THERMAL ANOMALIES IN STRESSED TEFLON

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ABSTRACT

In the course of testing polytetrafluoroethylene (Teflon) as a calorimetric gasketing material, serendipity revealed a thermal anomaly in stressed film that occurs concomitantly with the well-documented 25 °C transition. The magnitude of the excess energy absorption, *ca.* 35 cal/g, is suggested to be related to the restricted thermal expansion of the film.

INTRODUCTION

In the course of low-temperature heat capacity measurements on Rb_2SbBr_6 and Cs_2SbBr_6 to be reported[1] elsewhere, we undertook an investigation of polytetrafluoroethylene (PTFE) film used as a calorimetric gasket. Heat capacity measurements on PTFE have shown there to be two room temperature transitions, the larger at about 20 °C and the second, smaller, at about 30 °C. The total excess enthalpy of these two transitions has been found[2-7] to lie between 1.2 and 2.8 cal/g and to be a function of the percentage crystallinity of the sample. Indeed, Kuroda and Sakami[7] have found a linear relationship to exist between the excess enthalpy and the density of the sample (which, in turn, is directly proportional to the percentage crystallinity). Defining a 100% crystalline sample as one having a density of 2.315 g/cm³, an extrapolation of their data predicts a total excess enthalpy, ΔH_{xs}, of 3.2 cal/g. However Marx and Dole's measurements[2] on a highly crystalline powder showed a ΔH_{xs} of only 2.8 cal/g, not significantly greater than the 2.7 cal/g obtained for an 83% crystalline sample by Kuroda and Sakami[7].

Despite these anomalies, it was felt that PTFE'S mechanical and chemical properties made it a highly desirable gasketing material for our system. The excess enthalpy expected from gaskets of 0.035 g, *ca.* 0.07 cal, lies just at, or below, the observable threshold in a typical heat capacity measurement in the 20–30 °C range.

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EXPERIMENTAL

Sample

The circular gaskets (2 cm in diameter) were cut from a 0.002-in. (0.005-cm) thick sheet of PTFE film, No. 5000A Hi/D (Technical Fluorocarbons, Inc.) kindly supplied by the Cadillac Plastic and Chemical Company. They ranged in weight from 0.0341 to 0.0348 g, and were treated in no special manner before sealing.

Analyses

Although exhaustive analyses were not made, the IR spectra of both used and unused film proved to be identical with those of PTFE[8]. Furthermore, the melting point, obtained through differential scanning calorimetry, was identical with that of pure PTFE, 329°C[3].

RESULTS

The heat capacity of the calorimeter with the gasket was determined in a series of four overlapping measurements from 60 to 350°K. The normal sigmoid nature of the curve was broken by a small anomaly in the 285–300 K range (Fig. 1). These points were removed and the heat capacity from 60 to 285 K fitted by a least squares polynomial of degree seven. The points above 300 K were fitted with a least squares polynomial of the first degree. Of note is the observation of one transition, complete below 30°C, the temperature of the second room-temperature transition in PTFE.
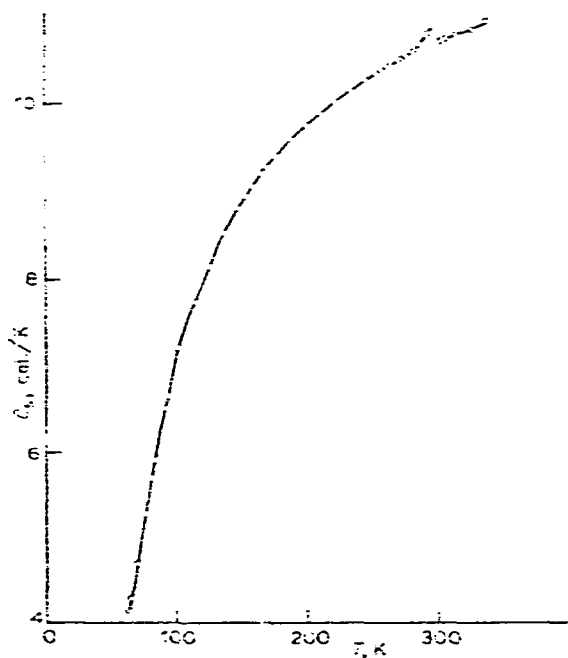

Fig. 1. The heat capacity of the "empty" calorimeter.

Upon cooling to below 280 K and reheating through this region the effect was reproduced. The average excess enthalpy for these runs was 1.2 ± 0.3 cal (Series I, Table I). Given the mass of the gasket this is equivalent to $ca.$ 35 cal/g.

