

Mechanical Shear Relaxation Spectroscopy in Experimental Viscoelasticity

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Synopsis

The applicability of experimental viscoelastic techniques involving sinusoidal mechanical shear is examined for several types of rheological systems. Data are first presented for NBS polyisobutylene to establish validity for the approach used. General categories that are investigated include elastomers, filled systems, pure liquids, slurries or suspensions, solutions and gels, foodstuffs, and polymer melts. A modification of the familiar time-temperature superposition routine is proposed by which both entropy and energy relaxation processes can be treated for liquids and polymers alike.

Introduction

In the study of dynamic viscoelasticity, experimental determinations of certain physical properties of matter are often accomplished by way of perturbing a sample material. The perturbation can be achieved by a variety of means. Ultrasonic¹ and dielectric² relaxation spectroscopy have been in use for many years, as have stress-relaxation techniques,³ constant-strain-rate experiments,⁴ vibrating reed devices,⁵ torsion pendulum schemes,⁶ and a resonance vibrator apparatus.⁷ In this paper, the authors report viscoelastic experiments made using yet another perturbation method—namely, sinusoidal mechanical shear. Our approach in some ways resembles other sinusoidal techniques,⁸ differing chiefly as follows: sub-resonant piezoelectric excitation is employed; stress sensor and strain generator are located on opposite sides of the viscoelastic sample; the apparatus can be regarded as a strain rather than a stress generator.

While no one technique is likely to satisfy all research and testing requirements, certain difficulties inherent in other approaches are avoided in the method exploited herein. Frequency is continuously variable as contrasted with the circumstance for techniques which operate at resonance. The apparatus utilized by the authors is relatively small and can be readily subjected to varying temperature and static pressure, as well as to different atmospheric environments. Sample loading is easily performed and only small amounts of sample are required. The theory of operation is simple and involves a minimum of restrictive assumptions. Real and imaginary components of complex shear modulus are obtained from voltage and phase measurements, and data reduction is accomplished without lengthy computation.

The aforementioned shear apparatus for mechanical spectroscopy has been employed by the authors during the course of various studies in liquid-state physics.⁹ Since the apparatus and associated experimental techniques have been reported in earlier literature,¹⁰ no further mention of these topics is made. Rather, in the major portion of the present paper, we devote attention to some results that have been obtained by applying mechanical shear spectroscopy to a variety of rheological substances. Motivation for the undertaking presented here stemmed from an interest and concern regarding the applicability in the field of polymer rheology of our dynamic methods that have been developed to study the liquid state. No attempt, therefore, has been made to exploit in depth any one polymer material or even a single class of polymer substances; instead, we cite results of several exploratory studies covering a rather broad spectrum of rheological systems.

In an appendix, a suggested scheme is set forth for modifying the conventional time-temperature superposition routine for application to relaxation phenomena in both liquids and polymers.

NBS Polyisobutylene

To establish a degree of validity for use of our sinusoidal shear apparatus with polymeric materials, we compare, at the outset, the cooperative polyisobutylene (PIB) data compiled by Marvin¹¹ at the National Bureau of Standards with data obtained by using our mechanical spectroscopy techniques on an NBS-prepared PIB sample. In Figure 1 is shown, by

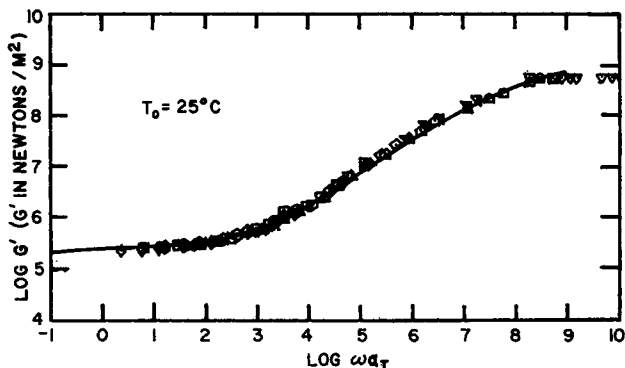


Fig. 1. Comparison of the frequency-dependent shear rigidity for NBS polyisobutylene with values determined by use of the sinusoidal shear apparatus.

the solid curve, the real component G' of shear modulus for a single batch of PIB as reported by Marvin. Isolated data points represent measurements made by the authors utilizing the sinusoidal shear generator. The conventional time-temperature superposition routine¹² has been employed in the figure, with reference temperature T_0 taken as indicated; ω designates angular frequency, and a_T is the usual shift factor. Close agreement

is evidenced between the shear spectroscopy results and the NBS data. This agreement is regarded as providing reasonable indication that our apparatus, developed for liquid-state research, can be of utility as well in the field of polymer rheology. We will now present some representative results of our studies on several classes of polymer substances.

Elastomers

Figure 2 displays shear relaxation data obtained with chlorobutyl rubber in various raw and cured states, wherein G'' represents the imaginary component of shear modulus. The low-temperature data have been multiplied in amplitude by the ratio $(G_\infty)_{T_g}/G_\infty$, where G_∞ is the asymptotic high-frequency shear rigidity, T is the sample temperature, and T_g is the glass transition temperature. The notation $(G_\infty)_T$ designates

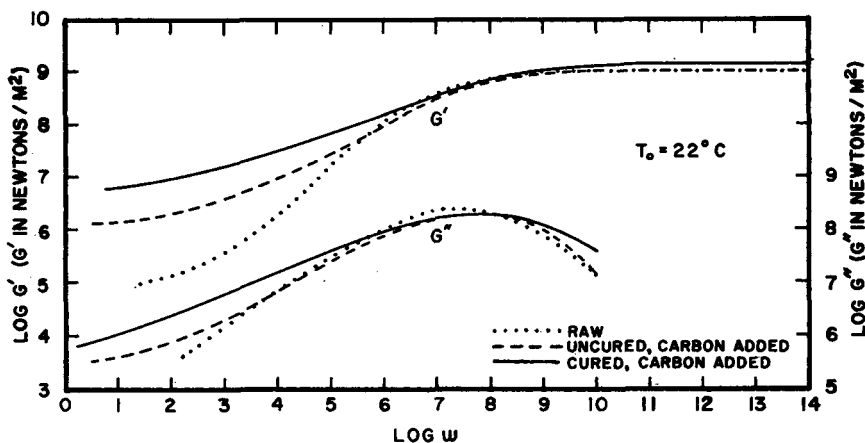


Fig. 2. Real and imaginary components of the frequency-dependent shear modulus for chlorobutyl rubber in various stages of cure.

