# Dynamic viscoelastic measurements of handsheet papers

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**ABSTRACT** *We studied the dynamic viscoelastic properties of beaten and unbeaten handsheet papers of bleached sulfite eucalyptus pulp. We obtained the storage and loss elasticity moduli in isothermal condition experiments at temperatures from 30°C to 70°C and frequencies from 0.3 Hz to 50 Hz. From these data, we evaluated and analyzed the modulus relaxation and the influence of temperature. The results were treated according to the use of Percolation Theory to derive a relationship between Young's modulus of an ideal paper and density. We also analyzed the influence of beating in an activation coefficient and in its derivative with respect to temperature and time.*

**KEYWORDS**
Analysis
Chemical analysis
Elastic strength
Physical properties
Viscoelasticity

The term "dynamic viscoelasticity" refers to measurements at oscillatory deformation. Such measurements provide information about the elasticity and about the loss, or damping, component of the sample. In spite of the increasing importance of dynamic viscoelasticity testing in materials science (especially in plastics), the dynamic testing of papers has received little attention.

Studies of the dynamic viscoelasticity of paper have shown the influence of the amplitude of the applied sinusoidal strain on the storage, or elastic, modulus and on the loss modulus. The storage modulus decreases with increasing amplitude of oscillatory deformation, while the loss modulus increases (*1-2*). With increasing network density, on the other hand, the storage modulus increases, and the loss factor decreases. This result is associated with interfiber friction and the shearing of cellulose fibers. As an example of the use of dynamic viscoelastic measurements, a recent study on mechanical properties of filled paper demonstrates that increasing clay content increased markedly the loss factor, reducing the stiffness, strength, and ductility of paper (*3*).

The influence of frequency (at a finite amplitude of strain) is of particular interest, because a dynamic measurement at frequency $\nu$ is equivalent to a transient one at $t = 1/\nu$. In the case of solid paper, the stress-strain measurements should include the time factor in order to study relaxation effects (*4*). Yet the mechanical behavior of paper is usually studied on the basis of the Young's moduli determined from the initial slope of load-elongation curves.

In our work, we measured the loss moduli and storage moduli of papers obtained at different beating conditions at a constant amplitude of strain but at frequencies ranging from $10^{-1}$ to $10^{-2}$Hz. The results are theoretically treated according to the Percolation Theory proposed by Nissan and Batten (*5*).

## Experimental procedures

The papers used were handsheets of bleached sulfite eucalyptus pulp beaten in Lampen and PFI mills and a Valley hollander. These beaters differ in that the beating organ of the Lampen mill has no filling at all, the PFI mill has a filling in only one beating organ, and Valley hollander beating organs are provided with knives. This equipment is used to macerate, cut, and fibrillate pulp fibers to increase their specific surfaces and their tendencies to bond. Some characteristics of the papers are presented in **Table I.**

In dynamic viscoelastic tests, the material sample is subjected to a sinusoidal deformation. The material response to the sinusoidal deformation is, at low enough deformation, a sinusoidal stress shifted in phase to the input deformation. The ratio of output stress amplitude and the input deformation amplitude is the complex modulus, which can be separated in a real part $E'$, the storage modulus, and an imaginary part $E''$, the loss modulus. The storage modulus represents the energy stored as reversible deformation in the sample during the test. The loss modulus represents the energy dissipated irreversibly by the motion of network segments. The ratio of loss modulus and storage modulus is defined as the loss factor, $\tan \delta$.

Dynamic mechanical properties

were measured in a Polymer Laboratories DMTA apparatus using bending deformations. These deformations are achieved by applying a sinusoidal current of known magnitude to a linear electromechanical vibrator. The amplitude of the displacement produced in the sample is monitored by an in-line, linearized, eddy-current displacement transducer.

From this type of bending experiment, the storage and loss components of the tensile modulus, or Young's modulus, can be derived (*6*). The amplitude of the oscillating displacement was 16 $\mu$. Isothermal experiments with samples 25 × 10 × 1 mm were carried out at temperatures from 30°C to 70°C at frequencies of 0.3, 1, 2, 3, 5, 10, 20, 30, and 50 Hz.

