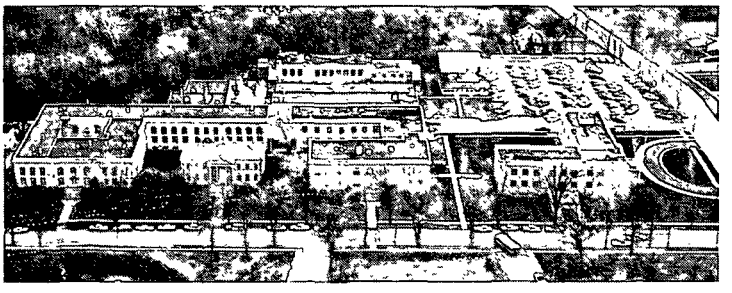

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INFLUENCES OF NONEQUILIBRIUM MOISTURE CONDITIONS ON THE IN-PLANE, ULTRASONIC STIFFNESSES OF CELLULOSE

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INFLUENCES OF NONEQUILIBRIUM MOISTURE CONDITIONS ON THE IN-PLANE, ULTRASONIC STIFFNESSES OF CELLULOSE

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ABSTRACT

Resonant and time-of-flight ultrasonic techniques were used to measure mass specific elastic stiffnesses and loss tangents for several papers and cellophanes during sorption, desorption, and at moisture equilibrium. When compared at equal moistures and temperatures, ultrasonic elastic stiffnesses and loss tangents obtained under nonequilibrium moisture conditions were identical to those at equilibrium. These results differ from published studies, which report transient increases in loss tangent and decreases in stiffness. Possible reasons for the different results are discussed. In any case, the nonexistence of an ultrasonic "moisture transient effect" simplifies the task of moisture-temperature compensation for on-line ultrasonic testers.

INTRODUCTION

Laboratory measurements of the in-plane, mass specific elastic stiffnesses of paper at ultrasonic frequencies have become routine (1,2). These provide a rapid, nondestructive determination of all of the in-plane, ultrasonic elastic parameters of paper. In addition to being important indicators of mechanical integrity, the ultrasonic stiffnesses can often be related to ultimate strength measurements (3,4). A major advantage of ultrasonic techniques is that they can be applied at the dry end of a paper machine (5), making real time evaluations of paper mechanical properties possible.

Paper moisture content and temperature fluctuations, occurring at the dry end of a paper machine, have considerable influence on the ultrasonic stiffnesses of paper (6). Therefore, in order for ultrasonic measurements to be useful for on-line quality control, the results must be converted to a standard temperature-moisture condition. On-line stiffness determinations may be further complicated by the "transient moisture effect". Several authors (7-12) report a transient decrease in stiffness (and/or a transient increase in loss tangent) in cellulose during nonequilibrium moisture conditions. Similar phenomena are reported in wool (13-21) and in other polymer-plasticizer systems (9). In other words, paper undergoing sorption or desorption may have a lower stiffness and a higher loss tangent at a given temperature and moisture content than at the same temperature and moisture content under equilibrium moisture conditions. Since moisture content is not at equilibrium during manufacture, the transient moisture effect could have repercussions for on-line ultrasonic measurements.

The purpose of this report is to present the results of ultrasonic elastic stiffness measurements on cellulosic materials obtained during sorption

and desorption. The tests were conducted over the range of temperatures and moisture contents commonly encountered at the dry end of the paper machine. The nonequilibrium stiffnesses are compared with the equilibrium values at the same moisture content and temperature.

BACKGROUND

It is well documented that paper exhibits the phenomenon of accelerated creep under cyclic humidity conditions (8,22-25). A material is said to undergo accelerated creep if it deforms far more and fails considerably sooner in a cyclic humidity environment than when tested under the same loads at the highest humidity. The fundamental mechanisms for accelerated creep are not well established. However, one conjecture is that accelerated creep is associated with a decrease in elastic stiffness during sorption and desorption.

Some of the first measurements of the effects of nonequilibrium moisture conditions on the elastic properties of polymers were conducted in 1959 on wool fibers with a freely oscillating torsion pendulum by Mackay and Downes (13). They observed transient minima between 30-60% in the torsional rigidity of fibers undergoing sorption. They demonstrated that these minima could not be explained by the fiber diameter changes accompanying sorption; that as sorption rate became greater rigidity minima increased; that the time of the rigidity minima were coincident with maximum sorption rates; and that moisture gain was essentially complete long before rigidity recovered to its final equilibrium value. Fibers undergoing desorption also exhibited a transient decrease in rigidity. That is, the rigidity during moisture change was less than at the same moisture content in equilibrium. Unlike sorption, however, transient modulus minima were not observed. Measurements of internal friction showed transient maxima on sorption as large as 100%.

