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Dynamic Mechanical Properties of Polyvinyl Stearate at Audio-Frequencies*†

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Measurements of the complex shear compliance ($J^*=J'-iJ''$) of polyvinyl stearate at frequencies from 50 to 5000 cps have resulted in the discovery of several sharp resonances in the compliance as previously described. The effects of temperature and static stress normal to the direction of the dynamic shearing stress have now been studied for this material. The two principal resonances observed at 25°C were located at (1) 180 and (2) 500 cps. At successive temperatures of 30, 36, and 42°C the first resonance remained essentially unchanged, but the second resonance shifted to higher frequencies and decreased in magnitude until it virtually disappeared at 42°C. A return to 25°C and a reapplication of a slight static stress resulted in the return of the second resonance (at 525 cps). At successively increasing static stresses corresponding to compressions up to 1.8% the second resonance now decreased in magnitude and shifted to higher frequencies. The first resonance disappeared at a static compression of 0.8%. Similar effects of static stress were observed at room temperature (~25°C) on a second set of samples of different dimensions. The reversibility of the effects of static compression were demonstrated by the second set of samples where for example, a resonance originally present at 2.8% static compression disappeared at 3.7% and reappeared when the static compression was reduced to 3.1%. The reversible nature of the effects of static stress seems to preclude the possibility of an explanation of the resonances in terms of changes in dislocation density.

I. INTRODUCTION

THE existence of multiple resonance dispersions in crystalline polymers has been demonstrated in a previous investigation of the dynamic shear compliance of polytetrafluoroethylene, polyethylene, and polyvinyl stearate.[1] Similar resonances have been observed at audio-frequencies in pure polycrystalline metals[2] and in single crystals of quartz.[3] In many cases the previous thermal and static stress histories (cold work) of the samples tested were found to have a profound effect on the location and magnitude of the observed resonances. The effects of temperature and static stress on the dynamic mechanical properties of polyvinyl stearate are presented in greater detail in the present investigation where the previous measurements[1] on polyvinyl stearate at 25.8°C and at frequencies from 100 to 2000 cps are extended to include temperatures from 25 to 50°C and frequencies from 50 to 5000 cps. Dynamic measurements are also reported with static compressions (at right angles to the direction of dynamic shear) varying from 0.1 to 3.7%.

II. MATERIAL STUDIED

The polyvinyl stearate samples were formed by heating to 80°C and casting in stainless steel molds. After casting the samples were slightly concave on top due to the contraction taking place upon solidification; these surfaces were then made plane by sanding with very fine sandpaper and emery cloth. The polyvinyl stearate was prepared as previously described[1] and had an average degree of polymerization of about 400. The crystallinity is estimated to be approximately 90% from x-ray determinations which assume the monomer (vinyl stearate) to be 100% crystalline.[4] The sample material melts sharply at 51.5°C according to capillary tube determinations of the melting point; this result is substantiated by the fact that the dielectric constant has a sharp discontinuity between 51 and 52°C[5] when the polymer is heated through this temperature range.

A summary of the sample properties and dimensions is adduced in Table I.

III. EXPERIMENTAL METHODS

Measurements of complex shear compliance were made by means of an electromagnetic transducer method which has been described in previous publications.[1,2,6] In this method two small disks of the sample material are clamped between metal surfaces and subjected to sinusoidal dynamic vibrations in a

TABLE I. Summary of sample dimensions and static compressions for polyvinyl stearate.

Sample No.	28	28*a*	28*b*	28*c*	28*d*	28*e*	37*a*	37*b*	37*c*
Percent stat. comp.	2.3	<0.1[a]	0.3[a]	0.8[a]	1.2[a]	1.8[a]	2.8	3.7	3.1
Dimensions diam. (in.)	0.377	0.380					0.500		
thickness (in.)	0.215_1	0.210_0					0.109_8		
	0.214_7	0.209_9					0.109_6		
Sample coefficient (cm)	2.74 at 2.3%						9.12 at 2.8%		
Weight (g)	0.369_0						0.332_0		
							0.331_6		

[a] Based on the thickness of sample 28 after heating to 41.7°C, i.e., 0.210_0 and 0.209_9 in. In other words, these compressions are in addition to the permanent deformation of No. 28 amounting to 2.3%.

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[2] Edwin R. Fitzgerald, Phys. Rev. 108, 690 (1957).
[3] Edwin R. Fitzgerald, Society of Rheology, Annual Meeting, Princeton, New Jersey (1958).
[4] W. S. Port (private communication).
[5] M. G. Broadhurst and E. R. Fitzgerald, Bull. Am. Phys. Soc. Ser. II, 3, 108 (1958).
[6] E. R. Fitzgerald and J. D. Ferry, J. Colloid Sci. 8, 1 (1953).

direction perpendicular to the static (clamping) stresses. The static stresses are of the order of 10^7 dynes/cm^2 ($\sim$150 psi) while the amplitude of the dynamic stress is less than 5×10^3 dynes/cm^2 ($\sim$0.08 psi) resulting in strain amplitudes of 10^{-4} to 10^{-6}. The value of the dynamic stress and strain amplitudes can be obtained directly from the alternating current used to drive the samples in shear and the magnetic constants of the apparatus. At present, however, there is no provision for a direct measurement of the static clamping stresses.

