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AN APPARATUS FOR DIFFERENTIAL THERMAL ANALYSIS OF FILAMENTOUS MATERIALS IN CONTROLLED ENVIRONMENTS

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INTRODUCTION

Differential thermal analysis is usually performed with the sample placed in a cup or cylindrical well which is in contact with a sensing thermocouple junction. Recent design trends have shown a preference for the shallowest possible sample container to reduce thermal gradients and sharpen the differential response. With this reduced volume, it is no longer feasible to dilute the sample with an inert heat transfer medium (*e.g.* alumina), and the problem of reproducible and efficient sample packing can become significant. This is especially true where the material to be analyzed can adopt a variety of bulk and surface configurations, such as is the case with bundles of textile fibers or filaments. These materials have a characteristic ability to partially resist deformation; usually by a combination of elastic recovery, inherent curl, and the resistance produced by fiber–fiber entanglements. Thus, packing fiber samples into a well or cup for DTA or DSC studies introduces some doubt as to their placement in relation to temperature or heat sensing elements. In addition, many fibers shrink, uncoil, or flow on being heated, leading to the possibility of misleading deflections in the thermal scans. Some commercial instruments deal with possible sample movement by arranging to have samples sealed in their holder cups by a crimped metal cover. Even under these conditions, we have found that most textile fibers do not permit reliable packing for good analytical results. The net effect is that fibers cannot be depended on to either make good contact with the sample holder or to maintain the same degree of contact during a heating program.

An additional problem arises for anyone interested in the thermal behavior of fibers in specific gaseous environments. Here, neither dilution with an inert solid nor crimped covering are satisfactory. In both cases there is restrictive gas flow both to and from the sample, and, if there are any volatile products formed, the sample will be responding to an atmosphere possibly quite different from that intended for the particular investigation. The technique of allowing environmental gas to flow right through a packed sample is not generally feasible with thermoplastic fibers, since shrinkage or fusion will affect the pressure drop across the sample. The resultant changes in gas flow can upset the base line and significantly interfere with accurate thermal analysis. This report describes a DTA sample chamber for filamentous materials designed to overcome the aforementioned objections.

DESIGN OF THE APPARATUS

The general design of the unit is shown schematically in Fig. 1. The major change from conventional DTA assemblies is in the mounting of the sample on the outer surface of an aluminum cylinder. The latter has been externally machined to form what is known as a square thread (thread grooves all with faces perpendicular to

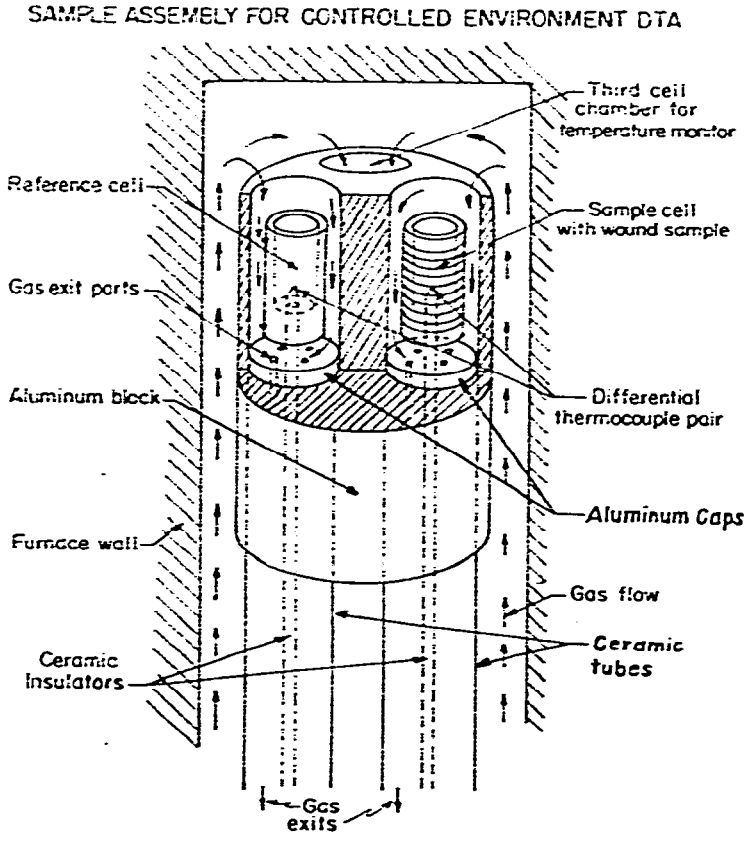

Fig. 1. Sample holder and furnace assembly for controlled environment DTA.

