A Method for Calculating Dynamic Mechanical Properties Using Fourier Transforms of Pulse Deformation Experiments

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Synopsis

A general method for determining the dynamic mechanical properties of a material is presented. It involves Fourier transforms of the stress and strain responses of a material subject to arbitrary deformation. As an example, uniaxial pulse-strain deformations were used to calculate the dynamic properties of a cured epoxy. A comparison of the properties calculated from uniaxial sinusoidal deformations and those obtained by Fourier transform analysis of the uniaxial pulse-strain indicate excellent agreement over a wide range in mechanical behavior. These results suggest that dynamic mechanical properties may be obtained when deformations other than that of a sine wave are used.

INTRODUCTION

Dynamic mechanical methods have been widely used to characterize the properties of polymers. The determination of the storage modulus (E'), loss modulus (E''), or equivalently, the complex modulus (E^*) and $\tan \delta$ can provide information on the glass transition temperature, (T_g) and secondary molecular relaxations.

Traditional dynamic mechanical methods involve determining the steady-state response of a material to a "clean" and continuous sinusoidal stress or strain disturbance. The term clean implies that there are no sine waves of other frequencies. The properties are determined by measuring the ratio of the amplitudes and the phase lag of the input and output sinusoidal signals. While these measurements are valuable, it would be convenient if one could generate these data using other disturbances.

In this article, we will demonstrate how dynamic mechanical data can be determined by evaluating the Fourier transforms of the stress and deformation responses of a material subject to arbitrary deformation. In order to verify the validity of our approach, a cured epoxy sample was subjected to dynamic deformation and uniaxial pulse-strain deformation. The Fourier transform-based dynamic properties were compared with those obtained using traditional methods.

THEORY

Before proceeding with the general methodology for determining dynamic mechanical properties using Fourier transforms, it is useful to include the

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Journal of Applied Polymer Science, Vol. 36, 403–413 (1988)

CCC 0021-8995/88/020403-11$04.00

derivation of some established results. The relationship between the storage (E'), loss (E'') and complex (E^*) moduli for a linear viscoelastic material are outlined below.

Equation (1) is a generalized linear viscoelastic constitutive equation where the tensile relaxation modulus $E(t)$ contains both time-dependent and time-independent contributions.[1]

$$\sigma(t) = \int_0^t E(t-\tau)\frac{\partial\epsilon}{\partial\tau}\,d\tau \tag{1}$$

where

$\sigma(t)$ = stress response

$\epsilon(t)$ = strain history

$E(t)$ = tensile relaxation modulus, where $E(t=\infty)$ = Eeq

Eeq = equilibrium tensile modulus

t = time

τ = time parameter

The dynamic mechanical properties can be calculated from the mechanical response of a material to sinusoidal deformation as follows. Substituting the harmonic strain input given in Eq. (2) into Eq. (1) yields Eq. (3) or (4):

$$\epsilon(\tau) = \epsilon_0 \sin\omega\tau \tag{2}$$

$$\sigma(t) = \epsilon_0\omega\int_0^t E(t-\tau)\cos\omega\tau\,d\tau \tag{3}$$

or

$$\sigma(t) = \epsilon_0\omega\int_0^t E(\tau)\cos(\omega t-\omega\tau)\,d\tau \tag{4}$$

Since $\cos(\omega t-\omega\tau) = \cos\omega t\cos\omega\tau + \sin\omega t\sin\omega\tau$ it is possible to simplify Eq. (4):

$$\sigma(t)/\epsilon_0 = \sin\omega t\left[\omega\int_0^t E(\tau)\sin\omega\tau\,d\tau\right] + \cos\omega t\left[\omega\int_0^t E(\tau)\cos\omega\tau\,d\tau\right] \tag{5}$$

At conditions of steady state ($t=\infty$), Eq. (5) can be simplified as follows:

$$\sigma(t)/\epsilon_0 = E'(\omega)\sin\omega t + E''(\omega)\cos\omega t \tag{6}$$

where

$$E'(\omega) = \omega\int_0^\infty E(\tau)\sin\omega\tau\,d\tau \tag{7}$$

$$E''(\omega) = \omega\int_0^\infty E(\tau)\cos\omega\tau\,d\tau \tag{8}$$

Note how the determination of the dynamic mechanical properties assumes a single-frequency harmonic input and conditions of steady state. In the discussion on the general methodology which follows, these limitations are not required.

