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# VISCOELASTIC PROPERTIES OF PAPER

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*SUMMARY*

*Paper specimens of the type commonly used in high-frequency loudspeaker cones have been subjected to dynamic viscoelastic characterisation using a Rheovibron Viscoelastometer. The paper exhibited a broad, relatively weak transition which was amenable to phenomenological modelling using a Wiechert spring–dashpot representation. The Wiechert model, once adjusted to fit the experimental data, provides an analytical tool the loudspeaker designer can use to predict the elastic and dissipative properties of paper at arbitrary temperatures and driving frequencies.*

## INTRODUCTION

Paper is a planar assemblage of cellulosic wood pulp fibres which achieves its mechanical integrity primarily by hydrogen bonding at fibre–fibre contact points.[1] Although paper is not commonly regarded as having appreciable strength and stiffness, its use in a wide variety of such demanding applications as packaging and loudspeaker cones attests to its often remarkable mechanical properties. A good many of the design methods aimed at utilising these properties have up to now been largely empirical, but the recent literature provides several demonstrations that paper can be characterised in a manner similar to that for other engineering materials, and that this more thorough characterisation may lead to improved efficiency in the design process. Given the macromolecular nature of cellulose, it is not surprising that many of these developments in characterisation methodology have drawn extensively on the methods of polymer and fibre science.

The need for a more quantitative model of paper properties is particularly felt in loudspeaker cone design, since the acoustic performance of the paper cone is governed principally by the elastic and dissipative properties of the paper material itself.[2] This article will present recent experimental data concerning the viscoelastic properties of loudspeaker paper, and the data will be rationalised in terms of a



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phenomenological model for thermorheologically simple materials. Such a model is necessary for a proper application of current loudspeaker design methods, which require that the real and imaginary components of the complex modulus be known as functions of temperature and driving frequency.

Detailed numerical techniques for the analysis of loudspeaker cone dynamics have become available only recently. This may be one reason for the lack of interest in paper viscoelasticity as compared with the very extensive literature of viscoelasticity in fibrous and bulk polymer forms. Steenberg *et al.*[3-5] noted that the load–elongation response of paper required some consideration of material viscoelasticity for its proper description, and Andersson[6] described a graphical procedure by which the viscous contribution could be inferred from the load–elongation diagram. Onogi and Sasaguri[7] made further contributions in this area by developing a statistical means of relating the complex behaviour of a paper network to the array of fibre–fibre contact bonds and the underlying viscoelastic properties of the cellulose fibres. They also compared their model predictions with experimental distributions of relaxation times obtained from cotton and rayon textile fibres,[8] and showed that paper should be expected to exhibit viscoelastic response similar to these polymeric fibres. However, the literature available to date has not contained a viscoelastic characterisation of a paper type over a sufficiently large rate or temperature scale to permit a broad analysis, and neither have the limited data available to date been cast in a form suitable for engineering design in which viscoelastic considerations are necessary.

## EXPERIMENTAL

Specimens for this present study were cut from flat sheet stock paper intended for use as high-frequency (tweeter) loudspeaker cones. These are lightweight papers obtained from ground softwoods (poplar, pine) high in hemicellulose content, mechanically pulped and rendered chemically neutral with an aluminum sulphate treatment. The stock is bleached with chlorine, then compounded with small quantities of ground limestone and rosin. A synthetic binder varnish is impregnated into the sheet to increase stiffness. The sheet stock averaged 0·25 mm in thickness, with a mean density as determined from direct weighing of 586 kg/m$^3$. Mechanical testing indicated a slight anisotropy to the material, but this was considered to be sufficiently small as to permit a general assumption of isotropy. The spatial arrangement of pulp fibres is evident in the scanning electron micrograph of Fig. 1, which also reveals the presence of the binder varnish.

