

Simultaneous Dynamic Mechanical and Dielectric Measurements on Polymers

Edwin R. Fitzgerald

Johns Hopkins University, Baltimore, Maryland 21218, USA

Introduction

A comparison of dielectric and mechanical retardation spectra for the same polymer is often helpful in elucidating the effects of molecular structure and/or microstructure on the observed macroscopic behavior. However, variations in the exact composition, impurities, different thermal and stress histories, or changing microstructural states of separate polymer samples used for electrical and mechanical testing can alter properties, mask correlations, or yield erratic, spurious correlations. Simultaneous measurements of mechanical and electrical properties on the same sample are necessary for meaningful comparisons; this is true for all polymers, but is especially important for biopolymers where time can have a profound effect on mechanical properties, for example. (FITZGERALD, 1975, 1977). Polymers in which temperature or stress induced phase or crystalline transitions take place also have time-sensitive properties as the transitions can occur over long times and produce marked changes in both electrical and mechanical properties (FITZGERALD, 1961).

A method and means for simultaneous measurements of the complex shear compliance ($J^* = J' - iJ''$) and the complex dielectric constant ($\epsilon^* = \epsilon' - i\epsilon''$) on the same samples of viscous liquids, gels, and solids is reported here. Some data are adduced from simultaneous dielectric and dynamic mechanical measurements on a 10% polyvinyl chloride/di-2-ethyl-hexyl phthalate gel at audiofrequencies and temperatures from - 50 to 100°C.

Measurement Method

Dynamic mechanical measurements are made of the complex shear compliance, $J^* = J' - iJ''$, or complex fluidity, $\mu = \mu' + i\mu''$ (or their inverses, rigidity and viscosity, respectively) as a function of frequency and temperature using a modified version of the electromagnetic transducer method of Fitzgerald (FITZGERALD, FERRY, 1953; FITZGERALD, 1957). The stainless steel sample slabs, which press a pair of disk-shaped samples outward against inside flat portions of a vibrating "driving" tube in this method, were each

modified to include a central portion insulated electrically from the rest of the slab. These insulated, cylindrical central portions with coplanar faces are mechanically rigid but form guarded electrodes, while the inside flats in the aluminum alloy driving tube are then the opposite, (parallel) high-voltage electrodes in a three-terminal dielectric cell. The outer parts of the sample slabs form the guard rings which are kept at the same, (grounded) potential as the central, cylindrical electrodes. Measurements of complex dielectric constant were carried out using a Model B221 Wayne Kerr Transformer ratio-arm bridge (CALVERT, MILDWATER, 1963); this transformer ratio-arm bridge is capable of measuring small capacitances and conductances from 50 to 20,000 Hz with an accuracy of $\pm 0.1\%$. The dynamic mechanical measurement apparatus cited yields values of the elastic modulus, J' , and the loss modulus, J'' , from 25 to 5000 Hz with a precision of $\pm 2\%$.

The dielectric "cell" constant (cross-sectional area/thickness) of the modified mechanical measurement apparatus is easily found for a given distance between the sample slab faces and the inside flats of the driving tube by measurements of the capacitance without a sample (C_a). Separate connections to each sample slab are made so that the exact centering of the slabs relative to the driving tube can be checked by separate air capacitance measurements on each slab. Some typical calibration data for the dielectric cell constants are presented in Table I.

TABLE I
Calibration Capacitance* Measurements
Modified Fitzgerald Apparatus
(Guarded electrode diameters 0.500")

Sample Slab Drive screw setting	Measured Air Capactance		
	Top Slab	Bottom Slab	Total
10 \equiv 1 turn	(mmf)		
0**	0.51	0.52	1.04
20	0.56	0.56	1.12
50	0.65	0.64	1.31
100	0.86	0.86	1.72
150	1.30	1.31	2.60
200	2.57	2.74	5.32
220	electrodes touching		

* conductance measured with air is always zero.

** distance between electrodes (also shearing faces) is 0.20 inches at zero setting.

While the transformer ratio-arm bridge is being used to measure the parallel capacitance and conductance of a sample pair, no disturbance is produced by the small-amplitude vibrations imposed during the dynamic shear compliance measurements - even when these vibrations are at the same frequency as the alternating electric field.

The modified driving tube - sample slab arrangement is shown in Figure 1 where it can be noted that the alternating electric field is transverse to the shearing direction or alternating mechanical field in this method.

