# Dynamic Mechanical Spectra and Limit of Linear Viscoelasticity of High Polmers

BRYCE MAXWELL and CLAUDE GUIMON

Princeton University Plastics Laboratory, Princeton, New Jersey

# INTRODUCTION

The design of plastics parts and components which are to be subjected to mechanical stress requires a knowledge of the time dependent and temperature dependent characteristics of polymeric materials.<sup>1</sup> In contrast to more traditional engineering materials, such physical properties as modulus of elasticity, tensile strength, ultimate elongation, and energy to break are markedly dependent on the rate of load application or time of duration of load and the temperature of application. The assumption of constancy of physical properties for common engineering materials such as steel or concrete leads to design by the use of the known relationships between stress and strain of classical strength of materials. It is the purpose of the work reported herein further to develop the subject of the response of plastics to mechanical loading so that similar relationships can be developed for the application of time dependent materials.

For example, the typical stress-strain curve for mild steel shown in Figure 1 contains many useful design data for the applications engineer. Since the response of this material is essentially independent of the rate at which the stress-strain data is obtained, design constants may be specified for the material. The curve is linear up to the point Pand hence a Hookean elastic modulus (E) may be determined. By careful study of the recovery characteristics of the material an elastic limit (L)can be found. Since the shape of the curve is essentially independent of the straining rate, a specific value of yield stress (Y) may be used in design. The maximum strength (M) and the ultimate elongation (U) can be specified from the curve. Of these physical constants perhaps the most useful to the design engineer are the proportional limit (P) and the Hookean modulus (E), since below the proportional limit he may use a linear relationship between stress and strain in application design.

By contrast, not so much useful design information is available from the stress-strain curve of a typical plastic material, shown for comparison in Figure 1. The shape of this curve is dependent on the rate at which stress or strain is applied<sup>2</sup> and also the temperature. In addition, since there is essentially no straight line portion in the initial part of the curve, even a time and temperature dependent linear relationship between stress and strain is not available from these data.

In order to determine useful relationships between stress and strain for these time dependent materials it is necessary to test them in a manner that controls the effect of time on their response. Several methods are available: stress relaxation, creep, and controlled frequency dynamic tests. Each method permits the determination of the relationship between stress and strain at a constant time scale of load application. Data taken in such a manner on plastic materials that exhibit linear viscoelastic behavior should produce a stress-strain relationship of the general type shown schematically in Figure 2.

If the time scale of load application is held constant by any of the three test methods mentioned above, the relationship between various magnitudes of stress and strain may be determined. If the material exhibits linear viscoelasticity, a line of constant slope (O-V) is obtained which indicates a linear, constant relationship between the time dependent stress and strain. Therefore, by this method a material parameter comparable to the Hookean modulus may be obtained for design purposes for these time dependent materials. At some point, V, the response of the material deviates from this linear relationship. This is termed the limit of linear viscoelastic response and indicates that the mechanical loading above this point has changed the response of the structure of the material so that it no longer responds in the same manner. Therefore, we may say that the limit of

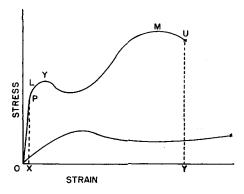


Fig. 1. Comparison of typical stress-strain curves for a mild steel and a rubbery state high polymer.

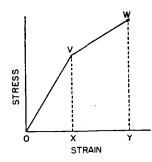


Fig. 2. Schematic dynamic stress-strain curve for a viscoelastic material.

linear viscoelastic response (V) is another important design characteristic of the material, in this case comparable to the proportional limit (P) of the traditional engineering materials.

The area O-V-X under the curve in Figure 2, when expressed in terms of energy per unit volume of material, represents the amount of energy the material can absorb without having the mechanical loading effect the structural response. This then is comparable to the area O-P-X of Figure 1 for ideal elastic response. This energy is often called the resilience of the material and is again an important design parameter.

The selection of materials for applications involving shock or catastrophic loadings involves consideration of the impact strength or total energy absorbing characteristics of materials. This energy is given by the area under the total stress-strain curve of Figure 1. Similar data on time dependent materials should be found from the area under O-V-W-Y of Figure 2.

