A Surface Acoustic Wave (SAW) Probe for the Thermomechanical Characterization of Selected Polymers

JOHN A. GROETSCH III* and RAYMOND E. DESSY, *Chemistry Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*

Synopsis

Specially designed surface acoustic wave devices may be used to examine the physical characteristics of the surfaces of thin polymer samples. Both cast films and thin film samples may be employed. The devices uniquely offer an opportunity to study: (1) very thin films, (2) surface-segregated materials, (3) the effect of diffusion of vapor into the surface region, and (4) simultaneous measurements of exterior surfaces of laminates. No special sample preparation is required. The T_g, T_m, T(alpha-c), and beta transitions observed agree with values taken with more complex, time-consuming apparatus.

INTRODUCTION

Although there has been a considerable amount of work on the characterization of bulk polymer properties, exploration of surface phenomena is still a relatively uncharted area. Methods for examining the chemical nature of surface changes are available, but, as yet, there are few methods for elucidating the physical properties of polymer surfaces. This paper will describe such a method and examine some applications for the technique.

Preliminary studies in the application of surface acoustic wave devices to the analysis of gas mixtures and polymer samples have been reported from this laboratory.[1] This study outlines the construction of a useful testing laboratory instrument and examines the theory behind the method.

Periodic distortions in piezoelectric substrates may be induced by application of RF energy to sets of interdigitized electrodes laid down on the substrate by standard photolithographic and etching techniques (Fig. 1). For the present work the transmitter consisted of 50 finger "pairs." Each finger 1 mil wide with 2 mil spacings between adjacent fingers. Finger length was 300 mil.

As RF energy is applied to such a transmitter, energy is coupled into the substrate in a number of ways. First, a longitudinal bulk (compressional) wave is induced which propagates through the medium. Second, a transverse wave (shear) is produced. Third, a surface or Rayleigh wave is excited. This third mode is traditionally called a surface acoustic wave (SAW).

By increasing the number of finger pairs beyond 15, it is possible to have most

* Present address: Exxon Chemicals America, Chemical Plant Laboratory, Baton Rouge, LA 70821.

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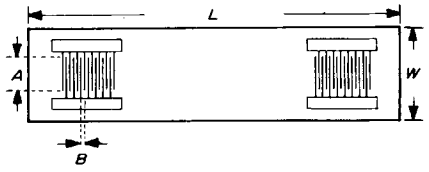


Fig. 1. Surface acoustic wave device: top view.

of the energy inserted into the substrate appear in the form of SAW energy. The SAW wave propagates down the surface of the substrate, at a velocity characteristic of the anisotropic media. For quartz, ST cut and X propagating, the velocity is 3.158 km/s. The wave length of the SAW wave is determined by the finger spacing with $\lambda = 4l$, where l is the interdigitized finger separation. Therefore, the present device has a SAW wavelength of 100 μm and an operating frequency of ~32 MHz.

The SAW wave propagates along the surface as an elliptical displacement (Fig. 2) of substrate perpendicular to the surface, with particle motion retrograde to the phase velocity of the SAW wave. The major axis of the ellipitical motion is perpendicular to the surface. All of the energy in the "surface wave" is dissipated within one wavelength of the surface. Vertical displacements are usually of the order of $10^{-5} \times \lambda$, or a few nm.

As the SAW wave propagates along the surface, it may be viewed in the same manner as a light beam exiting from a slit. In the latter case, the beam propagates through a Fresnel region in which dispersion is minimal, into a Frounhaoufer region where noticeable dispersion occurs. The length of the Fresnel region is determined by the ratio of the slit aperture to the wavelength involved. With an acoustic aperture of 0.75 cm and a wavelength of 100 μm, the SAW wave is well collimated for ~10 cm. With the separation of transmitter and receiver 2 cm, the probing SAW wave used in this work is very tightly collimated during its transit.

During the transit of this collimated beam several mechanisms can lead to change in the characteristics of the SAW wave. First, if a layer of material is laid down on the surface of the acoustic pathway, and the shear wave velocity in that layer is higher than the substrate shear wave velocity, the layer is said to stiffen the substrate. As the layer thickness increases, the surface limited Rayleigh wave increases in velocity until the shear wave velocity in the bulk substrate is reached. At this point the Rayleigh wave mode can phase match and couple to the bulk shear wave, and amplitude is lost from the Rayleigh wave.

Second, if the layer shear wave velocity is less than that of the substrate, the

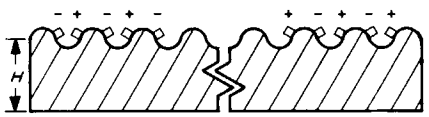


Fig. 2. Surface acoustic wave device: cross section.

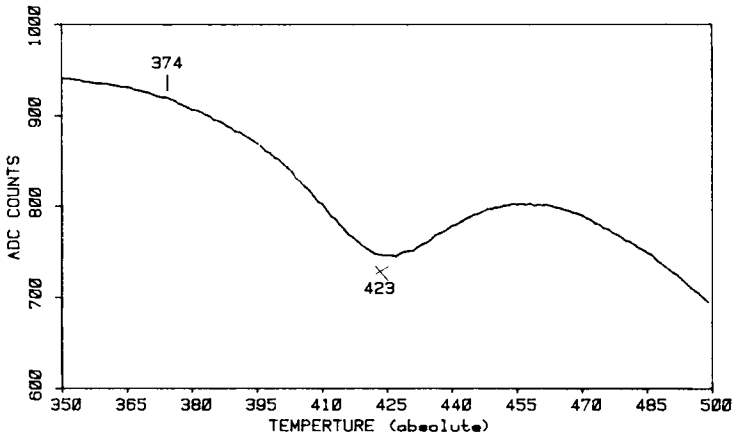


Fig. 3. Cast film; 0.01 g/mL poly(methyl methacrylate).

layer is said to load the substrate. In this case, as the layer thickness increases, the Rayleigh wave decreases in velocity until it approaches the shear wave velocity in the layer. Again, energy is lost as the particle displacement distributions approach those of sagittal plane plate modes in the layer material perturbed by the presence of the substrate.

Finally, surface perturbations, involving roughness or discontinuity, within the transmission path result in reflections of the propagating surface wave, and in bulk waves radiating into the substrate. Again energy is lost.