Estimates of the static stresses were obtained by noting the percent compression of the samples in the apparatus (obtained from micrometer readings which are made with the samples clamped in place) and then separately determining a compressive stress-strain curve for the samples after removing them from the apparatus. This was done by observing the deformation of the sample between two plates as weights were added to the upper plate. The results for a given sample are reproducible to within $\pm6\%$ but vary for different samples of the same material. Estimates of the static compressive stress, therefore, were obtained from static stress-strain data obtained on the samples actually used in the dynamic testing. The deformation at strains less than 2.0% was found to be entirely recoverable at room temperature ($\sim$25°C) and a linear function of the compressive stress.

IV. EXPERIMENTAL RESULTS

1. Frequency Dependence of Compliance at Various Temperatures and Compressions

The variation of J' and J'' with frequency for polyvinyl stearate (sample No. 28, cf., Table I) at 25.8°C is shown in Fig. 1. These results, from 100 to 2000 cps, were obtained at 312.5 to 344.8 hr after the application of a static compression of about 2.3%. Resonances are evident at 185, 490, 650, 720, 1235, 1400, and 1790 cps. The variation of complex shear compliance with frequency at 30.5°C is given in Fig. 2. These measurements were taken about 840 hr after the application of static compression and show a definite decrease in the magnitude of the largest resonance (490 cps) previously observed at 25.8°C together with a shift in frequency to 530 cps. The resonance at 185 cps is practically unchanged while there are indications of small resonances at 690 and 1410 cps. Results at 36.4 and 41.7°C taken at approximately 1015 and 1225 hr, respectively, (Fig. 3) demonstrate the continued existence of the resonance previously found at 185 cps which now seems to shift slightly to 195 cps at 41.7°C but is otherwise little changed. At the same time the largest resonance found near 500 cps at 25.8 and 30.5°C almost completely disappears at 36.4°C with only a small doublet at 525 and 560 cps remaining in this region. A doublet is also evident at 700 and 720 cps. The results at 41.7°C show a shift in the frequencies of the first doublet (525, 560 cps observed at 46.4°C) to 550 and 515 cps while the second doublet (700, 720 cps at 36.4°C) seems to split into two distinctly separate resonances at 690 and 760 cps. There is also evidence of a resonance near 1375 cps. At the conclusion of measurements at 41.7°C the samples were returned to room temperature and now found to be loose instead of tightly clamped between the shearing members of the transducer apparatus. The samples were removed and their thickness remeasured; a permanent reduction in thickness was found amounting to 2.3% of the original thickness.

A second series of measurements to determine the effect of the static compression on the same set of samples was instituted a few months later. The first of these measurements were made with the samples

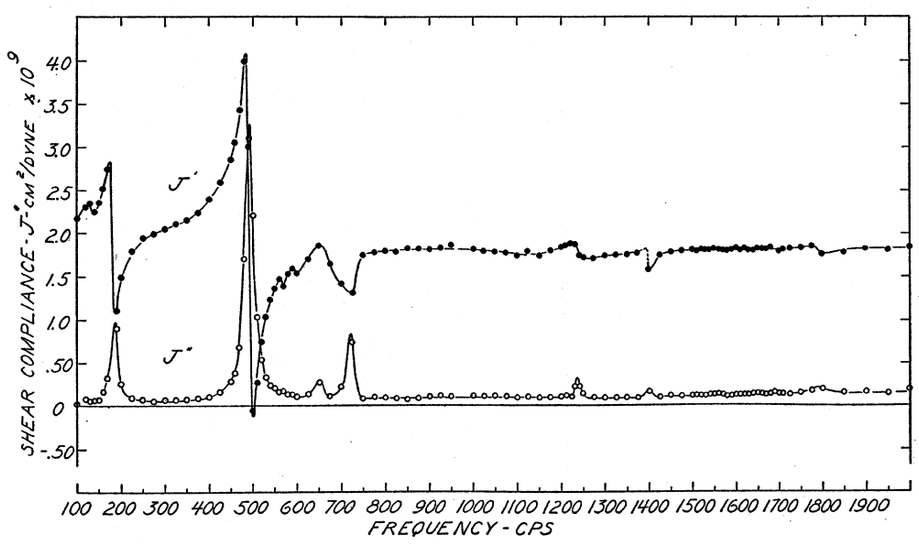

FIG. 1. Variation of complex shear compliance ($J^*=J'-iJ''$) with frequency for polyvinyl stearate at 25.8°C and 2.3% static compression. Solid points, J'; open points, J''. (First set of samples.)

