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Shrinkage Behavior of Oriented PVC by Thermomechanical Analysis

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Synopsis

This paper describes a novel application of thermomechanical analysis. Observation and measurement of the thermal recovery of stresses induced in oriented PVC by stretching at elevated temperature is achieved by the modification of a commercial TMA instrument. Employment of an electronic signal differentiation system, in combination with this instrument, permits the simultaneous recording of the rate of shrinkage as a function of temperature. Specific examples are given which demonstrate the performance of the instrument and illustrate its application to problems of practical interest, such as effects of stretching and annealing conditions on shrinkage behavior.

INTRODUCTION

Thermally induced shrinkage of oriented polymers is a phenomenon of great practical interest, since it limits the dimensional stability of plastics at elevated temperatures and also provides a convenient method of characterizing the degree of orientation. Conventional methods of measuring thermal shrinkage of oriented film or sheet samples[1–4] generally involve the introduction of samples of known dimensions into an oil bath or hot-air oven; after a given time at constant temperature, the sample is removed and its dimensions remeasured. While such procedures do yield useful results, they are tedious and time consuming; furthermore, curling or nonuniform shrinkage of a large sample can interfere with accurate measurements. Determination of shrinkage rate, or of degree of shrinkage under programmed-temperature conditions, is difficult. Consequently, a convenient method of measuring and automatically recording thermal shrinkage was sought.

Thermomechanical analysis (TMA) is a convenient technique for measuring and recording dimensional changes in polymers under both programmed-temperature and isothermal conditions. Recent reports[5,6] have indicated that TMA can be used for measurement of thermal shrinkage. We wish to report the successful modification of a commercial thermomechanical analyzer (du Pont Model 941) to permit the recording of shrinkage data. Use of an electronic signal differentiation system in combination with the TMA permits the recording of the shrinkage rate, as well as the degree of shrinkage, as functions of temperature. We have utilized the TMA technique to study the effects of stretching and annealing conditions on subsequent thermal shrinkage of oriented poly(vinyl chloride) (PVC).

EXPERIMENTAL

The sample-holding arrangement is shown in Figure 1. The sample is a rectangular section of film or sheet, typically 7 mm long and 1.5 mm wide. The sample is placed between two beryllium–copper clips, which are designed so as to increase clamping tension with increasing temperature. True sample length is the distance between the pinch points of the clips and is nominally 5 mm. The clips are mounted on the "fiber probe" assembly of the du Pont Model 941 thermomechanical analyzer. The upper clip remains stationary while the lower clip fits into the circular harness of a movable quartz frame attached to the core of a linear variable differential transformer (LVDT). The upper end of the movable member is connected to a plastic float immersed in a fluid reservoir mounted on top of the TMA support frame. The buoyancy of the float counteracts the combined weight of probe, clip, and sample.

For programmed-temperature measurements, the sample assembly (Fig. 1) is placed in the miniature furnace (air thermostat) normally used with the TMA; the furnace temperature is controlled by the programmer in a du Pont 900 console. For isothermal measurements the furnace is replaced by a small constant-temperature bath containing silicone oil, thereby minimizing thermal gradients in the vicinity of the sample. As the sample is heated, shrinkage forces cause an upward movement of the lower clip and quartz frame assembly. This movement is detected by the LVDT and the resulting signal (proportional to probe displacement) is plotted as a function of temperature or time.

In practice, operation under true "zero load" conditions leads to excessive noise, sample flexing, and probe overshoot. In order to obtain reproducible and meaningful results, it is therefore necessary to apply some tension (typically 200 mg) to the sample by placing a weight on the plastic float. This tension can be

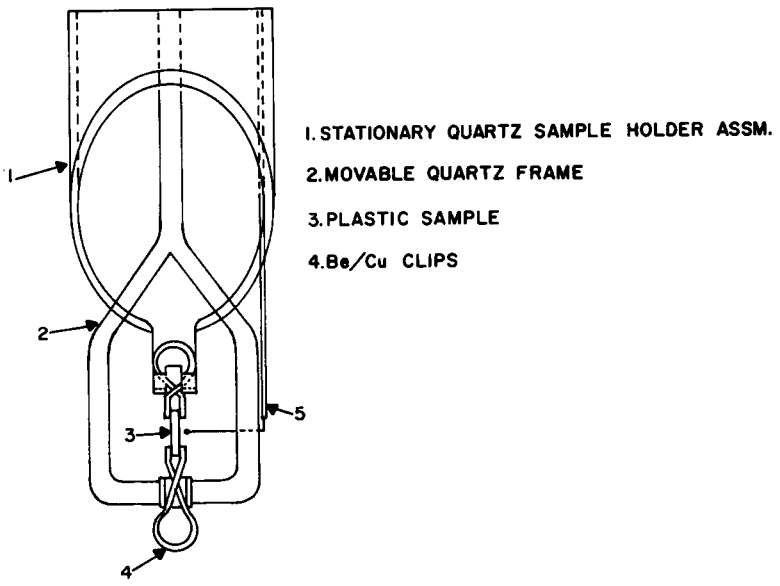

Fig. 1. Sample holder for shrinkage measurements.

sufficient to cause elongation and eventual failure of the sample in the range of 150° to 200°C.

