EVALUATION TECHNIQUES FOR SMALL POLYMER SAMPLES

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In earlier reports on evaluating experimental polymers, the General Engineering Laboratory has presented empirical methods for assessing the intrinsic thermal stabilities of small research samples, including those furnished in the form of intractable powders or gels (1). The more recent work to be reviewed here has been directed toward the development of methods for the further evaluation and characterization of the survivors of thermal stability testing. Again, such secondary screening methods have been chosen from among those which can be applied to small samples of indefinite form.

Of the dozen or so techniques which have been considered so far, only five will be discussed here. Two of them arose as logical extensions of the scopes of the two principal empirical thermal stability methods used in the earlier work, namely, thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The three additional techniques are: nuclear magnetic resonance spectroscopy (NMR), the micro-softening-range test (MSR) and dielectric testing.

All of these techniques, excepting TGA, have been studied as means of determining whether the survivors of thermal stability screening can be expected to retain useful properties over appropriately broad temperature ranges. TGA, on the other hand, has been applied to the problem of expressing empirically demonstrated thermal stability in terms of the kinetics of volatilization in inert atmosphere.

A single TGA graph of residual weight fraction vs temperature constitutes a rich source of kinetic data, since it is equivalent to a vast number of comparable isothermal aging curves. Much of this generous store of information is wasted, however, when the kinetic analysis is accomplished in the usual way by plotting the Arrhenius rate equation. This is because it is only in the knee regions of

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1. Doyle, C.D., Anal. Chem. <u>33</u>, 77-9 (1961)

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thermograms that slopes can be determined and matched to their corresponding temperatures with anything like reasonable precision.

To circumvent this difficulty, the equation of the TGA curve itself is used, rather than that of its slope. This expression, obtained by integrating the simple Arrhenius equation, is given at the top of Figure 1. Here, a and b are the desired kinetic constants, namely, the apparent frequency factor and the apparent activation energy for volatilization. They are found by first approximating b separately with the help of the second and third equations in Figure 1, then closing in on the value of b which affords the best fit of the equation to the experimental TGA curve. The great advantage of this procedure is that the resulting kinetic constants for a volatilization step of interest are valid over the entire step, rather than just the knee region.

The constants B and R are the TGA heating rate and the molar gas constant. The variable T is the absolute TGA temperature, preferably as measured in the sample material. The negative reciprocal thermogram slope dT/dv is measured at a point, denoted by the subscript - a, on the knee of the curve. The variable h is the true residual weight fraction calculated on the total weight fraction H lost during a particular volatilization step.

The functions p(x) and q(x), having been tabulated for the commonly encountered range of x (2), are readily evaluated. The evaluation of f(h) and g(h), on the other hand, is not straightforward, since the specific forms of these functions depend on the order of the rate process (2). Fortunately, it is frequently possible to describe matters adequately in terms of one of the simpler processes. Failing this, however, b can be determined without reference to the nature of the kinetic process by the use of the fourth equation in Figure 1. In this approach, compensation for the lack of information about the type of process is furnished by an additional data curve, namely, an aging curve determined at a constant temperature, denoted by the subscript - c, with all other experimental conditions kept identical with those of the corresponding TGA run. The equivalent life equation gives the relationship between isothermal aging times and TGA temperatures at equal residual weight fractions, as denoted by the subscript - i.

The reason why it is possible to determine b for undefined kinetic processes by using the equivalent life equation is that,

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2. Doyle, C.D., J. Appl. Pol. Sci. 5, 285-92 (1961)

fortunately, log p(x) is a nearly linear function of x for values of x greater than about 20. Thus b (in Kcal) can be approximated from a plot of log t_i vs $10^3/T_i$ by multiplying its slope by -4.351 (3). Thereafter, the best-fit value of b can be sought, using tabulated values of p(x) in the equivalent life equation.

The equations in Figure 1, together with the tables of p(x) and q(x), have proven most helpful in utilizing the TGA curve as a source of preliminary kinetic information.

In considering other secondary screening test methods, interest has been centered on heat softening and such underlying causes of heat softening as relaxations and thermodynamic transitions. Of the techniques to be discussed briefly here, differential thermal analysis (DTA) is applied solely as a means of observing thermodynamic transitions, while nuclear magnetic resonance spectroscopy (NMR) and dielectric testing are used in observing both transitions and relaxations. Dielectric testing has the added advantage of affording information of immediate value to designing engineers. The micro-softening-range test (MSR) was developed as a means of observing heat-softening directly and quantitatively. As an added advantage, the mechanical creep characteristics of a material can be inferred from its MSR curve.

For the observation of transitions by DTA up to about 300°C, the sample holder shown in Figure 2 has been devised for use on an ordinary lab hotplate plugged into a temperature programmer. The unit is highly sensitive and comparatively easy to load and clean. It comprises three 3-in. dia. x ½-in. thick aluminum discs bolted together in a stack. The top disc serves to position three Baldwin-Lima-Hamilton micro-miniature thermocouples, each of which is contained in and insulated from a 14-mil dia. stainless steel sheath. The thermocouples were specially ordered with long leads to minimize the number of junctions in the heated zone.

The thermocouple sheaths terminate within ¼-in. dia. sample and reference wells equally spaced on a ¼-in. radius in the center disc. Since these wells pass completely thru the center disc, they are easily cleaned by disassembling the stack. As a further aid to cleaning, a layer of aluminum foil is inserted between the bottom and center plates.