In view of the above it is apparent that, for proper application of time dependent polymeric materials, an understanding of the linear viscoelastic relationships between stress and strain and the values for the limit of linear viscoelastic responses for the various plastic materials must be developed if we are to have the ability to apply these materials with a degree of accuracy comparable to that developed for the more traditional materials.

## BASIC THEORY

The term viscoelastic response is used to describe material behavior which exhibits a combination of both viscous and elastic response upon the application of mechanical load. The combined response is not necessarily a simple cumulative addition of simple elastic and viscous behavior, but can be any complex combination of these two ideal responses. For example, a real material may exhibit some ideal elastic response combined with elastic response that is retarded by viscous flow combined with ideal viscous flow. This general definition of viscoelasticity must be modified and restricted if the response is linear.

For linear viscoelastic response the elastic effects must be Hookean and the viscous effects must be Newtonian. That is, for each elastic effect there must be a single elastic constant that relates stress to strain in a manner that is linear and independent of time, and for each viscous effect there must be a single constant of viscosity which relates the strain rate to stress. In addition, for a material to obey linear viscoelasticity all viscous and elastic responses must be acting at all times and strain, stress, or time cannot change the number or character of the combined individual responses. For any real material, as the magnitude of loading is increased. a point will be reached at which the elastic and viscous response mechanisms will be changed as to number and character or parameters as a result of the mechanical loading. At this point the original viscoelastic character no longer holds and either a new linear viscoelastic behavior will be introduced or the response will become one of nonlinear viscoelasticity. The point at which the first deviation from linear viscoelasticity is found is called the limit of linear viscoelastic response.

These definitions say that, below the limit of linear viscoelastic response, the time dependent modulus will be independent of the magnitude of the stress or strain applied. If a set of stress relaxation curves (Fig. 3) are obtained on a material at various magnitudes of strain ( $\epsilon_a$ ,  $\epsilon_b$ , etc.), the stress ( $\sigma$ ) at any time will be related to the strain by a constant time dependent modulus (*E*) provided the linear limit is not exceeded:

$$E(t) = \sigma/\epsilon \qquad (1)$$

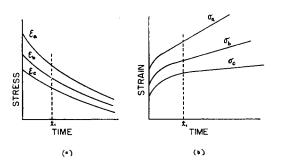


Fig. 3. Typical stress relaxation curves for strains below the limit of linear viscoelasticity. (a). Typical creep curves for stress below the limit of linear viscoelasticity (b).

Similarly if creep data (Fig. 3) were taken at various magnitudes of constant stress ( $\sigma_a$ ,  $\sigma_b$ , etc.) the time dependent modulus would be constant below the linear limit. In both cases we see that, if the time dependent relationship between stress and strain is studied in a manner by which the time dependency can be evaluated, a linear relationship between stress,  $\sigma(t)$ , and strain,  $\epsilon(t)$ , will result. Therefore, either the stress relaxation test or the creep test can be used to obtain data on  $\sigma(t)$  and  $\epsilon(t)$  up to the point V in Figure 2.

In addition, a third and perhaps more easily applied technique may be used to determine this time dependent limit. If an oscillatory stress or strain is applied to a specimen of material for evaluation and the response of the material both in-phase with the loading and ninety degrees out of phase with the loading is measured, a complex time and temperature dependent modulus,  $E^*$ , may be obtained:

$$E^* = E_1 + jE_2$$
 (2)

Here  $E_1$  represents the in-phase or real modulus and  $E_2$  is the out-of-phase or loss modulus. Any or all of these three moduli may be studied as a function of the magnitude of the applied stress or strain. If the frequency of the sinusoidally oscillating load is held constant, the time scale of load application per cycle is then independent of the magnitude of the applied stress or strain. Therefore, in order to determine the limit of linear viscoelastic response all that is necessary is to determine a dynamic modulus as a function of the maximum oscillatory loading applied, and again a plot similar to Figure 2 will be obtained. This is the technique that has been used to obtain the data presented in this paper, since both the magnitude of the applied loading and the time scale or frequency may be easily controlled. This makes possible the rapid determination of the dynamic moduli and the linear viscoelastic limit, and also permits the controlled study of the response above this limit.

