Synergic Action of Aging and Moisture on Native and Different Grades of Commercial Gutta-Percha (*trans*-Polyisoprene)

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SYNOPSIS

The aim of this paper was to study the plasticizing effect of subjecting native/commercial gutta-percha samples to controlled levels of different humidities. It was expected that this study would provide the practicing endodontist with invaluable insight into the mechanical properties of commercial gutta-percha cones (i.e., retrievability, malleability, flexibility, and torsional and bending ability). The "conditioning" of the gutta-percha samples depended greatly on the percentage of compatible/incompatible substances. The mixtures of native gutta-percha with compatible (i.e., wax) showed greater elongation, tensile strength, and number of rotations, but lower deformation angle than the mixtures of native gutta-percha with incompatible substances (i.e., salts, metal oxides). The observed lower values for tensile strength and torsional strain, relative energy to break, and the Young's modulus and the higher values for elongation and number of rotations for wet samples compared to the dry ones were attributed to the plasticizing effect of gutta-percha due to the insertion of water molecules in the polymer chains. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Previous publications on gutta-percha were focused on the study of its thermal[1,2] and mechanical properties[3-7] and the effect of aging.[8] The effect of composition of commercial gutta-percha on its mechanical properties was studied to a limited extent since only commercial samples were analyzed.[8,9] Therefore, the necessity arose for a further detailed study of the effect of each modifier/filler in mixtures with gutta-percha, so that, later, their synergic action upon gutta-percha could be interpreted. The present publication attempts to clarify the effect of different modifiers/fillers on the mechanical properties of gutta-percha in conjunction with the aging effect (storage time) at different relative humidities. It is the first time that an attempt has been made to correlate simultaneously the overlapping effect of the above-mentioned factors on the mechanical properties of native and commercial gutta-percha. Similar studies were made in the past by Struik[10,11] on amorphous and semicrystalline polymers where the physical aging was considered as a thermoreversible process affecting their properties by drastically changing the relaxation times. Physical aging of polymers has its practical implications, i.e., their gradual stiffening with time enables them to resist high mechanical loads for long times.

The effect of aging and storage over relative humidities affects greatly the retrievability of the dental gutta-percha cone, which is of great clinical interest for the practicing endodontist. The term "cone" denotes the form in which gutta-percha is currently used in dentistry.

Table I Manufacture Composition % (According to Manufacturer), Mean ($\bar{x}$), and Standard Deviation of Percentage Weights from Chemical Assay, K% Crystallinity, and Glass Transition (T_g °C)^2 of Commercial Gutta-Percha

| | Gutta-percha | | Zinc Oxide (ZnO) | | Barium Sulfate (BaSO$_4$) | | Cadmium Sulfate (CdSO$_4$) | | Bismuth Oxide (Bi$_2$O$_3$) | | Thermoplast[b] | Wax | Wax[c] Thermoplast Color | | | | |
	TC[a]	($\bar{x}$) ± SD	TC	($\bar{x}$) ± SD	TC	($\bar{x}$) ± SD	TC	($\bar{x}$) ± SD	TC	($\bar{x}$) ± SD	TC	TC	TC	($\bar{x}$) ± SD	%K	T_g (°C)	Manufacturer
1	20.0	20.1 ± 0.1	60.0	59.8 ± 0.4	18.0	18.2 ± 0.1	—	—	—	—	—	2.4	1.0	1.7 ± 0.01	15.9	23.1	United Dental Manufacturers, Florida, U.S.A.
2	29.6	29.6 ± 0.1	47.8	47.8 ± 0.2	21.0	20.8 ± 0.1	1.0	1.0 ± 0.004	—	—	—	—	—	3.1 ± 0.1	17.8	26.0	Produits Dentaires, Vevey, Switzerland
3	33.0	33.2 ± 0.2	33.0	33.2 ± 0.2	6.0	6.1 ± 0.03	—	—	22.0	22.4 ± 0.1	2.8	2.8	0.4	2.8 ± 0.01	21.6	28.0	Becht, Offenburg, Germany
4[d]	—	40.7 ± 0.3	—	50.2 ± 0.3	—	7.5 ± 0.06	—	—	—	—	—	—	—	1.5 ± 0.01	27.2	33.0	Hygenic, Akron, Ohio
5	100	99.8 ± 0.2	—	—	—	—	—	—	—	—	—	—	—	—	33.4	38.5	Produits Dentaires, Vevey, Switzerland

[a] TC = Theoretical composition.
[b] A commercially formulated plasticizer that is a mixture of low molecular weight compounds aiming to increase the flexibility and moldability of gutta-percha.
[c] Mean ($\bar{x}$) and standard deviation of the total percentage weights for thermoplast, wax, and color from chemical assay of commercial gutta-percha.
[d] No composition was given in the manufacturer's prospectus.