For the observation of first-order transitions, especially the melting of crystalline materials, the apparatus shown in Figure 2

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3. Doyle, C.D., to be published in J. Appl. Pol. Sci. in 1962

has been highly satisfactory. This has held true even for those powdered polymers which shrink to as little as 10% of initial volume on melting. Second-order transitions and glass transitions, on the other hand, are usually difficult to distinguish from capriciously varying base-line drift in DTA, and in this regard, the apparatus of Figure 2 offers little or no advantage over previous designs.

Where DTA senses only changes in heat content and can, therefore, be used only in observing thermic events, such as thermodynamic transitions, NMR senses molecular motions and therefore permits the observation of both transitions and relaxations. This powerful technique has been studied briefly thru the courtesy of Dr. C.M. Huggins, of the G.E. Research Laboratory, using a family of styrene-divinylbenzene copolymers kindly furnished by Dr. G.F.L. Ehlers, of A.S.D.

The findings are presented in Figure 3, where the effect of increased degree of crosslinking is shown as an increase in the temperature of the relaxation observed at about 20 kc. In each case, this relaxation involves molecular motions which commenced at the glass transition temperature some 40°C lower than the corresponding relaxation temperature.

NMR is a fascinating research tool, but for use in general prospecting for transitions and relaxations, it has some serious disadvantages. For one thing, the method is insensitive to molecular motions at frequencies below about 10 kc, so that most of the frequency range of interest in the study of mechanical behavior is inaccessible. Further, NMR is insensitive even to transitions if sufficiently vigorous molecular motions have already begun in preceding transitions.

From the standpoint of broad practical interest, both DTA and NMR are of questionable value as secondary screening tests for experimental materials. In this view, a direct heat-softening test which sums up the contributions of all the underlying causes of heat-softening is preferable to specialized methods for observing relaxations and transitions. To fulfill this need, the micro-softening-range apparatus shown in Figure 4 was devised for use with small powdered samples.

The MSR apparatus affords means of heating the sample under a weighted foot whose vertical height is recorded continuously along with the temperature of the sample holder. The stationary assembly of the apparatus comprises an aluminum baseplate and sample holder (again designed for use on an ordinary lab hotplate), a set of three Invar 36 support columns, an aluminum topplate bolted to the housing of a Starrett No. 25-611 dial gage, which in turn, supports a Schaevitz 100 SSL linear variable differential transformer (LVDT). The LVDT is loosely supported by a ringstand clamp to permit free expansion and contraction of the stationary assembly. The movable assembly comprises an Invar 36 loading rod connected to the dial gage foot and, thru the dial gage, to the movable core of the LVDT, which in turn, supports a pan for added weights. The LVDT core can also be positioned independently on its threaded supporting stud by turning the weight pan.

Before conducting a test, the $\frac{1}{4}$-in. dia. loading foot and the inner surface of the sample cup, 5/16-in. dia. x 50 mils deep, are covered with metal foil, usually a layer of 0.5 mil aluminum. Then, with the foil pressed firmly in place and with the weighted loading foot firmly bottomed in the sample cup, the dial indicator is zeroed. Next, the sample cup is filled, and the powdered sample in tamped under the loading foot by repeatedly lifting and lowering the weight pan with the weight in place. When the dial indicates a tamped sample depth near 50 mils, and when any creeping of the sample under load has become imperceptibly slow, the recorder is zeroed by turning the weight pan, and the heating program is started.

The instruments used with the MSR apparatus are shown in Figure 5. They comprise a temperature programmer, a demodulator for the output of the LVDT and a two-channel, time-base recorder. The temperature programmer, shown on the shelf in the upper portion of Figure 5, consists of four basic units mounted in a shop-made case: a Leeds and Northrup "10170" cam-type program unit, a "Speedomax H" recorder for the hotplate temperature, a "2-Action Duration-Adjusting Type"("DAT") control unit and an H.B. Instrument Company mercury relay, Cat. No. 7080, not visible in the photo.

To the right of the MSR test apparatus in Figure 5 is the demodulator for the output of the LVDT, a Schaevitz "DM-60-C" unit, powered by a "PS12A" supply. The output of the demodulator is fed to one channel of a Varian "G-22" recorder. The second channel receives the output of the sample thermocouple, a Baldwin-Lima-Hamilton "TCS-IS-50", specially supplied with long leads.

The gratifying reproducibility and sensitivity of the MSR test are illustrated in Figure 6 for a family of emulsion copolymers of styrene and divinylbenzene, some members of which were also examined by means of NMR, as noted earlier. Figure 6 clearly shows that, as contrasted with DTA and NMR, the MSR test indicates not only the temperature range, but also the extent of heat-softening. In further contrast with DTA and NMR, which are sometimes insensitive to the underlying causes of heat-softening, the MSR test affords a consistently dependable means of determining softening temperatures. Moreover, the MSR data curve has immediate practical value as an index of the temperature range where the rate of creep under load becomes rapid.

Considerations of potential practical value, more than anything else, led to the study of dielectric testing as a secondary screening procedure for experimental polymers--in spite of all the well-documented ancient and essentially still-unsolved problems associated with measuring the dielectric characteristics of powders. Even as a means of observing relaxations and transitions in distinctly formed specimens, the scope of dielectric testing is limited by insensitivity to the motions of non-polar molecular aggregations.

Primarily as a matter of ultimate engineering interest, then, a comparative study was made of the temperature-dependence of the dielectric characteristics of compressed powdered materials and the same materials in solid disc form. The standard disc specimens carried circular silver-painted electrodes on the opposite faces. One electrode was made smaller than the other and covered with a guard electrode during the measurements to eliminate fringing capacitance and loss.

