

Use of a Dynamic Mechanical Analyzer to Study Supported Polymers

HOWARD W. STARKWEATHER, JR. and MYLAR R. GIRI,* *E. I. du Pont de Nemours and Company, Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898*

Synopsis

The real and imaginary parts of the complex modulus of polymers which must be supported can be determined with the Du Pont Dynamic Mechanical Analyzer. Polymer coatings of equal thickness are laminated on both sides of a thin metal sheet. The flexural modulus of the laminate is given by $E = E_1x^3 + E_2(1 - x^3)$, where E_1 and E_2 are the moduli of the metal and the polymer, respectively, and x is the thickness fraction of metal. Under some conditions, the dynamic viscosity of the polymer can also be determined.

INTRODUCTION

The Du Pont Dynamic Mechanical Analyzer (DMA)¹ has proved to be a useful and efficient tool for characterizing the internal motions of polymers. This is especially true when it is coupled to a computational device to automate the calculation and plotting of quantities of scientific and engineering importance.² A need has been recognized for a technique for measuring the properties of materials which are fluid or simply too soft or tacky to be self-supporting. Such materials have sometimes been applied to fiber braids, fabrics, or springs to provide the necessary mechanical support. These techniques permit one to observe the temperatures and relative magnitudes of loss peaks, but the complex modulus cannot usually be determined quantitatively because of the geometric complexity.

We have demonstrated a technique which is applicable to the DMA or any device which is based on flexural deformations. Layers of polymers of equal thickness are laminated to both sides of a thin, loss-free sheet of metal.

Mathematical Relationships

The detailed nature of the deformations of the polymer samples in the DMA experiments has not been studied until now. As a first approach to the problem, we assume here that the motion of the polymer-coated sheet of metal in our experiments can be described by pure bending vibrations. We therefore neglect all shear strains in the sample and consider the deformation to consist only of extension and contraction of the longitudinal elements.

In pure bending, the compressive and elongational forces on any cross section cancel each other so that there is no net force on the laminate. The bending is

* Present address: Dept. of Physics, Pennsylvania State University, Hazleton Campus, Hazleton, PA 18201.

then characterized by the bending moment M . For a laminate of width b and thickness t , which is bent to a radius r , the bending moment is given by

$$M = EI/r \quad (1)$$

where E is the elastic modulus of the material of the laminate and $I = bt^3/12$. The product EI is called the flexural rigidity and is a measure of the resistance to bending. For example, for three-point loading, the central deflection of the beam due to a force F is given by $y_0 = (F/EI)l^3/48$, where l is the distance between the outer support points. Similar results hold for other configurations. These results and the derivation of the equation for M can be found in standard texts on elasticity.³

If the laminate (width b , total thickness t) is made up of two or more viscoelastic materials, the bending moment M^* will be a frequency-dependent complex quantity which can be written in the form

$$M^* = E^*I/r \quad (2)$$

This defines the complex effective elastic modulus $E^*(\omega) = E'(\omega) + iE''(\omega)$ of the composite laminate. We consider the symmetric case of a three-layer laminate, the inner layer having a thickness d_1 and the two outer layers being of equal thickness d_2 . Here the subscripts refer to two materials which have elastic moduli:

$$E_1^* = E_1' + iE_1'' \quad \text{and} \quad E_2^* = E_2' + iE_2'' \quad (3)$$

Assuming the validity of linear viscoelasticity theory, it is straightforward to calculate M^* in the required form. In terms of E_1^* and E_2^* we can then express the effective modulus E^* as

$$E^*(\omega) = E_1^*x^3 + E_2^*(1 - x^3) = E_2^* + (E_1^* - E_2^*)x^3 \quad (4)$$

where

$$x = d_1/(d_1 + 2d_2). \quad (5)$$

In our experiment, 2 corresponds to films of polymer coated on the two sides of a metal plate (1). Then $E_1^*(\omega)$ can be assumed known and $E_1''(\omega) \simeq 0$. The DMA experiment measures $E'(\omega)$ and $E''(\omega)$, and the elastic modulus of the polymer can then be extracted from this as

$$E_2'(\omega) = [E'(\omega) - E_1'x^3]/(1 - x^3) \quad (6)$$

$$E_2''(\omega) = E''(\omega)/(1 - x^3) \quad (7)$$

or

$$\tan\delta_2 = \tan\delta/[1 - (E_1'/E')x^3], \quad \text{where} \quad \tan\delta_2 = E_2''/E_2', \quad \tan\delta = E''/E' \quad (8)$$

Alternatively, E_2' can be obtained as the intercept of a plot of E' vs. x^3 by analogy with the right-hand side of eq. (4). Since x , the thickness fraction of metal is less than 1, x^3 decreases rapidly as the thickness of the polymer layers is increased, thereby narrowing the difference between E_2' and E' or E_2'' and E'' .

