

Audio-Frequency Mechanical Spectra of a Butadiene Terpolymer

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Synopsis

Measurements of complex shear compliance ($J^* = J' - iJ''$) as functions of frequency and temperature for an unvulcanized sample of a butadiene terpolymer are presented. The measurements reveal the existence of a broad retardation dispersion at audio frequencies and temperatures between -30° and $+35^\circ\text{C}$; but at temperatures below 0° and above 24°C , there are superimposed several series of sharp resonance dispersions. The appearance of these fine spectra below 0° and above 24°C correlates well with observed transitions in specific volume-temperature curves for the material at 1° and 24.5°C . Analyses of the spectra at 35.7°C reveal four separate spectral series each with mode frequencies increasing as 1, 4, 9, 16, . . . , etc. in agreement with predictions of the momentum-wave description of nonelastic deformation. Further, the ratios of frequencies for a common mode are in good agreement with the inverse atomic mass ratios of the atoms or atomic group to which each series is assigned. Thus, for the first mode of each series at 35.7°C , the frequency ratios are 1.000:1.142:1.220:1.335 for modes assigned to oxygen, nitrogen, the CH group, and carbon. These ratios, in turn, are in good agreement with the inverse atomic mass ratios, 1.000:1.142:1.230:1.333, as expected from momentum-wave deformation theory. Examination of the microstructural and stress requirements for observation of nonelastic resonances in vibration experiments suggests that some type of one-dimensional order extending over about 6 micrometers is present in the terpolymer below 0° and above 24°C , but is absent between these temperatures. The successful explanation of the dynamic mechanical behavior of this terpolymer, together with previous results cited for other materials, indicates the usefulness of the momentum-wave theory of mechanical deformation in correlating microstructure and macroscopic mechanical response.

INTRODUCTION

Butadiene terpolymers (and copolymers) are fabricated for use in a variety of situations where intermittent or sustained mechanical vibrations are present. Thus, some knowledge of the audio-frequency spectra of a terpolymer should be of immediate practical value, as well as of intrinsic or theoretical interest. Such terpolymer materials in most common use are, of course, vulcanized or cured, and measurements on samples prepared and cured with various types of vulcanizing agents have been made over the same temperature and frequency ranges as those reported here for an unvulcanized ("raw") terpolymer sample. The results for vulcanized samples of the same terpolymer will be reported subsequently, but are of the same general type as those found for the raw stock which has the advantage of fewer chemical constituents to be accounted for in analysis attempts.

TABLE I
Butadiene Terpolymer^a Samples Used for Dynamic Mechanical Measurements
(In Mold at 5000 psi for 5 Minutes at 145°C; Cooled in Press)

Sample	Diameter, in.	Thickness, in.	Mass, g	Sample pair coefficient <i>C</i> , cm
Measured immediately after removal from mold 1/2/68				
Top	0.462 (min.) 0.500 (max.)	0.0652 (mean)	0.1881	14.5
Bottom	0.471 (min.) 0.505 (max.)	0.0640 (mean)	0.1890	(both samples compressed to .064 thickness in apparatus)
Measured immediately after removal from apparatus 3/26/68 ^b				
Top	0.432 (min.) 0.525 (max.)	0.0685	0.1881	
Bottom	0.452 (min.) 0.524 (max.)	0.0690	0.1890	

^a 66:28:6 Parts by wt butadiene, acrylonitrile, methacrylic acid, respectively; purified by methanol extraction.

^b Subsequently, the unconfined samples curled into distorted shapes.

The unvulcanized sample material to be discussed in this article consisted of 66:28:6 parts by weight of butadiene ($\text{CH}_2=\text{CHCH}=\text{CH}_2$), acrylonitrile ($\text{CH}_2=\text{CHCN}$), and methacrylic acid ($\text{CH}_2=\text{CCH}_3\text{COOH}$), respectively, prepared by free-radical polymerization. A purified (methanol extracted) batch of the terpolymer (Hycar 1072, furnished by Dr. J. J. Shipman of the B. F. Goodrich Co., Brecksville, Ohio) was obtained, and a pair of sample disks was prepared from it in a stainless steel mold under 5000 psi pressure for 15 min at 145°C. Prior to molding, the samples were warmed in the press for 5 min at 145°C; and then, after molding, they were allowed to cool to room temperature in the press during a 4-hr period. When removed from the mold after this treatment, the samples remained of fairly uniform thickness but assumed a slightly noncircular (elliptical) cross section, as indicated by the data adduced in Table I. The samples were placed between metal shearing plates in the dynamic mechanical measurement apparatus soon after their removal from the press and compressed very slightly to a thickness of 0.064+ in. Each sample was positioned with its major axis transverse to the shearing direction during measurement. Immediately after their removal from the apparatus at the conclusion of the measurements (about 66 days later), the samples were remeasured and were found to have "relaxed" to the new dimensions listed in the bottom of Table I. Subsequently, the samples continued to distort with time into curled shapes. These observations indicate that at the molding temperature used (kept low to minimize oxidation), considerable residual or unrelaxed static stresses remained in the molded sample disks during the dynamic mechanical measurements.

The observed frequency variations of complex shear compliance, $\mathbf{J}^* = J' - iJ''$, reveal the existence of a broad retardation (or relaxation) dispersion of the type often found¹ (over some temperature range) for amorphous polymeric substances; but at temperatures above 20°C and below 0°C, there are in addition several superimposed series of sharp resonance dispersions as described in the next section.

A discussion, explanation, and the quantitative "assignment" of these resonance spectral modes is a principal aim of this article. Considerable success is achieved, but some unanswered questions remain for further investigation.