For the measurements on powders, the cell shown disassembled in Figure 7 was used. It comprises an alumina ceramic ring with a close-fitting stainless steel cylinder in the bottom serving as one of the electrodes. The other electrode is a ceramic cylinder metallized with platinum paint on the side and on one end, and with a platinum wire run thru from the metallized end to the opposite end. A guard gap 18 mils wide and 15 mils deep was machined in the metallized end.

Measurements at 1 kc on an epoxy resin in disc form and in the form of a powder under 15,000 psi are compared in terms of their temperature dependence in Figures 8 and 9. In Figure 8, it is seen that, while the apparent dielectric constant of the compressed mixture of powdered resin and air scarcely resembles that of the solid resin, the same temperature-dependence is found in both cases. Similarly, from Figure 9, the temperature-dependence of the dissipation factor is the same in both cases.

Again for reasons of practical interest, dielectric testing will be studied further in future work, with special emphasis on developing ways of measuring the true dielectric constants of powdered materials. At this writing, however, the best of the secondary screening methods developed so far are the micro-softening-range test and TGA applied as a means of determing preliminary kinetic constants. In the further development of the MSR test, it will be interesting to conduct parallel creep tests on distinctly formed specimens. Presumably the further development of TGA as a source of kinetic data would proceed along the lines of separate studies aimed at applying preliminary kinetic constants in solving practical problems involving special conditions of geometry, function and environment.

