

# Study of the Effect of Annealing, Draw Ratio, and Moisture upon the Crystallinity of Native and Commercial Gutta Percha (Transpolyisoprene) with DSC, DMTA, and X-Rays: Determination of the Activation Energies at $T_g$

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## SYNOPSIS

The transitions occurring in gutta-percha (transpolyisoprene) below the melting point were determined with DMTA and DSC. A comparison of the results obtained with these two methods showed satisfactory agreement. The thermal properties of native and commercial gutta-percha samples ( $T_g = 38 \pm 2^\circ\text{C}$  and  $T_m = 69 \pm 3^\circ\text{C}$ ) were investigated, both before and after annealing (at different times and temperatures), and at environments of different relative humidities. An increase in the draw ratio also proved to enhance the percentage crystallinity (%  $K$ ) and improve the thermal stability (higher  $T_g$ s and  $T_m$ s) of gutta-percha. Finally, the activation energies  $\Delta E$  (33.9–40.2 kJ/mol  $\times K$ ) at glass transition temperature were determined and correlated to the percentage content (%) of the commercial gutta-percha samples in native gutta-percha. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Great interest has been shown in the field of natural and commercial gutta-percha (trans-polyisoprene). Investigations of dental gutta-percha have been directed mainly towards its thermal (DSC),<sup>1</sup> thermomechanical (DMA),<sup>2,3</sup> mechanical,<sup>4–8</sup> physical properties,<sup>5–9</sup> and the effect of aging on mechanical properties.<sup>10–12</sup> Extensive reviews concerning the history, storing, and production of gutta-percha, and its impact on dentistry as one of the most important endodontic filling materials, have been made by Williams<sup>11</sup> and Goodman et al.<sup>2</sup>

It has been previously reported that gutta-percha could exist in two distinctly different crystalline forms, termed “alpha” and “beta” modifications.<sup>3</sup> These forms could be converted to each other, but not into natural rubber, which suggested that both

were of the trans isomer of polyisoprene, differing only in single bond configuration and molecular repeat distance.

Pure gutta-percha is rigid at ordinary temperatures, becomes pliable at 25–30°C ( $T_g$ ), softens and melts at 55–80°C,<sup>1</sup> depending on the mol wt (18,000–60,000), the percentage crystallinity, and the “alpha” or “beta” crystalline structure.

The transition region ( $T_g$ ) of gutta-percha has attracted the interest of research workers<sup>1–3</sup> because of the initiation of micro-Brownian motion in the molecular chains. A frozen-in segment can store much more energy for a given deformation than can a free-to-move, rubbery segment. Every time a stressed, frozen-in segment becomes free to move, its excess energy is dissipated as heat. Micro-Brownian motion is concerned with the cooperative diffusional motion of the main chain segments.

Apart from the above mentioned transition ( $\alpha$ -peak), there are a number of peaks designated as  $\beta$ ,  $\gamma$ , etc., in order of decreasing temperature. Side-chain motion and motion of methyl groups are re-

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sponsible (80–90% degree of crystallinity) and semicrystalline polymers (20–50% degree of crystallinity) have disclosed the existence of another transition called  $\alpha_c$ , attributed to the frictional viscosity among specific crystalline planes or molecules inside the crystals.<sup>14</sup>

The purpose of the current investigation was (a) to determine any correlation between the composition of gutta-percha and its thermal properties (heat of fusion, melting point, heat of crystallization, recrystallization point, and glass transition point), (b) to compare the results obtained by DSC and by the DMTA (for first time used on gutta-percha samples) before and after annealing and/or drawing of the samples, and (c) to calculate the activation energies of  $T_g$  and, finally, to show the effect of moisture absorption on the glass transition point ( $T_g$ ), which is essential for the appropriate storage and preservation of gutta-percha cones.

## MATERIALS AND METHODS

### Samples

Natural gutta-percha was kindly provided by Vevey S.A., Produits Dentaires, Suisse. It was of beta-form, similar to that available commercially.

### Chemical Assay

Five specimens of gutta-percha cones from each company were quantitatively assayed for organic and inorganic fractions.<sup>1</sup> The relative amounts of the ingredients were given in Table I.

### Annealing of the Samples

The samples were annealed in sealed glass ampoules, under DC 550 silicone fluid, at  $T_m - 5^\circ\text{C}$ ,  $T_m - 10^\circ\text{C}$ , and  $T_m - 15^\circ\text{C}$  ( $T_m$  is the DSC melting peak temperature of each commercial grade) for 10–2000 h.

### Measurement of the Thermal Properties ( $T_m$ , $T_g$ ) of DSC

All the thermal properties (melting point, heat of fusion, crystallization) were measured by recordings run at heating and cooling rates of  $2.5^\circ\text{C} \times \text{min}^{-1}$ . The samples of finely divided polymer (less than 10 mg in weight) were sealed in an aluminium pan. An empty sample pan was used as a reference and all measurements were carried out under a stream of oxygen free, dry nitrogen. The samples were kept at

temperatures ( $^\circ\text{C}$ )  $T = T_m + 10^\circ\text{C}$  for 10 min in order to erase any past thermal history of the material; the required recrystallization of the sample was attained at a cooling rate of  $2.5^\circ\text{C} \times \text{min}^{-1}$ , using liquid nitrogen. Indium was used to calibrate the DSC both to temperature and heat capacity. A DSC-30 Mettler, connected to an IBM PS-2/60 computer and an EPSON X-60 printer, were used for calorimetry measurements.  $T_g$  (glass transition) and  $T_m$  (melting points) were evaluated by taking the temperature at which one-half of the change in heat capacity ( $\Delta C_p$ ) had occurred and at the midpoint of inflection, respectively. Five samples were tested; the mean value and the standard deviation were calculated.

