The Dynamic Mechanical Behavior of Paper during Drying

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Synopsis

The dynamic mechanical properties of paper during restrained drying are reported in this article. The apparatus used was a servohydraulic material testing system (MTS), connected to a computer unit. It has been found that the ratio of drying stress to elastic modulus at a given dry solids content corresponds to the instantaneous linear contraction of the sheet when the drying stress is relieved. It is therefore deduced that paper behaves as a linear viscoelastic body during restrained drying. The finding of a maximum loss coefficient and the drastic change in elastic modulus during drying of paper are interpreted in terms of a transitional change in the amorphous regions of wood polymers plasticized by water.

INTRODUCTION

This article describes the measurement of dynamic mechanical properties of paper during restrained drying. Complex moduli in tension and loss coefficients (loss factors) at various dry solids contents have been measured. In addition, the ratio of the drying stress to the elastic modulus evaluated by extrapolation to zero strain amplitude has been compared with the immediate contraction of the sheet when the stress is released.

Previously, dynamic mechanical studies have only been performed in the region in which the cellulosic material was in equilibrium with ambient relative humidities.[1–3]

In resonant techniques with a low frequency it has been noted that transient phenomena may lead to significant changes in the loss factor.[1,2] In such cases, the rate at which diffusion takes place may have been so fast in relation to the testing frequency that resonant phenomena may have arisen in the evaluation of the damping value.

The dynamic mechanical technique used in this study makes it possible to study the elastic modulus, drying stress, and loss coefficient under non-equilibrium conditions by applying sinusoidal vibration at frequencies which are higher in comparison with the rate of evaporation as well as by applying low strain amplitudes.

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EXPERIMENTAL

Materials

Commercially manufactured, bleached kraft pulp from pine was used. The pulp consisted of 76% cellulose and 24% hemicellulose and the degree of polymerization (DP) was 1400. The carbohydrate content and DP of the pulp was determined according to the methods described in Refs. 4 and 5.

The pulp was beaten to 20 SR in a Valley beater, according to the scan-test procedure. Handsheets (200 g/m^2) were formed on a Formette Dynamique former[6] and the sheets were wet-pressed to a density of approximately 600 kg/m^3.

The wet-pressed sheets were then cut into samples with dimensions 150 mm $\times$ 250 mm. The cross-sectional area used for stress determination was determined on the dried samples.

Drying

All the samples were dried under restraint. Each sample was placed between two pairs of specially designed clamps mounted on a servohydraulic forced vibration dynamic tester (MTS). The clamped regions of the sample were heated to insure that they were drier than the exposed part of the sample to avoid breakage and slippage at the clamps. The distance between the upper and lower clamp pairs was 220 mm. The strain was measured by means of an extensometer attached to the clamps. The dry solids content of the sample was evaluated indirectly by weighing an identical piece suspended on an electronic balance (Sauter). Thus evaluation of the dry solids content of the sample may of course be subject to error due to, e.g., differences in moisture gradient, variations in basis weight, etc., between the sample used for dry solids content measurement and the sample used for evaluating the mechanical properties. The results of a calibration show however that the variation is within $\pm$ 2%. The drying climate was 25°C and 25% relative humidity. The surface temperature of the sample, during drying, was 20°C until the dry solids content had reached 75%. Thereafter the temperature rose to that of the surrounding climate.

Apparatus and Dynamic Testing

The apparatus used was a servohydraulic materials testing system (MTS) connected to a computer unit. One of the clamp pairs was attached to a hydraulic cylinder and the other clamp pair was mounted on a load cell.

Under cyclic loading conditions, viscoelastic behavior in general leads to energy dissipation. This means that the stress–strain curve is not a single-valued function, but forms a hysteresis loop, the area within the loop being proportional to the energy absorbed. The loss factor is dependent on the area within the loop, which can be a function of both frequency and stress (or strain) amplitude.