Alternatively, the Fourier transform of Eq. (1) can be given by Eq. (9), where it is assumed that the material starts from rest:

$$\tilde{\sigma} = i\omega\tilde{E}\tilde{\epsilon} \tag{9}$$

where

$$\tilde{\sigma}(\omega) = \int_0^\infty \sigma(t)e^{-i\omega t}\,dt \tag{10}$$

$$\tilde{\epsilon}(\omega) = \int_0^\infty \epsilon(t)e^{-i\omega t}\,dt \tag{11}$$

Note that Eqs. (10) and (11) are given by definition of the Fourier transform.[2] The angular frequency ω can be related to the linear frequency f by Eq. (12):

$$\omega = 2\pi f \tag{12}$$

Using Euler's formula, Eq. (9) can be rearranged and simplified as follows:

$$\tilde{\sigma}/\tilde{\epsilon} = i\omega\int_0^\infty E(t)e^{-i\omega t}\,dt = i\omega\int_0^\infty E(t)\cos\omega t\,dt - i^2\omega\int_0^\infty E(t)\sin\omega t\,dt \tag{13}$$

$$\tilde{\sigma}/\tilde{\epsilon} = \omega\int_0^\infty E(t)\sin\omega t\,dt + i\omega\int_0^\infty E(t)\cos\omega t\,dt \tag{14}$$

Substituting Eqs. (7) and (8) into Eq. (14) yields the desired result:

$$\tilde{\sigma}/\tilde{\epsilon} = i\omega\tilde{E} = E'(\omega) + iE''(\omega) = E^*(\omega) \tag{15}$$

Some of the mathematics involved in the calculation of the dynamic mechanical properties from arbitrary deformation have already been described.[3] A summary and the specifics regarding the numerical aspects of the method follow. Applying Euler's formula to the Fourier transforms of the stress and strain functions in Eq. (15), yields Eqs. (16) and (17):

$$\tilde{\sigma}(\omega) = \sigma_c - i\sigma_s \tag{16}$$

$$\tilde{\epsilon}(\omega) = \epsilon_c - i\epsilon_s \tag{17}$$

where

$$\sigma_s(\omega) = \int_0^\infty \sigma(t)\sin\omega t\,dt \tag{18}$$

$$\sigma_c(\omega) = \int_0^\infty \sigma(t)\cos\omega t\,dt \tag{19}$$

$$\epsilon_s(\omega) = \int_0^\infty \epsilon(t)\sin\omega t\,dt \tag{20}$$

$$\epsilon_c(\omega) = \int_0^\infty \epsilon(t)\cos\omega t\,dt \tag{21}$$

Equations (18)–(21) can be combined to yield the dynamic mechanical properties as follows:

$$E'(\omega) = \frac{\sigma_c(\omega)\epsilon_c(\omega) + \sigma_s(\omega)\epsilon_s(\omega)}{\epsilon_c^2(\omega) + \epsilon_s^2(\omega)} \tag{22}$$

$$E''(\omega) = \frac{\sigma_s(\omega)\epsilon_c(\omega) - \sigma_c(\omega)\epsilon_s(\omega)}{\epsilon_c^2(\omega) + \epsilon_s^2(\omega)} \tag{23}$$

$$|E^*(\omega)| = [E'^2 + E''^2]^{1/2} \tag{24}$$

$$\tan\delta = E''/E' \tag{25}$$

There are, however, several subtleties which should be noted in order to avoid erroneous results. Accordingly, care should be taken when choosing the frequencies at which the dynamic properties are to be calculated. First, the data collection rate of the stress and strain responses must be considered. In order to adequately calculate the dynamic mechanical properties at a given frequency, a sufficient number of data points should be collected so that a sine wave of that particular frequency can be adequately described. Clearly, higher collection rates will result in more accurate properties. Conversely, for a given data collection rate, the properties calculated at the lowest frequency will be the most accurate. As a general rule, the collection frequency should be ten times larger than the highest frequency to be calculated. Should high frequency dynamic properties be desired and high data collection rates are not feasible, interpolation of the collected data is recommended.