Table II Relative Humidity (RH) of Air Over Saturated Salt Solutions at 0°C

Saturated Salt Solution	RH %
Potassium nitrate	97
Potassium chloride	89
Sodium chloride	76
Magnesium nitrate	60
Magnesium chloride	35
Potassium acetate	25
Lithium chloride	15

MATERIALS AND METHODS

a. Samples

Native gutta-percha was kindly provided by VEVEY S. A. Produits Dentaires, Switzerland. It was of beta form, similar to that available commercially (Table I).

Fresh native and commercial gutta-percha cones, standardized size of 100 and hand-rolled, were obtained within 15 days after fabrication and stored at 0°C at different relative humidities (RH) for 120 days. The cones of dental gutta-percha were stored at 0°C because at this temperature the gutta-percha showed higher mechanical strength and elongation. The glass transitions (T_g) of native and commercial gutta-percha at low moisture contents ($< 5\%$) were determined by differential scanning calorimeter (DSC) and dynamic mechanical thermal analyser (DMTA)[2] and are given in Table I.

To gain a deeper insight into the fracture mechanism of commercial dental gutta-percha, mixtures of natural gutta-percha and salts or oxides were prepared by mixing all the constitutents thoroughly in an Ultrasonic Bath (Dowrs PW 1020) for 30 min and then pressed in a press (Moore, England) for 20 min at 60°C. Since commercial dental gutta-percha from different batches might present considerable changes, mixtures of pure gutta-percha and compatible (wax, thermoplast) or incompatible substances (zinc oxide, barium sulfate, coloring agents) were tested at the same time. The percentage crystallinity of native and commercial gutta-percha was determined with DSC and X-ray diffraction patterns as in a previous study.[12]

Saturated solutions of various salts in water were used to obtain known relative humidities of air circulated in sealed enclosures that were maintained at 0°C with the precision of $0.0 \pm 1.0°C$ with the aid of an economic incubator with a fan (size 2, Gallenkamp). Table II shows the relative humidity of air over saturated salt solutions.[13] The degree of humidity was equally measured with a hygrometer (J 3309-60 LCD Thermohygrometer, Cole-Parker) according to ASTM D 4230 within the atmospheres of the various salt solutions.

b. Chemical Assay

Five specimens of gutta-percha cones from each company were quantitatively assayed for organic and inorganic fractions, as in a previous study.[2]
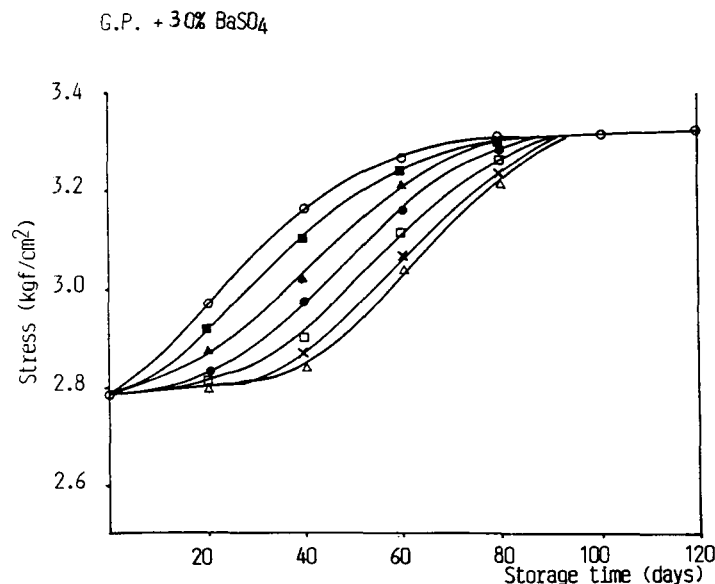

