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# SPECIFIC HEATS OF GUAYULE AND NATURAL RUBBERS ABOVE THE GLASS TRANSITION TEMPERATURE

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## ABSTRACT

Heat capacities of guayule and natural rubbers were measured between 228 and 333 K using a DuPont 990 Differential Scanning Calorimeter. Data obtained were fitted to a straight line. We obtained the following equations where $C_p$ is given in cal $g^{-1}$ $K^{-1}$. For guayule rubber, $C_p = 22.6152 \times 10^{-4}\ T + 0.7731$ (correlation factor = 0.99). For natural rubber, $C_p = 16.9195 \times 10^{-4}\ T + 0.9209$ (correlation factor = 0.98). Furthermore, some theoretical considerations and instrumental conditions were analyzed so that the determinations of heat capacities could be improved.

## INTRODUCTION

Gyayule rubber, extracted from Parthenium Argentatum Gray, has a similar chemical structure to natural rubber (extracted from the tree *Hevea brasiliensis*) with respect to its content of *cis*-1,4-polyisoprene [1] and to its molecular weight distribution [2]. Therefore one would expect the heat capacities of a purified sample of guayule rubber to be the same as the respective values for natural rubber. The specific heats of natural rubber were reported a long time ago [3,4]. The samples that were used to determine such values probably presented crystalline zones [5]. Therefore we need to re-evaluate the results for amorphous rubbers. This paper attempts to rectify this situation. By a thermal treatment (heating—quenching) of the sample almost completely amorphous rubbers (over 99%) were obtained. Determinations of the degree of crystallinity ($X$) by DSC are based fundamentally [6] on the measurement of the enthalpy of fusion from the crystalline zones ($\Delta H_{f_1}$) and it is calculated from eqn. (1), where $\Delta H_{f_2}$ represents the enthalpy of fusion of 100% crystalline rubber [7]

$$X = \frac{\Delta H_{f_1}}{\Delta H_{f_2}} \tag{1}$$

$\Delta H_{f_1}$ can be measured by calculating the fusion area from the endotherm obtained from the sample thermal analysis, because

$$\Delta H_{f_1} = \int C_p \, dT \tag{2}$$

$T_1$ and $T_2$ are the temperature limits of the fusion interval and $C_p$ is the value of the specific heat of the sample obtained using eqn. (3).

Determinations of the specific heat by DSC are made by the following sequence [8,9].

(1) The thermal capacity of a material like sapphire, whose heat capacity is known, plus the holder is measured and then compared with that of the empty holder.

(2) Thermal capacities of the sample plus holder are compared with that of an empty holder and the resulting trace will show a displacement which is dependent on the specific heat of the sample.

(3) Values of heat capacities of the sample ($C_{\mathrm{pr}}$) are calculated from eqn. (3)

$$C_{\mathrm{pr}} = C_{\mathrm{ps}} \frac{m_{\mathrm{s}} \Delta Y_{\mathrm{r}}}{m_{\mathrm{r}} \Delta Y_{\mathrm{s}}} \qquad (3)$$

where $C_{\mathrm{ps}}$ is the specific heat of sapphire, $m_{\mathrm{s}}$ and $m_{\mathrm{r}}$ are the weights of rubber and sapphire, $\Delta Y_{\mathrm{r}}$ and $\Delta Y_{\mathrm{s}}$ are the rubber and sapphire trace displacements related to the empty holder trace.

Figure 1 shows that the heating rate of the DSC apparatus is not constant over a one hundred degree interval, from 246 to 346 K, but increases continually. In addition, if we start at different temperatures we obtain different heating rates. This fact is important as it necessitates starting the runs at

