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MODIFIED SAMPLE PANS FOR USE IN PERKIN-ELMER DSC-2

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ABSTRACT

To increase sensitivity to weak transitions in polymer—solvent systems, sample pans have been developed with up to 10 times greater volume and two times greater contact area than standard hermetically sealed sample pans. The design and function of the dies to produce the pans as well as modified pan sealer are described. Examples of applications to water—polyurethane and epoxy systems are presented.

INTRODUCTION

Differential scanning calorimetry (DSC) is recognized as a standard technique for studying various transitions in polymeric systems. The small sample size employed assures the rapid attainment of thermal equilibrium and may be useful in studying new polymers where little material is available. However, occasions arise where there are very weak transitions (particularly glass transitions) which could be studied more accurately with larger samples. It has been found that this is particularly true in studies of diluent depression of the melting or glass transition which dictates the use of hermetically sealed pans. It should be noted that the standard all metal hermetically sealed sample pan provided by Perkin-Elmer affords only half the contact area of the sample pans (0.250 in. diameter) used with solids. Larger sample pans are also useful in a study of thermosetting liquid polymers such as epoxies [2,3]. In water—polyurethane systems, the problem of sensitivity and volatility of solvent becomes acute. To overcome these problems we used the larger sample pans originally designed for the Perkin-Elmer DSC-1B and subsequently employed with the DSC-2 [1]. However, effects were observed — principally large shifts in transition temperatures and broadening of melting peaks — which suggested the occurrence of strong temperature gradients. The problem was traced to the fact that the pans caught on the inner rim of the DSC sample holder, due to expansion of the lids during the sealing operation. This paper describes the modified design which solves this problem and also, for the first time, provides full details on the improved dies and procedures for the fabrication and use of these pans.

DESIGN AND FUNCTION OF DIES

The first concern is choice of the metal. Aluminum was the original material used. As long as care is taken to use very pure metal, and further, to work with nonoxidizing solvents, this is satisfactory. However, it was found that with time, sealed-in water gradually reacts with the aluminum pan leading to the loss of water from the sample. Since it occurs without a change in total weight in a properly sealed pan, the concentration of water in the sample becomes indeterminant. When one is concerned with low water concentrations this is unacceptable. Hence, our preference is to employ 99.999% pure gold foil, 0.005 in. thick, in working with water—polymer systems. Another advantage of gold is that it provides a consistently reliable hermetic seal whereas aluminum frequently does not. However, the much greater density of gold [2] is a disadvantage in working with reactive systems where rapid thermal equilibration is required.

The fabrication of both pans and lids requires four separate operations. Figure 1 shows the die used to prepunch the 7/16 in. discs as the first step in making either pans or lids. Figure 2 shows the five-station die set with which the remaining three operations are performed. The upper dies are all spring loaded to keep them raised during placement of material in each stage. The lower dies are press fit into the base. Both upper and lower dies are case hardened after machining to prevent excessive wear and to maintain dimensions. The handle is used to exert the pressure required to complete each operation and is moved from station to station as needed.

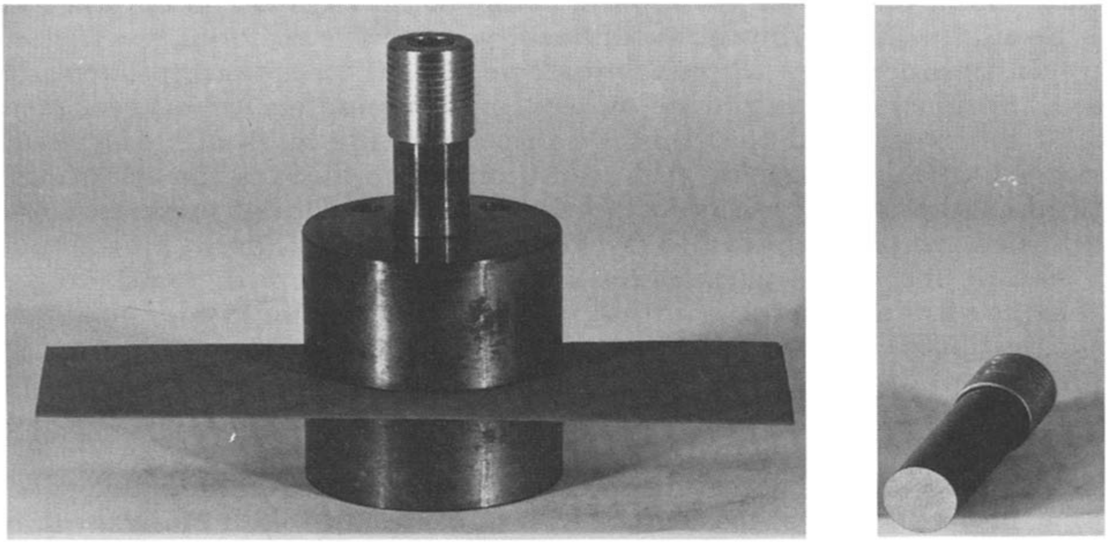

Fig. 1. Die to punch discs.