**I.** Characteristics and results for the different samples, including values for E, the storage modulus taken at a frequency of 1 Hz and extrapolated to w = 0, according to Eq. 3

| | Freeness, °SR | Ratio of water to solid, g $H_2O$/ g paper | Density, kg/m³ | E' v = 1, GPa | $E'_0$, GPa | Activation coef.,* $\gamma$ |
|---|---|---|---|---|---|---|
| Unbeaten paper | ... | 0.0646 | 509 | 0.94 | 1.12 | 0.36 |
| PFI mill | 26 | 0.0674 | 698 | 2.24 | 2.70 | 0.46 |
| | 43 | 0.0682 | 892 | 2.60 | 3.16 | 0.33 |
| Lampen mill | 26 | 0.0677 | 723 | 2.90 | 3.50 | 0.56 |
| | 41 | 0.0710 | 932 | 2.96 | 3.66 | 0.35 |
| Valley beater | 25.5 | 0.0639 | 615 | 3.02 | 3.56 | 0.78 |
| | 43.5 | 0.0629 | 759 | 2.68 | 3.14 | 0.45 |

*Obtained from Eq. 10.
SR = Schopper-Riegler freeness.

## Results and discussion

**Figures 1 and 2** present, respectively, the storage modulus, $E'$, and loss modulus, $E''$, plotted against frequency at a constant temperature of 30°C, for all the samples.

The relaxation modulus $E(t)$, presented in **Fig. 3**, was calculated by the equation proposed by Ninomiya and Ferry (*7*):

$$E(t) = | E'(\nu) - 0.4E'' (0.4\nu) + 0.014E'' (10\nu) | \; \nu = 1/t \qquad (1)$$

The influence of the temperature on the storage modulus can be seen in **Fig. 4** for unbeaten paper. Similar results are obtained for the rest of the samples.

The storage modulus dependence on frequency $\nu$ can be expressed, for all the samples (Fig. 1) at all temperatures (Fig. 4), by the equation:

$$\log E' = \log(E')_{\nu=1} + 0.002 \log \nu \qquad (2)$$

To study the influence of beating on the viscoelastic properties, we have compared the storage moduli, $(E')\nu$ = 1, of the different samples obtained at a frequency of $\nu$ = 1 Hz and a temperature of T = 30°C. These moduli, together with densities, are presented in Table I. Humidity has a considerable effect on Young's modulus, and humidity is expressed in Table I as the ratio of water to solid (g $H_2O$/g paper). Because of this effect, we have to refer to a common moisture content when comparing different papers.

An equation proposed recently by Batten and Nissan (*8*) is

$$\ln (E'/E'_0) = 0.2433 - 6.4074\, w \qquad (3)$$

where $w$ represents the ratio of water to solid. Using this equation, we can obtain the modulus $E_0'$, when $w$ = 0. In Table I, we can compare the values of $E_0'$ obtained for each sample, taking $E' = (E')\nu = 1$.

Recently, Nissan and Batten have used Percolation Theory to derive a relationship between the tensile modulus of an ideal paper and density, for given values of moisture and temperature (*5*). In their use of the Percolation Theory, Nissan and Batten define the total number of bonds available for elastic energy storage per unit mass as a fraction of the total when the space is fully tesselated:

$$S = \rho/\hat{\rho} \qquad (4)$$

where

$S$ = the solid fraction of the total space
$\rho$ = the apparent density of paper
$\hat{\rho}$ = the density of crystalline cellulose = 1540 kg/m³.

When $0.2322 < S < 1$, they obtain

$$E/\rho = (\hat{E}/\hat{\rho})S \qquad (5)$$

where $\hat{E} = \hat{E}_{w,\,T(\hat{\rho})}$ is the maximum value of Young's modulus of an ideal, isotropic, cellulosic paper at the density of the crystalline cellulose. The value of $\hat{E}$, in GPa, is given by the equation

$$\hat{E} = 28.79 \exp | -[( w + 0.0024)(T - 25°)]| \qquad (6)$$

This equation gives a value of $\hat{E}$ = 28.45 for $w$ = 0 and $T$ = 30°C.