Soon afterward, Nordon (14) performed a similar study on wool fibers using a forced oscillation torsion pendulum. This permitted a greater frequency range and smaller oscillation amplitudes. Torsional rigidity was measured during sorption for a variety of step changes in relative humidity. A transient minimum of approximately 5% was observed, regardless of the magnitude of the humidity change. The transient minima observed by Nordon are considerably smaller than the ones found by Mackay and Downes. Nordon attributed this to a difference in fiber diameter (45 μm rather than 30 μm). He also stated that some of the difference in the size of the minima was due to the smaller strain amplitude used in his study (0.03% rather than 2%). Feughelman, Robinson, and Haly reported effects, similar to those observed by Nordon in torsion, in stress relaxation studies of wool fibers held under axially tensile strains of approximately 1.5% (15-18). However, the transient stress minima increased as the magnitude of the humidity step was increased.

More recently, a dynamic sinusoidal extension technique (axial strain amplitude 0.01%), has been used by Danilatos and Postle (19) to study horse hair and wool fibers during sorption. They found a transient maximum in loss angle of around 20%, when a horse hair sample, initially at 53% RH, was submerged in water. This maximum coincided with the completion of swelling and was not accompanied by a transient minimum in modulus. Loss angle maxima were smaller or nonexistent when sorption in wool fibers was induced by step humidity changes. Transient minima in modulus accompanying sorption were again absent. These researchers (20) also tested wool fibers axially during desorption and found no transient minima in modulus values or maxima in loss tangents.

Transient maxima in loss tangent, modulus minima, and moduli lower than those at comparable equilibrium conditions have been reported in cellulosic

materials undergoing sorption and desorption. Using a freely oscillating torsion pendulum, De Ruvo, Lundberg, Martin-Lof, and Soremark (8) found a transient maximum in the logarithmic decrement of about 25%, when testing sulfate fibers undergoing sorption induced by an increase in RH from 10-22%. Kubat and Lindbergson (9) used thin strips and a torsion pendulum (strain amplitude ≈ 0.01%) in free oscillation in their measurements of the effects of moisture change on the loss tangent for the in-plane shear modulus. They also tested a variety of other polymer-plasticizer systems and found, in all cases, transient maxima in loss tangent (some as large as 100%) accompanying both sorption and desorption. Changes in loss tangents occurred long after plasticizer equilibrium had been reached. The results of the study are taken by the authors to demonstrate that the occurrence of a transient loss tangent maximum during moisture change is a general phenomenon, since it was found in all of the polymer-plasticizer systems tested. Another report by these authors, considering just the paper-water system (10), reported that, even though transient maxima in torsional loss tangents of approximately 100% were observed, no transient minima were found in the real part of the shear modulus.

As reported by Back, Salmen, and Richardson (7), extensional stiffnesses, obtained by measuring the initial slopes of load-elongation curves for kraft sack papers, passed through minima during sorption and desorption and were lower than equilibrium data when compared at the same moisture content. Equilibrium and sorption data did not converge after 20 minutes, even though the majority of the moisture change was accomplished in the first 10 minutes. The time lag in the recoverability of stiffness corresponds to results discussed earlier (13,14,17). The shallow minimum in stiffness accompanying sorption is also similar to previously discussed results (14-17). The unique feature of

this study is the initial transient decrease in tensile stiffness on desorption. The results from Mackay and Downes, although showing decreases with respect to comparable equilibrium values, did not display desorption transient minima. Transient minima in the extensional stiffnesses of paper were not observed in sorption or desorption by Berger (11) using an Instron tensile tester in a cyclic stress mode (strain amplitude 0.025-0.15%). Loss tangent maxima of around 25% were found to occur during sorption and desorption.

Evidence, from other than mechanical tests, supports the proposition of a transient moisture effect in polymers. Dielectric measurements on wool (21) indicate increased molecular mobility during nonequilibrium moisture conditions. Large transient maxima were found to occur in the real part of the dielectric constant of samples undergoing small sorptions from initially dry conditions. Larger sorption steps resulted in smaller maxima. Shishoo and Lundell (12) performed NMR testing on cotton and wool samples. They argue that the broad peak half width of the proton absorption curve is a measure of matrix rigidity and show that this half width exhibits a minimum during sorption.

The reason for subjecting the reader to the literature review was to demonstrate that there is a body of often conflicting data indicating that the linear physical properties of polymers are influenced by sorption history. A more detailed examination of these publications reveals that their authors rarely consider the effects of temperature changes during sorption and rarely compare transient measurements with the corresponding equilibrium numbers. At this point, it appears that there is something going on, but inconsistencies in the literature make it impossible to even make qualitative phenomenological statements with confidence.

EXPERIMENTAL

Resonance (6,26) and time-of-flight techniques (2,6) were used to measure viscoelastic parameters of cellulosic materials at ultrasonic frequencies while moisture was changing. Shear and longitudinal mass specific planar stiffnesses were measured on extended sheets with the time-of-flight approach. Both the real and imaginary parts of the in-plane, mass specific Young's moduli of narrow strips were determined with the resonance equipment.

The resonance apparatus has been previously described by Pankonin and Habeger (26). The approach, which is diagrammed as a part of Figure 1, is to determine the mass specific modulus (E/rho) and the loss tangent from the frequency and width at half height of the resonant peaks in standing wave vibrations of a narrow strip. The strip is coupled between a pair of ceramic piezoelectric transducers: one is excited with a sinusoidal voltage and the signal resulting at the other is measured as a function of frequency. Sample lengths were chosen to produce first harmonic resonance peaks near 60 kHz when measured at 22°C and 50% RH.