### Measurement of Thermomechanical Properties by DMTA

The sample temperature was varied from  $-100^\circ\text{C}$  to  $+100^\circ\text{C}$ . The use of a microcomputer and the IEEE interface allowed the frequency to be multiplexed during a slow thermal scan ( $2.5^\circ\text{C}/\text{min}$ ) and all data was stored for subsequent manipulation. The mode of deformation geometry employed involved bending small bars as dual single cantilevers.

The dynamic mechanical technique, in which a small oscillating mechanical strain is exercised on a solid or viscoelastic liquid and the stress is resolved into real and imaginary components, can provide valuable information about all changes in the state of molecular motion as temperature is scanned. Therefore, this technique is considered to be one of the most effective for studying the influence either of molecular structure or of phase morphology on the physical properties of natural and synthetic polymers.<sup>15–19</sup>

Five specimens, each approximately 2 mm thick, were molded for each material and the small plaques were returned to room temperature for about a day before the experiment.<sup>16–18</sup>

### Uniaxial Drawing of the Films

Drawing was carried out by solid-state extruder. Each gutta-percha film was inserted into split, high-density, polyethylene (HDPE) billets, which were press-fitted into the barrel of an Instron rheometer. The billet assemblies were then pushed through conical brass dies of  $20^\circ$ , including the entrance angle at  $180^\circ$  and  $90^\circ$ , for the gutta-percha and polyethylene, respectively. The draw ratio was determined from the displacements of ink markers in the

**Table I Manufacture Composition % (According to Manufacturer) and Mean ( $\bar{x}$ ) and Standard Deviation of Percentage Weights from Chemical Assay of Commercial Gutta-Percha (5 Specimens)**

Nr	Gutta-Percha		Zinc Oxide ZnO		Barium Sulfate BaSO <sub>4</sub>		Cadmium Sulfate CdSO <sub>4</sub>		Bismuth Oxide Bi <sub>2</sub> O <sub>3</sub>		Thermo-plast		Coloring Agent					
	Theoretical Composition	( $\bar{x}$ ) ± S.D.	Theoretical Composition	( $\bar{x}$ ) ± S.D.	Theoretical Composition	( $\bar{x}$ ) ± S.D.	Theoretical Composition	( $\bar{x}$ ) ± S.D.	Theoretical Composition	( $\bar{x}$ ) ± S.D.	Theor. Comp. (%)	Theor. Comp. (%)	Wax	Wax <sup>b</sup> Thermopl. Color ( $\bar{x}$ ) ± S.D.	Theoretical Composition	Theor. Comp. (%)	Manufacturer	
																		Wax
1*	—	40.7 ± 0.3	—	50.2 ± 0.3	—	7.5 ± 0.006	—	—	—	—	—	—	—	—	—	—	1.5 ± 0.01	Hygenic, U.S.A. Roeko,
2*	—	37.3 ± 0.2	—	57.4 ± 0.3	—	2.4 ± 0.02	—	—	—	—	—	—	—	—	—	—	3.4 ± 0.01	Roeschelsen GMBH, Germany
3	33.0	33.2 ± 0.2	33.0	33.2 ± 0.1	6.0	6.1 ± 0.03	—	—	22.0	22.4 ± 0.1	2.8	2.8	2.8	0.4	0.4	2.8 ± 0.01	2.8 ± 0.01	Becht GMBH, Germany
4	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 ± 0.01	Produits Dentaires Vevey, S.A. Suisse
5	20.0	20.0 ± 0.1	60.0	60.1 ± 0.3	18.0	17.9 ± 0.09	—	—	—	—	—	—	2-4	1.0	1.0	2.1 ± 0.01	2.1 ± 0.01	Vereinigte Denta Werke, Munchen, Germany
6	20.0	20.1 ± 0.1	60.0	59.8 ± 0.4	18.0	18.2 ± 0.1	—	—	—	—	—	—	2-4	1.0	1.0	1.7 ± 0.01	1.7 ± 0.01	United Dental Manufacturers Florida, U.S.A

\* No composition was given in the manufacturer's prospectus.

<sup>b</sup> Mean ( $\bar{x}$ ) and standard deviation of the total percentage weights for Thermoplast, Wax, Color from chemical assay of commercial gutta percha.

films before extrusion ( $R_1$ ) and after extrusion, that is,

$$\lambda = R_1/R_2^{20,21}$$

### Measurement of Moisture Content

This procedure was done by weighing the samples before and after conditioning over salt solutions and by using an automatic moisturemeter (Mitsubishi CA-05) after the samples have remained under these conditions. In both methods, the measurements were conducted on five specimens of every sample after these specimens (10 mg) had remained overnight in 2.5 mL of anhydrous formamide. The titrations were conducted on the suspended liquid and a blank test (titration of formamide) was also made.

Variation in the results showed that gutta-percha cones tended to absorb a greater quantity of water if they remained in a closed container that had solutions of high relative humidity, which are related to the influence of relative humidity on the storage preservation of gutta-percha.

### Measurement of % Crystallinity with Wide-Angle X-ray Diffraction Patterns

Wide-angle X-ray diffractograms were recorded by a Philips–Elicon X-Ray powder diffractometer PW1050.25 using Cu–K $\alpha$  radiation ( $\lambda = 0.154$  nm).