The correlation of mechanical properties with the internal structure of materials is the fundamental discipline underlying the science of materials application. The time dependent mechanical response of polymeric materials may be associated with a series of several internal structural motions or distortions. These may be qualitatively described as follows: (1) The distortion of the bond angles and lengths in the polymer chain backbone. This must by nature be a distortion of relatively high modulus which is essentially ideally elastic or independent of time. (2) The distortion by rotation and uncoiling of segments of chains. Depending on the chemical structure of the polymer and the temperature, a series or spectrum of uncoiling mechanisms can take place. Each of these mechanisms will respond in a delayed elastic manner which may be thought of in the linear viscoelastic case as Hookean elasticity delayed or retarded by Newtonian viscosity. The number and character of these delayed elastic responses will depend upon the magnitude of the applied mechanical loading, the time scale or rate of load application, and the structure of the polymer at any given temperature. (3) The distortion of the polymer structure by the relative motion or slipping of individual chains with respect to each other. In a linear, noncrosslinked polymer this translational motion of chains will take place under any condition of mechanical loading unless prevented by crystalline structure or chain entanglements. In the case of linear viscoelastic response this mechanism of structural distortion may be considered as Newtonian flow.

At a long time scale of loading, analogous to a low frequency in a dynamic test, all of the structural mechanisms will be manifested in the response of the material. The result will be a large distortion or strain for a given applied stress. This results in a low value for the in-phase modulus  $(E_1)$ . At a short time of loading, or high frequency, many of the delayed structural distortions cannot respond to produce a large strain for a given stress. As a result the in-phase modulus is higher and in principle at infinite frequency would have the value associated with the distortion of the bonds in the chain backbone alone. Similarly the out-of-phase or loss modulus will be dependent on the rate at which structural distortion mechanisms can respond. At long time scales of loading the delayed elastic mechanisms of uncoiling and segmental motion will have time to respond in-phase with the loading, and as a result the out-of-phase response will be small. At very short time scales of loading, or high frequencies, the response will be essentially ideal elastic, and the out-of-phase response should approach zero. In between these two extremes of rate of loading the loss modulus should reach a maximum at time scales of loading at which the retarded elastic distortional mechanisms are out-of-phase with the loading. Another dynamic property that is often reported is the loss factor that represents the ratio of loss modulus to storage or in-phase modulus. Since the loss modulus is high in the range of time scales of loading where the modulus is highly time dependent, then a high loss factor indicates a very time dependent in-phase modulus.

In view of the above, we should also expect the limit of linear viscoelastic response to be dependent on the rate of loading or time scale of test. At very low frequencies all structural mechanisms of response are able to respond, and a high strain limit might be expected. At very rapid rates of loading only the ideal elastic mechanisms of structural distortion have time to respond, and hence a low strain limit should be expected.

The above general consideration of the time dependency of the limit must be further modified by structural response considerations. At low frequencies of testing, long time under load may result in the possibility of structural distortion mechanisms taking place that may be of a nonlinear nature, such as disentanglement of chains or distortion of crystalline structure. This may result in a lowering of the linear limit at long time scales of loading. On the other hand, at high frequencies, since fewer mechanisms of structural distortion are available for response, the stress at any given strain will increase. This increased stress may produce degradative or nonlinear structural responses, which further reduces the strain limit of linear viscoelastic responses. Since for any given time scale of loading it is the strain that determines the number and character of structural distortion responses, it would seem more fundamental to designate the limit as a strain value rather than a stress value.

At the present time it is not possible to make any generalization about the interaction of these structural considerations, which hold for all materials. Therefore, it is necessary to take data on the limit for purposes of application design with specific materials.

