moisture; (6) it should be bacteriostatic, or at least not encourage bacterial growth; (7) it should be radiopaque; (8) it should not stain tooth structure; (9) it should not irritate periapical tissue; (10) it should be sterile, or easily and quickly sterilized immediately before insertion; and (11) it should be easily removeable from the root canal if necessary.

Grossman evaluates gutta percha endodontic filling material as a good canal filling material because it does not shrink after being inserted, unless it is used in conjunction with a solvent; it is impervious
to moisture; it does not encourage bacterial growth; it does not irritate periapical tissue except when under pressure; it is radiopaque; it does not stain tooth structure; it may be kept sterile by immersion in an antiseptic solution; and it is removed easily from a root canal if necessary.

Luks, in 1965 (18), recognized gutta percha as the filling material that most closely meets the requirements of an ideal root canal filling, and stated emphatically that the use of any other material represented a compromise or second choice.

Nevertheless, the need for an improved, more ideal root canal filling material grows as our knowledge and sophistication of endodontic therapy grows. Although presently used filling materials seem to fulfill most requirements and afford the practitioner a high degree of success, the obliteration techniques in root canal treatment leave room for much improvement. Filling materials and techniques introduced over a century ago are still in use today. Grossman still expects the next great advance in endodontics to be in the realm of the root canal filling (12).

Interest in alternative and supplementary filling materials has been directed primarily toward plastics. In studying acrylic, polyethylene, polypropylene, nylon, Teflon, vinyls, and epoxies, Grossman proposed in 1958 and again in 1963 that synthetic plastic cones supplement or replace gutta percha as a root canal filling material (15,19); this has
not come to pass and gutta percha endodontic filling material retains its role as the material of choice today (1973).

Gutta percha

Gutta percha is the purified, coagulated milky exudate of several trees indigenous to the islands of the Malay archipelago and their immediate vicinity (20).

Swain, in 1890 (16), described the historical development of gutta percha. Its introduction into Europe was primarily as an article of curiosity in the form of sticks, whips, and other articles. About 1843, the value of gutta percha as a material was brought to the attention of scientists and manufacturers by Sir Jose d' Almedia, a resident of Singapore, who presented specimens to the Royal Asiatic Society of England. He had observed the material in use among the natives as handles for their knives and other utensils.

At the same time, William Montgomerie, a Scotish surgeon residing in Singapore, presented the material to interested scientists and manufacturers in London and described some of its many possible uses. Gutta percha was suggested as an insulator by Faraday, because of its poor conduction of both heat and electricity. This property, combined with its indestructibility by fresh or salt water, rendered it useful as protection for marine cables, and it was so used in 1857 with much success (16). The valuable qualities of the substance were quickly
recognized soon after its introduction to western cultures, and a great demand for it arose almost immediately. The import of gutta percha to Europe increased from 200 pounds to 2,500,000 pounds between 1844 and 1848.

Almost immediately after the attention of the world had been directed to the properties of gutta percha, several members of the dental profession began experimenting with it. However, they found that pure gutta percha would not meet the needs of the dental practitioner, but that the hardness or softness of the material could be altered by the admixture of zinc oxide or zinc sulfide, aluminum, whiting, precipitated chalk, lime or silex in various combinations (16).

Gutta percha was first used as a temporary filling in dentistry about 1847. Koch (21) recalled that "Hill's stopping" was introduced in 1848 in an attempt to render gutta percha available for permanent as compared to temporary usage. This special preparation of gutta percha had several additives such as quicklime, powdered quartz, and feldspar (a nineteenth century composite!). Soon a considerable number of gutta percha compounds were made and sold. Each varied in the amount and character of foreign substances incorporated with it to alter either its hardness or softening temperature.

Koch mentions that some operators probably filled root canals with gutta percha soon after its introduction to the profession as a "stopping" for carious cavities. He recalled that his preceptor was doing so in 1865.
Ordinary baseplate gutta percha was heated in a small porcelain dish until it became very soft and sticky. It was then transferred to the dry canal with a hot instrument.

Bowman (22), at a clinic given by the St. Louis Dental Society in 1867, demonstrated the use of gutta percha for the "perfect" filling of the root canals of an extracted lower molar.

Composition and structure

Gutta percha is a natural polymer composed of isoprene units, \( \text{CH}_2=\text{CHC(CH}_3)=\text{CH}_2 \), joined in regular fashion into a long chain. There are two possible geometric configurations of polyisoprene: the \textit{trans} form, gutta percha, and the \textit{cis} form, typical of India rubber. The \textit{trans} and \textit{cis} forms are identical chemically. The difference in physical character lies in the geometry of the molecules (20). A nonplanar chain configuration is produced by the repulsion between the \( \text{CH}_3 \) and adjacent \( \text{CH}_2 \) groups (28). This nonplanar configuration has the potential for protecting approximately 20 percent of the double bonds from the effects of oxidation (26).

Character and properties

Before waxes, fillers, and opacifiers are added to gutta percha to make the root canal filling material with which we are familiar, it appears in commerce as gray blocks, often with a reddish tinge. It is rigid at ordinary temperatures, becomes pliable at 25 to 30°C, softens
at 60°C, and melts at 100°C with partial decomposition. Gutta percha is a hydrocarbon, and chloroform, carbon disulfide, and benzene are its best solvents. Alkaline solutions or dilute acids do not affect it. Strong sulfuric acid chars it when warm, and nitric acid produces its complete oxidation. When exposed to light and air, gutta percha rapidly oxidizes, absorbing oxygen and producing a brittle resin. Ozone and sulfur also attack gutta percha with similar results. The attack by air is slowed greatly by the addition of antioxidants such as aromatic amines or phenols (20,23).

About 60 percent of gutta percha is normally crystalline at ordinary temperature, the remainder being amorphous. Two crystal modifications of gutta percha exist: a low melting form termed beta, with a melting point range of 56 to 64°C, and a high melting form termed alpha, with a melting point range from 68 to 74°C. Melting points depend upon the condition under which crystallization has occurred and upon the rate of heating. Gutta percha from the tree is in an alpha crystalline form. Upon heating and slow cooling, this gutta percha returns to the alpha crystalline form, but with rapid cooling, the beta crystalline form is obtained. These two forms differ in the pattern in which the molecules are arranged. The beta form is unstable and can be converted to the alpha form by slight warming.

Because gutta percha is a polymer, it can be expected to exhibit a property common to all polymers known as viscoelasticity. This term
implies that the material possesses not only elastic properties, but also some properties of viscous liquids (31). The viscoelasticity of gutta percha will be discussed further in Chapter 5.

Research

As noted previously, research on gutta percha has been limited in relation to its use in endodontics. However, several investigators over the years have provided direction toward a greater understanding of this unique substance.

In 1902, Sir William Ramsay (27) presented a paper to the London Section of the International Congress of Applied Chemistry. Utilizing acceptable analytical techniques at the time, Ramsay stated that gutta percha had three components, the principal constituent being the hydrocarbon gutta, with the empirical formula C₅H₈, and having a molecular weight of about 30,000. The remaining fractions were reported to be albane, a whitish crystalline resin, and fluavile, a yellowish non-crystalline resin. These findings, however, have not been substantiated by more recent research.