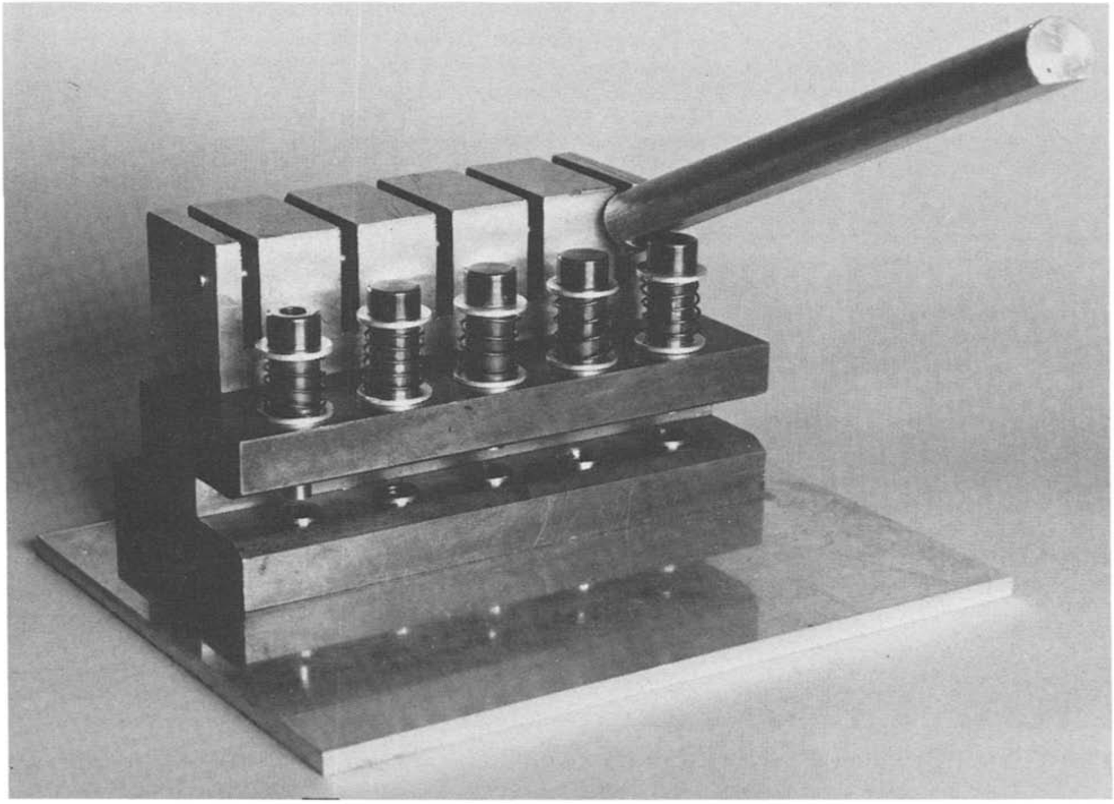

Fig 2. Five-station die set to form pans and lids

Figure 3 shows side view and face view of the upper (male) dies. Shown above each die is the metal formed (top and bottom views) following each stage. The lower dies are the female companions in stations 1, 2, and 4. The lower dies in stations 3 and 5 are hollow cylinders with sharpened edges to trim excess metal from pan or lid. From right to left the operations are as follows.

(1) Station No. 1 produces a preform which assures flatness of the portion of the disc to become the pan or lid and aids in centering the metal in the bottom die for the next stage. The disc (A) is pressed into a recess in an aluminum collar, which is then centered on the lower die. (Centering is critical in all of these operations.) The preform (B) is made by exerting pressure with the handle on the upper die.

(2) Station No. 2 forms the lid. The preform from Station No. 1 is placed in a second collar and centered on the die. Pressure is again exerted on the upper die to form the lid (C).

(3) Station No. 3 trims the excess metal to finish the lid (D). Once the lid is cut it drops through the lower die. The excess ring remains on the upper die. It has also been found that the lids can be formed and cut from the preform in one step at this station.