Figure 1 here

The time-of-flight technique, which is described elsewhere (6), is also diagrammed in Figure 1. Briefly, the technique uses three piezoelectric bimorph transducers arranged in-line, with a receiver located between two transmitters. The receiver is 30 mm from one transmitter and 60 mm from the other. The transmitters are pulsed alternately, and the difference in the time-of-flight along the two paths is determined by a cross correlation analysis. The difference in the transducer displacement distances is divided by the time difference to calculate ultrasound velocity. The square of this velocity equals

the mass specific planar stiffness. Shear and longitudinal stiffnesses were obtained by rotating the bimorph transducers 90° about their axes.

The specially designed environmental chamber used to study the effects of moisture and temperature on the ultrasonic moduli has been described previously (6) and is diagrammed in Figure 1. It is a Blue M model CF temperature/humidity oven modified to hold the ultrasonic testers. A computer controlled fan was added to maintain humidity and temperature uniformity and to achieve rapid moisture changes in the samples. A hole was drilled in the top of the oven, so that moisture could be determined by weighing a test sample in the chamber. Sample temperature is monitored by imbedding a thin thermocouple in another test sample. The computer-controlled testing sequence, which accompanies a rapid moisture change, is a temperature recording, followed by an interruption of the fan, a sample weighing, a resumption of the fan, and an ultrasonic measurement. The sequence automatically repeats and data are continually recorded. For more detail, see the earlier publication (6).

Several commercial samples were tested including two different calipers of unplasticized cellophane, typing paper, blotter stock, an alkaline made bond paper, and two different basis weight linerboards. An effort was made to choose a variety of samples including ones with different basis weights, crystallinities, microstructures, and apparent densities.

RESULTS

Figure 2 shows the change in sample moisture content produced by a rapid humidity change in the oven. In this case, commercial blotter paper was tested at approximately 55°C. The figure is generated from three sorption and three desorption runs. Notice that the runs are reproducible and that the

majority of moisture change is complete within the first five minutes. It was found that the rate of moisture change generally became greater as the sample size was decreased, the basis weight was lowered, or the oven air temperature was raised.

Figure 2 here

Figure 3 presents the accompanying changes in MD mass specific Young's modulus measured using the strip resonance technique. These modulus data are also reproducible. Notice the continuous increase in modulus during desorption and decrease upon sorption. Transient minima do not occur in sorption or desorption. Similar data were obtained using the time-of-flight technique for shear as well as longitudinal mass specific stiffness. Figure 4 shows loss tangent data for the same runs. Loss tangent increases with sorption and decreases uniformly with desorption. The slight overshoot with sorption is probably a result of sample temperature changes as will be discussed later.

Figures 3 and 4 here

The largest difference between equilibrium and transient modulus and loss tangent data was found to be a result of transient changes in sample temperature. The temperature rises as moisture is sorbed and falls with desorption. Figure 5 shows the temperature changes encountered during sorption and desorption. The maximum temperature change, which occurs after two minutes, is 5°C. Notice that the time of maximum temperature change coincides with the maximum rate of moisture change. The magnitude of the temperature change depends primarily on the rate of moisture change, and temperature excursions as large as 8°C were recorded. Similar temperature transients have been reported by others in newsprint and linerboard using an infrared technique (27). Even

larger temperature drops were measured (up to 17°C) when paper samples were tested in an evacuation chamber (11).

Figure 5 here

The viscoelastic properties of cellulosic materials depend upon temperature. Therefore, to determine modulus values at a constant temperature during rapid moisture changes, compensations must be made for evaporative cooling and sorptive heating. By using temperatures acquired during the nonequilibrium moisture runs and established equilibrium temperature-modulus relationships (6), linear thermal corrections in the transient moduli data were made. Figure 6 presents the uncorrected sorption and desorption moduli for the blotter paper, along with the equilibrium moduli. Note the moisture-modulus hysteresis loops in the transient data. These loops are similar to those presented previously in a conductivity study of filter paper (28). In that study, the loop was assumed to be due to moisture induced temperature changes, and conductivity differences were used to calculate seemingly reasonable temperature changes. The present study has the advantage in that temperature measurements are actually made. When thermal effects are accounted for, the moisture-modulus hysteresis loops in Figure 6 disappear as shown in Figure 7. Within the limits of the experiment, the equilibrium and nonequilibrium moduli are equal. This was true for all the samples listed above whether examined with the resonance or the time-of-flight (shear or longitudinal) technique (11). Loss tangent equilibrium-transient equivalence was also established for all samples (11). Thus, if temperature variations are accounted for, no transient change in ultrasonically measured viscoelastic parameters was detected during rapid moisture changes!