$$g(h) = \frac{ab}{BR} p(x)$$

$$x = \frac{b}{RT}$$

$$q(x_a) = H\left[\frac{f(h)g(h)}{T}\left(\frac{dT}{dv}\right)\right]_a$$

$$t_i = \frac{be^{x_c}}{BR} p(x_i)$$

FIGURE I VOLATILIZATION KINETICS EQUATIONS

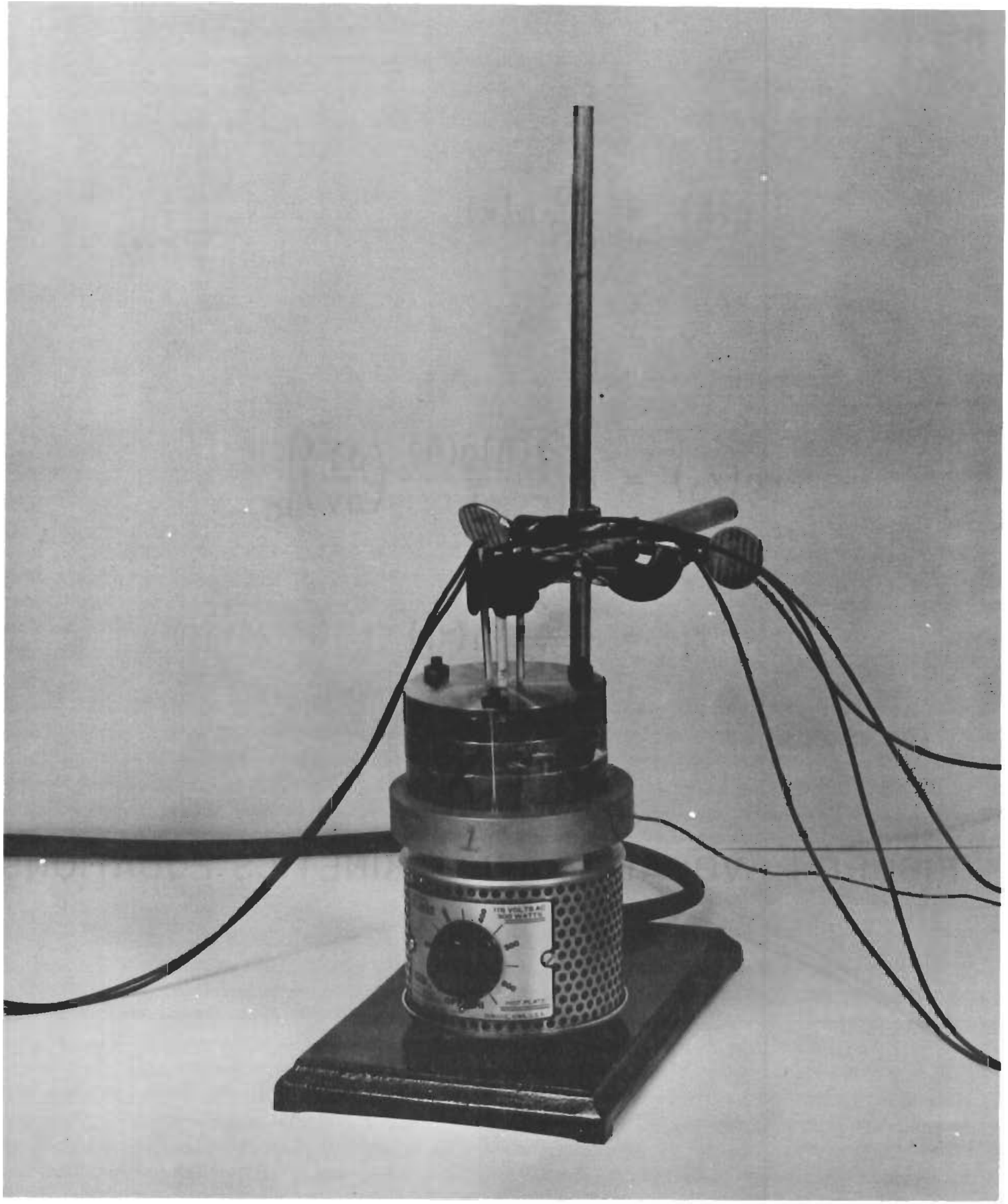

FIGURE 2 DTA APPARATUS

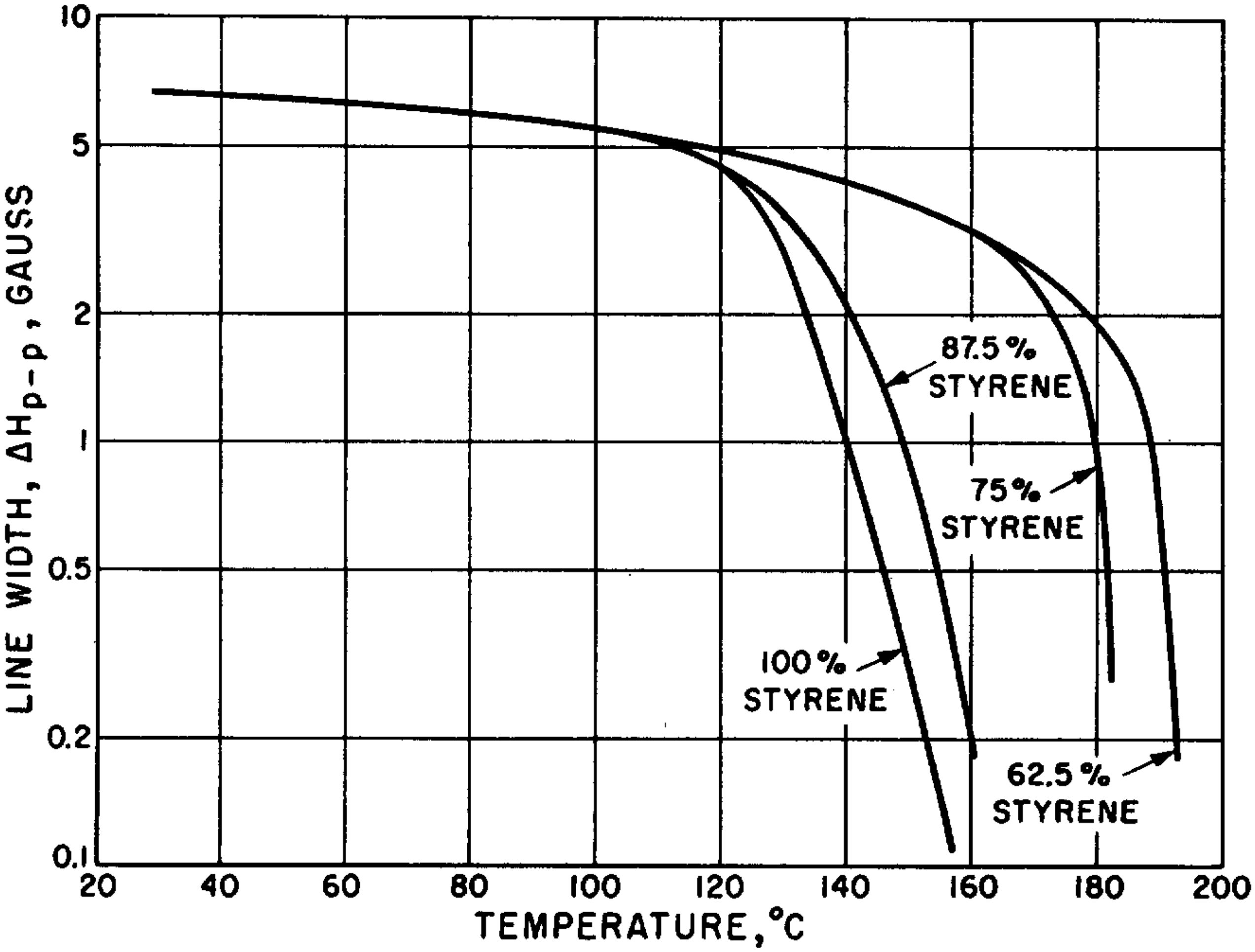

FIGURE 3 TEMPERATURE DEPENDENCE OF THE PROTON MAGNETIC RESONANCE LINE WIDTH FOR CO-POLYMERS OF STYRENE AND DIVINYLBENZENE