Using this result and combining Eqs. 4 and 5, we obtain the following expression for ideal paper of zero moisture content at 30°C:

$$E_0 = \rho^2 (28.45 \times 10^9/1540^2) \qquad (7)$$

Nissan and Batten (*5*) compared theoretical and experimental results for three pulps, observing deviations except in the case of Corsican pine kraft pulps. The authors attributed these deviations from the theoretical prediction to variations in pulps that affect the density of hydrogen bonds at a given density of paper. (These variations include different lignin or hemicellulose contents, as well as different bonding or debonding agents.) To include these effects in the theory, they propose the following relationship:

$$E_{real}(\rho) = \gamma\, E_{ideal}(\rho) \qquad (8)$$

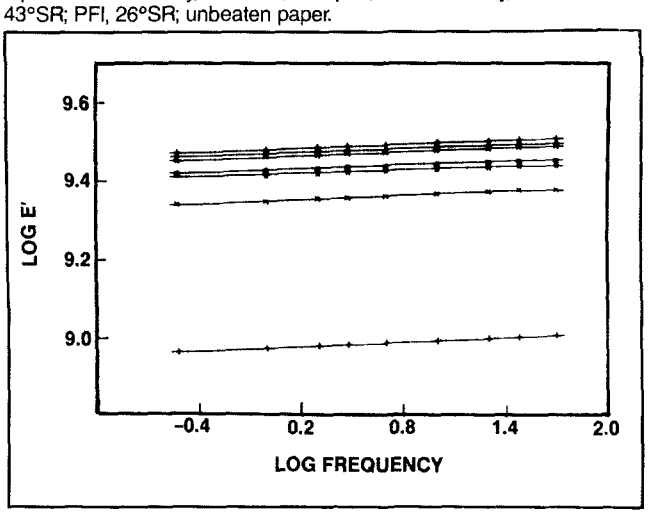
where $\gamma$ is an activation coefficient that accounts for variation in pulps and the presence of bonding or debonding agents.

In our particular case, at a frequency of $\nu$ = 1 Hz, $T$ = 30°C, and $w$ = 0, we have

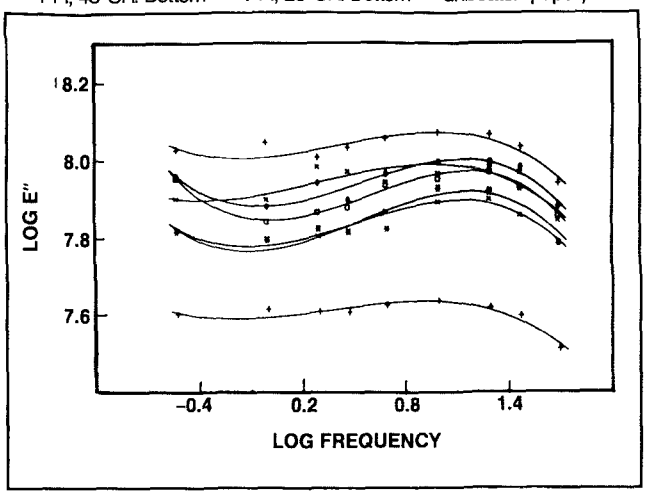
$$E_0 = \gamma\rho^2 (28.45 \times 10^9/ 1540^2) \qquad (9)$$

In **Fig. 5**, we present the plots corresponding to Eq. 9 for $\gamma$ = 1 (ideal case), $\gamma$ = 0.7, $\gamma$ = 0.5, and $\gamma$ = 0.3. The experimental values presented in Table I are also plotted. Our papers, made from bleached, sulfite, eucalyp-