The second subtlety concerns the numerical methods used to calculate the mechanical properties. Consider Eqs. (20) and (21) and a rapidly applied uniaxial pulse-strain deformation of magnitude ϵ_0. Mathematically this is equivalent to multiplying $\cos\omega t$ and $\sin\omega t$ by the constant ϵ_0. For pulse durations which are integer multiples of the desired frequency fc, the values for $\epsilon_c(\omega)$ and $\epsilon_s(\omega)$ will be equal to zero. This results in the calculation of erroneous dynamic properties. In order to maximize the values of $\epsilon_c(\omega)$ and $\epsilon_s(\omega)$, the desired frequency or pulse duration should be chosen so as to result in an noninteger number of sine or cosine waves. Equation (26) states the criterion that should be employed when using uniaxial pulse-strain deformations. In order to obtain the highest degree of accuracy, one should choose parameters such that $r = 0.5$. While the choice of $r = 0.5$ is not fixed, the accuracy that one obtains decreases as r decreases.

$$(p)(fc) = n + r \tag{26}$$

where

p = pulse duration [s]

fc = desired frequency of calculated properties [Hz]

n = integer

r = fractional part of a sine wave ($0 < r < 1$)

In general, for a deformation of arbitrary shape, the intergral of the product of $\epsilon(t)$ and $\sin \omega t$ or $\cos \omega t$ will not be zero and Eq. (26) can be disregarded. For the experiments described below, which use uniaxial pulse-strain deformations, these considerations have been taken into account. The choice of the frequencies at which the dynamic properties are calculated and the pulse duration employed result in $r = 0.4$.

For deformations which result in $\epsilon_c(\omega)$ and $\epsilon_s(\omega)$ equal to zero, the dynamic mechanical properties of a material can still be recovered. The method involves the ratio of time-weighted moments of the stress and strain histories as described below. Differentiation of Eq. (9) with respect to ω yields:

$$\frac{\partial \tilde{\sigma}}{\partial \omega} = i\tilde{E}\tilde{\epsilon} + i\omega\tilde{\epsilon}\frac{\partial \tilde{E}}{\partial \omega} + i\omega\tilde{E}\frac{\partial \tilde{\epsilon}}{\partial \omega} \tag{27}$$

Since $\tilde{\epsilon} = 0$, the first and second terms of the right-hand side equal zero. This simplifies Eq. (27) to Eq. (28):

$$\frac{\partial \tilde{\sigma}}{\partial \omega} = i\omega\tilde{E}\frac{\partial \tilde{\epsilon}}{\partial \omega} \tag{28}$$

It can be shown that expressions for $\partial\tilde{\sigma}/\partial\omega$ and $\partial\tilde{\epsilon}/\partial\omega$ are given by Eqs. (29) and (30):

$$\frac{\partial \tilde{\sigma}}{\partial \omega} = -i\int_0^\infty t\sigma(t)e^{-i\omega t}\,dt \tag{29}$$

$$\frac{\partial \tilde{\epsilon}}{\partial \omega} = -i\int_0^\infty t\epsilon(t)e^{-i\omega t}\,dt \tag{30}$$

Substitution of Eqs. (29) and (30) into Eq. (28) yields the desired result:

$$i\omega\tilde{E} = \frac{\partial\tilde{\sigma}/\partial\omega}{\partial\tilde{\epsilon}/\partial\omega} = \frac{\int_0^\infty t\sigma(t)e^{-i\omega t}\,dt}{\int_0^\infty t\epsilon(t)e^{-i\omega t}\,dt} \tag{31}$$

Hence, the dynamic mechanical properties can be calculated by evaluating the ratio of the time-weighted moments of the stress and strain transforms. For those deformation histories whose time-weighted moment of strain equals zero this method can be further generalized to yield the desired results. Repeated differentiation of Eq. (9) with respect to ω results in successively higher moments of stress and strain. Differentiation is continued until the denominator of Eq. (31) becomes nonzero. At that point the dynamic properties can be determined. It should be noted, however, that since these calculations utilize higher order moments of stress and strain, the resulting properties calculated from such information are subject to more inaccuracy.

