

Thermal Expansion Measurements and Transition Temperatures, First and Second Order*

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INTRODUCTION

When any pure material goes through a change in state, its physical properties change greatly. In each phase the physical properties are relatively constant or change slowly enough with temperature that the rate of change of a property such as volume is a constant. This rate of change of volume is the thermal expansion coefficient, $(\partial V/V)/\partial T$.

The thermal expansion coefficient is almost constant, experimentally, as long as the temperature range over which measurements are made does not include a phase transition. At the transition temperature, abrupt changes in volume are found as illustrated in Figure 1.

Polymeric materials often show changes in physical properties not necessarily accompanied by abrupt changes in volume, even though the expansion coefficient does change. Since the expansion coefficient changes, some change in

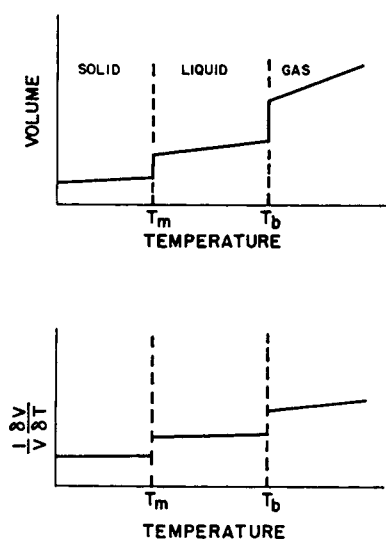


Fig. 1. Typical changes in volume and coefficient of expansion for ordinary materials.

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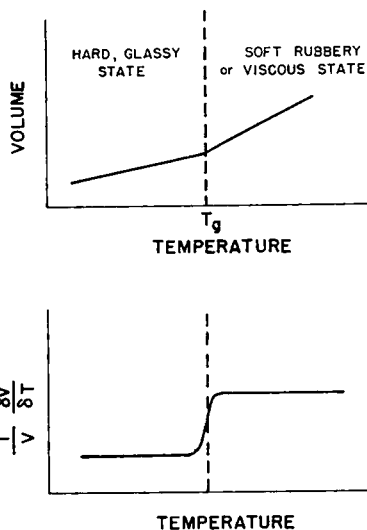


Fig. 2. Typical changes in volume and coefficient of expansion for amorphous polymeric materials.

internal structure is suspected, and the name second-order transition (T_g) has been adopted. This kind of change is roughly diagrammed in Figure 2.

This latter change at the second-order transition temperature can be found in every known polymer, even though many polymers possess clear, first-order, crystalline transitions as well. Hevea rubber, for example, has a crystalline melting point of 28°C ., compared to its T_g about -70° . These data are shown, copied from Boyer and Spencer,¹ as Figure 3.

APPARATUS

Since the transition which takes place at any observed temperature is accompanied by changes in the other physical properties, an attempt was made to identify transitions in some new polymers to aid in the understanding of their other properties. A simplified form of dilatometer utilizing the principle of differential thermal expansion was constructed and modified in two important ways

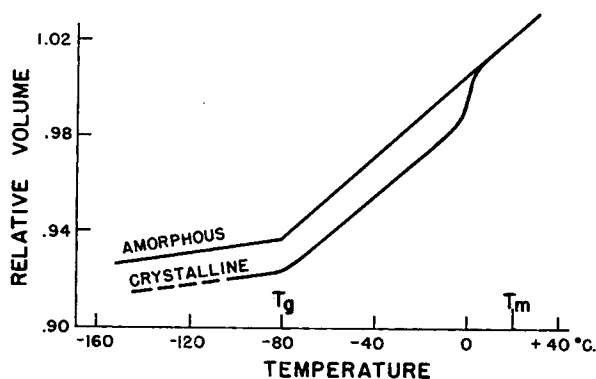


Fig. 3. Changes in volume of Hevea rubber showing both crystalline and amorphous transitions.

from a design published by K. L. Floyd.² Since some polymers were very difficult to prepare and only limited amounts were available, sample size was reduced to about one cubic centimeter. Also, direct and continuous measurement of temperature eliminated the need for a constant temperature bath, and further removed the restrictions imposed by contact fluids. An additional advantage accrued in that the thermal range of measurement was increased.