(4) Station No. 4 forms the pan (E). In this case, however, the preform is inverted in a second collar, which is then centered on the lower die. The

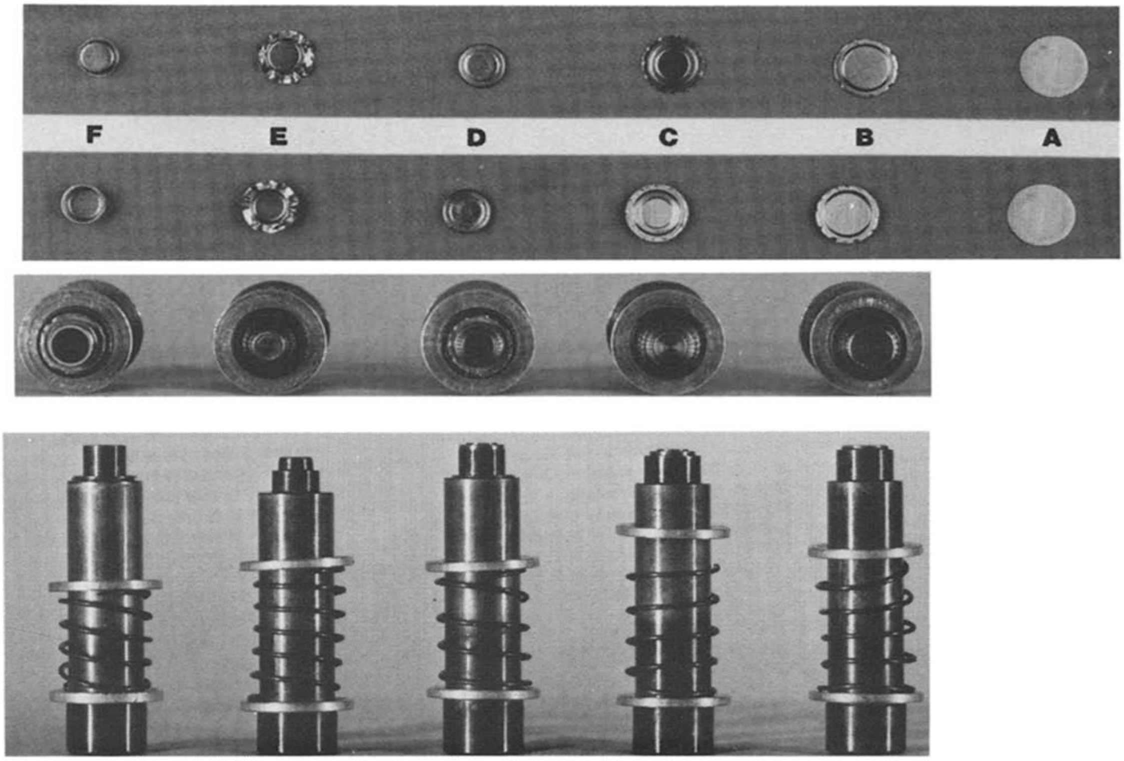

Fig. 3. Detail of upper dies and resultant metal pieces.

drawing or forming step should be performed slowly to avoid tearing the metal. The total depth of the pan may be varied by insertion of a shim of appropriate height in the bottom die. Pan depth can be varied from 0.010 to 0.080 in. (0.2—2.5 mm)

(5) Station No. 5 trims the excess metal from the pan (F). The formed pan is inverted in the upper die before cutting. This allows the die to exert force such that the sealing rim remains flat during the cutting operation.

The newly formed pans and lids should be cleaned with methylene chloride or hydrocarbon solvent to remove any grease or oils. If the sealing rim and inside of the lid are not clean a hermetic seal will not be formed. Final inner dimensions of the large compared to standard pans are. diameter 6 mm as opposed to 4 mm; height up to 2.5 mm as opposed to 0.5 mm.