The electronic signal differentiator was developed at Owens-Illinois for the express purpose of generating time derivative curves of the probe movement signals from the du Pont 900 console. Simple modifications of the du Pont console allowed direct transfer of x-axis, sample temperature, signals to an auxiliary recorder. Time derivatives of y-axis signals from any of the du Pont thermal analytical instruments are plotted against sample temperature through the signal differentiator on the auxiliary recorder. In the experiments described in this paper, the y-axis represents probe displacement.

The PVC composition used in this investigation was supplied in sheet form by American Hoechst, Inc., Delaware City, Delaware, and contained less than 1% total additives (stabilizer and lubricant only). Sheet samples were subjected to uniaxial or biaxial extension via a film stretching instrument at elevated temperatures of from 90° to 120°C.

The film-stretching instrument (LET) was developed by the T. M. Long Company of Somerville, New Jersey. It consists of two draw bars operating at right angles to each other by hydraulically driven rams. The four edges of the sample specimen are attached to the opposed moving and/or fixed draw bars by clips. Stretching may be accomplished either uniaxially or biaxially at a constant rate of from 0.05 to 20 in./sec, and at a constant force of from zero to 25 pounds per inch of edge before stretching. Samples can be heated uniformly to temperatures in excess of 200°C in a matter of minutes.

In an attempt to improve upon the orientation effect induced in the PVC by the LET, some of the samples were subjected to a process referred to as "heat setting," wherein the sample is stretched and held at temperature for a period of time before quenching. (The stretching temperature not necessarily being the same as the heat-set temperature.)

RESULTS AND DISCUSSION

Figure 2 shows measured shrinkage curves of samples cut from two different uniaxially oriented sheets of PVC. Stretching was performed at 100°C, with the sheets unconstrained in the direction perpendicular to the direction of stretch. One sample (2X) was obtained from a sheet stretched to twice its original length, the other (3X) from one stretched to three times the original length. Measurements were performed in the direction of stretching. In each case, the total shrinkage (obtained at ca. 140°C) corresponds, within experimental error, to a return to the original length of the sample prior to stretching, e.g., the "2X" sample shrinks to half its length. Control runs made on unoriented samples produced a flat base line through the temperature range of interest, thus indicating minimal preorientation as a result of the sheet forming process.

Figure 3 shows the shrinkage curves of two similar biaxially oriented PVC sheets stretched at different temperatures (105° and 115°C, respectively). Each sheet was stretched to three times its original length and twice its original width, with the shrinkage measurement being performed in the direction of greater stretch. The corresponding differential (shrinkage rate) curves are displayed in Figure 4. The sample stretched at the higher temperature tends to exhibit shrinkage at higher temperatures.

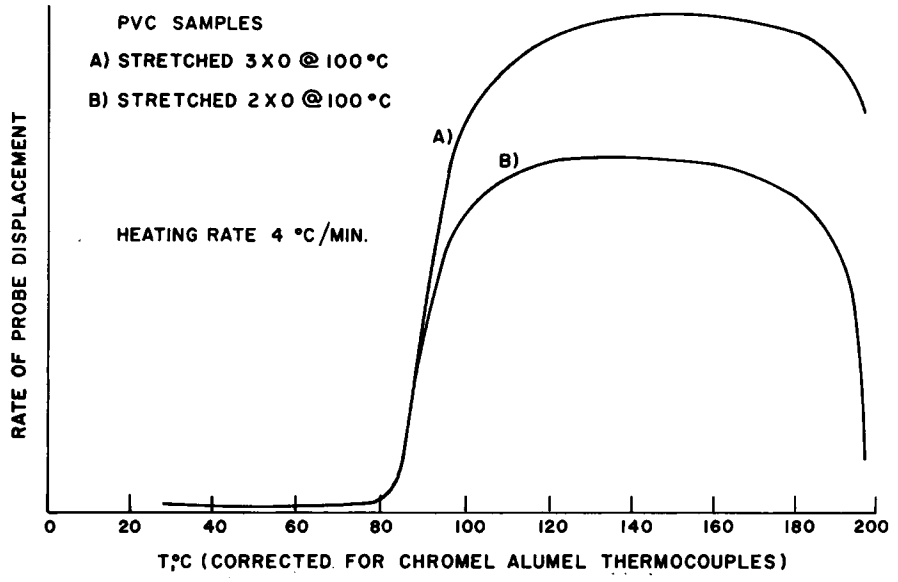

Fig. 2. Effect of degree of stretch on shrinkage of unaxially oriented PVC.

