Determination of Phase Transitions in Gutta-Percha by Differential Thermal Analysis

HILLAR M. ROOTARE *and* JOHN M. POWERS

Department of Dental Materials, School of Dentistry, University of Michigan, Ann Arbor, Michigan 48109, USA

Pure gutta-percha was heat-treated in a differential thermal analyzer. The high melting form crystallized on cooling when gutta-percha was heated to 70 C or less. Above 74 C, crystallization into the low melting form predominated. Either polymorph can be selectively crystallized by control of the heat-treatment temperature before cooling.

Gutta-percha, which occurs naturally as trans-1,4-polyisoprene, has been found to exist in at least two crystalline states, a low melting or β-form and a high melting or γ-form.[1-4] Bunn[1] predicted and Fisher[2] confirmed by electron diffraction the existence of three configurations (α, β, and γ) of the trans-polyisoprene chain. The α-form was observed only in stretched samples of gutta-percha.[2] Recently, Takahashi et al[4] determined by x-ray diffraction that the crystal structure of the α-form was identical to that of the γ-form.

Thermal analysis of experimental and commercial gutta-percha points used in endodontics has demonstrated the presence of up to seven thermal transitions.[5-7] Further, transition temperatures and penetration were shown to be affected by heat treatment of the samples.[6-7] The ability to convert gutta-percha from one crystalline form to another by heat treatment may be a useful technique for both the manufacturer of points and the endodontist.

The purpose of this study was to determine

by differential thermal analysis (DTA) the effect of nonequilibrium heating and cooling on the formation of low and high melting forms of gutta-percha crystallized from the bulk.

Materials and Methods

A differential thermal analyzer* was used to determine peak temperatures of endotherms on heating and exotherms on cooling of samples of purified gutta-percha.† Small shavings (about 5 mg) of the gutta-percha were placed into the sample capillary tube and the sample thermocouple inserted. Glass beads were used in conjunction with the reference thermocouple. DTA was carried out in air at a heating rate of 20 C per minute. A series of runs was made on the same sample, each time heating it to a different maximum temperature up to 100 C, in order to follow the phase transitions of the low and high melting polymorphs. After each run, the sample was cooled to room temperature (~ 25 C) by flowing air at a low rate through the sample block. This procedure allowed sufficient time for the cooling exotherm to develop reproducibly.

X-ray diffraction patterns were determined over the 2Θ range from 10 to 35 degrees with nickel-filtered, $CuK\alpha$ radiation ($\lambda = 1.540$ Å) on a diffractometer.‡ The gutta-percha sample ($2.0 \times 1.5 \times 0.1$ cm) was mounted on a heated copper block ($4.5 \times 4.0 \times 0.9$ cm) which was inserted into the goniometer. Hot water from a constant temperature bath§ was circulated through the block until the desired temperature was reached. A chromel-alumel thermocouple, imbedded under the surface of the sample, was used to monitor the sample temperature on a digital millivoltmeter.¶

Results

Four thermograms for heating rates of 5, 10, and 20 C per minute are shown in Figure 1 with

their corresponding cooling exotherms for the high melting polymorph of gutta-percha. There was no change in the major endotherm temperature of 57.5 C with the varying heating rates. A heating rate of 20 C per minute was chosen in subsequent runs because of the sharpness and the reproducibility of peaks.

The dependence of the size of the endotherm and peak temperature on the amount of the high melting polymorph present (5-mg sample) is shown in Figure 2. For this sequence of DTA runs, the maximum temperature to which the sample was heated for each run did not exceed 65 C. This assured the formation of only the high melting polymorph upon cooling. The end temperature at which cooling was stopped and the next DTA run started was reduced from 49 C to 39 C in steps of approximately one-degree intervals (Fig 2, right column) in order to control the amount of the crystalline phase formed during each cooling cycle. With each successive step in lowering the cooling temperature, more crystalline high melting polymorph was formed, as indicated by the corresponding increase in the endotherm peak heights. An ac-
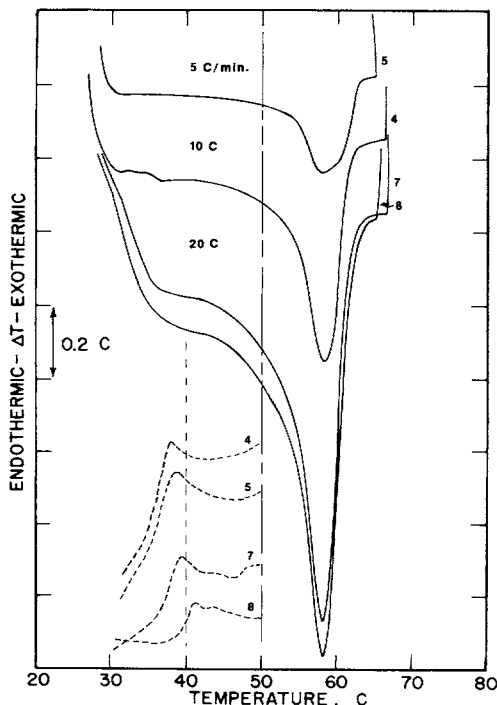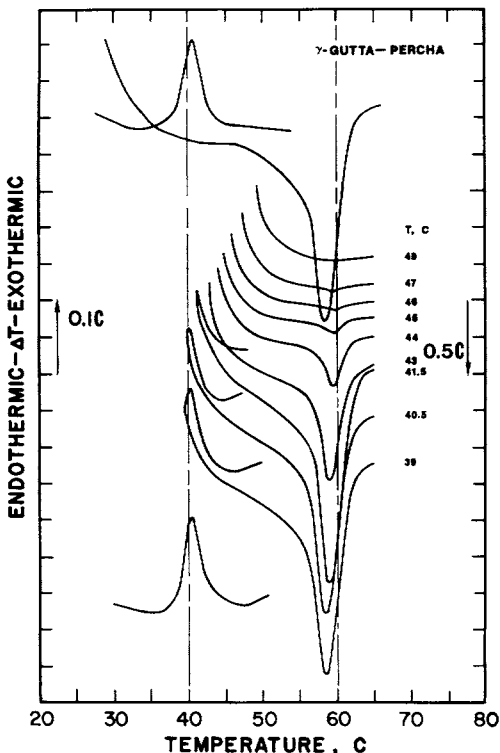

