

# The thermomechanical properties of gutta-percha

## II. The history and molecular chemistry of gutta-percha

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

BOSTON UNIVERSITY SCHOOL OF GRADUATE DENTISTRY

The various early uses of gutta-percha are reviewed, and its molecular chemistry is discussed.

**T**he early history of gutta-percha is obscure. The Malays and Chinese are said to have used it in a remote and undetermined epoch long before Western civilization had any knowledge of its existence.<sup>1, 2</sup> The recorded evidence of this material in Europe comes from a well-known English family of travelers and curiosity hunters, the Trandescants, in the middle of the seventeenth century. The Trandescants, father and son, were the proprietors of a collection of curiosities assembled near London known as "Trandescant's Arc." John Trandescant, the son, published a small book in 1656 entitled *Museum Trandescantium, or A Collection of Rareties Preserved at South Lambreth Near London*. In this book he made the statement: "The plyable mazer wood, being warmed in water, will work to any form." This was thought to apply to gutta-percha since no other material suitable for mazers† was known to possess such properties. Gutta-percha, as formerly prepared by the natives of Asia, had a yellowish brown color and showed a decidedly fibrous texture. Even experienced observers mistook it for wood. It is interesting that, in the vernacular, one name for the tree that yielded gutta-percha became the "mazer wood tree."

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\*Instructor, School of Graduate Dentistry.

\*\*Assistant Dean, Professor and Chairman, Department of Endodontics.

\*\*\*Assistant Professor, College of Engineering, Boston University.

†Mazers—Large drinking bowls originally made of hard wood.

Although "Trandescant's Arc" was a curiosity of its age, frequented by greats, including kings and queens, the unusual properties of the remarkable "mazer wood" passed quite unnoticed by practical men. After the death of the younger Trandescant in 1662, Elias Ashmole obtained possession of the collection and moved it to Oxford where, in 1682, it became the nucleus of the famed Ashmolean Museum. The historical sample of which young John wrote was never found, but there is little doubt that his "mazer wood" and gutta-percha are identical substances.<sup>1-5</sup>

For almost 200 years "mazer wood" was brought into England as a curiosity from the tropical regions of Asia without coming into practical use. In the early 1840's it was reintroduced into Europe, under the name gutta-percha, in a manner which led to its rediscovery as a valuable substance to be applied in art, science, and manufacturing.<sup>2-4</sup> There were two rival claimants for the honor of this reintroduction. Both were residents of Singapore, and both belonged to the medical profession.

Dr. Jose D'Almeida<sup>1, 3, 6</sup> brought specimens with him to London in 1843 and presented them to the Royal Asiatic Society. A list of D'Almeida's specimens was printed in the *Journal of the Royal Asiatic Society*, volume 8, in 1844, in an article entitled "A List of Donations to the Museum from April 1842 to June 1844." Dr. William Montgomerie<sup>1-6</sup> communicated his findings to the Medical Board of Calcutta in 1842 and later to the Society for the Encouragement of Arts, Manufactures, and Commerce in London.

Some of the samples and a copy of Montgomerie's letter originally sent to the Medical Board in Calcutta were forwarded to the Agricultural and Horticultural Society of India, where Dr. Fred Mouat, Chemical Examiner to the Government of Calcutta, wrote the first published record referring to gutta-percha since the quotation in the Trandescant catalog 186 years earlier.

The rediscovery of gutta-percha at that moment in history when dynamic electricity began to play an important role in Western life and the unalterability of gutta-percha in cool water, especially salt water, led to its use in the insulation of telegraph cables. Prior to 1848 many attempts were made to find a suitable insulation for underseas cables, but none of the materials tested could withstand long periods of immersion. The first successful insulation for an underwater line was gutta-percha, used by Ernst Werner von Siemens in 1848.<sup>2, 6</sup> Gutta-percha occupied an unrivaled position as the most desirable insulator of electric cables until its replacement by vulcanized rubber late in the nineteenth century.