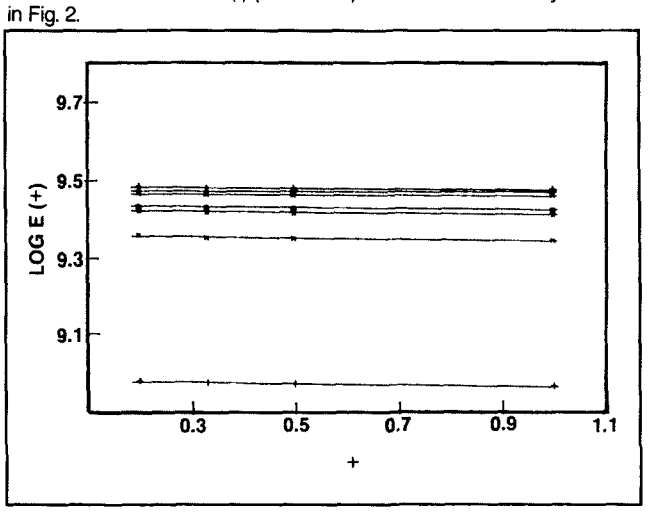
1. Storage modulus $E'$ (in Pascals) against frequency at 30°C. From top to bottom: Valley, 25.5°SR; Lampen, 26°SR; Valley, 43.5°SR; PFI, 43°SR; PFI, 26°SR; unbeaten paper.



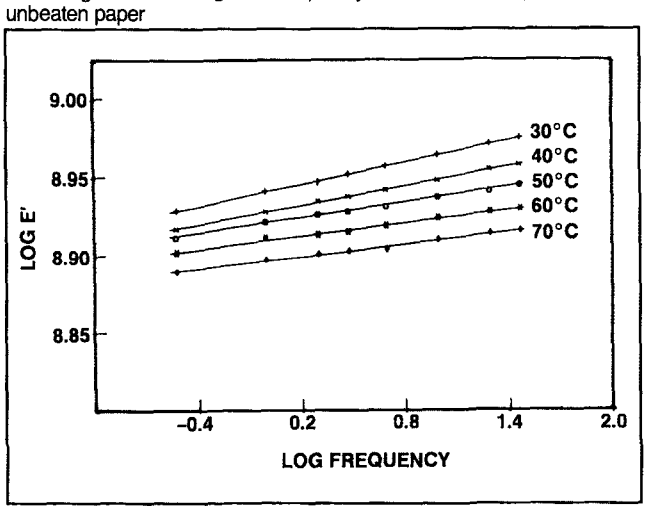

2. Loss modulus $E'$ (in Pascals) against frequency at T = 30°C. (Top+ = Valley, 25.5°SR. • = Lampen, 41°SR. × = Lampen, 26°SR. o = Valley, 43.5°SR. * = PFI, 43°SR. Bottom × = PFI, 26°SR. Bottom+ = unbeaten paper.)




3. Relaxation modulus $E(t)$ (in Pascals) at T = 30°C. Same symbols as in Fig. 2.




4. Storage modulus against frequency at different temperatures for unbeaten paper




tus pulp, correspond to a relatively low value of $\gamma$, especially when we compare it to values for white birch pulps (*9*) ($\gamma$ = 0.88), larch kraft pulps ($\gamma$ = 0.74), and Corsican pine kraft pulps ($\gamma$ = 1).

With Eq. 8 having been proposed so recently, there is no more information to our knowledge concerning values of $\gamma$ for different samples. Results presented in the literature we have referenced include data of the Young's moduli determined from the initial slope of a load-elongation curve, rather than stress relaxation and $E'$ against frequency curves. Therefore, it is difficult to compare our results with those obtained from published studies, which usually do not include information on time effects and deformation speeds. Nevertheless, from **Table II** we conclude that tensile moduli for other pulps are similar to ours, except when the test was made in the machine direction.

One of our aims was to find a parameter that might be affected by beating. The effect of beating is to transfer bonds from within the fibers to between the fibers; consequently, $\gamma$ should be the parameter affected by beating since it is presented as a measure of the bonding in real paper relative to an ideal cellulosic paper at the same density.

As we can see from results presented in Fig. 1 and Table I, beating gives the final paper sheet a higher density and tensile modulus. However, we observe in Fig. 5 that the data of unbeaten pulp and pulp beaten in the Lampen and PFI mills and the Valley hollander do not correlate according to different values of $\gamma$. In fact, we can obtain an estimated value for each sample from Eq. 9:

$$\gamma = E''_0 / 11{,}996\rho^2 \qquad (10)$$

The values of $\gamma$ obtained from this equation and presented in Table I do not show evidence of the influence of beating.

