## On the Calculation of Tensile Stress Relaxation Modulus for Varying Stress and Strain

### INTRODUCTION

Recently we have constructed an environmental stress relaxometer and creep apparatus for operation in vacuo or vapor environment.[1]  The principle, first utilized by Berry,[2] essentially involves the polymer sample in series with a spring of known compliance.  Although stress relaxation measurements can be made with this instrument, it would be much simpler from our experimental viewpoint to subject the spring to a sudden strain and just observe the displacement of the polymer/spring contact with time.  The procedure for determining the stress relaxation modulus from such an experiment has been formulated by Hopkins[3] using the basis of linear viscoelastic theory.  We therefore decided to investigate the usefulness of this procedure for an amorphous polymer using a series of springs of varying compliance.

### THEORY

The equation derived by Hopkins is

$$\int_0^t M(t - \tau)[x_0 - x(\tau)]d\tau = \int_0^t N(\tau)x(t - \tau)d\tau \tag{1}$$

where $M$ and $N$ are the stiffnesses of the spring and the polymer sample, respectively, $x$ is the displacement of the sample/spring contact, $x_0$ is the instantaneous displacement of the spring, and $t$ is time.  The object is to solve eq. (1) numerically for $N$ since $M$, $x$, and $x_0$ are all known from the experiment.  The technique for solution was derived by Hopkins and Hamming[4] and can be written as

$$N(t_{n+1/2}) = \frac{K(t_{n+1}) - \sum_{i=0}^{n=1} N(t_{i+1/2})[X(t_{n+1} - t_i) - X(t_{n+1} - t_{i+1})]}{X(t_{n+1} - t_n)} . \tag{2}$$

The log $t$ axis is subdivided $t_0 = 0$, $t_1$, $t_2$...$t_n$.  $K(t)$ is the value of the left hand side of eq. (1), and $X$ is given by

$$X(t) = \int_0^t x(\tau)\, d\tau \tag{3}$$

so that $K$ and $X$ are readily available from numerical integration of experimental data.  Hence the value of $N$ at each time can be calculated using

the known values at earlier times; $N(t_{1/2})$ is given by

$$N(t_{1/2}) = \frac{K(t_1)}{X(t_1)}. \tag{4}$$

Having obtained the stiffness $N$ of the sample as a function of time, the tensile modulus $E$ follows after multiplication by a form factor, i.e.,

$$E(t) = \frac{N(t) \cdot l}{A} \tag{5}$$

where $l$ and $A$ are the length and cross-sectional area of the sample, provided that the polymer is in the form of a thin strip.

## EXPERIMENTAL

The polymer used was Rhoplex AC-34 resin, a copolymer of esters of acrylic acid and methacrylic acid, and was obtained from Rohm & Haas Co. The copolymer has a softening point of about 5°C and is completely amorphous

The envir nmental instrument is described elsewhere.[1] For this work, operations were carried out under normal atmospheric pressure. Four springs each having a different compliance were used. Small spring extensions were nonlinear with respect to the applied load so that the stiffnesses $M$ varied somewhat with time, thus complicating the analysis. The equilibrium stiffnesses of the springs, i.e., the slope of load–extension plots, for moderate and large loads are given in Table I.

TABLE I
Equilibrium Spring Stiffness

| Spring | Stiffness, g/cm |
|--------|-----------------|
| G | 86.7 |
| H | 41.7 |
| I | 19.1 |
| J | 10.3 |

The initial stress put on the sample was maintained fairly constant at about $1.7 \times 10^6$ dynes/cm² for each of the springs. The maximum strain observed was about 30%. The stress on the polymer decreased only to about 90% of the initial stress for the most extensible spring J, but to about 40% for the least extensible spring G.

In addition to the Hopkins procedure, pure stress relaxation experiments were carried out using both the environmental instrument and an Instron tensile tester.

## RESULTS AND DISCUSSION

The tensile modulus $E$ as a function of time, calculated both from the Hopkins procedure and from pure stress relaxation, is shown in Figure 1.
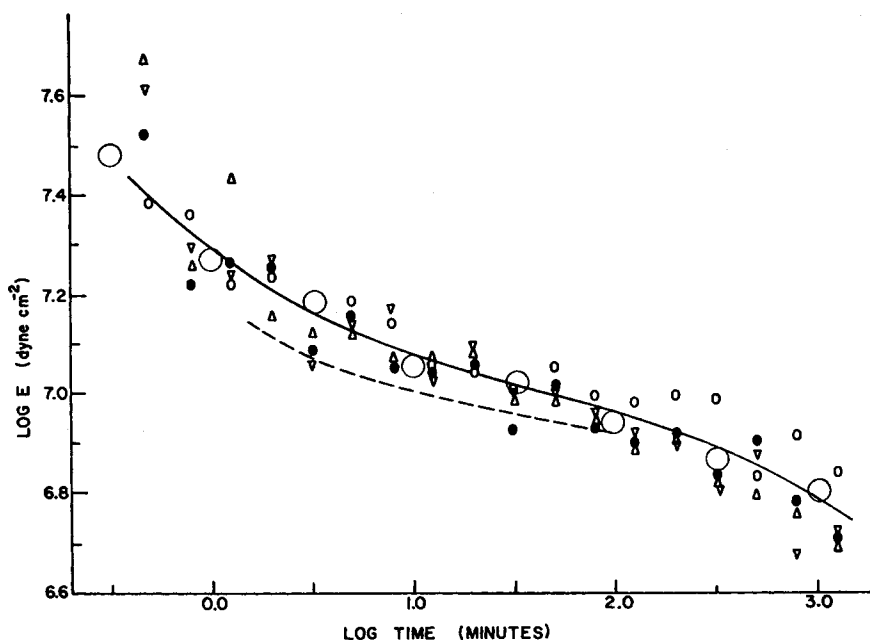
Fig. 1. Tensile modulus from Hopkins' analysis, log $E$ (dynes/cm$^2$) versus log time (min). Rhoplex AC-34, 23°C: (O) spring G; (●) spring H; (△) spring I; (▽) spring J; (———) estimated mean of four springs; (– – –) pure stress relaxation (mean of determinations on two instruments); (⊖) mean of four springs, independent calculation (eq. [6]).