People became infatuated with this new material. Patents for its use multiplied rapidly. Gutta-percha was employed for the manufacture of corks, cements, thread, surgical instruments, garments, pipes, and sheathing for ships. Even boats were made wholly of gutta-percha, one as early as 1850. It was constructed by Messrs. Searle and Company of South Lambreth, England, and used in an Arctic expedition. Maps and globes were made of the material, and, because of the thin sheets into which it could be rolled, gutta-percha seemed destined to replace paper. The variety of manufactured articles became bewildering. Musical instruments, candelabra, gaiters, garters, suspenders, window shades, carpets, gloves, mattresses, pillows, tents, umbrellas, and a host of other articles were

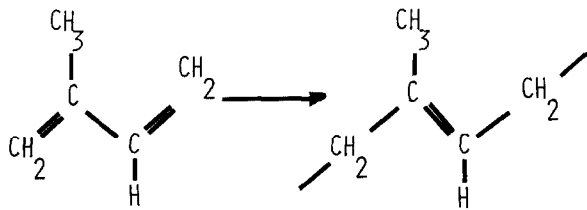


Fig. 1. Isoprene monomer  $\rightarrow$  Isoprene mer.

fabricated of gutta-percha. Gutta-percha golf balls were introduced by the later part of the nineteenth century, and until 1920 "gutties" was the term used for golf balls on links in this country and abroad.

Of all these commercial applications, except for its use in golf balls, there remains only a memory, and if it were not for certain special uses, the gutta-percha of Sumatra would have been abandoned by industry, for the very properties of the material are such that they are opposed to most of the uses to which it was first assigned. It is an eminently plastic substance at slightly elevated temperatures, and it was not unusual to see garments, as well as slippers, soften with the heat of fire. Vulcanization of the chemically related material, rubber, proved much more successful than vulcanization of gutta-percha, and rubber soon dispelled the gutta-percha illusion.

It was this characteristic of plasticity of gutta-percha at relatively low temperatures that determined the failure of the new industry. As its essential properties became better understood, gutta-percha was left with a less utilized but still significant place in those areas where it could be more suitably applied.<sup>2, 3, 5</sup>

Gutta-percha, the naturally occurring polymer of isoprene, has been known to dentistry for approximately 125 years,<sup>7-9</sup> but man's use of such natural polymers antedates recorded history. The science and understanding of polymers is more recent, and only in the last 25 to 30 years has this understanding produced the widespread use of synthetic polymers as we know it today.

The characteristic feature of the organic polymer molecule is a chain of covalently bonded atoms, built by the repetitive chemical linking of small, simple units. The chains are long with molecular weights ranging from  $10^4$  to  $10^6$ . Their large size and chainlike structure result in fields of attraction between individual molecules (Van der Waals bonding). This bonding, along with natural physical entanglement of the long chains, produces unique and interesting properties in the bulk specimen.<sup>10</sup>

Bonding and mechanical interaction of polymer chains vary with the length of the molecule and the orientation and character of its side radicals. Even slight changes in bond orientation of two otherwise identical polymer chains (isomerism) result in remarkable differences in mechanical and thermal properties.<sup>11</sup> Natural rubber and gutta-percha represent, perhaps, the most interesting example of isomerism. Both are high-molecular-weight polymers, and both are structured from the same basic building unit or isoprene mer (Fig. 1).

The basis for the remarkable properties of natural rubber and gutta-percha, as well as for their differences, was not explained in terms of molecular physics until 1942.<sup>12</sup> "Cis" polyisoprene, it was discovered, exists with its  $\text{CH}_2$  groups

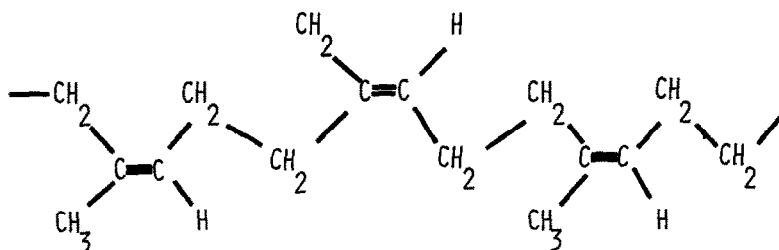


Fig. 2. Natural rubber.