each other), and the sample is wound in the grooves and anchored by means of a slit cut in the end of the cylinder. In this way a length of yarn or filament can be placed securely in position without changing its structure and without the necessity of diluting it with another substance. The cylinder is drilled out as much as possible, leaving just enough wall thickness to accommodate the threads. In use, it sits on a thin aluminum disc platform mounted on the ceramic insulator containing the thermocouple (not shown in the illustration). Three identical cylinders are mounted symmetrically in the center of a vertical furnace that is open only at the bottom. Two of these cylinders are used for the sample and reference junction with a chromel–alumel differential thermocouple pair while the third serves to monitor the actual temperature by being paired with an ice-bath reference junction. The differential

thermocouple output is fed to a DC amplifier and the amplified signal to a strip chart recorder; the combination offers a maximum sensitivity of 0.125°C/inch. The temperature signal is fed directly to a second channel on the same recorder, so that simultaneous plots of ΔT and T as functions of time are produced.

The three cylinders are enclosed by a cylindrical aluminum block having three holes coincident with the positions of the three smaller cylinders. These holes are somewhat larger than the outside diameter of the sample holders and consequently, there is an annular space between the two metal surfaces. Below the sample holders, the block is supported by three ceramic tubes topped by perforated aluminum covers. The latter have supporting rims which fit snugly in the block holes and serve to keep the block in position. The parts are designed so that the block and any of the smaller cylinders can be removed and replaced securely in the same position. Other smaller holes have been drilled in the block to reduce its mass (not shown in Fig. 1).

The dimensions of each component of the apparatus were chosen through a combination of general background knowledge and some trial and error experiences. They are listed as follows, without any inference that the choices made produced optimum performance (all dimensions in centimeters).

Furnace height	19.0	Sample cylinder length	1.7
Furnace i.d.	5.5	Sample cylinder o.d.	0.8
Aluminum block length	3.9	Sample cylinder i.d.	0.6
Aluminum block o.d.	3.6	Distance between cylinders	
Aluminum block holes (diam.)	1.3	(center to center)	1.9
Distance from base platform		Distance from base platform	
to top of block	17.0	to top of cylinders	16.0

The furnace is connected to a proportional temperature programmer (F. and M., model 240) and the programming rate controlled by means of a fourth thermocouple just below the sample assembly (not shown in Fig. 1). The optimum position for this controlling thermocouple was determined by trial and error. By means of a counterweighted pulley the furnace can be lowered over the sample assembly to rest on the O-ring seal at the base platform of the apparatus. Gas is fed into the sample chamber below the aluminum block and, in order to leave the chamber, must pass up the furnace enclosure, down the annular spaces inside the block, and out the exit holes that lead down through the ceramic supports. In this way a flow of environmental gas continually passes by the well exposed sample and gaseous by-products are removed as they are formed.

EVALUATION OF THE APPARATUS

Temperature response

The ability of the apparatus to locate the actual temperatures of first order transitions has been studied using the freezing points of at least 99% pure metal wires. Each material was mounted as previously described and scanned at a heating

rate of 5°C/min. In most cases the metals were allowed to cool until a freezing exotherm was generated, and then recycled to produce another melting peak. Each metal was run at two levels of sample size, with the smaller sample wound only about the middle region of the threaded cylinder. Indium, tin, and zinc wire were used, as well as a single sample of lead ribbon for which no record of purity was available. Table I lists the on-set, peak, and interpolated melting temperature for each sample.