Frequency and Temperature Dependence of the Complex Shear Compliance

Logarithmic plots of the elastic (J') and loss (J'') components of the complex shear compliance versus frequency are presented in Figures 1 and 2 at temperatures from -30.3° to 35.7°C . Measurements were made first at 19.1°C , revealing a broad, smooth retardation dispersion as J' drops from 112×10^{-9} cm^2/dyne at 25 cps to 8.80×10^{-9} cm^2/dyne at 2200 cps, for example. A slight indication of the presence of superimposed resonance dispersions near 1800 and 2100 cps is given by both J' and J'' data, however. As the temperature was lowered in succeeding measurements, the indications of superimposed resonance dispersions gradually became smaller and are essentially absent in the data at 10.3° and 2.9°C . The curves of J' and J'' are smooth within the experimental precision ($\pm 2\%$), but there is a slight plateau or "bump" in the J' -versus-frequency curve between 1500 and 1750 cps at 2.9°C . As the tempera-

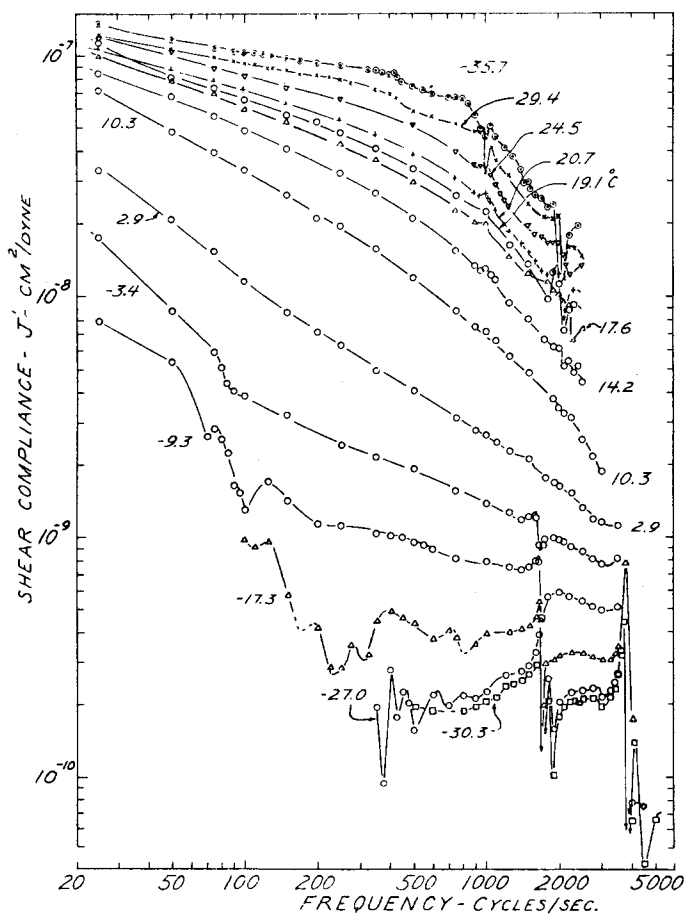


Fig. 1. Frequency dependence of the elastic component J' of complex shear compliance ($J^* = J' - iJ''$) for the butadiene terpolymer at 15 temperatures, as indicated.

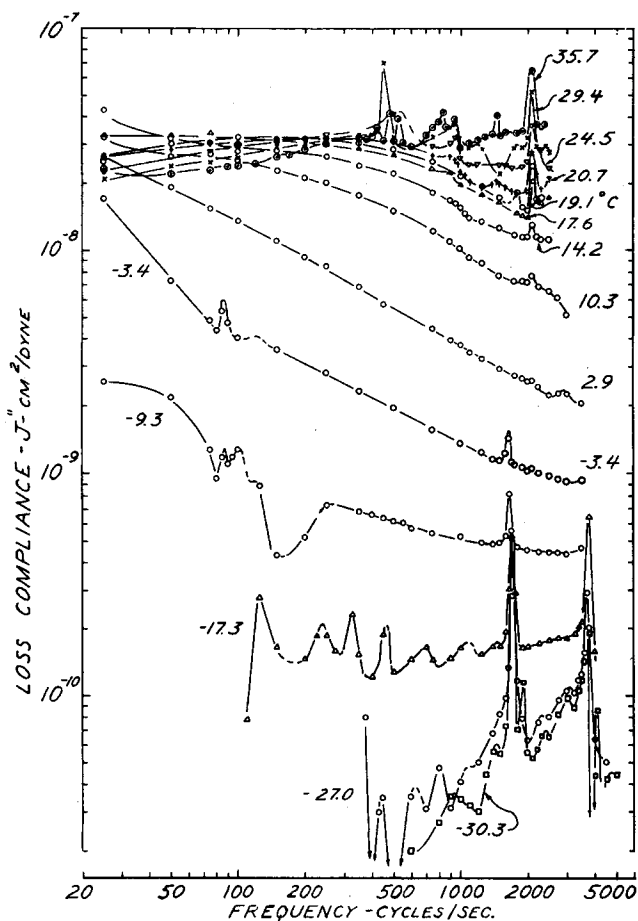


Fig. 2. Frequency dependence of the viscous (loss) component J'' of complex shear compliance ($J^* = J' - iJ''$) for the butadiene terpolymer at 15 temperatures, as indicated.

ture was subsequently lowered, a number of increasingly prominent resonance dispersions appeared at temperatures of -3.4° , -9.3° , -17.3° , -27.0° , and -30.3°C . In particular, a resonance centered at 1650 cps became more intense as the temperature was lowered and many additional resonances appeared at other frequencies.

The temperature was then raised, and many of the resonances found at very low temperatures disappeared, but others lingered for a while. Thus, at -6.6°C , resonances near 90, 405, 1640, and 3650 cps are prominent; but at 15.9°C , these have nearly all disappeared to be replaced by small irregularities near 1000 and 2100 cps. A very small remnant of a 1650 cps resonance is evident from a careful inspection of the compliance curves at 15.9°C . At 20.7°C , the 1650-cps resonance has completely disappeared, but the resonances near 1000 and 2100 cps have grown, and they continue to grow at 24.5° , 29.4° , and 35.7°C . Additional resonances not present at all between 2.9° and 20.7°C are clearly evident at 24.5° , 29.3° , and 35.7°C .