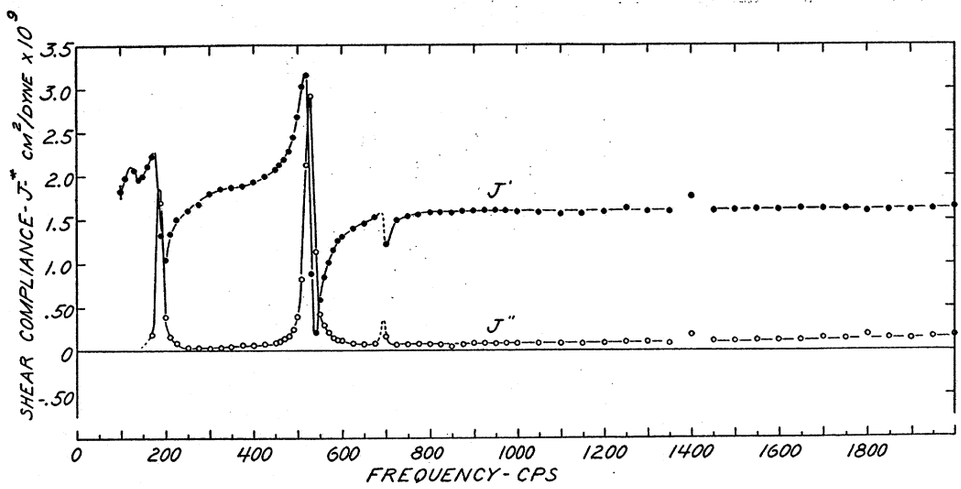

FIG. 2. Variation of complex shear compliance ($J^*=J'-iJ''$) with frequency for polyvinyl stearate at 30.5°C and 2.3% static compression. Solid points, J'; open points, J''.

compressed very slightly (<0.1%)[7] and although it is probable that the samples were not slipping during the dynamic measurements, this cannot be stated with complete certainty. At subsequent static deformations the samples were tested for slipping as previously described[1,2] and found not to slip at forces much greater than those corresponding to the amplitudes of the applied dynamic stresses. The results of measurements at 0.1% static compression are adduced in Fig. 4. A huge resonance is present at 170 cps together with a much smaller one at 575 cps and low, broad resonances at 1080 and 1260 cps. These results did not change with time.

The samples were next compressed to 0.3% and values of J' and J'' determined from 100 to 2000 cps as shown in Fig. 5. A small resonance is present at 190 cps together with a much larger one at 525 cps and a small one at 1775 cps. It should be noted that the

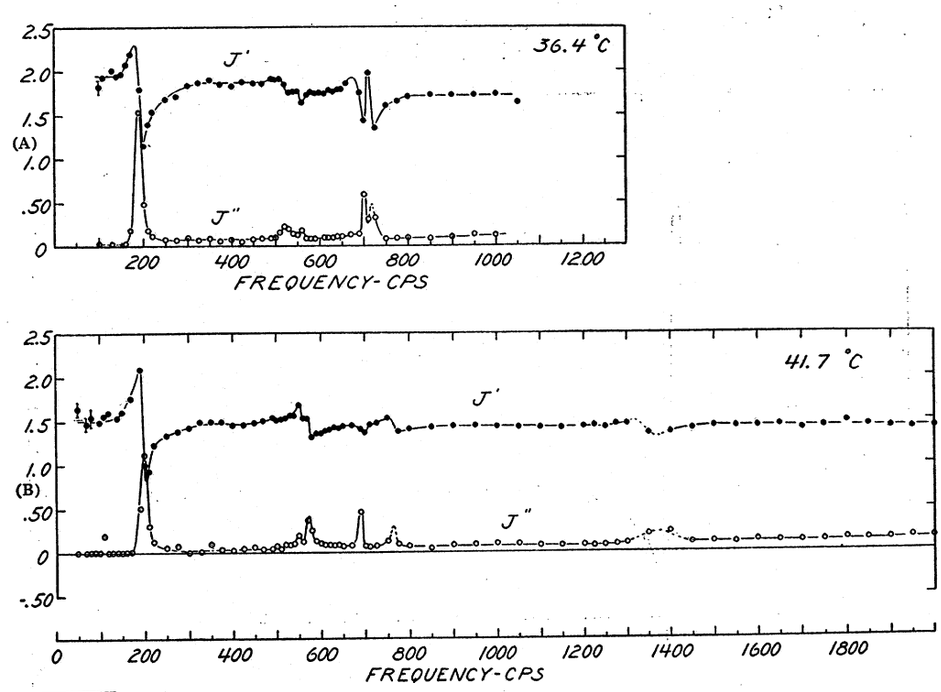

FIG. 3. (A) Variation of complex shear compliance ($J^*=J'-iJ''$) with frequency for polyvinyl stearate at 36.4°C and 2.3% static compression. (B) Variation of complex shear compliance with frequency for polyvinyl stearate at 41.7°C and 2.3% static compression. Solid points, J'; open points, J''.

[7] The static compressions subsequently listed are with respect to the new, decreased thickness found after the measurements at 41.7°C.

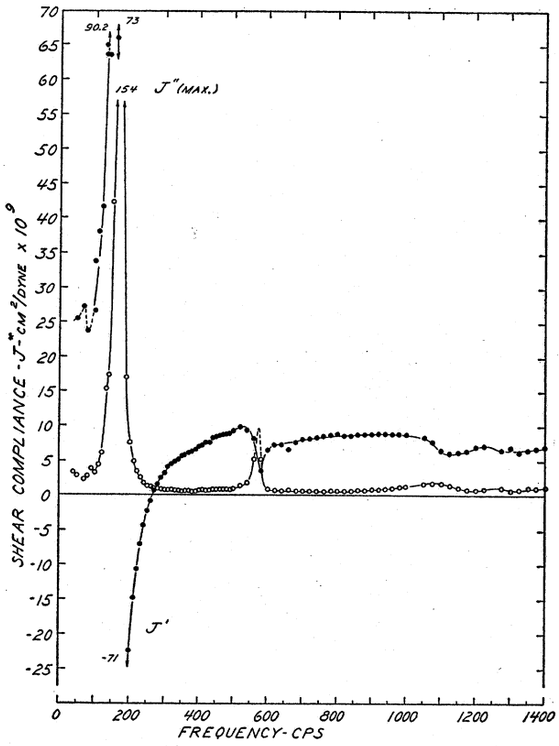

FIG. 4. Variation of complex shear compliance ($J^*=J'-iJ''$) with frequency for the polyvinyl stearate samples of Figs. 1–3 at 24.8°C after removal and reinsertion in the apparatus. A static compression of about 0.1% was applied in addition to the 2.3% previously applied as the samples were found to have a permanent set of 2.3% after heating to 41.7°C. Solid points, J'; open points, J''.

two principal resonances originally found at 25.8°C in Fig. 1 were located at nearly the same frequencies (i.e., 185 and 490 cps) as those in Fig. 5.