The apparatus, basically, is a dilatometer in which the actual dilation of the sample is measured mechanically in one chosen direction or dimension; that is, this is a linear differential thermal expansion method. The length of a sample is compared to that of a stainless steel post, conveniently hollowed to form a cup which holds the sample.

The apparatus is sketched schematically in Figure 4. Details of the cup and tripod are shown in Figure 5. Several assemblies, differing in size and in kind of metal, have been made. The mirror tripod rests one leg on the sample, the other two on the stainless steel cup. A washer prevents indentation of the sample. Movement of the sample relative to the cup tips the tripod and mirror, and thus moves the galvanometer spot. An auxiliary mirror on the cup checks zero, making the differential measurements independent of slight shifts in the level of the cup. The sample may range from 10 to 12 mm. in height, but must have fairly flat faces. Clean, knife-cut surfaces are acceptable. The sample need not be cured, since creep can usually be reduced to a negligible value by appropriate heat or relaxation treatments.

Temperature of the sample is measured by an iron-constantan thermocouple inserted close to the midpoint. The thermocouple is made of No. 38-gage wire to eliminate false movements of the sample arising from the springiness of heavier

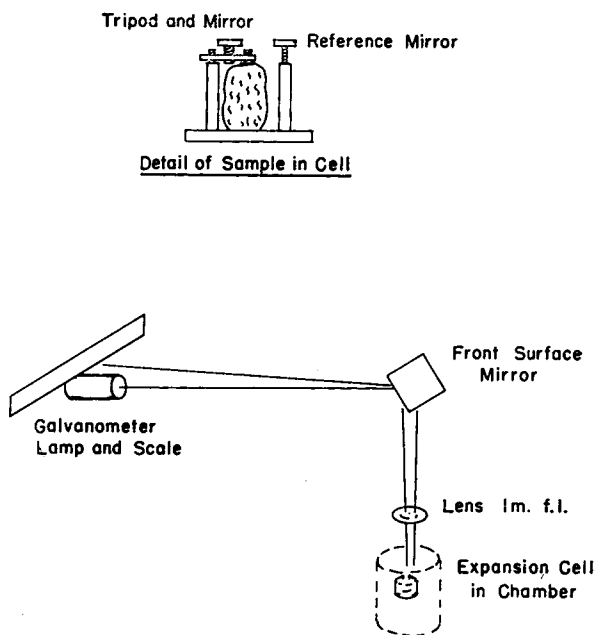


Fig. 4. Schematic illustrations of experimental arrangements.

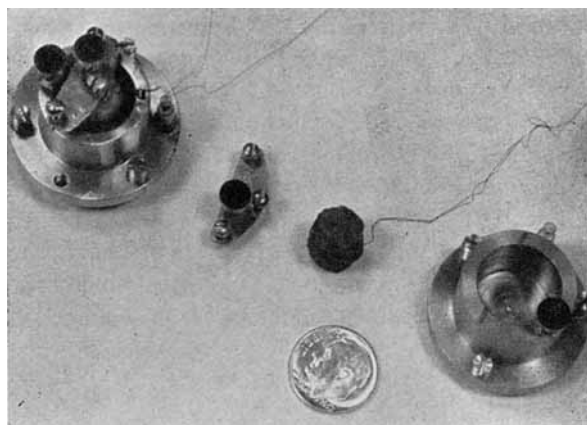


Fig. 5. The loaded differential expansion cell and components.

gage wires. An ice junction is used. Individual calibrations of the junctions are not attempted, since values read from tables are considered accurate enough.

Two alternate procedures have been used, the first being preferred as more convenient. In the first procedure, the assembled cup containing the sample and tripod is flooded with liquid nitrogen in an insulated chamber or in a vacuum flask. After the excess nitrogen has boiled away, expansion of the samples in warming to room temperature is followed. The rate of rise near -150°C . is about 1° per minute; near 0° , less than $1/2^{\circ}\text{C}$. per minute. With this initial, fairly rapid, temperature rise, the sample is not at constant temperature throughout. The gradient is estimated at 3°C . maximum,