These results were obtained using a dynamic mechanical measurement apparatus which has been described in detail^{2,3} and in summary⁴⁻⁶ in a number of

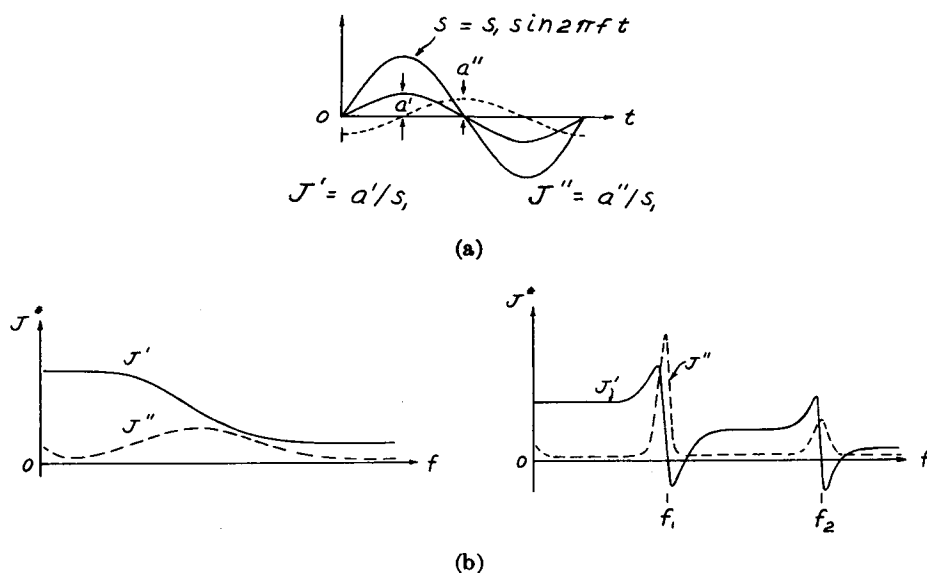


Fig. 3. (a) Division of delayed sinusoidal strain into components a' and a'' , leading to definitions of the corresponding complex shear compliance components J' and J'' , as shown. (b) Frequency dependence of complex shear compliance for retardation dispersion (left) and two resonances dispersions (right) centered at f_1, f_2 .

previous publications, so that no lengthy explanation of the apparatus or method is needed here. An electromagnetic transducer method was used in which values of the complex mechanical shear compliance are obtained in terms of measured electrical impedances, calibration constants of the apparatus, and dimensions of the pair of test samples. The very small-amplitude sinusoidal shearing stresses applied (<0.08 psi) result in small strain amplitudes of 10^{-5} to 10^{-7} , and both J' and J'' are found to a usual precision of $\pm 2\%$. J' is the ratio of the amplitude of the strain component in phase with the applied sinusoidal stress to the stress amplitude, while J'' is the ratio of the component strain amplitude 90° out of phase with the applied stress to the stress amplitude.

A useful summary of the definitions of J' and J'' together with typical retardation and resonance dispersion curves for compliance are given in Figure 3.

Variation of Specific Volume with Temperature: Two Transitions

The occurrence of numerous resonances or fine spectra at temperatures above 24° and below 0°C and the virtual absence of such spectra between 0° and 24°C suggests at once the existence of some type of structural or other transitions in the terpolymer near 0° and 24°C . Accordingly, determinations of specific volume versus temperature were made for the terpolymer using the same mercury dilatometer apparatus described in previous publications.^{7,8} The results, shown in Figure 4, reveal clearly the presence of two sharp transitions centered at 47.5° and 24.5°C , along with two others, more gradual, between 2.5° and -2.0°C and between -11° and -15°C . The transitions occurring between 25° and 24°C and from 2.5° to -2.0°C correspond very closely to the temperature regions above and below which the mechanical compliance fine spectra are prominent. Further, the slopes of the specific volume-temperature lines from

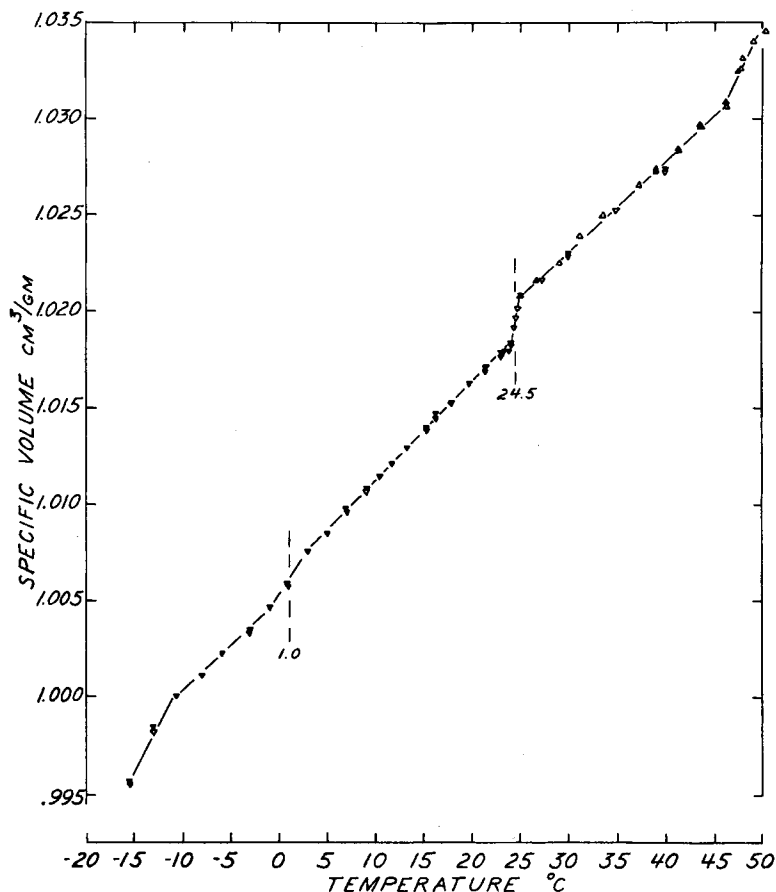


Fig. 4. Specific volume temperature dependence for the butadiene terpolymer showing transitions at 1.0° and 24.5°C, along with two at -12° and 47.5°C. Results for descending temperatures are indicated by inverted triangles (▽); for ascending temperatures, by upright triangles (△).

-11° to -2.5°C and from 25° to 46°C are nearly the same, while the slope from 2.5° to 24°C is smaller than the slopes above and below these temperatures.

Dynamic mechanical data were not obtained at temperatures above the transition at 47.5°C. There were no sudden changes in the type of compliance-frequency curves (Figs. 1 and 2) below -11°C; the number and frequencies of the resonance modes remained about the same, while the general or "background" levels of compliance dropped with decreasing temperature.

Specific volume-temperature measurements on an unpurified, "commercial" grade sample of this same terpolymer revealed very similar behavior with transitions between 48° and 46°C, 26° and 24°C, and also transitions centered at -6° and -10°C.