For the polymer systems studied, the velocities in the layers placed on the surface of the SAW detector lead to loading; reflection also occurs. Both processes lead to an observed loss in amplitude. Typical bulk shear velocities for polymers lie in the range of 0.75–1.5 km/s, some four times lower than for quartz. The bulk and shear moduli for polymer samples typically lie in the range of $0.1–1.0 \times 10^{10}$ N/m^2, some 10 times lower than for quartz.

The interested reader is referred to the seminal works of North and Pethrick[2] or Hartmann[3] on acoustic measurements. Further work on frequency and phase changes using the present system is in progress.

Cast Films: The simplest test of the SAW device as an instrument for examining polymer samples is a simple cast film. Varying concentrations of

TABLE I
Comparison: SAW Technique with DSC and 1-Hz DMA

Polymer	T_g by DSC (°K)	SAW "knee" (°K)	Loss peak by DMA (°K)	SAW min. (°K)
Polystyrene	373	371	373–392	383
PMMA	378	374	393	423
Polysulfone	449	452	457–468	476
Polycarbonate	422	411	428	431

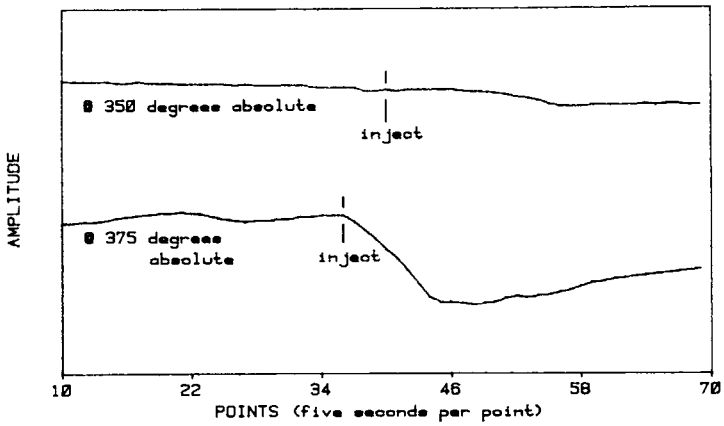


Fig. 4. Plasticizer effect. Solvent injection study.

poly(methyl methacrylate) (PMMA) dissolved in methyl ethyl ketone were used to lay down very thin samples on the quartz substrate between the interdigitized electrodes. ESCA studies were used to screen the graded series of preparations, to delineate at what point complete surface coverage was achieved. These samples represented the thinnest films that provided uniform coverage. Their estimated thickness, from concentration/area calculations, was about 0.1 mil (2.5 μm).

The amplitude of the SAW wave seen at the detector as a function of temperature is shown in Figure 3. The "knee" in the thermogram occurs at the temperature found near the glass transition of the materials using classical differential scanning calorimetry. At higher temperatures, an amplitude minimum, associated with a loss maximum, occurs at a temperature near that reported for such a phenomenon by dynamic mechanical analysis at 1 Hz.

If this same experiment is repeated on a fresh film upon which a drop of water

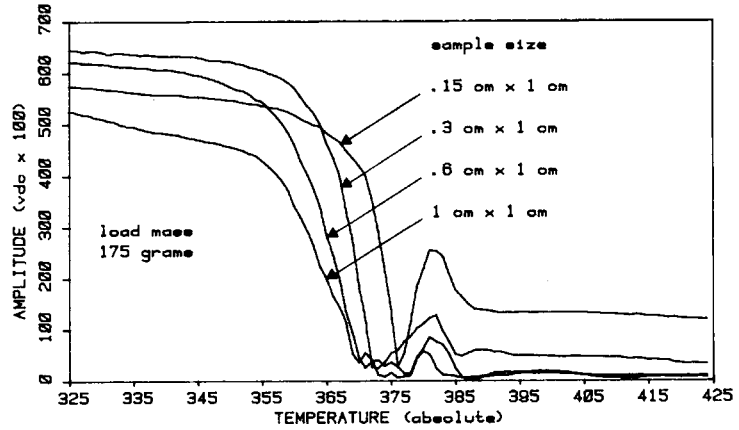


Fig. 5. LDPE Study #1. Decreasing sample pressure.

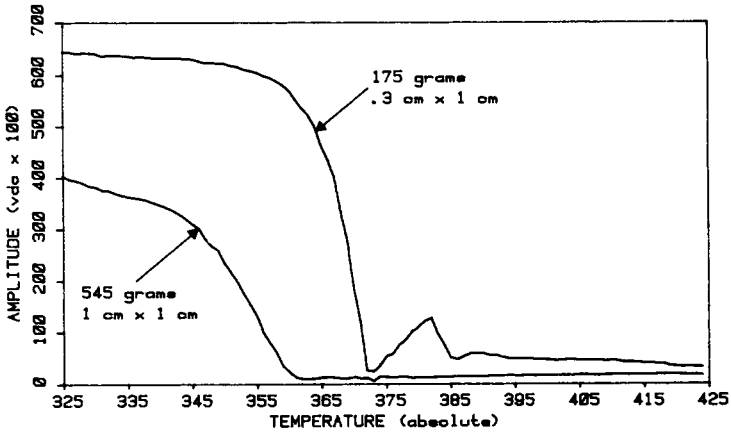


Fig. 6. LDPE Study #2. Constant sample pressure.

is placed, an identical thermogram is obtained. Such small amounts of liquid placed directly on the quartz surface completely "quench" the SAW wave by mode conversion and reflection. Therefore, the SAW device must "probe" or penetrate into the cast films only a short distance. The inability to cast thinner films precludes an exact estimate. However, a minimum can be set by recalling the small vertical displacements involved in the surface wave, approximately 1 nm at the frequency of these studies. The 1-μm value imposed by the PMMA/water experiment sets the maximum.

Other cast films were studied. Table I shows the relationship between the "knees" and minima observed for the series, and the classically derived values. The agreement is quite good except for the PMMA sample.