Figure 1 Effect of storage time and different relative humidities (RH) on the tensile strength of mixture of native Gutta-Percha and 30% BaSO$_4$ at 0°C (test diameter 1.00 mm; strain rate 2.0 mm/s).
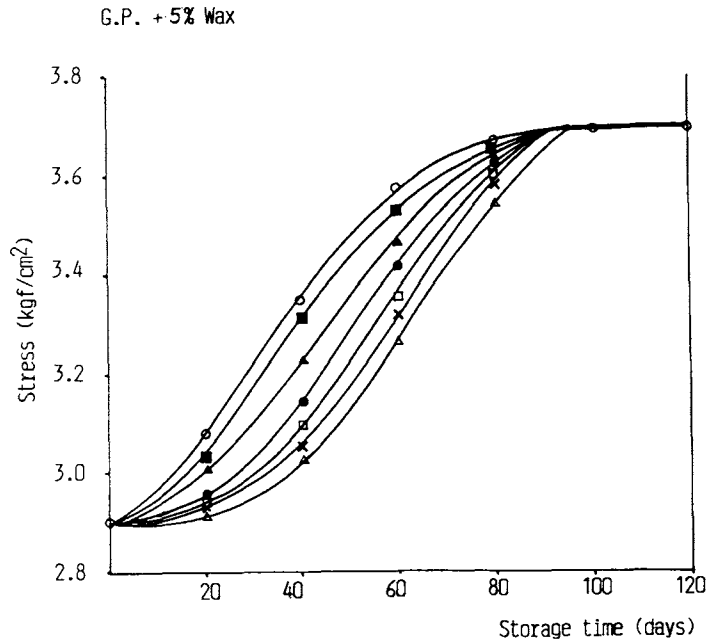
G.P. + 5% Wax

Figure 2   Effect of storage time and different relative humidities (RH) on the tensile strength of mixture of native Gutta-Percha and 5% wax at 0°C (test diameter 1.00 mm; test length 1.00 mm; strain rate 2.0 mm/s).

c. Mechanical Testing

1. Mechanical Properties (Tension–Elongation)

Tests of tension and elongation were made with a texture analyzer SMS (stable microsoft system) IA XT2 connected to an AMSTRAD/640K (PC2080/

30 8Hz) and an EPSON printer (LX-400). The unit was also supplied with an Analisa program. Measurements were made under the following conditions: elongation rate 2 mm/min; recording rate 4 mm/min. The specimens were gripped with the aid of clamps provided by the SMS that manufactures this apparatus.
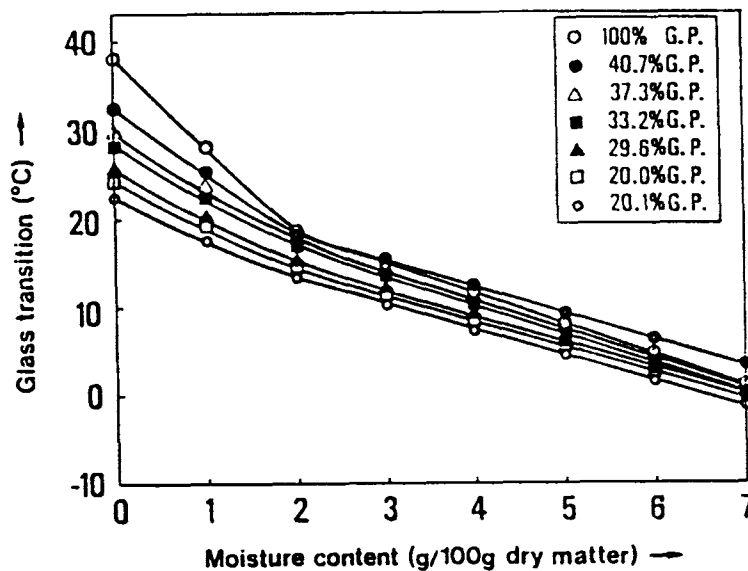
Figure 3   Effect of moisture content on the glass transition point (T_g) for various grades of commercial and native (pure) gutta-percha.
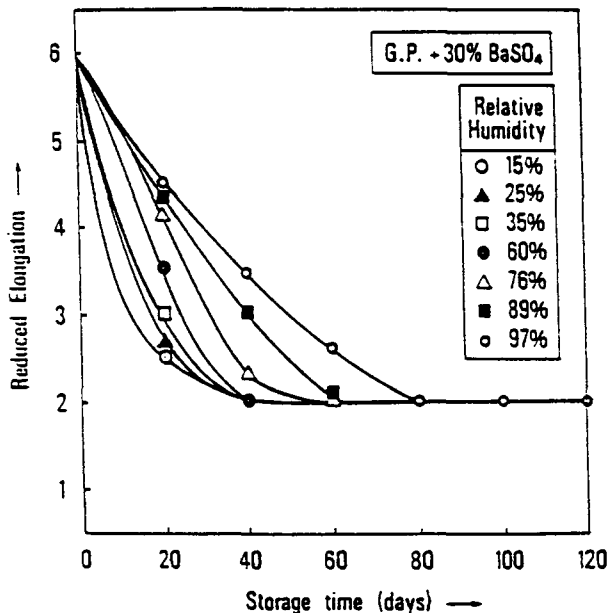
Figure 4 Effect of storage time and different relative humidities (RH) on the reduced elongation of mixture of native Gutta-Percha and 30% BaSO₄ at 0°C (test diameter 1.00 mm; test length 1.00 mm; strain rate 2.0 mm/s).
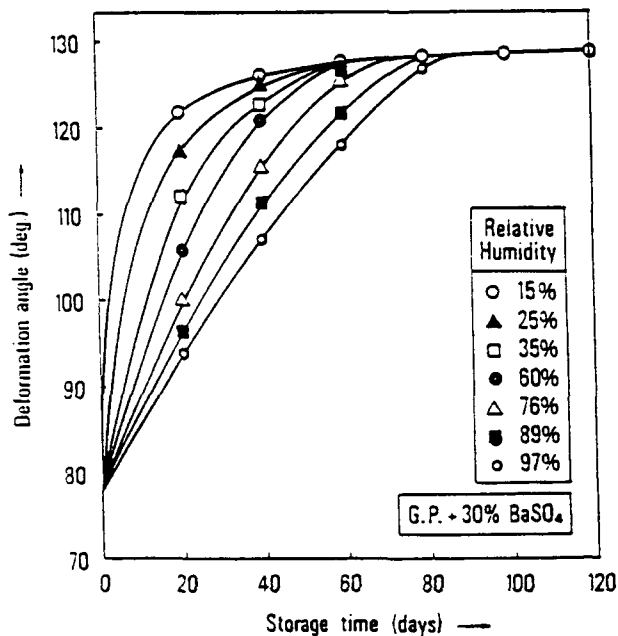