Results at 0.8% static compression were obtained as shown in Fig. 6. The resonance previously found at 190 cps (0.3%) has vanished and that found at 525 cps at 0.3% has shifted to 670 cps and apparently decreased in magnitude although the exact value of J'' (max) is not well defined because the frequency intervals (25 cps) were too large. These measurements were taken approximately 241 hr after those at 0.3% static compression. In order to obtain better resolution, measurements in the resonance region were repeated at smaller frequency intervals at 339 hr and 507 hr as shown in Fig. 7 (B and C) where they are compared with the original measurements (A). From Fig. 7 it is clear that the single resonance of Fig. 6 [and Fig. 7(A)] is in reality a triplet or series of three peaks occurring very close to one another, or more specifically at 645, 665, and 685 cps. This situation appears to be relatively stable but there is an indication that the 685-cps resonance has increased at the expense of those at 645 and 665 cps at 507 hr [Fig. 7(C)].

Results from 100 to 2000 cps at 1.2 and 1.8% static compression are given in Fig. 8. At 1.2% the resonance found near 685 cps at 0.8% has shifted to 735 cps and is reduced in size. At 1.8% a further decrease and shift to 775 cps takes place. Results from 2000 to 5000 cps at 1.2% are presented in Fig. 9 showing a resonance at 2810 cps. At 1.8% this resonance occurs at 2820 cps (Fig. 10) and thus does not seem to be affected much by an increase in compression.

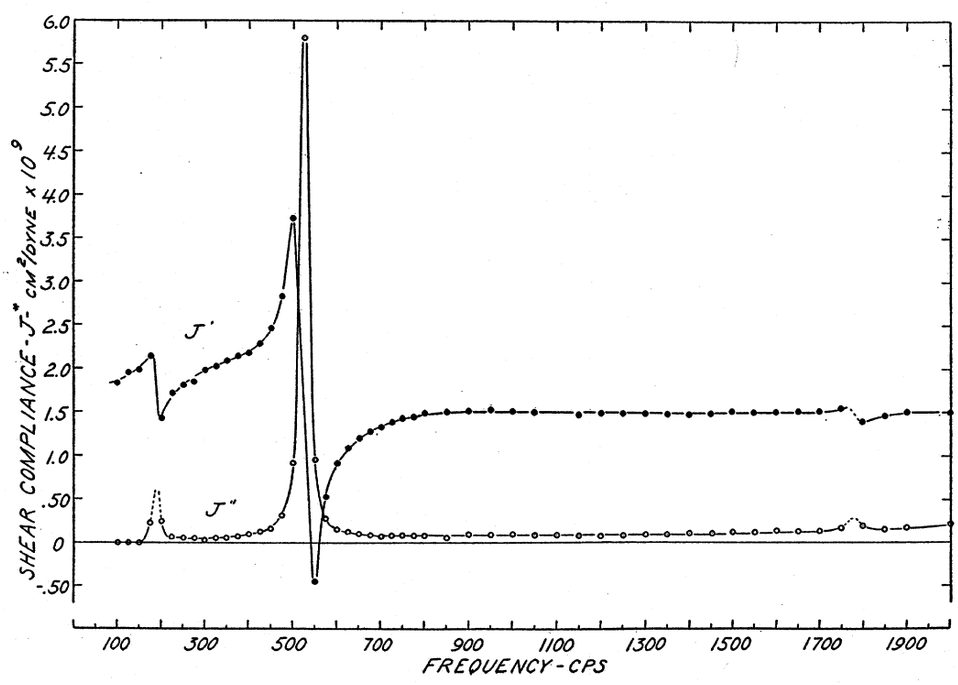

FIG. 5. Variation of complex shear compliance ($J^*=J'-iJ''$) with frequency for the polyvinyl stearate of Fig. 4 at 24.8°C and a static compression of 0.3%. Solid points, J'; open points, J''.