high-frequency shear rigidity at temperature T . All high-temperature results have been multiplied in amplitude by the conventional ratio T_0/T . Even though the reference temperature T_0 and the glass transition temperature are not identical in Figure 2, the low-temperature amplitude-reduction scheme noted above was particularly employed here so as to include in the G' display the shear rigidity at the glass transition temperature. We note that this technique differs somewhat from that recommended in the appendix. However, the frequency values in Figure 2 have been shifted in accordance with the procedure recommended in the appendix. All amplitude reductions displayed in the present paper, with the exception of those shown in Figure 1, take account of the following relations:

$$\begin{aligned}
 dG_\infty/dT > 0, T > T_g & \quad (\text{Entropy or rubbery region}) \\
 dG_\infty/dT < 0, T < T_g & \quad (\text{Energy region}) \\
 dG_\infty/dT = 0, T < T_g < T_c & \quad (\text{Glassy region})
 \end{aligned}$$

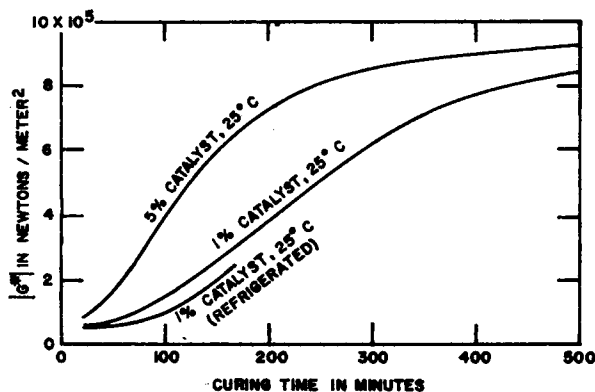


Fig. 3. Increase during curing time of the shear-modulus amplitude for various mixtures of silicon rubber and catalyst.

In these relations, T_c is the apparent temperature of transition from entropy to energy storage relaxation.

In Figure 3 is shown the change with time, during the curing cycle, of the shear-modulus amplitude $G^* = [(G')^2 + (G'')^2]^{1/2}$ for a sample of liquid silicon rubber containing two different amounts of curing agent. The effect on the working and curing times of various amounts of curing agent is clearly in evidence. Note that the final modulus after cure is not affected greatly by the amount of curing agent. By the lower curve of Figure 3 is shown the influence on the cure cycle of refrigerating the uncatalyzed rubber at 0°C ., then adding a fixed concentration of curing agent and observing the shear moduli at room temperature.

In an extension of the above study we have found from the shear modulus versus frequency curves that curing is accompanied by three physical phenomena: (a) the relaxation time increases many orders of magnitude; (b) G_∞ increases anywhere from 10% to 50%; (c) the distribution of relaxation times becomes broader. All three effects can be explained on the basis of growth in polymer chains and/or increased chain crosslinking during cure.

Filled Systems

As an example of a filled polymer system, a type of solid-propellant formulation was studied to obtain the shear moduli displayed in Figure 4. All data have been reduced in amplitude and shifted in frequency in accordance with the scheme employed for Figure 2. The moduli shown in Figure 4 are nearly an order of magnitude larger than the corresponding moduli for the same material as measured by means of traditional stress-relaxation techniques¹³ at strain magnitudes larger than 1%. However, in a comparison of constant-strain-rate data taken at strains of 0.5% or less with the results of Figure 4, Beyer¹⁴ found agreement with our data to within 2%. It is of interest to compare, for the solid-propellant mate-

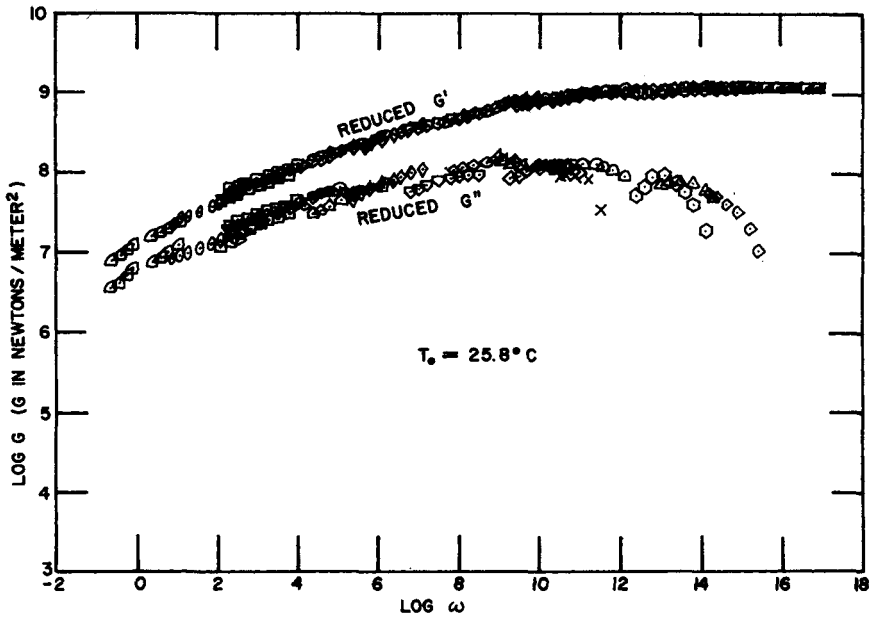


Fig. 4. Frequency dependence of the shear moduli for a typical filled solid-propellant system.

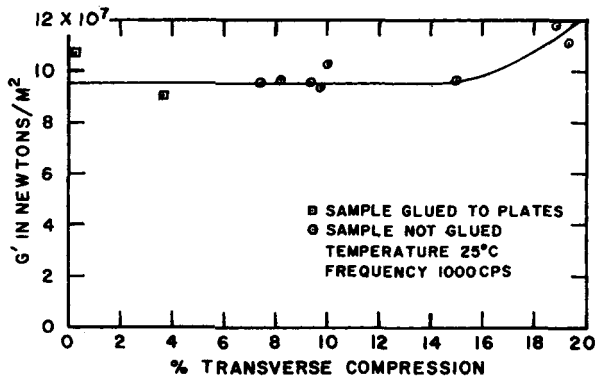


Fig. 5. Variation with per cent transverse compression of the real component of shear modulus for a filled solid-propellant system.

rial, the degradation of shear moduli with increasing tensile strain and the increase in shear moduli realized with increasing compressive strain (the latter shown in Fig. 5). The data of Figure 5 at low transverse compressions were obtained by affixing the propellant sample to the plates of our sinusoidal shear apparatus by means of epoxy resin.