A large number of specimens (more than twenty) were subjected to viscoelastic characterisation using a Rheovibron Viscoelastometer. This instrument applies a small cyclic displacement to the specimen, oscillating about a mean value just large enough to prevent unloading the specimen at the point of minimum cyclic displacement. The amplitude ratio and the phase angle between the oscillating


Fig. 1. Scanning electron micrograph of paper surface, nominal 300 × magnification.

displacement and the resulting cyclic load are recorded directly, while the environmental chamber containing the specimen is heated slowly (approximately 3 °C/min) from near liquid nitrogen temperature to the onset of thermal degradation of the specimen. The data were converted to values of complex modulus by means of the appropriate geometrical scaling factors, then stored on computer discs for later model fitting and plotting. The plots given in Figs 2 and 3 are typical presentations of the results; such plots are often termed 'dynamic mechanical spectra'.

The specimens were not conditioned in any way before testing. Most of the data therefore show the effect of imbibed water in the specimens, which is manifest primarily by a transition at 0 °C. This may reflect an ice–liquid transition of the free water entrapped in the paper, and as such is not a true viscoelastic relaxation. It was noted that this transition was attenuated considerably by first heating the specimen to drive off free water.

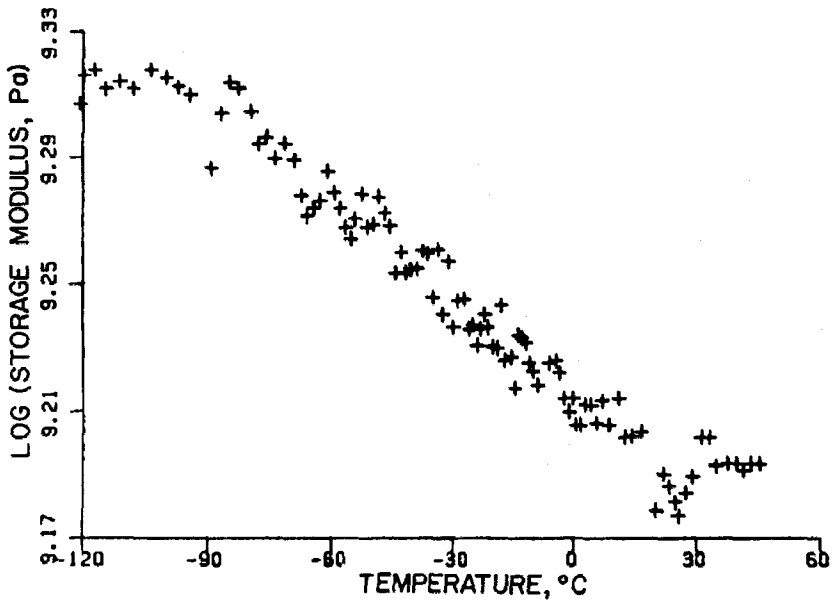


Fig. 2. Dynamic mechanical spectrum of paper specimen at 110 Hz—storage modulus.