Finally, with regard to the path of deformation, it is best to use a displacement which returns to its predeformation level. Under these conditions, the assumption of linear viscoelasticity requires the stress to return to zero, and ensures that the intergrals used in the above calculations are defined. Similarly, it should be noted that by virtue of the assumption of linear viscoelasticity, if $\tilde{\epsilon}$ equals zero then $\tilde{\sigma}$ must also equal zero. For nonlinear viscoelastic materials this is not necessarily true. Thus, this technique can also be used as a test for the linearity of a material.

EXPERIMENTAL

A cured epoxy was chosen as a sample for the purposes of this comparison. Specifically, Epon 828, a DGEBA epoxy resin was cured for 1 h at 115°C with a stoichiometric amount of polyamide V-40. Both materials were obtained from the Shell Chemical Company. Based upon curing studies on this sample using the technique of Impulse Viscoelasticity, these curing conditions resulted in a fully cured sample.[4] In this way, measurements were made without the complication of continued polymerization.

Sinusoidal deformations, in a uniaxial mode, were conducted at frequencies of 0.12, 0.52, and 0.92 Hz on a Dynastat mechanical spectrometer (Imass, Inc., Hingham, MA). Measurements were made in the displacement control mode using the low range displacement transducer. $|E'|$, E', E'', and $\tan\delta$ based upon dynamic deformations were calculated by the Dynastat's microprocessor.

Approximately 1 min after the dynamic testing was complete, a uniaxial pulse-strain deformation of 20 s duration was applied to the sample. Analog signals of the stress and strain were collected and digitized at a rate of 10 Hz. At this data collection frequency, this corresponds to 83, 19, and 11 points per sine wave for the 0.12, 0.52, and 0.92 Hz frequencies, respectively. Data collection began 10 s prior to the uniaxial deformation and continued for 100 s. Because of fast sample relaxation at the higher temperatures, the data collection period was reduced to 50 s. The numerical calculations indicated in the previous section [Eqs. (18)–(25)] were then used to determine $|E^*|$, E', E'', and $\tan\delta$ at 0.12, 0.52, and 0.92 Hz using simple quadrature integration routines that were written specifically for these calculations. As mentioned, these frequencies were specifically chosen to avoid the numerical complications associated with uniaxial pulse-strain deformations.

For both modes of deformation, sample strain was kept small ($< .05\%$) in order to help assure conditions of linear viscoelasticity. Two measurements were made at 30, 40, 50, 60, 70, 75, 80, 90, 100, 110, and 115°C. Temperature was controlled to ± 0.1°C. Prior to deformation the samples were allowed to come to thermal equilibrium.

RESULTS AND DISCUSSION

Figure 1 plots the storage modulus E' at 0.12 Hz as calculated by the Dynastat as a function of temperature for the cured epoxy sample. For such data, a T_g of 85–90°C can be estimated. This value is in agreement with that obtained from Impulse Viscoelastic measurements.[4]

Figures 2(a-e) plot the stress response to the uniaxial deformation for the epoxy sample at temperatures of 30, 50, 70, 90, and 110°C, respectively. In each of these figures the stress relaxation during the deformation pulse is indicative of the viscoelastic nature of the material. The slow relaxations in stress shown in Figures 2(a) and (b) are evidence for the relatively long relaxation times associated with the glassy state. There is a trend toward increasingly viscoelastic character as the temperature is increased. This can be