Anonymously low transitions in films which had not been completely desolvated were observed. This led to a series of experiments in which thoroughly

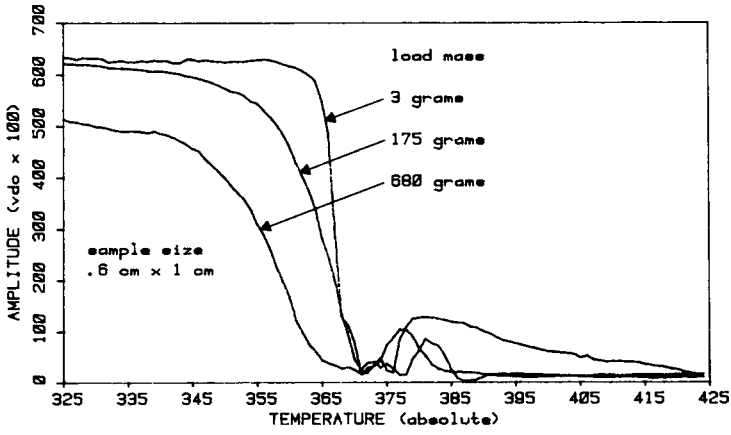


Fig. 7. LDPE Study #3. Increasing sample pressure.

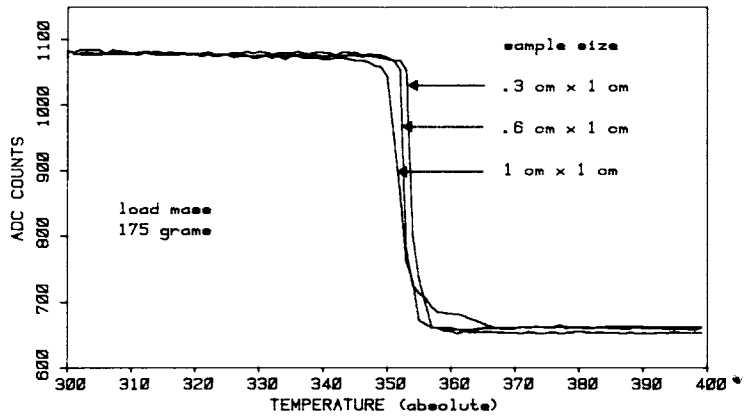


Fig. 8. Study #1 on PET. Decreasing sample pressure.

degassed samples of cast polystyrene films were exposed to solvent vapor of chloroform at a fixed temperature, well below the glass transition. This latter is an "observation point" from which changes in glass transition temperature can be observed as the solvent vapors begin to occupy free volume within the polymer sample and act as plasticizers. The resulting plot of amplitude vs. time has the same general shape as an amplitude/temperature curve. It provides a convenient mechanism to observe film/gas interactions (Fig. 4).

Thin Films: The major effort in the study was to characterize thin film samples taken from larger sheets of single polymer, copolymer, or laminate construction. These samples may be easily prepared by cutting square samples a few mm on each edge from the specimen. Or a paper punch can create circular samples a few mm in diameter. These samples were placed on the optically flat quartz substrate in the path of the acoustic beam. Their surface irregularities preclude intimate contact with the propagating surface. Loss in SAW amplitude is due to mode conversion and reflection. Obviously, the quality and quantity

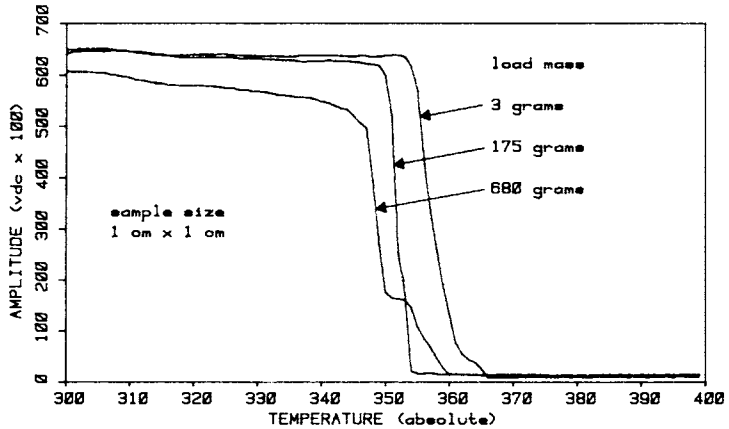


Fig. 9. Study #3 on PET. Increasing sample pressure.

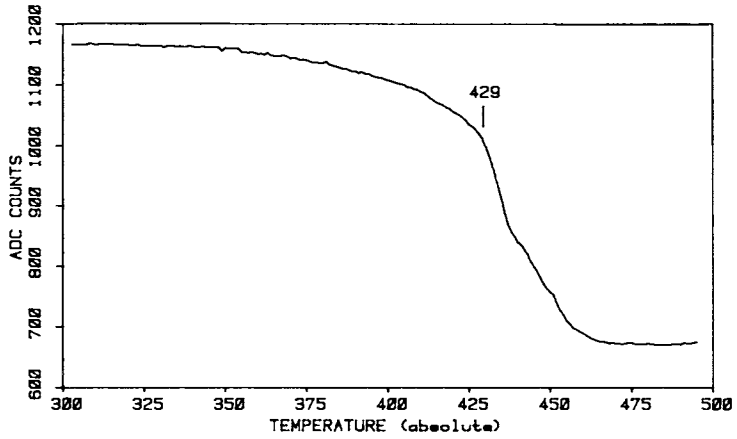


Fig. 10. Thin film. T_m in poly(vinylidene fluoride).

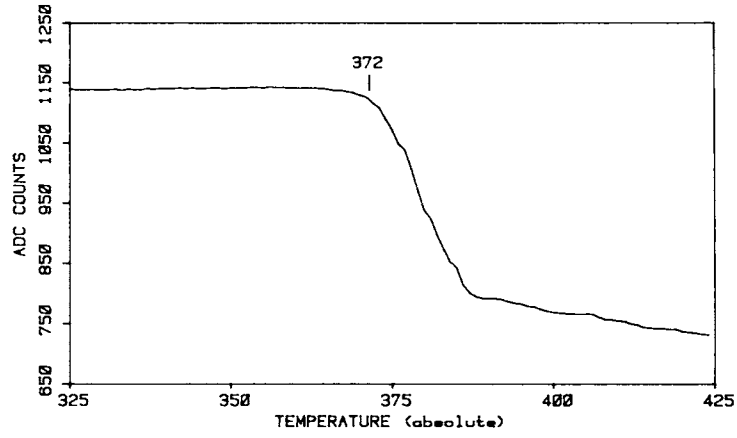


Fig. 11. Thin film. T_g in polystyrene; 90 g load; 0.6 cm × 0.15 cm.