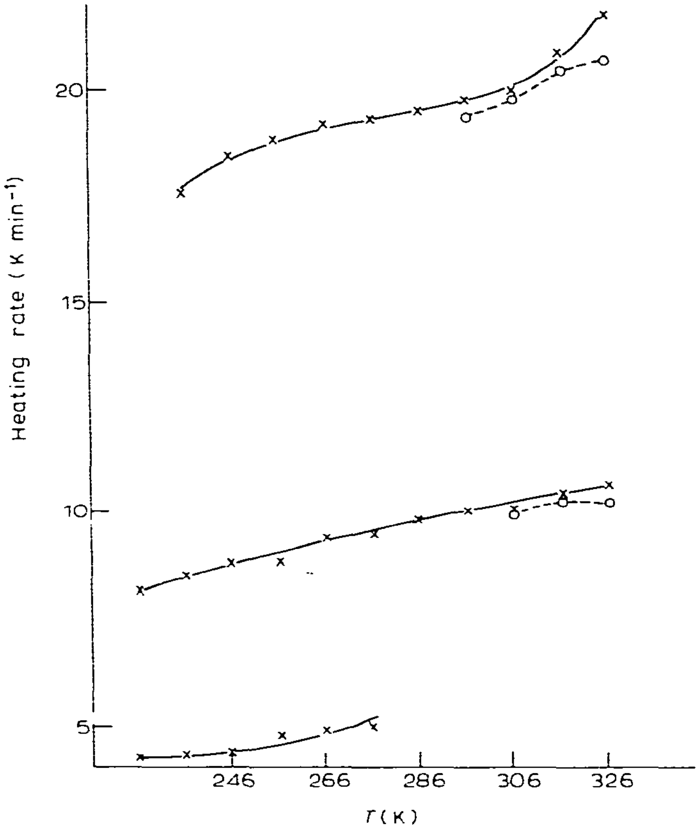

Fig. 1. Variation of the heating rate. ×, Heating started at 220 K; ○, heating started at room temperature.

the same temperature. To avoid this we consider that it is better and more accurate to calculate the values of the specific heats using eqn. (3) instead of the more commonly used eqn. (4)

$$C_{pr} = \frac{60\, q_s \Delta Y_r E}{H_r m_r} \tag{4}$$

where $q_s$ is the apparatus sensitivity, $\Delta Y_r$ is the sample trace displacement from the empty holder trace, $E$ is the cell calibration coefficient, $H_r$ is the heating rate and $m_r$ is the sample weight.

## EXPERIMENTAL

### *Sample preparation*

#### *Hevea rubber*

This rubber was obtained from the National Bureau of Standards (NR No. 40). By dissolving the rubber in tetrahydrofuran, coagulating it in acetone and finally centrifuging it, the antioxidant, proteins and macrogel that it contains were eliminated. Microgel was eliminated by repeated filtrations in a filter press. The total amount of gel was 13.35%. The rubber was finally obtained as a film by evaporating off the THF in a vacuum dessicator.

#### *Guayule rubber*

Guayule bush was chopped, deresinated with acetone in a Soxhlet for 8 h. Then it was purified using the same procedure followed for natural rubber.

BHT was added as an antioxidant to both rubber samples to avoid degradations before the thermal analysis was performed.

### *Calorimeter calibration*

The registered temperature was calibrated by using selected standards whose melting point temperatures are in the range 230 to 330 K [10]. Among the standards used were mercury, nitrobenzene and maleic anhydride.

The calibration coefficient of the calorimeter cell ($\Delta Y_s$) was measured by means of a sapphire disc under the same instrument conditions used for the rubber samples.

### *Sample conditioning*

To eliminate possible crystalline zones [11], samples were heated from room temperature, ca. 20°C, to 60°C. After this treatment the rubbers were quenched at 213 K in a dry ice—acetone bath.

### *Sample runs*

Samples were analyzed in a DuPont Calorimeter provided with a DSC cell.

They were cooled by a dry ice—acetone bath in contact with the cell. The procedure for the runs was as follows.

(a) After sample conditioning the nitrogen flow was stabilized and the temperature adjusted to 221 K.

(b) The heating was started; the trace was obtained from 222 to 333 K.

(c) The heating program was then interrupted by the "hold" button.

(d) The sample was removed from the DSC cell and the cell was then heated to 423 K to eliminate any traces of water; the cell was then ready to make another analysis.

## RESULTS AND DISCUSSION

(1) The heat capacity results are listed in Table 1 and shown graphically in Figs. 2 and 3. The variation in values was ±3%. Data were adjusted by square minima and gave the following equations.