Measurements of the height of the mercury column in the dilatometer capillary were made at intervals of 20 to 30 min after a constant temperature was reached in order to assure equilibrium results. Temperatures were measured using a two-junction iron-Constantan thermocouple placed in the unsilvered Dewar

flask next to the dilatometer bulb; variations at equilibrium were less than 0.1°C. Small pieces of the terpolymer sample with a total mass of 3.6458 g were placed in the dilatometer (dilatometer volume 34.0861 cm³), which was then degassed by cooling and heating slightly under vacuum (10⁻² mm Hg). Degassed, clean mercury was then added and the dilatometer bulb connected to a 2-mm precision-bore capillary. The height of the mercury column in the capillary was read to the nearest 0.001 cm by a cathetometer. Values of specific volume were calculated by reference to the known specific volume of mercury at 25°C and subtraction of the known expansion for mercury. Measured values of the sample density at 25°C indicated that the volume of the 3.6458-g sample used was 3.8860 cm³ (density 0.9382 g/cm³). Relative accuracy of the specific volume values are estimated to be within 5 × 10⁻⁴ cm³/g, but the existence of the two transitions at 24.5° and 1°C is of the most significance for present purposes, as will be seen from succeeding remarks.

Momentum-Wave Modes at Audio Frequencies

Microstructural Requirements for Modes

Sharp resonance dispersions of the type found to be so prominent below 0° and above 25°C in this butadiene terpolymer have been previously reported at audio frequencies for a number of materials. These have included polymers,^{9,10} biological polymers,^{6,11} organic and inorganic crystals,^{7,12,13} and metals and metal alloys.^{2,4} Such resonances have been attributed to the presence of momentum-wave modes in crystalline (ordered) lattice segments,^{14,15} and under some conditions, the mode frequencies ν_q are given to a good approximation by

$$\nu_q \cong \frac{h}{8mS^2} q^2 \quad (1)$$

where $q = 1, 2, 3, \dots$, h = Planck's constant, m is the atomic mass in grams, and S is a characteristic length such as a lattice segment length or some other length of regularly spaced atoms of mass m in the material. In a conventional crystalline material, S is a measure of the space extent of the individual perfect crystalline units forming the mosaic structure (subgrains) within polycrystal grains or the slightly misaligned (1 to 2 degrees) sections making up the corresponding mosaic patterns in a single crystal.¹⁵ The requirement of three-dimensional translational periodicity, however, is not necessary for the existence of such modes, only the repetition of a common atomic spacing d in one direction within the material is needed.¹⁶ Then, if $N + 1$ is the number of atoms with a common spacing, d , in any *one* direction, the characteristic length in the direction becomes,

$$S = Nd \quad (2)$$

and the *exact* expression for the frequencies of the $N - 1$ standing-wave modes expected is¹⁵

$$\nu_q = \nu_m' \sin^2 \left(\frac{q\pi}{2N} \right) \quad (3)$$

for $\nu_m' = \hbar/m\pi d^2$ and $q = 1, 2, 3, \dots, N - 1$.

From eq. (3), it is evident that the approximation given by eq. (1) is a good one for large values of N and small values of q ; errors in ν_q from eq. (1) are less than 1% for $N/q \geq 9$, for example. Values of $S = Nd$ of the order of 10^{-4} cm (10^{-6} m) lead to predictions of concentrated modes with values for ν_q in the audio range (10^2 to 10^4 cps), and a second set of concentrated modes with frequencies from 10^9 to 10^{10} cps when values of h and atomic mass m are substituted in eq. (1).

The existence of such characteristic micrometer lengths in many materials (including biological substances) is a well-documented experimental fact.¹⁵

The predictions of eqs. (1) and (3) apply to a monatomic material, but can be usefully extended to polyatomic substances as described elsewhere.^{6,16} That is, for a common characteristic length S , a series of discrete modes will be present for each type of atom:

$$\nu_{1q} \cong \frac{h}{8m_1S^2} q^2; \nu_{2q} \cong \frac{h}{8m_2S^2} q^2; \dots \nu_{kq} \cong \frac{h}{8m_kS^2} q^2 \quad (4)$$

where m_1, m_2, \dots, m_k are the atomic masses of each type of atom, and $q = 1, 2, 3, \dots$ as before. Then the ratios of the frequencies corresponding to the same modes for each series are given by

$$\begin{aligned} \nu_{11} : \nu_{21} : \nu_{31} : \dots : \nu_{k1} &= 1/m_1 : 1/m_2 : 1/m_3 : \dots : 1/m_k \\ \nu_{12} : \nu_{22} : \nu_{32} : \dots : \nu_{k2} &= 1/m_1 : 1/m_2 : 1/m_3 : \dots : 1/m_k \end{aligned} \quad (5)$$

etc. Thus, even in the absence of knowledge of a characteristic length, the identification of spectral series with frequencies increasing as 1, 4, 9, 16, 25, \dots , etc., and the frequency ratios for a common mode can be used to assign series to the particular atomic masses known to be present in the material.

Stress Requirements for Mode Activation

The existence of intrinsic momentum wave modes with frequencies dependent on a characteristic micrometer length in the material substructure does not in itself guarantee that enhancement or resonance will occur for applied mechanical vibrations at a mode frequency or frequencies. In addition, the modes must be activated by residual or applied steady (or slowly varying) stresses acting to produce forces on certain field-free atoms within the material.¹⁵ For an ordered row of atoms of some finite length S , only certain discrete forces F_{pq} result in momentum-wave generation by these "free" atoms according¹⁵ to

$$F_{pq} = \frac{h^2}{8mdp} \frac{q^2}{S^2} \quad (6)$$

where F_{pq} is the force/atom; $q = 1, 2, 3, \dots$; d is the atomic spacing; m is the atomic mass as before; and p is a dimensionless parameter dependent on the mean extent of field free regions ("degree of freeness") within which free atoms exist. That is, $s = pd$ is the (mean) field-free distance that a free atom moves before its momentum is transferred to an ordered row of bound atoms (along which the momentum wave then propagates). Rearrangement of eq. (6) gives

$$F_{pq} \cdot pd = F_{pq} \cdot s = \frac{h^2}{8mS^2} q^2$$

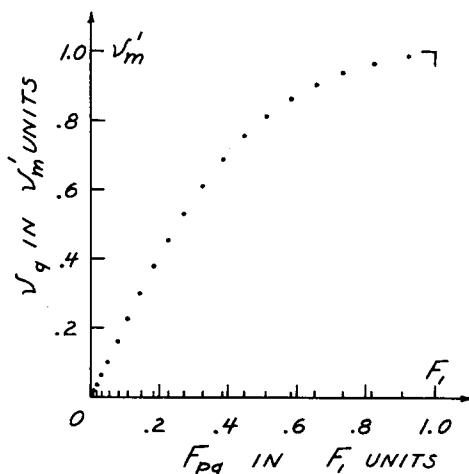


Fig. 5. Variation of (activated) momentum-wave mode frequency ν_q with force per atom, F_{pq} according to eq. (8) of text and reference 15. The force per atom, in turn, depends on the applied or residual mechanical stress state of the material. The case shown is for an interatomic spacing d and characteristic length $S = Nd$ within the material, where N is taken as 21 for illustrative purposes (20 discrete modes).