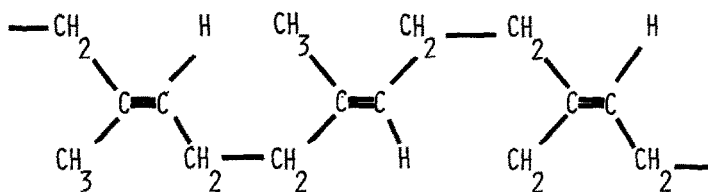


Fig. 3. Gutta-percha.

(the chain forming links of individual isoprene units) on the same side of the double bond to form the polymer of natural rubber (Fig. 2). "Trans" polyisoprene, on the other hand, exists with its chain forming  $\text{CH}_2$  groups on opposite sides of the double bond to form the polymer known as gutta-percha (Fig. 3).<sup>13</sup> It may be observed that the "cis" form is more kinked, which complicates alignment, allows for mobility of one chain with respect to another, and gives natural rubber its elastomeric character. The "trans" form is more linear and crystallizes more readily. Consequently, gutta-percha is harder, more brittle, and less elastic than natural rubber.<sup>14</sup>

Most polymers do not represent a completely random entanglement of long-chain molecules but are, to some extent, crystalline, that is, ordered. Perhaps the simplest model of polymer crystallinity is the "fringed micelle" (Fig. 4), which may be thought of as regions within a bulk polymer where the molecular chains pass from disordered areas into more ordered, parallel arrangements.<sup>13</sup> These regions of close packing and alignment of molecules result in increased intermolecular attraction, producing greater mechanical strength and reduced plasticity. Density is increased, resulting in a reduction in volume for the bulk specimen.

Temperature radically affects the physical state and molecular arrangement of linear polymers. At sufficiently high temperatures a linear polymer is an amorphous, rubbery melt in which the molecular chains can be envisioned as random coils, continually changing orientation as a result of thermal excitation. At sufficiently low temperatures the same polymer is a rigid solid with its chains locked in position. There are two mechanisms by which solidification takes place with cooling. One method is through crystallization into an ordered, molecular arrangement. The other is by random freezing or vitrification. Specific polymer systems solidify by means of varying amounts of each of these mechanisms.

A critical event occurred in 1942, when C. W. Bunn reported an interesting complication in the molecular chemistry of gutta-percha. He found that the polymer could exist in two distinctly different crystalline forms, which he termed

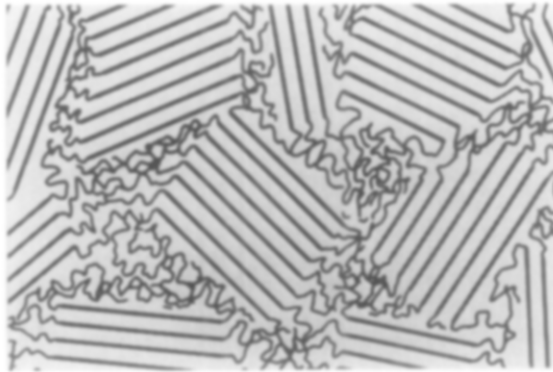


Fig. 4. Fringed micelle structure of semicrystalline polymers. (Reprinted from Paul J. Flory: Principles of Polymer Chemistry. Copyright 1953 by Cornell University. Used by permission of Cornell University Press.)