The percentage crystallinity of gutta-percha samples (before and after annealing and/or drawing) was calculated according to Alexander.<sup>22</sup>

### Small-Angle Scattering Measurements

Small-angle scattering measurements were made with pinhole collimation at a specimen-to-film distance of 32 cm. Ni-filtered Cu–K $\alpha$  radiation was used. The small-angle photographs were scanned with the microdensitometer and, from the resulting trace, the position of the small-angle maximum was determined. The long period ( $d$ ) was calculated from the following equation:

$$d = \frac{\lambda}{2 \sin \theta} \quad (1)$$

where  $\theta$  is half the Bragg angle at which the small-angle maximum occurred.

## RESULTS

The results ( $T_m$ ,  $T_g$ ,  $\Delta H_m$ , and  $\Delta H_c$ ) obtained from two different techniques (DMTA and DSC) are shown in Table II. Table II shows that the mentioned thermal properties are dependent upon the composition of commercial gutta-percha and, in addition, higher for pure gutta-percha than for commercial gutta-percha.

The effect of moisture content (g/100 g dry matter) on the glass transition point ( $T_g$ ) is shown in Figure 1. It is obvious that the initially significant difference in  $T_g$ , due to the effect of the moisture content upon the plasticization of gutta-percha, seems to be overcome as the moisture content increases and, consequently, the plasticization effect is manifested. This occurs in all samples to almost the same extent. The activation energies at glass transition, both for native and commercial gutta-percha, are presented in Table III and their calculation is shown in Figure 2. Table III shows the effect of different frequencies (0.33–30 Hz) upon the  $T_g$  values ( $^{\circ}\text{C}$ ). Figure 2 shows the effect of different frequencies ( $\log f$ ) against the inverse peak temperature of tangent  $\delta$  ( $\tan \delta$ ).

The effect of annealing temperature on the long period of crystals ( $\text{\AA}$ ) is shown in Figure 3. The annealing temperature did not exceed the melting point in order not to induce any additional crystallization.

Dynamic modulus  $E'$ ,  $\tan \delta$ , and loss modulus  $E''$ , as a function of temperature before and after annealing for native and commercial gutta-percha of various crystallinities (1 Hz), are presented in Table IV and Figures 3, 4, 5 and 6.

The effect of draw ratio on the position of the maximum in  $E''$  ( $^{\circ}\text{C}$ ), the degree of crystallinity, and on the width of the  $E''$  peak for gutta-percha is shown in Table V.

## DISCUSSION

From Figure 1, it is concluded that the glass transition point ( $T_g$ ) decreases with increasing moisture content and theoretically reaches the  $T_g$  of pure water. This decrease of the glass transition point is due to the plasticization of the amorphous part by water. It is obvious that the lower the percentage of gutta-percha in the mixture, the less the influence of the moisture content on the content. Therefore, the commercial samples did not show the dramatic decrease that was observed in the case of pure gutta-percha. It should be noted that the estimation of

drying conditions and storage stability presupposes extended knowledge of the effect of small amounts of moisture on  $T_g$ , because, at this temperature, the gutta-percha becomes much more pliable than at lower temperatures.<sup>23-25</sup> The same effect (of moisture on  $T_g$ ) has been observed and studied extensively in the case of carbohydrates<sup>26</sup> and synthetic polymers.<sup>27</sup>

From Table II, it was concluded that both the  $T_m$  and  $T_g$  values were in the following order:  $\tan \delta > \text{DSC} = \log E'' > \log E'$ , which is confirmed by previous publications.<sup>15-19</sup> It is a feature of all dynamic mechanical data that  $\tan \delta$  does not peak at the same point as the loss modulus,  $E''$ .<sup>15,16</sup>

The observation of a damping generally signifies the inception of a new mode of molecular motion, at the specific measurement frequency, with increasing temperature. The interpretation of the gutta-percha (pure or commercial) thermal spectrum with decreasing temperature is as follows<sup>3</sup>:

$\tan \delta$	45.0–72.3°C	
$\log E'$	47.8–66.7°C	$\alpha_c$
$\log E''$	42.1–69.8°C	

The above interpretation shows the process  $\alpha_c$  due to inception of liquid behavior. It occurs at temperatures in the vicinity of melting point ( $T_m$ ) and it relates to rotation about the chain axis of chain-folded polymers to a second-order expansion of lattice parameters perpendicular to the chain direction in the crystalline phase.

$\tan \delta$	28.3–42.2°C	
$\log E'$	18.5–34.9°C	$\alpha$
$\log E''$	23.0–38.7°C	

The above interpretation shows the process  $\alpha$  due to onset of rotational freedom of the backbone chain, which is called the  $T_g$  process (softening point). The initiation of the micro-Brownian motion of the amorphous chains can be equally described as cooperative diffusional motion of the main chains.<sup>28-31</sup>

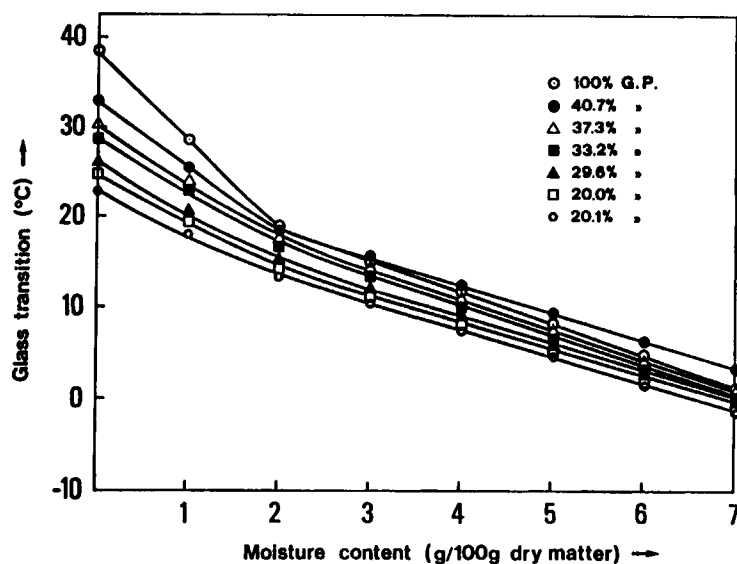
$\tan \delta$	-18.1–(-31.0)°C	$\beta$
$\log E'$	-23.1–(-42.5)°C	or
$\log E''$	-18.7–(-36.1)°C	$\gamma$