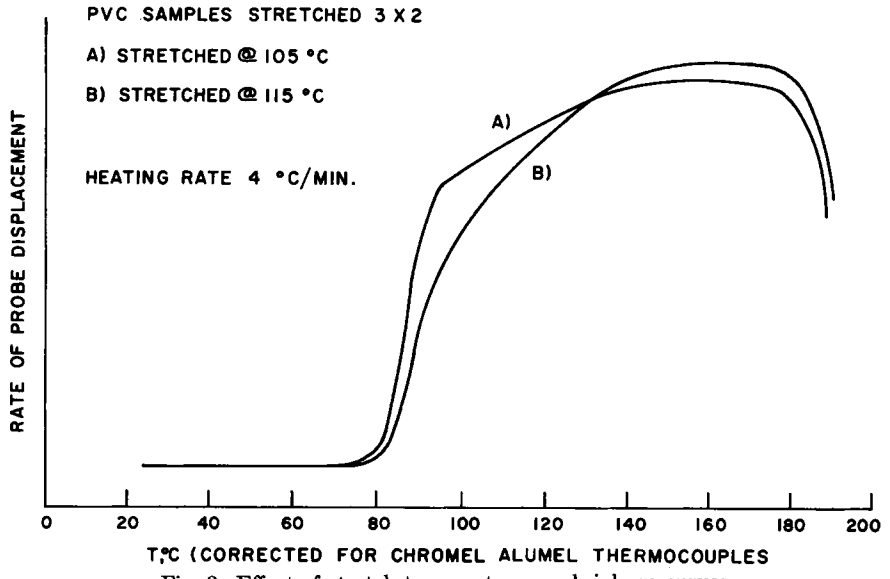

Fig. 3. Effect of stretch temperature on shrinkage curves.

Still more pronounced effects on shrinkage are caused by "heat setting" processes, wherein a film or sheet is stretched at elevated temperature and subsequently restrained in the stretched, heated condition for a period of time. Figure 5 shows the shrinkage behavior of three different PVC samples each stretched biaxially 3 × 2 at 100–105°C and measured in the 3X direction. Sample A was quenched immediately. Sample B was heat set for 15 min at 110°C, then quenched. Sample C was heat set for 180 min at 120°C, then quenched. The differences in shrinkage behavior appear even more pronounced when the corresponding differential curves are examined (Fig. 6); note the reduction in in-

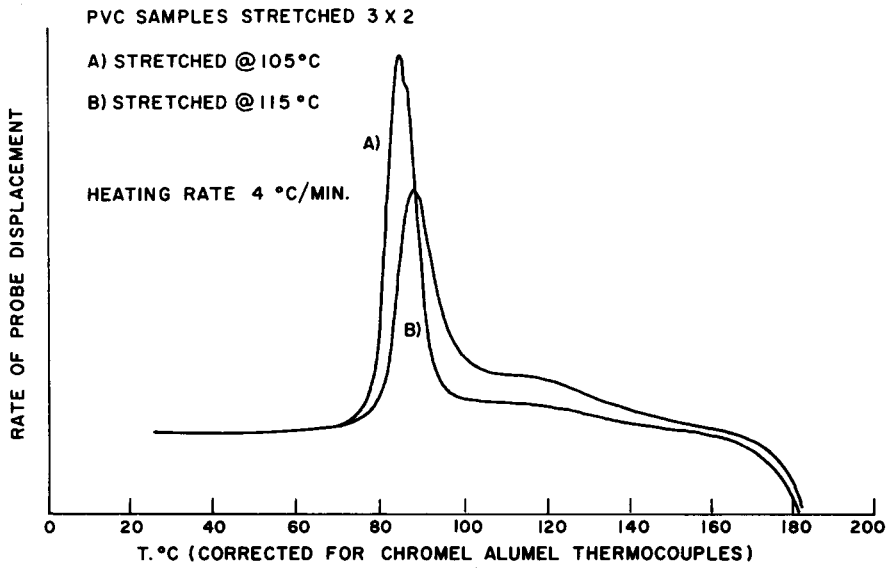

Fig. 4. Effect of stretch temperature on differential (shrinkage rate) curves.