Degradation of stress moduli for rubberlike polymers at strains above 1% was reported as early as 1952 by Marvin;¹⁵ however, it has not been generally acknowledged that the moderate strains commonly imposed by

stress-relaxation experiments can cause so severe a degradation as an order of magnitude, even in a filled polymer. Such order-of-magnitude degradation as found by the authors seems to suggest that the true linear

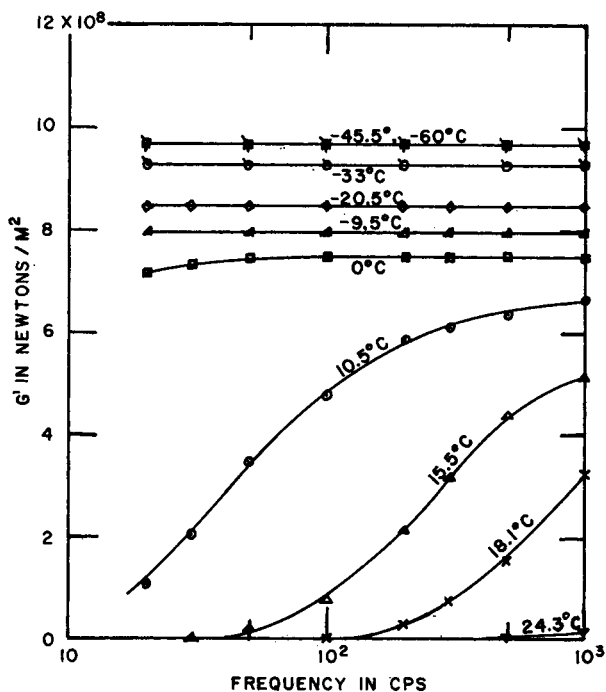


Fig. 6. Frequency-dependent shear rigidity of liquid diphenyl hexachloride at various temperatures.

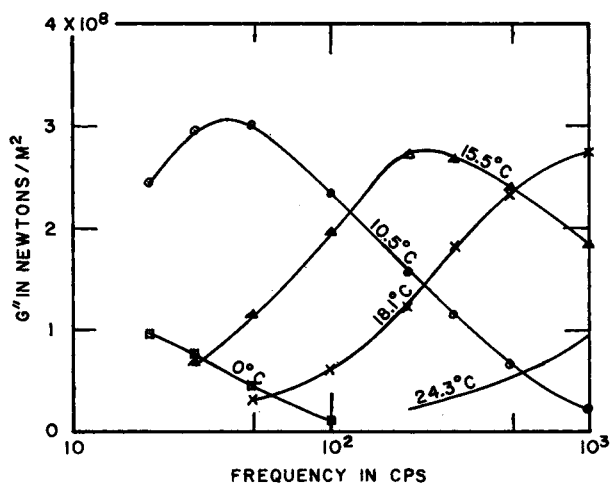


Fig. 7. Frequency-dependent imaginary component of shear modulus for liquid diphenyl hexachloride at various temperatures.

viscoelastic moduli of at least some highly filled polymeric materials perhaps are not revealed by experiments which subject the material to strains of 1% or greater. We suggest that the dynamic modulus of a

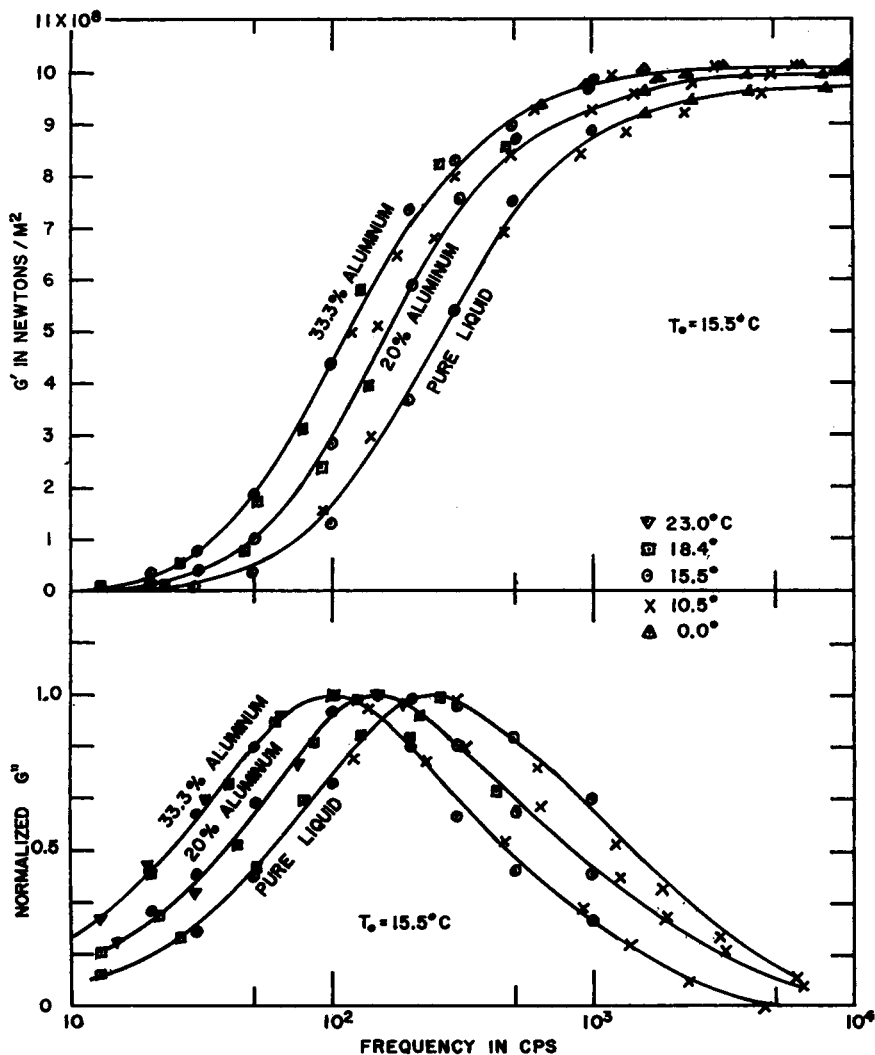


Fig. 8. Shear moduli associated with a suspension of aluminum powder in liquid diphenyl hexachloride.

material be displayed over a wide range of strains; the true linear modulus as given by microstrain measurements of the type employed by the authors then forms an upper bound to the family of macrostrain curves obtained with conventional apparatus.