The stress and strain signals obtained in a dynamic test using a sinusoidally varying strain may be combined into a stress–strain diagram to

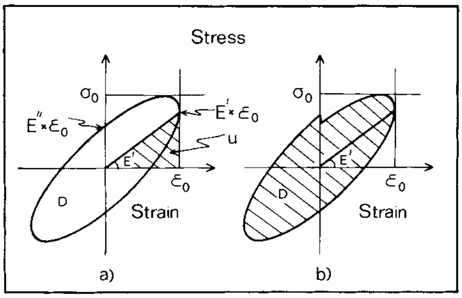

Fig. 1. The hysteresis loop: relation between stress and strain in a dynamic mechanical test with sinusoidally varying stress and strain: (a) closed loop ellipse; (b) nonclosed loop.

form an elliptical hysteresis loop, as shown in Figure 1(a). Half the strain amplitude ϵ_0 and half the stress amplitude σ_0 are indicated in the figure. Note that the origin of the ellipse is not necessarily situated at zero stress and strain. The slope of the straight line through the origin is the real (storage) part of the complex modulus, E' (simply denoted as elastic modulus in this paper). Here E'' denotes the loss modulus, and δ is the loss angle. The area of the loop, D, is the energy per unit volume dissipated during each cycle:

$$\begin{aligned} D &= \pi \cdot E'' \cdot \epsilon_0^2 \\ &= \pi \cdot \sigma_0 \cdot \sin \delta \cdot \epsilon_0 \end{aligned} \tag{1}$$

The elastic strain energy u, represented by the area of the shaded triangle in Figure 1(a), is

$$\begin{aligned} u &= \frac{1}{2} \cdot E' \cdot \epsilon_0^2 \\ &= \frac{1}{2} \cdot \sigma_0 \cdot \cos \delta \cdot \epsilon_0 \end{aligned} \tag{2}$$

The loss coefficient (loss factor) is determined from u and D:

$$\begin{aligned} \tan \delta &= \frac{D}{2 \cdot \pi \cdot u} \\ &= \frac{E''}{E'} \end{aligned} \tag{3}$$

In the present investigation, all runs were carried out under strain-controlled conditions, i.e., the strain amplitude was kept constant while the stress was allowed to increase as a result of the increasing drying stress during the run. Occasionally, when the rate of drying is faster than the experimental frequency, the loop is not closed at lower frequencies, as shown in Figure 1(b). In this case, an equivalent linear damping is defined by eq. (3). D is the shaded area in Figure 1(b), and u is the shaded triangle defined as in Figure 1(a).

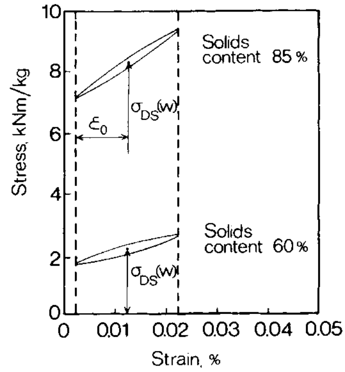

Fig. 2. Schematic illustration of stress and strain loops during drying. $\sigma_{DS}(\omega)$ is the drying stress at a given solids content (ω). ϵ is the strain amplitude.

The frequency range studied was 0.1–10 Hz and the strain amplitude ranged from 0.02% to 0.2%. Figure 2 shows hysteresis loops with a strain amplitude of 0.02% measured at two solids contents during drying. The drying stress $\sigma_{DS}(\omega)$ is defined at the average stress in the loop. Note that the dynamic studies are performed so that only tensile forces act on the sample.

Because paper has a porous network structure, stress σ and elastic modulus E, which are expressed in terms of force per unit cross-sectional area (MPa, GPa), are less suitable quantities. These properties are, furthermore, sensitive to changes in sheet thickness. Therefore, it is more relevant to express the mechanical properties in terms of specific properties, i.e., stress and modulus divided by the sheet density. The density used is that obtained by measurement of the grammage and dimensions of the dry sheet at 50% relative humidity and 23°C. The sheet thickness was measured by employing two spherical anvils one attached to a LVDT.

RESULTS

Drying Stress

The relationship between the drying stress and the elastic modulus at various drying solids content during drying was evaluated from dynamic mechanical measurements.

In order to enable a comparison to be made with static drying stresses, i.e., no superimposed strain amplitude, the strain amplitude was varied and the curve of drying stress was extrapolated to zero strain amplitude (Fig. 3). The corresponding elastic modulus was also obtained by extrapolation to zero strain amplitude (Fig. 4). This enabled the complicating factor of superimposed creep and plastic flow during the experiment to be avoided.

