Abrupt increases in the thermal conductances of Apiezon N and T grease have been observed, and it is surmised that these discontuities, as well as published anomalies in the specific heat, are related to glass transition temperatures (T_g (*N*) = *273 K and* T_g (*T*) = *210 K*) *of the greases.*

A correlation between thermal conductance and specific heat anomalies and the glass temperature of Apiezon N and T greases

M. M. Kreitman, T. Ashworth, and M. Rechowicz

Apiezon N and T grease are often used to effect thermal bonds over a temperature range extending from less than 1 K up to their melting points. Published data on the specific heat of these greases have disclosed the presence of anomalies [1,2] and in both cases, the authors have reported serious decreases in the reproducibility of the measurements within the anomalous temperature regions. Furthermore, while observing the heat transfer across pressed contacts being cooled to low temperatures, Rechowicz, Ashworth, and Steeple [3] have noted abrupt decreases in heat flow for Apiezon N and T grease respectively.

In a separate study of the low temperature thermal conductivity of Apiezon N grease Kreitman and Callahan [4] noted a glass temperature of 237 K for the grease and it was surmised elsewhere [5] that the glass temperature transitions of the N and T greases could have a bearing on the anomalies in the specific heat. The importance of the glass transition temperature in observations of the physical properties of polymers is well established and studies have indicated the possibility of predicting the fracture energy (from studies of tensile stress–strain properties) since its maximum is believed to be associated with changes in the viscoelastic properties accompanying the main glass transition. In this paper, we wish to examine data which describes the abrupt changes in heat flow mentioned in reference 3 and compare these results with the glass transition temperatures and the published specific heat anomalies.[6]

Results

Thermal conductances of N and T grease were determined using the apparatus illustrated in Fig.1. Surface A was maintained at 77 K by immersion in liquid nitrogen and the rate of heat flow through the grease G was determined from the cooling curve of the copper block S; corrections were made for radiative cooling. In Fig.2, the rate of loss of heat Q from S, which is a measure of the conductance of the grease, is plotted as a function of tne temperature of S. Sufficient pressure was applied to ensure good contact but not cause the grease to flow out from between the surfaces. The layer of grease was of the order of 0.02 cm

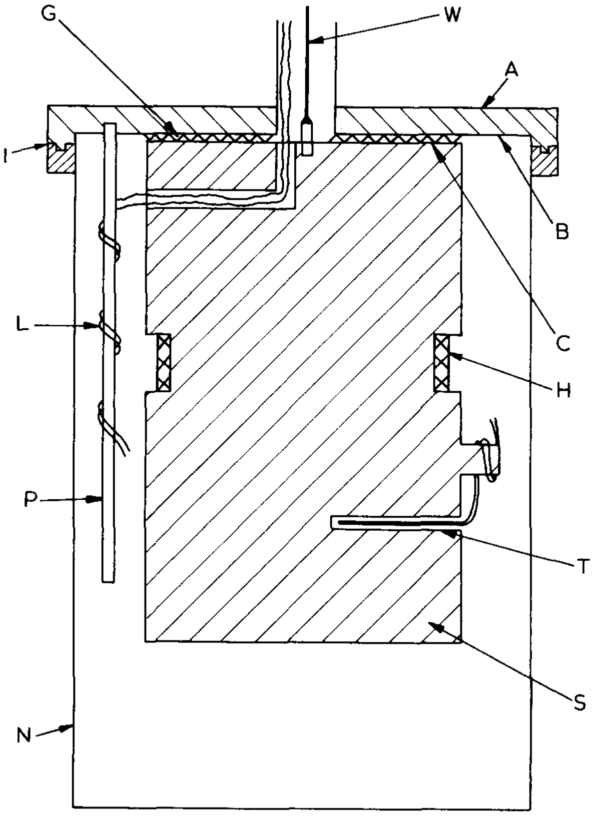

Fig.1 Apparatus used to determine the thermal conductance of greases
G – grease, H – heater, I – indium seal (clamping device not shown), L – leads, N – vacuum-tight chamber immersed in liquid nitrogen, P – thermal strapping post, S – copper block, T – platinum resistance thermometer, W – Suspension wire, A, B – surfaces of the chamber top, C – surface of the copper block

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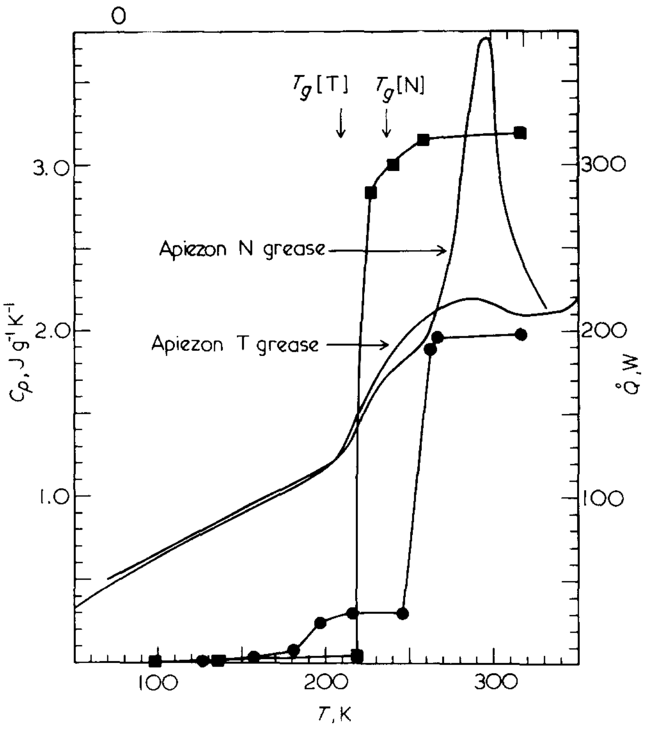

Fig.2 Glass transition temperatures, thermal conductance and specific heat of Apiezon N and T greases. Smooth curves represent the specific heat data of references 1 and 2
●—conductance of N grease; ■—conductance of T grease

thick. Abrupt decreases in the conductances of Apiezon N and T greases were observed as shown in Fig.2.