## APPARATUS AND PROCEDURE

The dynamic testing apparatus used in this study has been described.<sup>3</sup> The test specimen is a 0.25-in. diameter rod, approximately 2.5 in. long, which is subjected to a flexural loading as a cantilever beam in such a manner as to produce a sinusoidally oscillating tension and compression in the specimen. The frequency of the dynamic loading may be varied and controlled over a wide range and the test temperature may be controlled and determined.

Since the response of polymeric materials is time dependent no unique or specific relationship exists between stress and strain. Therefore, it is necessary to treat either stress or strain as a controlled variable and to study the response of one in terms of the other. If the maximum applied oscillatory stress is controlled we have a dynamic test similar to a creep test. If the maximum applied oscillatory strain is controlled we have a dynamic test similar to a stress relaxation test. In view of the greater fundamental significance of strain from a structural point of view, as brought out in the theory section, the data presented here were taken with this as the controlled variable.

The specimens were molded in vertical injection machines under controlled temperature, pressure, and time of pressure application cycles. The best molding cycle for each material was selected after exploratory study and was held constant for those series of materials for which a controlled internal structural variable was to be studied. Table I presents a list of the materials studied together with the molding cycle used.

The dynamic spectra were examined in most cases over a frequency range of  $10^{-2}$  to  $10^2$  cycles/ sec. Where temperature effects were also studied, data were taken from  $-10^{\circ}$ C. up to the softening point of the material. The procedure for taking data was to start at the lowest temperature and frequency and to study the entire frequency range at that temperature, then to raise the temperature and again cover the frequency range starting from the low end.

The limit of linear viscoelastic response was determined by determining the relationship between stress and strain at controlled intervals of strain. The magnitude of strain to be applied to the specimen in the dynamic test can be preset on the apparatus directly by micrometer adjustment of the magnitude of deflection to be applied in an oscillatory manner to the free end of the cantilever beam specimen.

				Molding conditions			
		Materi	al	Temp., °F.	Press., psi	Time, sec.	
Α.	Polyethyle	ne, 0.14 C	H <sub>3</sub> /100 C	350	8000	10	
В.		0.70	44	350	8000	10	
С.	"	0.85	"	350	8000	10	
D.	"	1.80	44	350	8000	10	
E.	"	2.20	44	350	8000	10	
F.	" "	3.30	"	350	8000	10	
G.	Polypropyl	ene		335	16000	240	
H.	Polybutene-1			350	8000	10	
I.	Polystyrene			Extruded			
J.	Styrene-bu	tadiene co	polymer	410	8000	30	
K.	Styrene-ac	rylonitrile	methylstyrene terpolymer	410	8000	30	
L.	Cellulose acetate			300	8000	30	
M.	1. Cellulose acetate-butyrate			300	8000	30	
N.	Polycarbonate			$\mathbf{Extruded}$			

TABLE I

Starting from essentially zero deflection, individual determinations of the dynamic stress as a function of strain were made at intervals of 0.01 in. of increased deflection. A typical set of data for both the in-phase and out-of-phase dynamic stress-strain relationship is shown in Figure 4 for pure polystyrene at 10 cycles/sec. and 25°C. The vertical ordinate represents both the in-phase and out-of-phase stress on an arbitrary linear scale. The horizontal ordinate shows the magnitude of deflection applied to the specimen and is directly proportional to dynamic strain.

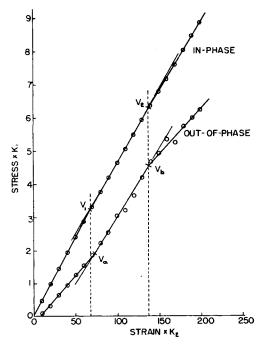


Fig. 4. Dynamic stress-strain curves for polystyrene at 25°C. and 10 cycles/sec.

As the strain magnitude is increased from zero, the in-phase stress increases in a manner directly proportional to the applied strain, as shown by the straight line  $O-V_1$ . Above this point the stress and strain are again linearly related but by a different constant in the range  $V_1-V_2$ . At  $V_2$ another limit is found, followed by an apparently linear relationship up to the breaking point. These strain limits are also confirmed by breaks in the curve of out-of-phase stress vs. applied dynamic strain,  $V_a$  and  $V_b$ . The strain limit of linear viscoelastic response can easily be determined from such data, since they represent the intersection of two straight lines, or linear regions of response.