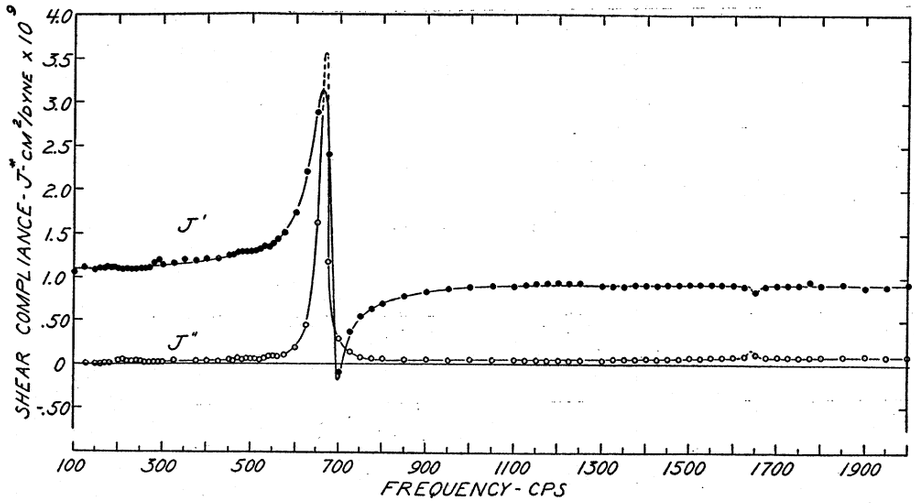

FIG. 6. Variation of complex shear compliance ($J^* = J' - iJ''$) with frequency for the polyvinyl stearate of Fig. 4 at 25.0°C and 0.8% static compression. Solid points, J'; open points, J''.

Measurements were also carried out at room temperature (~25°C) on a second set of samples of different dimensions (No. 37, cf., Table I). The results at an initial static compression of 2.8% are shown in Fig. 11. Resonances occur at 385, 3180, and 3310 cps. Measurements extended to 5000 cps (not shown) revealed no additional resonances. The magnitude and position of the resonances did not change within a period of 230 hr. At the end of this time these samples were compressed to 3.7% with the results shown in Fig. 12. The 400-cps resonance is reduced and shifted to 475 cps while the 3180-cps resonance disappears and the one at 3310 shifts to 3670 cps. Measurements from 3900 to 5000 cps (not shown) again revealed no resonances in this region. Additional small resonances are present at 1400, 1520, and 2980 cps at this static compression. The results were again unchanged with time at the end of 317 hr after the additional compression.

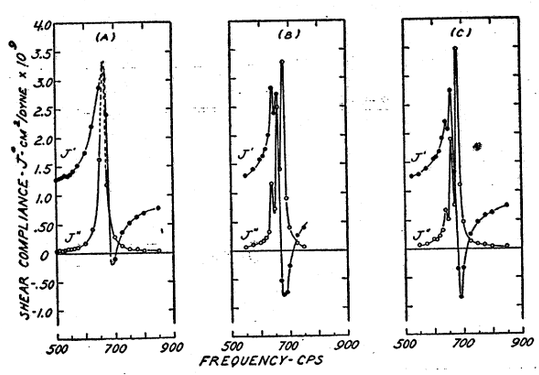

FIG. 7. Variation of complex shear compliance with frequency in the vicinity of the main resonance (~670 cps) at different times at a static compression of 0.8%. (A) 241 hr after 0.3% deformation (same data shown in Fig. 6). (B) 339-hr and 10-cps intervals. (C) 507-hr and 10-cps intervals.

In order to observe the possible reversible nature of static stresses the samples holders were moved in to correspond to approximately the initial static compression of 2.8%. Because of some play in the adjusting screw and uncertainties in the measurements of sample thickness the resulting compression of 3.1% was about as close to the original compression as could be expected. With the return of the samples to their original static compression the resonances also returned essentially to their original positions and magnitudes. The effect of static compression and its reversible nature in connection with the dynamic resonances is demonstrated in Fig. 13 where data in the region of the low-frequency and high-frequency resonances are shown for successive static compression of 2.8, 3.7, and a return to 3.1%.

2. Static Stress-Strain Characteristics

Static stress-strain measurements in compression were carried out for the set of two samples used in the first series of dynamic measurements (No. 28, cf., Table I). Two series of measurements were made on each of the two samples of the set. The results for the two samples did not agree although measurements on each were reproducible. The differences may be due to microscopic surface irregularities which generally make reliable compressive stress-strain tests difficult at small strains. The densities of the samples were determined to be the same (0.978 g/cm³) which seems to rule out large variations in total percent crystallinity or possible voids. On the other hand, variations in dislocation densities could result in large differences in the static mechanical properties. Additional measurements on other samples with a more exact experimental method (e.g., the use of strain gauges) are needed to establish the general extent of the variation in static modulus to be expected. In the meantime the results on the two-