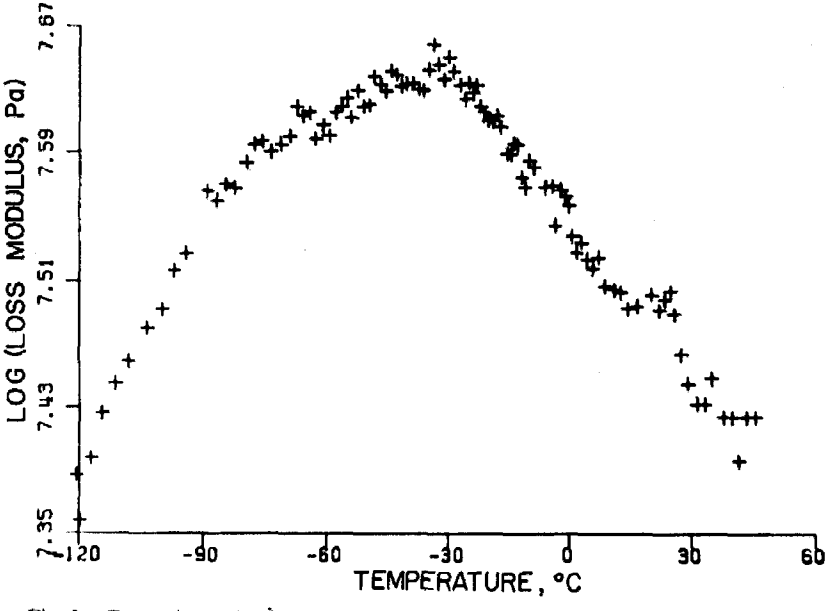


Fig. 3. Dynamic mechanical spectrum of paper specimen at 110 Hz—loss modulus.

In addition to the anomalous effect of water, the paper specimens differed from the usual synthetic polymer specimens in that the heterogeneous nature of the paper microstructure produced somewhat more scatter than is usually seen in bulk polymers, and the paper specimens exhibited a tendency to fail during the test due to a fatigue-like process which evidently operates even at the small displacements applied by the instrument. Nevertheless, the mechanical spectra obtained from several specimens were of sufficient quality to permit viscoelastic modelling.

## A PHENOMENOLOGICAL MODEL

Although considerable insight may often be derived simply by examining the dynamic mechanical spectra directly, these data must be phrased in terms of a closed-form or numerical model before they may be used directly in viscoelastic structural analyses. For the purpose of loudspeaker design, the viscoelastic model must be able to provide a reasonable prediction of the elastic and loss modulus of the material at arbitrary temperatures and driving frequencies. The Wiechert spring–dashpot array shown in Fig. 4 provides a convenient means of obtaining such a model. These mechanical analogs are amenable to numerical calculations involving discrete–variable methods, and their parameters may usually be related to the molecular mechanisms of the relaxation process. For a more thorough treatment of this and other models of polymer viscoelasticity, the reader is referred to the extensive literature of this subject, but notably the text of McCrum *et al.*[9]

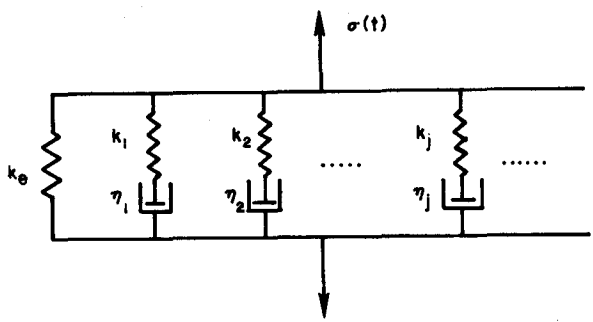


Fig. 4. The Wiechert model for linear viscoelastic response.

In its usual linear formulation, the Wiechert model uses Hookean springs and Newtonian dashpots, defined by the relations:

$$\sigma_{\text{spring}} = k\varepsilon \tag{1}$$

$$\sigma_{\text{dashpot}} = \eta D\varepsilon \tag{2}$$

where $\sigma$ and $\varepsilon$ are the stress and strain, k is the spring constant and $\eta$ the dashpot viscosity, and $D = \partial/\partial t$ is the time-derivative operator. The stress in the $j$th arm of the model is then given by the operator equation:

$$D\sigma_j + \frac{1}{\tau_j}\sigma_j = k_k D\varepsilon \tag{3}$$

where $\tau_j = \eta_j/k_j$ is a characteristic relaxation time. Solving operationally for the stress:

$$\sigma_j = \frac{k_j D\varepsilon}{\left(D + \frac{1}{\tau_j}\right)} \tag{4}$$

The stress transmitted by the entire model at a total strain $\varepsilon$ is the sum of the various $\sigma_j$ plus the stress in the equilibrium spring:

$$\sigma = \left[k_e + \sum_{j=1} \frac{k_j D}{\left(D + \frac{1}{\tau_j}\right)}\right]\varepsilon \tag{5}$$

In the case of sinusoidal loading, the stress and strain are of the form:

$$\sigma = \sigma_0^* \exp(i\omega t) \tag{6}$$

$$\varepsilon = \varepsilon_0^* \exp(i\omega t) \tag{7}$$

where $i = \sqrt{-1}$, $\omega$ is the cyclic frequency, and the asterisk denotes a complex quantity.