FIG 2. — The effect of cooling temperature on endo- and exotherms of the high melting polymorph. The scale of the T axis is 0.1 C for the exotherms and 0.5 C for the endotherms.

companying shift in the peak temperature of the endotherm from 60 C down to 57.5 C was observed which was attributed to increased crystallinity. A cooling exotherm at 40 C (crystallization temperature) corresponds to the endotherm at 57.5 C. The peak areas represent the relative proportions of crystalline phase present. Integration of the peak areas resulted in a linear relationship with the corresponding peak temperatures (T_{en}). An analysis of linear regression[8] that assumed no imprecision in values of peak temperature resulted in:

$$\text{Peak area} = 152 - 2.56\, T_{en}.$$

A correlation coefficient (r) of -0.996 was obtained. The critical value of r- which the hypothesis of independence of peak area and T_{en} could be rejected was 0.950 at the 95% level of confidence.

Some typical thermograms have been reproduced in Figure 3. In this figure, the cooling curves (exotherms) are indicated by broken

FIG 1. — DTA curves of gutta-percha at three rates of heating. The exotherms on subsequent cooling are shown with broken lines (— — —).
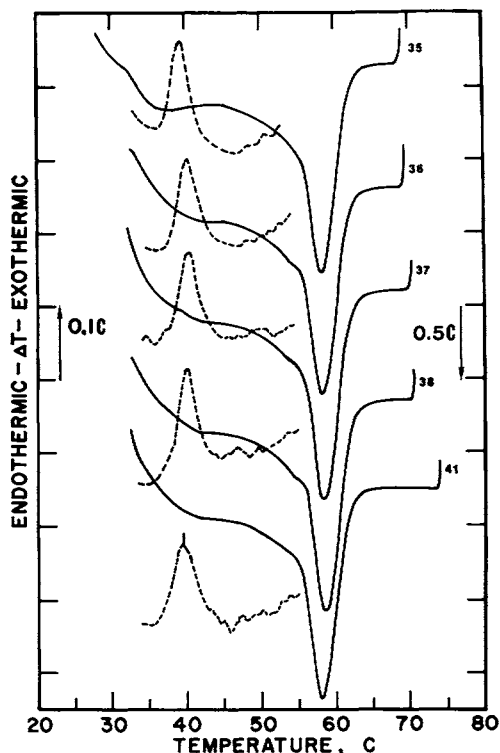
FIG 3a. — The effect of the maximum sample temperature on endotherms of high melting polymorph of gutta-percha. Cooling exotherms are drawn in broken lines (— — —). The maximum sample temperature increased from 68 C to 74 C for runs 35 to 41.

about 48 C and the reduction in size of the peak at about 58 C. The exotherms in Figure 3b show two peaks, one for each polymorph formed. The peak of the low melting polymorph was 3 to 4 degrees lower in temperature and was also identifiable by the sharp pip.

The conversion to the low melting polymorph is shown to be completed in Figure 3c (runs 49 to 53) as indicated by the sharp, symmetrical exotherm at about 34 C. Because of the slow cooling rates, adequate time was available for small amounts of the high melting polymorph with an endotherm at 55 C to crystallize out simultaneously with the low melting polymorph (runs 52 and 53). The high melting polymorph was produced upon cooling the specimen slowly through the temperature range of approximately 60 C to 40 C. In order to eliminate the formation of the high melting polymorph when the low melting polymorph was desired, rapid cooling was required from temperatures above 80 C. This was achieved by quenching the sample in an ice bath, so that

lines intersecting the heating curves. The gutta-percha sample, converted in the previous runs to the high melting polymorph, was subjected to a maximum sample temperature increasing from 68 C to 75 C. The appearance of a small pip (very rapid release of energy) on the exotherm of the high melting polymorph (Fig 3a, run 41, broken line) was the first indication that the low melting polymorph was crystallizing out simultaneously. Not until several runs later (Fig 3b, runs 43 and 45) where the sample was heated from 76 C to 83 C, was a shoulder observed on the endotherm that could be attributed to the presence of the low melting polymorph.