Figure 6 Effect of storage time and different relative humidities (RH) on the deformation angle of mixture of native Gutta-Percha and 30% BaSO₄ at 0°C (test diameter 1.20 mm; bend diameter 3.1 mm).

2. Bending Test

After a number of preliminary trials to ensure the reliability of the recorded results, the conditions for the bending test were selected. Cones were bent to

a 180° angle (U-shaped) for 15 min at a test diameter of 1.20 mm over a 3.0 mm diameter metal rod. A measurement was made of the angle of deformation after bending and releasing the thinner end of the test cone.[9] Resilience was noted as a function of the rapidity with which the bent cone re-
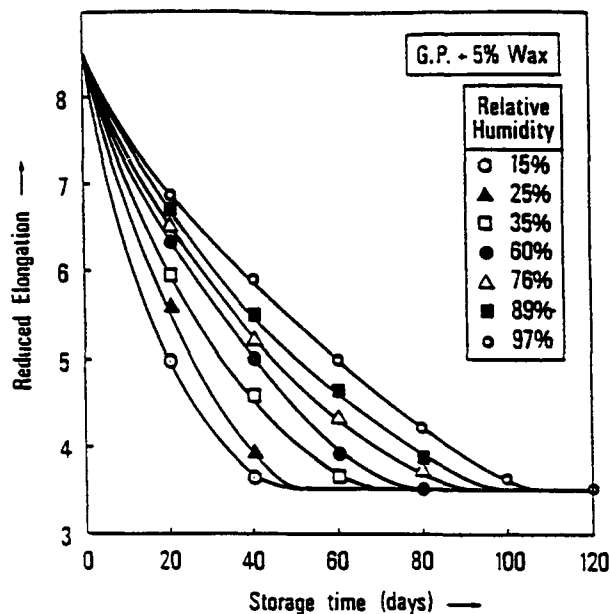