TABLE II
Comparison: SAW Technique with Standard Methods

Polymer	Transition type	Standard method (°K)	SAW technique (°K)
PVDF	T_m	429–441	429
PS	T_g	373	372
PMMA	T_g	378	368
PC	T_g	422	421
PET	T_g	342–350	348
Polypropylene	T(alpha-c)	391	393
Teflon	Beta	~300	280–290
Polyethylene	Beta	~150	152–159
TPU-40	Beta	~140	149–155
PC/Polysulfone	T_g's	433/460	431/464

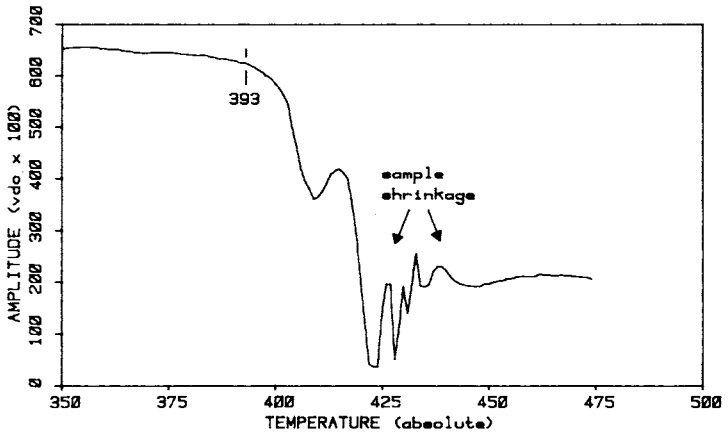


Fig. 12. Thin film. T (alpha-c) in polypropylene; 3 g load; 0.3 cm × 1 cm.

of surface contact plays an important role in the initial loss in SAW amplitude as the sample is placed on the surface. Further changes in the quality and quantity of surface contact can be observed as thermally induced transitions occur. These might well be affected by any pressure used to hold the sample on the surface. A polymer with very low moduli shear, tensile, and bulk was chosen for a series of pilot studies to exaggerate any such effects.

Various sizes and shapes of low density polyethylene, 60 μm thick, were prepared. All were 10 mm wide but the lengths increased from 1.5 mm to 3.0 mm and from 6.0 mm to 10 mm. The samples could thus block the acoustic path to the same extent normal to the propagating wave, but would offer differing "path lengths" to the SAW wave.

At a fixed load mass (brass weights, thermally insulated by Teflon spacers from the sample) Figure 5 shows that narrow samples give a response reminiscent of the cast films, with "knee" and minimum. Samples with a longer acoustic path

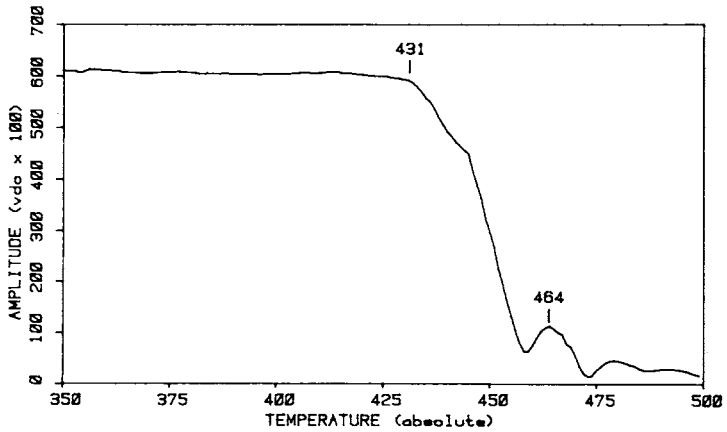


Fig. 13. Thin film. T_g's in polycarbonate/polysulfone block copolymer; 90 g load; 0.6 cm × 0.6 cm.

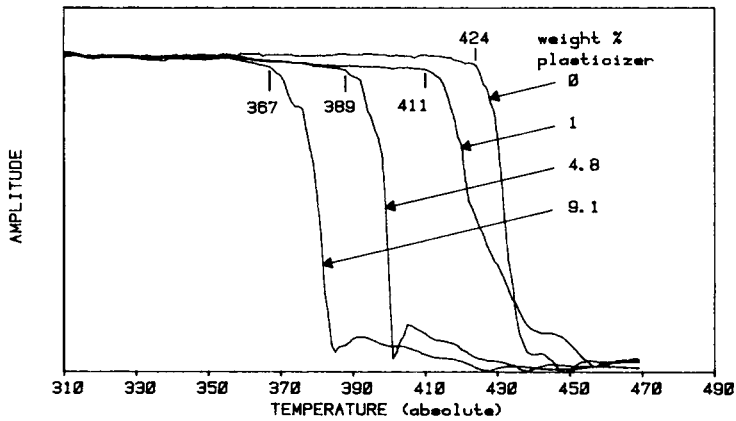


Fig. 14. Thin film. T_g's for homogeneous solution Lexan/plasticizer blends; 3 g load; 0.6 cm × 1 cm.

length begin to attenuate the signal earlier. The characteristic minima becomes less well defined until it finally disappears. Figure 6 shows the effect of constant pressure. Sample preparation should then involve samples with an acoustic pathlength of 1–5 mm for clean observations. For a fixed sample size, Figure 7 demonstrates that the sample pressure should be maintained in the region of 5,000–25,000 dyn/cm^2 for optimum observations. This factor of 5 in dimension and load range makes sample preparation and mounting only a modestly critical process, a desirable feature for a routine procedure.

As expected, when similar studies were conducted on poly(ethylene terphthalate) the family of curves involved at constant load mass (Fig. 8) and constant pressure (Fig. 9) were much closer together. This would increase the tolerance factors in dimension and load to a range of about 10.

With this information in hand, a large number of different sample types were investigated by the technique.

Typical thermograms are shown in Figures 10 and 11 for samples of a homopolymer. Table II shows results from the series studied as compared with the temperatures found by standard methods. The agreement is excellent. The scope of the method is demonstrated by the variety of transition types that have been observed. These cover the range from beta transitions in the polurethane sample (TPU-40 at 140°K) to the T_m of polyvinylidenedifluoride at 430°K.