Using eqns (6) and (7) in eqn (5), the complex modulus of the Wiechert model is obtained as:

$$E^* = \frac{\sigma_0^*}{\varepsilon_0^*} = k_e + \sum_{j=1}^{n} \frac{k_j(i\omega)}{1 + i\omega\tau_j} \tag{8}$$

Rearranging,

$$E^* = k_g - \sum_{j=1}^{n} \frac{k_j}{1 + i\omega\tau_j} \tag{9}$$

where $k_g = k_e + \sum k_j$ is the 'glassy' or short-time modulus of the model.

The real ('storage') and imaginary ('loss') components of the complex modulus may be written explicitly by further rearranging eqn (9):

$$E^* = E' + iE'' \tag{10}$$

$$= \mathrm{k_e} + \sum_{j=1}^{n} \frac{\mathrm{k}_j \omega^2 \tau_j^2}{1 + \omega^2 \tau_j^2} + i \sum_{j=1}^{n} \frac{\mathrm{k}_j \omega \tau_j}{1 + \omega^2 \tau_j^2} \tag{11}$$

It is sometimes convenient to relate the above quantities to the phase angle $\delta$ by which the strain lags the stress in these sinusoidal loading tests as:

$$\tan \delta = E''/E' \tag{12}$$

The Rheovibron Viscoelastometer provides values of tan $\delta$ and magnitude of the complex modulus $|E^*|$, from which $E'$ and $E''$ may be computed easily.

Typically, polymers exhibit a relatively large viscoelastic transition corresponding to the onset of large-scale segmental rearrangements, and several other 'secondary' transitions corresponding to smaller-scale molecular flow mechanisms. An obvious application of the Wiechert model to polymer viscoelasticity uses one arm for each of the observed transitions: the $\mathrm{k}_j$ are chosen to provide the correct change in storage modulus through the transition, and the $\tau_j$ are chosen so as to place the transition at the correct time or temperature. This procedure thus assigns a single relaxation time to each transition.

Single-relaxation time models, however, do not usually provide acceptable descriptions of experimental data, since the molecular mechanisms involved even in a single transition are sufficiently dissimilar to create a wide distribution of relaxation times. The single-relaxation time models usually predict too sharp a transition, with too large a maximum in the loss modulus. One means of improving the model is to assign several Wiechert arms to each transition, choosing the $\mathrm{k}_j$ and $\tau_j$ of each to obtain a good fit to the data. Another often used approach, somewhat simpler in application, is to modify eqn (9) slightly to include a 'Cole–Cole broadening parameter', $\beta_j$, on each arm:

$$E^* = \mathrm{k_g} - \sum_{j=1}^{n} \frac{\mathrm{k}_j}{1 + (i\omega\tau_j)\beta_j} \tag{13}$$

A reasonable temperature dependence for the model may be obtained by writing the relaxation time as an Eyring relation:

$$\tau = \tau_0 \exp(H/RT) \tag{14}$$

where $\tau_0$ is a pre-exponential with units of time, $H$ is an apparent activation energy for the process, $T$ is the absolute temperature, and $R = 8{\cdot}314$ J/mole °K is the gas constant. The Eyring formulation here assumes a thermally activated rate process with a temperature independent activation energy and is thus somewhat limited in its

applicability, but its use is justified in many instances. The numerical value of $\tau_0$ may be obtained by noting that $\omega\tau = 1$ at the centre of the transition, where $E''$ passes through a maximum:

$$\tau_0 = 1/\omega \exp(H/RT_0) \tag{15}$$

where $T_0$ is the temperature at the transition midpoint.