The presence of both crystalline polymorphs was quite evident in samples where endotherms for both polymorphs were observed (Fig 3b, runs 46 to 48). The conversion of the high to low melting polymorph is illustrated in Figures 3b and 3c by the growth in size of the peak at
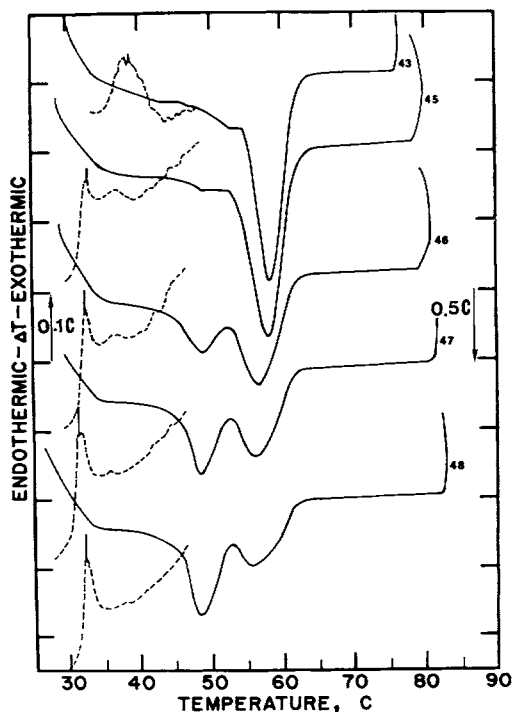

FIG 3b. — The effect of maximum sample temperature on the conversion of the high to low melting polymorph of gutta-percha. The temperature was increased from 76 C to 83 C for runs 43 to 48.

only the low melting polymorph crystallized below 35 C. On reheating, however, a new endotherm appeared between 35 C and 37 C which was not reversible and might have been caused by the relief of the internal stresses developed during quenching. When the sample was reheated through the endotherm peak to 40 C, cooled to room temperature and rerun, the endotherm did not reappear.

In order to complete the cycle and reconvert the low to high melting polymorph, the sample temperature was reduced to 70 C in runs 54 and 55 (Fig 3c). The effect of the temperature drop is shown in Figure 3d (run 56), where endotherms appeared for both polymorphs. Further lowering of the temperature from 68 C to 59 C in the following thermograms (run 56 to 62) completed the conversion to high melting polymorph.

In order to identify the DTA endotherms with the correct polymorpic crystalline phase, x-ray diffractograms were made of the original

FIG 3d. — The effect of decreasing the maximum heating temperature from 68 C to 59 C on the transformation of the low to the high melting polymorph (runs 56-62).
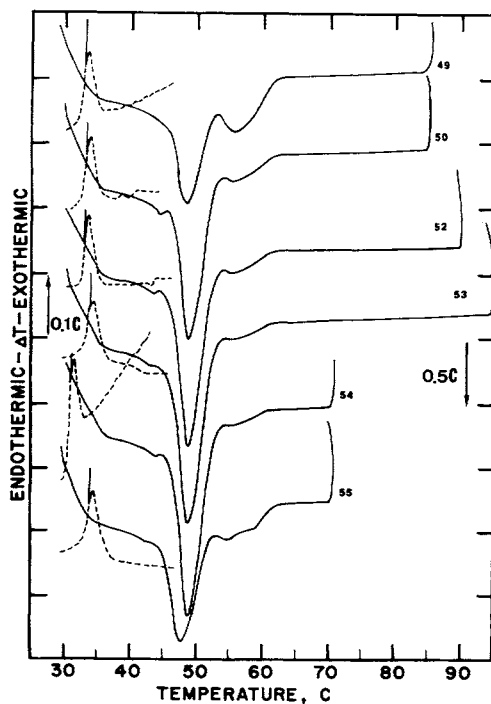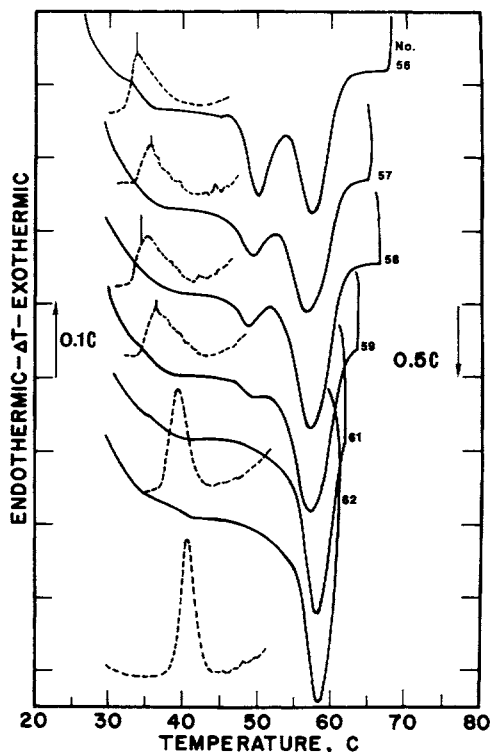

FIG 3c. — The effect of increasing the maximum heating temperature from 85 C to 95 C on the completion of the transformation to the low melting polymorph (runs 49-53). In order to reverse the process, the maximum temperature was reduced to 70 C in runs 54 and 55.