For guayule rubber

$C_p = 22.6152 \times 10^{-4} T + 0.7731$

For natural rubber

$C_p = 16.9195 \times 10^{-4} T + 0.9209.$

TABLE 1

Specific heats of guayule and natural rubbers

| Temp. (K) | $C_p$ (cal $g^{-1}$ $K^{-1}$) | |
|---|---|---|
| | Guayule | Hevea |
| 228 | 0.3079 | 0.3107 |
| 233 | 0.3107 | 0.3150 |
| 238 | 0.3131 | 0.3155 |
| 243 | 0.3157 | 0.3172 |
| 248 | 0.3178 | 0.3166 |
| 253 | 0.3190 | 0.3187 |
| 258 | 0.3222 | 0.3290 |
| 263 | 0.3252 | 0.3275 |
| 268 | 0.3292 | 0.3276 |
| 273 | 0.3424 | 0.3387 |
| 278 | 0.3346 | 0.3299 |
| 283 | 0.3378 | 0.3337 |
| 288 | 0.3404 | 0.3367 |
| 293 | 0.3417 | 0.3379 |
| 298 | 0.3441 | 0.3396 |
| 303 | 0.3463 | 0.3414 |
| 308 | 0.3500 | 0.3447 |
| 313 | 0.3528 | 0.3464 |
| 318 | 0.3553 | 0.3479 |
| 323 | 0.3571 | 0.3484 |
| 328 | 0.3633 | 0.3525 |
| 333 | 0.3667 | 0.3542 |

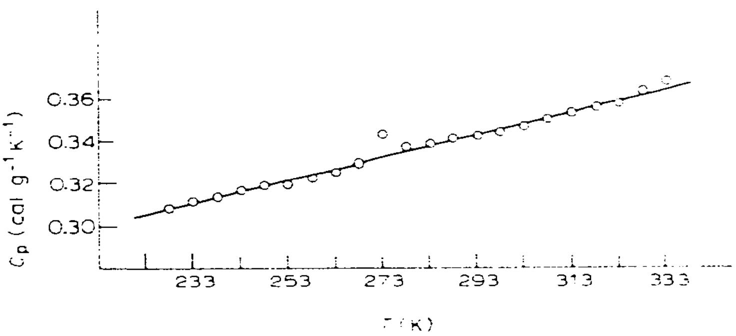

Fig. 2. Specific heat of guayule rubber.

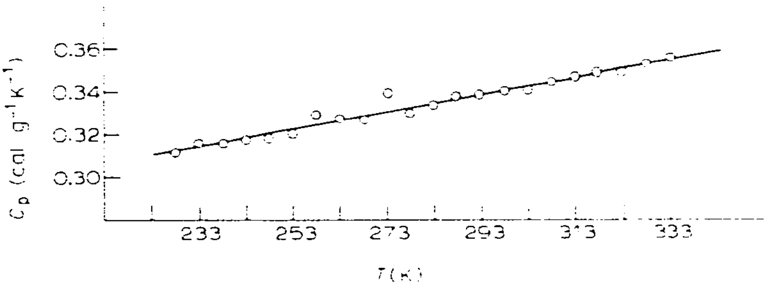

Fig. 3. Specific heat of natural rubber.

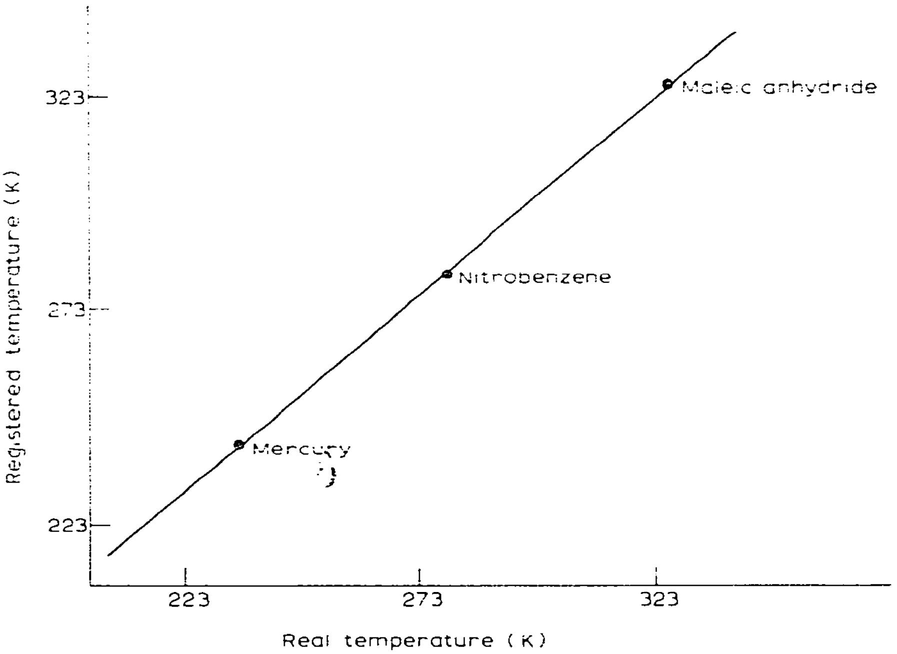

Fig. 4. Temperature calibration.