Figures 6 and 7 here

DISCUSSION

As demonstrated in the present study, thermal corrections must be made to transient data. Moisture-induced temperature changes cause sorptive modulus data to be lower and desorptive data higher than equilibrium values. It is possible, therefore, that the modulus minima accompanying sorption, reported in the literature, are due to the increased temperature of samples. This would help to explain why transient changes are more dramatic at low moisture contents where the heat of sorption is the greatest (14,21). However, due to the lack of pertinent moisture and temperature data, it is difficult to determine which results might be thermal effects. Temperature corrections affect desorption data in the opposite way. That is, if a transient decrease in modulus is observed in data uncorrected for evaporative cooling effects, the decrease will be even larger when corrections are made. Therefore, temperature changes cannot be responsible for the initial decrease in stiffness found by Back, Salmen, and Richardson (7) in samples undergoing desorption. It is also unlikely that transient temperature changes can explain the loss tangent maxima. At room temperature and low test frequencies, increases in temperature are expected to increase loss tangent values. Sorptive heating might cause loss tangent maxima to occur. However, maxima were found accompanying desorption, where temperatures fall initially. Also, inordinately large temperature increases are required to explain observed sorptive loss tangent maxima. Finally, changes in loss tangents occur long after moisture induced temperature transients are complete.

The results of this study stand in marked contrast to all earlier reports of the transient sorption effect on the linear viscoelastic properties of polymers. To our knowledge, this is the first time that nonequilibrium and

equilibrium elastic stiffnesses were found to be equal and the first time no transient effect was observed in the loss tangents. The ultrasonic techniques differ from mechanical measurements previously made in two ways: they operate at higher frequency and at lower strains.

It seems unlikely that test frequency is the critical difference. Over the range of temperatures and moistures of the ultrasonic tests, the same viscoelastic relaxations, active at lower frequencies, are encountered. Therefore, the fundamental physical processes that influence the viscoelastic behavior in the different frequency regimes are the same. If the time frame of the experiment is not much smaller than the sorption time, anomalous errors can arise in low frequency, loss tangent calculations (29). However, transient loss tangent behavior has been reported long after sorption is essentially complete (9) and when experimental times are much less than sorption times (8,9,11,19). Also, Berger (11) found that the transient loss tangent results remained in cyclic tensile tester measurements after making corrections for modulus changes during an instrument cycle.

There is more reason to presume that the null results in the ultrasonic tests are due to their low strain amplitude. The ultrasonic tests are conducted at much lower strains than the other mechanical measurements. An upper limit on the strains produced in the time-of-flight experiment can be calculated by assuming that all of the electrical energy applied to the transmitter is converted into a circularly uniform ultrasonic wave. Taking the physical parameters (of the samples tested above) that give the highest results, the strain amplitude maximum was calculated to be 0.005%. Realistic estimates for actual strains are at least an order of magnitude lower than this.

There is support in the literature for the contention that the transient effect decreases as strain amplitude is lowered. Far larger transient minima in the torsional rigidity of wool fibers were found by Mackay and Downes (30-60%) than by Nordon (5%). Nordon suspected the smaller minima were due to his smaller angular amplitudes and larger fiber diameters. Fiber diameter does affect sorption rate, which obviously plays a role in the transient phenomenon. However, it can also affect the shear strain amplitude, since, at constant oscillation amplitude, maximum shear strain is proportional to fiber diameter. Nordon also states that, in his experience, transient minima become greater as oscillation amplitude is increased.

It is certainly possible that the transient effect is a nonlinear phenomenon. As pointed out earlier, accelerated creep is a dramatic and well-established effect. Accelerated creep tests are conducted at large strains and nonlinear behavior is clearly important. When low frequency measurements are operated at lower strains, conflicting reports of moisture transients arise. However, ultrasonic tests, which are at very low strains, detect no transient behavior. The two known reports of transient phenomena at low strain amplitudes and high frequencies (12,21) can probably be explained by sorption induced temperature effects.

CONCLUSIONS

The practical benefit of this study is that it supplies evidence that it is unnecessary to correct for transient moisture effects in making on-line ultrasonic measurements. The origin of the transient effect, observed in other mechanical tests, is still open for investigation.

ACKNOWLEDGMENT

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Figure Captions

Figure 1. A schematic of the resonant and time-of-flight experiments enclosed in the variable humidity oven.

Figure 2. Moisture content-time data for commercial blotter stock undergoing sorption and desorption.