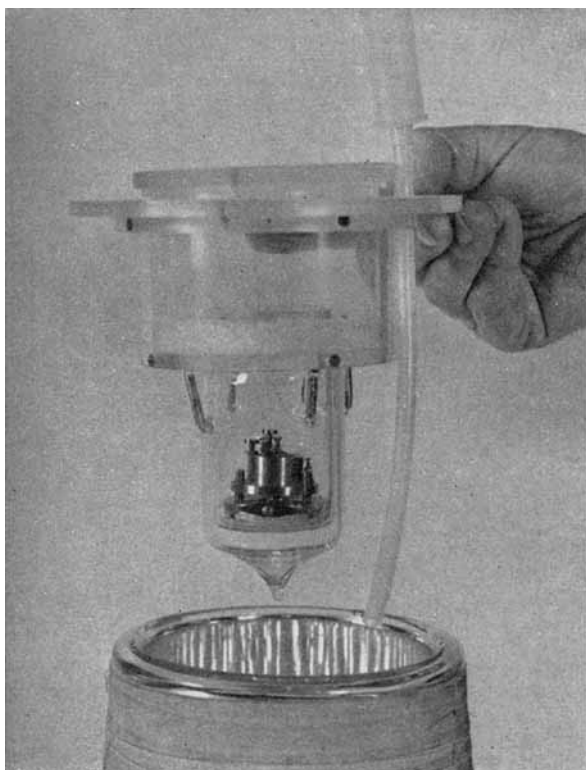


Fig. 6. The expansion cell in vacuum wall flask ready for a cooling cycle run. Liquid nitrogen can be poured into the Dewar flask through the polyethylene sidearm.

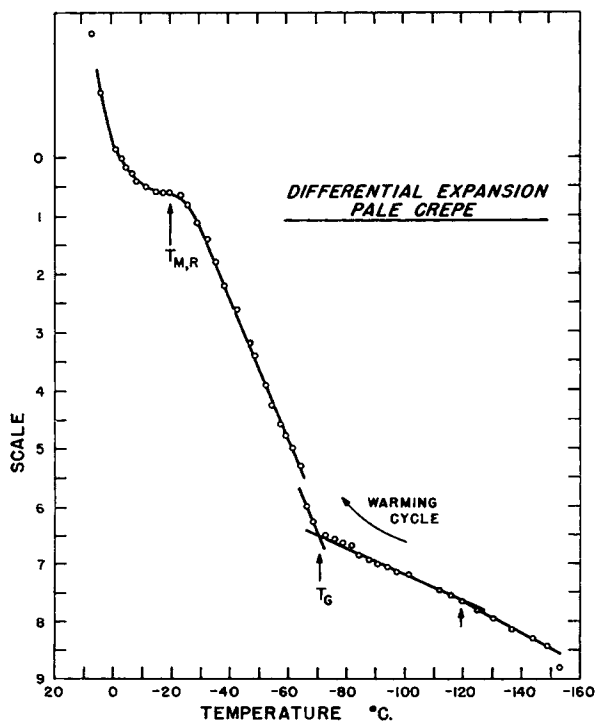


Fig. 7. A typical differential expansion curve for a sample of pale crepe.

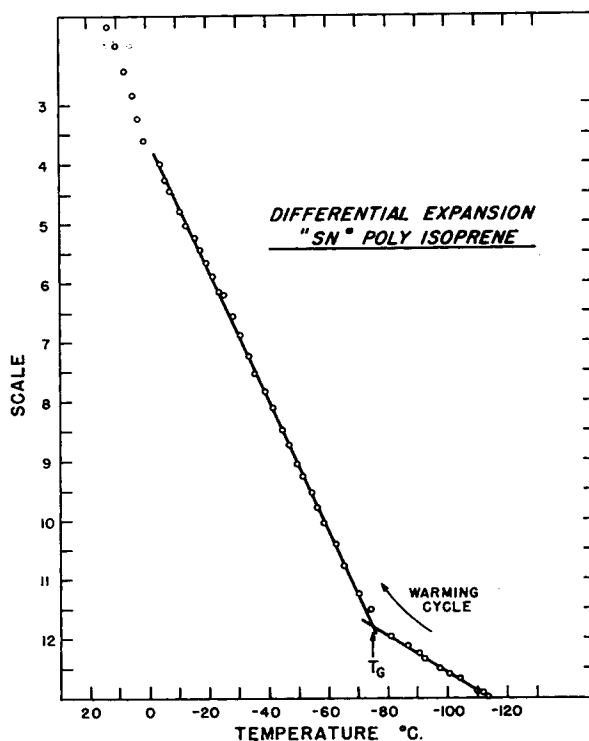


Fig. 8. A typical differential expansion curve for a sample of SN rubber (polyisoprene, about 95% *cis* 1,4-structure).