Suspensions

The rheology of slurries and suspensions nowadays is becoming increasingly more important.¹⁶ Many of the conventional techniques in experimental rheology do not apply for such substances. We present some preliminary investigations in which the dynamic behavior of a liquid-solid mixture is determined by means of our sinusoidal shear apparatus.

The components of shear modulus for a pure suspending liquid (diphenyl hexachloride or Aroclor 1260) were determined first, resulting in the temperature curves displayed in Figures 6 and 7. These plots lead to the composite pure-liquid curves (valid at a single temperature T_0) appearing in Figure 8, wherein the G' amplitudes have been reduced in the same manner as noted for Figure 2 and the G'' amplitudes have been normalized to unity. Aluminum powder of random particle size (estimated to be in the diameter range 2–30 μ) and of irregular particle shape was added to the liquid to form a suspension. Two samples containing volumes of aluminum particles (calculated from powder weight and the density of aluminum) amounting to 20 and 33.3% of the volume of the final suspension were prepared. The dynamic behavior of the suspension was determined exactly as in the case of the pure liquid, and the temperature data again reduced as noted previously. These results are also displayed in Figure 8.

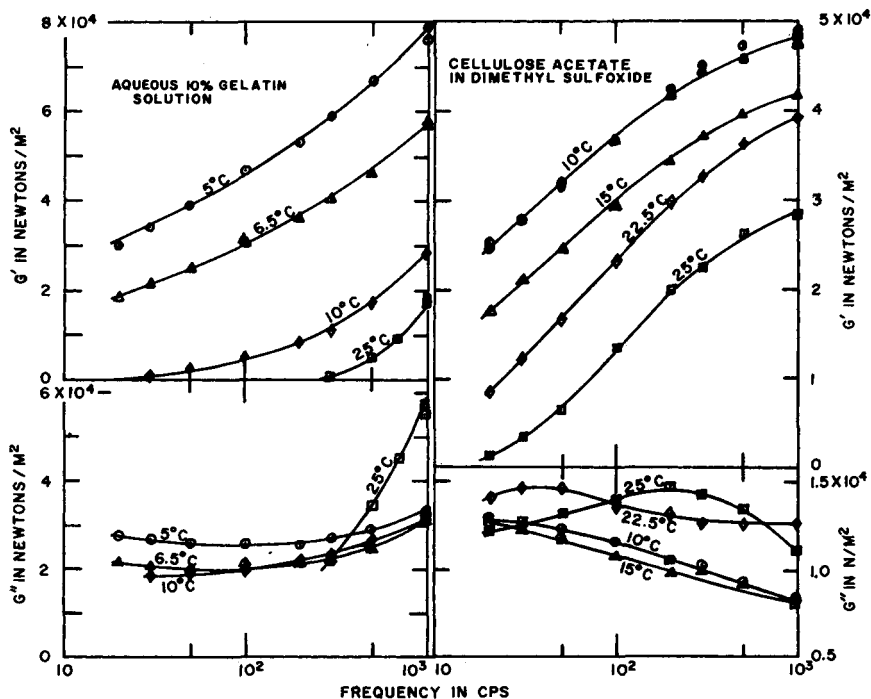


Fig. 9. Frequency dependence of the shear moduli for two different solutions at various temperatures.

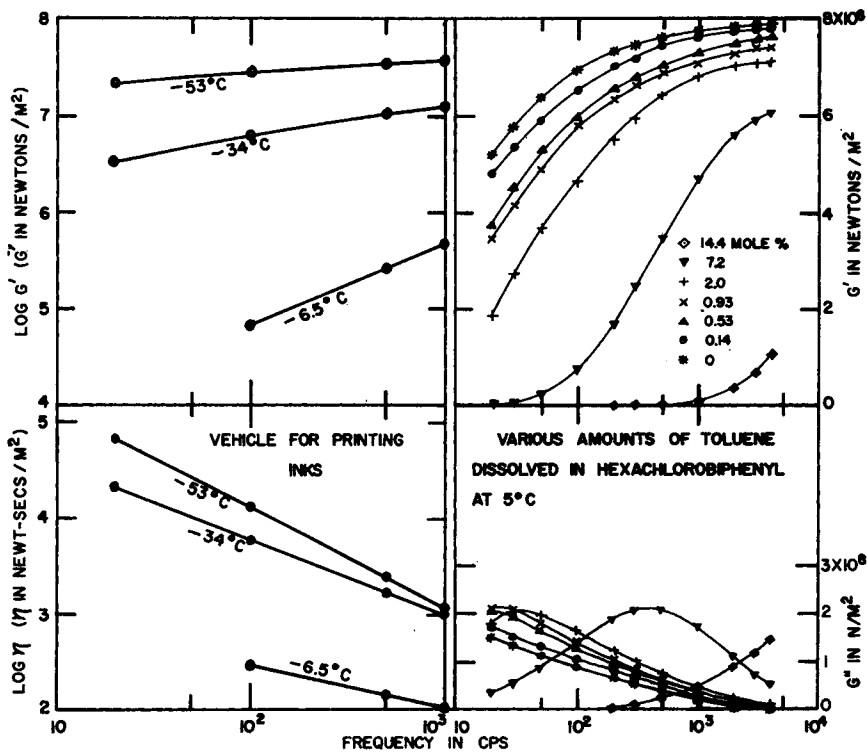


Fig. 10. Frequency dependence of the shear rigidity and shear viscosity associated with a commercial vehicle for printing inks and with a solution consisting of various mole concentrations of toluene in liquid hexachlorobiphenyl.

It can be seen from Figure 8 that the addition of aluminum powder to the liquid (a) increases the high-frequency asymptote of the energy-storage modulus, (b) increases the relaxation times, and (c) shifts the peak of the energy-dissipation modulus to lower frequencies. Examination of the temperature curves reveals that any effect of the aluminum on the distribution of relaxation times associated with the unadulterated liquid is small in comparison with experimental scatter. However, in subsequent experiments with aluminum oxide powders containing particles of very small diameter, a pronounced effect on the distribution function was observed, a result to be discussed further in a later publication.