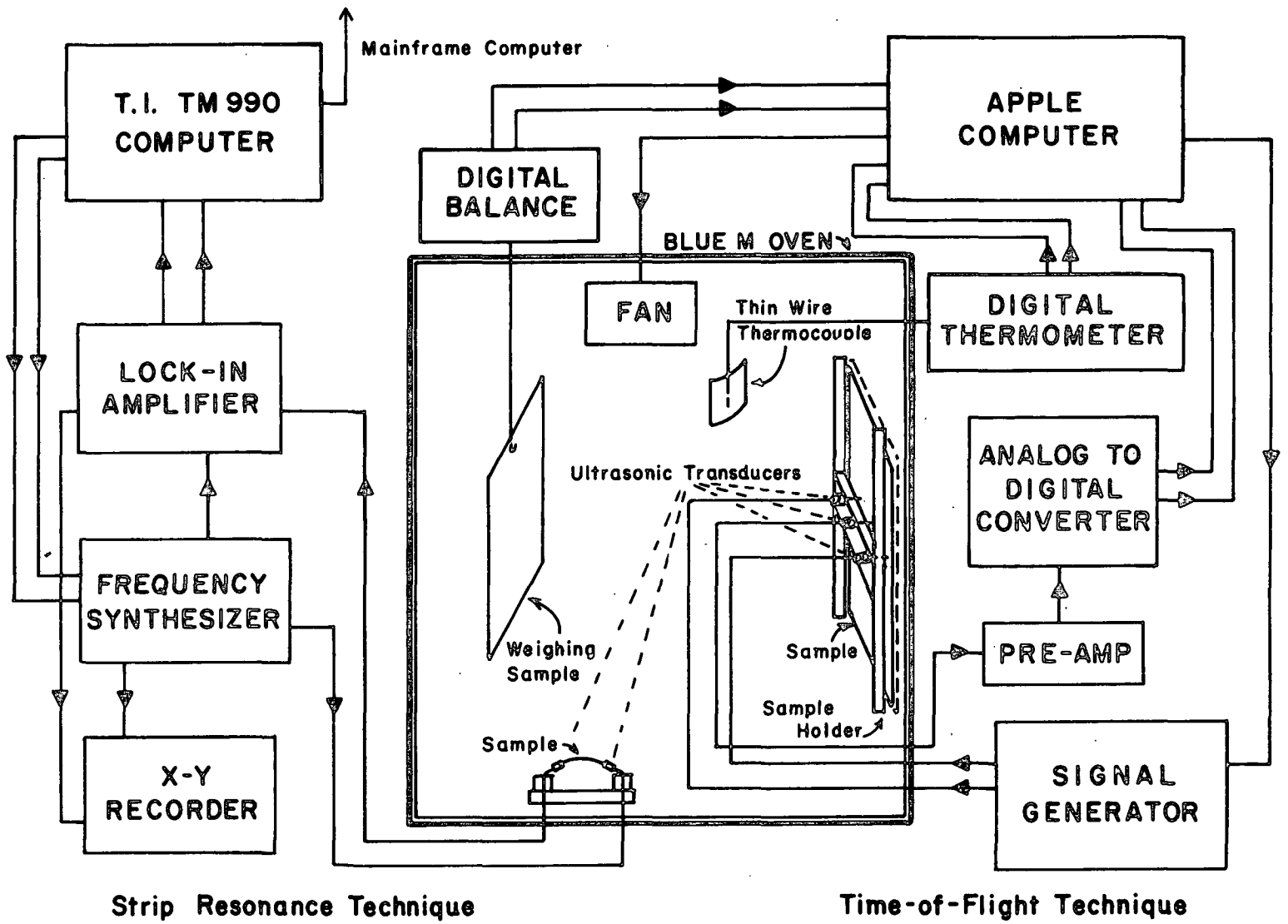
Figure 3. Strip resonance MD mass specific Young's modulus-time data for commercial blotter paper undergoing sorption from 2.5-6% and desorption from 6-2.5% moisture.

Figure 4. Strip resonance MD loss tangent-time data for commercial blotter stock undergoing sorption from 2.5-6% and desorption from 6-2.5% moisture.

Figure 5. Temperature-time data for commercial blotter stock undergoing sorption and desorption.

Figure 6. Strip resonance MD mass specific Young's modulus-temperature-moisture data for commercial blotter stock under equilibrium and transient moisture conditions.

Figure 7. Strip resonance MD mass specific Young's modulus-temperature-moisture data (corrected for temperature) for commercial blotter stock under equilibrium and transient moisture conditions.