but may be less. In the second procedure, the assembled cup is placed in a vacuum wall flask, which, in turn, is immersed in liquid nitrogen. In this procedure, the sample cools slowly by radiation to the cold surroundings. Similar measurements of contraction with decreasing temperature can be followed. Multiple windows enclosing dry, dead air spaces permit observations without excessive frosting troubles. The expansion cell in its chamber is shown in Figure 6. The data are usually plotted as galvanometer curves vs. temperature. Breaks or discontinuities identify transitions. Coefficients of expansion were computed from smoothed curves in some cases.

POLYMER TRANSITIONS

A typical expansion curve for a sample of pale crepe natural rubber is shown in Figure 7. Quick cooling with liquid air is followed by linear expansion as the cell and sample warm up. At about -70°C . the sample increases its rate of expansion, clearly defining the second-order transition temperature. The break at about -60°C . is due to relaxation of stress frozen in by the shock cooling of direct contact with the liquid air. This break, in contrast to other changes, is irregular, not repeatable, and can be eliminated by slower cooling techniques. Further increase in tempera-

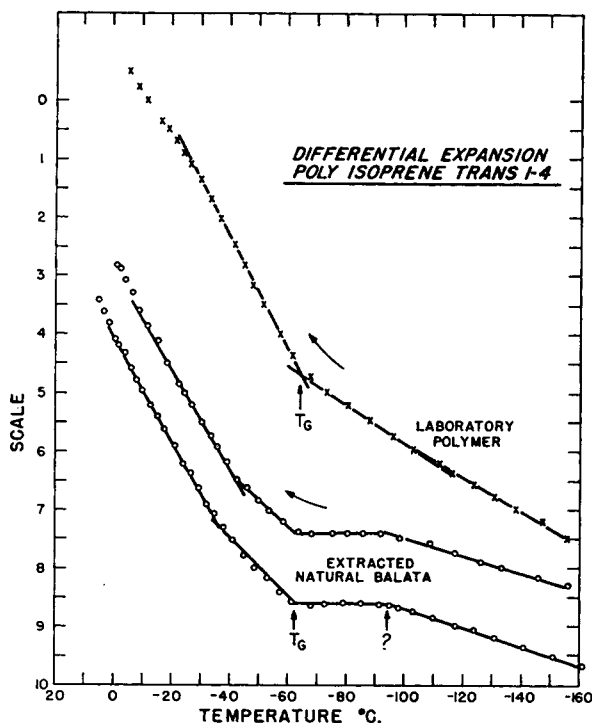


Fig. 9. Typical differential expansion curves for polyisoprene, *trans* 1,4-structure.

ture is accompanied by linear expansion up to about -25°C ., at which temperature the rubber crystallizes rapidly. The decreased height and increased rate of rise of temperature are related to the increased density of the crystalline phase and the liberation of the latent heat of crystallization. Further warming results in a more rapid expansion as the crystalline phase melts to the amorphous rubber. The small change in slope to about -125°C . is believed to be an artifact of the stainless steel used in the cell, in that this material undergoes a first-order phase change at about this temperature. A pure nickel cell has been used to check ambiguities of this kind.