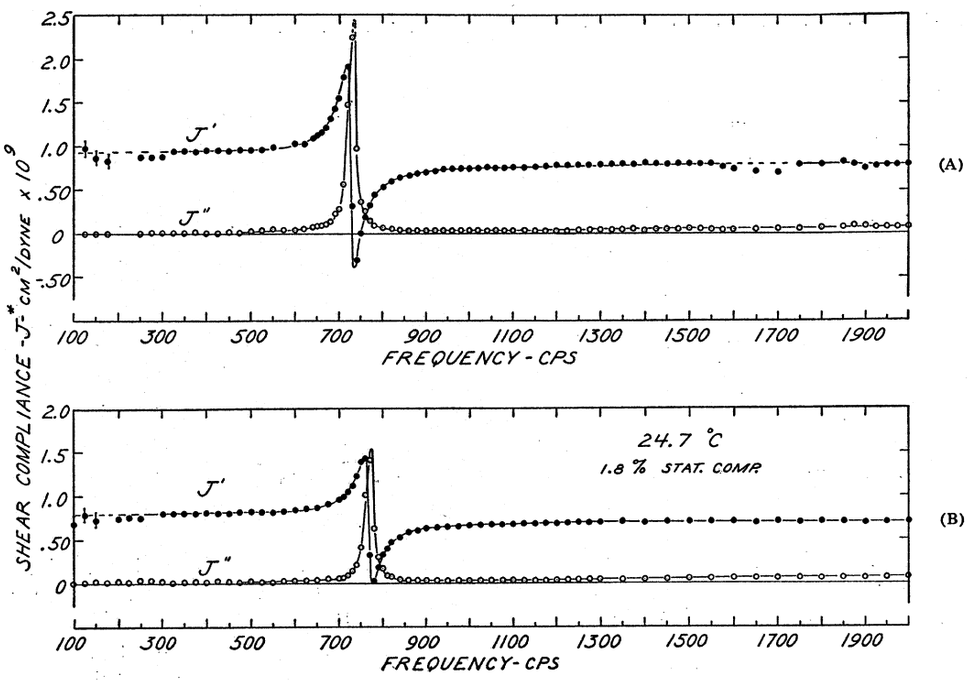

FIG. 8. (A) Variation of complex shear compliance ($J^*=J'-iJ''$) with frequency for the polyvinyl stearate of Fig. 4 at 24.6°C and 1.2% static compression. (B) Variation of complex shear compliance with frequency for the polyvinyl stearate of Fig. 4 at 24.7°C and 1.8% static compression. Solid points, J'; open points, J''.

sample system can be used to estimate the average static stress corresponding to the deformations present during dynamic testing.

The static modulus in compression was found to be approximately 1.0×10^7 dynes/cm² for the set of two samples (No. 28) previously cited. In all cases the deformation did not change with time during an interval from 1 to 10 min after the application of each increment

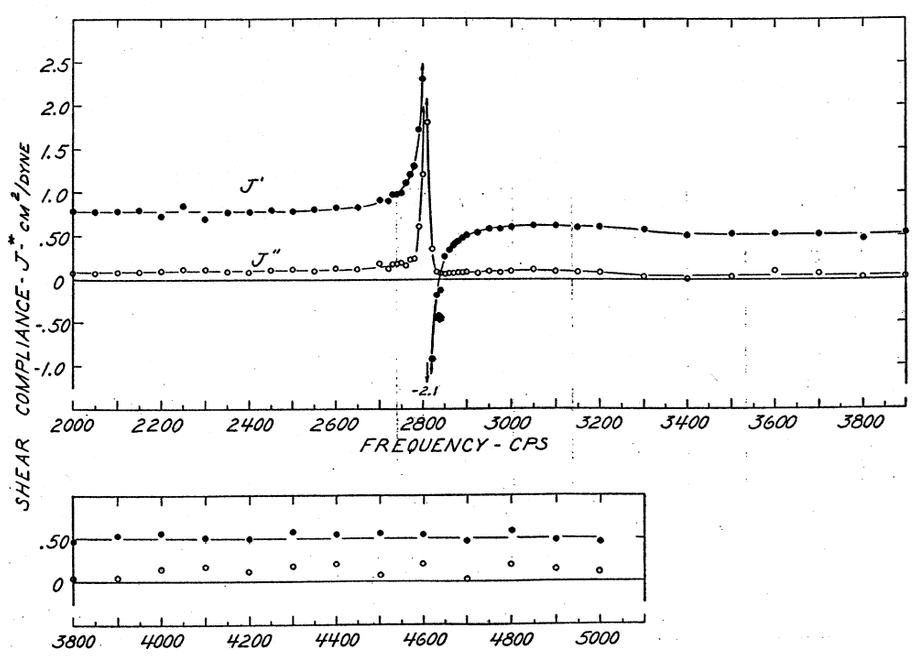

FIG. 9. Variation of complex shear compliance ($J^*=J'-iJ''$) with frequency for the polyvinyl stearate of Fig. 7 (1.2% static compression above 2000 cps). Solid points, J'; open points, J''.

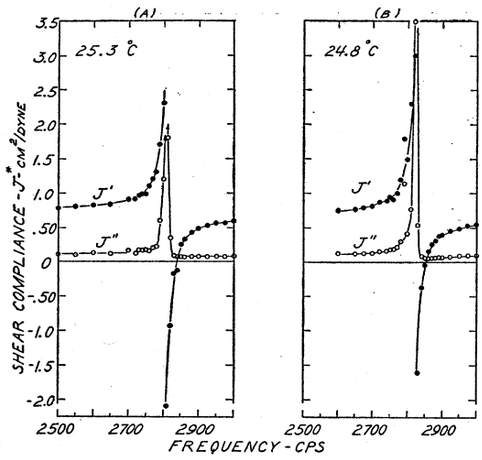

FIG. 10. A comparison of the high-frequency compliance resonance (~2800 cps) in polyvinyl stearate at (A) 1.2 and (B) 1.8% static compression. Solid points, J'; open points, J''.

in loading. The samples recovered completely after removal of the maximum applied load which had resulted in a compression of 2.0%.