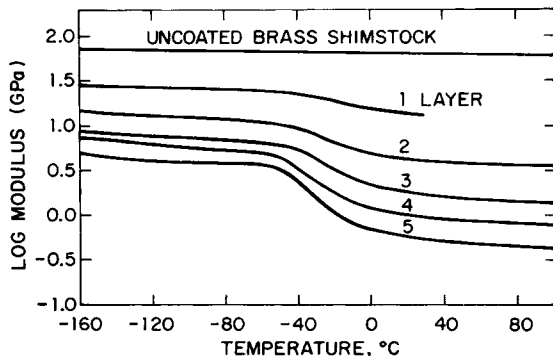


Fig. 1. Modulus of brass shimstock coated with one to five layers of 3M rubber cement tape adhesive on each side.

APPLICATION TO A MODEL SYSTEM

For the central metal layer, we used 5.1-mil brass shimstock. This material has a modulus E'_1 , of 67.4 GPa at 250°C and 75.9 GPa at -150°C. Its loss modulus is less than 10^{-3} GPa. For a soft, tacky polymer, we chose the adhesive from 3M rubber cement tape. A DSC scan showed a glass temperature (onset) of -55°C and a small ($\Delta H = 0.12$ cal/g) endotherm at -10°C. From an infrared spectrum, it was concluded that at least the major component is poly(*n*-butyl acrylate). The thickness of each layer of adhesive is 1.8 mils. Thus, the thickness fraction of brass is

$$x = 5.1 / (5.1 + 3.6n) \tag{9}$$

where n is the number of layers of adhesive on each side.

DMA measurements were made on laminates with n from 1 to 5. Thus, x^3 varied from 0.20 to 0.01. The dependence of the modulus on temperature for each of these laminates and the uncoated shimstock is shown in Figure 1. The modulus data at -150°C and +25°C are plotted against x^3 in the left side of Figure 2. At 25°C, the intercept is essentially zero. Under these conditions,

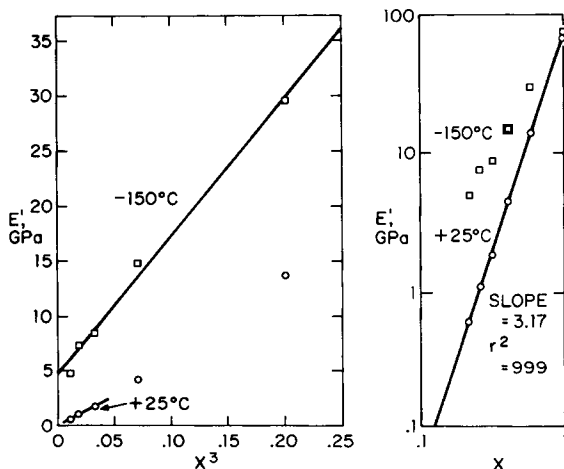


Fig. 2. Dependence of the modulus of brass-adhesive laminates on the thickness fraction of brass.

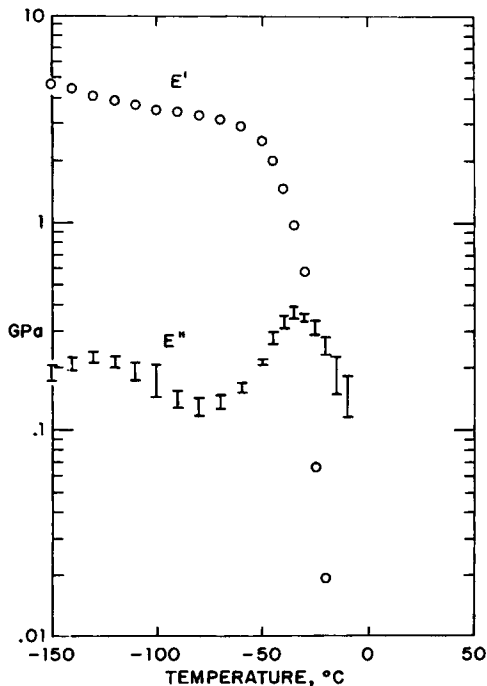


Fig. 3. Dynamic mechanical modulus for the adhesive from 3M rubber cement tape.

E' should be proportional to x^3 . From the log log plot on the right side of Figure 2, the experimental exponent is 3.17. Since the thicknesses are not known with a high degree of precision, the agreement between theory and experiment is considered satisfactory.

Values of E'_2 and E''_2 , the properties of the polymer, were calculated at 10° intervals using the intercept method for E' and using data for $n = 3-5$ for E'' . These data are plotted in Figure 3. The α and β -relaxations are seen at about -35 and -130°C ., respectively. It should be noted that we have not corrected for the differences in thermal expansion coefficients between the metal and the polymer. This would cause x to vary with temperature.