(Fig 4, curve A) and the heat-treated samples (Fig 4, curves C and D) of gutta-percha. Heating a sample to 65 C on a hot stage resulted in a broad x-ray diffraction band characteristic of an amorphous, molten phase of gutta-percha (Fig 4, curve B). When the gutta-percha was heated to about 70 C and cooled to room temperature, the high melting polymorph was produced (Fig 4, curve C) with a 58 C endotherm (Fig 3a). Reheating the sample to 100 C and cooling it to room temperature resulted in the high melting polymorph transforming back to the low melting crystalline phase (Fig 4, curve D) with a 48 C endotherm (Fig 3c).

Discussion

Earlier observations have shown that two subsequent DTA runs on the same sample of gutta-percha did not yield identical curves.[6,7] Quite often it was possible in the third run to reproduce the second run very closely when the sample was heated beyond 80 C. This indicated

that the second DTA run served to heat treat the sample. The samples usually were heated above 80 C with the result that the endotherm at 58 C always diminished in size and the endotherm below 50 C was either enhanced in size or split into two peaks.[6,7]

In order to relate the peak temperatures of the endotherms and exotherms to the maximum temperatures to which the sample was heated, Figures 5 and 6 were plotted. The dominant endotherm peak temperatures (solid points) appear to align themselves along the

46 C and 49 C line for the low melting polymorph and along the 57.5 C line for the high melting polymorph (Fig 5). The two dominant endotherms, as observed in Figures 3-b, c, and d and plotted as half solid points in Figure 5, indicate the presence of both polymorphs to a significant degree in the sample. The presence of a minor endotherm, indicative of very small amounts of a minor phase coexisting with a dominant polymorph, is indicated by open points.
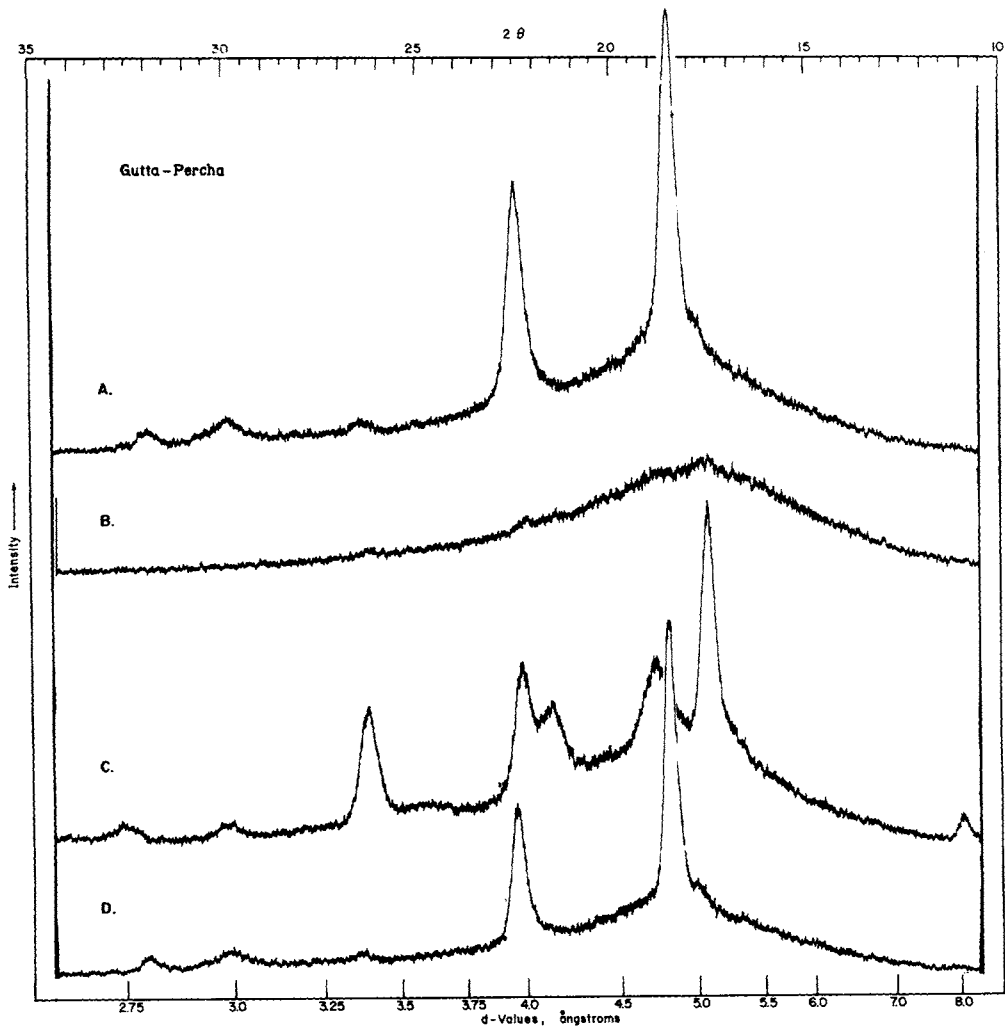