V. DISCUSSION

1. Effect of Temperature on Dynamic Mechanical Properties

The chief result of the dynamic shear compliance measurements is to demonstrate the complexity of the investigated phenomena. The effect of temperature on the principal resonance initially found (~490 cps, Fig. 1) is demonstrated by the data of Figs. 1–3. As the temperature increases the 490-cps resonance shifts to higher frequencies and then virtually disappears at 36.4°C, breaking into a very small double resonance which persists at 41.7°C. This behavior is similar to that found for polytetrafluoroethylene[1] but a much greater change occurs in a smaller temperature range. On the other hand, the resonance near 185 cps shows practically no change in going from 25.8 to 41.7°C. The background level of the real part of the compliance (J') decreases from about 1.80×10^{-9} cm²/dyne at 25.8°C to 1.45×10^{-9} cm²/dyne at 41.7°C. Thus an increase in temperature decreases the compliance which is the reverse of the usual effect of temperature on amorphous polymers.

One might question whether the temperature effect alone is studied in these measurements since an increase in static stress might arise due to the thermal expansion of the sample between metal parts of much lower thermal expansion coefficients. The fact that the 185-cps resonance remains practically unchanged, however, seems to preclude this possibility since this resonance was subsequently found to disappear with increased pressure. In fact the samples were found to have suffered a permanent deformation of 2.3% after being returned to 25° from 41.7°C so any increased pressure due to thermal expansion was most probably relieved

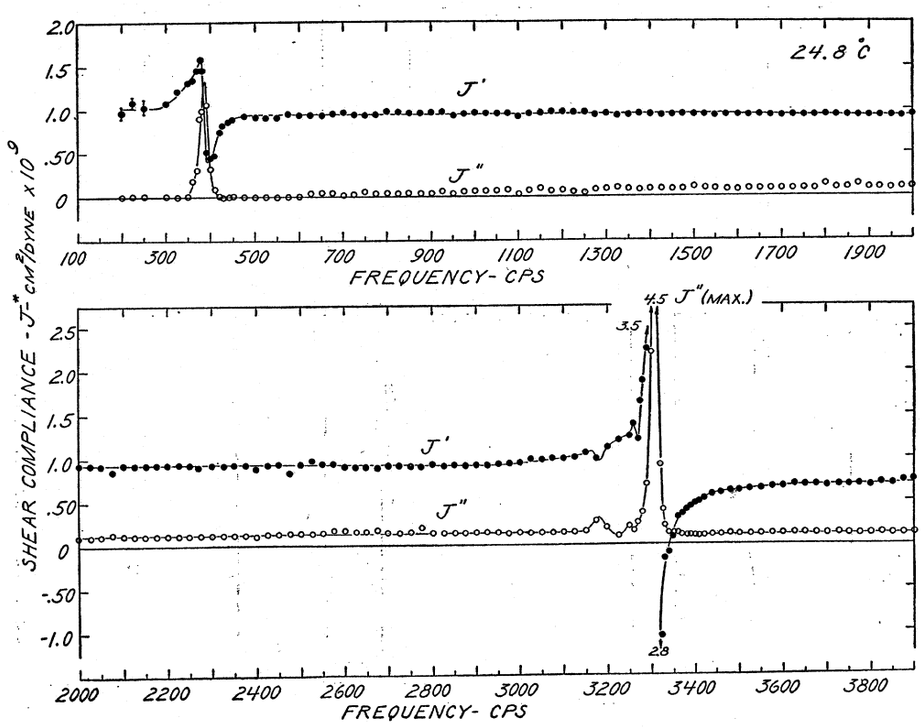

FIG. 11. Variation of complex shear compliance ($J^*=J'-iJ''$) with frequency for polyvinyl stearate at 24.8°C and 2.8% static compression. (Second set of samples.) Solid points, J'; open points, J''.

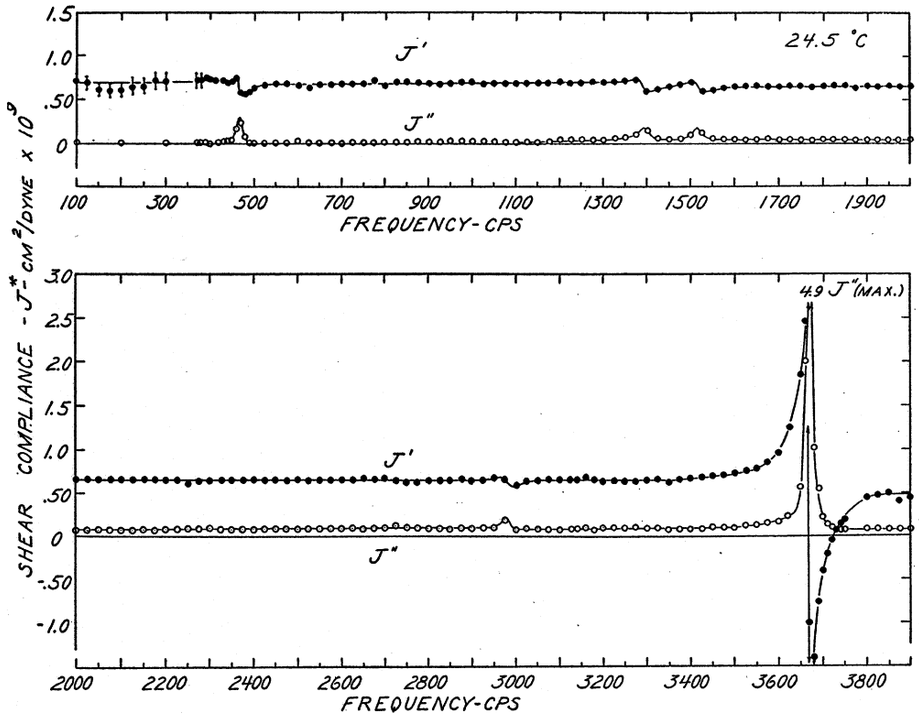

FIG. 12. Variation of complex shear compliance ($J^*=J'-iJ''$) with frequency for polyvinyl stearate at 24.5°C and 3.7% static compression. Solid points, J'; open points, J''.