In an attempt to provide a closer correlation to the use of gutta percha in root filling techniques, Price in 1918 (4), reported the first work on the investigation of the physical properties and filling efficiencies of the various forms of dental gutta percha. This study concentrated upon an analysis of the two gutta percha filling techniques
that were in vogue at that time -- hot gutta percha and solvent-gutta percha. In studying gutta percha, Price noted that it was a gum, and postulated that it would therefore behave similarly to commonly known gums and waxes. The propensity for such substances to retain a "locked elasticity" led Price to theorize that the heating of gutta percha prior to insertion into the canal only resulted in a smaller filling than hoped for, due to contraction after cooling to body temperature.

Price packed glass cylinders with gutta percha, softened the material with heat, and then submitted the gutta percha to high pressures during cooling. After cooling, ink was applied to each cylinder. Shrinkage was demonstrated by diffusion of the ink between the gutta percha and the glass wall. Price concluded therefore that gutta percha fillings should always be inserted with a cement.

Next, Price evaluated the post-insertion shrinkage of the solvent-gutta perchas, chloropercha, eucapercha, and chlororosin. Price observed that there was not much shrinkage difference between the compounds, but that shrinkage was usually relative to the amount of solvent added. Chlororosin had the favorable quality of adhering to the canal wall.

Included in Price's article were several tests by Miller and associates, who also studied volumetric changes of dental gutta percha after heat and solvent treatment. They reported the shrinkage of a sheet of gutta percha after the application of heat. Miller concluded that gutta percha should be "annealed", by heating it to a temperature of 75°C, before it is used to fill the root canal. Miller also placed the three
solvent-gutta perchas in graduated cylinders and observed the shrinkage due to evaporation over a period of several months. Shrinkage did occur, but was very slow, which led him to forecast that complete solidification of the materials would require a year or more!

These studies were highly empirical, and in addition, the knowledge gained from them in regard to today's gutta percha endodontic filling materials is questionable.

Buchbinder, in 1931 (29), repeated Price's experiment evaluating the shrinkage of the solvent-gutta perchas. Chloropercha, chlororosin, and eucapercha were packed into glass tubes. Buchbinder observed shrinkage visually without the use of a stain.

McElroy, in 1955 (13), acknowledging the problem of shrinkage with solvent-gutta perchas, estimated that use of the chloropercha technique resulted in 7.5 percent of the canal remaining unfilled after evaporation of the chloroform. He therefore recommended the use of a cement in conjunction with a well-condensed gutta percha point to minimize volumetric change.

In the last twenty years, the use of condensed gutta percha with an appropriate root canal cement has increased in popularity, thereby reducing the problem of post-fill contraction of the material. Lately, interest has been geared toward modification of gutta percha endodontic filling material to permit easier manipulation within the root canal. Also, emphasis has been stressed upon standardization of the size of
the points in accordance with root canal instruments so that quicker, more exact root fillings can be achieved.

Anticipating future developments, Grossman, at the International Conference on Endodontics in 1958 (15), stated that gutta percha could be improved as a root filling material by formulating it so that it would become stiffer, and so that it would more closely conform to the sizes of root canal instruments. As an example, he suggested that gutta percha might be powdered and combined with a small amount of thermosetting plastic, also in powder form. The powders could then be molded under pressure to the desired widths and tapers producing both a stiffer cone, and a more precise filling material. This manufacturing procedure has not proved practical, as hand-rolling of gutta percha points still predominates.

Ingle, at the same international conference (30), emphasized the total absence of standardization of both root canal instruments and filling materials. Today, a standarized system of root canal instruments and filling materials has become, in most respects, a reality. However, the deviations allowed manufacturers from these proposed standards have often been exceeded. Standardization remains far from perfected, and no specifications for either instruments or root canal filling materials exist.

Mayne, Shapiro, and Abramson, 1971 (10), studied the reliability and validity of the standardization of five commercial brands of
gutta percha points. They revealed the presence of significant deviations in the size accuracy of the points. The study also included a subjective test of the rigidity of the gutta percha points by six endodontists. These practitioners rated the rigidity of the points from one to three depending upon their empirical assessment of the points for clinical use. Only two of the five brands studied were judged to have satisfactory rigidity without excessive brittleness.

Also in 1971, Gurney and associates (11) studied the hardness, linear expansion, water absorption/desorption, and rigidity of Mynol endodontic gutta percha.

It appears that with over 100 years of use of gutta percha for filling root canals, there is very little that can be regarded as scientific fact concerning the properties and behavior of this material. Information supplied to the profession by the manufacturers is limited to the ingredients of their particular gutta percha filling materials, the proportions of the ingredients being held as trade secrets. It is the purpose of this investigation to provide essential, basic information about these filling materials.
CHAPTER 3
METHODS AND MATERIALS

The five brands of gutta percha endodontic filling materials studied by Mayne et al (10) were judged representative of the gutta percha filling materials available commercially, and were therefore included for analysis in this study. Size #100 gutta percha points were requested from the following manufacturers: Mynol Chemical Co., Premier Dental Products Co., Charles B. Schwed Co. (Dent-O-Lux), Star Dental Co. (Tempryte), and Union Broach Co. (Indian Head). All companies supplied size #100 points except Schwed Co., which does not stock this size (10), and therefore sent alternate sizes (#90 and #110).

Chemical Assay

Premier, Mynol, and Schwed supplied information about the composition of their gutta percha endodontic points. The following basic components were noted: gutta percha, zinc oxide, barium sulfate, and coloring agent. In addition, Premier listed strontium sulfate, and Schwed mentioned the presence of a small amount of paraffin wax.

Since it was not the purpose of this investigation to concentrate upon the exact formulation of the gutta percha endodontic filling materials, and the nature of the contents were known, emphasis was
placed upon the proportions of the stated ingredients in relation to the mechanical properties. Samples of gutta percha filling material from each company were quantitatively assayed for an organic fraction (gutta percha; wax and/or resin), and an inorganic fraction (heavy metal sulfates; zinc oxide) (Figure 1).

One gram of each sample was dissolved in 10 ml of chloroform in a 15-ml centrifuge tube, and centrifuged at 10,000×G for 15 minutes. The supernatent was poured into a 100-ml beaker, and 10 ml of acetone were added to precipitate the pure gutta percha. The chloroform-dissolution and centrifugation step was repeated three times to remove as much gutta percha as possible. After each centrifugation, 10 ml of acetone were added to the supernatent to precipitate the gutta percha. The resultant mixture of chloroform/acetone/gutta percha was filtered through a tared Selas #2010 filtering crucible* (nominal maximum pore diameter of 8.8 microns). The filtrate was transferred from the 250-ml filtering flask to a 100-ml beaker, and was partially evaporated at 60°C to reduce its volume for final evaporation on a tared watch glass. The resulting substance was weighed (wax and/or resin).