The calorimeter was removed from the cryostat, loaded with 1.0581 g (corrected to vacuum) of shredded film, fitted with a new gasket, sealed, and reloaded. The three sets of runs contained in Series II were made through the anomalous region. The first runs (Series II A) were those in which the calorimeter was cooled to just below the transition region and measurements made from there. Since in both Series II B and II C the calorimeter was cooled to well below the transition region, to 90 K and 150 K, respectively, before the runs were begun, the difference in thermal pretreatment forced us to eliminate the results of Series II A. Also, in cooling well below the transition region, it is felt that the large molecules, of which Teflon is consitututed, are better able to achieve an equilibrium situation before measurements are begun. The average $\Delta \bar{H}_{xs}$ for Series II is then 2.2 ± 0.3 cal, when corrected for the small amount of excess enthalpy above the highest measured temperature.

Series III is a series of runs made by replacing the shredded film with 1.3864 g (corrected to vacuum) of manually stretched Teflon film and changing the gasket. Runs A, B, and C were all treated similarly in being cooled to far below the transition region and heated up to begin the measurements. Run D was made one month after A, B, and C, and showed no evidence of a relaxation process having taken place. The average ΔH_{xs} for the stretched Teflon film is 2.4 ± 0.3 cal. Heat capacities in the anomalous region are depicted in Figure 2. The increases in ΔH_{xs} for series II and III can be attributed wholly to the greater mass of film added. It is, then, apparent that manual stretching does not produce more than an immediate stress, and the stretched Teflon may be regarded to be no different than the shredded Teflon.
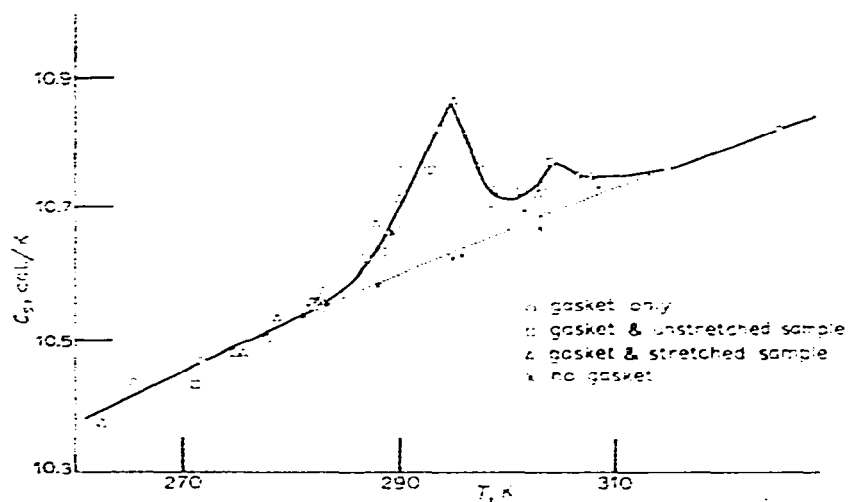

Fig. 2. Heat capacities in the anomalous region.

TABLE I

VALUES OF ΔH_{xs} FOR TEFLON

Experiment	ΔH_{xs} (cal)	$\Delta\bar{H}_{xs}$ (cal)
Teflon gasket		
Series I		
A	0.85	1.2±0.3
B	1.51	
Teflon gasket plus Teflon film		
Series II		
A	1.38	
B	2.14	2.1±0.3
C	1.97	
Teflon gasket plus stretched Teflon film		
Series III		
A	2.13	2.4±0.3
B	2.28	
C	1.99	
D	2.37	

What was observed, then, is ; (a) an excess enthalphy of 1.2±0.3 cal for a gasket of 0.0348 g, or about 35 cal/g, gained between 285 and 300 K and (b) almost normal ΔH_{xs} values of 0.95 and 0.83 cal/g for the unstretched and stretched samples, respectively, over the 285–313 K range.

DISCUSSION

Two obvious discrepancies exist between this work and previous studies. The excess enthalpy for the bulk film appears to be slightly lower than reported values, and a ΔH_{xs} of ca. 35 cal/g for the gasket is unique.

The easier to explain is the small ΔH_{xs} for the bulk material. Since it has been established that the enthalpy of transition is a function of the percentage crystallinity, a smaller ΔH_{xs} would be expected if the sample were less crystalline than those examined previously. Crude density measurements, together with a comparison of the IR bands[8] suggest that the sample used in this study was of a lower percentage crystallinity, about 39%, than those on which measurements had been made previously. If a cooperative transition from crystalline to amorphous can be assumed to occur with an enthalpy of transition, ΔH_t, dependent on the mole fraction of the polymer which has already undergone the transition, i.e.

$$\Delta H_t = A(1-X_a)^n = AX_c^n \qquad (1)$$

where A is a constant, X_a the mole fraction of polymer which has become amorphous, and n the power of the dependence of the enthalpy of transition on the mole fraction, or the sharpness of the transition, values of A and n can be determined approximately.