The above interpretation shows that  $\beta$  is a broad relaxation attributed to libration of the  $-\text{CH}_3$  about

Table II Thermal Properties of Pure and Commercial Gutta-Percha Determined with DSC and DMTA (Mean  $\pm$  Standard Deviation of Five Specimens)<sup>a,b</sup>

Manufacturer	$T_m$ (°C)					$T_g$ (°C)					$\Delta H_c$ (J/g)	$\Delta H_m$ (J/g)	$\Delta H_c$ (J/g)	%K
	DMTA					DMTA								
	DSC	$\log E'$	$\log E''$	$\tan \sigma$	DSC	$\log E'$	$\log E''$	$\tan \sigma$	DSC	$\log E'$				
Pure Gutta-Percha	70.1 $\pm$ 0.4	66.7 $\pm$ 0.4	69.8 $\pm$ 0.5	72.3 $\pm$ 0.6	38.5 $\pm$ 0.6	34.9 $\pm$ 0.5	38.7 $\pm$ 0.5	42.2 $\pm$ 0.6	35.1 $\pm$ 0.6	32.3 $\pm$ 0.6	33.4	33.4		
Nr 1	52.2 $\pm$ 0.2	49.8 $\pm$ 0.3	52.3 $\pm$ 0.4	55.1 $\pm$ 0.5	33.0 $\pm$ 0.5	28.9 $\pm$ 0.4	32.8 $\pm$ 0.4	37.1 $\pm$ 0.5	16.2 $\pm$ 0.4	15.1 $\pm$ 0.5	27.2	27.2		
Nr 2	51.0 $\pm$ 0.3	47.9 $\pm$ 0.4	50.8 $\pm$ 0.4	53.9 $\pm$ 0.5	30.1 $\pm$ 0.5	26.0 $\pm$ 0.3	30.2 $\pm$ 0.4	34.0 $\pm$ 0.5	14.9 $\pm$ 0.4	13.8 $\pm$ 0.4	25.8	25.8		
Nr 3	48.2 $\pm$ 0.2	45.1 $\pm$ 0.3	48.0 $\pm$ 0.4	52.0 $\pm$ 0.5	28.0 $\pm$ 0.4	24.1 $\pm$ 0.3	28.3 $\pm$ 0.4	33.0 $\pm$ 0.4	14.1 $\pm$ 0.5	12.3 $\pm$ 0.4	21.6	21.6		
Nr 4	46.3 $\pm$ 0.2	42.0 $\pm$ 0.3	46.5 $\pm$ 0.3	49.8 $\pm$ 0.3	26.0 $\pm$ 0.3	21.9 $\pm$ 0.3	26.0 $\pm$ 0.3	30.2 $\pm$ 0.3	11.4 $\pm$ 0.3	10.1 $\pm$ 0.4	17.8	17.8		
Nr 5	43.0 $\pm$ 0.4	38.9 $\pm$ 0.4	43.3 $\pm$ 0.4	47.2 $\pm$ 0.4	25.2 $\pm$ 0.4	21.3 $\pm$ 0.2	25.1 $\pm$ 0.3	29.8 $\pm$ 0.3	7.8 $\pm$ 0.2	6.9 $\pm$ 0.3	16.3	16.3		
Nr 6	42.1 $\pm$ 0.3	37.2 $\pm$ 0.3	42.1 $\pm$ 0.5	45.0 $\pm$ 0.3	23.1 $\pm$ 0.3	18.5 $\pm$ 0.2	23.0 $\pm$ 0.2	28.3 $\pm$ 0.3	7.7 $\pm$ 0.1	6.7 $\pm$ 0.2	15.9	15.9		

<sup>a</sup> ( $T_m$ ) melting point (°C), ( $T_g$ ) glass transition temperature (°C), ( $\Delta H_m$ ) enthalpy heat (J/g), ( $\Delta H_c$ ) crystallization heat (J/g), (%K) average crystallinity. From WAX-ray diffraction patterns and D.S.C. measurements.  $\Delta H^\circ$  for 100% crystalline gutta-percha was calculated theoretically according to Van Krevelen.<sup>42</sup>



**Figure 1** Glass transition point ( $T_g$ ) vs. moisture content for different contents of gutta-percha.

its axis, or  $\gamma$ , in which some chains may undergo angular cooperative motion in the glass to give local configurational change (single bond flips). A representative example is the cyclohexyl group chair-chair transition.<sup>32</sup> End-group rotation, crystalline defects, backbone chain motions of short segments or groups, and a phase separation of impurities or diluents (grades of commercial gutta-percha) can provide some other probable interpretations of the  $\gamma$ -peak.<sup>13</sup>