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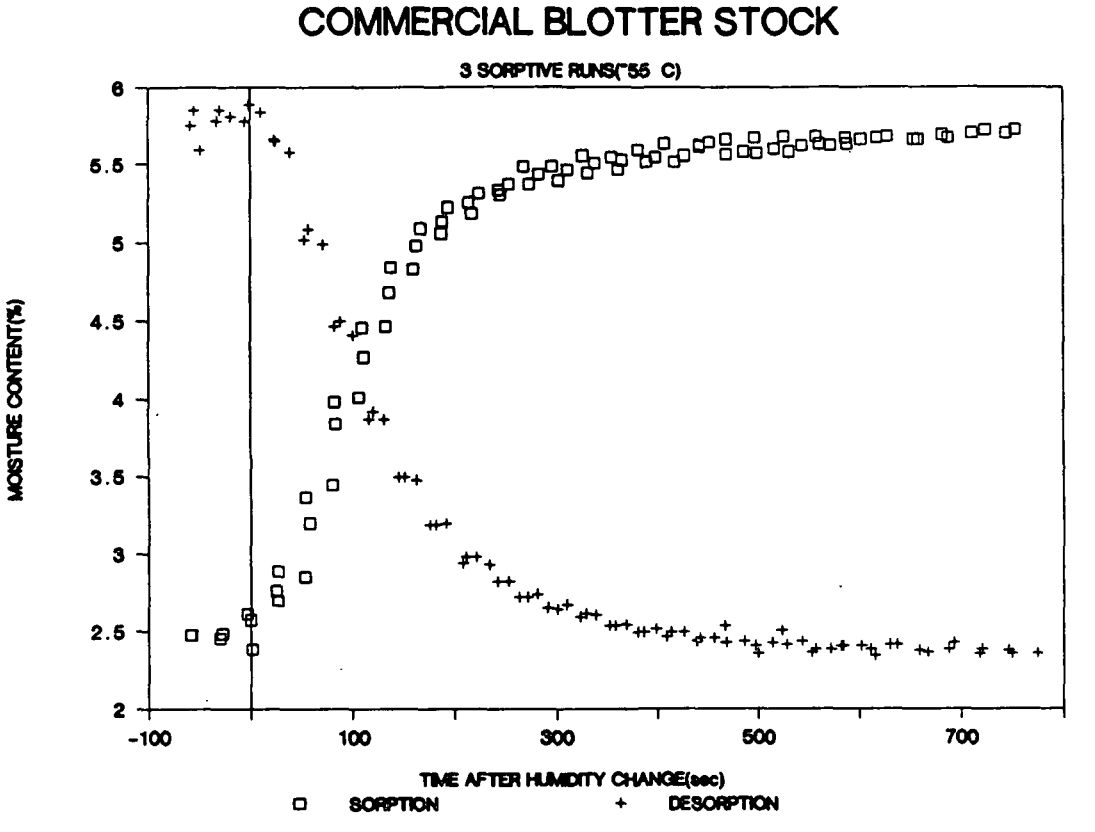

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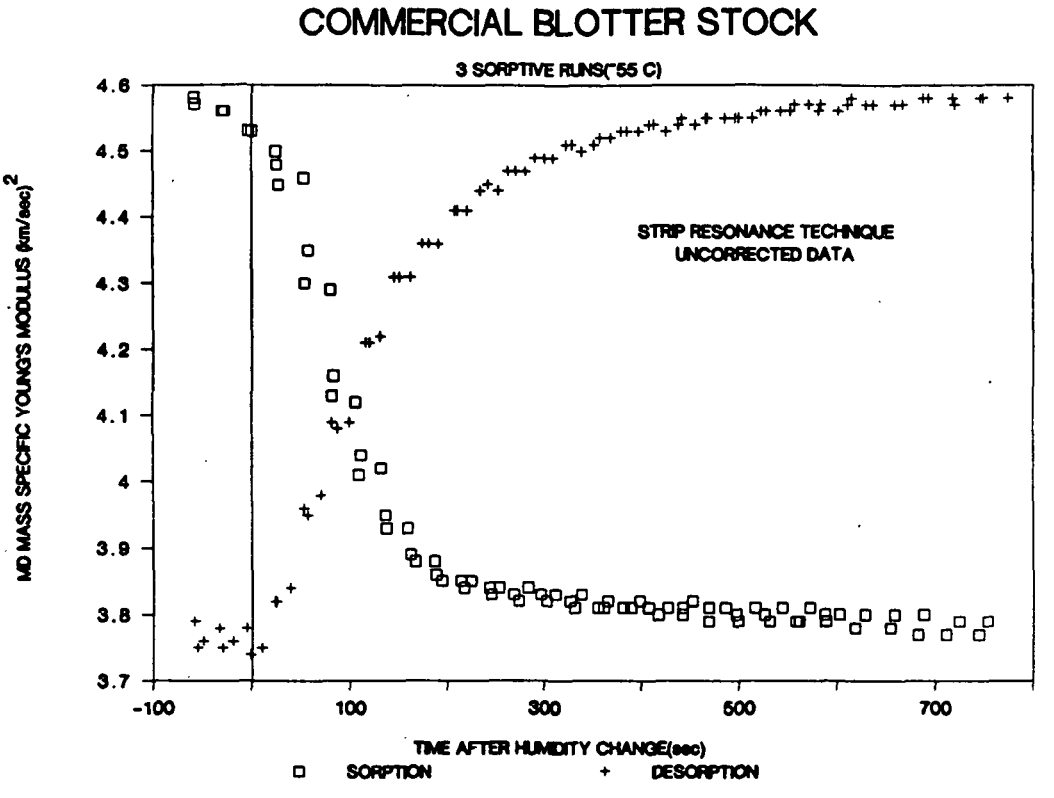
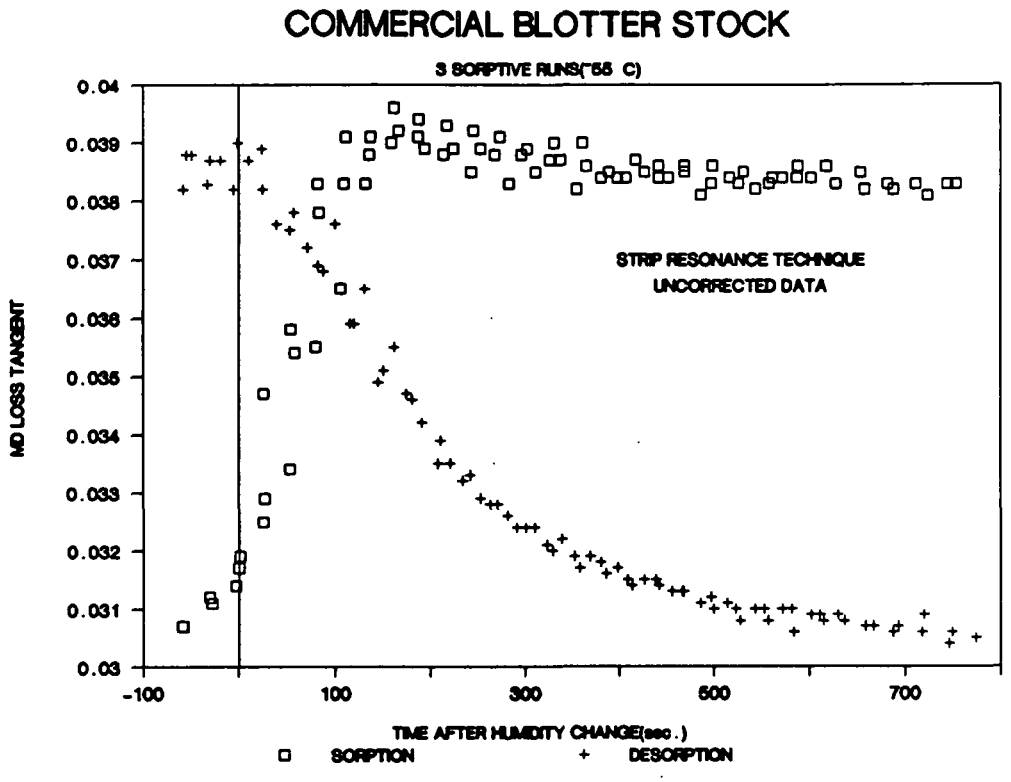