FIG 4. — X-ray diffractograms of gutta-percha samples. A) An original sample of gutta-percha in the low melting or beta crystalline polymorph, B) heated to 65 C to an amorphous or molten state, C) heated to 70 C and cooled to room temperature to transform the sample to the high melting or gamma crystalline polymorph, and D) reheated to 100 C and cooled to room temperature to convert the sample back to the low melting crystalline polymorph.
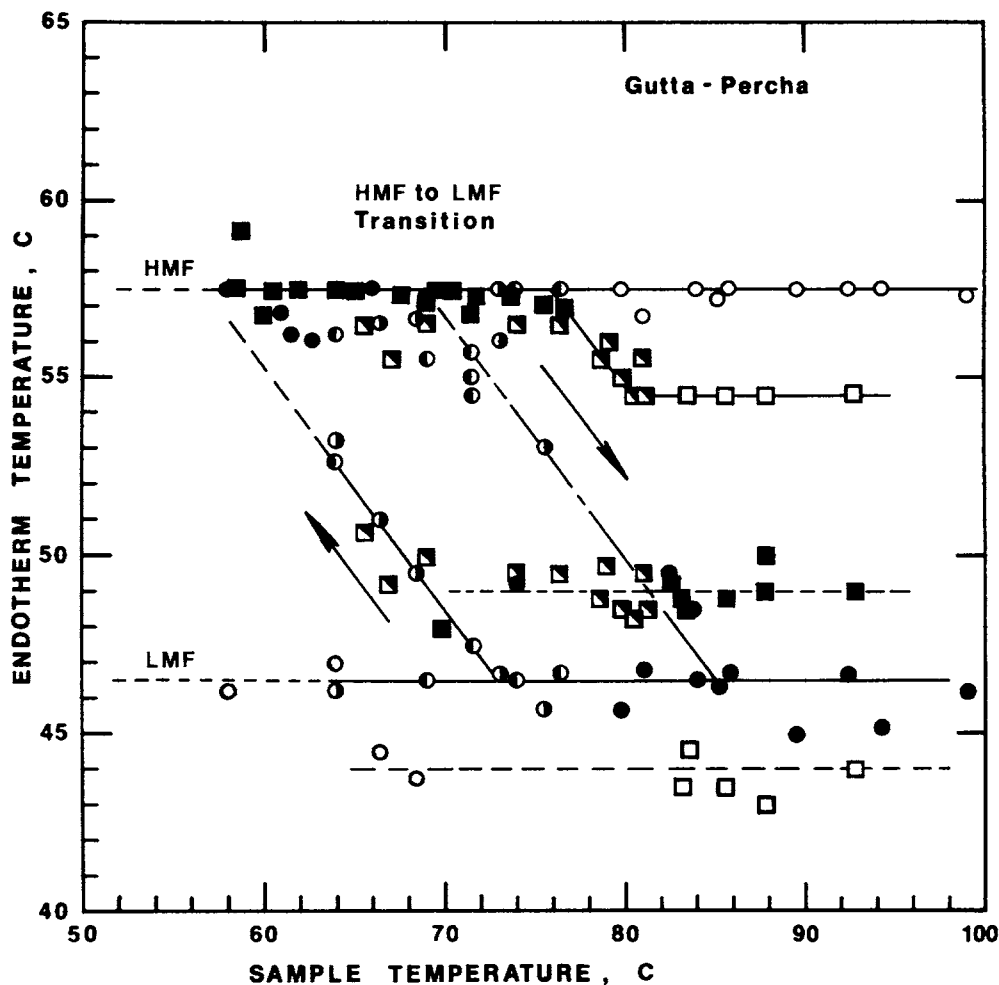
FIG 5. — Plot of endotherm peak temperatures as a function of maximum sample temperature. The dominant endotherms are indicated by solid points (●, ■), two coexisting peaks by half solid points (◑, ◨), and minor peaks by open points (○, □). Circles represent first set of data and squares the second set. The downward arrow indicates the conversion of the high melting to the low melting polymorph with increasing sample temperature. The upward arrow indicates the conversion in reverse direction.