Solutions

Since our apparatus was designed for the study of liquids, it is well adapted to investigations of solutions and gels. When the solvent is volatile, care must be exercised to prevent evaporation from the sample during the course of an experiment. Evaporation is effectively prevented by operating the apparatus in an enclosed atmosphere containing enough

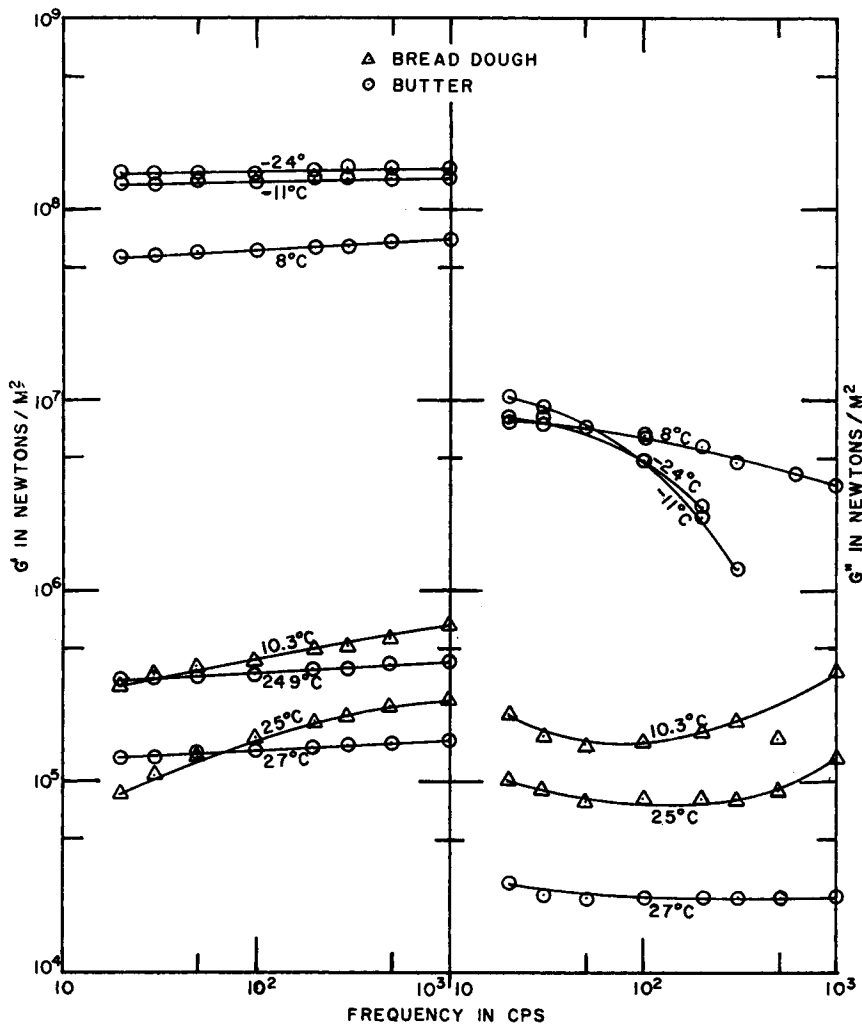


Fig. 11. Shear moduli for a flour-water mixture and for commercial butter at various temperatures.

of the volatilized solvent to establish an equilibrium between the sample and the atmosphere.*

In Figure 9 are shown the real and imaginary components of the shear modulus for an aqueous 10% gelatin solution as well as for a solution of cellulose acetate in dimethyl sulfoxide. In Figure 10, the shear rigidity and the shear viscosity (rather than the real and imaginary components of shear modulus) are displayed for a commercial vehicle used with printing

*This condition may be achieved conveniently by exposing to the enclosed atmosphere a second quantity of the sample material whose mass is large in comparison with the sample mass and whose volume occupies an appreciable portion of the enclosure.

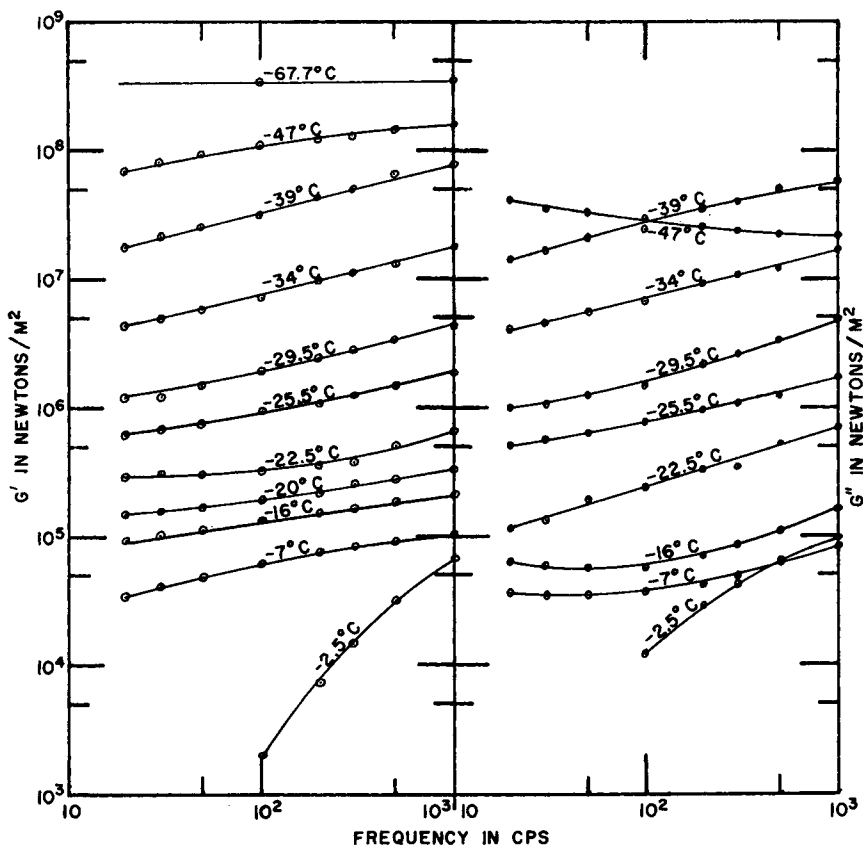


Fig. 12. Frequency dependence of the shear moduli for a sample of toothpaste at various temperatures.

inks. Also in Figure 10 are displayed data for a solution containing various proportions of toluene dissolved in diphenyl hexachloride. The addition of increasing amounts of toluene causes an increase in the width of the distribution of relaxation times, a decrease in the relaxation time itself, and a decrease in the high-frequency shear rigidity. Of additional interest in the latter case is the extended frequency range realized with our apparatus by providing means for positive tightening of each threaded part.

Foodstuffs

Figure 11 contains plots of the real and imaginary shear components as measured for raw bread dough and also for commercial butter. No data are presented below 0°C . for the dough substance since it has appreciable water content. It is particularly noted that the butter data apparently indicate that a rather broad distribution of relaxation times is extant and that upwards of fifty decades of frequency are probably required to reveal the entire relaxation process.