TABLE III
Comparison: SAW with DSC

Film wt % Plast.	SAW T_g onset (°K)	DSC T_g onset (°K)
0	424	423.5
1.0	411	414.6
4.8	389	389.3
9.1	367	367.2

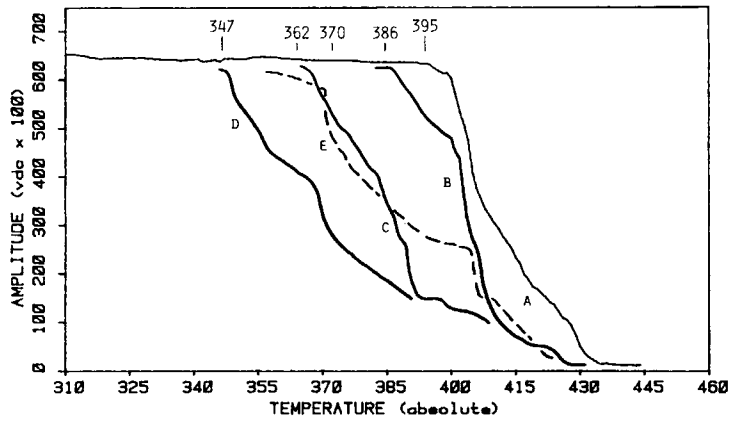


Fig. 15. Surface mobility transition for treated Lexan; 90 g load; 0.6 cm × 1 cm. Samples at 125 K (% plasticizer): (A) 0; (B) 1; (C) 5; (D) 10; (E) 10. Baking period: (A–D) 5 min; (E) 60 min.

Unique Applications: There are a number of interesting applications for a polymeric testing device which is: (1) surface-oriented; (2) sensitive to contact quality/quantity, and (3) surface dimension normal to the propagating wave.

First, an examination of the thermogram for polypropylene, which has been treated by radiation so as to "shrink" upon heating, indicates that the classic T_g is observed (Fig. 12). The curve also shows excellent evidence near 425°K for the shrinkage process. As the material reduces its dimension perpendicular to the propagating wave, the acoustic beam is attenuated to a lesser extent. This would provide an excellent quality control test.

Figure 13 shows a thermogram for a block copolymer sample composed of polycarbonate and polysulfone segments. The two T_g's shown are identical to those found by classical means.

Another interesting application has been done in collaboration with Schultz.[4]

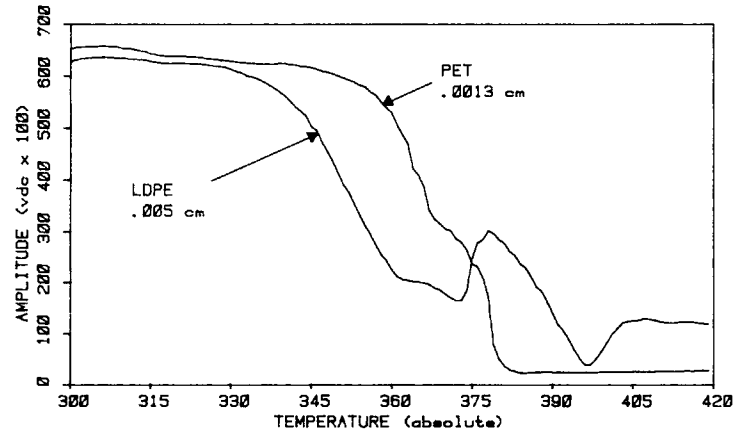


Fig. 16. Transitions from both surfaces of a PET–adhesive–LDPE laminate; 10 g load; 0.6 cm × 1 cm.

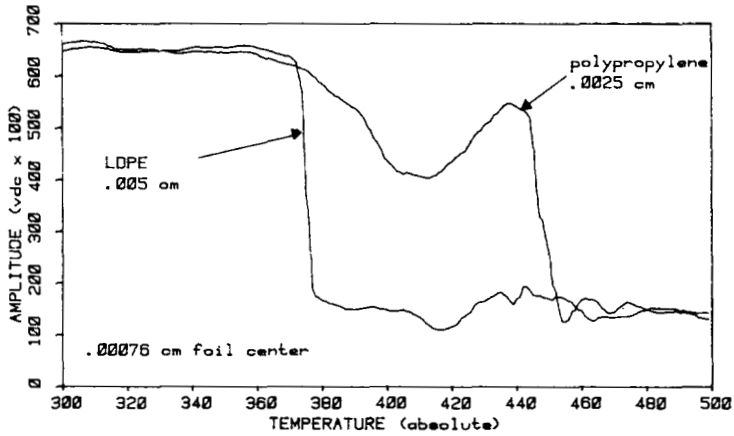


Fig. 17. Transitions from both surfaces of a polypropylene–adhesive–foil–adhesive–LDPE laminate; 20 g load; 0.6 cm × 1 cm.

This worker prepared several samples of poly(bisphenol A carbonate) that had been bulk treated with 4-dodecyloxy-2-hydroxy-benzophenone. The films were 2.5 μm thick. The amount of plasticizer and the relevant thermal data are shown in Figure 14. Table III compares the SAW and DSC measurements. Next, a series of thicker samples, 25 μm each, were diffusion treated in a series of concentration/time/temperature studies. The plasticizer solution was placed on

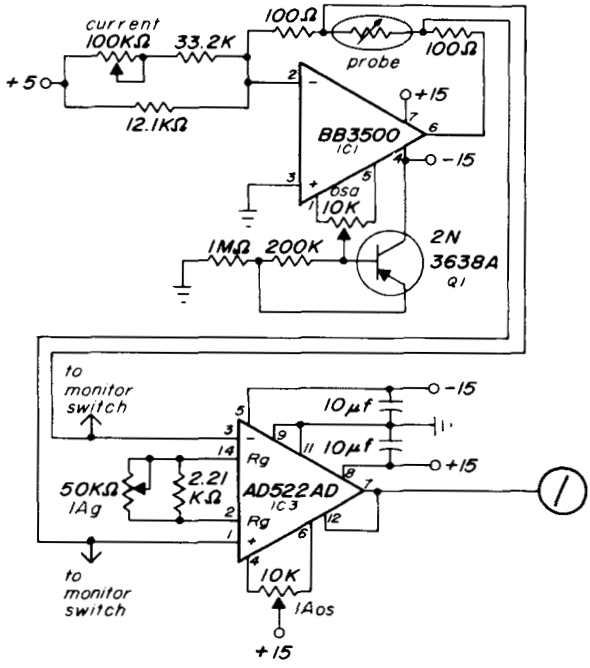


Fig. 18. Schematic probe support circuitry.