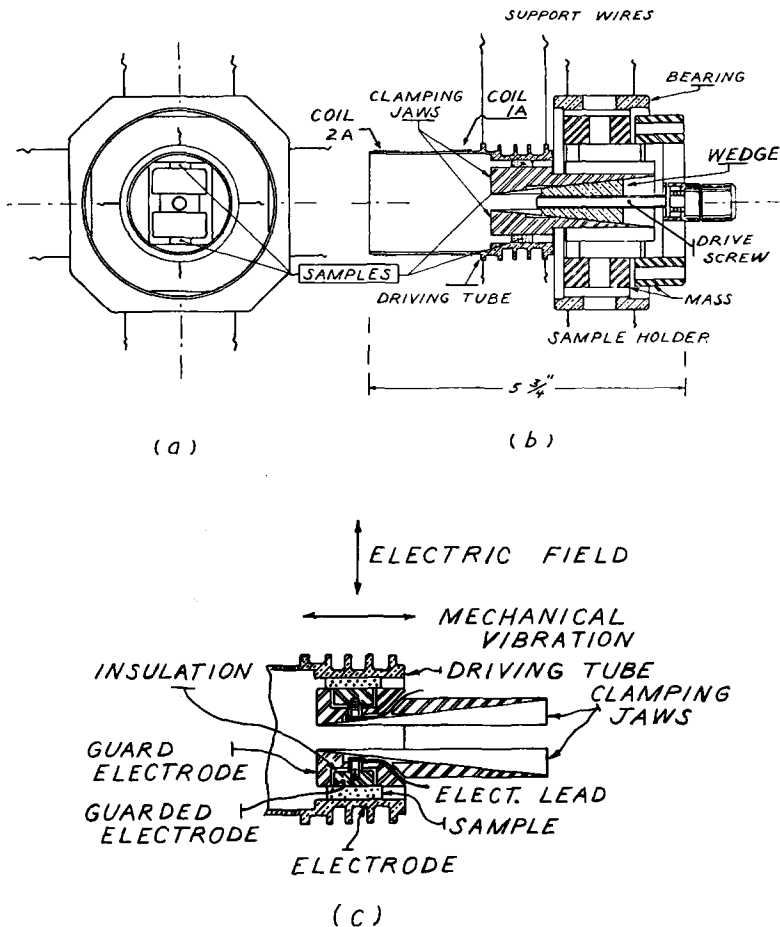


FIG. 1 End view (a) and side view section (b) of sample holder and driving tube of dynamic mechanical measurement apparatus. Enlarged sectional view (c) of sample slabs (clamping jaws) shows modification to allow simultaneous dielectric measurements as described in text.

Experimental Results

Some results of simultaneous dielectric and dynamic mechanical measurements on a 10% by volume polyvinyl chloride/di-2-ethyl hexyl phthalate gel are shown in Fig. 2 where values of complex shear compliance and complex dielectric constant at 100 Hz are plotted from -60 to 30°C. The sample was prepared from polyvinyl chloride powder (PVC) and redistilled di-2-ethyl hexyl phthalate (DOP) furnished by the B. F. Goodrich Co. Research Center, Brecksville, Ohio. The PVC powder was stirred into the DOP at 125°C and formed a gel within a few minutes. The gel was heated for 10 minutes at 125°C to remove air bubbles, and the sample pair was then cast from the gel into disks of 0.875" diameter and .031" thickness using a stainless steel mold in which the samples were pressed at 135-140°C for 5 minutes and then cooled to room temperature. In the measurement apparatus the drive screw was adjusted to give a distance between the sample slabs and driving tube flats of about .0305" in order to assure complete contact with the shearing/dielectric faces of the apparatus.

Many more dynamic mechanical and dielectric data were obtained for this gel sample, but the data of Fig. 2 suffice to illustrate the simultaneous mechanical/electrical measurement method. The dipolar dispersion region for this gel (at 100 Hz) is between -20 and -70°C with maxima in ϵ'' at -42 and -66°C. Since di-2-ethyl hexyl phthalate itself (DOP) has a dielectric loss maximum near -68°C at 100 Hz, it seems reasonable to conclude that the gel sample contained some "free" or uncombined DOP along with the 10% PVC-DOP gel, or perhaps is a mixture of gels varying from 2 to 10% PVC by volume. Values of complex dielectric constant vs. temperature at 1000 and 10,000 Hz show similar double dispersions with maxima in ϵ'' at -57 and -28°C; -48 and -18°C, respectively.

A single, broad maximum in the shear loss compliance, J'' , seems to occur near 12°C and 100 Hz for this same sample, but could result from the superposition of two or more separate maxima not clearly resolved.