The glass temperature, T_g, was determined by Kreitman [5] as that temperature at which the grease became hard when a small quantity of the grease was gently prodded with a wire as the temperature was slowly decreased through the transition. Details of the measurement technique have been described previously.[5] Values of T_g(N) = 236.5 ± 0.5 K and T_g(T) = 209.5 ± 1.0 K were found for the N and T greases, respectively; these are included in Fig.2.

Fig.2 also contains the published heat capacity results of Bunting, Ashworth, and Steeple [1] on Apiezon N grease and the results of the earlier work by Westrum, Chou, Osborne, and Flotow [2] on Apiezon T grease.

Discussion

The physical properties of polymers and factors influencing the glass transition temperature have been discussed by Bueche.[7] Boyer [8] has shown for partially crystalline polymers that the glass transition temperature and the melting temperature T_m, are linearly related with diluent as a common parameter. Tabulations of the ratio T_g/T_m have been given by Beaman,[9] Boyer,[8] and Bueche [7] for a number of polymers, and it is well known that $0.50 \lesssim T_g/T_m \lesssim 0.75$. T_g/T_m is observed to be close to 0.5 for symmetrical polymers, while for unsymmetrical polymers, the ratio is close to 0.7.

Using the values of T_m obtained from the supplier,[10] ratios of 0.75 and 0.53 are obtained for the N and T greases, respectively. If the Boyer–Beaman rule is applicable, it may be surmised that the T grease is a more symmetrical structure. (The composition of the greases previously have been discussed briefly.[1,2]) This observation is also supported by the experimental data in Fig.2 since the specific heat and the heat conduction curves for the N grease both clearly indicate the presence of a secondary peak.

The thermal expansion coefficient (associated with the slope increase of the specific volume versus temperature curve at the glass transition) is larger above T_g, and the specific heat and the thermal conductivity is expected to be increased also. The rise in the specific heat curves immediately on the high temperature side of T_g in Fig.2 conforms to these expectations. (It is surmised that the rise in the heat conductance curves also coincides with the glass temperatures, since these curves are believed to be displaced too far to the right for reasons to be given below.)

The size of the slope increase mentioned above is less for samples with greater amounts of crystallinity, and therefore, it may be taken as a rough indication of the amount of crystallinity in a particular sample. The sizable increase in heat capacity above T_g indicates that both grease samples are not highly crystalline and this indication is supported by the fact that their glass temperatures were easily observable. Nevertheless, some crystallization has occurred as the sample has been cooled between T_m and T_g, and it has been suggested [5] that the main peak ($\sim$296 K) in the heat capacity of the grease is due to partial crystallizations.[11]

In regard to crystallization kinetics and mechanisms, it is known for polymer segments in bulk amorphous systems, that the crystallization temperatures are observed to range from 40 to 70 K above the glass temperature, and in this temperature range, a strong increase in the free transport activation energy with temperature is expected. Using these values, we obtain crystallization temperature regions of 250–280 K and 277–307 K for the N and T greases, respectively. It may be observed that these regions are found to occur within the anomalous regions of the heat capacities.

The comparative decreases in reproducibility reported [1,2] for the regions of the heat capacity anomalies might be explained by slight variations in the sample cooling process. Such variations could lead to small variations in crystallization which in turn would cause variations in the heat capacity. However, in regard to the measurements on the T grease, it should be noted that, although the authors did not employ the full capability of their measuring techniques, nothing was observed to indicate that the thermal history was relevant – either in cooling down or warming up.[12] It appears that the crystallization variation effect, if present, is small enough to escape detection even by sensitive measurements.

The problems of conductivity in amorphous or semicrystalline polymers has recently assumed considerable importance. The electrical conductivity of polyelectrolyte polymers has been observed to vary linearly with temperature with a break in slope in the vicinity of the glass transition temperature.[13] The thermal conductivity, λ, of most polymeric materials also shows a definite change in slope at the glass transition temperature. Although there is considerable variation in the measured values of the thermal conductivity reported by various investigators (variations may arise due to differences in sample preparation, mean molecular weight polymer morphology, presence of diluents, etc), a clearly defined maximum value, λ_{max}, is often found in the immediate vicinity of the reported T_g.

The relationship between the sharp increase in thermal conduction and the glass temperature is very clear for the greases in Fig.2. Abrupt and reproducible increase in thermal conductance were observed at block temperatures of 246 K and 219 K for the N and T greases, and it is noted that the difference between these two temperatures is identical to the difference of 27 K between T_g(N) and T_g(T). Subsequent estimates of the temperature difference between surfaces A and B of the chamber top inferred mean grease temperatures of 233 ± 10 K and 211 ± 10 K (for N and T grease respectively) for the thermal conductance increases. It is surmised that the anomalies in thermal conductance in fact occur exactly at the glass transition temperature. It must be observed that the large increase in the thermal conductance of the grease at T_g should not necessarily be interpreted as caused by a correspondingly large increase in thermal conductivity. Such a conclusion would be contrary to the λ_{max} results found to occur at or near T_g for various polymers and glasses. However, much of the decrease in heat flow at T_g could arise from a favourable differential thermal contraction, since a change in the coefficient of thermal expansion at T_g is expected. In order to separate these two effects, thermal expansion and thermal conductivity experiments are necessary.

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