TABLE 2

DSC cell calibration coefficients

| Temp. (K) | $\Delta Y_s$ (cm) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 228 | 7.45 | 7.62 | 7.67 | 7.52 | 7.56 | 7.57 | 7.56 | 7.85 | 7.92 |
| 233 | 7.80 | 7.97 | 7.92 | 7.90 | 7.88 | 7.76 | 7.88 | 8.42 | 8.32 |
| 238 | 8.02 | 8.17 | 8.17 | 8.17 | 8.13 | 8.07 | 8.13 | 8.70 | 8.56 |
| 243 | 8.30 | 8.38 | 8.45 | 8.41 | 8.37 | 8.28 | 8.37 | 8.93 | 9.04 |
| 248 | 8.50 | 8.62 | 8.66 | 8.62 | 8.57 | 8.50 | 8.57 | 9.18 | 9.04 |
| 253 | 8.80 | 8.87 | 8.90 | 8.87 | 8.82 | 8.75 | 8.82 | 9.43 | 9.32 |
| 258 | 9.10 | 9.15 | 9.18 | 9.20 | 9.12 | 9.05 | 9.12 | 9.76 | 9.64 |
| 263 | 9.37 | 9.42 | 9.45 | 9.50 | 9.38 | 9.28 | 9.38 | 10.05 | 10.00 |
| 268 | 9.65 | 9.65 | 9.67 | 9.75 | 9.60 | — | 9.60 | — | 10.20 |
| 273 | 9.82 | 9.82 | 9.82 | 9.95 | 9.79 | 9.78 | 9.79 | 10.56 | 10.40 |
| 278 | 10.00 | 10.00 | 10.05 | 10.12 | 10.02 | 9.94 | 10.02 | 10.78 | 10.57 |
| 283 | 10.15 | 10.17 | 10.20 | 10.27 | 10.13 | 10.12 | 10.13 | 10.95 | 10.76 |
| 288 | 10.30 | 10.33 | 10.35 | 10.43 | 10.32 | 10.29 | 10.32 | 11.17 | 10.83 |
| 293 | 10.47 | 10.52 | 10.50 | 10.61 | 10.45 | 10.42 | 10.45 | 11.26 | 11.07 |
| 298 | 10.62 | 10.61 | 10.65 | 10.72 | 10.59 | 10.53 | 10.59 | 11.50 | 11.21 |
| 303 | 10.75 | 10.77 | 10.80 | 10.91 | 10.72 | 10.65 | 10.72 | 11.61 | 11.36 |
| 308 | 10.90 | 10.93 | 10.95 | 11.06 | 10.86 | 10.82 | 10.86 | 11.75 | 11.50 |
| 313 | 11.05 | 11.10 | 11.10 | 11.20 | 10.98 | 10.93 | 10.98 | 11.91 | 11.65 |
| 318 | 11.20 | 11.24 | 11.25 | 11.35 | 11.14 | 11.10 | 11.14 | 12.04 | 11.83 |
| 323 | 11.35 | 11.42 | 11.40 | 11.52 | 11.28 | 11.23 | 11.28 | 12.25 | 11.98 |
| 328 | 11.50 | 11.62 | 11.57 | 11.72 | 11.47 | 11.47 | 11.47 | 12.41 | 12.17 |

Their correlation factor was above 0.98.

(2) In Figs. 2 and 3, we can observe that in the range 268—278 K there is a discontinuity, very probably due to the fusion of tiny crystalline zones present in the rubbers. We evaluated their degree of crystallinity using eqn. (1) and found it to be 0.3% for guayule rubber and 0.7% for natural rubber. These crystalline zones were probably formed during the thermal analysis. We thought initially that these discontinuities could be due to frozen water present in the sample. However, we heated one sample at 333 K for one hour and this sample also presented the same discontinuity.

(3) The relation between the real temperature measured with the temperature calibration standards and the registered temperature is shown in Fig. 4.

(4) Table 2 shows the results for the calibration coefficient. A very good reproducibility (a mean deviation of 0.62%) was obtained.

## CONCLUSIONS

(1) We can adequately represent the specific heat values for amorphous guayule and natural rubbers as a straight line for the range 228 –333 K.

(2) The specific heat values, within experimental error, show the physical similarity between guayule and natural rubbers.

(3) A special thermal treatment to render rubber samples amorphous was optimized.

(4) The instrument conditions for performing runs at the calorimeter was optimized.

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