The precipitate remaining within the crucible (gutta percha) was dried in a drying oven at 60°C, allowed to cool in a dessicator, and weighed. Each dessicator used in the experiment contained calcium chloride, to remove moisture from the samples, and paraffin cubes, *

*Sargent-Welch Scientific Co., Chicago, Ill.
1 gm of sample dissolved in 10 ml of chloroform centrifuged at 10,000 x G for 15 minutes repeated three times

INORGANIC

60°C 2.4 M HCl wash repeated five times filtered

heavy metal sulfates

ORGANIC

10 ml of acetone added after each centrifugation filtered

zinc chloride gutta percha wax and/or resin (after evaporation)

Figure 1. Flow sheet for the chemical assay of the five brands of gutta percha endodontic filling materials.
to extract excess chloroform remaining within the gutta percha samples.

Precipitate remaining within the centrifuge tube (inorganic salts -- zinc oxide and heavy metal sulfates) was transferred with an acetone wash, to a second tared filtering crucible, dried, cooled in a desiccator, and weighed (total salt).

To separate the two salts, five washes with 60°C 2.4 M HCl extracted the zinc oxide as the chloride. The resultant heavy metal precipitate was washed with distilled water, then acetone, dried, cooled, and weighed. The weight of the heavy metal precipitate was subtracted from the weight of the total salt to yield the zinc oxide weight.

Three samples of each brand of gutta percha endodontic filling material were quantitatively assayed according to the above procedure.

**Mechanical Properties Testing**

An Instron Universal Testing Machine Model 1130* with a 0-100 pound load cell and "C" grips, was used to provide data on the mechanical properties of the gutta percha filling materials.

The metal grips were modified because they severely crushed the gutta percha points and thus resulted in inaccurate data. To overcome this, a soft gum rubber was attached to each grip with rubber adhesive. In addition, 600-mesh silicon carbide paper was cemented to the gum rubber to reduce slippage of the gutta percha points during testing (Figure 2). Slippage did occur, however, when using high stresses to

*Instron Corp., Canton, Mass.
Figure 2. Modified grip apparatus. Note that the specimen (S) is held by the metal grips (MG) to which have been added soft rubber (R), and silicon carbide paper (P).
test for ultimate tensile strength, because only a small area of the point could be clamped. Therefore, to determine the value of this property, ten (except where noted) previously tested, stretched gutta percha points of each brand were again fastened in the grips at the original gauge length. Slippage no longer presented a problem with higher stress loads, because the stretched points could be secured by a larger area of the grips as compared to the much smaller area clamped on the original, untested points. They were then stressed to their fracture point.

Trial testing revealed that these materials are extremely temperature sensitive, and that representative curves of the gutta percha points were achieved only when they were slightly warmed to a temperature of approximately 31°C. During testing, therefore, a No.1 photoflood lamp provided this constant temperature as verified regularly by a centigrade thermometer.

The crosshead speed of the Instron was set at ten inches per minute, the chart speed at 20 inches per minute, and a load range was calibrated from 0-10 pounds. Gauge lengths for all tests was set at 15 mm.

Size #100 points from Mynol, Premier, Star, and Union Broach were tested. Sizes #90 and #110 Dent-O-Lux (Schwed Co.) gutta percha points were tested because size #100, as mentioned earlier, was not available. The Dent-O-Lux sample size was also lower than the other brands, because
of the limited amount received from the manufacturer.

All data was recorded on chart paper within the Instron machine.
CHAPTER 4
RESULTS

Chemical Assay

Results of the chemical assays on the five brands of gutta percha endodontic filling materials are shown in Table 1. The relative amounts of the ingredients are: gutta percha, 18.88--21.79 percent; zinc oxide, 59.10--75.27 percent; heavy metal sulfates, 1.51--17.33 percent; and waxes and/or resins, 1.00--4.07 percent. Recovery of the constituent ingredients was 98.99--100.29 percent, indicating an approximate recovery error of ± 1.0 percent.

The final fraction containing gutta percha was qualitatively indistinguishable from purified, commercially available gutta percha.

Two types of coloring agents, incorporated into the gutta percha filling materials, were revealed by the assays. Dent-O-Lux and Tempryte filling materials possessed a dye that was rapidly affected by chloroform, causing an immediate discoloration and dissolution. On the other hand, the assay of Premier, Mynol, and Indian Head endodontic filling materials demonstrated the presence of a chloroform-insoluble, acid-insoluble dye that therefore followed the inorganic pathway of the assay, ending in association with the metal sulfates. The chloroform-soluble coloring agents remained with the organic components, gutta percha; wax and/or resin.
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<th>Zinc Oxide</th>
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<td>Indian Head</td>
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<td>21.66</td>
<td>1.15</td>
<td>17.40*</td>
<td>59.45</td>
<td>99.66</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>22.02</td>
<td>0.83</td>
<td>17.00*</td>
<td>59.55</td>
<td>99.40</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>21.68</td>
<td>1.03</td>
<td>17.58*</td>
<td>59.70</td>
<td>99.99</td>
</tr>
<tr>
<td></td>
<td>x ± s</td>
<td>21.79 ± 0.20</td>
<td>1.00 ± 0.16</td>
<td>17.33 ± 0.30</td>
<td>59.57 ± 0.13</td>
<td>99.68 ± 0.30</td>
</tr>
<tr>
<td>Dent-O-Lux</td>
<td>1</td>
<td>19.82</td>
<td>2.63</td>
<td>1.54*</td>
<td>75.39</td>
<td>99.38</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>20.17</td>
<td>2.96</td>
<td>1.75*</td>
<td>74.77</td>
<td>99.65</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>19.75</td>
<td>2.66</td>
<td>1.24*</td>
<td>75.66</td>
<td>99.31</td>
</tr>
<tr>
<td></td>
<td>x ± s</td>
<td>19.91 ± 0.23</td>
<td>2.75 ± 0.18</td>
<td>1.51 ± 0.26</td>
<td>75.27 ± 0.46</td>
<td>99.45 ± 0.18</td>
</tr>
<tr>
<td>Tempryte</td>
<td>1</td>
<td>22.23</td>
<td>2.73</td>
<td>3.66*</td>
<td>73.12</td>
<td>101.74</td>
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<tr>
<td></td>
<td>2</td>
<td>19.82</td>
<td>3.19</td>
<td>5.38*</td>
<td>71.52</td>
<td>99.91</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>19.66</td>
<td>2.91</td>
<td>1.16*</td>
<td>75.50</td>
<td>99.23</td>
</tr>
<tr>
<td></td>
<td>x ± s</td>
<td>20.57 ± 1.44</td>
<td>2.94 ± 0.23</td>
<td>3.40 ± 2.12</td>
<td>73.38 ± 2.00</td>
<td>100.29 ± 1.30</td>
</tr>
</tbody>
</table>

*Colored residue found with heavy metal sulfate

** x ± s of total recovered: 99.68 ± 0.86
Three of the brands of gutta percha filling materials (Indian Head, Dent-O-Lux, and Tempryte) had a leathery residue which remained with the metal sulfates after treatment with HCl. The color of the residue varied from a reddish-brown pigment in the Indian Head filling material, to grayish-brown in the Tempryte and Dent-O-Lux filling materials. These residues were insoluble in chloroform, hydrochloric acid, and acetone, and were only sparingly soluble in warm toluene.