A similar expansion curve for a sample of Ameripol SN is shown in Figure 8. This material is polyisoprene, polymerized about 95% as the *cis*-1,4-isomer. Rapid cooling followed by slow warming shows the same change in expansion but at about -75°C .. Further warming shows no evidence of crystallization. This lack of crystallinity merely reflects the purity of the material, in that nucleating centers for the crystalline phase are not present in sufficient concentrations to initiate this action in the time duration of this run. Other independent measurements have shown crystallization rates and crystal phase structure identical with natural rubber when the proper seeding impurities are added. The same

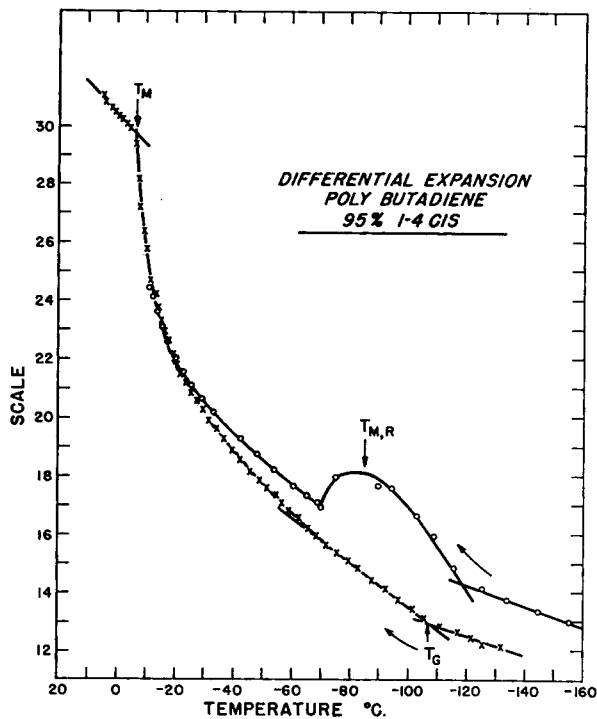


Fig. 10. Typical differential expansion curves for polybutadiene, 1,4-structure.

transition temperature, -75°C ., was obtained for a highly purified sample of natural rubber furnished by Dr. D. Craig of this laboratory.

Expansion curves for samples of extracted balata and a laboratory-polymerized polyisoprene are shown in Figure 9. The experimental polymer was believed to have a *trans*-1,4 isomer content over 90% and was a hard, leathery material at room temperature. The abrupt change in expansion about -60°C . is clear evidence for the glass transition, even in the presence of the crystalline phase. The two curves for the natural balata were obtained on specimens cut from the same original sheet about a week apart. Both curves show the same breaks and changes, confirming each other very nicely. The glass transition at -60°C . is clearly identifiable. The change in slope at about -80°C . cannot be explained.

Expansion curves for several samples of polybutadiene with *cis*-1,4-isomer contents of about 95% have been obtained, all of which can be made to show certain common features illustrated in Figure 10. Shock cooling followed by warming causes expansion in the glassy state. The increase in the rate of expansion above about -120° for the data shown is accompanied by an abrupt increase in the rate of warming to about 15°C . per minute, in contrast to the $\frac{1}{2}^{\circ}\text{C}$. per minute at both lower and higher temperatures. This peculiar volume

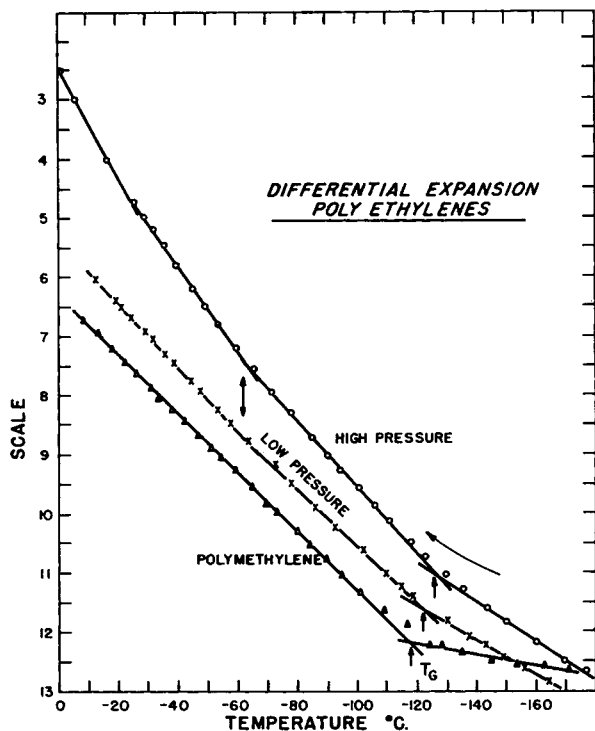


Fig. 11. Typical differential expansion curves for polyethylenes.