and from the approximate relations for ν_q given in eq. (1), we obtain

$$\nu_q \cong F_{pq} \cdot s/h \quad (7)$$

for the first few modes. That is, for a given (mean) value of the field-free distance s available to the free atoms, the order of an activated mode (and the observed mode frequency) is directly proportional to the force/atom resulting from residual or applied stresses. An exact expression relating the (activated) mode frequency and the force per atom, F , can also be written with the aid of eq. (3) and the relation between wave vector (k) and force per atom (F)¹⁵:

$$\nu_q = \nu_m' \sin^2 (b \sqrt{F_{pq}}) \quad (8)$$

where $\nu_m' = \hbar/\pi md^2$ as before and $b = (d/\hbar) \sqrt{sm}/2$. The variation of (activated) mode frequency with force per atom will then be as shown in Figure 5. Again, we note that at low-mode frequencies (small values of q), there is a linear dependence of frequency on force per atom. The force per atom in a material can be related to the applied external stress through use of a proper orientation (directional) factor and a knowledge of the number of atoms per unit cross-sectional area. Thus, for a given material and direction of applied load, an approximately linear dependence of mode frequency on load magnitude is expected. Of course, the field free parameter s may sometimes itself be a sensitive function of the load (the changes in defect structure produced by loading or "cold working" will often change s), and this might result in nonlinear frequency-load behavior.

In any case, a wide distribution of steady stress magnitudes throughout a material is necessary to activate all the momentum-wave modes of a particular series.

Conversely, an unloaded and well-annealed sample with all residual and applied stresses zero will show no resonances when subjected to low-amplitude vibrational loads.

The appearance of some modes and the absence of others for a particular series during vibration measurements may thus be a useful indication of the actual stress distribution (on a microscopic scale) within the sample.

Some Previous Experimental Results

The earliest quantitative correlations obtained between predictions of the momentum-wave theory outlined above and experimental observations were found for a stretched natural-rubber gum stock.¹⁵ From x-ray diffraction, this material is known to be in an unordered or amorphous state at room temperature below 300% elongation, but shows an increasing extent of crystallinity or order at higher elongations. In addition, light-scattering measurements by Yau and Stein¹⁷ reveal the presence of a superstructure in stretched gum stocks corresponding to a length of around 2×10^{-4} cm; the superstructure is absent in unstretched rubber. Dynamic mechanical measurements of compliance on gum rubber samples, in turn, reveal no resonance dispersions in the unstretched or stretched states below 300% elongation, but mechanical compliance resonances occur at 310% and higher elongations.¹⁸ The exact frequencies of the resonances changed with time at each elongation. At 310% elongation, for example, the principal resonance shifted from 1020 to 1100 cps. Using the value of "about 2×10^{-4} cm" identified from the light-scattering observations as the characteristic length S in eq. (1) and the atomic mass of carbon for m , the initial predicted first mode frequency is 1040 cps.¹⁵ Conversely, the characteristic length S can be calculated from the observed mode frequencies as between 1.94 and 2.02×10^{-4} cm. In either case, good agreement between experiment and theory is found.

It is evident that both the necessary static stress and microstructural requirements are present in these vibration measurements on stretched rubber. Additional evidence for the stress requirement is afforded by measurements on a poly(tetrafluoroethylene) bar (extruded Teflon bar obtained from E. I. du Pont de Nemours and Co.) in transverse vibration reported by Fitzgerald and Woodward.^{15,19} With no tension, only a broad elastic-mode resonance at 375 cps is found; but under axial tension (produced by long, thin metal wires pulling from nodal points), additional, sharp resonances were observed to be superimposed to the elastic-mode response curve for the bar in the region from 350 to 450 cps. The resonance dispersions found in this region agree in general with prior results⁹ reported for complex shear compliance measurements on poly(tetrafluoroethylene) measured (under a static compression transverse to the shearing direction) with the electromagnetic transducer described here. Thus, at 1.36% static compression and 55.6°C, resonances in shear compliance were observed in poly(tetrafluoroethylene) at 105, 417, 1000, 1650, and 2500 cps in good agreement with expected ratios of 1:4:9:16:25 if the 105 cps resonance is taken as the first-mode frequency, for example. Substitution of the atomic mass of fluorine in eq. (1), taking $\nu_1 = 105$ cps, results in a calculated characteristic length of 5.0 micrometers. This is in reasonable agreement with the primary particle sizes of 2 to 5 micrometers reported by Sperati²¹ for some samples of poly(tetrafluoroethylene) polymer, but no specific particle-size determinations were made on the polymer of this particular sample. The characteristic length S will, of course, necessarily be less than or equal to the particle (grain) size in any polycrystalline material.

Momentum-wave mode identifications have also been made by Fitzgerald and Freeland⁶ from dynamic mechanical shear measurements on dog intervertebral disks resulting in assignments of two observed spectral series (with series frequencies in the ratios 1:4:9:etc.) to nitrogen and carbon atoms. Observed frequency ratios at $q = 1$ and $q = 4$ were 1.168 and 1.173, respectively; these values agree well with the predicted ratio m_2 (nitrogen): m_1 (carbon) of 1.167, cf. eq. (5). For these series, a common characteristic segment length of $S = 8.40 \times 10^{-4}$ cm was calculated. This is exactly 30 lengths of the collagen molecule, but no experimental evidence for such a characteristic length in collagen has been reported. The existence of ordered or "paracrystalline" regions *within* molecules of collagen and other biopolymers, however, now seems well-established (e.g., see review by Hosemann²⁰).