**Mechanical Properties**

Tensile testing of the gutta percha endodontic filling material specimens produced load vs. elongation curves on the Instron chart paper. Several points on each curve were selected to characterize the following data: upper yield point, lower yield point, elastic modulus, total elongation, and ultimate tensile strength. These parameters will be defined and thoroughly discussed in the next chapter.

Most curves displayed a sharp upper yield point (Figure 3), however, one brand (Dent-O-Lux) revealed the total absence of this point, and so a four percent offset was selected to determine its yield strength (Figure 4).

Flexibility was measured as elongation of the specimen from zero elongation to the upper yield point.

The lower yield point was designated as the lowest point on the curve where the load either became constant or started to increase, after
Figure 3. A representative load vs. elongation curve. Note the yield strength or the upper yield point (UYP), the lower yield point (LYP), the increasing slope characteristic of strain hardening (SH), and the ultimate tensile strength (UTS).
Figure 4. A typical load vs. elongation curve of the Dent-O-Lux specimens. Note the absence of a lower yield point. The dashed line represents the four percent offset technique used for measuring the yield strength of these specimens.
decreasing from the upper yield point. Most samples demonstrated a lower yield point with the exception of Dent-O-Lux. This brand consistently failed to exhibit an upper or lower yield point on the samples that were tested (Figure 4). The lower yield point values were used in preparing the stress-strain curves.

Recording total elongation presented a problem because many of the gutta percha points slipped from the grips before the ultimate tensile strength was reached. To determine total elongation, therefore, elongation was measured on the ultimate tensile strength curves from a point where loss of linearity occurred to the fracture point. The mean value of these measurements was then added to the portion of the original curve where the samples had slipped from the grips. Total elongation was then measured from zero to the ultimate tensile strength.

Values of the mechanical properties were recorded for each specimen tested, and units of measure were converted where necessary. The means and standard deviations were calculated, and were then used to determine the following mechanical properties: yield strength, flexibility, ultimate tensile strength, elastic modulus, resilience, and percentage elongation (Table 2).

Stress-strain curves were prepared for each brand (Figures 5 and 6). The character and slope of the curves, from the lower yield point to the ultimate tensile strength, were approximated from the test curves.
<table>
<thead>
<tr>
<th>Brand</th>
<th>Yield Strength (psi)</th>
<th>Flexibility (in/in)</th>
<th>Ultimate Tensile Strength (psi)</th>
<th>Elastic Modulus (psi)</th>
<th>Resilience (in. lbs.)</th>
<th>Percentage Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Premier (61)*</td>
<td>1173.36 ± 93.93</td>
<td>0.08 ± 0.008</td>
<td>2025.63 ± 147.53 (10)**</td>
<td>16544.3 ± 3095.1</td>
<td>51.75 ± 7.56</td>
<td>401 ± 132</td>
</tr>
<tr>
<td>Mynol (50)*</td>
<td>1194.5 ± 188.62</td>
<td>0.07 ± 0.02</td>
<td>2414.38 ± 188.06 (10)**</td>
<td>22149.6 ± 5386.4</td>
<td>42.98 ± 11.99</td>
<td>476 ± 105</td>
</tr>
<tr>
<td>Indian Head (47)*</td>
<td>1717.0 ± 187.17</td>
<td>0.08 ± 0.02</td>
<td>2855.63 ± 288.46 (10)**</td>
<td>27329.3 ± 6996.6</td>
<td>76.44 ± 22.47</td>
<td>308 ± 91</td>
</tr>
<tr>
<td>Dent-O-Lux (26)*</td>
<td>1273.69 ± 78.08</td>
<td>0.12 ± 0.02</td>
<td>1733.68 ± 113.29 (5)**</td>
<td>21415.3 ± 8789.6</td>
<td>77.34 ± 13.58</td>
<td>173 ± 86</td>
</tr>
<tr>
<td>Tempryte (62)*</td>
<td>1234.38 ± 142.3</td>
<td>0.12 ± 0.02</td>
<td>2036.11 ± 192.15 (9)**</td>
<td>15499.6 ± 4045.6</td>
<td>71.17 ± 19.68</td>
<td>216 ± 96</td>
</tr>
</tbody>
</table>

*Sample size for all values except ultimate tensile strength

**Sample size for ultimate tensile strength values

***Four percent offset used in place of upper yield point
Figure 5. Stress-strain curves of the five brands of gutta percha endodontic filling materials.
Figure 6. Stress-strain curves of the five brands of gutta percha endodontic filling materials illustrating the elastic portion of the curves.
CHAPTER 5
DISCUSSION

Materials researchers have been seeking the ideal root canal filling material since the first root canal was filled well over one-hundred years ago. However, it seems as though investigations in this area have been directed along myopic approaches to the problem. In studying root canal filling materials, gutta percha material in particular, efforts have been centered around techniques, such as the pros and cons of solvents and/or warm gutta percha methods, or lateral versus vertical condensation procedures. Today, with the availability of modern scientific investigations, the researcher is allowed to use more sophisticated techniques in solving experimental problems. Knowledge of root canal filling materials should not be by trial and error investigation of clinical root canal filling procedures with little or no control of the many variables therein, but should begin with the collection of basic information on the material itself. In studying gutta percha as an endodontic filling material, knowledge of the ingredients of this unique material should include the effects of its ingredients upon its mechanical properties. Nielson (31), who is involved in the study of polymers notes that "the synthetic polymer chemist wants to know how mechanical behavior
is related to chemical structure in order that he can tailor-make materials with any desired properties."

A study of dental materials requires a basic knowledge of mechanical properties, and the rather rigid definitions that have been assigned to them.

Material properties are usually related to the effect of external forces upon a body. Force is an action which produces, or has a tendency to produce, a change in the motion of a body, and it always has direction (32).

Stress is the internal reaction to the external force, and is measured as force per unit area. Stress therefore varies directly with the magnitude of the force, and inversely with the area over which the force is applied (32,33). Three types of stress are delineated, depending upon the direction of the forces. Tensile stress results when a body is subjected to two forces which are directed away from each other in the same straight line; compressive stress occurs when two forces act on a body toward each other in the same straight line; and shear stress develops when two forces are directed toward each other, but not in the same straight line.

The effect of stress upon a body usually produces a deformation. The deformation per unit of original dimension is known as strain. Strain can be classified as either elastic or plastic depending upon
its reversibility. Elastic strain is reversible, disappearing after the stress is removed, and is nearly proportional to the amount of applied stress. A perfectly elastic material will immediately recover its original size and shape when the load is removed (33,34). The amount of elastic strain does not ordinarily exceed one percent before some amount of plastic deformation results (35). Once the elasticity of a substance is surpassed, permanent strain occurs. This is the result of the irreversible displacement of the atoms inside the material. Elastic strain is considered to be the retention of neighboring atoms (33).

The relationships of stress and strain are best illustrated in materials science with the use of stress-strain curves. In these diagrams, the stress is plotted vertically and the strain is plotted horizontally (Figures 5 and 6). These curves facilitate an understanding of the following mechanical properties.