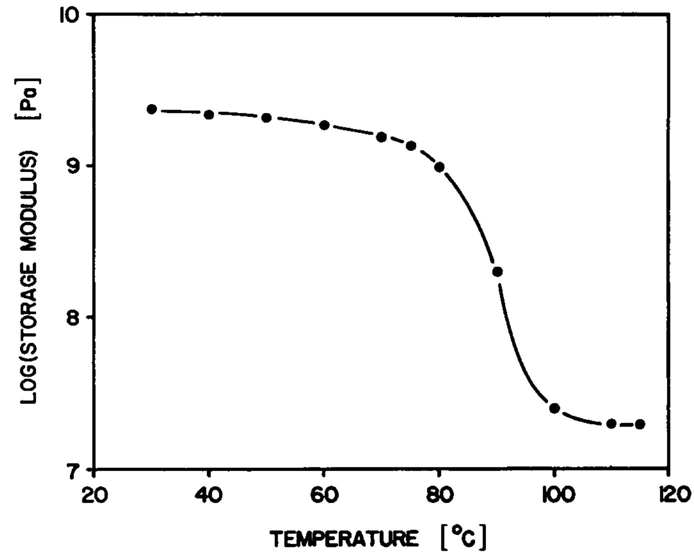
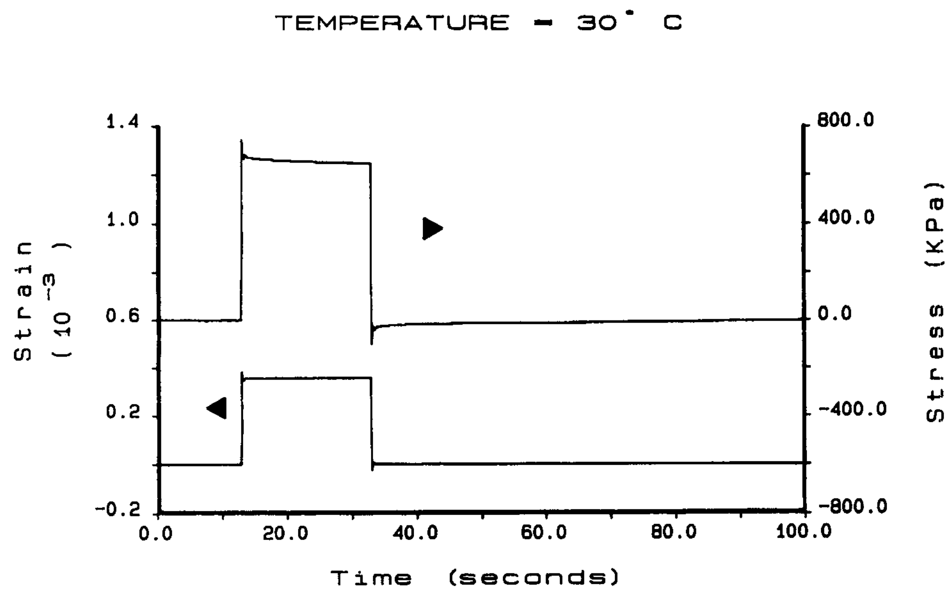


Fig. 1. Plot of E' at 0.12 Hz as a function of temperature the V-40/Epon 828 epoxy. The figure was generated from data based upon dynamic deformations.

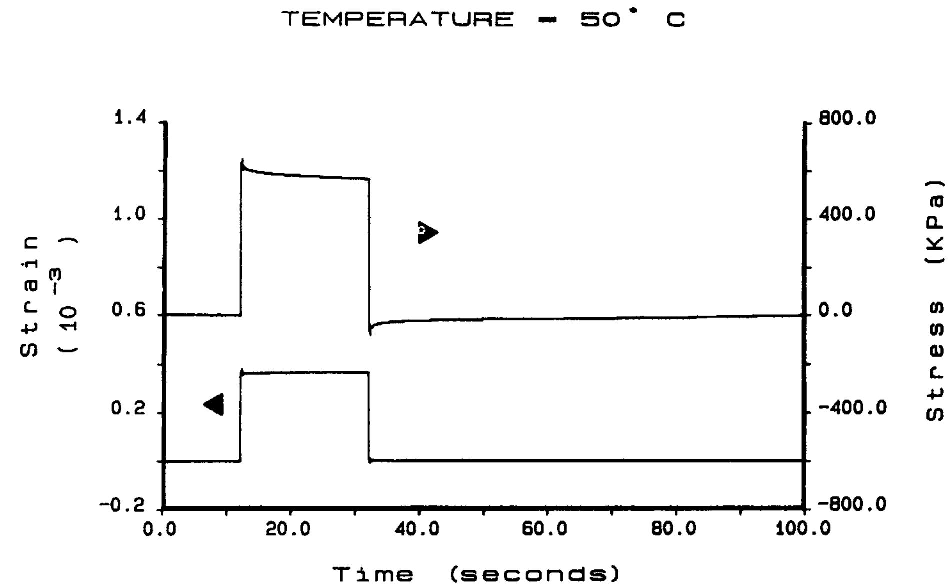


(a)