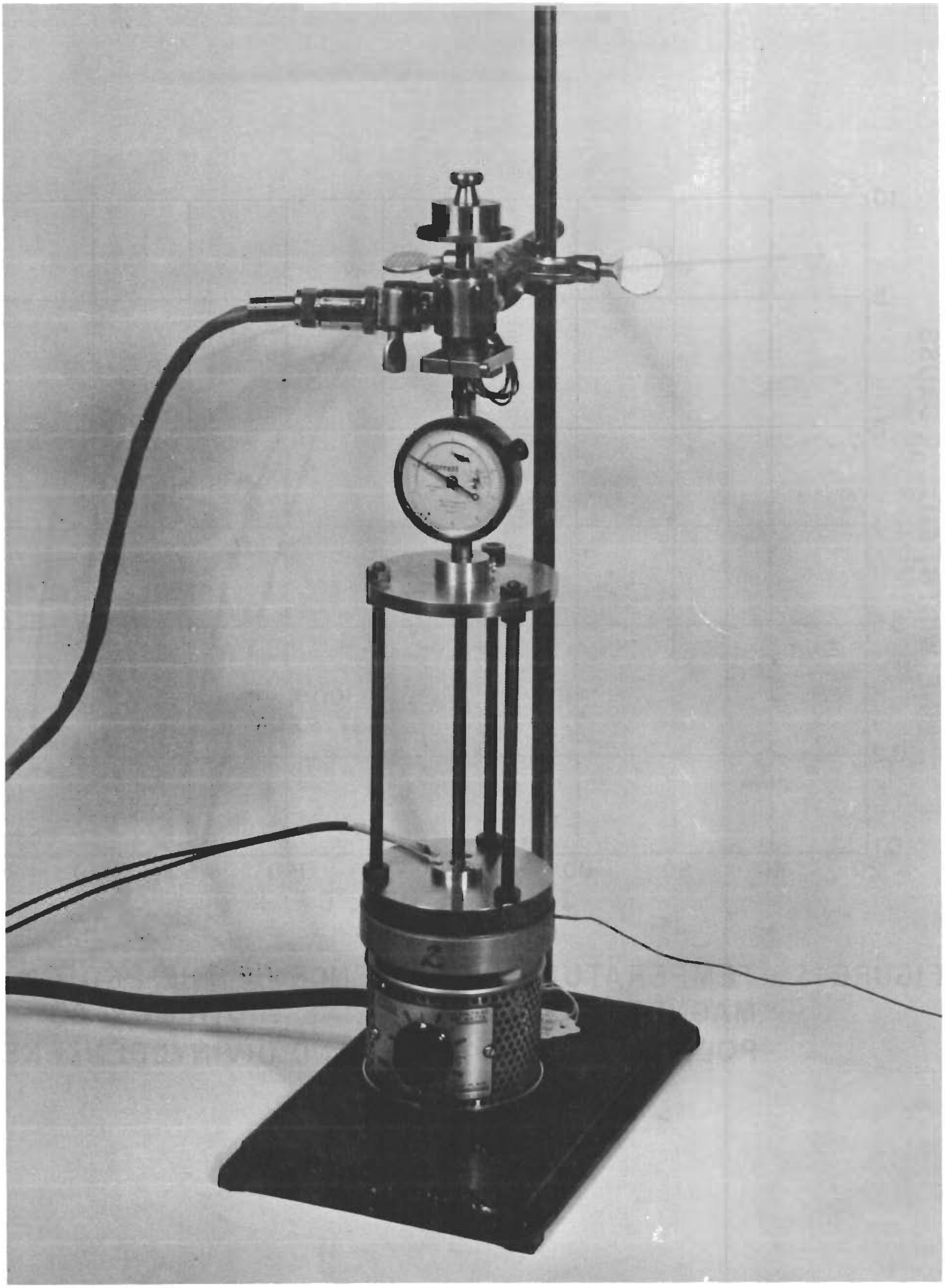

FIGURE 4 MSR APPARATUS

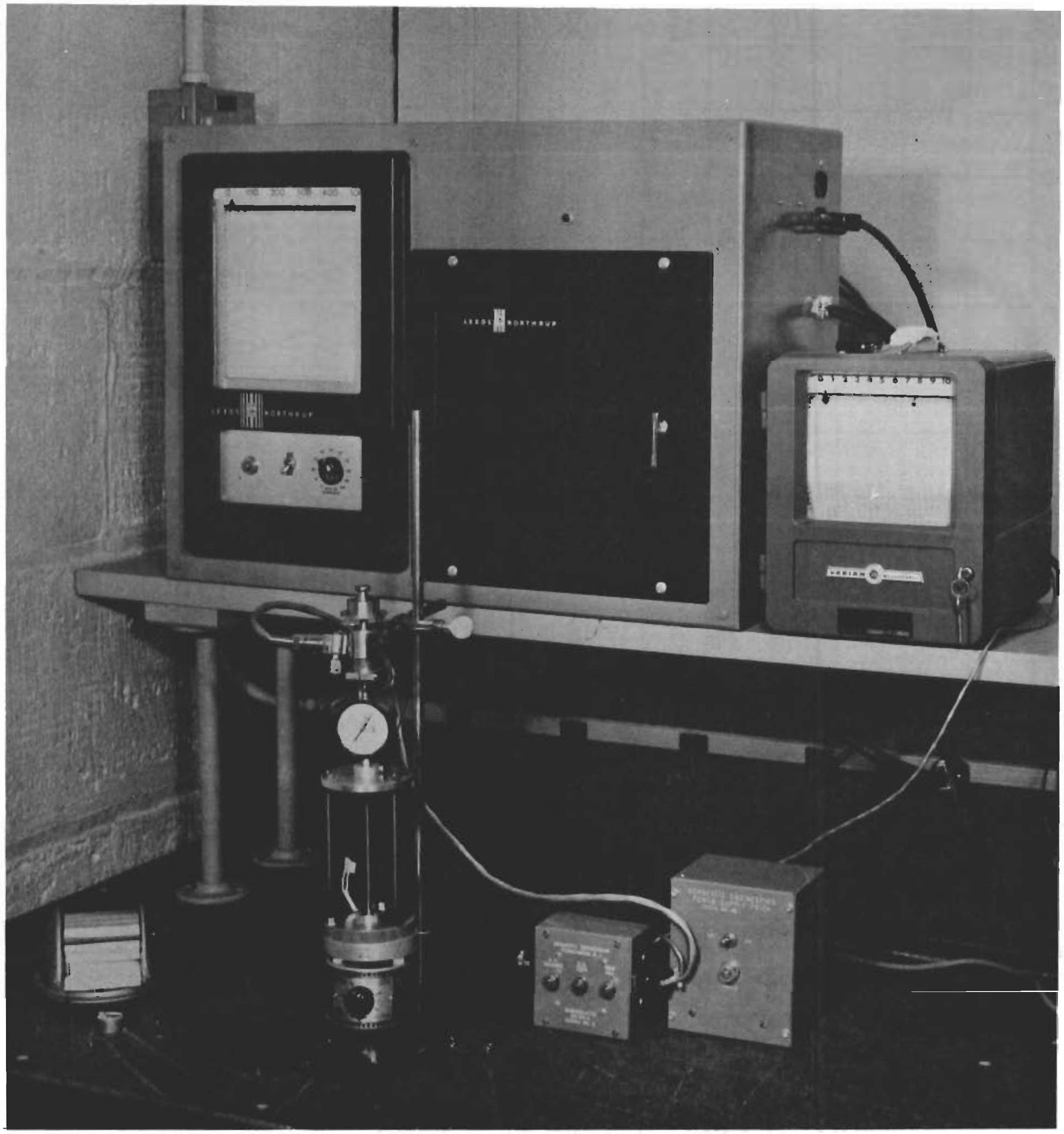

FIGURE 5 MSR APPARATUS AND INSTRUMENTATION