The proportional limit is the greatest stress that a material will sustain without a deviation from the proportionality of stress to strain (32). Below the proportional limit, theoretically no permanent deformation occurs within the structure; therefore, this portion of the curve is considered to represent elastic strain. However, the application of stress greater than the proportional limit will produce a permanent deformation. This region, beyond the proportional limit, is termed the plastic region.
The **elastic limit** is the maximum stress that a material will withstand without permanent deformation (32). This term is therefore used interchangeably with proportional limit. However, one expression describes the elastic behavior of a material, while the other depicts the proportionality of strain to stress within the structure.

*Yield strength* is the stress at which a material exhibits a specified limited deviation from the proportionality of stress to strain (32). Beyond the yield strength, the material begins to function in a plastic manner.

The proportional limit, elastic limit, and yield strength are considered to represent the most important properties of a material (32).

The **elastic modulus** expresses the ratio between the applied stress and the elastic strain that results (33). It represents the slope of the elastic portion of the stress-strain curve, and is a measure of the relative stiffness or rigidity within the elastic range.

**Flexibility** is a measure of the strain that results when a material is deformed to its proportional limit. Its value is a function of the elastic modulus and the proportional limits of a material.

**Resilience** is the amount of energy absorbed by a material when it is stressed to its proportional limit. It is measured by the area under the elastic portion of the stress-strain curve.

The **ultimate strength** of a material is the maximum stress that the material can withstand before its failure. In tensile tests, its value is measured by dividing the maximum load in tension by the original
cross-sectional area of the test sample.

The elongation of a material is the strain measured at a particular point on the stress-strain curve, and is usually used to describe the total elongation before fracture. The resultant strain value can be multiplied by 100, and then expressed as percentage elongation.

As mentioned previously, to measure the mechanical parameters of the gutta percha endodontic filling materials, six properties were chosen: yield strength, flexibility, ultimate tensile strength, elastic modulus, resilience, and percentage elongation.

The yield strength was selected, rather than the proportional limit or the elastic limit, because most of the test curves displayed a sharp upper yield point which prompted an interest in its study. Actually, when comparing the yield strengths of various materials, any amount of permanent strain can be arbitrarily chosen for recording (32). An alternative to selecting a specific point on the stress-strain curve for the yield strength, is the use of the percent offset. In this method, a percentage of total strain is selected for the yield strength measurement. Because Dent-0-Lux failed to display any upper yield points, a four percent offset was selected to determine its yield strength (Figure 4).

The choice of using tensile tests to study the mechanical properties of the gutta percha endodontic filling materials was based upon the
following criteria. Hayden, et al (35), report that the tensile test is probably the most useful of all the tests used in evaluating mechanical properties; results gained from tensile testing are an extremely useful adjunct in designing new materials. In addition, compression tests are mainly used in testing brittle materials such as iron and concrete. Extremely ductile materials are seldom tested in compression because the sample is constrained by friction at the interface with the platens of the apparatus, thus causing a "barreling" effect. The resultant complicated stress distribution then can only be analyzed in an approximate fashion (35).

The proper crosshead speed on the Instron machine was determined on a trial and error basis until an appropriate strain rate was selected. The necessity of this procedure will be explained by speaking briefly of the "strain rate sensitivity" of polymers.

Polymers such as gutta percha are not perfectly elastic, but have both elastic properties and some properties of viscous liquids; therefore being known as viscoelastic materials. For a viscous material, the force resisting deformation is proportional to the "velocity gradient" (31).

Theoretical models of springs and dashpots, as developed by Kelvin and Maxwell, simplify the concepts of the unique strain-velocity dependency of viscoelastic polymers (31). The model that best describes the reaction of a polymer such as gutta percha to tensile stress is the "Maxwell element". This model illustrates a spring and a dashpot assembled in
series, in resistance to two opposite, uniaxial forces. When these forces are activated, the initial deformation is linear due to the concentration of the stress in stretching the spring -- the ideal elastic element. However, as the spring elongates, more and more of the stress is carried by the dashpot. Eventually, the spring can stretch no more, and all of the additional stress goes into the flow of the dashpot. As the dashpot is involved in deformation, the proportionality of stress to strain, common to the spring, will disappear. Deformation now is totally dependent upon the strain rate. Since the piston in the dashpot will only move at a constant rate, an increase in the elongation rate will produce an elevated stress. If a sufficient load to activate the dashpot in a viscoelastic material is held constant, a stress will be produced within the material that will eventually deform with time. However, if enough compensatory deformation does not occur, and a stress remains, the internal forces may be rearranged by molecular shifting. This is called "stress relaxation", and is common to all viscoelastic materials -- including gutta percha. Price, in 1918 (4), observed the phenomenon of stress relaxation, when he commented on the tendency of gutta percha, like waxes and gums, to return to its original shape after the stresses were removed.

The phenomenon of stress relaxation is closely related to the strain rate sensitivity of polymers. If a high rate of strain is
imposed upon a polymer, sufficient time for stress relaxation will not occur, and a brittle fracture will result. When trial testing, this appeared to be problematical when crosshead speeds were set above ten inches per minute. Curiously, however, when strain rates below ten inches per minute were utilized, a high occurrence of fractures also resulted (Figure 7). In considering this phenomenon, the following observation by Nielson (31) seems to offer a possible explanation. Nielson proposes that in a viscoelastic material energy resulting from the load is not stored as in a spring, but is dissipated as heat when a viscous material is deformed. Since viscoelastic materials, such as gutta percha, are extremely temperature dependent, the production of heat by the straining process produces an increased interatomic spacing, which in turn results in a sufficient softening temperature. If the crosshead speed is too low, on the other hand, adequate heat is not generated to reach the softening temperature, which could then explain the brittle fractures.

The effect of strain velocity on mechanical properties of polymers is noted by Nielson (31) who reports that an increase in the rate of elongation will result in an increased ultimate tensile strength, an increased elastic modulus, and a decrease in total elongation. Hayden et al. (35) also described a generally higher stress-strain curve as the strain rate increases.
As previously mentioned, gutta percha is extremely temperature dependent: softening and deformation begin at relatively low temperatures. The stress-strain sensitivity and the marked brittleness, and they may be fractures, a definite inflection in the stress-strain character with a high ultimate strength is similar to that of the stress-strain curve with many decrease resilience that exceeds 30°C (25°C). At high temperatures both raising the gutta percha at room temperature, elongation has been heated to 31°C during the testing procedure; this elevated temperature yielded curves which were identical to those reported for similar polymers in the literature (31, 34, 35, 37).

Figure 7. Premature fracture of a test specimen.
As previously mentioned, gutta percha is extremely temperature dependent, softening with an increased temperature and becoming easily deformable. It is therefore described as being "thermoplastic" (35).

The stress-strain curves of polymers reflect much of this temperature sensitivity. At low temperatures, polymers tend to be brittle, and they may break before a yield point is attained (31). At high temperatures, a definite yield point may even disappear being replaced by an inflection in the curve. Different temperatures can change the stress-strain characteristics of a polymer from brittle to soft, with a high ultimate strength and elongation. The result of lower temperatures is similar to the effect of an increased elongation rate, both raising the stress-strain curve (31,35). An increased temperature will also decrease resilience, especially when the temperature of the gutta percha exceeds 30°C (35,36). Testing of the gutta percha points at room temperature (25°C), therefore, resulted in unsatisfactory load vs. elongation curves with many premature fractures. The samples were then heated to 31°C during the testing procedure; this elevated temperature yielded curves which were identical to those reported for similar polymers in the literature (31,34,35,37).