Most striking are the recent dynamic mechanical measurements of complex longitudinal modulus ($E^* = E' + iE''$) on human bones reported by Pugh et al.¹¹ Two spectral series with frequencies increasing as 1, 4, 9, 16, . . . , etc. are found and assigned to calcium and phosphate atoms. Observed common-mode frequency ratios for the series varied from 0.711 to 0.805 in agreement with the expected atomic mass ratio phosphorous:calcium of 0.773. In addition, the characteristic length S calculated from each series was 2.82 and 2.93 micrometers, in very good agreement with the *known* lamellar thickness of about 3 micrometers in the bone samples.

Comparison of Calculated and Observed Frequency-Mode Ratios at 35.7°C

Analysis of the frequency spectra for the butadiene terpolymer is confined to the results at 35.7°C, where the most detailed (closely spaced in frequency) results were obtained. To aid in identification of the mode frequencies, linear plots of J' and J'' versus frequency were constructed as adduced in Figures 6 and 7. A quick glance at these shows a "bump" around 100 cps, "clusters" of four resonances centered at 420 and 950 cps, several resonances above and below 1750 cps, pronounced resonances near 2050 cps, and a well-defined resonance near 2300 cps. This cursory inspection is promising, since it indicates that some frequency-mode ratios of 1:4:9:16; etc. might be inferred from the curves. Before any detailed analysis is attempted, however, it is useful to recall some results to be expected from the addition of several simultaneous resonance dispersions which are (a) closely spaced and shaped as shown in Figure 8a, (b) closely spaced and shaped as in Figure 8b. In the first case, the three loss compliance resonances add to give what looks like a larger broadened single resonance; in the second, two resonances add to give what might incorrectly be taken as three maxima. Finally, from Figure 8c, we see that the addition of a broad "background" retardation dispersion and a resonance dispersion can produce an apparent frequency shift in the maximum value of the loss compliance maximum and hence an erroneous value for the mode frequency if it is taken as that at the maximum of the unresolved compliance curve. Similar apparent frequency shifts also occur in the J' -versus-frequency curves when several resonance modes are closely spaced or superimposed on broad retardation dispersions.

With due attention to the above precautions, the data of Figures 6 and 7 were analyzed *separately* for locations of the mode frequencies; that is, mode frequencies were assigned to the maxima in J'' and also to the inflection or "half-way" point in the rising and falling values of J' on each side of a resonance. In

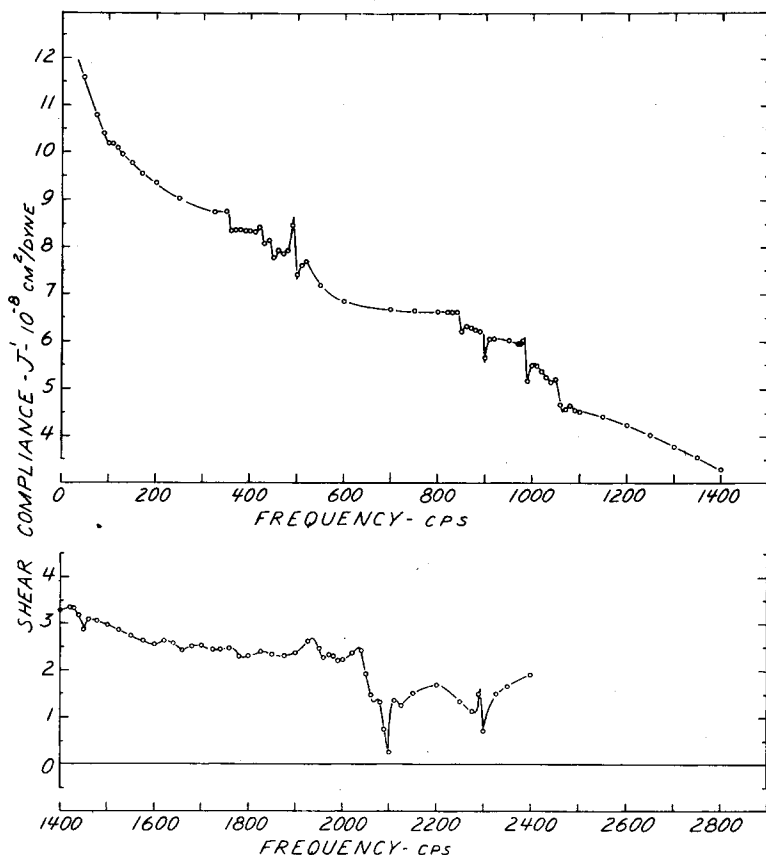


Fig. 6. Linear plot of elastic component J' , of complex shear compliance ($J^* = J' - iJ''$) vs. frequency for the butadiene terpolymer at 35.7°C . Groupings or clusters of four resonance modes around 400 and 900 cps are clearly evident as described in text.

addition, a second set of selections were made at a much later time (when memories of previously selected resonance frequencies were dim) without prior reference to the first set. Differences between the selection of mode frequencies from J' and from J'' data always amounted to less than 5 cps; many identical values were selected. The results of the two time-separated analyses were also very similar, as shown in Tables II and III. In each case, four series were identified from the experimental data and assigned to atoms of oxygen (16), nitrogen (14), the C—H group (13), and carbon (12) occurring in some ordered fashion within the terpolymer and extending over the same characteristic length $S = 5.83 \times 10^{-4}$ cm. The composition of the terpolymer guarantees the presence of large numbers of carbon and nitrogen atoms; in addition to the oxygen atoms originally present in methacrylic acid, there are undoubtedly others produced because of oxidation of the terpolymer during molding, etc. From Tables II and III, the good agreement between predicted common-mode frequencies and the inverse atomic mass ratios is evident. From Table III, for example,

$$\nu_{10} : \nu_{1N} : \nu_{1CH} : \nu_{1C} = 1.000 : 1.142 : 1.220 : 1.335$$

and the expected ratios are

$$1/16 : 1/14 : 1/13 : 1/12 = 1.000 : 1.142 : 1.230 : 1.333$$

On the other hand, resonances at 1990, 2060, and 2140 cps (cf. Table III) are unexplained and unassigned; their ratios are 1.000:1.035:1.075.