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Since there are only two forms involved the change in state is represented by

PTFE(crystalline)$\rightleftharpoons$PTFE(amorphous)

and the excess heat absorption $d(\Delta H_{xs})$, is given by

$$d(\Delta H_{xs}) = \Delta H_t dX_c \tag{2}$$

or

$$d(\Delta H_{xs}) = \int_{X_c}^{0} \Delta H_t dX_c = \int_{X_c}^{0} AX_c^n dX_c, \tag{3}$$

and

$$d(\Delta H_{xs}) = [A/(n+1)] X_c^{(n+1)} \tag{4}$$

then if ΔH_{xs} values for percentages crystallinity of 50 and 80% can be introduced[2-7], a table of ΔH_{xs} as a function of the percentage crystallinity can be constructed (Table II).

TABLE II

EXCESS ENTHALPY AS A FUNCTION OF PERCENTAGE CRYSTALLINITY

Percentage crystallinity	ΔH_{xs} (calculated) (cal/g)
100	2.8
90	2.4
80	2.0[a]
70	1.6
60	1.3
50	1.0[a]
40	0.7
30	0.5
20	0.3
10	0.1

[a]Assumed values, leading to $A = 4.2$ cal/g and $n = 0.5$ for Eq. (1).

The ΔH_{xs} for a sample of such low percentage crystallinity as ours fits well within the range of values calculated.

Because the only observable is the ΔH_{xs} for the room-temperature transition on the gasket the second discrepancy is harder to explain. The physical evidence seems to suggest that the gasket was under stress, by having been placed on the lip of the calorimeter well and pressed tightly into the groove in the lid as a result of the sealing process (see Fig. 3). The presence of a transparent or nearly transparent ring in the gasket where the seal was made — a phenomenon induced either by screwing the lid on with a gasket over the orifice, or induced in the bulk film by pressing with a sharp instrument — together with the fact that other gasketing materials tried, including thinner film, were cut during the sealing process suggests that stress is, indeed,

present. The thermochemical evidence available leads to the conclusion that the elongation of PTFE at 20 °C is an endothermic process[9], but leads one to hypothesize that this energy absorption is related to stress relaxation. The room-temperature transitions in PTFE, particularly the 20 °C one, with its uncoiling of helix chains from 13 CF_2 groups per repeat distance to 15 CF_2 groups per repeat distance[10], seem likely
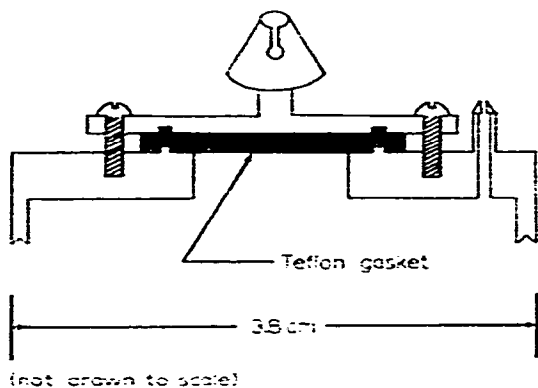

Fig. 3. Diagram of the gasket seal in the calorimeter.

candidates as stress removal mechanisms. At the present time it can only be speculated as to whether the stress was induced entirely by the sealing process, or if in fact the sealing together with the passing through a temperature region where chain movement should, but could not occur, caused the stress. The fact that the ΔH_{xs} is fairly reproducible seems to suggest the latter to be the case. But it is also apparent that the lowest temperature to which the sample is cooled affects the excess enthalpy obtained (c.f. Table I, Series IB, which was cooled to only 280 K while IA was cooled to 60 K); for other runs, however, it was found to be the case that samples cooled lower showed a larger ΔH_{xs}, so the relationship here remains a mystery. Series IIA represents measurements on a sample cooled to ca. 260 K, while IIB and IIC were cooled to and held at 100 K before C_p measurements were begun.

There is evidence[11] to suggest that deformations in PTFE are controlled by a large energy of activation. If this is the case, it is tempting to suggest the following process as taking place in the gasket; defining V_1 and V_2 as being "equilibrium" specific volumes of PTFE at some low ($T_1 = 100$ K) and high ($T_2 = 285$ K, where a mechanism for stress relaxation exists) temperatures, respectively, fix the gasket in place at T_2, cool it and hold it at T_1 for a time sufficiently long to allow its contraction to V_1, then heat it rapidly to T_2. It may be possible that relaxation will not occur quickly, and the sample will not have reattained its original volume at T_2. Then, if the relaxation can be induced concurrently with the crystalline–amorphous transition, an extra energy absorption would be observed.

$$\Delta H_{xs} = \int_{V_1}^{V_2} (\partial H/\partial V)_p \, dT = \int_{V_1}^{V_2} (C_p/\alpha)(1/V)\, dV$$

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Using room temperature values of C_p^2 and α^{12}, the isothermal coefficient of expansion, and taking V_1 and V_2 to be the volumes at 100 and 290 K^{12}, a ΔH_{xs} of ca. 29 cal/g can be calculated. The reasonable accord between this value and that observed for the gasket, suggests that a calorimeter should be developed in which larger amounts of PTFE can be held under similar stress during the measurement of its heat capacity.

ACKNOWLEDGEMENTS

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