# **RESULTS AND DISCUSSION**

The frequency and temperature dependent response of polystyrene is shown in Figures 5 and 6

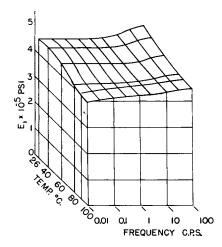


Fig. 5. In-phase modulus of polystyrene as a function of frequency and temperature.

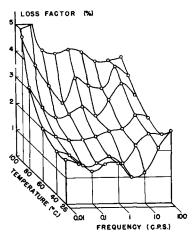


Fig. 6. Loss factor of polystyrene as a function of frequency and temperature.

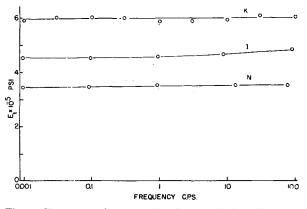


Fig. 7. Frequency dependent in-phase modulus of styrene terpolymer (K), polystyrene (I), and polycarbonate (N).

as an example of the dynamic mechanical spectra of a glassy state amorphous polymer. From Figure 5 it is apparent that this material exhibits a high, essentially constant in-phase modulus over the range studied. This behavior is confirmed by the loss values shown in Figure 6. Although considerable variation of loss factor values is found, the values themselves are all very low, less than 3%, except at temperatures near the glass transition. This should be expected for a material exhibiting a constant in-phase modulus with frequency and temperature. Similar behavior was also found for the polycarbonate material (N) and the styrene terpolymer (K), shown together with polystyrene (I) at room temperature in Figure 7.

For comparison the dynamic mechanical spectra of a typical polycrystalline polymer (linear polyethylene B) are shown in Figures 8 and 9. In the ranges of temperature and frequency studied this material exhibits a much greater time and temperature dependency of the in-phase modulus. This is confirmed by the frequency and temperature dependent loss factor peak of Figure 9. All of the data on both glassy state amorphous and linear polycrystalline materials presented above were taken at load values below the limit of linear viscoelastic response. Such data, then, are independent of the magnitude of stress or strain applied; that is, these spectra can be considered as constant below the limit.

In order to know the range of mechanical loading over which these dynamic spectra can be used as

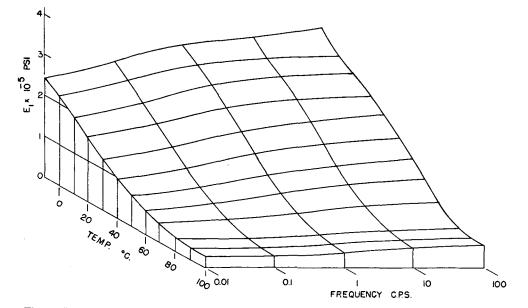


Fig. 8. In-phase modulus of linear polyethylene as a function of frequency and temperature.

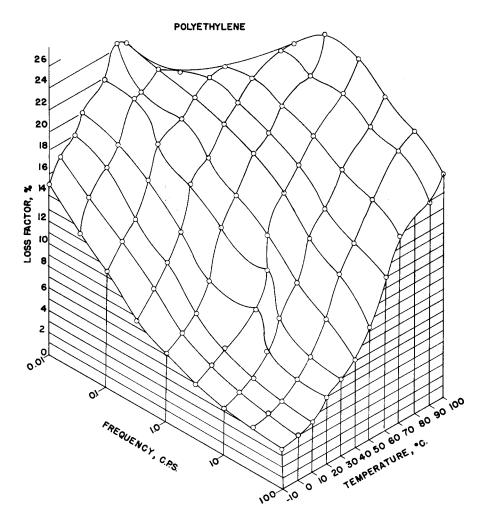


Fig. 9. Loss factor of linear polyethylene as a function of frequency and temperature.

design application data, the value of the various limits must be known. The values of the stress limit and strain limit  $(V_1)$  for the series of polyethylenes (A through F of Table I) of various degrees of branching are shown in Figure 10. A general trend of decreasing stress limit with increasing degree of branching, as shown by methyl group content, is found. A pronounced trend of increasing strain limit is found with increasing degree of branching. Since the dynamic properties of polycrystalline polymers is primarily associated with the amorphous regions between crystallites,<sup>4</sup> these data must be analyzed from the point of view of amorphous content and the response of the amorphous material.