SAMPLE PREPARATION AND SEALING

Use with polymer/solvent systems

Polymer discs or powder are loaded into the pan and the weight of polymer determined. Desired amounts of solvent or diluent can then be added. Care must be used to avoid any contamination of the rim by solvent or polymer or a hermetic seal will not be produced. Pan and lid are then placed in the sealer shown in Fig. 4. This sealer was a standard Perkin-Elmer volatile

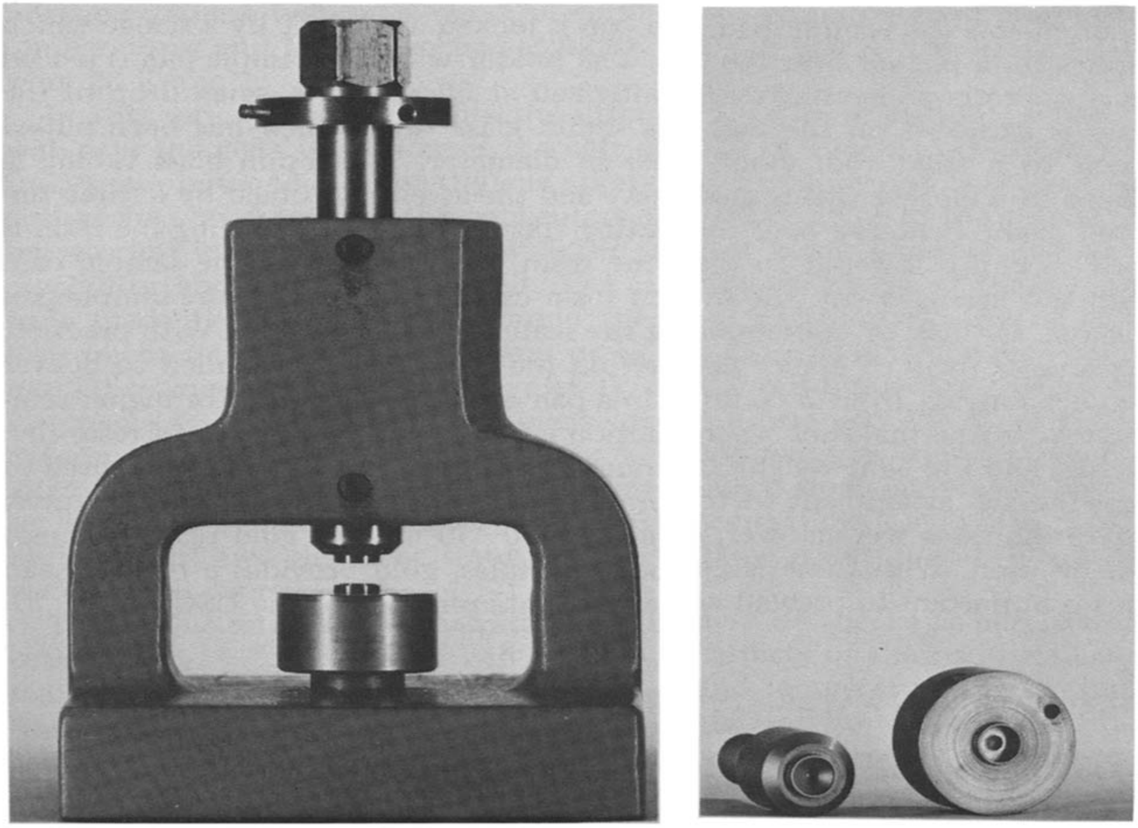

Fig. 4. Modified sealing device.

pan sealer which was adapted for the new pans. The torque necessary to cold weld the lip of the pan and lid is determined by experiment. For our gold pans 80—90 in. pounds produced good seals. The seal is formed by applying the necessary torque with click-stop torque wrench. The sealing process frequently shears the rim from the pan. If necessary, Station No. 5 of the die set may be used to remove the rim. Following sealing, reweighing will allow calculation of the actual concentration of volatile constituent added. The criterion for hermeticity of the seal with water was met by placing the sealed pan in a vacuum oven at 50°C for 1 h. A change of less than 5 μg in weight was considered evidence of a hermetic seal.

Use with thermosetting resins

Another application of these larger hermetically sealed sample cells is in the study of the curing of epoxy resins. The neat resins are tacky or nearly rigid solids at room temperature which makes transfer of small quantities especially difficult if standard hermetically sealed pans are used. The following procedure was developed with the larger pans.

A sample pan holder was fabricated consisting of an aluminum disk 1 inch in diameter and one-eighth inch in thickness with a central cavity which accomodates the sample pan. The pan is locked into place by a flange which rotates on a pin set into the disk. The holder with the sample pan is placed on a microscope heating stage controlled at 50—60°C. A small drop of the resin is gathered on the end of a 4 mm glass tube which has been pulled down to a solid rod about 1 mm in diameter. The 4 mm glass tubing is placed in a closely fitting glass sleeve and the assembly is held by a three fingered clamp centered over the heating stage. The tubing carrying the resin is then carefully lowered to place the resin in the center of the sample pan. With this arrangement, the drop of resin can be melted into the sample pan without the risk of contaminating the sealing edge of the pan. With practice, the size of drop of epoxy gathered on the rod can be controlled to deliver samples ranging from 5 to 30 mg in a pan of 0.5 mm height. For higher temperature isothermal runs where reaction is rapid, smaller samples of resin (5—15 mg) and the light-weight aluminum sample pan (30 mg) should be used to expedite the attainment of temperature equilibrium. At lower temperatures, where the rates were slower, samples of 20—30 mg and gold pans (220 mg) can be used. With these larger epoxy samples, gold provides a reliable seal. This is important to prevent accidental contamination of the DSC.

