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A SAMPLE MOUNTING TECHNIQUE FOR THE DYNAMINC MECHANICAL ANALYSIS OF CELLULOSE AND PAPER SHEETS

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ABSTRACT

A sample clamp assembly has been devised for the dynamic mechanical analysis of thin cellulose and paper sheets. The assembly, used with the DuPont 981 DMA, provides an arched sample cross-section to prevent buckling deformation of the sample. The applicability of this technique is demonstrated by measurements on original and thermally-aged newsprints.

INTRODUCTION

The mechanical characteristics of cellulose and paper are, on the one hand, very important for the user, and, on the other hand, reflect the differences and changes in the microscopic structure of the materials. There are several methods (usually standardized) of measuring the mechanical characteristics of paper. Yet, practically all these methods have their shortcomings (low sensitivity to significant changes, poor reproducibility, pure empirical character of the test, etc.). Thus, new mechanical test methods may still be needed, without expecting any of them to overcome all the difficulties at the same time.

One of the new possibilities is the measurement of dynamic mechanical properties as a function of temperature. These properties are sensitive to changes in the internal motion of polymer molecules and molecule segments. Cellulose itself usually consists of crystalline and amorphous parts. The latter were reported to show several second-order transformations during heating: at 190–200 [1], 280–300 [2], 390–400 [3] and 490–500 K [4,5], the last being the glass transition. Several transformations before glass transition

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have also been detected by acoustic spectroscopy [6] most of which could not be precisely assigned to molecular motions. The effect of plasticizers (including water) on the glass transition was also studied by several authors [2,4,7,8].

As a part of a complex research program on cellulose and paper aging (for previous results see ref. 9), this paper is an account of investigations on the applicability of dynamic mechanical analysis for testing cellulose and paper sheets.

DEVELOPMENT OF A SAMPLE MOUNTING TECHNIQUE FOR THE DYNAMIC MECHANICAL ANALYSIS OF PAPER SHEETS

Measurements were made on a DuPont 981 dynamic mechanical analyser (DMA), measuring the resonant frequency and energy dissipation of a system containing the sample during a temperature program [10,11]. Since the mechanical load on the sample is very low in the apparatus, most solids are rigid enough to be measured in the form of sheets, rods, etc.

Quite often, however, the material to be investigated cannot simply be mounted on the arms of the apparatus, since it is either a liquid at the beginning of the experiment (e.g., synthetic resins or adhesives) or it forms a thin film which undergoes a buckling mode of deformation in the apparatus. In order to overcome these difficulties, different ways of sample mounting have been proposed and found useful in several important cases: horizontal mounting of thin samples often prevents buckling [12]; materials which are not self-supporting can be measured with the aid of support techniques.

Soft materials (resins, adhesives) can be investigated with the aid of shim, wire and hollow beam supports [12–15], offering the possibility of determining both the elastic modulus and damping. The most widely used glass cloth support provides tan delta and non-quantitative stiffness (modulus) curves [12].

Figure 1 contains the resonant frequency and damping curves of a cellulose sheet (an industrial intermediate product). The thickness of the sample (1.0 mm) allowed normal, vertical sample clamping. (In all the experiments discussed in this paper samples were heated with a rate of 5 °C min^{-1} in flowing nitrogen.)

First, from room temperature to about 130 °C, both frequency and damping decreased gradually. The most probable reason for this is the change in the properties of the sheet as a consequence of water desorption. From 130 to 220 °C the decrease of the resonant frequency was slower but gradual; the damping curve, however, formed a distinct step. In the third section (230–280 °C) a sharp decrease in both modulus and damping occurred. The onset of this change is quite close to the reported temperature (220–230 °C) of cellulose glass transition [4,5]. At the same time, thermal

decomposition also starts in this temperature range: thermogravimetric curves recorded under similar conditions indicated that the sample lost about 3% of its mass up to 280 °C. Consequently, glass transition is probably mainly responsible for the changes starting at 230 °C, thermal decomposition may have a minor, though not negligible, role.

Thin cellulose and paper sheets could not be tested in the normal way, because buckling deformation occurred both to vertically and horizontally clamped samples. The support techniques mentioned above were also regarded as unpromising, because changes in the frequency and damping were expected to be very small (in comparison to the drastic changes during, e.g., a resin cure).

Therefore, instead of using plane sheets, it seemed reasonable to look for a different sample geometry to ensure the necessary stiffness and to avoid buckling.

On the basis of preliminary tests a sample clamp assembly was devised to provide an arched sample cross-section. Thus, the clamped sample has the shape of a cylindrical tube segment. The jaws of the assembly and the arrangement of the clamped sample on the instrument arms are shown schematically in Fig. 2.

APPLICATION OF THE NEW CLAMPING ASSEMBLY TO PAPER SAMPLES

First, samples from an accelerated aging experiment were measured with the clamping technique described above. Two sorts of newsprint were treated

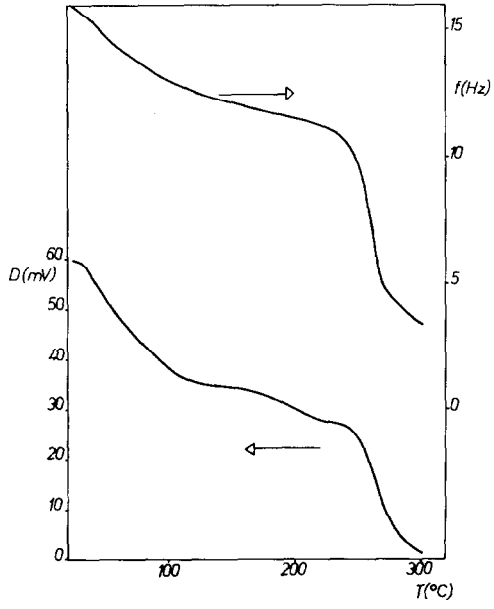

Fig. 1. Frequency and damping curves of a bleached poplar cellulose sheet (sample size: $18 \times 10 \times 1.0$ mm; heating rate: 5 °C min^{-1}).