Figure 5 Effect of storage time and different relative humidities (RH) on the reduced elongation of mixture of native Gutta-Percha and 5% wax at 0°C (test diameter 1.00 mm; test length 1.00 mm; strain rate 2.0 mm/s).
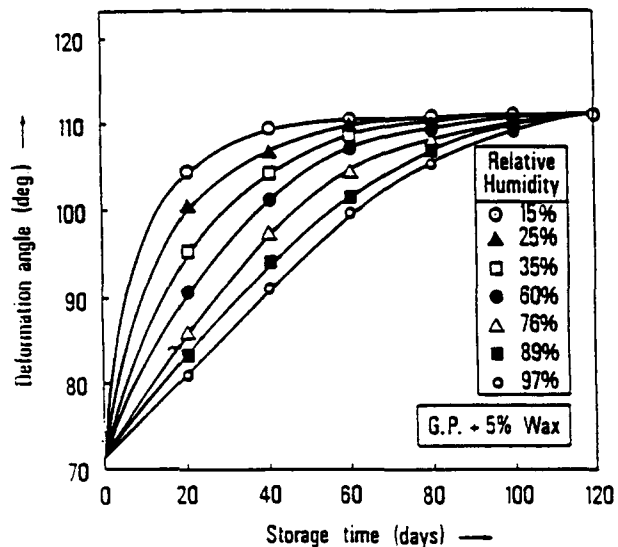

Figure 7 Effect of storage time and different relative humidities (RH) on the deformation angle of mixture of native Gutta-Percha and 5% wax at 0°C (test diameter 1.20 mm; bend diameter 3.1 mm).
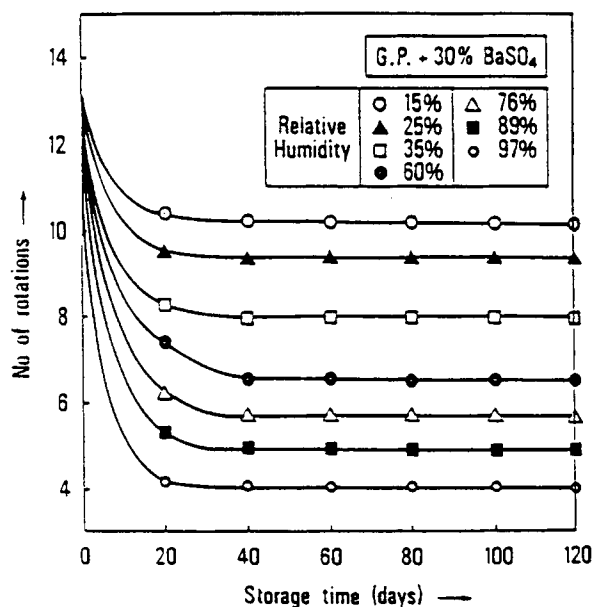
Figure 8 Effect of storage time and different relative humidities (RH) on number of rotations to fracture of mixture of native Gutta-Percha and 30% $BaSO_4$ at 0°C (test diameter 1.20 mm; test length 2.01 mm; torsional strength 150 Gm cm).

turned to the final deformation angle. If the cones returned relatively fast, they were considered resilient. The specimens were allowed to warm to room temperature for 15 min before testing.

3. Torsion Test

Gutta-percha samples were tried for torsion with a torsion tester (modification of Clash-Berg). A detailed description is provided in the *American Standards Testing Methods* (ASTM, D1043).[14] The calibration of the torsion tester was carried out with a wire spring made of tempered steel and a polyethylene rod. Five specimens were tested for each sample.

RESULTS AND DISCUSSION

a. The Effect of Humidity on Mechanical Properties and Glass Transition Temperature (T_g)

The effect of a salt solution with a large range of relative humidities (15–19% RH) provides us with useful information about the effect of water on the mechanical properties (stress, reduced elongation, deformation angle, torsional stress) of commercial dental gutta-percha cones in the oral cavity (Figs. 1–9).

The absorption of water has a plasticizing effect on the dental cones of commercial gutta-percha. Therefore, their stress is higher the higher the RH and, consequently, the greater the content of absorbed water (Figs. 1 and 2). It is noteworthy that all curves of stress vs. storage show a maximum within 80–100 days. Although the nature of this phenomenon is not quite clear, it could be suggested that this maximum is due to the perturbation of the chain orientation because of insertion of water molecules. The intrachain and then interchain bonding is affected, resulting in a modified structure provided that the molecules can act as a network. As water content increases, the material begins to behave more and more as a single-chain species, thus leading to higher stress values.[3] A further crystallization of gutta-percha might be a probable explanation for the higher stress values.