The extrapolated drying stress closely corresponded to the drying stress obtained in experiments in which the sample was subjected to no sinusoidal vibrations. The elastic modulus did not exhibit the same sensitivity to strain amplitude, but at a strain above 0.1% a drop in modulus was observed, indicating that plastic deformation is a factor contributing to the loss of energy in the cyclic deformation.

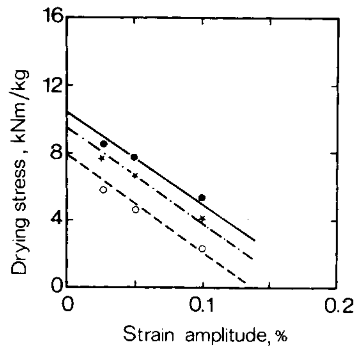

Fig. 3. Drying stress at different dry solids contents vs. strain amplitude: (●) 85%; (✱) 75%; (○) 65%.

Table I shows the ratio of the extrapolated drying stress to elastic modulus at three different solids contents and the immediate sheet contraction observed on release of the stress at these solids contents. The table shows that the calculated drying strain is equal to the instantaneous contraction of the sample on release of the stress at a given solids content. Drying stress is consequently a product of elastic modulus times drying strain.

In an earlier work,[7] it was found that drying stress corresponded to the yield stress of paper, i.e., the highest stress at which the stress is linearly related to strain. Drying stress and drying strain when the paper is dried under restraint consequently correspond to yield stress and yield strain.

A schematic presentation of the drying process under restrained conditions is given in Figure 5. As drying proceeds, the drying stress builds up to the level of the yield stress. If the stress is released, the sheet contracts by an amount equal to the drying strain. The elastic modulus of the sheet at a given solids content may in principle be determined from the slope of the stress–strain curve.

Loss Coefficient and Elastic Modulus

Figure 6 shows the loss coefficient vs. solids content at various frequencies. The large deviation in the loss coefficient evaluated at 0.1 Hz may be at-

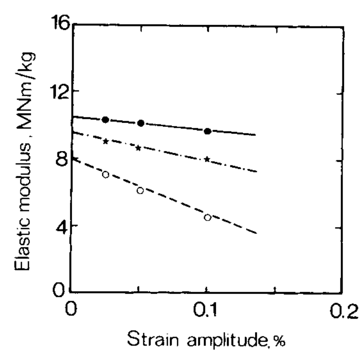

Fig. 4. Elastic modulus vs. strain amplitude at different dry solids contents: symbols as in Figure 3.

TABLE I
Ratio of Drying Stress to Elastic Modulus and Contractions Obtained on Release of Drying Stress at Different Dry Solids Contents

Dry solids content (%) (ω)	Calculated drying strain (%) $\epsilon_{DS} = \sigma_{DS}(\omega)/E(\omega)$	Contraction (ϵ) (%)
65	0.090	0.093
75	0.10	0.11
85	0.10	0.11

tributed to transient conditions during drying. These phenomena may be encountered when the drying rate or rate of change in mechanical properties is rapid in relation to the measuring frequency. Above 1 Hz this effect was neglible. A slight shift in peak value of the loss coefficient towards lower dryness values was observed when the frequency was increased, indicating the frequency dependence behavior of a viscoelastic process.

Figure 7 reveals that the loss coefficient (tan δ) displayed a maximum at a dry solids content of about 50% (1 g water/1 g dry sheet). The storage elastic modulus of paper changed drastically after passing the maximum, and the loss modulus reached a peak at a dry solids content of about 85%. During the drying process, the sample thus displayed a change in loss coefficient and elastic modulus analogous to a second-order transition in a polymer system.

Since paper is composed of fibers based on semicrystalline polymers, the observed changes in modulus and loss coefficient are expected to be lower than for pure amorphous systems.

DISCUSSION

In a paper by Page and Seth,[8] it was demonstrated that the elastic modulus of dry paper can be quantitatively calculated using Cox's theory,[9] which predicts that the elastic modulus of paper will be one-third of the elastic modulus of the fibers.