The value of the activation energy may be obtained by noting the extent to which the transition shifts along the temperature axis as the frequency is varied (or vice versa), but it is often more convenient to use the observation[9] that the activation energy is related inversely to the area under a plot of $E''$ versus $1/T$:

$$H_j = (\mathrm{k}_j R\pi/2) \div \int E'' \,\mathrm{d}\left(\frac{1}{T}\right) \tag{16}$$

The above relation can be used even when a distribution of relaxation times is present, in which case one views $\tau_0$ as being distributed while $H$ is held constant. Each arm of the Wiechert model thus requires four constants for its specification: $k_j$, $\beta_j$, $T_{0j}$, and $H_j$.

## ANALYSIS OF RESULTS

Dynamic mechanical spectra obtained from the various specimens showed consistent results, although many of the spectra contained anomalies due to scatter or premature breakage. A smaller number of the spectra, obtained after operator techniques had been adjusted for the unusual experimental difficulties inherent in this material, appeared as smooth plots. The model fitting to be presented here will be restricted to just one of these better experimental runs, but it is argued that these data are representative of the paper material studied.

As seen in Figs 2 and 3, the material exhibits a relatively weak transition (approximately 30% change in storage modulus) extending over a very broad temperature range from $-100\,^{\circ}\mathrm{C}$ to $40\,^{\circ}\mathrm{C}$. A transition of this width is likely a superposition of several overlapping relaxations. Nevertheless, the initial attempts at modelling the paper response consisted of a single viscous arm in the Wiechert model, with the thought that the broad distribution could be incorporated by the Cole–Cole broadening parameter.

Even in the data of Fig. 2, which represents the highest quality data obtained during this study, too much scatter is present to permit the computation of an apparent activation energy directly from the shift in dynamic spectra as the frequency is varied. However, the evaluation of activation energy by integration of the loss curve according to eqn (16) is straightforward, and this approach yields a value of 60 kJ/mole for the paper material. This value is reasonable for moderate-scale conformational rearrangements in high polymers, but it must be remembered that a broad distribution of relaxation mechanisms is undoubtedly present in the

paper materials, so that the above figure represents only an averaged indicator of temperature sensitivity.

A convenient means of selecting the other numerical parameters for the Wiechert model employs an Argand diagram in which $E''$ is plotted as the ordinate against $E'$. In the case of single-relaxation time transitions, this diagram appears as a semicircle which intersects the abscissa at the maximum and minimum values of the storage modulus and whose height is just half the difference between these intersection values. The equilibrium spring constant $k_e$ is taken as the minimum storage modulus, and $k_1$ is set to the difference between the minimum and maximum storage moduli. In the case of distributed relaxation times, the semicircles are depressed to arcs, and it can be shown that the height of the arc is related directly to the Cole–Cole broadening parameter as:

$$\beta = \frac{4}{\pi}\tan^{-1}\frac{2E''_{max}}{E'_{max} - E'_{min}} = \frac{4}{\pi}\tan^{-1}\frac{2E''_{max}}{k_1} \tag{17}$$

When the data of Figs 2 and 3 are crossplotted, the Argand diagram of Fig. 5 is obtained. Examination of the extreme points of these data yield for the single-arm Wiechert model the numerical parameters $k_e = 1{\cdot}44\,\text{GPa}$, $k_1 = 0{\cdot}68\,\text{GPa}$, $\beta = 0{\cdot}157$. The smooth curve drawn through the data in Fig. 5 represents the prediction of the single-arm Wiechert model for this choice of numerical constants.