However, this assumption requires further experimentation with DSC and X-rays. The glass transition point (T_g) decreases with increasing moisture content and, theoretically, reaches the T_g of pure water (Fig. 3). This decrease in the glass transition is due to the plasticization of the amorphous part of gutta-percha by water. The lower the percentage of gutta-percha in the mixture, the less is the influence of the moisture content. Therefore, the commercial samples did not show the dramatic
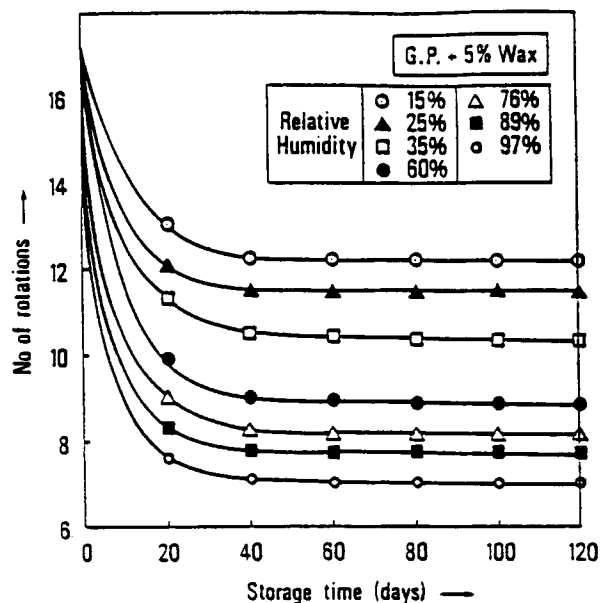

Figure 9 Effect of storage time and different relative humidities (RH) on number of rotations to fracture of mixture of native Gutta-Percha and 5% Wax at 0°C (test diameter 1.20 mm; test length 2.01 mm; torsional strength 150 Gm cm).

fall observed in the case of pure gutta-percha.[2] The water gain was within 1–7% w/w.

An increase in the reduced elongation ($\Delta l/l_0 = l - l_0/l_0$), where l_0 = initial length and l = final length after elongation, could be attributed to the higher pliability and flexibility caused by the insertion of water molecules into polymer chains. This time, the higher the relative humidity, the more intense is the plasticizing effect on gutta-percha cones, as can be seen from Figures 4 and 5. After the first 70–90 days, no further change in reduced elongation was observed. A possible explanation is that the gutta-percha cones have undergone a certain saturation of water absorbance during that period of time (70–90 days) after which no further absorption is feasible.

Water absorption of gutta-percha increased the deformation angle ($\simeq$ 10–20%) compared to samples of gutta-percha not being previously conditioned over salt solutions of different relative humidities (RH).[13] It was found that the values of the deformation angle become stabilized after 70–90 days (Figs. 6 and 7) probably for the above-mentioned reasons as in the case of reduced elongation. The angle of deformation was measured after bending and releasing the thinner end of the test cone.

Finally, the number of rotations needed for fracture decreased, compared to wet samples,[12] and a further decrease was observed due to the aging effect (Figs. 8 and 9). These results were consistent with our expectations according to which plasticization of gutta-percha cones should lead to increase of the necessary number of rotations for fracture. The observed discrepancy is possible due either to partial plasticization of gutta-percha or to nonuniform dis-tribution of water over the gutta-percha cone. The latter explanation is less probable because in 20–40 days the number of needed rotations to fracture becomes constant.

The relative energy at break and the Young's modulus vs. storage time at different RH (Figs. 10–13) follow the behavior of stress vs. storage time and torsional strain obviously for the same, already previously mentioned, reasons.

b. Effect of Storage Time and Chemical Composition

Although the incorporation of suitable filler materials is a well-known and effective technique for improving the mechanical strength of polymers,[15–17] in the case of gutta-percha, a distinction should be made between the addition of compatible (wax, thermoplast) and the incompatible substances (salts, oxides, coloring agents). However, in both cases, it can be said that there is a competitive action of these "fillers":