The effect of temperature on the storage modulus, $E'$, is presented in Fig. 4, for unbeaten paper. Similar plots are obtained for the rest of the samples. In all cases, the influence of temperature is independent of frequency. To analyze this influence in the framework of the Percolation Theory, we express Eq. 9 in the form:

$$E = \gamma (\rho/\hat{\rho})^2 E \qquad (11)$$

Taking the logarithm of both sides and differentiating with respect to

temperature, we obtain (assuming the variation of $(\rho/\hat{\rho})^2$ with temperature is negligible):

$$d\ln E/dT = (1/\gamma)(d\gamma/dT) + (d\ln \hat{E}/dT) \quad (12)$$

Batten and Nissan have obtained a value for $d\ln \hat{E}/dT$ of $-2.4 \times 10^{-3}$ deg$^{-1}$ for ideal paper considered as an H-bond-dominated solid. Therefore, we can express:

$$(d\gamma/dT) = \gamma[(d\ln E/dT) + 2.4 \times 10^{-3}] \quad (13)$$

Our experimental values of $(d\ln E/dT)$ and the estimated $(d\gamma/dT)$ values are presented in **Table III**. These data of $(d\ln E/dT)$ are in the range of the experimental values presented by Batten and Nissan for various pulps—from $-1.3 \times 10^{-3}$ to $-3.6 \times 10^{-3}$ deg$^{-1}$. As to the values of $(d\gamma/dT)$, for unbeaten paper there is a decrease of $\gamma$ with temperature, whereas for beaten paper samples the activity coefficient increases with temperature. In general, according to Eq. 13, the sign of the variation of $\gamma$ is determined by the value $-2.4 \times 10^{-3}$ deg$^{-1}$. Actually, among the experimental data of Batten and Nissan (*8*), we find higher and lower values than this critical value.

In any case, for the experimental data available until now, the variation of $\gamma$ with temperature is small: a change of 50°C in temperature produces a variation of less than 10% in the activity coefficient.

The relaxation modulus $E(t)$ obtained according to Eq. 1 and presented in Fig. 3 can be expressed for all the samples by the equation:

$$E(t) = E(0)\exp(-0.013t) \quad (14)$$

where $E(0)$ is characteristic of each sample and $t$ is given in seconds.

To analyze these results, we differentiate Eq. 11 with respect to time, which yields:

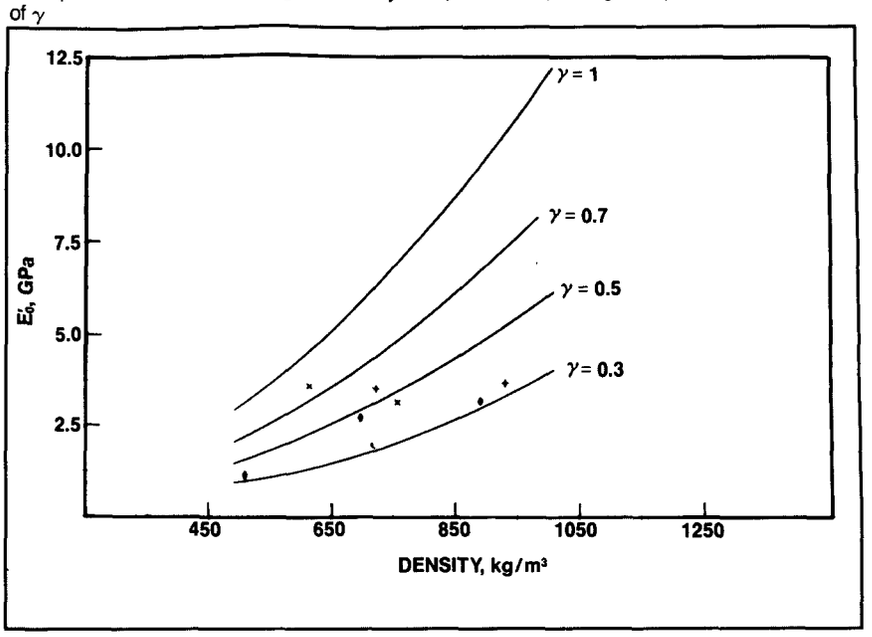
$$dE/dt = (\rho/\hat{\rho})^2 \hat{E} d\gamma/dt + \gamma(\rho/\hat{\rho})^2 (d\hat{E}/dt) \quad (15)$$