An attempt to use standardized test specimens of the gutta percha endodontic filling materials proved to be fruitless. Only one manufacturer was able to supply the gutta percha filling material in slab form,
and so consideration was given to preparing standard test specimens from the gutta percha points supplied by the other manufacturers. This would have required heating and packing the points into a mold, possibly altering the chemical and mechanical properties of the material. Instead, the gutta percha points themselves were used as tensile specimens. Gutta percha points are not uniform in cross-sectional area, but are tapered approximately 0.3 mm along their length, a fact which could result in less accurate data. Nevertheless, most points demonstrated a strain pattern which was considered identical to polymer tensile specimens. In fact, the tapered points displayed more accurate test curves than standardized test samples made from slabs of gutta percha material. The cross-sectional area used for determination of the mechanical properties was selected at the middle of the gauge length (cross-sectional areas: #100 points = 0.0016 in²; #90 points = 0.0013 in²; and #110 points = 0.0019 in²).

Determination of the ultimate tensile strengths and the total elongations may have also afforded reduced accuracy. As reported in Chapter 3 (Methods and Materials), the samples usually slipped from the grips before the ultimate tensile strength was attained. Reapplication of strained gutta percha points securely in the grips produced an additional elongation to the fracture point when stressed. Since these curves continued to exhibit plastic regions before fracture, their mean elongation was accepted as a valid extension of the test curves, and was
therefore, added to each curve for determination of total elongation.

Chemical assay of the brands of gutta percha filling materials revealed interesting ingredient proportions that usually differed from information supplied by the manufacturers (Table 1). The precision of the results allowed the sample size of three assays per brand to be selected. This precision is best exemplified by the relatively small statistical variations for the ingredients of each brand.

In studying these quantitative values, several trends were found. By comparing the organic components (gutta percha; wax and/or resin) and the inorganic components (zinc oxide; heavy metal sulfates) the proportionality of the different fractions became apparent. Regardless of the brand, the organic and inorganic fractions were essentially the same. The mean organic percentage was 23.14 percent with a standard deviation of only ±0.48 percent, while the mean inorganic percentage was 76.37 percent with the small standard deviation of ±0.68 percent.

Why then, is there a difference in the mechanical properties between the brands? The answer is related to the substance incorporated into these two fractions. In general, the gutta percha content was inversely proportional to the wax and/or resin fraction, as was the zinc oxide content to the heavy metal sulfates. If a brand possesses a high gutta percha content, as Indian Head does for example, its wax and/or resin fraction is relatively lower in weight. Likewise, Dent-O-Lux exhibits
the largest zinc oxide weight, but its metal sulfate fraction is the lowest of the five brands. A variation of this trend was never exhibited. The importance of these interrelationships will be discussed later in this chapter.

A relatively high heavy metal sulfate content, in three of the five brands of gutta percha filling materials, was found to conform to the ingredient proportionalities just discussed. Premier, Mynol, and Indian Head revealed high metal sulfate contents, but had low zinc oxide fractions.

As shown in Table 1, the mean total recovery of the assays was 99.86 ± 0.86 percent. In the samples assayed, Tempryte and Mynol yielded apparent recoveries above 100 percent. The retention of small quantities of residual moisture and chloroform probably accounts for this excess.

Some manufacturers described the presence of wax in their gutta percha filling materials. In addition, resinous materials have been revealed in gutta percha itself (20,27). The amounts of these two organic substances were not ascertained, because the likelihood of the presence of either or both of them was not considered to be of utmost value to this investigation. They probably have similar chemical and mechanical properties, and since their combined weight was usually less than four percent, they were placed under the single category -- wax and/or resin.
The chloroform-insoluble, acid-insoluble residues found with Dent-0-Lux, Tempryte, and Indian Head metal sulfates were described in Chapter 4. The unsolved question of their nature possibly accounts for a source of error in the assay as the real weight of heavy metal sulfates is probably somewhat less than that reported. The significance of the difference in weight, however, is regarded as small.

Tensile testing of polymers, such as gutta percha, results in a characteristic strain pattern. Most polymers demonstrate a concentration of plastic deformation in a localized region of the sample under tension (35). This characteristic is called "cold-drawing" or "necking". The specimens do not elongate uniformly, but at the yield point, a constriction develops in the specimen. Material in the constricted region undergoes very large elongations, and as stretching continues, the constricted area grows in both directions toward the clamps. The cross-sectional area of the drawn portion remains constant during stretching, and it is separated from the undrawn region by a well-defined shoulder (31).

Samples of the gutta percha points, when stressed, reproduced the cold-drawing characteristic of polymers (Figure 8). This similarity to polymers, together with the conformity of the stress-strain curves of gutta percha filling materials and polymers, will be shown later in this chapter to be an explanation of the predominance of the mechanical properties of the natural polymer -- gutta percha.

Tensile testing of the gutta percha filling materials revealed
Figure 8. "Necking" phenomenon illustrating the cold-drawn area (CD) separated from the undrawn portion (UD) by well-defined shoulders. Note the grip modifications: metal grip (MG), soft rubber (R), and silicon carbide paper (P).
significant differences in the mechanical properties of the five brands (Table 2). Indian Head displayed the highest yield strength, ultimate tensile strength, and elastic modulus, and a relatively high resilience. On the other hand, Mynol and Premier revealed low resiliences and yield strenths, but high percentage elongations.

According to the stress-strain curves (Figures 5 and 6), Dent-0-Lux appeared to be the most brittle of the five brands, because of its low percentage elongation and ultimate tensile strength. Dent-0-Lux and Tempryte did, however, exhibit high flexibility values.

High standard deviations of the mechanical properties were thought to be a reflection of poor quality control in the manufacturing process (Table 2). Defects in the points often produced an early fracture. The resultant small elongations of these specimens, when used to compute the mean percentage elongation, therefore contributed to large standard deviations.

Large standard deviations of the elastic modulus values, however, were believed to be related to an inaccurate method of measurement. It was discovered, after the collection of data was completed, that an extension of the slope of the linear portion of the test curve to intersect with a projected load value would have produced more accurate data. Nevertheless, values for the elastic moduli did appear to be fairly accurate for a comparison of the five brands. Dent-0-Lux, however, exhibited an unusually high elastic modulus that was possibly related to
its low sample size.

Chemically, gutta percha is the natural polymer, trans-polyisoprene. Billmeyer (37) defines a polymer as "a large molecule built up by the repetition of small, simple chemical units." All polymers have high molecular weights, and are generally in the form of long chains (31). Gutta percha consists of isoprene units that are joined in a linear fashion by strong primary bonds. The resultant chains are usually arranged in folds. Relatively weak secondary (Van der Waals) bonds help to maintain these folds, and to bind the adjacent chains to each other. High molecular weights allow these forces to build up enough yield good strength, dimensional stability, and other mechanical properties (37).