“alpha” and “beta” modifications. These forms could be converted into each other but not into natural rubber, which suggested that both were of the “trans” isomer, differing only in single bond configuration and molecular repeat distance (Fig. 5). These modifications have never been reported previously in the dental literature, and failure to make this distinction has retarded a more complete understanding of the thermophysical properties of dental gutta-percha.

Most commercial gutta-percha exists as the “beta” crystalline structure.<sup>15</sup> The “alpha” form occurs in the tree. If the natural “alpha” form is heated above 65° C., it becomes amorphous and melts. If this amorphous material is cooled extremely slowly (0.5° C. per hour), the “alpha” form recrystallizes. If, on the other hand, the amorphous melt is cooled routinely, the “beta” form recrystallizes.<sup>12</sup> It is in this form that most commercial gutta-percha, including dental gutta-percha, exists. If the “beta” form is now reheated, the polymer becomes amorphous at 56° C., 9 degrees lower than the melting point for the “alpha” form. It is apparent, therefore, that the factor determining the melting point of “alpha” and “beta” gutta-percha is the rate of cooling which, in turn, controls the extent and character of crystallinity in the congealed material. In addition, the purity of a sample,<sup>16</sup> as well as its average molecular weight and molecular weight distribution, affects these melting points. Isoprene polymer material obtained from chicle, for example, has a molecular weight of 16,000 to 18,000, while the isoprene polymer material obtained from plants producing gutta-percha has a molecular weight of 30,000 to 60,000.<sup>17</sup> Although these materials are the same chemically and structurally, a wide variation in molecular weight and per cent crystallinity results in a notable discrepancy in melting points.

To complicate the situation further, differences in crystallization are found even within similarly identified materials. For example, the melting point of “alpha” gutta-percha has been “documented” at 65° C.,<sup>12, 18</sup> 74° C.,<sup>19</sup> and 79° C.,<sup>20</sup> pointing out the multiple variants that are included in the make-up of so-called pure samples. An awareness of these variations is essential to an understanding of the properties and behavior of these materials.

There is apparently no difference in the mechanical properties of “alpha” and

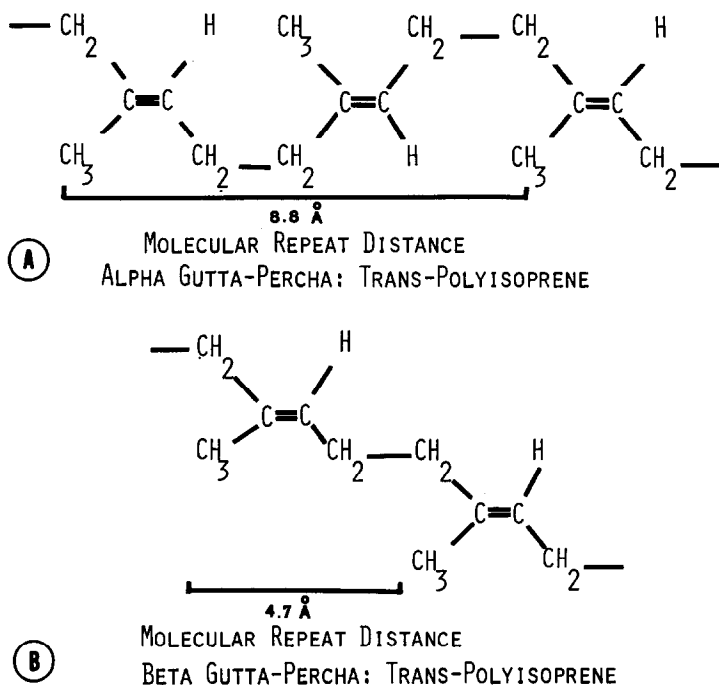


Fig. 5. A, Alpha gutta-percha: Transpolyisoprene. B, Beta gutta-percha: Transpolyisoprene.