1. Crack arrestors and improvement of mechanical properties.
2. Crazing agents.

Figures 1, 4, 6 and 8 show that in the case of salts, oxides, and color agent, it is the crazing action of the filler that prevails, thus making possible the description of the fracture as spatially heterogeneous. On the contrary, compatible substances such as wax and thermoplast turn in favor of crack arrestors
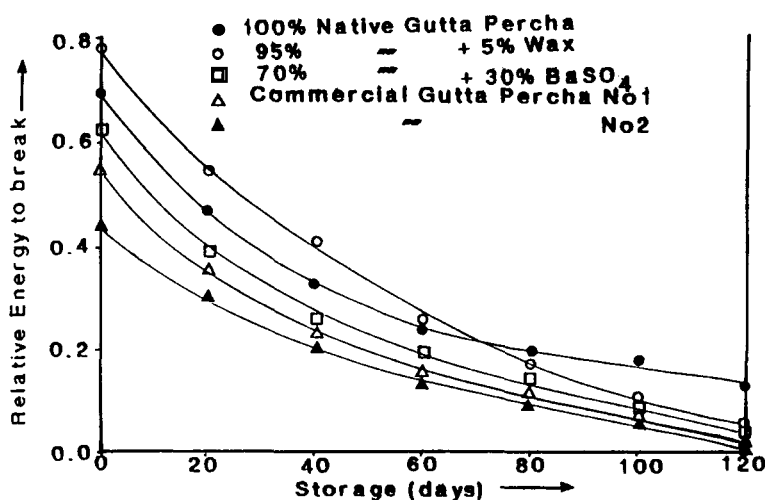

Figure 10 Relative energy to break vs. storage (days) for native and commercial dental gutta-percha conditioned at 0°C (RH = 25%).
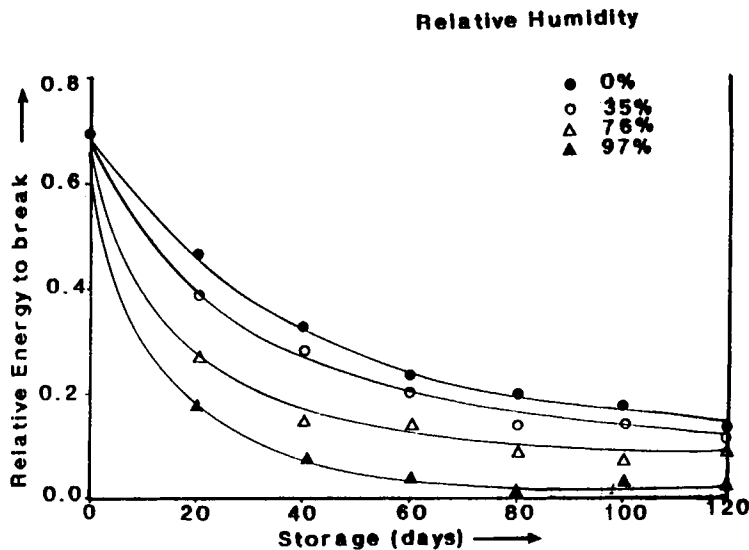
Relative Humidity

Figure 11 Relative energy at break vs. storage (days) for native gutta-percha conditioned at 0°C at different relative humidities.

because of their plasticizing effect (Figs. 2, 5, 7, and 9).

The relative energy at break and the Young's modulus of native and commercial gutta-percha

(Figs. 10 and 12) seem to be greatly affected by storage time since their values decreased dramatically. Addition of a compatible substance (i.e., wax) acts beneficially to an increase of relative energy at break,
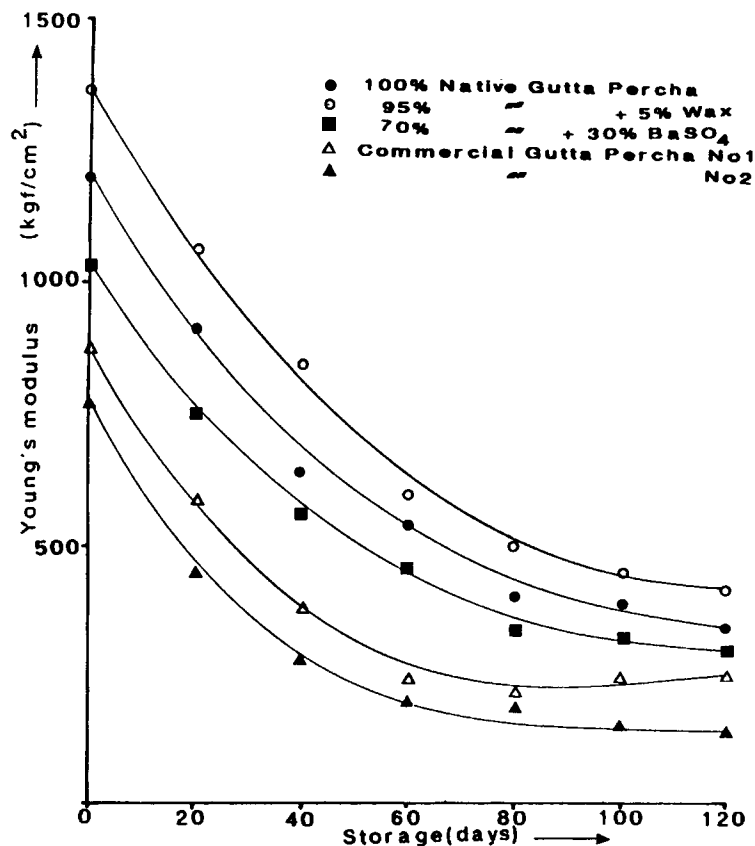