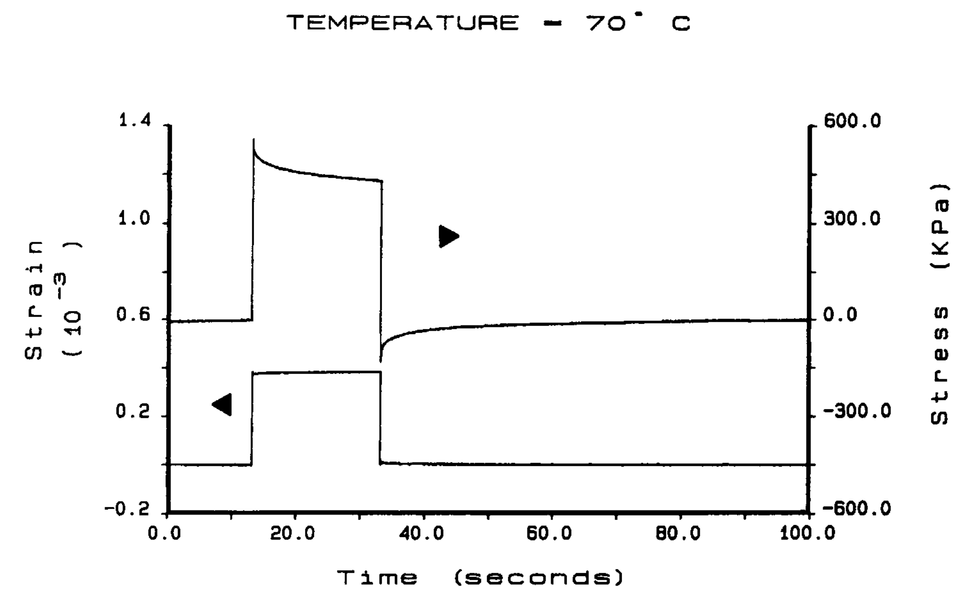
Fig. 2. Plot of the stress response to a uniaxial pulse-strain deformation for the V-40/Epon 828 epoxy sample at temperatures of (a) 30, (b) 50, (c) 70, (d) 90, and (e) 110°C.

seen on Figures 2(c) and (d). About 20°C above T_g the sample behaved almost elastically, as evidenced by Figure 2(e).

Table I compares the dynamic data generated by both methods at the three frequencies for all temperatures. The agreement between the two methods appears to be excellent over the entire range in mechanical behavior. A



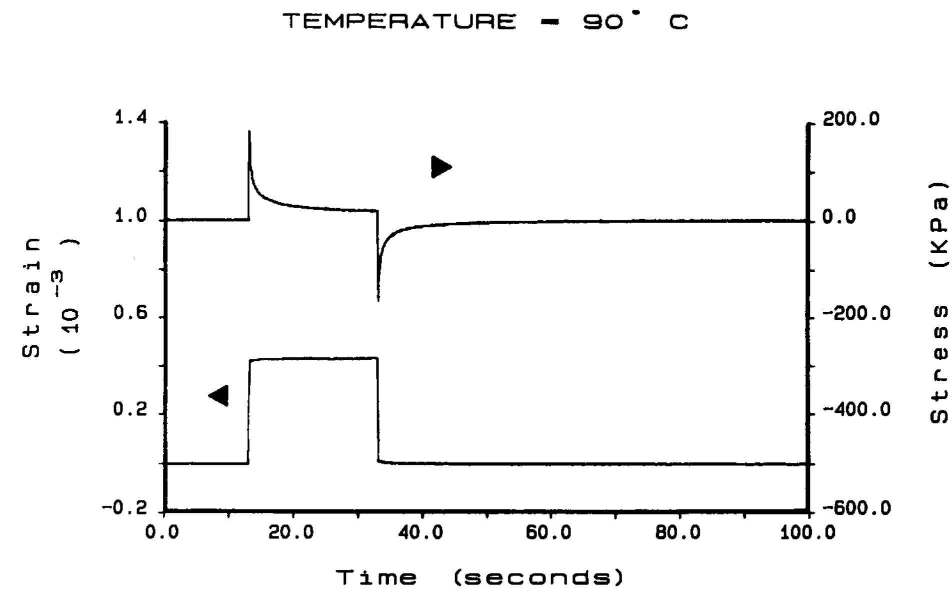
(b)