POLYURETHANE—WATER SYSTEMS

One of the many applications for these pans is illustrated by studies of polyurethane—water samples. The scans were run in a Perkin-Elmer DSC 2 equipped with its sub-ambient accessory, which was cooled with liquid

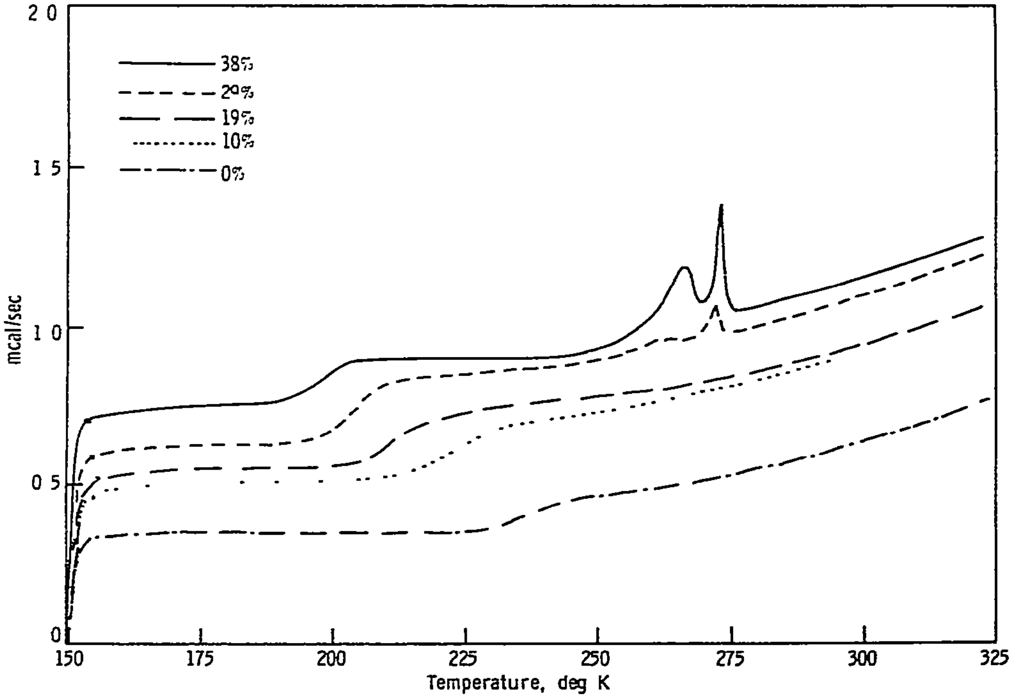

Fig. 5 DSC scans of polyether polyurethanes with various amounts of added water.

nitrogen under a helium purge. The samples were equilibrated at preselected temperatures and then quenched at 320 K min^{-1} to 150 K. The heating rates were 20 K min^{-1}.

In this series of experiments the effect of increasing amounts of added water on the glass transition of the soft segment of a methylenediphenyldiisocyanate/butanediol/polyethylene oxide polyurethane was measured. We also wished to determine the concentration at which some of the sorbed water was not interacting directly with the polymer, but was mobile enough to crystallize and subsequently melt. The larger contact area of these sealed pans made it possible to determine the glass transition readily at lower instrument sensitivity. This allowed us to scan the 175 K temperature range needed to measure both the polymer T_g, and the water melt regions in a single scan. As Fig. 5 shows, the scans are noise free and the T_g is readily determined. The decrease in T_g with increasing water content is obvious. With 29% added water, it becomes apparent that a small amount of the water is free to melt beginning at 260 K with the main peak at 273 K. This is indicative of two different states of crystallizable water in addition to the water which depresses T_g.

These illustrations demonstrate the usefulness of the large hermetically sealed pans. A future paper will explore the effects of the pan height and temperature gradients in the cell upon shape and temperature of the transitions as seen in DSC scans; further aspects of the polyurethane—water interactions have been treated elsewhere [4,5].

ACKNOWLEDGEMENTS

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