A sample of toothpaste (Crest) was chosen for investigation and proved to be an interesting material dynamically. The corresponding shear moduli are plotted in Figure 12, wherein the entire entropy modulus is revealed in clear detail as well as a portion of the energy modulus. A pronounced tendency for plateau leveling occurs between the two modulus regions.

Polymer Melts

The dynamic moduli for a sample of commercial polyethylene over the temperature interval 23–174°C. are displayed in Figure 13. The crystal-

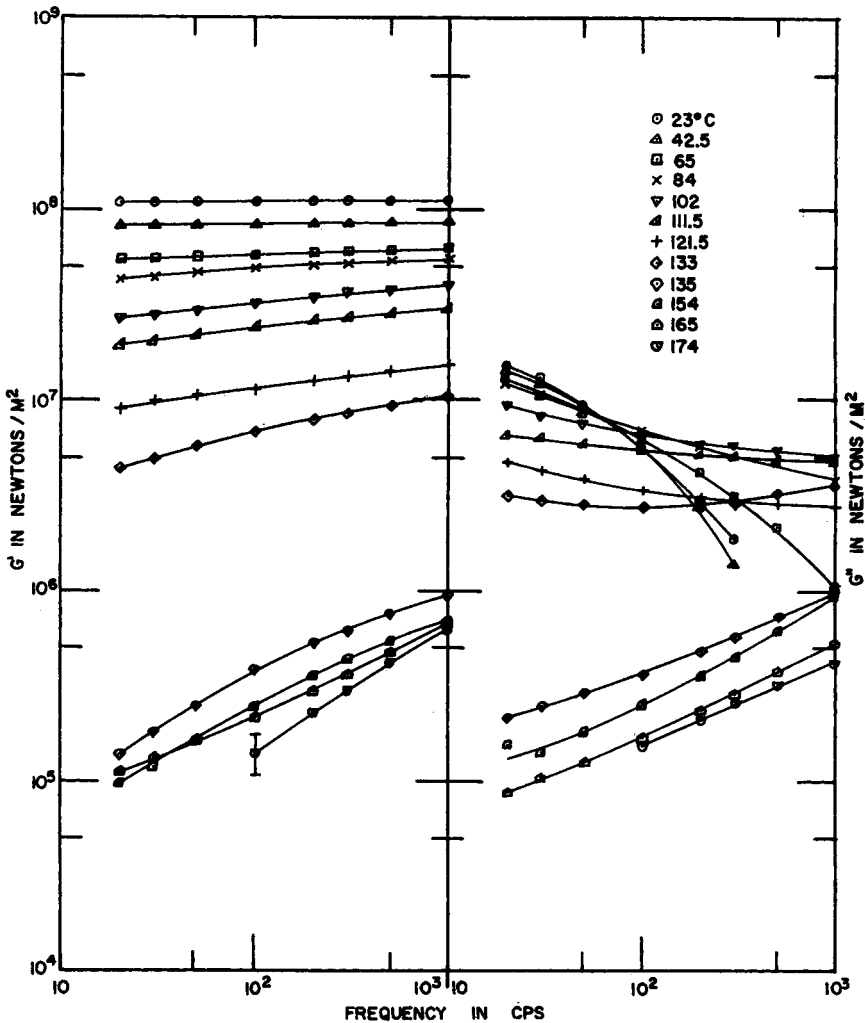


Fig. 13. Shear moduli for a commercial polyethylene material (of low cross-linking) at various temperatures. The crystalline melting point is approximately 135°C.

line melting point of the sample chosen is about 135°C., and hence the moduli drop by more than an order of magnitude in going from 132.5 to 137°C. Measurements in the intervening region are not presented, since consistent temperature curves could not be obtained. We remark that the measurements at room temperature shown in Figure 13 are found to agree with those made by Lethersich.¹⁷

Since the magnitude of the shear moduli for polyethylene at elevated temperatures is so low, the force developed in the monitor shear plate of our dynamic sinusoidal apparatus is not adequate to yield a good signal-to-noise ratio using the standard detection circuitry. By employing a Hewlett-Packard spectrum analyzer, we have overcome this problem through selective filtering and thereby have extended the sensitivity of the apparatus by more than an order of magnitude. It has thus been possible to obtain the high-temperature results reported in Figure 13.

APPENDIX

Proposed Time-Temperature Superposition Routine for Liquids and Polymers

The relaxation mechanism in liquids is primarily an energy-storage process,* whereas in polymers it is partly an energy-storage and partly an entropy effect.¹⁸ When dealing with polymer data, an effort should be made to differentiate energy from entropy processes so that the two mechanisms can be treated differently.¹⁹ The methods presently employed in the well-known time-temperature superposition routines are based on the assumption of entropy processes only,²⁰ wherein the rigidity is taken to be proportional to T , the absolute temperature.²¹ This assumption is not valid for pure liquids in the experimental temperature and frequency ranges of present interest to the authors, and is only partially valid in the case of polymers, as pointed out by Mason.¹⁹

To demonstrate a time-temperature superposition routine that is valid for both liquids and polymers, we superpose the data of Figure 6 to obtain the plots of Figure 14. In this procedure we utilize the temperature dependence of both the high-frequency modulus G_∞ and the relaxation time τ_r . These are found, for the liquid under consideration, from Figures 6 and 8 of ref. 22. For each reference temperature T_0 noted in Figure 14, the temperature (T) curves of Figure 6 have been adjusted in amplitude so that their asymptotic high-frequency values agree with that high-frequency modulus indicated for T_0 by Figure 6 of ref. 22—that is, for each T_0 , all curves of Figure 6 are multiplied by the factor $(G_\infty)_{T_0}/(G_\infty)_T$. Also, each

* Judging from all experimental evidence to date, we attribute the relaxation process in liquids totally to an energy storage mechanism. However, for some associated liquids whose molecules are large and complex, the authors have found evidence, at relatively warm temperatures, of a tendency for the relaxation to display behavior characteristic of an entropy process.^{9e,f} Such liquids may possibly be on the borderline between liquid and polymer states.