“beta” gutta-percha, but there are thermal and volumetric differences. Gutta-percha undergoes internal structural conversions or crystalline phase changes with respect to its “alpha” and “beta” forms at specific transition points during heating and cooling cycles. This results in molecules with different repeat units, producing, in turn, different crystallographic structures, the variations of which are reflected in volume changes induced in gutta-percha by heating and cooling.

As a solid material is heated, there is usually a linear increase in volume resulting from the thermal excitation of individual atoms or molecules. This dimensional change is *reversible* with cooling, so that the volume of most substances at a given temperature is the same during the heating as during the cooling process. This constancy of volume at a given temperature does not hold true for materials with crystalline phase changes. Consequently, for that class of materials to which gutta-percha belongs, the thermal history of a sample must be considered in a determination of those volume changes which occur upon further thermal manipulation.

The effect of phase and phase changes on volume and electrical and mechanical properties was recognized and reported in 1934 by Bekkedahl<sup>21</sup> at the National Bureau of Standards. With the use of dilatometric techniques, he identified the phases, amorphous and crystalline, occurring in natural rubber and rubber-sulfur compounds, relating them to thermophysical properties and property changes.

These were not, however, the first observations of this type of phenomenon. In 1918 Price,<sup>22</sup> a dentist, recorded suggestive evidence of irreversible volume

changes on heating and cooling baseplate gutta-percha, but was unable at that early date to attribute valid and significant meaning to his findings.

The importance of crystalline phase transformations in the gutta-percha type of polymers has not been subsequently investigated by the dental profession; it has, however, been studied by the rubber industry. In 1932 Dean<sup>16</sup> discovered profound and irreversible changes in the density (hence, volume) of gutta-percha with varying temperatures. By means of volume dilatometry, he monitored these changes and obtained data representing alterations up to 54° C. Dean pointed out that impurities markedly altered transition temperatures and behavior.

In 1963 Leeper and Schlesinger<sup>17</sup> studied the thermal interconversion of "alpha" and "beta" transpolyisoprene derived from chicle and found that the "beta" to "alpha" transition occurred between 60° and 64° C. They also reported the effect of impurities and solvents on lowering the transition temperatures, as well as the effects of prior mechanical and thermal conditioning.

Mandelkern, Quinn, and Roberts,<sup>23</sup> in 1955, indicated the melting point of the "beta" form of gutta-percha to be 64° C. and that of the "alpha" to be 74° C. Again, the thermal history and per cent purity were related to transformation temperatures.

The most recent investigation in this field was that by Flanagan and Rijke<sup>20</sup> in 1972. They studied the equilibrium melting and transformation temperatures of "Trans-Pip," a synthetic gutta-percha product. A combination of dilatometry, calorimetry, radiography, and dissolution techniques was employed. The melting temperatures of the "beta" and "alpha" forms were reported specifically as 79.5° C. and 82.4° C. It should be pointed out that the base material had a molecular weight of  $1.6 \times 10^5$ , an order of magnitude greater than the naturally occurring polymer, which in itself will elevate observed temperatures through increased interchain bonding.

Phase transitions are of central importance in a study of the temperature-related volume changes which occur in dental gutta-percha, for, as a result of these transitions, irreversible volume changes take place.<sup>15-17, 21-23</sup> These phase transformation temperatures are affected by molecular weight, purity, compounding, thermal and mechanical history, and degree of crystallinity. Manufacturers of dental gutta-percha have refused to divulge information with respect to the nature and source of their base material, as well as the mixing and time-temperature cycling involved in processing. This secrecy, or lack of knowledge in the dental industry, necessitated our further study of this problem as a prerequisite to clinically related investigations of the thermal-volumetric properties of gutta-percha in endodontics.

#### REFERENCES

1. Obach, E. F. A.: *Canter Lectures on Gutta-Percha*, London, 1898, Williams Trowce.
2. Seelingmann, T., Torriten, G. L., and Faronnet, H.: *India Rubber and Gutta-Percha*, London, 1910, Scott, Greenwood & Sons.
3. Terry, H. L.: *India Rubber and Its Manufacture*, London, 1907, Archibald Constable & Co., Ltd.
4. Brannt, W. T.: *Practical Treatise on Caoutchouc and Gutta-Percha*, London, 1883, Lampson, Low, Marston, Searle & Rivington.