Two independently obtained sets of data are plotted in Figure 5. The data from the first set of experiments are represented by circles and from the second set by squares. In the first set, the sample was cooled rapidly with a fast air flow to room temperature, whereas in the second set, the sample was cooled very slowly (about 1 C/min). Because of the slower cooling rate, these samples had adequate time in the 60 C to 40 C temperature range to form some of the high melting phase before crystallization of the low melting phase took place. The presence of small amounts of the high melting poly-

morph with the low melting polymorph resulted in a slight elevation of the endotherm temperature of the low melting polymorph. As observed in Figure 5, the endotherms of the low melting polymorph leveled off at the 49 C instead of the 46.5 C line as in the first experiment. A corresponding 3 C change can be observed in the endotherms of the high melting polymorph that show a change from 57.5 C to 54.5 C. The high melting phase is only a minor constituent here. The arrows between the two horizontal lines indicate the direction of the endotherm temperatures with the change in sam-

ple temperature. The downward arrow indicates the path of the transformation of the high melting polymorph into the low melting crystalline phase. This transformation occurs between temperatures of 70 C and 80 C. Hysteresis was demonstrated by reversal of this transformation. The path of converting the low melting back into the high melting polymorph lowered the temperature by approximately 10 C.

Exotherms were recorded on cooling the sample after the heating cycle. They represent the crystallization temperature of the poly-

morph. In Figure 6, the peak temperatures were plotted as a function of the maximum temperature to which the specimen was heated. The exotherms followed the same pattern as the endotherms. In the first experiment, the gutta-percha sample was heated first to 100 C and then each subsequent time to progressively lower temperatures ending at about 63 C (open squares). The exotherm temperatures remained at about 30 C as the maximum sample temperature decreased to about 73 C. Further lowering of the sample temperature to 65 C
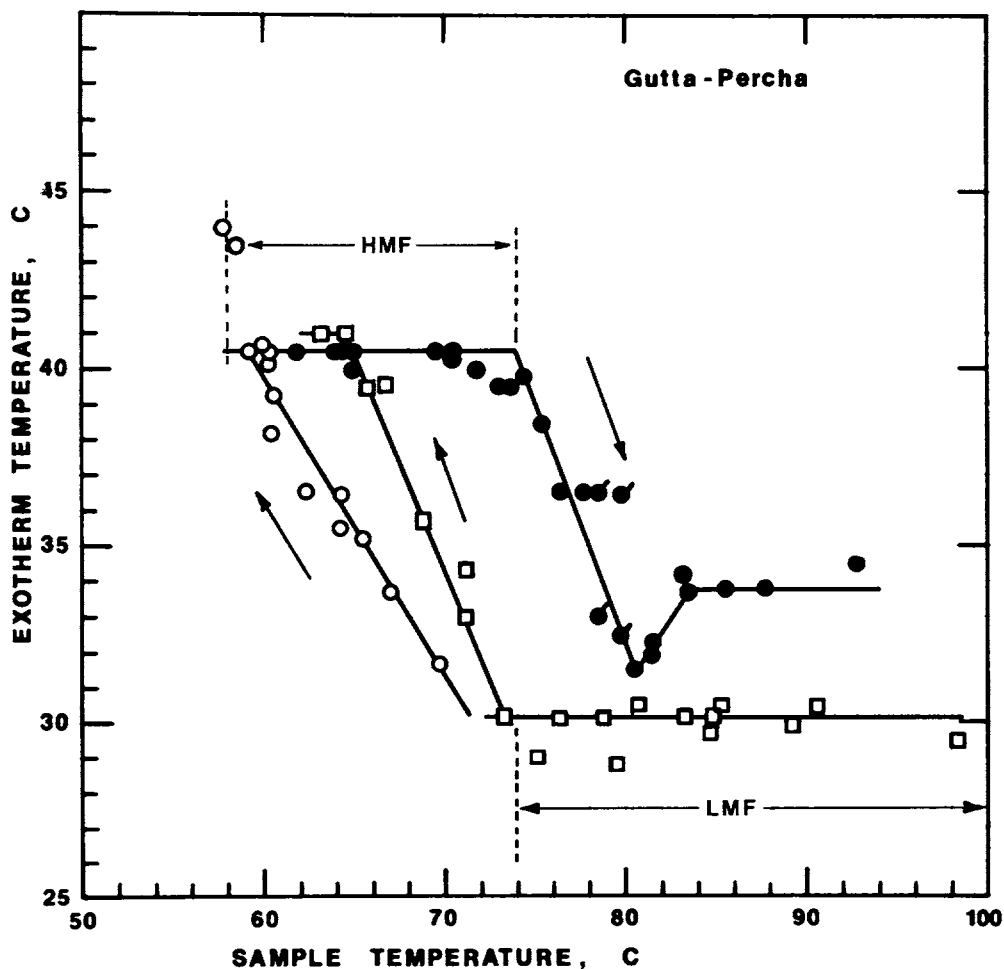