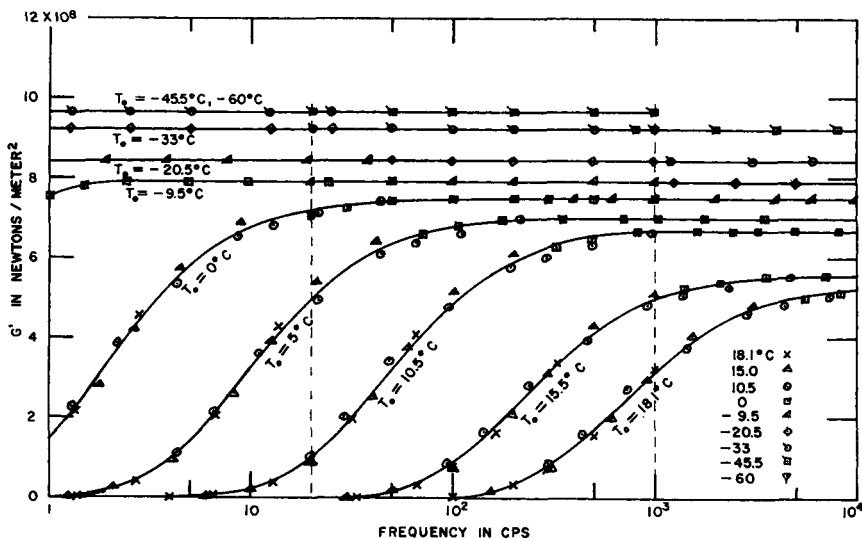


Fig. 14. Reduction of the data in Figure 6 (using a variety of reference temperatures) to extend the frequency range presented but preserve the original data curves (shown between the dotted lines).

curve in Figure 6 has been so shifted in frequency that its relaxation time agrees with that value given by Figure 8 of ref. 22 for temperature T_0 , i.e., all frequencies associated with data at temperature T are multiplied by the ratio $(\tau_r)_T/(\tau_r)_{T_0}$. Thus, the curves of Figure 14 between 20 and 10^3 cycles/sec. have not been altered from the original data of Figure 6; rather, use has been made of the similarity in shape of the curves to extend the frequency range.* In the reduction, the temperature dependence of G_∞ in the energy region as well as the temperature independence of G_∞ below T_g (appropriate for experiments whose temperature is varied over time scales of the order of hours) are taken into account, and the frequency independence of G_∞ at all temperatures is preserved. The resultant plot reveals the temperature change for both G_∞ and τ in a single display. Note that T_0 need not necessarily be chosen equal to an experimental temperature T (witness the case at $T_0 = 5^\circ\text{C}$).

If, in attempting to superpose the temperature curves of Figure 6, we had followed convention and multiplied all amplitudes by T_0/T rather than by $(G_\infty)_{T_0}/(G_\infty)_T$, the high-frequency asymptotes would not have coincided for reference temperature T_0 . In polymer theory, the validity of normalizing amplitudes of temperature curves by the factor T_0/T prior to superposition is based upon (a) the relaxation mechanism being an entropy process ("rubberlike" behavior), and (b) a rigidity which is proportional to

* Note that the above routine ignores (as do all others) the temperature dependence of the distribution of relaxation times, as reflected in the changing width of the relaxation spectrum with varying temperature.^{9b} Conceivably, a frequency compression could be included in the superposition routine to account for this effect.

the absolute temperature.²¹ If, in any temperature range, the dynamic temperature data for a polymer reveals an energy relaxation mechanism or a rigidity that is not proportional to the absolute temperature, the usual routine of reduction by the ratio T_0/T is questionable.

In Figure 15 are displayed dynamic temperature data for a representative polymer. The high-temperature data suggest, typically, an entropy process with corresponding rigidity modulus of approximately 10^6 Newtons/m.², whereas the low-temperature data indicate an energy-storage

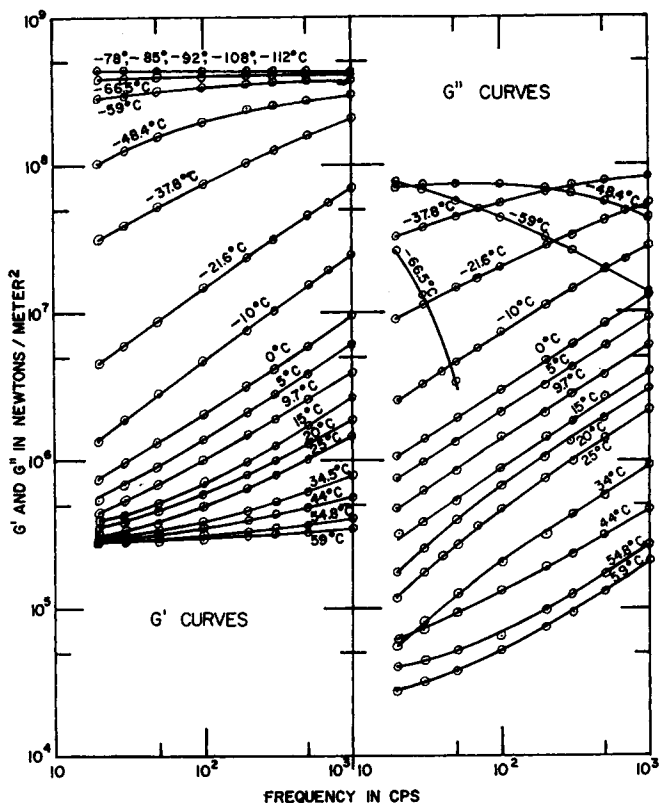


Fig. 15. Frequency dependence of the shear moduli for a typical polymer at various temperatures.

mechanism with typical modulus of nearly 10^9 Newtons/m.². Furthermore, one can see (although not as lucidly as for the liquid data in Fig. 6) that at low temperatures G_∞ is roughly proportional to T^{-1} rather than to T . Below the glass transition temperature T_g , G_∞ ceases to be dependent on T and remains fixed, just as for the liquid data of Figure 6. Clearly, at some temperature the relaxation mechanism changes from primarily an entropy process to predominantly an energy-storage process, and the usual T_0/T reduction becomes invalid.

Application of the proposed reduction scheme to the data of Figure 15 yields, for reference temperature T_0 , a reduced curve for which the high-frequency asymptote is that modulus actually encountered for the temperature T_0 . If $T_0 = T_g$, the reduced curve may lie along an asymptote whose magnitude increases with the time scale of the measurement,²³ but which is nevertheless constant with frequency. If the T_0/T reduction procedure is employed in the energy region, the aforementioned curve increases without limit as successively lower temperature data are shifted to higher frequencies. Such behavior is not regarded as a realistic representation of actual materials.