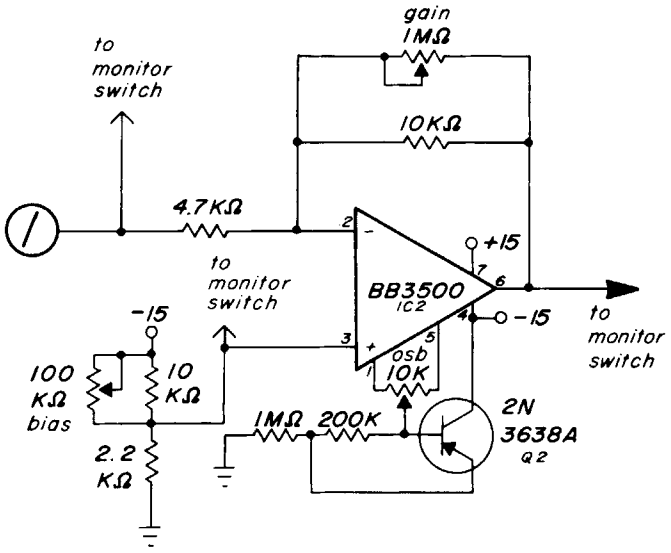


Fig. 19. Schematic (continued) probe support circuitry.

the surface. Then a post-application heat treatment was used to diffuse the material into the polymer. The surface into which diffusion took place was analyzed by the SAW method. The results are shown in Figure 15. As expected,

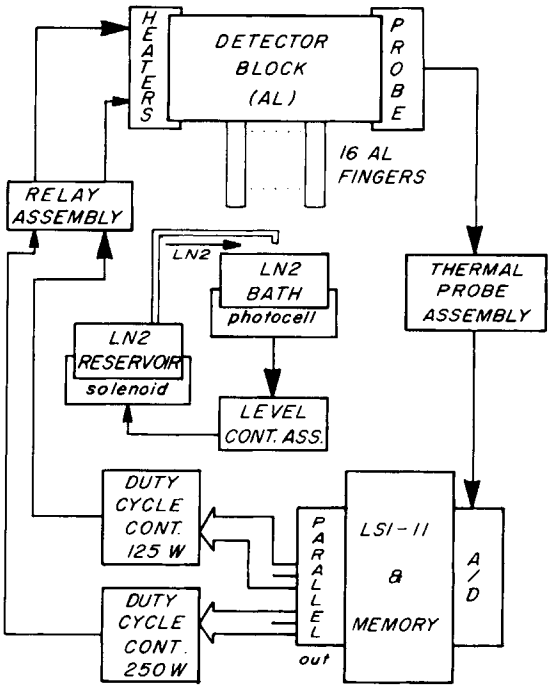


Fig. 20. Block diagram temperature measurement and control.

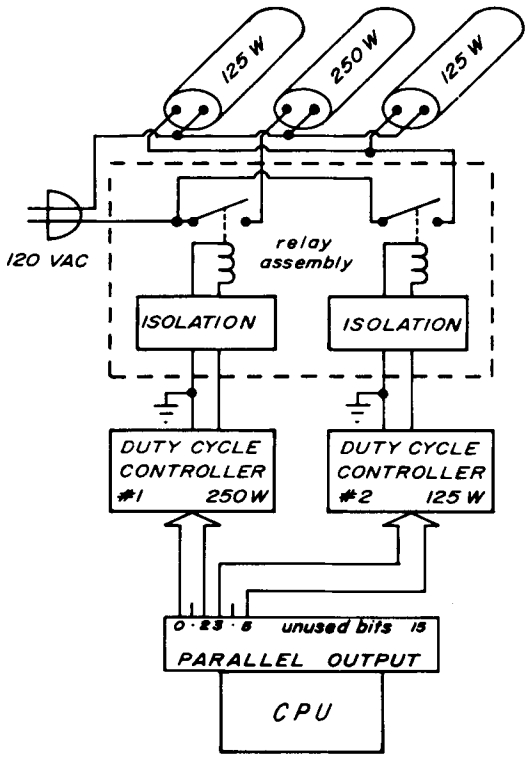


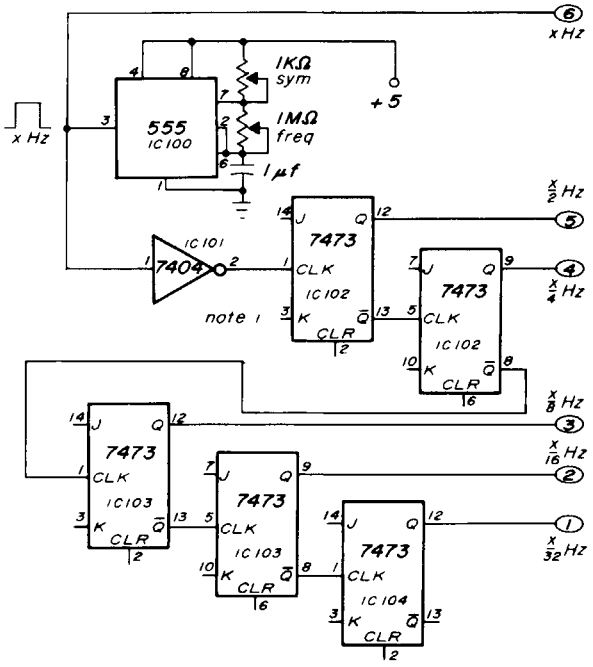
Fig. 21. Expanded block diagram heater control assembly.

for identical time/temperature values, the observed T_g decreased as the percentage of plasticizer in the diffusing environment increased. However, as curve E (cf. curve D) shows, extended post-heat treating apparently leads to increased evaporative loss, a process in competition with the diffusion process into the surface area. The SAW techniques provide an inexpensive, quick way to explore surface-resident mobility changes.