Figure 3. Strip resonance MD mass specific Young's modulus-time data for commercial blotter paper undergoing sorption from 2.5-6% and desorption from 6-2.5% moisture.



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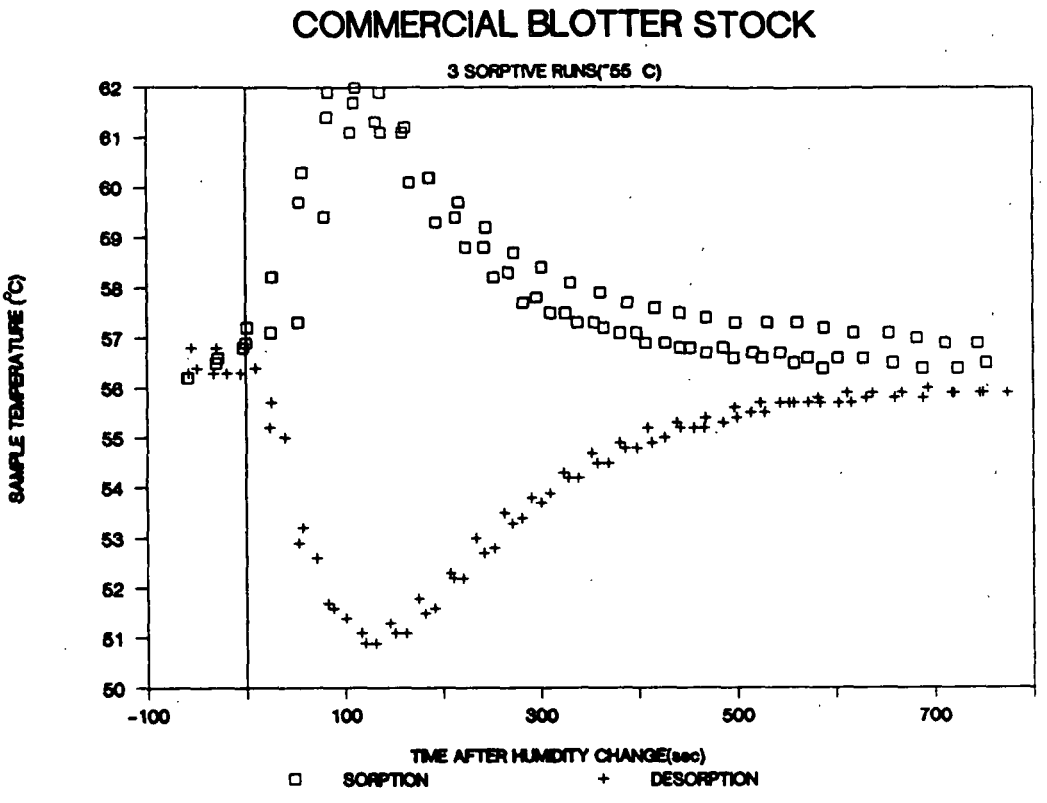