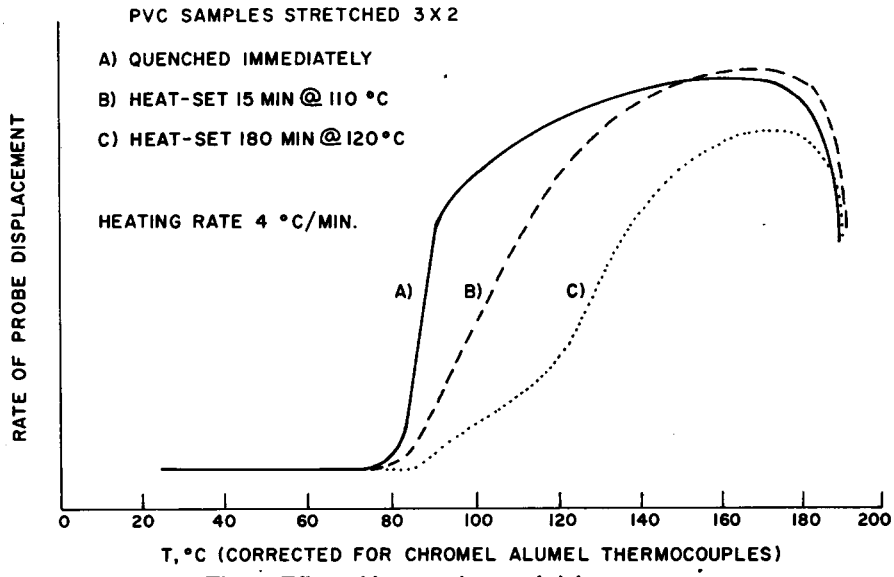

Fig. 5. Effect of heat setting on shrinkage curves.

tensity of the original shrinkage activity peak, accompanied by the appearance of a second peak at higher temperatures, in the heat-set samples.

While the technique described here is convenient and useful, it is not without limitations. The measurements must be performed on small samples (typical length 5 mm between clips), owing to the limited dynamic range of the LVDT; this restriction, combined with uncertainty as to the effective length of the sample between clamping points, leads to an uncertainty of a few percent in the degree of shrinkage. Elongation of the sample at elevated temperatures, under the influence of the required minimum tension, imposes an upper limit of approximately

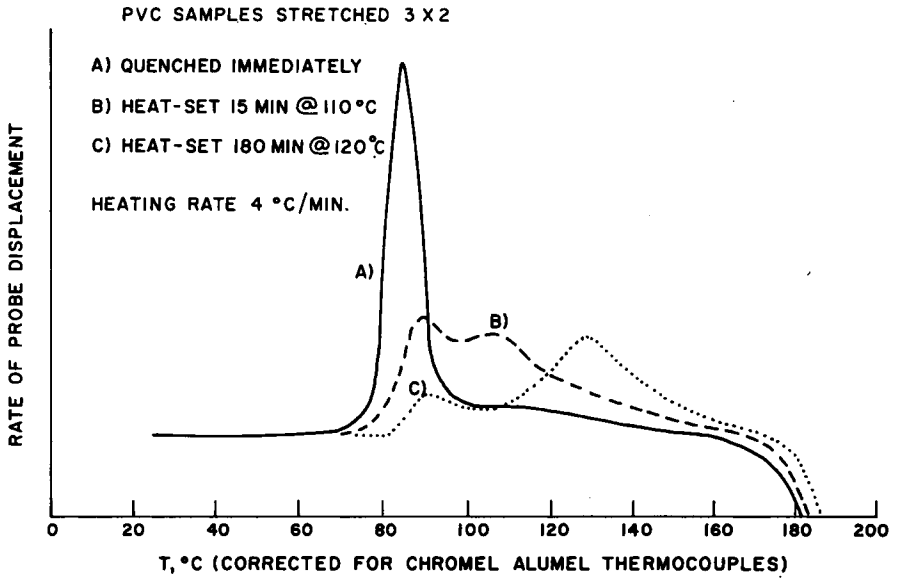

Fig. 6. Effect of heat setting on differential (shrinkage rate) curves.

200°C on the usable temperature range (note "fall-off" of shrinkage curves in Figure 2 in the 160–200°C range). Reliable results are obtained only at low heating rates (below about 5°C/min).

In spite of these limitations, the technique has provided valuable information on the effects of stretch temperature, degree of stretch, and thermal history on shrinkage of oriented samples. Work is currently in progress on an improved instrument which is expected to overcome the limitations of the present system.

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