TABLE I

TEMPERATURE RESPONSE FOR MELTING OF METAL WIRES (°C)

Sample	*Wt. (mg)*	*On-set*	*M.p.*	*Peak*	*M.p. (lit.)*
Indium	88.7	149, 150	155, 153	157, 156	157
	165.6	153, 152	156, 155	159, 158	
Tin	64.1	224, 222	231, 229	236, 232	232
	307.0	228	233	238	
Lead	—	318, 320	323, 323	327, 325	328
Zinc	162.5	415, 415	423, 423	427, 427	419.5
	167.3	417	423	429	
	322.9	415, 415	422, 423	427, 427	

The latter was determined as the temperature (of the reference) at a point half way up the low temperature side of the melting peak. Values obtained by recycling are listed sequentially on the same line for each sample. Response to melting was quite rapid, as indicated by the small temperature intervals between on-set and peak. At the on-set the differential traces moved sharply away from the base line without the usual indication of thermal lag. Allowing for the small amount of impurities in the metal samples, the temperature response seems to be reasonably accurate.

Reproducibility of peak area

Polypropylene multifilament yarn was used in a test of the ability of the unit to reproduce the peak area of a transition. Seven runs were made under nitrogen at a

TABLE II

POLYPROPYLENE MELTING PEAK AREAS

Sample wt. (mg)	*Melting peak area (inch²/g)*[a]
33.5	20.3
33.0	20.3
32.5	20.9
30.9	19.4
29.7	18.5
27.4	20.1
27.2	18.4

[a]Mean value 19.7; coeff. of variation 4.9%.

flow rate of approximately 100 ml/min, using a scanning rate of 5° C/min. The results are shown in Table II, and indicate a high degree of area reproducibility for a sample size of the order of 30 mg.

Influence of sample size

Thermal response as a function of sample size has been evaluated by comparing the results for a series of three runs on a rayon yarn in which sample size was varied over a four-fold range. The peak under study was a sharp endotherm, coincident with partial volatilization of the material. Results are tabulated in Table III.

TABLE III

THERMAL RESPONSE FOR DIFFERENT SIZE RAYON SAMPLES

Sample wt. (mg)	*Peak temp. (°C)*	*Peak area (inch²/g)*
12.7	251[a]	35.4
26.3	250	37.2
49.3	249	33.1

[a]The material was a flame-proofed rayon and, consequently, had a relatively low decomposition temperature.

Calorimetric response

Data for the same four metals were used to determine the calorimetric response of the instrument, that is, the correlation of the generated peak area to the actual heat of fusion. Fig. 2 indicates the trend of this correlation factor (using known heats of

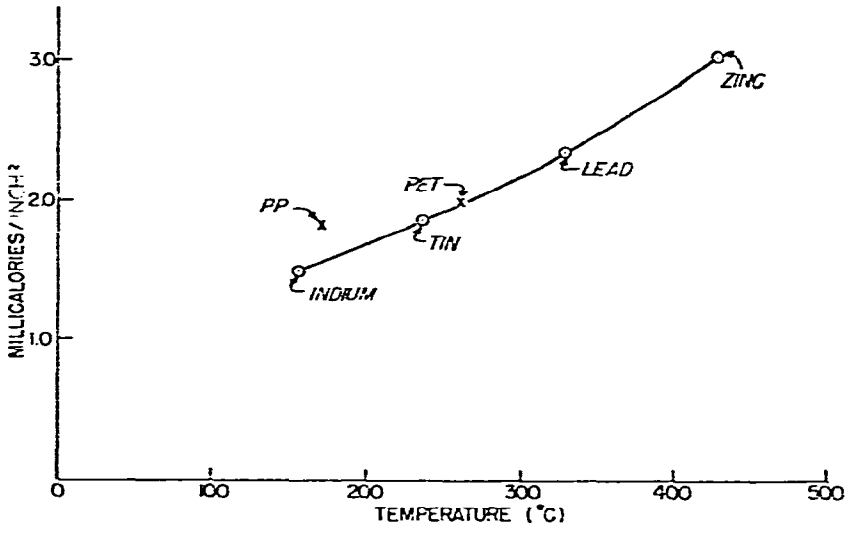

Fig. 2. Calorimetric response as a function of temperature.

fusion and expressed as the amount of heat required to generate a square inch of peak area), showing that sensitivity decreases with temperature. This is a common

characteristic for enthalpy-calibrated DTA units. Included in the plot are similar results for two yarn samples in which the polymer heats of fusion were estimated from the most appropriate literature values. Considering the uncertainty introduced by the latter, it seems that calibration using metal wires can be utilized in the determination of enthalpy effects in fibers.