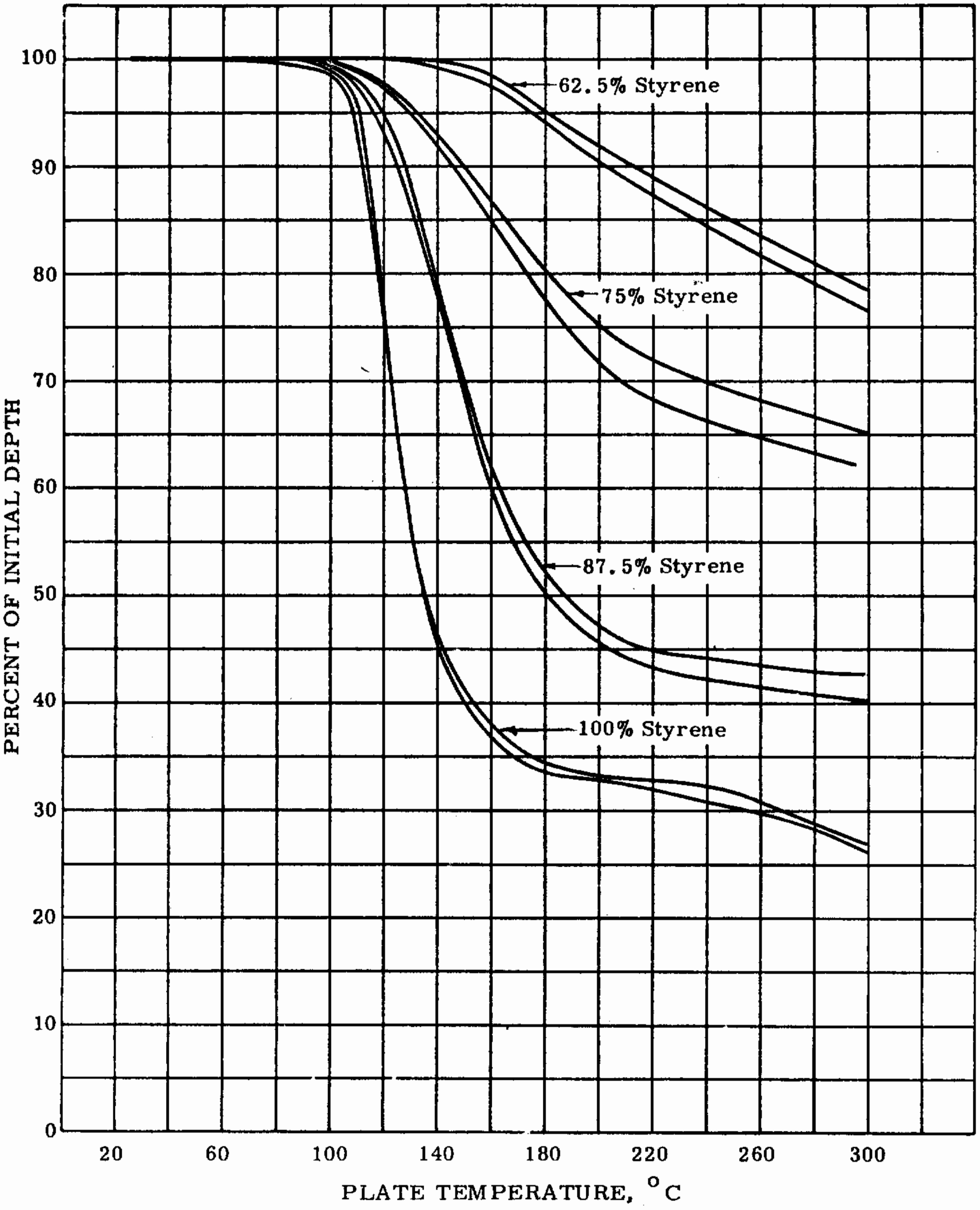

Figure 6 MSR Test at 10°C per Minute, under 100 g Added Load, Styrene - Divinylbenzene Copolymers