Laminates: Finally, the surface nature of the SAW method suggests that it would have unique application to laminates. The simple, noncritical sample preparation would make it possible to explore each surface separately. Or an apparatus which sandwiched the sample disk in between two SAW devices could be constructed. Although this has not been fabricated, it is conceptually and technically rather simple. To demonstrate the viability of the concept, we can examine Figures 16 and 17, which show two commercial laminate samples. In each, the transitions expected from the surface contacted material were observed. The quality control applications in stored, surface-treated materials, whether that treatment is deliberate or accidental, is obvious.

EXPERIMENTAL

SAW Transducer: The SAW transducer was fabricated from commercially available ST cut quartz plates, X propagating (Valpey-Fisher Corp.). The plate



notes:
1. all J, K, and CLR inputs tied to +5V

Fig. 22. Schematic duty-cycle controller #1.

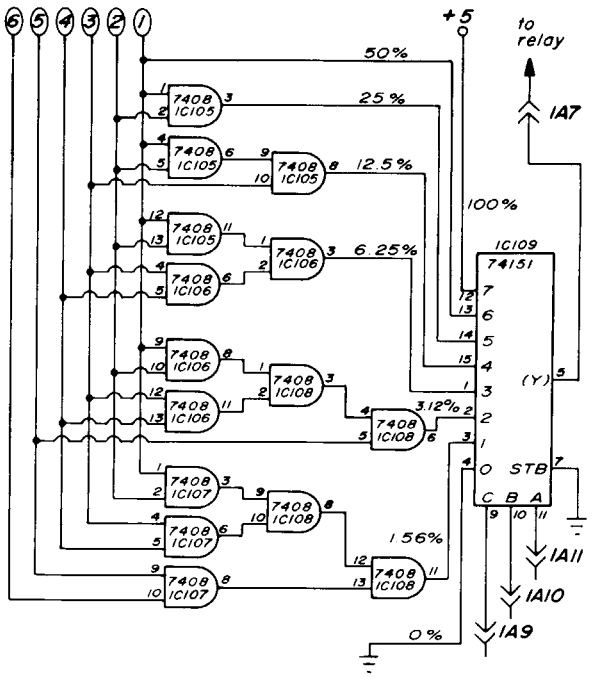
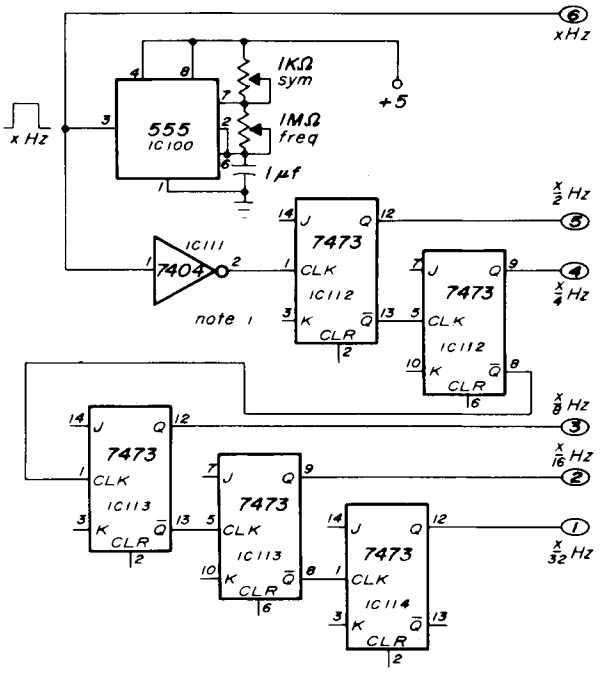


Fig. 23. Schematic (continued) duty-cycle controller #1.



notes:
1. all J, K, and CLR inputs tied to +5V

Fig. 24. Schematic duty-cycle controller #2.

was 2 in. × 0.5 in. × 0.035 in. Standard photolithographic techniques were used to lay down interdigitized transducers with the following specifications: acoustic aperture, 0.30 in.; finger spacing, 2 mil; finger width, 1 mil; number of finger pairs, 50; operating frequency, 31.58 MHz.

Transducer Support Block: An aluminum block, milled to accept two identical quartz SAW plates, was inletted with appropriate holes to accept cartridge heaters (1 × 250 W, 2 × 125 W), 25 aluminum fingers that could be immersed in liquid nitrogen, and a platinum resistance temperature probe. The block (2.5 in. × 1.75 in. × 1.0 in.) was large enough to provide a good thermal mass. The block was in turn mounted upon a large cylindrical block of Teflon (6 in. in diameter × 1.5 in. thick) that was gasketed on the bottom to a nitrogen Dewar and on the top to an inert atmosphere enclosure hood.

The platinum resistance temperature probe (Omega Inc.) was incorporated into the support circuitry shown in Figures 18 and 19. The output was digitized by a successive approximation ADC (12-bit + sign) subsystem incorporated into a Digital Equipment Corporation LSI-11 based microcomputer with 16K word of memory. The system was programmed in FORTH.

A lookup table approach was used to linearize the response/temperature function. This consisted of a thermocouple placed inside an oil-filled glass jacket inserted into a hole drilled immediately below the sample area, as a standard.

Proportional, closed-loop temperature control was developed through the interaction of FORTH defined vocabulary words and the hardware shown in

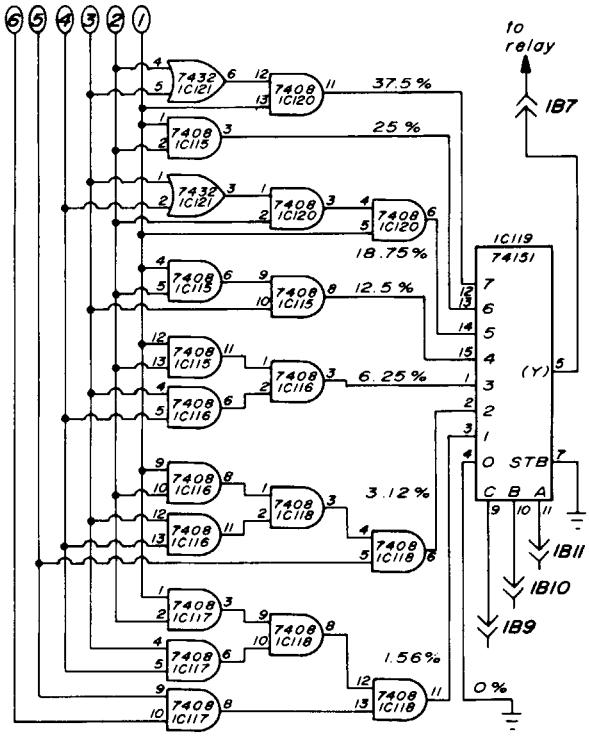


Fig. 25. Schematic (continued) duty-cycle controller #2.