$$\tan \delta = -52.4 - (-64.1)^\circ\text{C}$$

$$\log E' = -60.4 - (72.3)^\circ\text{C} \quad \delta$$

$$\log E'' = -51.9 - (67.6)^\circ\text{C}$$

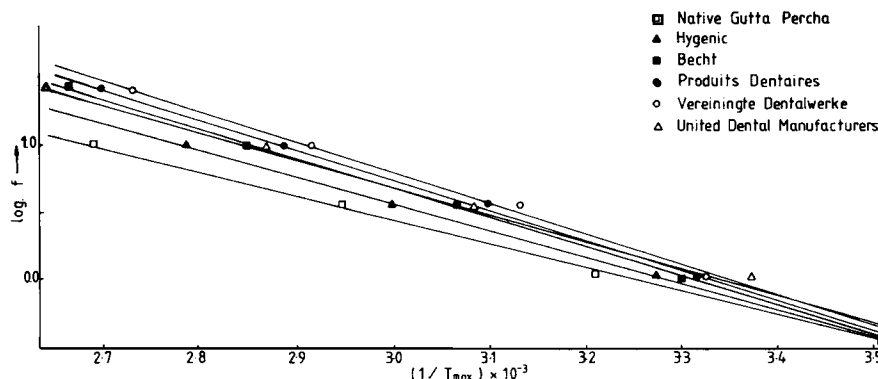
The above interpretation shows the broad relaxation process  $\delta$  of an origin that is not yet identified. It was thought<sup>32</sup> that the origin may have been the local mode motion predicted for chain molecules due to the cooperative torsional excursion about bonds without change of configuration, that is, within the same potential well.

A shift to higher temperatures with higher impressed frequencies ( $f$ ) was observed and the corresponding  $T_g$  values upon different frequencies from  $\log E''$  spectra for native and commercial gutta-percha are shown in Table III.

The shift of  $T_g$  in relation to change in the frequency allows the activation energy of the glass transition temperature to be determined<sup>17,19,32</sup> as  $\Delta E = -R [d \ln f / d(1/T)]$ , where  $R = 8.314 \times 10^{-3}$  KJ

**Table III** Glass Transition Temperature ( $^\circ\text{C}$ ) from Log  $E''$  Relaxation Spectra for Various Frequencies (Hz) and Calculated Activation Energy for  $T_g$  ( $\Delta E$ , KJ/mol  $\times K$ ) of Native and Commercial Gutta-Percha

	$T_g$ ( $^\circ\text{C}$ )					$\Delta E$ (KJ/mol)
	0.33 Hz	1 Hz	3 Hz	10 Hz	30 Hz	
Native Gutta-Percha	12.1	38.7	65.9	98.6	—	33.9
Hygenic, U.S.A.	10.5	32.8	60.3	85.6	—	40.2
Roeko, Germany	10.0	30.2	53.2	77.9	102.9	39.3
Becht, Germany	9.4	28.3	49.6	73.6	97.4	38.3
Produits Dentaires, Suisse	9.0	26.0	46.2	69.1	93.3	38.9
United Dental						
Manufacturers, U.S.A.	7.9	23.0	51.3	75.9	99.3	38.3



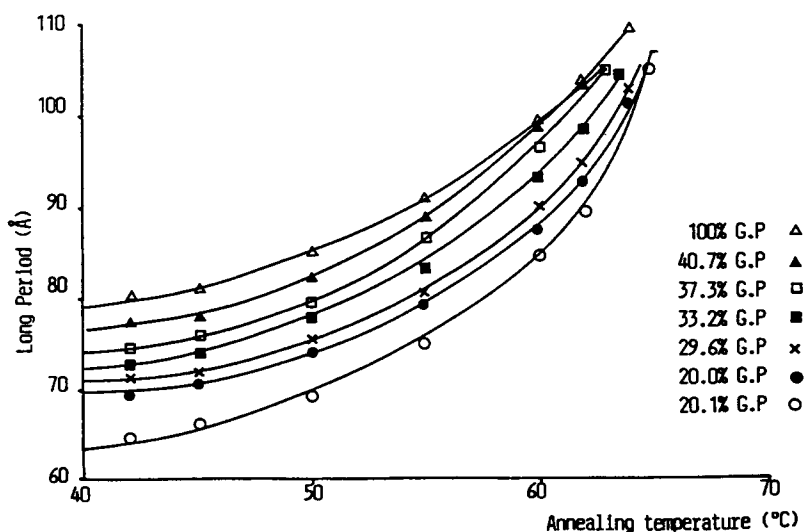
**Figure 2**  $(1/T_g) \times 10^{-3}$  vs.  $\log f$  (frequency) for determination of glass transition activation energies.

$\times \text{mol}^{-1} \times \text{K}^{-1}$  and  $T = T_g$  ( $^{\circ}\text{K}$ ). Thus, from the slopes of the plots of  $\log f$  vs.  $1/T$  (Table III), shown in Figure 2, the activation energies of the  $T_g$  process for the gutta-percha were derived.

The activation energies ( $\Delta E$ ) for the calculated values were considerably lower than those found for polymethacrylates,<sup>33</sup> crosslinked epoxies,<sup>19</sup> and aromatic and aliphatic copolyamides.<sup>34,35</sup> The relationship of  $\Delta E$  vs. the composition of the gutta-percha samples showed that the minimum value was found for native gutta-percha with the lower crystallinity (Table II). This should be attributed to the fact that in the amorphous or semicrystalline polymers ( $\%K < 40$ ), the chain segments are freer from restraints imposed by crystalline polymers in the

glass transition region. As in the case of polyethylene terephthalate (PET)<sup>36,37</sup> and polyamides (nylon 66),<sup>38</sup> a linear relation was established between the height of the  $\alpha$ -relaxation ( $T_g$ ) and the crystallinity. An increase in crystallinity induced a decrease in the height of the  $\alpha$ -peak (Fig. 7) and an increase in the width of the  $E''_{\text{max}}$  peak at  $E''_{\text{max}}/\sqrt{2}$  (Table V).