Gutta percha is approximately 60 percent crystalline, the remainder being amorphous (20). Hayden et al (35) state that the relative amounts of crystalline and non-crystalline regions in polymers vary with the chemical composition, molecular configuration, and processing. Generally, the higher the crystallinity, the higher the strength of the material will be, because stress must work in opposition to the restoring forces of the primary bonds (35). Hayden et al (35) note that the mechanical properties of organic polymers are highly sensitive to molecular configuration, which is itself sensitive to the mode of manufacture. Different processing techniques that are held as trade
secrets by the manufacturers of gutta percha endodontic filling materials could possibly account for many of the variables in mechanical properties. The differing processes of hand-rolling versus machine-rolling of gutta percha points alone could contribute different characteristics to the final product.

The weakest portions of polymers are the secondary bonds between the chains. Vulcanization is the formation of cross-links between adjacent chains at positions where double bonds originally existed (35). This adds considerably to the strength of the material, while increasing its brittleness.

Gutta percha is therefore analogous to the molecular configuration of a linear polymer with weak interchain bonds. A more complex system is presented, however, when speaking of gutta percha endodontic filling materials, because of additional substances that are present. The reasons for incorporation of zinc oxide, heavy metal sulfates, and occasionally, wax, are the key to understanding the properties of gutta percha endodontic filling materials.

Zinc oxide has long been used as a filler in many dental materials, because of several characteristics and properties that make it ideal for this purpose. It is inexpensive, relatively inert, and non-toxic; its white color is desirable, and its particle size can be made extremely fine. The purpose of its use in gutta percha endodontic filling materials
is either related to its ideal filler characteristics, or to its possible vulcanizing effects (38).

Heavy metal sulfates (barium sulfate and strontium sulfate) are most probably incorporated into gutta percha endodontic filling materials solely because of their excellent radiopacity, a desirable characteristic of any root canal filling.

The reasons for incorporating waxes into some of the gutta percha filling materials is not clearly evident. Waxes are possibly added as a dilutant to maintain the constant organic content when a lower portion of gutta percha is desired. Paraffin waxes have been reported to form an adhesive boundary with gutta percha molecules (39), which might produce intrinsic interferences with the arrangement and movement of the gutta percha chains.

Hypothetically, at the molecular level, gutta percha endodontic filling materials are probably composed of a continuous phase of gutta percha in the form of folded chains. Folds in the chains are maintained by secondary bonds, and the chains themselves are probably bonded to each other by both secondary bonds and zinc oxide cross-links. Molecules of metal sulfates are likely to be interspersed at random, and waxes might conceivably interact with the folded chains of gutta percha. Pure gutta percha is mostly crystalline, and is therefore hard and tough. The rigid structure of pure gutta percha is likely to be interrupted by
either the bonding interferences of waxes or zinc oxide molecules. The effects of these molecular arrangements on mechanical properties will be discussed next.

In studying the stress-strain curves for the five gutta percha filling materials (Figures 5 and 6), the following analysis of the data is proposed. At the constant strain rate of ten inches per minute, all specimens produced an immediate linear strain. Upon release of the load, the strain would return to zero, thus illustrating the elastic effects of the spring in the "Maxwell element" mentioned earlier. If the load was increased, the curves demonstrated a yield point. Hypothetically, at the yield point, most of the stress should be converting to the dashpot effect of the Maxwell element. From this point, the stress decreased to a short, constant level in most samples (except Dent-0-Lux), and then gradually began to increase to the ultimate tensile strength.

At the molecular level, the elastic portion of the stress-strain curve is likely to be associated with the stretching of the secondary bonds between the folds in the gutta percha chains. The slope of this linear portion (elastic modulus) should be associated with the amount and position of the secondary bonds. As the yield point is approached, more secondary bonds are broken, and slipping of the polymer chains
results in increasing plastic deformation. When the majority of the secondary bonds have been eliminated (chain unfolding), the decrease in stress corresponds to the lack of opposing molecular bonds. Amorphous and crystalline regions at this stage are unoriented to the direction of force. As the strain continues, these elements become oriented to the vector force resulting in a new crystalline pattern. An increased stress now results as the primary bonds in the oriented chains are opposed. Some secondary bonds and zinc oxide cross-links between the oriented chains may still be present at this stage only if they can adequately oppose the stress of chain slippage. Orientation produces a "strain-hardening" effect that continues until enough primary bonds in the chain are broken to yield a fracture in the test sample.

The assumption that most of the mechanical properties of these filling materials are the result of the weakest component, gutta percha, is not supported by the relative weights of the fractions found by the chemical assay. According to the assay, gutta percha only accounts for about 20 percent of the total weight, as opposed to approximately 75 percent for zinc oxide. In studying the relative densities of gutta percha and zinc oxide, however, it is revealed that zinc oxide is approximately five times as dense as gutta percha (40). This accounts for the predominance of the mechanical properties of the gutta percha and its relatively low percentage weight. If, in fact, zinc oxide was responsible
for the predominant effect upon mechanical properties, curves typical of ceramics would be observed, with high yield strengths and extreme brittleness.

Nielson (31) reports that hard, tough polymers produce curves showing high elastic moduli, yield points, tensile strengths, and elongations. Statistical analysis of the results of this investigation show that at the 0.05 significance level, gutta percha, like hard, tough polymers, is positively correlated with yield strength. Because of the production of a high yield strength, mechanical properties, such as resilience and elastic modulus, that are associated with the elastic portion of the curve, also showed a positive trend with increased gutta percha content. In addition, the ultimate tensile strength increased proportionally with gutta percha content. However, although the resilience, elastic modulus, and ultimate tensile strength exhibited strong trends, they were not statistically significant at the 0.05 level. These findings appear to relate to the hard, tough polymers to which Nielson refers. Only the elongation of the gutta percha filling materials differed completely from the forecasted properties of hard, tough polymers. Reasons for this discrepancy will be discussed next.

The inverse proportionality of zinc oxide content and the percentage elongation is statistically correlated (P > 0.05). This accounts for the lowering of percentage elongation in gutta percha filling materials as the
zinc oxide content increases. Similarly, an increase in zinc oxide content tended to decrease the ultimate tensile strength. Nielson (31) reports that the addition of fillers, in the form of fine powders, to polymers results in a decrease in both elongation and ultimate strength. Zinc oxide, by forming strong chain cross-links, could prevent the slippage of the gutta percha chains, resulting in increased brittleness as the amount of zinc oxide increases. This was observed with Dent-0-Lux and Tempryte filling materials, which contained the highest zinc oxide contents (Figure 5).

The Dent-0-Lux stress-strain curve revealed the absence of a lower yield point. Since this brand had the highest zinc oxide content, inter-chain bonding could have been so strong that breakage of the secondary bonds, which would produce a yield point, was inhibited. Tempryte, which also had a high zinc oxide content, exhibited a rather vague lower yield point. The sharpest yield points were exhibited by Mynol and Premier, which had low zinc oxide contents.