According to Eq. 14, the left part of this equation can be expressed as:

$$dE/dt = -0.013E \quad (16)$$

In our case, $dE/dt$ varies from $-1.237 \times 10^7$ Pa/s for unbeaten paper ($E = 9.52 \times 10^8$ Pa) to $-3.978 \times 10^7$ Pa/s for Valley-beaten paper ($E = 3.06 \times 10^9$ Pa).

**5.** Experimental values of $E'_0$ against density and plots corresponding to Eq. 9 for different values of $\gamma$




**II.** Young's moduli of different papers, obtained from referenced literature

| $E_0$, GPa | Observations | Ref. |
|---|---|---|
| 2.86 | Commercial paper. Cross-machine direction. | 10 |
| 7.03 | Commercial paper. Machine direction. | 10 |
| 3.6 | | 1 |
| 1.5 | Machine-ground kraft paper. Nonlinear viscoelastic measurements. | |
| | $\epsilon = 1.3 \times 10^{-6}$ s. $\sigma_0 = 2.3 \times 10^7$ Pa. | |
| 2.1 | $\epsilon = 4.17 \times 10^{-6}$ s. $\sigma_0 = 3 \times 10^7$ Pa. | 11 |
| 4 | $\epsilon = 5 \times 10^{-3}$ s. $\sigma_0 = 3 \times 10^7$ Pa. | 11 |
| 2.38 | Handsheet, unbleached kraft softwood. | 12 |
| 7.36 | Linerboard, 20% R.H., machine direction. | 12 |
| 2.88 | Linerboard, 20% R.H., cross-machine direction. | 12 |

**III.** Experimental values of $d\ln E/dt$ in the range of 30–70°C and $d\gamma/dT$ and $d\gamma/dt$ obtained according to Eqs. 13 and 15, respectively

| Sample | Freeness, °SR | $d\ln E/dT$, deg.$^{-1}$ | $d\gamma/dt$, deg.$^{-2}$ | $d\gamma/dT$, deg.$^{-1}$ |
|---|---|---|---|---|
| Unbeaten paper | ... | $-3.45 \times 10^{-3}$ | $-3.78 \times 10^{-4}$ | $-3.98 \times 10^{-3}$ |
| PFI mill | 26 | $-2.76 \times 10^{-3}$ | $+4.71 \times 10^{-4}$ | $-5.02 \times 10^{-3}$ |
| | 43 | $-3.68 \times 10^{-3}$ | $+1.85 \times 10^{-4}$ | $-3.96 \times 10^{-3}$ |
| Lampen mill | 26 | $-1.38 \times 10^{-3}$ | $+5.69 \times 10^{-4}$ | $-6.00 \times 10^{-3}$ |
| | 41 | $-2.33 \times 10^{-3}$ | $+2.45 \times 10^{-5}$ | $-3.72 \times 10^{-3}$ |
| Valley beater | 25.5 | $-1.84 \times 10^{-3}$ | $+1.16 \times 10^{-3}$ | $-8.76 \times 10^{-3}$ |
| | 43.5 | $-2.30 \times 10^{-3}$ | $+5.60 \times 10^{-4}$ | $-5.10 \times 10^{-3}$ |

SR = Schopper Riegler freeness.

What is the relative influence of the term $\gamma(\rho/\hat{\rho})^2 (d\hat{E}/dt)$ in $dE/dt$?

For maximally tesselated, crystalline cellulose, $E$ is related to the number of H bonds by means of Eq. 13:

$$\hat{E} = <K_R> n^{1/3} \quad (17)$$

where

$K$ = force constant

$R$ = distance $R$ between two O atoms (in O-H-O type bonds)

$n$ = the effective number of H bonds per unit volume involved in taking up the strain under uniaxial stress conditions.