Figure 12 Young's modulus (kgf cm²) vs. storage (days for native and commercial gutta-percha conditioned at 0°C (RH = 25%).
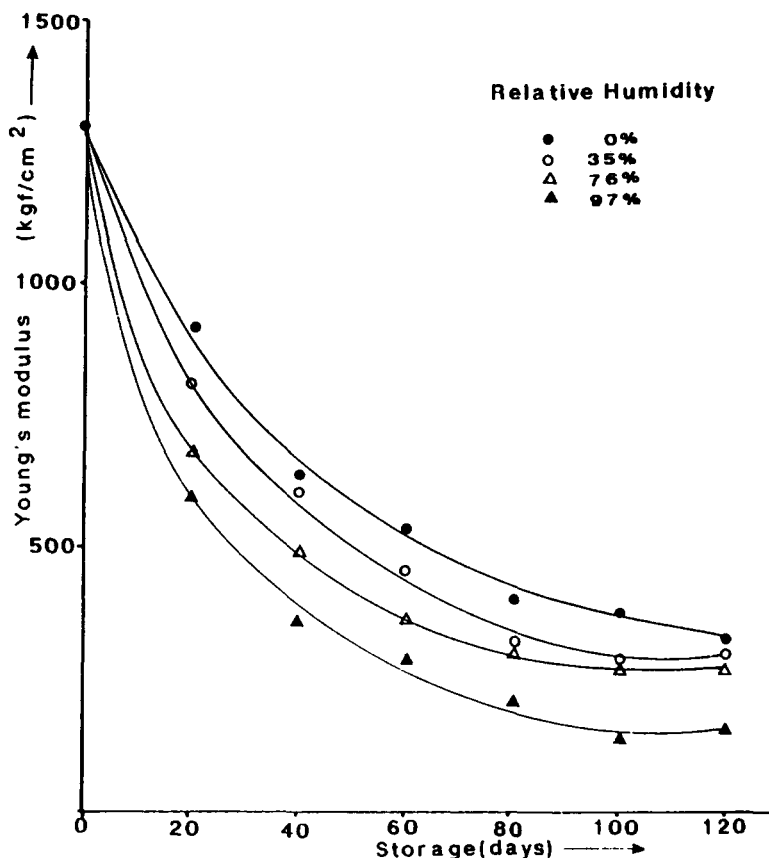
Figure 13 Young's modulus (kgf cm²) vs. storage (days) for native gutta-percha conditioned at 0°C at different relative humidities.

whereas the insertion of incompatible substances in gutta-percha decrease the relative energy at break due probably to their own action as crazing agents.

Commercial dental gutta-percha cones had a much higher percentage composition in incompatible substances than in compatible ones (Table I). Therefore, their behavior was closer to the one in the mixtures of native gutta-percha and incompatible substances.

The nonuniform distribution of the internal stresses that results in the development of high critical stresses is considered responsible for the rupture of covalent bonds in commercial gutta-percha.[18-21] The presence of a high percentage of incompatible substances, acting as crazing agents, promotes the rupture of bonds, and the higher the content of incompatible substances, the greater the number of ruptured covalent bonds.

The depression of tensile strength, torsional strain, relative energy at break, and the Young's modulus of gutta-percha with storage at different RH should be due to a depression of glass transition point once the water molecules have been absorbed

by gutta-percha. This conclusion has proved to be valid for amorphous and semicrystalline synthetic and natural polymers[22,23] and it does not apply only in the case of the highly crystalline ones.

CONCLUSIONS

The lack of thermodynamic equilibrium of polymers in the glassy state is the main reason for the phenomenon of aging followed by a tendency toward a volume relaxation. The physical aging and plasticization of gutta-percha, due to insertion of water molecules, can be explained with the aid of the "free-volume" theory, i.e., the packing density is the major factor determining the mobility of particles. Both native and commercial gutta-percha age in the same way as is shown in the figures where an increase in relaxation times is proportional to the aging time.

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