Ferry²⁴ has recently proposed a time-temperature reduction scheme which is a modification of that presented earlier by Ferry and Fitzgerald²⁵ and which is suggested as possibly applicable to data both in the energy-modulus and the entropy-modulus region. Ferry's reduction scheme is equivalent to that of the authors in the entropy region, but does not appear to be as appropriate in the energy-modulus region. Details of the foregoing as well as further elaboration on the present proposed reduction scheme will appear in a future publication.

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References

- (a) Mason, W. P., *Phys. Rev.* **73**, 1074 (1948); (b) J. J. Markham, R. T. Beyer, and L. B. Lindsay, *Revs. Mod. Phys.*, **23**, 353 (1951); (c) T. A. Litovitz, *J. Acoust. Soc. Am.*, **31**, 681 (1959).
- (a) Kauzmann, W., *Revs. Mod. Phys.*, **14**, 12 (1948); (b) G. McDuffie and T. A. Litovitz, *J. Chem. Phys.*, **37**, 1699 (1962); (c) J. K. Hartt and E. F. Carr, *J. Chem. Phys.*, **36**, 2523 (1962); (d) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
- (a) Catsiff, E., and A. V. Tobolsky, *J. Colloid Sci.*, **10**, 375 (1955); (b) A. V. Tobolsky and J. R. McLaughlin, *J. Poly. Sci.*, **8**, 543 (1952).
- Smith, T. L., *Trans. Soc. Rheol.*, **6**, 61 (1962).
- (a) Nolle, A. W., *J. Appl. Phys.*, **19**, 753 (1948); (b) H. S. Sack, J. Motz, H. Raub, and R. Work, *J. Appl. Phys.*, **18**, 450 (1947).
- Nielsen, L. E., *Rev. Sci. Instr.*, **22**, 690 (1951).
- (a) Rorden, H., and A. Grieco, *J. Appl. Phys.*, **22**, 842 (1951); (b) I. Hopkins, *Trans. Am. Soc. Mech. Engrs.*, **73**, 195 (1951).
- (a) Ferry, J. D., L. D. Grandine, and E. R. Fitzgerald, *J. Appl. Phys.*, **24**, 911 (1953); (b) E. R. Fitzgerald, L. D. Grandine, and J. D. Ferry, *J. Appl. Phys.*, **24**, 650 (1953).
- (a) Miles, D. O., *Phys. Fluids*, **4**, 1482 (1961); (b) D. O. Miles and A. S. Hamamoto, *Nature*, **193**, 644 (1962); (c) D. O. Miles, *J. Appl. Phys.*, **33**, 1014 (1962); (d) D. O. Miles, *Bull. Am. Phys. Soc.*, **7**, 452 (1962); (e) D. O. Miles, *Bull. Am. Phys. Soc.*, **7**, 607 (1962); (f) D. O. Miles, *J. Appl. Phys.*, **36**, 866 (1965).

10. (a) Miles, D. O., *J. Appl. Phys.*, **33**, 1422 (1962); (b) D. O. Miles and G. C. Knollman, *J. Appl. Phys.*, **35**, 2549 (1964); (c) D. O. Miles, G. C. Knollman, and A. S. Hamamoto, *Rev. Sci. Instr.*, **36**, 158 (1965).
11. (a) Marvin, R. S., *Proceedings 2nd International Congress of Rheology*, Academic, New York, 1954, p. 156; (b) R. S. Marvin, R. Aldrich, and H. S. Sack, *J. Appl. Phys.*, **25**, 1213 (1954).
12. Ferry, J. D., *Viscoelastic Properties of Polymers*, Wiley, New York, 1954.
13. Cantey, D., *Solid Propellant Structural Integrity Investigations*, Lockheed Propulsion Company Documentary Report No. RPL-TDR64-32, April, 1964.
14. Beyer, R. B., and D. O. Miles, to be published separately.
15. Marvin, R. S., *Ind. Eng. Chem.*, **44**, 696 (1952).
16. Ellis, H. S., P. J. Redberger, and L. H. Bolt, *Ind. Eng. Chem.*, **55**, 18 (1963).
17. Lethersich, W., *J. Sci. Instr.*, **27**, 303 (1950).
18. Smith, T. L., *Symposium on Stress-Strain-Time-Temperature Relationships in Materials*, ASTM Special Technical Publication No. 325, Am. Soc. Testing Materials, Philadelphia, 1962, p. 60. See also Ref. 12, p. 210.
19. Mason, W. P., *Rheol. Abstr.*, **2**, 16 (1959).
20. Ref. 12, p. 210.
21. Ferry, J. D., *J. Am. Chem. Soc.*, **72**, 3746 (1950).
22. Miles, D. O., *Phys. Fluids*, **4**, 1482 (1961).
23. (a) Reiner, M., *Deformation, Strain and Flow*, Lewis, London, 1960; (b) R. W. Douglas, *Proceedings 4th International Congress of Rheology*, Academic, New York, 1963; (c) A. V. Tobolsky and J. R. McLaughlin, *J. Poly. Sci.*, **7**, 658 (1951).
24. Private communication.
25. Ferry, J. D., and E. R. Fitzgerald, *J. Coll. Sci.*, **8**, 224 (1953).

Résumé

On examine la possibilité d'application à plusieurs types de systèmes rhéologiques des techniques expérimentales viscoélastiques mettant en oeuvre le cisaillement mécanique sinusoidal. On présente en premier lieu les résultats pour le polyisobutylene NBS en vue d'établir la validité de la méthode d'investigation employée. Les principales catégories qui ont été étudiées, comprennent des élastomères, des systèmes chargés, des liquides purs, des bouillies ou suspensions, des solutions et des gels, des aliments et des polymères fondus. On propose une modification de la technique courante de superposition température-temps qui permet de traiter d'une façon identique l'entropie et la relaxation d'énergie, pour les liquides et les polymères.

Zusammenfassung

Die Anwendbarkeit viskoelastischer Versuchsmethoden unter Verwendung von sinus förmiger mechanischer Scherung wird für einige rheologische Systeme überprüft. Zunächst werden Daten für NBS-Polyisobutylene angegeben, welche die Brauchbarkeit des Verfahrens zeigen. Folgende allgemeine Kategorien werden untersucht: Elastomere, füllstoffhaltige Systeme, reine Flüssigkeiten, "Aufschlammungen" oder Suspensionen, Lösungen und Gele, Nährstoffe und Polymerschmelzen. Eine Modifizierung des üblichen Zeit-Temperatur-Superpositionsverfahrens wird vorgeschlagen, mit welcher Entropie- und Energielaxationsprozesse in gleicher Weise für Flüssigkeiten und Polymere behandelt werden können.

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