As the degree of branching is increased the branched points disturb the crystallite growth and thereby prevent a high degree of crystallinity being formed in the material. As a result the amorphous content increases with increasing branching. Since the strain takes place largely in the amorphous regions, the trend observed of increased strain limit with increased branching is to be expected. In addition to changing the amount of amorphous content, the branching also should affect the internal response mechanisms of the amorphous regions. The presence of branch points should tend to separate the chains so that interactions between chains are less frequent. With less frequent interactions along the chain lengths, large chain segments can contribute to the viscoelastic response of configurational distortion. This again should increase the limit.

A third contribution of increased branching to increased strain limit should also result from the interference of branches with crystalline growth. As the crystallite grows it feeds on the amorphous chains. If the material were perfectly linear the

Material		Stress limit, psi 542	Strain limit, in./in. $\times 10^{-3}$ 2.3	Strain limit $\times$ stress limit 1,240
A. Polyethylene, 0.14 C	H <sub>3</sub> /100 C			
B. " 0.70	44	585	4.3	2,520
C. " 0.85	"	425	6.7	2,850
D. " 1.80	44	200	6.00	1,200
E. " 2.20	"	265	8.2	2,170
F. " 3.30	"	236	12.9	3,040
G. Polypropylene		885	4.4	3,900
H. Polybutene-1		565	5.5	3,100
I. Polystyrene		2000	5.1	10,200
J. Polystyrene copolyme	r	2100	6.0	12,600
K. Polystyrene terpolym	er	4400	9.2	40,500
L. Cellulose acetate		2010	9.6	19,300
M. Cellulose acetate-but	vrate	2030	13.1	26,500

TABLE II

only limiting factor to crystallite growth would be the strain in the amorphous regions. But if the material is branched, the growth may be stopped by the branch points. This would produce a structure with less strain in the amorphous regions due to the growth of crystallites. Thus, less strained amorphous material should exhibit a greater strain limit of linear viscoelastic response.

The stress and strain limits of linear viscoelasticity  $(V_1)$  for the materials tested are listed in Table II. If we consider the series of polystyrene and copolymers of styrene, a trend of increasing strain limit with increasing heterogeneity of structure is found. The pure homopolymer has a strain limit of  $5.1 \times 10^{-3}$ , the copolymer  $6.0 \times 10^{-3}$ and the terpolymer  $9.2 \times 10^{-3}$ . Again, as in the case with the branching of polyethylene, we see an increase in the strain limit as the heterogeneity of the structure reduces interchain action and produces a larger magnitude configurational distortion before the linear limit is reached.

The two cellulosic materials also follow the same trend. The cellulose acetate-butyrate may be considered as a more heterogeneous structure than the pure cellulose acetate and exhibits a 35% higher strain limit of linear viscoelasticity.

Polypropylene at this frequency and temperature has a strain limit of  $4.4 \times 10^{-3}$ . When comparing this to the polyethylene data, one might think of polypropylene as a very branched polyethylene and expect a high strain limit, but if the structural requirement for a high strain limit is heterogeneity then it is not just branching but rather a randomness of structure that is required. Therefore, since polypropylene has a homogeneous structure we should expect it to exhibit a low strain limit of linear viscoelasticity. Polybutene-1 is known to have two crystalline forms or structures. The "as molded" structure changes slowly to a permanent structure. At room temperature this process takes from 10 to 20 days. Figure 11 shows the variation of the linear stress and strain limits for this material as a function of time after molding. The "as molded" structure exhibits low limits. During the transition from one structure to the other the limits rise to a maximum at about seven days at room temperature and