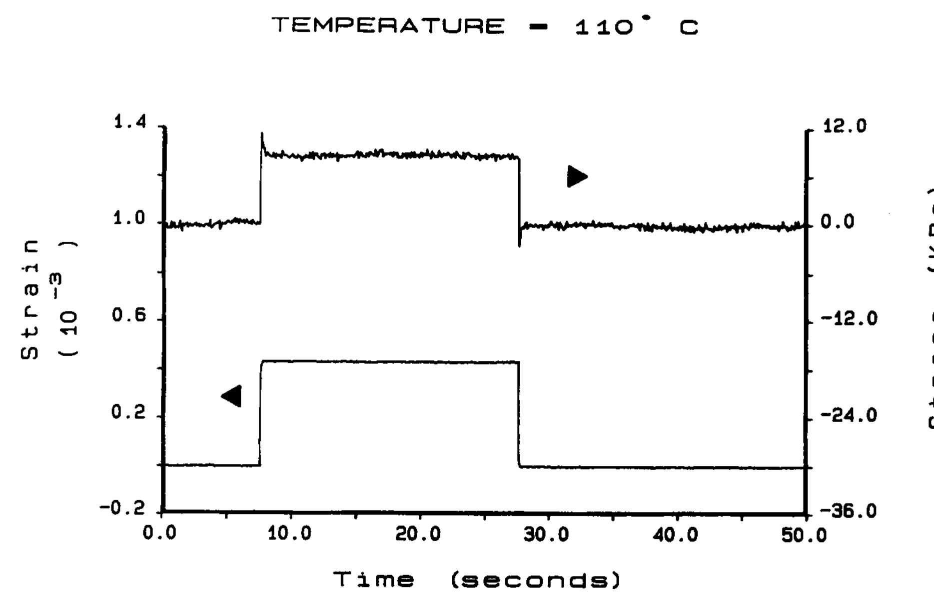
(c)

Fig. 2. (*Continued from the previous page.*)

comparison of both methods for $|E^*|$ and E' indicates differences of less than 1%. Because of the good agreement it was deemed that the differences in mechanical properties would not appear clearly on a figure. It should be noted that the results presented in Table I are the average of two measurements at each condition. In general, the agreement between the data obtained via



(d)



(e)

Fig. 2. (*Continued from the previous page.*)

dynamic methods was better than that obtained by the Fourier transform method.

The differences between the dynamic data and the Fourier transform data in the glassy state could be reduced by using longer pulse durations. In this way it would be possible to help recover some of the long-term relaxations

TABLE I
Comparison of the Dynamic Mechanical Data at 0.12, 0.52, and 0.92 Hz Using Dynamic Mechanical and Fourier Transform Methods at each Temperature