The existence of a characteristic length of the order of 6 micrometers has not been previously reported for this butadiene terpolymer. Ordered (paracrystal-

TABLE II
Dynamic Shear Compliance Spectrum of Butadiene Terpolymer* at 37.5°C; 1968 Analysis

q^2	Frequencies, cps							
	O ¹⁶		N ¹⁴		CH ¹³		C ¹²	
	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
1	yes	91.8	yes	104.8	yes	111.3	yes	122.4
4	367	(367)	419	(419)	445	(445)	490	(490)
9	840	826	900	943	985	1000	1060	1101
16	1445	1469	1650	1676	1770	1780	1950	1958
25	2295	2295	—	2620	—	2780	—	3060

Unassigned resonances at 1980, 2050, and 2100 cps (measurements made from 25 to 2500 cps)

* Terpolymer: butadiene, 66; acrylonitrile, 28; methacrylic acid, 6 parts by wt.

Observed frequency ratios ($q^2 = 4$): 1.000:1.141:1.212:1.333; pred. frequency ratios: 1.000:1.142:1.230:1.333 (1/16:1/14:1/13:1/12).

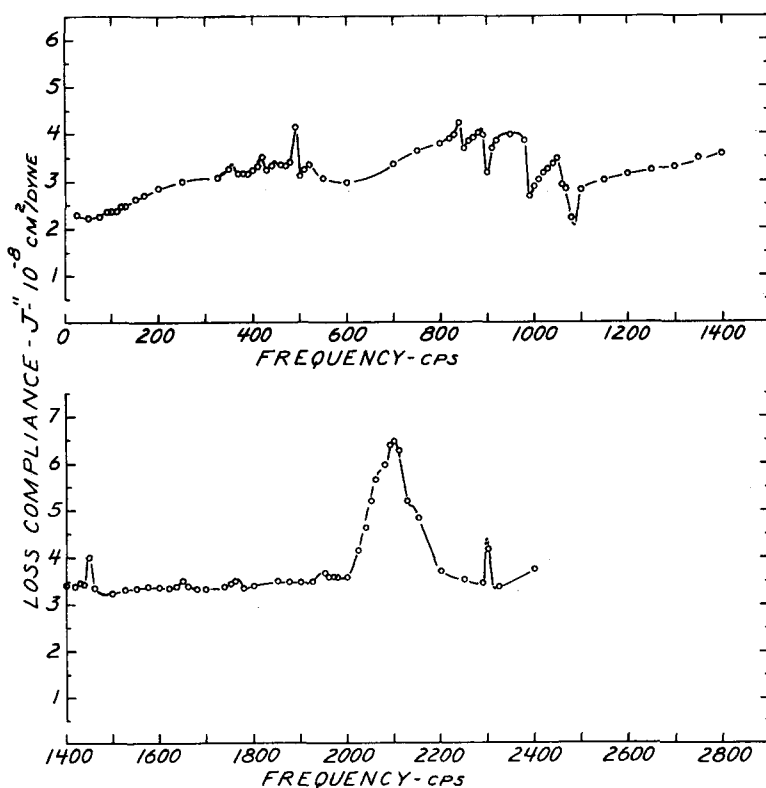


Fig. 7. Linear plot of loss component J'' of complex shear compliance ($J^* = J' - iJ''$) vs. frequency for the butadiene polymer at 35.7°C. Four-frequency resonance mode clusters near 400 and 900 cps are evident as in Figure 6. Apparent three-mode cluster at 2100 cps is considered to result from superposition of two modes at closely spaced frequencies (2060 and 2140) as discussed in text and demonstrated in Figure 8.

TABLE III
Dynamic shear compliance spectrum of butadiene terpolymer^a at 37.5°C; 1973 Analysis

q ²	Frequencies, cps							
	O ¹⁶		N ¹⁴		CH ¹³		C ¹²	
	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
1	yes	(91.0)	yes	(104.0)	yes	(111.0)	yes	(121.5)
4	360	364	420	416	445	444	495	486
9	845	819	895	936	985	999	1095	1094
16	1450	1456	1650	1664	1770	1776	1945	1944
25	2295	2275	—	2600	—	2775	—	3038

Unassigned resonances at 1990, 2060, and 2140 cps (measurements made from 25 to 2500 cps)

^a Terpolymer: butadiene, 66; acrylonitrile, 28; methacrylic acid, 6 parts by wt.
Calcd. frequency ratios ($q^2 = 1$): 1.000:1.142:1.220:1.335; pred. frequency ratios: 1.000:1.142:1.230:1.333 (1/16:1/14:1/13:1/12).

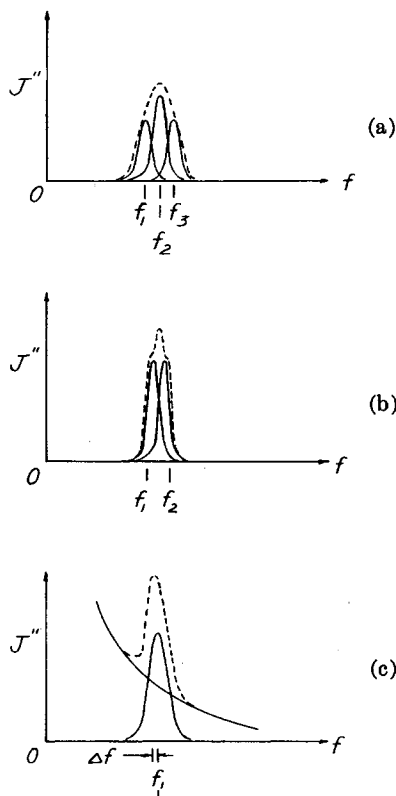


Fig. 8. (a) Superposition of three closely spaced but separate mechanical loss (J'') curves (solid lines) to give an apparent single-mode frequency (dashed line). (b) Superposition of two closely spaced maxima in J'' to give a resultant curve which might, at first glance, be considered to result from three separate modes (dashed line). (c) Shift in apparent mode frequency (from J'' data) caused by broad frequency-dependent "background" retardation dispersion in J'' as indicated for a single mode. These and similar effects on J' vs.-frequency curves must be considered in mechanical spectra analysis of closely spaced mode frequencies.

line) arrangements within synthetic polymers chains, however, are known to occur²⁰ as they do in biopolymers.