5. Ferguson, J.: All About Rubber and Gutta-Percha. In *The Indiarubber Planter's Manual*, Singapore, 1889, John Little & Co.
6. Henry, J.: Caoutchouc and Gutta-Percha. In *Annual Report of the Board of Regents of the Smithsonian Institute*, Washington, 1865, Government Printing Office.
7. Prinz, H.: *Dental Chronology*, Philadelphia, 1945, Lea & Febiger.
8. Payne, E. T.: Gutta-Percha, *Trans. Odontol. Soc.*, N. Y., 1884.
9. Hill, A., and Blackman, S. G.: Circular to the Members of the Dental Profession, *Dent. Newsletter* 1: 28-31, 1847-48.
10. Williams, D. J.: *Polymer Science and Engineering*, Englewood Cliffs, N. J., 1971, Prentice-Hall, Inc., pp. 1-42, 207.
11. Van Vlack, L.: *Materials Science for Engineers*, Reading, Mass., 1971, Addison Wesley Publishing Co., pp. 126-248.
12. Bunn, C. W.: Molecular Structure and Rubber-Like Elasticity, Part I. The Crystal Structures of Beta Gutta-Percha, Rubber and Polychloroprene, *Proc. R. Soc.* **A180**: 40, 1942.
13. Alfrey, T. and Gurnee, E.: *Materials Science for Engineers*, Englewood Cliffs, N. J., 1967, Prentice-Hall, Inc., pp. 1-20.
14. Baterman, L.: *The Chemistry and Physics of Rubber-Like Substances*, London, 1963, McLaren & Sons, Ltd., pp. 21-27.
15. Fisher, D.: Crystal Structures of Gutta-Percha, *Proc. Phys. Soc.* **66B**: 7, 1953.
16. Dean, J. N.: Heat Treatment and Polymorphism of Gutta-Percha and Balata, *Trans. Inst. Rub. Ind.* **8**: 25-37, 1932.
17. Leeper, H. M., and Schlesinger, W.: Gutta II, Interconversion of Alpha and Beta Forms, *J. Poly. Sci.* **11(4)**: 307-323, 1953.
18. Baterman, L. L.: Cis-Trans Isomerism in Natural Polyisoprenes, in the Chemistry and Physics of Rubber-Like Substances, London, 1963, McLaren and Sons, pp. 21-22.
19. Mandelkern, L.: *Crystallization of Polymers*, New York, 1964, McGraw-Hill Book Company, Inc., p. 119.
20. Flanagan, R. D., and Rijke, A. M.: Polymorphisms in Polymers. I. The Equilibrium Melting Temperature of Two Crystalline Modifications of Trans-1 4-Polyisoprene, *J. Polym. Sci. [A-2]* **10**: 1207, 1972.
21. Bekkedahl, N.: Forms of Rubber as Indicated by Temperature-Volume Relationship, Research Paper RP 717, *J. Res. Natl. Bureau Standards* **13**: 411-431, 1934.
22. Price, W. A.: Report of Laboratory Investigations on the Physical Properties of Root Filling Materials and the Efficiency of Root Fillings for Blocking Infection From Sterile Tooth Structures, *J. Natl. Dent. Assoc.* **5**: 1259-1280, 1918.
23. Mandelkern, L., Quinn, F. A., and Roberts, D. E.: Thermodynamics of Crystallization in High Polymers: Gutta-Percha, *J. Am. Chem. Soc.* **78**: 926-932, 1956.

*Reprint requests to:*

Dr. Herbert Schilder  
Boston University School of Graduate Dentistry  
100 East Newton St.  
Boston, Mass. 02118