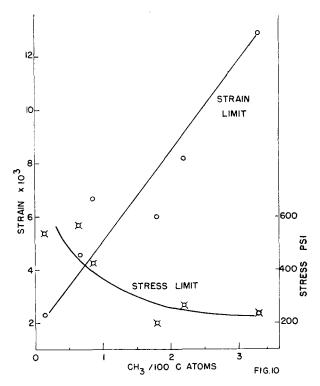


Fig. 10. Stress and strain limits of linear viscoelasticity as a function of degree of branching in polyethylene.

then fall as the new, permanent structure is formed. Again the structure existing during the change or transition may be considered as heterogeneous—in this case a heterogeneity of crystalline forms that should produce a greater amorphous content and a greater opportunity for linear structural configurational distortion. This is confirmed by the time dependent changes in the linear viscoelastic limits. The time or frequency dependence of the limits is shown in Figures 12 and 13 for polystyrene and polyethylene, respectively. Polystyrene at room temperature is in the glassy state, and because of the lack of rotation at the carbon bonds in the chain backbone no long range or high elasticity is exhibited. Both the first  $(V_1)$  and the second  $(V_2)$ strain limit of linear viscoelasticity exhibit a slight

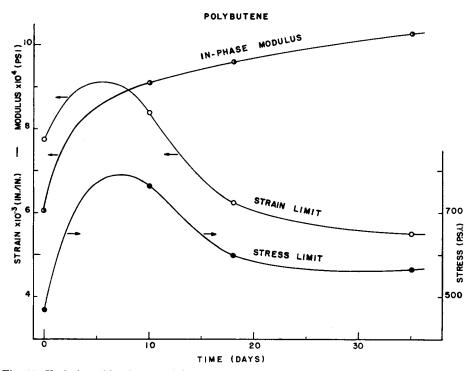


Fig. 11. Variation of in-phase modulus, stress limit, and strain limit with time in polybutene.

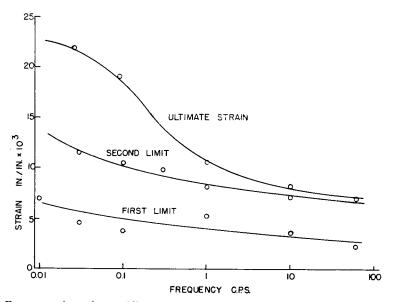


Fig. 12. Frequency dependence of linear viscoelastic limits and ultimate strain for polystyrene.

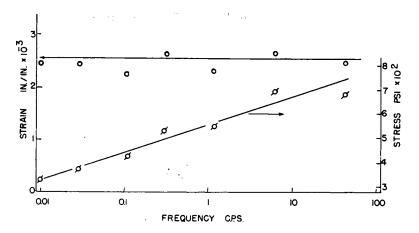


Fig. 13. Frequency dependence of the stress and strain limits of linear viscoelasticity for polyethylene.

decrease with increased frequency. This same trend is shown in the ultimate or breaking strain. Polyethylene, on the other hand, is an example of a rubbery state polycrystalline polymer at room temperature. It exhibits an essentially constant strain limit with frequency while the stress limit increases with frequency in accordance with the increasing in-phase modulus  $(E_1)$ .

The engineer using these materials in application design will be concerned with the energy that can be stored in the material in the linear viscoelastic region and with the limits themselves. The product of the stress limit times the strain limit is an indication of the relative energy-storing abilities of the materials up to the point at which the mechanical loading produces a change in the structural response mechanisms. These products are listed in Table II. In the series of polyethylenes, as the structural changes producing heterogeneity increase, the stress limit decreases while the strain limit increases. As a result the relative energystoring values vary with structure in a random manner with the methyl group content. In the styrene series both the stress limit and the strain limit increase with increased heterogeneity. This produces a distinct trend of increased energy storage below the limit with heterogeneity. The same trend is observed with the two cellulosic materials.

It is apparent that, among the materials investigated, the glassy state materials can store a great deal more energy in the linear viscoelastic range than can the rubbery state materials. To the design engineer this means that, if he must design for energy absorption without strain induced change in structure, a glassy state material would be preferable. But, if he must consider energy absorption for accidental shock or impact loading, a rubbery state material may be preferable since the ductility of these materials allows much greater energy absorption in the nonlinear region.