FIG 6. — Plot of exotherm peak temperatures as a function of maximum sample temperature. The ranges of crystallization for both polymorphs of gutta-percha are indicated. The intermediate slopes are the transition curves from one phase to the other. The arrows indicate the direction of the path. Open squares (□) represent the data from the first set of experiments. The data from the second set (Fig 3) are plotted as circles, with closed circles (●) indicating conversion of the high melting to the low melting polymorph, and open circles (○) indicating conversion back to the high melting polymorph.
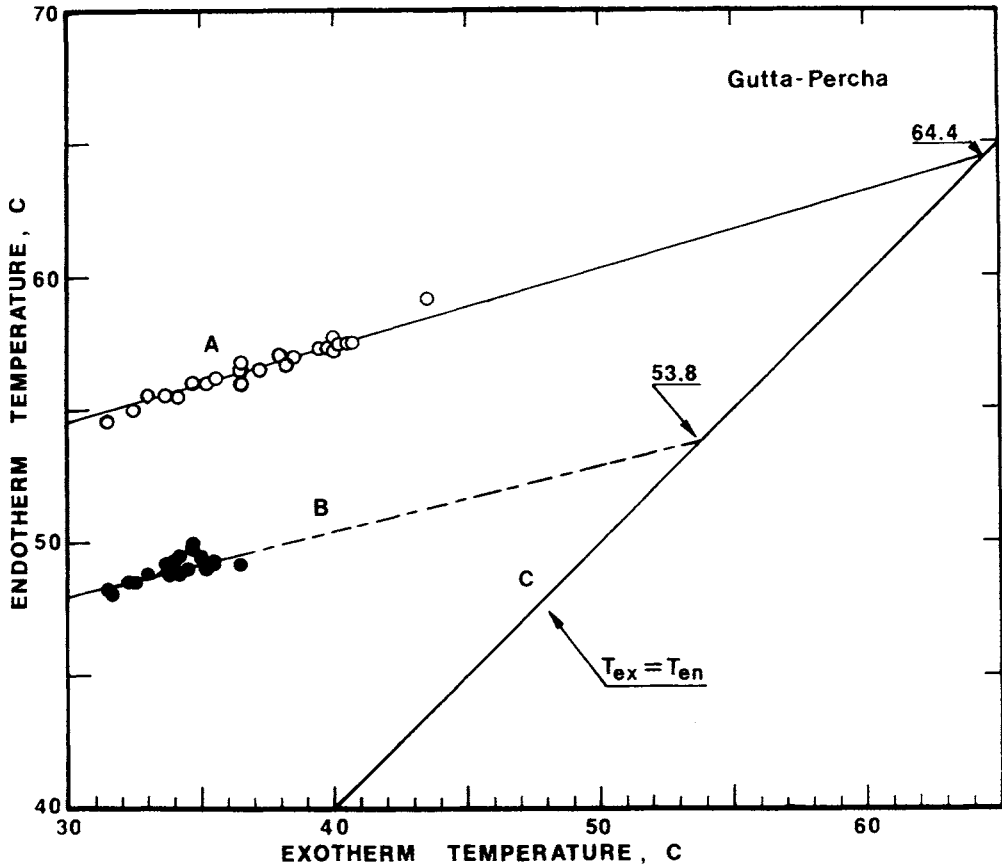
FIG 7. — Plot of endotherm peak temperatures (melting) determined experimentally as a function of exotherm peak temperatures (crystallization) for the high melting (A) and the low melting (B) polymorphs of gutta-percha. The isothermal line (C) is T_{ex} equals T_{en}.

brought about the conversion of the low melting to the high melting polymorph. This cooling curve (open squares) was generated with the specimen cooled relatively rapidly. When a very slow cooling rate was used in the second experiment (circles), the exotherms followed a different path from the low melting to the high melting polymorph (open circles). Decreasing the cooling rate shifted the transformation path to lower sample temperatures.

To reverse this process and transform the high melting back to the low melting crystalline phase, the specimen was heated to increasingly higher temperatures (closed circles). The hysteresis loop, identical to that of the endotherms, was again displaced by the shift of the downward slope of the exotherm temperatures (downward arrow) by approximately 10 degrees to a higher sample temperature. Also a sudden

elevation of the exotherm temperatures from 30 C to 34 C was observed in the sample temperature range of 80 C to 84 C. This elevation of the exotherm temperature is analogous to the behavior of the endotherms at that sample temperature level and is probably caused by small amounts of the high melting phase present in the low melting polymorph. When the sample was heated to above 84 C and cooled very slowly, the high melting phase had adequate time to crystallize before the low melting phase began to crystallize. Thus, the phase transitions in gutta-percha are reversible. The high melting crystalline phase can be converted to the low melting phase and back again by simple control of the temperature to which the gutta-percha sample is heated. The paths of the two transitions, however, are not reversible because of the hysteresis.