Here, $<K_R>$ = 18.42 N/m is the average value of the force constant for stretching or compressing the distance $R$ by a unit $n$.

Differentiating Eq. 17 and substituting in Eq. 15 yields:

$$\gamma(\rho/\hat{\rho})^2 (d\hat{E}/dt) = \gamma (\rho/\hat{\rho})^2 (<K_R>/3) (<K_R>/\hat{E})^2 dn/dt \quad (18)$$

The value of $dn/dt$ has been determined by Nissan and Batten (*14*) for a stress cycling experiment. This value is $-1.767 \times 10^{23}$ bonds/m$^3$·s.

The values of $E, \rho, <K_R>, \gamma$, and $\rho$ are known. For unbeaten paper ($\gamma = 0.36, \rho = 509$ kg/m$^3$), one obtains:

$$\gamma(\rho/\rho_c)^2 (d\hat{E}/dt) = -1.788 \times 10^4 \text{ Pa/s} \quad (19)$$

In the case of Valley-beaten pulp ($\gamma = 0.78$, $\rho = 615$ kg/m$^3$), the corresponding value is $-6.12 \times 10^4$ Pa/s. For both samples, the obtained values represent less than 0.2% of the experimental values of $dE/dt$.

We can conclude, therefore, that at least in our case, the main contribution to relaxation corresponds to the term in $d\gamma/dt$. In Table III, we present the values of $d\gamma/dt$ obtained from Eq. 15, neglecting the second term and taking $E$ for each sample at $t = 0.2$ s.

## Summary and conclusions

We carried out dynamic viscoelastic experiments to determine the tensile storage modulus, $E'$, and loss modulus $E''$ of handsheet papers, at different frequencies and temperatures.

One of the advantages of the dynamic mechanical analyzer used in this work is the small size of the samples (25 × 10 × 1 mm), which allows an accurate temperature control in isothermal experiments. On the other hand, the small amplitude of the oscillating displacement (16 $\mu$m), which corresponds to a maximum deformation of 0.06%, guarantees the linear character of the measurements.

Under these advantageous conditions, we have accurately determined the effect of temperature on the storage modulus. The results have been interpreted in the framework of the Percolation Theory of Nissan and Batten. We conclude that for unbeaten paper the activation coefficient $\gamma$ decreases with temperature, whereas for beaten paper samples $\gamma$ increases with temperature. (The activation coefficient accounts for the variation in pulps and the presence of bonding or debonding agents.)

The effect of time on Young's moduli can be determined, because measurements at different frequencies have been carried out. This analysis is made using the Ninomiya and Ferry equation, which provides the interrelation of a transient with the corresponding dynamic functions. The relaxation modulus so determined can be expressed for all the samples by the equation:

$$E(t) = E(0) \exp(-0.013\, t) \quad (20)$$

where $E(0)$ is characteristic of each sample.

The subsequent analysis of this result in the light of the Percolation Theory shows that the main contribution to relaxation corresponds to the variation of the activity coefficient with time.

Finally, dynamic viscoelastic measurements are an excellent means to help us understand the relationship between the structure of paper and its final properties. Further work in this field should cover other opportunities that dynamic viscoelastic tests offer. These opportunities include the study of the influence of the amplitude of deformation in $E'$, $E''$, and tan $\delta$. Dynamic viscoelastic tests should also be used to study the variation of moduli with time at constant amplitude and at constant frequency. (Both types of experiments can give us information on structure breakdown.) Multifrequency temperature sweeps should be carried out to analyze molecular motions, particularly in the presence of water.□

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This work has been supported by the CAICYT (Project number PR 83-3338). We would like to acknowledge the crucial contribution of Alfred H. Nissan and George L. Batten, Jr.

Received for review Sept. 21, 1989.

Accepted Nov. 17, 1989.


# CORRECTION

**Evaluating operating alternatives on a continuous digester with extended delignification**

On page 129 of the February issue, Figure 3, the ending totals for alternative number 2 should read 1574 H-factor and AA/wood.

*Tappi Journal* regrets any inconvenience due to this error.□