Wound sample versus packed sample

The sample holder has been designed so that materials can also be packed in the conventional way; that is, inside the aluminum cylinder and directly in contact with a thermocouple. A number of materials have been tested in this packing mode, using sintered alumina as diluent and as reference material for the other chambers.

In most cases, no gross differences were observed between the results obtained by each packing method, though there was appreciably poorer base line control for the interior packed runs. In a few instances, however, there appeared evidence that the difference in environmental control was enough to change the behavior of the material. An example of this is shown in Fig. 3, which illustrates the effect of packing

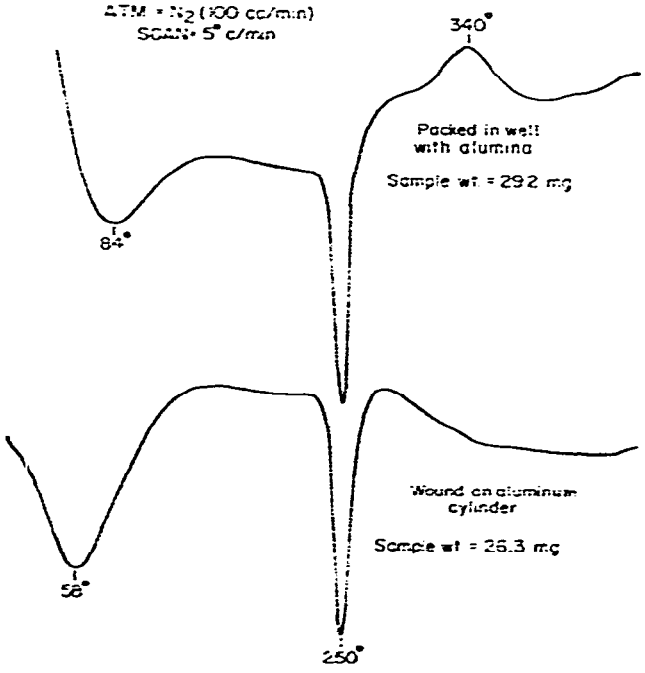

Fig. 3. Comparative DTA scans for interior and exterior sample mounting. Material: flame-proofed rayon.

on the behavior of a flame-proofed rayon. The externally wound sample, besides losing water over a lower temperature range, exhibited only an endothermic decomposition whereas the sample packed with alumina showed an additional exotherm such as it would in the presence of air. Whether the origin of this exothermic process lies in the restrictive packing or in the contact with alumina is a question still to be

resolved, yet it seems to be definite that superior control of environment is achieved with the wound sample arrangement, leading to less ambiguous thermoanalytical data.

Effect of winding tension

Most polymeric filaments exhibit longitudinal shrinkage on being heated and therefore would tend to be under increasing stress when constrained by being wound about the sample cylinder. The question has arisen as to whether this would be the cause of perturbations in the DTA thermograms. To investigate this possibility, nylon 66 monofilament samples were wound on the mounting cylinder using a range of winding tensions from 5 to 500 g per filament. This was accomplished by attaching an appropriate weight to the hanging free end of the sample and winding it onto the sample cylinder by rotating the latter. Two samples of nylon were studied, one with a high draw ratio and the other an undrawn filament (in general, drawn polymers show a greater degree of thermal shrinkage). For each combination of winding tension and extent of draw, subsequent DTA scans were indistinguishable from one another, indicating that these factors are not critical in such applications.

CONCLUSIONS

The basic concept and design of the apparatus appears to be feasible and to offer a more precise sample mounting for DTA studies on fibers and filaments. No significant loss of sensitivity is incurred, even though the sample is not in actual contact with the thermocouple. Over the range covered, peak areas are reproducible and proportional to enthalpy change, so that the apparatus is usable as a quantitative scanning calorimeter. Environmental control is improved and this should prove a source of considerable new information on the thermal behavior of fibers in specific environments.

An extremely helpful feature of the wound holder is that the sample cylinder can be removed without disturbing the mounted sample. Residue weights can thus be easily determined, post-scan material conditioned as desired, and rescanning carried out with confidence that there will be the same mounting condition as in the original scan. With only a few exceptions, materials tended to remain within the threaded grooves even after liquifying.

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