The significant brittleness, that was found to be associated with high levels of zinc oxide, tends to support the concept that zinc oxide is a vulcanizer in gutta percha endodontic filling materials. However, of equal significance, an increase in flexibility was found with a larger zinc oxide content. Similarly, although not statistically significant, the resilience increased with an increase in zinc oxide content. Dent-
O-Lux and Tempryte, with high zinc oxide contents, demonstrated high resilience and flexibility values. The role of zinc oxide as a vulcanizer cannot account for the elevated flexibility and resilience values; in fact, the values of these properties should be proportionately lower. The effects of oxidation, which are similar to those of vulcanization, do not increase flexibility, but rather produce a harder, more brittle substance (20). Therefore, the concept that zinc oxide is merely a filler, cannot be eliminated until the effects of zinc oxide on flexibility and resilience can be explained.

It can be debated that zinc oxide has no intrinsic chemical effect, but instead produces mechanical characteristics by its dilution of gutta percha alone. However, it must be remembered, as stated previously, that the relationships between the inorganic and organic components were constant. If a large zinc oxide content was present, the only fraction that suffered were the heavy metal sulfates.

Significant correlations of the metal sulfates to the mechanical properties were exactly opposite, but equal to the same properties affected by the zinc oxide content. Dilution of the zinc oxide content could be the principal effect of the metal sulfates upon the mechanical properties.

In studying the shortcomings of gutta percha endodontic filling materials as compared to the ideal filling material, Grossman (12) states that gutta percha filling material is not always easily introduced into the
canal, either as separate cones, or in combination with other cones or materials. Curved, irregular, or small canals are the major reasons for the lack of use of gutta percha filling material to fill a root canal. Even when the master gutta percha cone is negotiated the entire working length of the canal, it does not always seal laterally upon condensation, although perhaps sealing apically (12).

Speaking from a manipulative standpoint, the ideal semisolid root canal filling material should possess a manageable rigidity. The proper combination of flexibility and rigidity should permit the negotiation of almost any root canal regardless of its anatomical characteristics.

Nevertheless, the complete negotiation of the root canal by the master gutta percha point solves only half of the problem. At this stage, the gutta percha filling material must possess sufficient flow to allow its condensation to completely fill the root canal, from the apex to the floor of the chamber, vertically and laterally. The space between the condensed gutta percha filling material and the canal wall should ideally be minimal so that too much reliance need not be placed upon the paste-like root canal sealer for total obliteration of the root canal space. Finally, the gutta percha filling material must possess dimensional stability after its condensation.

From this study, it seems as though the desirable mechanical properties of gutta percha endodontic filling materials should include a high
rigidity (elastic modulus), a high flexibility, high yield strength, a large elongation, and a low resiliency.

To design an improved endodontic filling material involving gutta percha, therefore, simply vary the chemical composition. High gutta percha and low zinc oxide contents favor a high level of rigidity. This property, together with high flexibility and a high yield strength, would facilitate negotiation of canals. However, flexibility increases with a large zinc oxide component and a lower gutta percha component, while high yield strengths seem to be totally dependent upon gutta percha contents. To add to these antitheses, a large percentage elongation, a reflection of greater condensability, is achieved by lowering the zinc oxide content; and resiliency, an indication of post-condensation dimensional stability, is affected by both zinc oxide and gutta percha levels!

It therefore seems evident that it is almost impossible to develop an ideal root canal filling material utilizing gutta percha. The properties needed for one phase of canal obliteration (negotiation) are usually opposite to those required for the final phase (condensation). There is a need for two different material characteristics within the same material. In order to negotiate difficult canals, high values of rigidity, flexibility, and yield strength are required; and on the other hand, a readily condensable material should possess a high percentage elongation and a low resilience. Most of these properties require opposite chemical
proportions in gutta percha endodontic filling materials. It is evident, that a material chosen because of its properties facilitating negotiation of the canal will fall short of ideal when condensing; the opposite is also true.

To offer possible solutions to these problems is an encouragement to future research, for the two different materials requirements present a problem not easily overcome.

A material with sufficient rigidity, flexibility, and strength could easily be inserted to the full working length of a canal, and then have its material characteristics changed to afford good condensability and hopefully, dimensional stability. Agents such as increased temperature (3) and solvents (1,2) have been used for this purpose; however, these techniques may present a compromise in dimensional stability.

Since different brands of gutta percha endodontic filling materials exhibit differing mechanical properties, perhaps the choice of one over the other should be based upon root canal morphology. Likewise, manufacturers could market different types of gutta percha root canal filling materials with differing mechanical properties. The choice of a particular type then could be based upon the particular root canal morphology encountered, such as a type of dental gold is selected depending upon its use, from an inlay to a bridge. The disadvantage of this proposal, again, is the compromise of one phase to facilitate the other.
Semisolid filling materials with a soft apical portion and a rigid coronal portion might be an improvement if possible to manufacture, but lateral sealing would be compromised in the coronal portion of the canal. Perhaps a better solution is the development of a soft filling material with a rigid core.

Mechanical properties testing shows that the best technique for condensation of gutta percha filling materials is with the use of a large amount of force sustained over a long period of time to permit the viscoelastic material to plastically deform to its fullest extent. Generally, however, this is not the procedure used in clinical endodontic practice.

To aid in the development of a better gutta percha endodontic filling material, future research should include in depth investigations of the temperature and strain rate sensitivities of gutta percha root canal filling materials.

Also, examination of gutta percha root canal filling materials with the use of the scanning electron microscope should shed light upon the physical morphology of not only the filling material, but possibly differences which might exist between the core and the skin of processed gutta percha points.

Oxidation sensitivities of the gutta percha molecule, trans-polyisoprene, are noticed clinically in the form of increased brittleness of
gutta percha points with age. Investigation of this chemical change could help in the development of more oxidation-resistant root canal filling materials, or in the discovery of antioxidants which could be incorporated into the filling material itself.

Studies of the effect of sealers upon gutta percha endodontic filling materials might reveal mechanical and chemical changes which could be advantageous or detrimental to the ideal root canal filling. The chemical and mechanical effects of eugenol, common to most endodontic sealers, could have much bearing upon the manipulative properties of semisolid endodontic filling materials.

Finally, gutta percha is a natural commodity; it is subject to many factors which affect supply, while being in great demand. The supply of zinc oxide itself is presently nearing a crisis level because of an increasing demand for it in other chemical products. Perhaps research in the field of synthetics will result in better answers to the materials problems posed by endodontics, either by the use of synthetics in combination with gutta percha, or as a substitute for it.
CHAPTER 6
SUMMARY

Gutta percha has been predominant as a root canal filling material for over a century. It has been used in various filling techniques; its effect upon biologic tissues has been studied; but knowledge of its chemical and mechanical properties has grown little since its introduction into the field of dentistry, much less, endodontics.

In this investigation, the mechanical properties were compared to the chemical composition of five brands of gutta percha endodontic filling materials. Significant correlations were found to exist between these parameters; hypothetical molecular models and explanations of its mechanical properties were offered.

Knowledge acquired from this study creates new questions and the necessity for further investigations.
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APPROVAL SHEET

The thesis submitted by Dr. Charles E. Friedman has been read and approved by members of the Department of Oral Biology.

The final copies have been examined by the director of the thesis and the signature which appears below verifies the fact that any necessary changes have been incorporated, and that the thesis is now given final approval with reference to content, form, and mechanical accuracy.

The thesis is therefore accepted in partial fulfillment of the requirement for the degree of Master of Science.

May 17, 1973
Date

Signature of Advisor