Temp (°C)	prop.	Dynamic mechanical method (Hz)			Fourier transform method (Hz)		
		0.12	0.52	0.92	0.12	0.52	0.92
30	$\lvert E^*\rvert$	2376	2433	2452	2405	2460	2471
	E'	2375	2432	2451	2404	2459	2469
	E''	65	58	56	60	71	82
	$\tan\delta$	0.027	0.024	0.023	0.025	0.029	0.033
40	$\lvert E^*\rvert$	2201	2262	2289	2227	2280	2295
	E'	2200	2261	2288	2226	2278	2294
	E''	70	64	62	62	70	55
	$\tan\delta$	0.032	0.028	0.027	0.028	0.031	0.024
50	$\lvert E^*\rvert$	2033	2094	2126	2058	2125	2143
	E'	2032	2093	2125	2057	2124	2142
	E''	74	71	67	62	67	56
	$\tan\delta$	0.036	0.034	0.031	0.030	0.032	0.026
60	$\lvert E^*\rvert$	1842	1912	1946	1860	1931	1955
	E'	1840	1911	1944	1858	1929	1953
	E''	88	79	76	80	72	70
	$\tan\delta$	0.048	0.041	0.039	0.043	0.037	0.036
70	$\lvert E^*\rvert$	1558	1654	1687	1575	1632	1671
	E'	1554	1651	1684	1572	1629	1669
	E''	112	99	93	102	89	75
	$\tan\delta$	0.072	0.060	0.055	0.065	0.055	0.045
75	$\lvert E^*\rvert$	1325	1444	1485	1357	1439	1543
	E'	1317	1438	1481	1350	1433	1538
	E''	141	125	116	135	130	128
	$\tan\delta$	0.11	0.087	0.078	0.10	0.091	0.083
80	$\lvert E^*\rvert$	985	1138	1190	993	1131	1162
	E'	969	1126	1181	978	1123	1152
	E''	176	160	152	174	135	150
	$\tan\delta$	0.18	0.14	0.13	0.18	0.12	0.13
90	$\lvert E^*\rvert$	199	329	388	197	319	360
	E'	166	292	351	166	283	321
	E''	108	153	165	106	146	161
	$\tan\delta$	0.65	0.52	0.47	0.64	0.52	0.50
100	$\lvert E^*\rvert$	25.0	39.0	48.4	25.1	34.0	38.3
	E'	24.3	33.5	40.1	23.6	30.3	33.2
	E''	7.6	20.0	27.2	8.6	14.5	18.7
	$\tan\delta$	0.31	0.60	0.68	0.36	0.48	0.56
110	$\lvert E^*\rvert$	19.5	20.3	21.1	19.3	20.7	19.7
	E'	19.5	20.2	20.9	19.3	20.6	19.7
	E''	0.49	2.4	3.3	0.59	*	1.5
	$\tan\delta$	0.025	0.12	0.16	0.031	*	0.075
115	$\lvert E^*\rvert$	19.6	19.8	20.1	18.5	18.4	21.2
	E'	19.6	19.8	20.1	18.5	18.4	21.2
	E''	0.13	0.88	1.2	0.43	*	*
	$\tan\delta$	0.0066	0.044	0.061	0.023	*	*

Values for $\lvert E^*\rvert$, E', and E'' are in units of MPa. Data represent the average of two measurements. The asterisks (*) represent negative numbers.

present in the glassy state. For this study it was assumed that a 20 s pulse was sufficient. The negative loss moduli and tan δ data at 110 and 115°C can be attributed to the fact that it is very difficult to calculate the loss properties of a nearly elastic material without resorting to extremely high data collection frequencies. Negative values have also been observed when deforming other elastic materials using standard dynamic methods.

As a measure of the viscoelastic character of a material, one can also use the dependence of the dynamic mechanical properties upon frequency. Though the investigated range in frequency is less than a decade, near T_g there is a factor of 2 difference between the low and high frequency properties. The Fourier transform-based properties indicate excellent qualitative and quantitative agreement. In addition, this trend in viscoelastic character is qualitatively supported by Figures 2(a-e).

An additional feature of the Fourier transform method is that it is also possible to calculate the very low frequency or equilibrium properties. From such data, one can calculate the ratio of the equilibrium tensile modulus to the storage modulus. This is another measure of the viscoelastic character of a material.

SUMMARY AND CONCLUSIONS

A method has been presented showing that it is possible to accurately calculate dynamic mechanical properties ($|E^*|$, E', E'', $\tan\delta$) at several frequencies using the Fourier transforms of stress and strain responses to arbitrary deformations. While uniaxial pulse-strain deformations were used in this study, the method is applicable to deformations of arbitrary shape, provided that sufficient data are collected so that a sine wave can be adequately described over the frequency range of interest. This potential limitation can be overcome with higher data collection rates or data interpolation. In addition, the method presented can be used as a test for the linearity of a material.

In order to verify this approach, a comparison of the dynamic mechanical properties was made at frequencies of 0.12, 0.52, and 0.92 Hz for a cured epoxy. Using traditional dynamic deformations and the Fourier transform method, excellent qualitative and quantitative agreement was found in the range of the glassy to the rubbery state.

The authors wish to thank the Center for UMass-Industry Research on Polymers (CUMIRP) for financial support.

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Received May 28, 1987
Accepted October 8, 1987