### CONCLUSIONS

The dynamic mechanical spectra of polystyrene (a glassy state polymer) and polyethylene (a rubbery state polycrystalline polymer) have been determined and the values of the dynamic properties have been shown to be dependent on the magnitude of the mechanical loading with respect to the limit of linear viscoelastic response. Specific conclusions which can be drawn from this are as follows:

(1) The limit of linear viscoelastic response is an important material property which must be considered in the interpretation of data on time dependent materials and in the application of such data to engineering problems.

(2) The limit of linear viscoelastic response has been found to be dependent on temperature and on the time scale of load application (frequency).

(3) The relative energy storing capacity of glassy state polymers in the linear viscoelastic region is much greater than that of typical rubbery state polycrystalline materials.

(4) In several series of polymers of controlled internal structure the strain limit of linear viscoelastic response has been found to vary directly with the heterogeneity of the structure. This has been interpreted in terms of the effects of interchain interaction on configurational distortions.

#### References

1. Maxwell, Bryce, SPE Journal, 15, 6 (June, 1959).

2. Maxwell, Bryce, and J. P. Harrington, Trans. ASME, 74, 4 (May, 1952).

- 3. Maxwell, Bryce, A.S.T.M. Bull., No. 215 (July, 1956).
- 4. Kavafian, G., J. Polymer Sci., 24, 107 (1957).

### **Synopsis**

The dynamic mechanical properties of a typical polycrystalline polymer (polyethylene) and a typical glassy state amorphous polymer (polystyrene) have been studied as a function of both frequency and temperature. The response of these materials to mechanical loading was found to be dependent upon the magnitude of strain resulting from the mechanical load above the limit of linear viscoelastic response. Therefore, the limit of linear viscoelastic response must be considered as an important material characteristic in design application of high polymers. This limit has been studied as a function of time scale of loading and polymer structure for a series of materials. A general trend of increased strain limit of linear viscoelastic response with increased heterogeneity of internal structure has been found.

#### Résumé

Les propriétés mécaniques dynamiques d'un polymère polycristallin typique (polyéthylène) et d'un polymère amorphe vitreux typique (polystyrène) ont été étudiées en fonction de la fréquence et de la température. La résponse de ces matériaux à une charge mécanique dépend de l'importance de l'élongation résultant de la charge mécanique audessus de la limite de la réponse viscoélastique linéaire. En conséquence la limite de réponse viscoélastique linéaire doit être considérée comme une caractéristique importante du matériau pour l'élaboration de hauts polymères. Cette limite a été étudiée en fonction de la vitesse de charge et de la structure du polymère pour une série de matériaux. On a observé une tendance générale à l'accroissement de la limite d'élongation de la réponse viscoélastique linéaire avec l'augmentation de l'hétérogénéité de la structure interne.

#### Zusammenfassung

Die dynamischen mechanischen Eigenschaften eines typisch polykristallinen Polymeren (Polyäthylen) und eines typisch glasartigen amorphen Polymeren (Polystyrol) wurden als Funktion der Frequenz und der Temperatur untersucht. Es wurde gefunden, dass die Reaktion dieser Materialien auf mechanische Belastung von der Grösse der Verformung abhängig ist, die durch die mechanische Belastung oberhalb der Linearitätsgrenze des viskoelastischen Verhaltens ensteht. Daher muss die Linearitätsgrenze des viskoelastischen Verhaltens als wichtige Materialcharakteristik bei einer Anwendung von Hochpolymeren als Konstruktionselemente angesehen werden. Diese Grenze wurde als Funktion der Belastungszeit und der Polymerstruktur für eine Reihe von Materialien untersucht. Es wurde eine allgemeine Tendenz zum Anstieg der Linearitätsgrenze bei der Verformung für das viskoelastische Verhalten mit steigender Heterogenität der inneren Struktur festgestellt.

Received March 10, 1961