Values of ϵ'' , J'' and/or the loss tangents ϵ''/ϵ' , J''/J' when plotted against frequency at constant temperatures also display double maxima at certain temperatures; a more detailed discussion will be presented, along with these additional data, in a subsequent article.

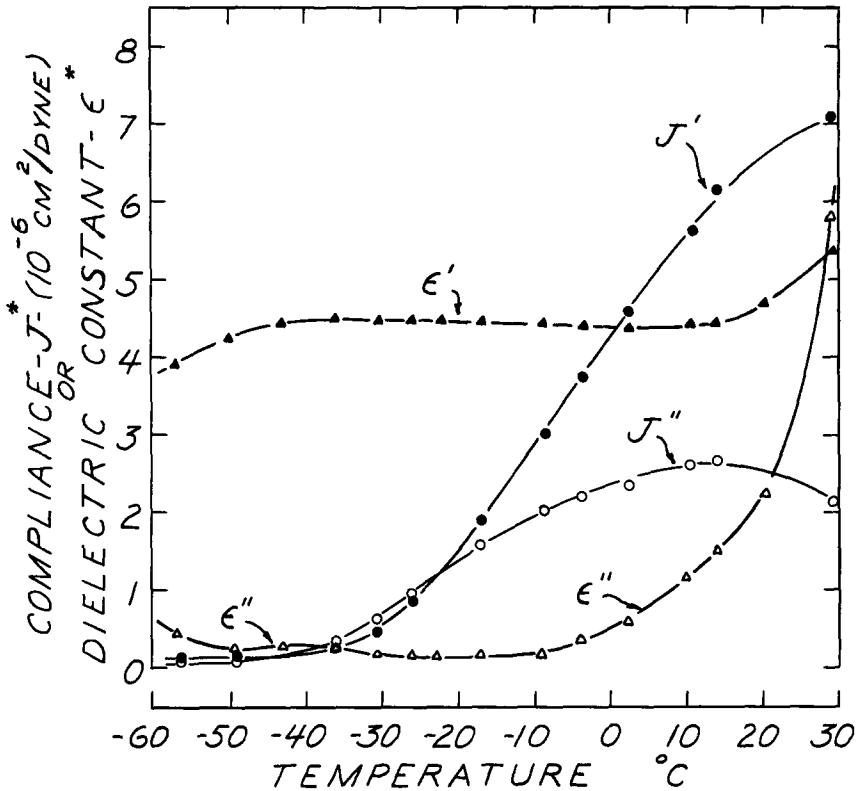


FIG. 2 Complex dielectric constant ($\epsilon^* = \epsilon' - i\epsilon''$) and complex shear compliance ($J^* = J' - iJ''$) variations with temperature at 100 Hz from simultaneous measurements on the same sample of a 10% by volume polyvinyl chloride-di-2-ethyl hexyl phthalate gel. Dipolar maxima in ϵ'' occur around -42°C and -66°C at 100 Hz; the general rise in ϵ' and ϵ'' above 20°C is attributed to interfacial (Maxwell) polarization arising from ionic impurities.

Conclusions

It is possible to carry out simultaneous dynamic mechanical and dielectric measurements on the same polymer sample at audiofrequencies and temperatures from -50 to 100°C using a modified electromagnetic transducer method developed originally for mechanical measurements only. Some representative data are cited for a 10% PVC-DOP gel, but measurements have also been made on solid samples of a butadiene acrylonitrile terpolymer and other materials. It is evident that such simultaneous measurements are likely to be most useful for polar polymers or other polar materials where dielectric dispersions can be attributed or "assigned" to particular molecular groups along the polymer chains.

Acknowledgements

This work was supported, in part, by a grant from the National Science Foundation. Mr. Frank Troska did the machine work necessary to modify the shear compliance-dielectric constant sample slabs (clamping jaws) for the transducer apparatus.

References

- R. CALVERT and J. MILDWATER:
Electr. Engr. 35, 782 (1963)
E. R. FITZGERALD and J. D. FERRY:
J. Colloid Sci. 8, 1 (1953)
E. R. FITZGERALD:
J. Chem. Phys. 27, 1180 (1957)
E. R. FITZGERALD
J. Acoust. Soc. Am. 33, 1305 (1961)
E. R. FITZGERALD:
Biorheology, 12, 397 (1975)
E. R. FITZGERALD:
Medical Phys. 4, 49 (1977)

Received and accepted August 4, 1980