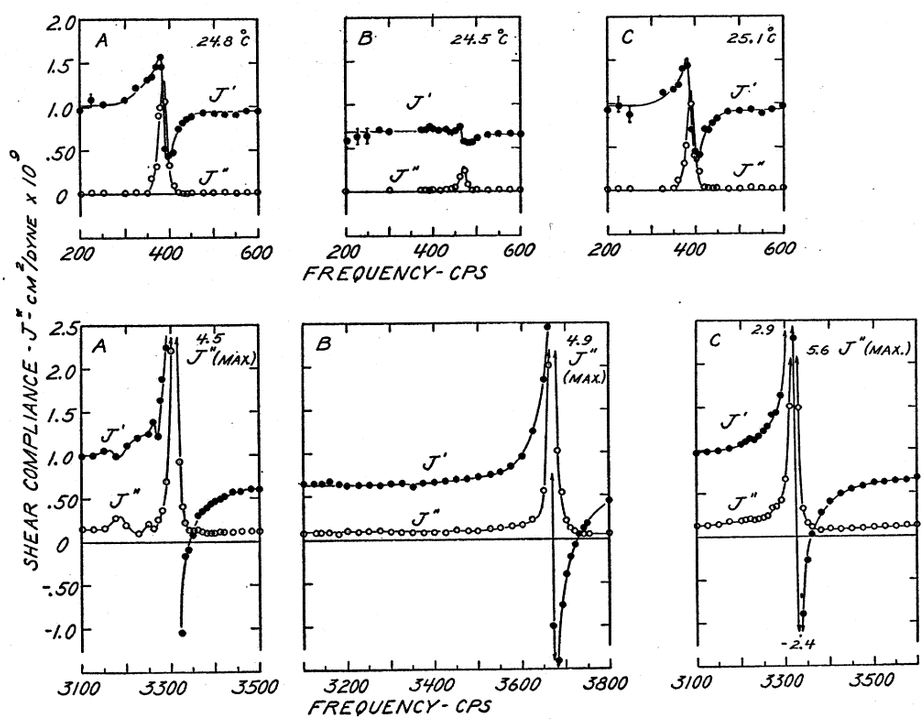

FIG. 13. Comparison of two resonances in dynamic compliance of polyvinyl stearate at successive static compressions of: (A) 2.8%; (B) 3.7%; and (C) a return to 3.1%. Solid points, J'; open points, J''.

TABLE II. Variation of resonance frequency with static stress for polyvinyl stearate at 25°C.

Percent stat. comp.	Static stress dynes/cm² ($\times 10^6$)	Resonance frequency f_r cps	J''_{max} cm²/dyne ($\times 10^{-9}$)	J' background level cm²/dyne ($\times 10^{-9}$)
0.1	Results not reliable			8
0.3	3.0	525	5.8	1.50
0.8	8.0	685[a]	3.50	0.90
1.2	12.1	735	2.4_5	0.7_7
1.8	18.0	775	1.5_5	0.7_0

[a] This is the principal resonance of 3 occurring in the region.

through recrystallization occurring below the melting point (51.5°C).

2. Effect of Pressure on Dynamic Mechanical Properties

The effect of increasing static compression (and hence stress) is demonstrated by Figs. 5–7 where a decrease in magnitude and shift to higher frequencies is found for the main resonance (~525 cps) as the static stress is increased.[8] The background level of the real part of the shear compliance (J') also decreases from 1.5×10^{-9} cm²/dyne at 0.3% to 0.70×10^{-9} cm²/dyne at 1.8%. This reduction in background compliance is again similar to results found for polytetrafluoroethylene with increasing static stress.[1] A summary of the effects of increasing static compression and stress is given in Table II.

[8] The results at 0.1% static compression are not considered here because of the possibility that slipping might have occurred as previously pointed out.

A comparison of Figs. 1 and 5 demonstrates that at a given pressure-temperature state the main features of the dynamic characteristics can be very nearly reproduced for the same set of samples.

Figure 13 shows that the effect of static compression (and thus stress) is reversible as long as the static strains are small enough so that no permanent set results.

3. Possible Origin of Resonances

No satisfactory explanation has been advanced for the existence or behavior of the mechanical resonance dispersion of the type described here. Existing concepts and theories of lattice vibrations and the motions of imperfections alike fail to account for the experimental results. While certain aspects of the behavior of the resonances seem to indicate that dislocations may be involved, other factors (such as the presence of similar resonances in fused quartz and the reversible nature of the effects of static pressure) seem to preclude an explanation in terms of dislocations alone. Further systematic studies of the effect of temperature, static stress, and sample size are needed in order to determine more precisely the influence of these parameters. Studies of similar resonances in systems of simpler structure (such as single crystals) may be of value in discovering the mechanism responsible for the resonance dispersions in polymers and polycrystalline metals.

ACKNOWLEDGMENTS

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