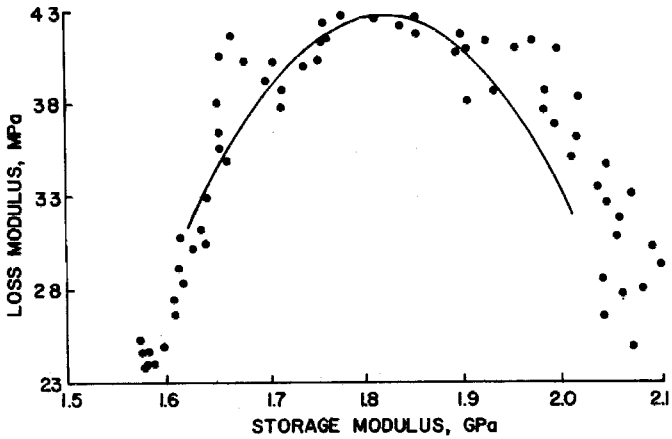


Fig. 5. Argand diagram for dynamic mechanical response of paper specimen at 110 Hz. Closed circles represent experimental values, drawn curve is a one-arm Wiechert model fit to the data.

It was found that the single-arm model, even with the above choice of the Cole–Cole parameter, was incapable of providing a good fit to the experimental data over the full range of temperatures. In particular, the loss modulus was underpredicted at temperatures far from the transition centre temperature. After some trials, it was found that a good predictive model could be obtained without

undue complexity by using three arms in the Wiechert model, each broadened with a Cole–Cole parameter of $\beta = 0{\cdot}177$. The previous activation energy of 60 kJ/mole was applied to all three arms. A tabulation of the numerical values employed in this final model is given in Table 1, and the comparison of the model prediction with experimental data is given in Fig. 6.

TABLE 1
WIECHERT MODEL PARAMETERS ($k_e = 1{\cdot}44$ GPa)

| j | $k_j$, *MPa* | $T_{0j}$, °C | $\beta_j$ | $H_j$, *kJ/Mole* |
|---|---|---|---|---|
| 1 | 166 | 13 | 0·177 | 60 |
| 2 | 237 | −34 | 0·177 | 60 |
| 3 | 277 | −75 | 0·177 | 60 |

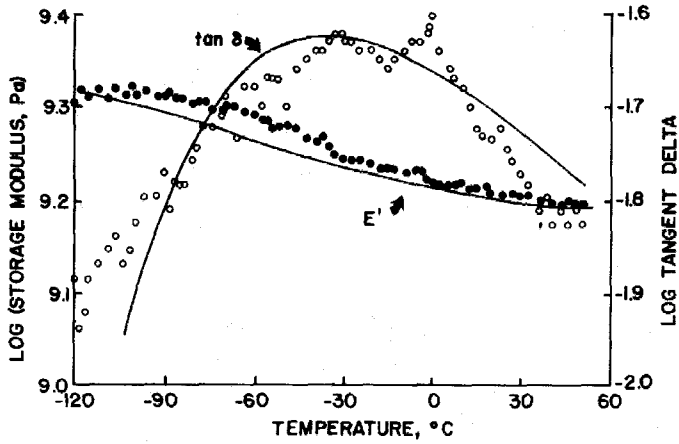


Fig. 6. Dynamic mechanical response of paper specimen at 110 Hz. Circles are experimental values and drawn curves represent a three-arm Wiechert model fit to the data.

## CONCLUSIONS

Although the heterogeneous microstructure of paper and its tendency to imbibe appreciable quantities of free water lead to some difficulties in performing dynamic mechanical analysis, the Rheovibron data obtained from loudspeaker paper specimens does exhibit a broad viscoelastic transition which is amenable to phenomenological modelling. It was found that the unusual breadth of the transition required the use of a multiple-arm Wiechert model representation. The resulting model provides insight as to the strength and temperature dependence of the molecular rearrangements underlying the transition, and in addition is a useful

tool in predicting the elastic and loss characteristics of loudspeaker papers at arbitrary temperatures and frequencies.

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