The fibers in the sheet used in this investigation consisted of 76% cellulose and 24% hemicellulose. Cellulose consists mainly of crystalline material,

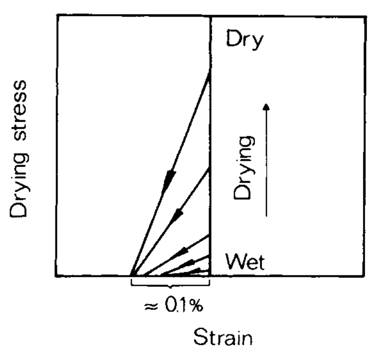

Fig. 5. A schematic presentation of the drying process under restraint. The slope of each line represents the elastic modulus of the sheet. The arrows indicate the direction of sheet contraction when the stress is released.

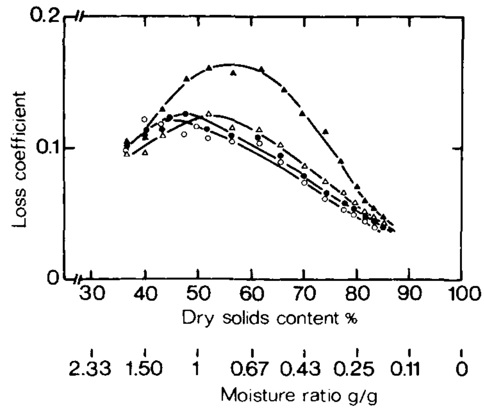

Fig. 6. Loss coefficient (tan δ) vs. dry solids content (strain amplitude 0.05%): (▲) 0.1 Hz; (△) 1 Hz; (●) 5 Hz; (○) 10 Hz.

and this crystalline material aggregates into microfibrils,[10] which are considered to be the reinforcing element in the fiber.[11-13]

The cellulose microfibrils contain irregularities or disordered zones which are accessible to water.[14-17] Due to these irregularities, changes in rigidity due to water may take place locally in the microfibrils.[18] Hemicelluloses are relatively unoriented or amorphous or short-chained polymers having DP values in the low hundreds and are easily softened by moisture.[19]

Following the above arguments, it is possible to establish a link between the constituent components of the cell wall and the elastic properties of the sheet at various moisture contents.

The findings that there is a maximum loss coefficient and that there is a drastic change in elastic modulus during the drying of paper can thus be interpreted in terms of a transitional change in the amorphous regions of wood polymers which are plasticised by water. This is in agreement with the results reported by Westman and Lindström for cellulose gels.[20] Westman and Lindström demonstrated earlier that cellulose gel displayed rubber

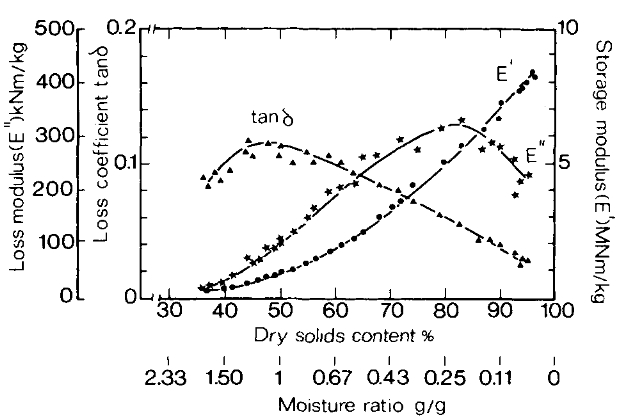

Fig. 7. Elastic modulus and loss coefficient vs. dry solids content for bleached sulphate sheet (5 Hz and 0.05% strain amplitude). (▲) loss coefficient; (●) storage elastic modulus; (★) loss elastic modulus.

elastic features at a certain critical water content in the amorphous phase. When the content of water was reduced, a rapid decrease in creep compliance took place.

FINAL REMARK

Maxima in loss coefficient and loss modulus are observed during the drying of paper. Another important finding in this work is the correspondence between the drying stress–elastic modulus ratio and the sheet contraction. This indicates that there is good experimental support for viewing the drying stresses as linear viscoelastic when shrinkage is not allowed during drying. The drying stress is then simply the modulus times the drying strain, which was fairly constant for the paper investigated.

It is therefore suggested that the drying stress is caused by the rapid increase in modulus of the network due to the loss in mobility of the amorphous components in the cell wall.

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