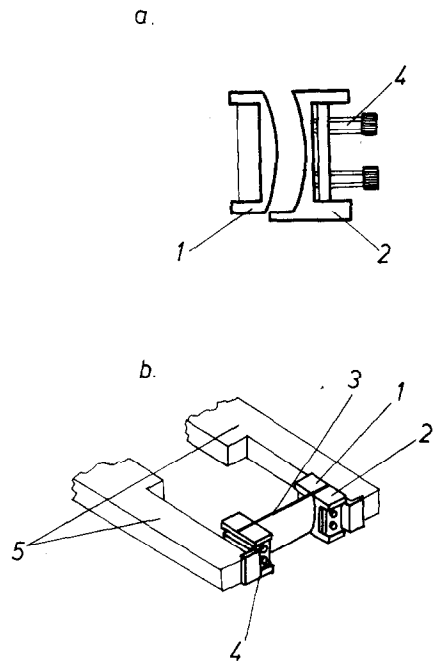

Fig. 2. Scheme of the clamp assembly for arched samples (a) and its arrangement on the arms of the 981 dynamic mechanical analyser (b). (1) Positive jaw, (2) negative jaw, (3) sample, (4) sample clamp screw, (5) DMA arms.

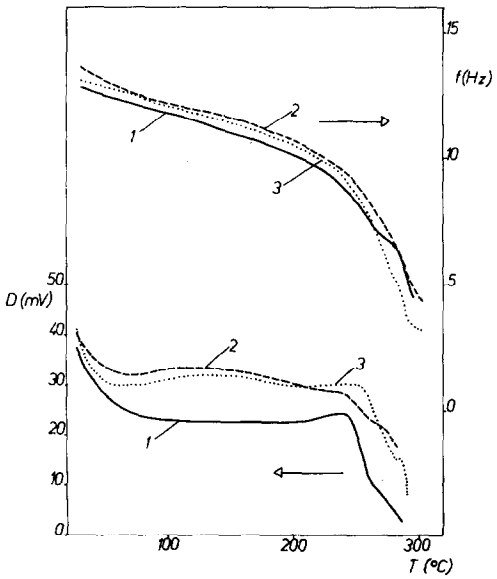

Fig. 3. Frequency and damping curves of a 53 g m^{-2} newsprint (sample: 6 parallel sheets of $18 \times 16 \times 0.1$ mm; heating rate: 5 °C min^{-1}). (1) Original, (2) after 10 days of accelerated aging, (3) after 30 days of accelerated aging.

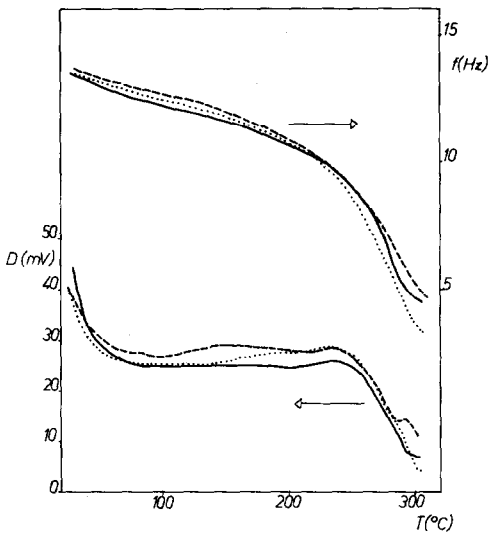

Fig. 4. Frequency and damping curves of a 60 g m^{-2} newsprint (sample: 6 parallel sheets of 18×16×0.1 mm; heating rate: 5 °C min^{-1}). (———) Original, (— — —) after 10 days of accelerated aging, (· · · · · ·) after 30 days of accelerated aging.

at 100 °C in air of 50% relative humidity. The DMA curves of the original and some aged samples are presented in Figs. 3 and 4 as examples; a detailed discussion of the results will be published later.

The resonant frequency and damping curves have some basic similarities to those of the thick cellulose sheet drawn in Fig. 1. A gradual decrease of the resonant frequencies was observed up to about 230 °C, when the change became faster. All the damping curves have a decreasing region from room temperature to about 80 °C (note that water evolution was easier from the thin sheets than from the thick cellulose sample discussed earlier) and a small maximum or shoulder near 240 °C, followed by a rapid loss of frequency and damping. These changes can also be explained by the glass transition and by the start of thermal decomposition.

In addition, the aged samples exhibit a broad peak (or shoulder) in the 100–220 °C temperature range, where the original samples had a virtually constant level of damping. This effect is quite promising from the point of view of aging studies.

CONCLUDING REMARKS

The first results (some of which have been discussed in the preceding section) show that the new sample mounting technique may be useful in

DMA studies on paper or other thin samples of similar properties. However, the question whether quantitative modulus and loss data can be obtained by means of this technique, has not been answered yet. For the usual sample geometries and supporting techniques, the elastic modulus and the loss factor (tan delta) can readily be estimated from the measured quantities [10–12]. A study is currently underway on the possibility of quantitative evaluations of measurements with the new mounting method, also including the problem of the mechanical anisotropy of paper.

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