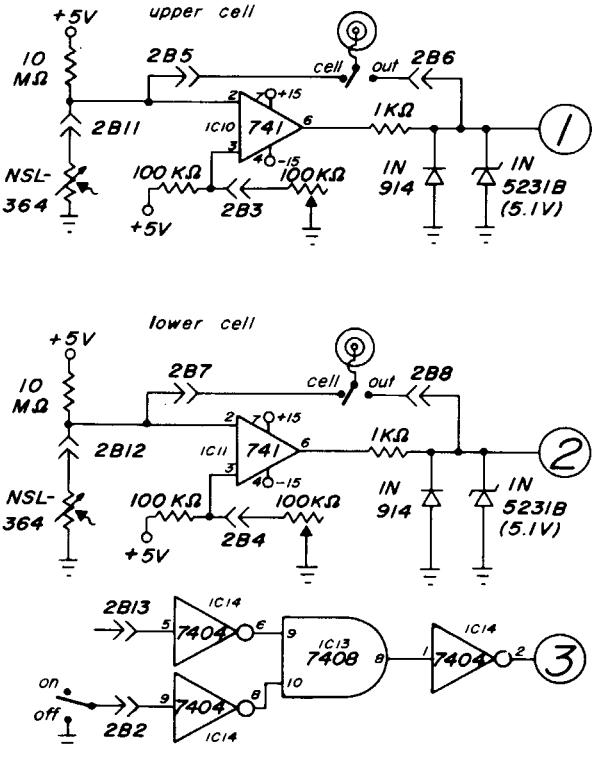


Fig. 26. Schematic liquid nitrogen level controller.

Figure 20. Heating was accomplished by means of two duty cycle controllers shown in Figure 21, using the schematics given in Figures 22–25. The cooling was controlled by keeping the level of liquid nitrogen in the Dewar constant. The level sensing mechanism involved a glass float riding on guide wires built into the Dewar. A reflective spot on its surface, in conjunction with an external light source and two photosensors, was used to generate "LEVEL LO" and "LEVEL HI" signals (Fig. 26). These were used in conjunction with solenoid activating circuitry (Fig. 27) to start and stop the flow of liquid nitrogen from a transfer Dewar into the cooling Dewar, by closing and opening, respectively, the venting solenoid on top of the transfer Dewar. (A safety vent was installed to purge overpressure). The solenoid was wired in series with a heater in the bottom of the vessel to provide driving pressure for the transfer.

Software was written to provide both the ability to set the temperature of the block to a desired single value, as well as to generate smooth temperature ramps from 150°K through 550°K, at speeds of 4–20°/min.

The RF energy input was provided by a Tektronix 191 constant amplitude signal generator coupled to the interdigitized transducers by a 2820 broad band amplifier (TRW, Inc.) and a 1 μH coil. The RF energy at the output was treated as shown in Figure 28, the final digitized data being correlated with the simultaneously measured temperature valve.

This X/Y data was stored in the local control computer and subsequently transmitted to a host computer over RS-232 9600 baud network link, where data storage and plotting could be accomplished. All network protocol, record management, and plotting was done in FORTH.

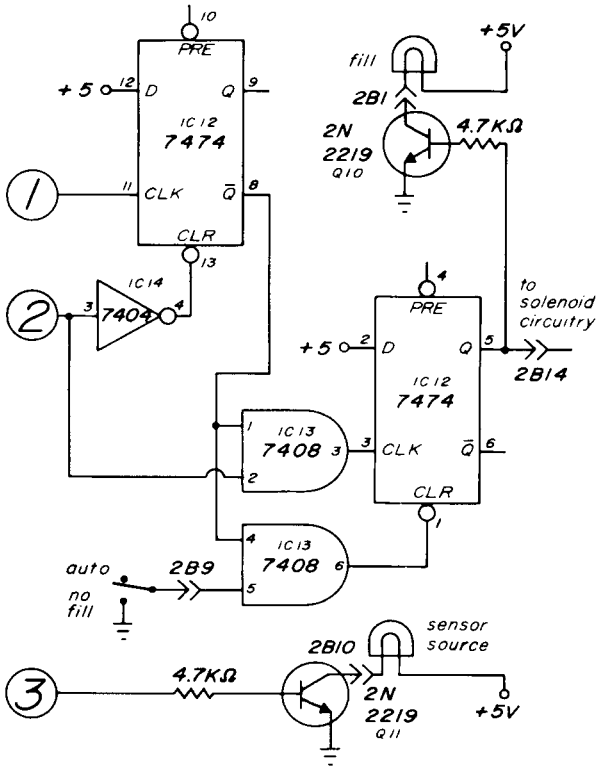


Fig. 27. Schematic (continued) liquid nitrogen level controller.

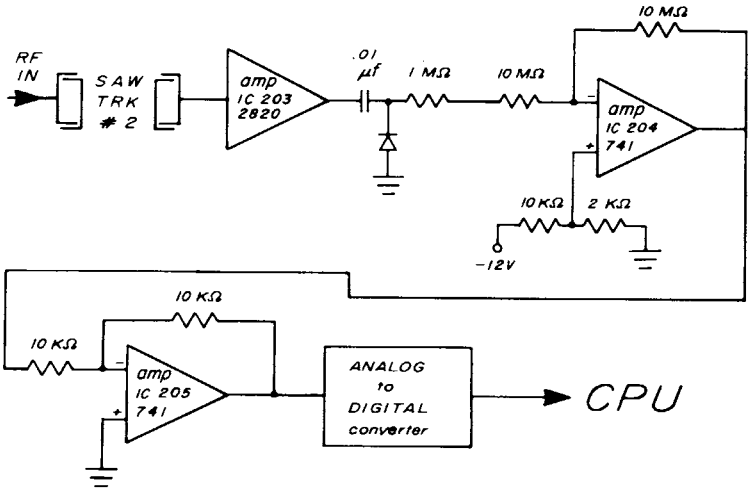


Fig. 28. Track #2 and post-plate circuitry.

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