change obviously is evidence of rapid crystallization at about $-85^{\circ}\text{C}.$, apparently starting at much lower temperatures. Curves of this type are not uniformly reproducible either in the "crystallization hump" or in the value of T_g . Reproducible curves can be obtained by slower cooling, followed by warming of the type also shown in Figure 10. Expansion changes abruptly at about $-108^{\circ}\text{C}.$, then continues linearly up to about $-70^{\circ}\text{C}.$ Deviations from linearity above this temperature are believed to represent partial melting of the crystalline phase of this material. Melting in this specimen is complete at $-6^{\circ}\text{C}.$ While the T_g is not sensitive to changes in structure in the range above about 85% isomer content, the final melting temperature T_m decreases as the *cis* content falls from 100%. The melting point of the 100%-*cis* polymer cannot be estimated from these data, since the influence and amount of impurities are too difficult to measure or estimate with confidence.

Expansion curves for two samples of polyethylene and a sample of polymethylene are shown in Figure 11. The high-pressure polyethylene, after shock cooling, shows a linear expansion with a distinct change in slope at about $-125^{\circ}\text{C}.$ The subsequent expansion curve has no extensive linear region, although it has been drawn or approximated by a series of chords. The low

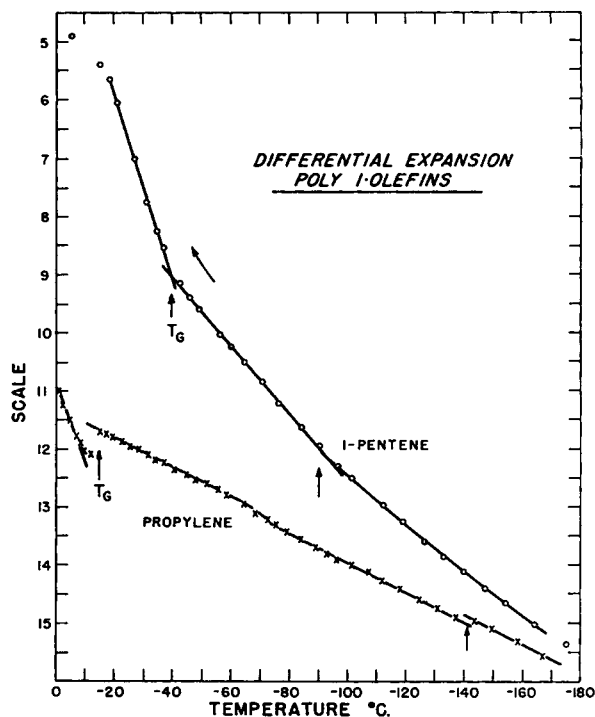


Fig. 12. Typical differential expansion curves for polyolefins.

pressure polyethylene similarly shows a distinct break at about $-122^{\circ}\text{C}.$, followed by linear expansion over a considerable temperature range. Subsequent expansion does not follow the same linearity, but the question about continuous curvature cannot be resolved. The sample of polymethylene, furnished by Dr. Franz Widmer, shows linear expansion up to $-120^{\circ}\text{C}.$, followed by further linear expansion at a different slope. The change in behavior of these three materials is believed to be significant and related to differences in their structure.

Expansion curves for samples of polypropylene and poly-1-pentene are shown in Figure 12. Both materials are isotactic polymers showing crystallinity at and above room temperature, with melting points near 150° and $75^{\circ}\text{C}.$, respectively. Both warming and cooling curves show the second-order transitions for polypropylene at about -20 and $-40^{\circ}\text{C}.$ for poly-1-pentene. Additional repeatable changes in the expansion curves can be identified, although their significance cannot be explained. It can be noted that the expansion curves for these two polymers differ in slope just below T_g , but are fairly comparable above that temperature. The coefficient of expansion below T_g has been computed from the graph and instrument constants and it is presented in Table I, together with similar information on other comparable polymers. The values of $\partial l/\partial T$ are reliable only to about 10%,

TABLE I
Transition Temperature and Expansion Coefficient

Polymer	T_g , °C.	$1/l \left(\frac{\partial l}{\partial T} \right)_{T < T_g}$ $\times 10^6$ cm./cm. °C.	T_{γ} , °C.
Polyethylene (high pressure)	-125	8	
Polyethylene (low pressure)	-122	7	
Polypropylene	-20	6	-70
Poly-1-butene	-25	12	-80
Poly-1-pentene	-40	15	-90
Poly-1-hexene	-50	16	-110
Poly-1-octene	-65	23	-105

since the tipping arm of the optical lever is difficult to measure accurately. Also listed are the temperatures of the additional low temperature discontinuity in the column labeled T_{γ} . The small change in slope makes these values less reliable than the corresponding T_g measurements.