Despite the scatter of the experimental points, broad agreement is obtained for each of the springs. The upper continuous line approximates to the best line through the points and represents a modulus some 10%–15% higher than that calculated from pure stress relaxation. Since $E$ measured with the environmental instrument differed by roughly 10% from the Instron results, in any case the agreement is considered reasonable, especially since the strains employed were somewhat larger than are normally used for tests of linear viscoelastic theory. The larger discrepancy at the earliest time is due to extrapolation outside the range of experimental measurements, which in our case is particularly difficult because finite times of the order of a few seconds were required for the springs to reach their initial extension. The large circles in Figure 1 represent the mean results of an independent calculation for the four springs. The equation used to calculate $E$ for the sample was

$$\int_0^t E(\tau)\epsilon(t - \tau)\, d\tau = \int_0^t \sigma(\tau)\, d\tau \qquad (6)$$

where $\sigma$ and $\epsilon$ are the stress and strain in the polymer specimen, respectively. In addition, at very short times, when the springs were in the process of being extended, it was assumed for convenience that both the
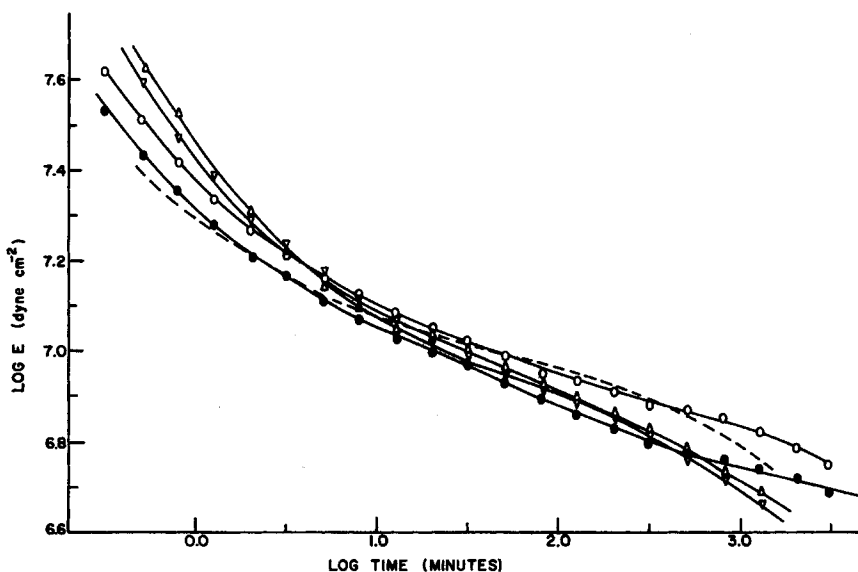
Fig. 2. Superficial tensile modulus using each spring, log $E$ (dynes/cm²) versus log time (min).  Rhoplex AC-34, 23°C:  (O) spring G;  (●) spring H;  (△) spring I;  (▽) spring J;  (– – –) estimated mean of four springs, Hopkins' analysis (from Fig. 1).

spring and specimen extensions were at a constant rate and that the stress in the specimen increased linearly with time.   Figure 1 illustrates that the results from this calculation are in very good agreement with those obtained using the Hopkins procedure.

In Figure 2, the best curve from the Hopkins procedure is compared with the superficial modulus (i.e., nominal stress divided by nominal strain at any time) using each of the four springs.   The comparison per se merely indicates that little difference exists between calculated and superficial modulus over most of the time scale used.   However, there is another aspect which might be of some interest.

Recently we proposed an approximate method of comparing tensile creep compliance with the compliance obtained from penetration experiments using a spherical indenter.[5]   Very good agreement was observed for a vinylacetate–dibutylmaleate copolymer, but small differences of up to 25% were found for Rhoplex AC-34, for which the creep compliance varied slightly more with time than did the penetration compliance.   Now, a penetration experiment differs from true creep in that the stress decreases as the strain increases.   If this were the cause of the discrepancy in the case of Rhoplex AC-34, then the superficial tensile compliance (or modulus) observed when spring G is used should vary less with time than that for spring J, which corresponds nearly to a pure creep experiment.   That this is the case is illustrated in Figure 2.

In conclusion, the Hopkins technique appears useful for calculating tensile modulus when simplicity of experimental design is an important

factor. The calculations, which were carried out by hand, tend to become somewhat tedious; and if the technique is to be used regularly, then a computer program is probably essential.

### References

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