The endotherms obtained from the DTA runs (Fig 5) were essentially the melting temperatures of the gutta-percha polymorphs crystallized from the melt at the exotherm temperatures (Fig 6). The endotherm temperatures (T_{en}) were plotted against the exotherm temperatures (T_{ex}) in Figure 7. This type of plot has been used previously to calculate the equilibrium melting points (T_m^o) of large crystals in which surface effects are negligible.[9-11] The equilibrium melting points can be used to derive thermodynamic parameters for the crystalline polymorphs; however, this study was concerned only with the dynamic aspects of rapid DTA analysis and the bulk melting and crystallization phenomena of gutta-percha. Since crystallization did not occur isothermally because of continuous cooling through the exotherm, and the endotherm data were obtained at relatively fast heating rates (20 C/min), the melting endotherm data could not be extrapolated to yield equilibrium melting temperatures for the two polymorphs. Nevertheless, a straight line relationship was determined by linear regression[8] for the high melting phase (A) to be:

$$T_{en} = 46.0 + 0.286\ T_{ex},$$

and for the low melting phase (B) to be:

$$T_{en} = 40.4 + 0.249\ T_{ex}.$$

The assumption that the peak temperatures were known with no imprecision was made. Correlation coefficients of 0.973 and 0.889, respectively, were obtained for the preceding equations. Critical values of r above which the hypothesis of independence of T_{en} and T_{ex} could be rejected were 0.423 and 0.514, respectively, at the 95% level of confidence. These equations extrapolated to the line, $T_{en} = T_{ex}$ in Figure 7 yielded equilibrium or, in this study, the limiting melting endotherm temperatures of 64.4 C for the high melting polymorph and 53.8 C for the low melting polymorph of gutta-percha. These values were each about ten degrees below the melting points obtained dilatometrically by Mandelkern.[3] The linear dependence of the endotherm temperatures on the exotherm temperatures for the low and high melting crystalline polymorphs of gutta-percha show that the actual melting endotherm for either polymorph can occur at any temperature along the line and is determined by the crystallization temperature for that polymorph. This estimated crystallization temperature (T_m^o) has

been found to be greater than the directly observed melting temperatures.[9-11]

Conclusions

DTA curves of the low and high melting crystalline polymorphs of gutta-percha were determined. Heat treatment of the gutta-percha was used to thermally induce the formation of either or both polymorphs in the sample.

By raising the temperature of the specimen from 70 C to 100 C and cooling it to room temperature, the high melting polymorph was transformed into the low melting polymorph. During slow cooling, some high melting polymorph crystallized with the low melting polymorph. When the sample was quenched at 0 C, the high melting polymorph was eliminated. On heating to 60 C, the high melting form was the dominant polymorph produced.

In all analyses, the endotherm temperatures were found to be dependent on the exotherm temperatures of the preceding run which acted as a heat treatment for the sample. The endotherm temperatures were found to depend linearly on the exotherm temperatures of the polymorph.

The transitions between the low and high melting polymorphs in gutta-percha were found to be reversible, cyclic phenomena with hysteresis. Either of the polymorphs could be produced by simple control of the temperature of heat-treatment of the sample.

References

1. BUNN, C. W.: Molecular Structure and Rubber-like Elasticity, I. The Crystal Structures of Beta Gutta-Percha, Rubber and Polychloroprene, *Proc Roy Soc* A180:40-66, 1942.
2. FISHER, DOROTHY.: Crystal Structures of Gutta-Percha, *Proc Phys Soc* 66:7-16, 1953.
3. 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.
4. TAKAHASHI, YASUHIRO; SATO, TAKEFUMI; TADOKORO, HIROYUKI; and TANAKA YASUYUKI.: Crystal Structure of Alpha Gutta-Percha: Modification of the Constrained Least-Squares Method, *J Polym Sci Polym Phys Ed* 11:233-248, 1973.
5. SCHILDER, HERBERT; GOODMAN, ALVIN; and ALDRICH, WINTHROP.: The Thermomechanical Properties of Gutta-Percha III. Determination of Phase Transition Temperatures for Gutta-Percha, *Oral Surg* 38:109-114, 1974.
6. ROOTARE, H. M.; POWERS, J. M.; and SMITH, R. L.: Thermal Analysis of Experimental and Commercial Gutta-Percha, *J Endodont* 2:244-249, 1976.

7. ROOTARE, H. M.; POWERS, J. M.; and SMITH, R. L.: Thermal Analysis of Dental Gutta-Percha, in PORTER, R. S. and JOHNSON, J. F. (eds), *Analytical Calorimetry.* Volume 4, New York, Plenum Press, 1977, 251 pp.

8. University of Michigan, Statistical Research Laboratory: *A Manual of Elementary Statistics Using MIDAS.* Ann Arbor, Statistical Research Laboratory, 1975, 301 p.

9. GOPALAN, M., and MANDELKERN, L.: The Effect of Crystallization Temperature and Molecular Weight on the Melting Temperature of Linear Polyethylene, *J Phys Chem* 71:3833-3841, 1967.

10. LOVERING, E. G., and WOODEN, D. C.: Transitions in Trans-1,4-Polyisoprene, *J Polym Sci* (A-2) 7:1639-1649, 1969.

11. LOVERING, E. G., and WOODEN, D. C.: Equilibrium Melting Points of the Low-Melting and High-Melting Crystalline Forms of Trans-1,4-Polyisoprene, *J Polym Sci* (A-2) 9:175-179, 1971.