DYNAMIC VISCOSITY

The relationship between a cyclic stress and strain can be expressed in terms of either a complex modulus or a complex viscosity. Ferry⁴ has given the following relationship between the real part of the complex viscosity, η' , and the imaginary part of the complex shear modulus, G'' :

$$\eta' = G''/\omega = G''/2\pi f \quad (10)$$

The dynamic viscosity may not be comparable with the steady state viscosity. For example, a crosslinked rubber could have a finite dynamic viscosity, even though there is no steady state flow. Entanglements may produce a similar contrast in polymers of high molecular weight. On the other hand, this approach is not applicable to materials of low viscosity because the damping in the mechanical linkage of the DMA may be greater than that due to the viscosity of the sample.

To demonstrate the concept, we chose polytetrafluoroethylene (PTFE) at temperatures between 50°C and the melting point. Data taken with a capillary rheometer exhibit strongly non-Newtonian behavior.⁵ Comparisons were made at an apparent strain rate $\dot{\gamma}$ equal to $2\pi f$, where f is the frequency of the DMA. Thus the shear stress from the capillary measurement may be compared with the loss modulus from the DMA. Since the resistance to shear is small compared to the resistance to compression, it is assumed that the shear modulus is approximately one third of the Young's modulus. Capillary data for several varieties of PTFE at 300°C were presented in Figure 1 of Ref. 5. At an apparent shear rate of 30 s^{-1} , the shear stress was $4-9 \times 10^5 \text{ Pa}$. The equivalent quantity computed from DMA data was $6 \times 10^5 \text{ Pa}$. Since brass has a significant level of internal friction at temperatures above 300°C, 3-mil stainless steel shimstock was used for the laminates with PTFE.

The dependence of equivalent shear stress at about 30 s^{-1} on temperature is shown in Figure 4. Several approaches were used with the DMA, including an unlaminated PTFE control, laminates with two values of x , the thickness fraction of metal, and an extrapolation of laminate data to $x = 0$ (the intercept method). At temperatures below 150°C, the DMA method gives higher stresses. In the middle range the two methods give the same order of magnitude. Above 300°C, the capillary method gives increasing stresses⁵ while the DMA method gives stresses which continue to decrease with increasing temperature. Above the melting point of PTFE, the DMA method indicates a dynamic viscosity below the limit of measurement. Using a tensile technique, Nishioka and Watanabe⁶

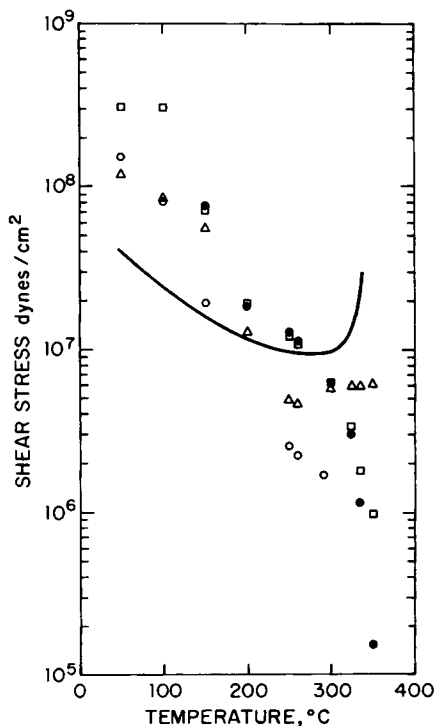


Fig. 4. Comparison of DMA and capillary data for the dependence of shear stress on temperature at an apparent shear rate of 30 s^{-1} . (○) Control, (●) intercept, (□) $X = 0.058$, (Δ) $X = 0.115$.

obtained a viscosity of 10^{11} – 10^{12} poises. They also reported that the melt was rubbery with an instantaneous Young's modulus of 2 – 3×10^7 dynes/cm² (10^{-3} GPa). Using DMA data on laminates and the intercept method of calculation, we obtained a modulus of 1.4×10^{-2} GPa at 350°C and 9.2×10^{-3} GPa at 380°C. Thus, PTFE above its melting point behaves like a rubber in having a low dynamic viscosity, a high steady state viscosity, and a modulus near 10^7 dynes/cm² (10^{-3} GPa).

CONCLUSIONS

The DMA laminate technique provides a convenient way to get quantitative or semiquantitative values of the dynamic mechanical properties of polymers which must be supported. In addition to fluid, soft, or tacky substances, it is applicable to coatings and systems which are undergoing changes such as drying, crosslinking, or reactions induced by light. These changes can be followed as functions of time, temperature, or environmental factors.

For the determination of relaxation temperatures and the comparison of samples, coatings as thin as 2 mils have proved useful. For quantitative measurements of modulus and loss modulus, thicker layers and especially a range of thicknesses are preferred.

References

1. R.L. Blaine and L. Woo, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **17**, 1 (1976).
2. R. M. Ikeda and H. W. Starkweather, *Polym. Eng. Sci.*, **20**, 321 (1980).
3. See, for example, L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, Pergamon, New York, 1970.
4. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, p. 33.
5. H. W. Starkweather, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 73 (1979).
6. A. Nishioka and M. Watanabe, *J. Polym. Sci.*, **24**, 298 (1957).

Received May 27, 1981

Accepted October 13, 1981