At low annealing temperature, the long period ( $d$ ), obtained from small-angle x-ray scattering measurements, changed slowly with temperature. On the contrary, a substantial increase in long period ( $d$ ) was observed for annealing temperatures approaching the melting point ( $T_m$ )<sup>13</sup> (Fig. 3). The effects of annealing temperature (40–65 $^{\circ}\text{C}$ ) and time (1–60 days) on  $\%$  crystallinity (average x-rays and



**Figure 3** Effect of annealing temperature for 24 h on the long period of crystals ( $\text{\AA}$ ).

**Table IV** Effect of Annealing Temperature and Annealing Time on % Crystallinity (%*K*),  $E''_{\max}$  (Temperature, *Pa*) and Long Period (Å) for Native and Commercial Gutta-Percha

Annealing Time (h)	Annealing Temperature	% <i>K</i> <sup>a</sup>	$E''_{\max}$ (°C)	DMTA ( <i>Pa</i> )	Long Distance (SMAX) (Å)	
12	40	36.2	39.4	8.5	70.5	Native Gutta-Percha = 100% G.P.
24	40	38.5	40.1	8.1	78.9	
72	40	39.4	40.8	7.8	90.2	
12	50	37.3	40.6	8.0	76.9	
24	50	39.1	41.5	7.7	85.2	
72	50	39.9	42.3	7.5	92.8	
12	64	43.8	40.9	7.8	99.8	
24	64	46.7	42.0	7.6	109.1	
72	64	49.8	42.7	7.3	118.0	
12	40	17.2	23.8	7.9	54.5	United Dental Manufacturers Gutta-Percha 20.1% G.P. Content
24	40	18.7	24.3	7.5	63.2	
72	40	19.8	25.0	7.2	70.4	
12	50	18.4	24.2	7.4	60.0	
24	50	20.3	25.3	7.2	68.8	
72	50	22.4	26.0	6.7	74.8	
12	64	25.8	25.0	7.1	93.9	
24	64	28.4	26.2	6.6	101.3	
72	64	31.6	27.1	6.2	108.5	

<sup>a</sup> Average from X-ray diffraction patterns and DSC measurements.

DSC measurements),  $E''_{\max}$  (temp. °C and *Pa*), and long period (Å) of native and commercial gutta-percha (trans polyisoprene) are shown in Table IV. The degree of crystallinity of gutta-percha increased considerably in temperature from 50 to 65°C. This particular behavior could be interpreted as the result

of the following two crystallization processes: the formation of nuclei and the subsequent growth of nuclei. The first process prevails at low annealing temperatures (40–50°C) whereas the second prevails at high annealing temperatures (50–65°C). The latter crystallization (high temperature) of gutta-

**Table V** Effect of Draw Ratio on the Position of Maximum in  $E''$  (°C), Degree of Crystallinity (%*K*) and on the Width of  $E''$  for Gutta-Percha (Native & Commercial)

	Draw Ratio	Maximum in $E''$ (°C)	Degree of Crystallinity* (% <i>K</i> )	Width of $E''$ peak at $E''_{\max}/\sqrt{2}$
Native Gutta-Percha = 100% G.P.	0	38.7	33.4	18.4
	1	40.6	35.2	21.9
	3	39.4	38.5	25.0
	5	37.0	41.4	29.0
United Dental Manufacturers Gutta-Percha = 20.1% G.P.	0	23.0	15.9	8.2
	1	24.2	16.7	9.5
	3	27.5	21.8	12.6
	5	31.4	24.2	15.0

\* From Wide Angle X-ray Diffraction patterns and D.S.C. measurements.  $\Delta H^\circ$  for 100% crystalline Gutta-Percha was calculated theoretically according to Van Krevelen.<sup>42</sup>



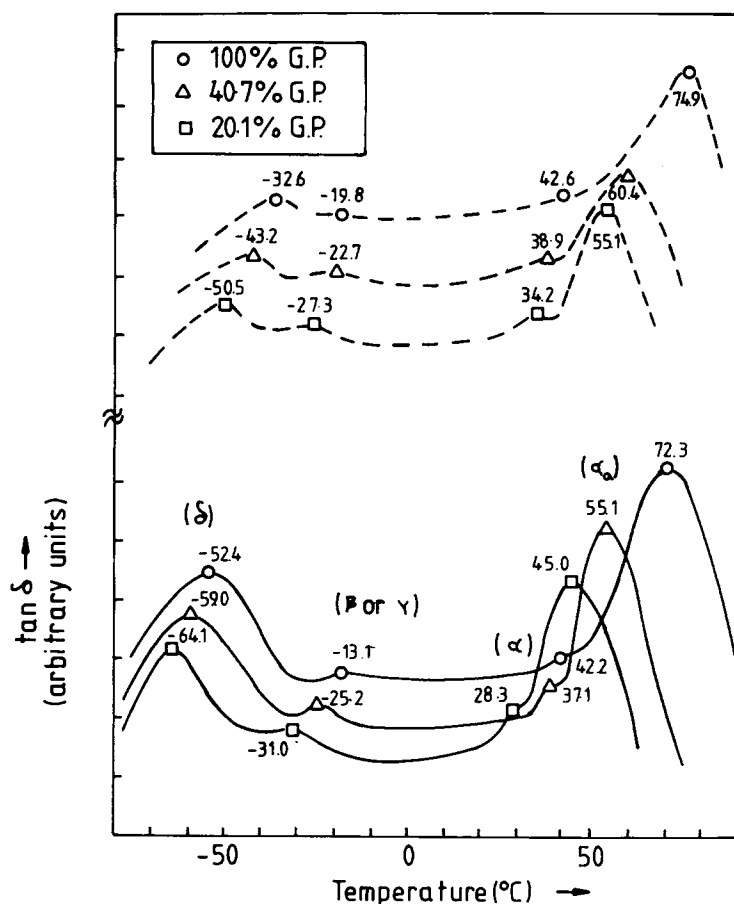


Figure 4 Tan  $\delta$  vs. temperature for samples with different contents of gutta-percha. (—) before annealing, (---) after annealing.