CONCLUSIONS

Understanding of the experimental observations cited for the butadiene terpolymer sample requires reexamination of the simultaneous microstructural and stress requirements outlined above. That is, the occurrence of enhanced responses or resonances like those cited can occur in a material subject to mechanical vibration if (1) the atomic constituents of the material with masses m_k are arranged in a regular or ordered manner over some characteristic length S in at least one direction; and (2) as a result of residual or applied steady stresses, there are forces per atom, F_{pq} , within the material such that the discrete force requirement, of eq. (7), is met.

According to eq. (1), the product of atomic mass and characteristic length squared must further have appropriate values,

$$m_k S^2 \cong \frac{h}{8\nu_q} q^2. \quad (9)$$

For resonance modes with frequencies ν_1 ($q = 1$) from 10 to 1000 cps, for example,

$$8.28 \times 10^{-31} < m_k S^2 < 8.28 \times 10^{-29} \quad (9a)$$

and atomic masses from 1 to 100 thus demand characteristic lengths from about 0.7 to 70×10^{-4} cm. At the same time, the actual microscopic stress distribution within the material must be such that for the macroscopic applied or residual stresses present, there is a mean force per atom, F_{pq} , where

$$F_{pq} \cdot s = \nu_q h \quad (7a)$$

where s is a (mean) characteristic field free length available to certain "free" atoms within the material. These forces, as given by eq. (7a), are needed to "activate" the intrinsic momentum-wave modes described by eq. (1). Thus, audio-frequency resonances will be observed in mechanical vibration measurements when (a) an ordered arrangement of like atoms with regular spacing d exists in at least one direction in a material; (b) the ordered arrangement extends over some characteristic length S , so that requirements like those of eqs. (9) and (9a) are fulfilled for any given atomic mass m ; (c) a residual or applied steady stress distribution is present throughout the sample to activate the modes as demanded by eqs. (7) and (7a).

The absence of any one of these three requirements will result in the absence of observed momentum-wave resonances. In particular, narrow stress distributions may activate only some modes leading to observation of some resonance frequencies in a series, but not others.

The appearance of strong resonance modes above about 24°C and below 1°C, together with their diminution or absence at intermediate temperatures in the butadiene terpolymer, most probably results from the occurrence of order-disorder transitions at 24° and 1°C. The existence of order-disorder transitions is also substantiated by the specific volume-temperature transitions observed at these same temperatures. Thus, above 24°C and below 1°C, requirements (a)

and (b) are apparently met. Conversely, ordered arrangements may be completely absent between 1° and 24°C, or are present only over such a short range (small value of S) that characteristic modes are at much higher frequencies. Of course, if no order at all exists, a characteristic length S necessarily vanishes and the mode frequencies become infinitely high.

A possible, alternative explanation is that the required stress distribution to cause mode activation is present above 24° and below 1°C, but disappears between 1° and 24°C. This is considered unlikely in the present case because of the strong evidence of residual stress concentrations previously cited and the observed second-order transitions in specific volume-temperature data just mentioned.

The observed values of frequency ratios for a common mode of the terpolymer are in excellent agreement with the inverse atomic mass ratio prediction from eqs. (4) and (5) for a common characteristic length S . In particular, the ratios oxygen/nitrogen/carbon agree so well that correct assignment of these observed series is strongly substantiated. On the other hand, assignment of a momentum-wave series to the CH group, acting as a single mass, is perhaps questionable even though good quantitative agreement with the predicted inverse atomic-mass frequency dependence again results.

An alternate assignment of this series is to the carbon isotope of mass 13, which, however, in usual concentrations amounts to only 1.1% of the total carbon content. Similarly, the CH₂ group has the same mass (14) as the nitrogen atom, so that this group mode cannot be easily distinguished from the atomic (nitrogen) mode.

Finally, it should be emphasized that three observed terpolymer resonances at 35.7°C (at 1990, 2060, and 2140 cps) are unassigned on the basis of the equations and ideas presented here. If the assignment of modes to atomic groups is accepted as valid, it should be noted that these three frequency ratios are in close agreement with the inverse group mass ratios for CO, NO, and COH, for example (e.g., inverse group mass ratios 1.000:1.035:1.072 compare to frequency ratios 1.000:1.035:1.075). This is not to be taken as a valid explanation without further investigation, however. In some of the materials mentioned in the discussion of previous experimental results, there are also "unassigned" (and unexplained) resonance frequencies; in particular, a splitting of modes into two or three frequencies with changes in time and/or temperature has often been observed. Some of these changes may result simply from the development of two or more predominant characteristic lengths within the material, but others may occur because the *effective* atomic masses at particular positions in the ordered arrangement vary in some regular fashion.

Multiple transitions in acrylonitrile-butadiene copolymers at low temperatures (below about -25°C) have been reported for copolymers with less than 36% acrylonitrile;²² these are attributed to the incompatibility of copolymer species of differing comonomer contents. Multiple transitions above 20°C have also been observed in copolymers of ethylene and acrylic acid as well as copolymers of butadiene and acrylic acid.²³ Thus, the occurrence of multiple specific heat transitions in this butadiene terpolymer between 50° and -20°C is perhaps to be expected. Further, copolymers of butadiene-acrylic acid are "ionomers"; i.e., they form intermolecular ionic bonds and are said to consist of crystalline phases and amorphous phases.²³ The acrylic acid groups are sometimes said to be

distributed randomly (as dimers) or as large ionic clusters (100 Å diam.) in the amorphous phase; a third "aggregate" model proposes acid aggregates of only 5 to 10 Å diameters homogeneously distributed in the amorphous phase.²³ Small-angle x-ray scattering indicates the existence also of polyethylene or butadiene crystalline lamellae in these ionomers.²³ Similar lamellar structures, if present in the butadiene-acrylonitrile-acrylic acid terpolymer could account for the observed dynamic mechanical spectra; the calculated characteristic length, $S = 6$ micrometers, might then correspond to the chief lamellar thicknesses.

For whatever detailed reasons they occur, the general existence of these sharp, nonelastic resonance responses to mechanical vibrations of materials is of considerable practical importance in many material uses. Unexpectedly high vibration amplitudes may occur at certain frequencies, for example; or other undesirable behavior, including early fatigue fractures, may ensue. The momentum-wave theory of mechanical deformation¹⁵ is clearly a useful means of correlating the microstructure and macroscopic mechanical response of materials such as the observed dynamic mechanical properties of this butadiene terpolymer.

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