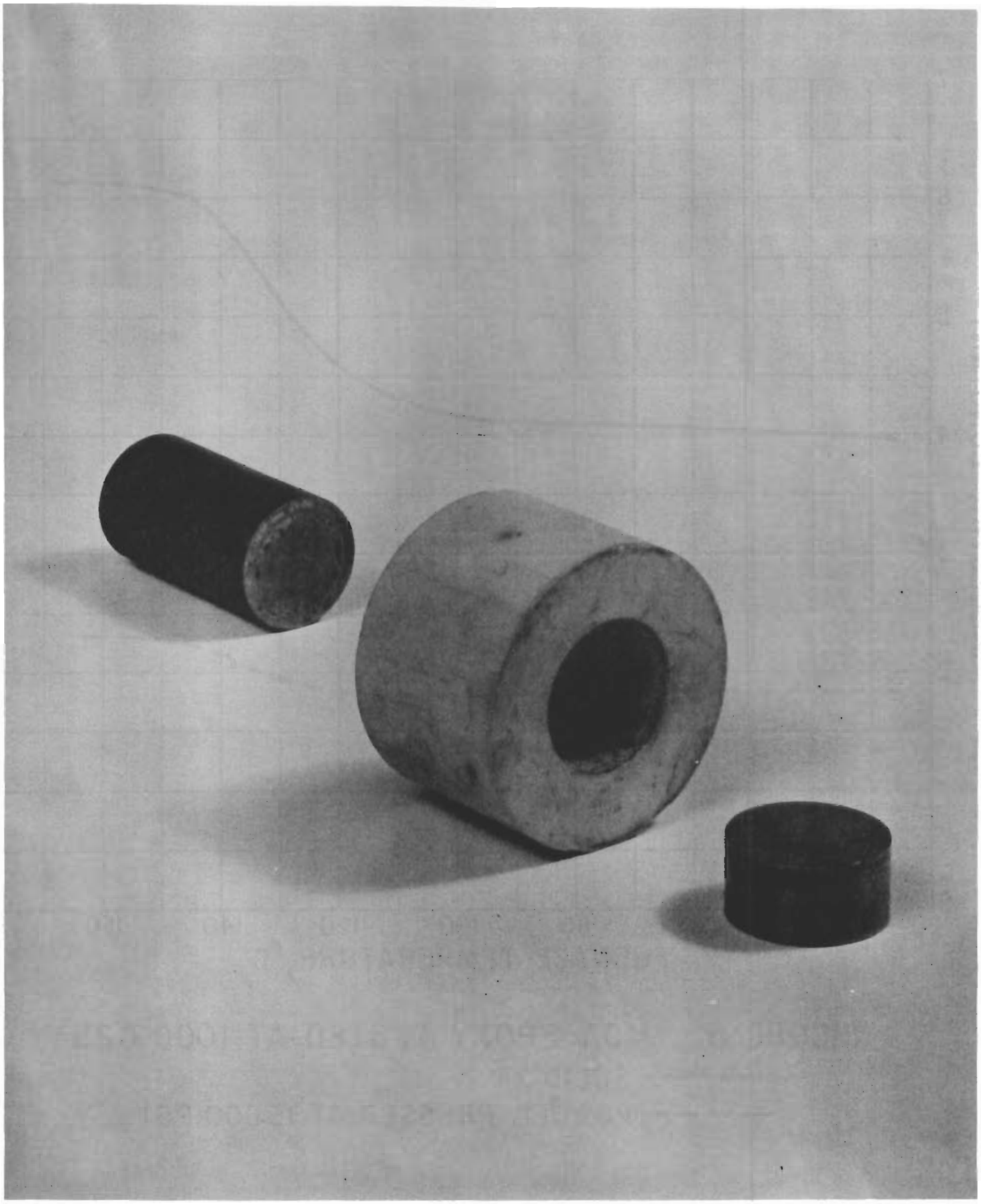

FIGURE 7 DIELECTRIC TEST CELL

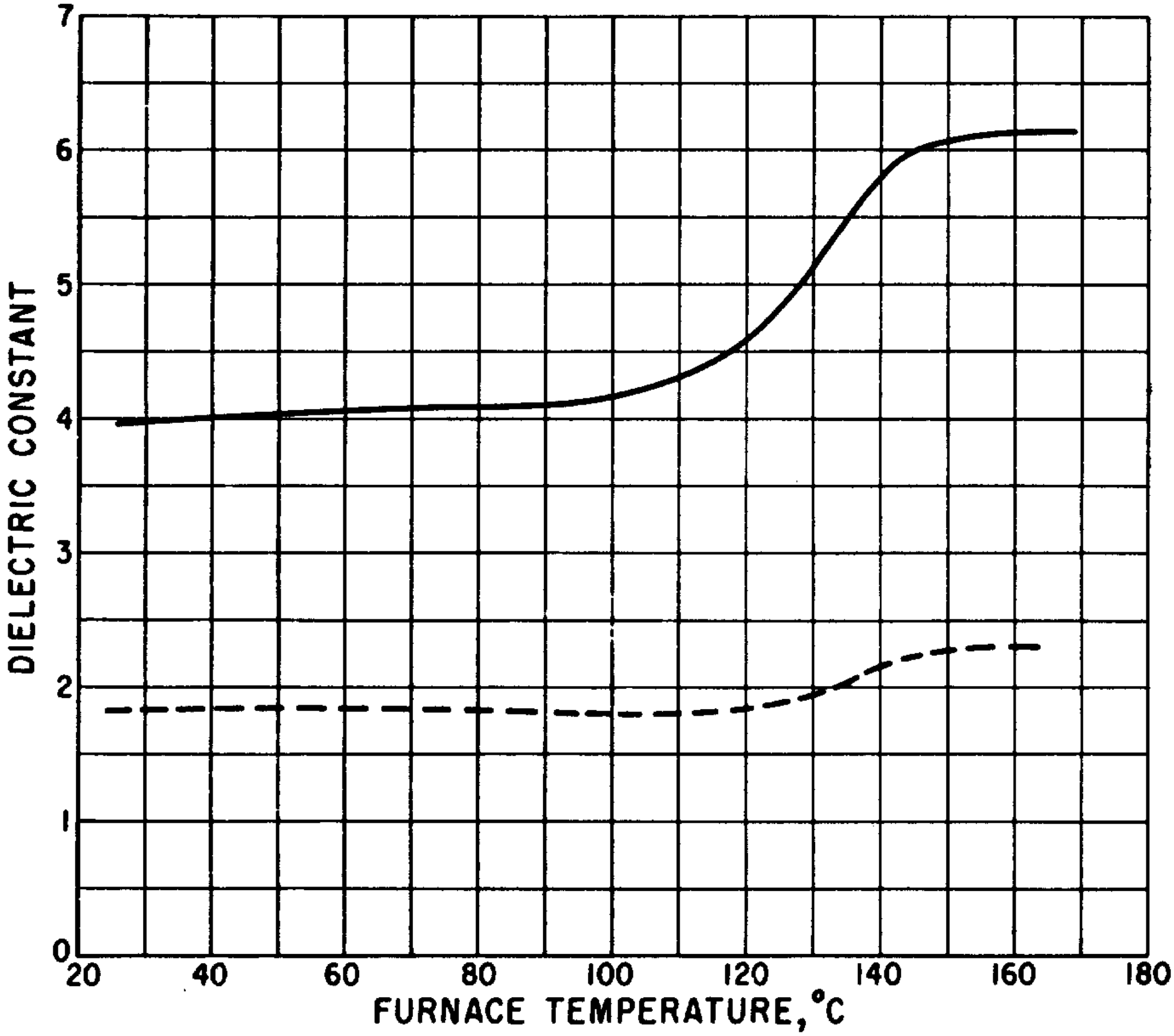

FIGURE 8 MDA EPOXY TESTED AT 1000 CPS

——— SOLID