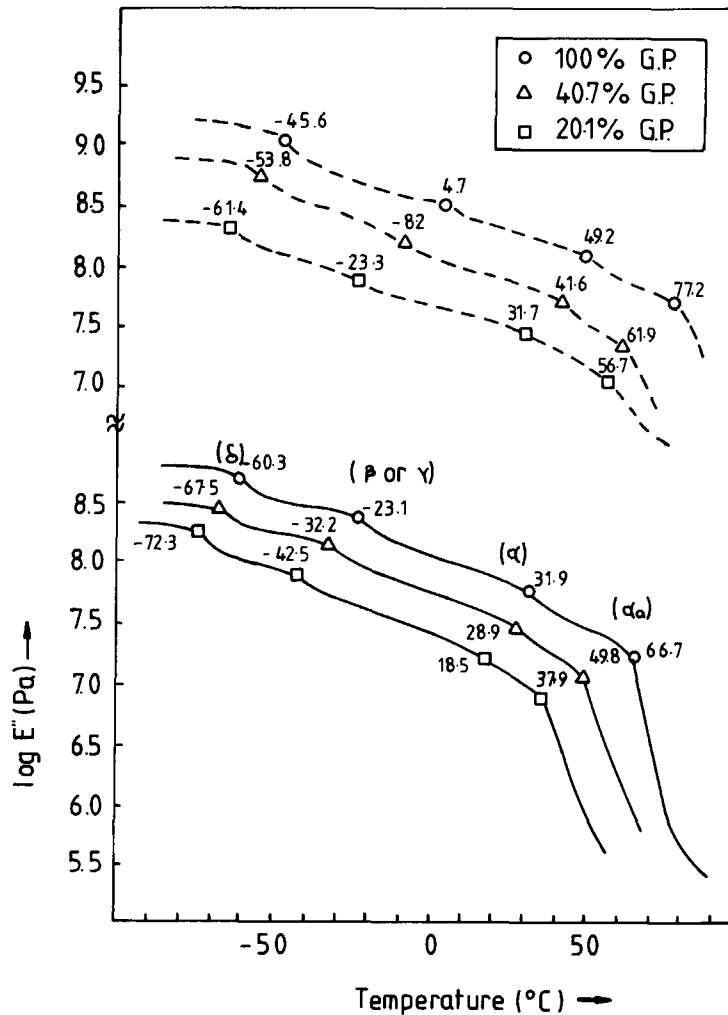
percha is described by a diffusion process, in which crystallites grow in size almost without any new nucleation. Similar crystallization processes were observed in a related study concerning the effect of annealing temperature on crystallinity and crystal size of PET.<sup>39</sup> It should be mentioned that occasionally the occurrence of many small crystallites is more effective in restraining motion than is the occurrence of a few large crystallites.<sup>13,40</sup> Therefore, 40°C is the threshold of the two processes of crystallization of gutta-percha.

The effect of mol wt on the glass transition temperature has been studied for PET<sup>36,37</sup> and nylon 66.<sup>42</sup> An increase in mol wt of gutta-percha has a large effect upon the glass transition range, transforming the behavior from viscous flow to a plateau range of rubberlike behavior. The length of the rubber plateau region increased as the mol wt increased.<sup>42</sup> A variety of mol wts of gutta percha, before and after having undergone mastication,<sup>12</sup> was examined and the results of  $T_{max}$  (°C), width of the

$\alpha$ -peak, and  $\tan \delta_{max}$  vs. the mol wts are shown in Figure 8.

Higher mol wt distribution grades of gutta-percha caused a shift of the  $\alpha$ -peak (glass transition) to higher temperatures. The reasons for this shift in temperature of  $T_g$  should be interpreted in terms of linear growth of molecules, increasing crystallinity, more closely packed morphology in conjunction with an increase in orientation, and a formation of the additional interlamellar connections.<sup>39</sup>

The  $\alpha$ -transition in gutta-percha samples occurs at higher temperatures from higher draw ratios (Table V). The shift in the position of the  $\alpha$ -transition due to annealing is interpreted in terms of the number of crystals, while the shift due to drawing is attributed to the orientation in the amorphous regions. Although the  $\alpha$ -peak shifted to high temperatures for crystallinities up to 35%, at higher crystallinities the  $\alpha$ -peak was shifted toward lower temperature. A similar behavior was observed for PET.<sup>13,41</sup> The effect of crystal size is considered cru-



**Figure 5** Log  $E'$  vs. temperature for samples with different contents of gutta-percha. (—) before annealing, (---) after annealing.

cial for the morphology of the amorphous regions. At low to medium crystallinities ( $\%K < 35$ ), there were many small crystallites acting as crosslinks and inhibiting the motion of the segments in the amorphous regions, whereas at high crystallinities, the crystallites were larger and fewer and, consequently, allowed the segments in the amorphous regions more freedom.

It should be noted for the purpose of this investigation that Native gutta-percha is a naturally occurring polymer (i.e., transpolyisoprene) that is free of commercial additives. Commercial gutta-percha is available in a variety of grades; it is native polymer modified with commercial additives.