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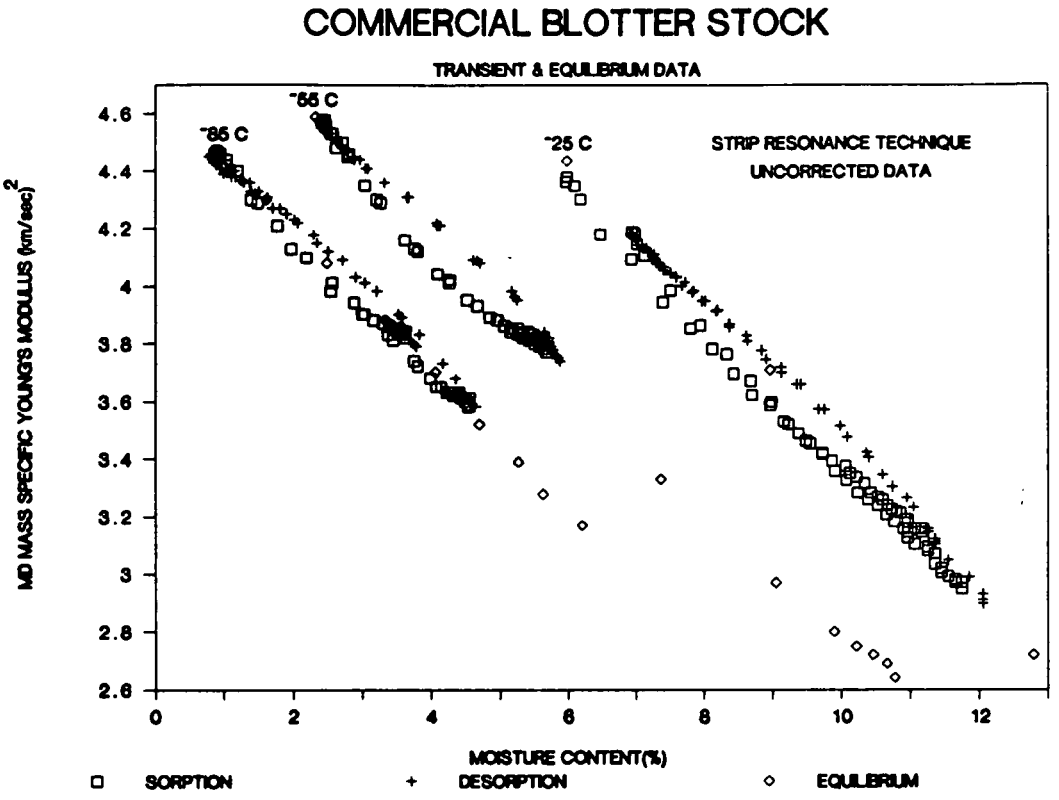

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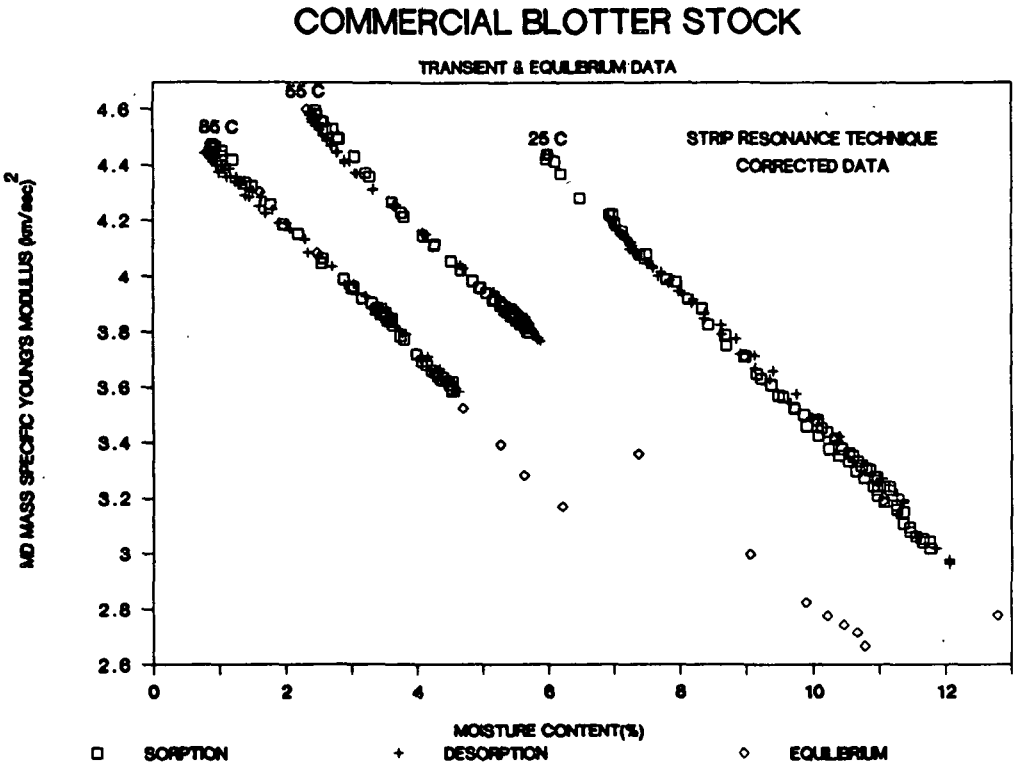

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