– – – – POWDER PRESSED AT 15000 PSI

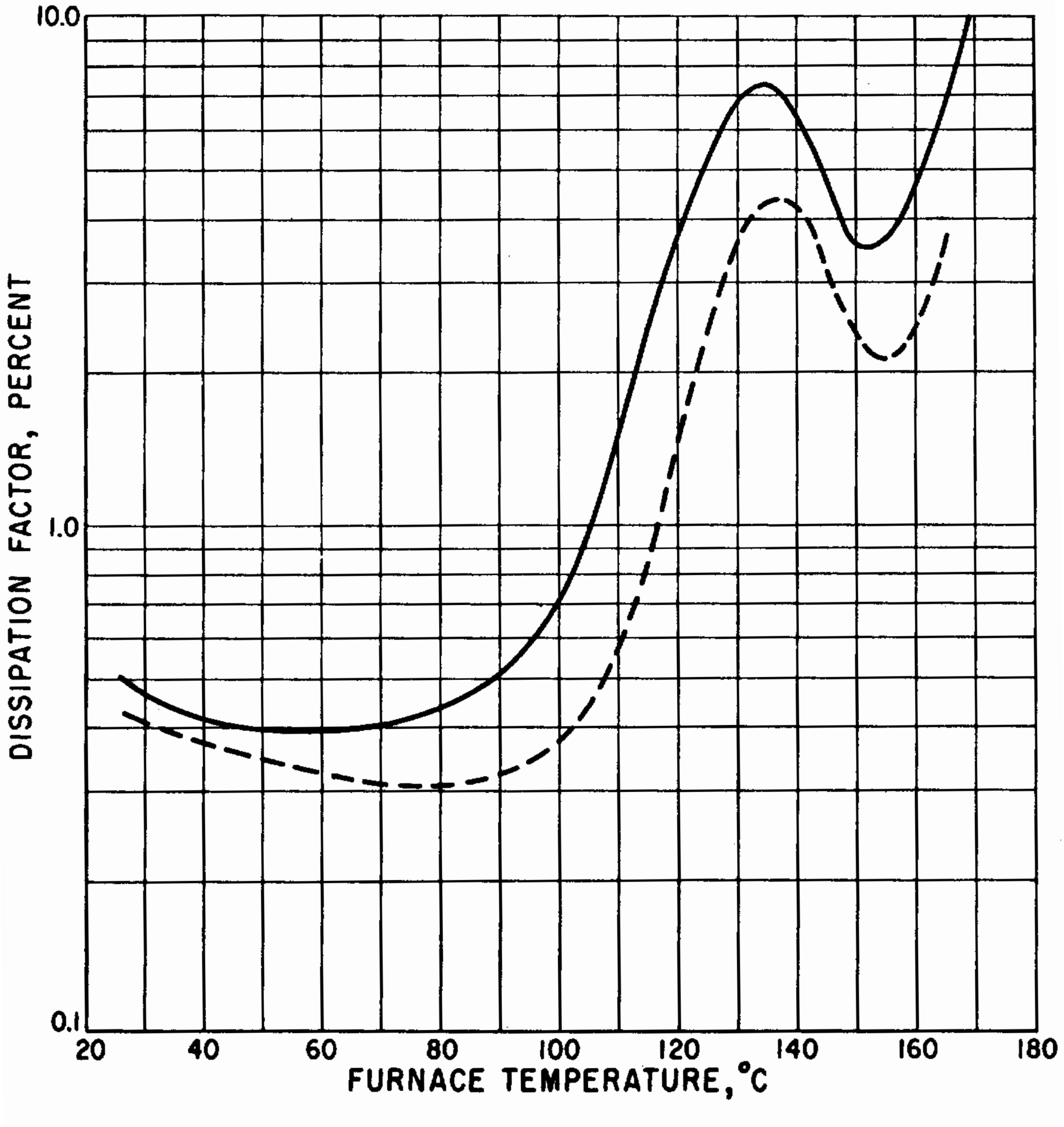

FIGURE 9 MDA EPOXY TESTED AT 1000 CPS

——— SOLID

– – – – POWDER PRESSED AT 15000 PSI