## CONCLUSIONS

The loss modulus  $T_g$  and  $T_m$  values, determined with DMTA, were found to be in agreement with the DSC values, whereas the storage modulus and  $\tan$  (DMTA) were lower or higher, respectively, than the DSC. The activation energies of gutta-percha at  $T_g$  were within the determined range of other crystalline polymers, that is, 20–40 KJ/mol K. Both annealing and draw ratio induce an increase in the percentage crystallinity ( $\%K$ ) of native and commercial gutta-percha. On the contrary, the absorption of moisture by gutta-percha resulted in a substantial depression of  $T_g$  values.

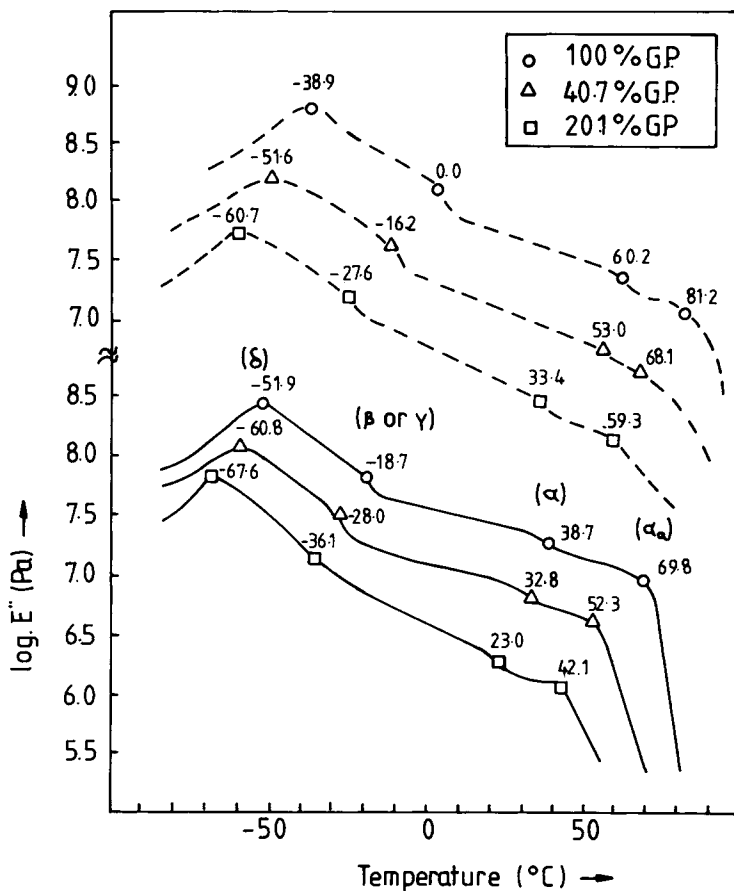


Figure 6 Log  $E''$  vs. temperature for samples with different contents of gutta-percha. (—) before annealing, (---) after annealing.

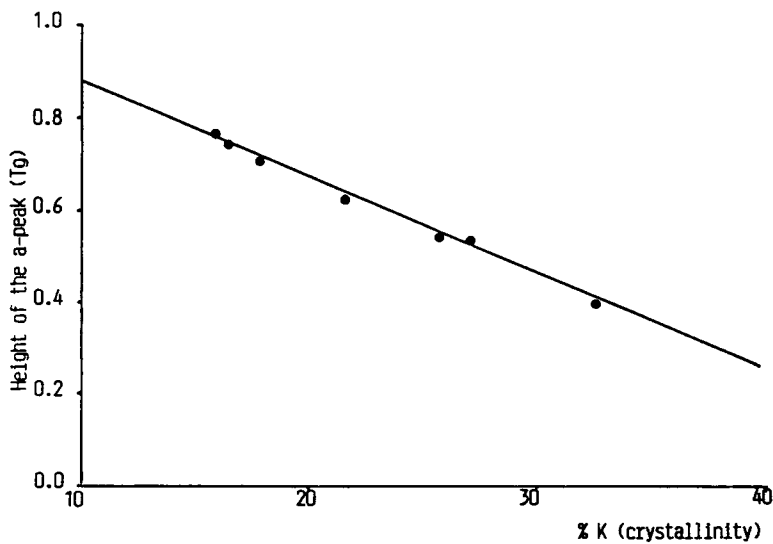
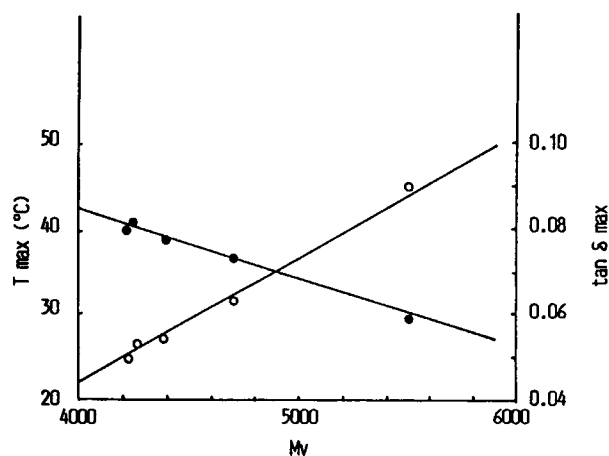


Figure 7 Crystallinity (%K) vs. height of the  $\alpha$ -peak ( $T_g$ ) of gutta-percha.



**Figure 8** Relation between mol wt ( $M_n$ ) of gutta-percha and parameters of the  $\alpha$ -peak ( $T_g$  and  $\tan \delta_{\max}$ ).

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