DISCUSSION

Differential expansion measurements on a variety of polymers have shown changes in state easily recognizable as first-order crystalline and/or second-order glassy phenomena. In addition to these obvious transitions, some materials show reproducible discontinuities in slope which can be interpreted as additional second-order transitions. If these discontinuities represent a loss of a degree of freedom for some portion of the molecule, then changes in dynamic mechanical properties would be expected in the vicinity of these temperatures. Changes of this kind have been reported before^{3,4} and where comparisons can be made, seem reasonable in magnitude.

The change in the expansion coefficient just below T_g , where the polymers are presumably in corresponding states, indicates that the polyolefins with the larger side groups retain excess volume as they cool from above the glass transition. The retention in volume is roughly proportional to the number of carbon atoms in the side chain. An alternate interpretation states that each side chain methylene group adds a constant increment of nonoccupied volume to the molar volume of the backbone chain. The expansion value for the polyethylenes is higher than for polymethylene, and is also out of place in the polyolefin series. This may be taken as further evidence of the side group structure of these materials, but any estimation of amounts or kinds of side structure are not justified.

References

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Synopsis

Transitions in polymers have been studied with the use of a differential expansion apparatus modified from a design described by K. L. Floyd. Materials ranging from uncured, soft rubbers to hard, waxy solids have been studied from above room temperature down to liquid air temperatures. Both the first-order transition temperature, T_m and the second-order transition temperature, T_p , can be identified. Multiple changes in slope of the expansion curves indicate the possibility of additional second-order transitions. Expansion curves for several diene rubbers are presented, illustrating typical transition phenomena. Expansion curves for several polyolefin materials are presented which illustrate changes in T_g and in the low temperature expansion coefficient with changes in the structure of the polymer.

Résumé

Les transitions ont été étudiées dans les polymères en utilisant un appareil d'expansion différentielle, modèle modifié au type décrit par Floyd. L'étude a porté sur des matériaux allant de caoutchoucs mous et non-traités aux solides durs et cireux, cela de la température de chambre jusqu'à la température de l'air liquide. Les températures de transition de premier et de second ordre soit T_m et T_p peuvent être identifiées. De multiples variations de la pente de la courbe d'expansion indiquent la possibilité de transitions de second ordre additionnelles. Les courbes d'expansions de différents caoutchoucs diéniques sont présentées illustrant des phénomènes typiques de transitions. Les courbes d'expansion de différents matériaux polyoléfiniques sont présentés illustrant la variation de T_g et du coefficient d'expansion à basse température accompagnant les modifications de la structure du polymère.

Zusammenfassung

Mit einer modifizierten Form des von Floyd angegebenen Differential-expansionsapparates wurden Umwandlungen in Polymeren untersucht. Es wurden Stoffe im Konsistenzbereich von unvulkanisiertem Weichgummi bis zu harten, wachsartigen Festkörpern bei Temperaturen oberhalb Raumtemperatur bis hinunter zur Temperatur der flüssigen Luft untersucht. Es kann sowohl die Umwandlungstemperatur erster Ordnung, T_m , als auch diejenige zweiter Ordnung, T_p , festgestellt werden. Mehrfache Änderungen der Neigung der Ausdehnungskurven deuten auf die Möglichkeit zusätzlicher Umwandlungen zweiter Ordnung hin. Ausdehnungskurven für einige Dienkautschuke werden vorgelegt, die die typischen Umwandlungserscheinungen aufweisen. Ebenso werden solche Kurven für einige Polyolefinsubstanzen gezeigt, die die Abhängigkeit des T_g und des Tieftemperaturexpansionkoeffizienten von der Struktur des Polymeren erkennen lassen.

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