

Characteristic Viscoelastic Parameters for Amorphous Polymers

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STRESS RELAXATION MASTER CURVES

Stress relaxation master curves for amorphous polymers are obtained by horizontal displacement of $\log E_r(t)$ data obtained at different temperatures along the log time axis.¹ A typical example is shown in Figure 1, for polyisobutylene in the transition region.

The general appearances of stress relaxation master curves for various amorphous polymers in the transition region are quite similar. Linear amorphous polymers or very slightly crosslinked amorphous polymers generally show a relatively linear region in the $\log E_r(t)$ vs. $\log t$ plot in the neighborhood of $E_r(t) = 10^9$ dynes/cm.², as seen in Figure 1.

For the sake of defining some very simple parameters to characterize the master curves of linear or slightly crosslinked amorphous polymers we shall select $E_r(t) = 10^9$ dynes/cm.² as an arbitrary point of reference for the modulus, and 10 sec. as an arbitrary reference time.

The characteristic relaxation time $K(T)$ at any temperature is the time required for $E_r(t)$ to attain a value of 10^9 dynes/cm.². T_i is the temperature at which $K(T) = 10$ sec.; i.e., $K(T_i) = K_i = 10$.

E_1 and E_2 are the "horizontal" asymptotes of the stress relaxation master curve in the transition region, otherwise defined as the glassy modulus and the rubbery modulus (in theory, E_2 varies proportionally to absolute temperature; E_1 also has a slight temperature dependence and time dependence).

We define another characteristic parameter n ; the negative slope of the $\log E_r(t)$ vs. $\log (t)$ master curve at $E_r(t) = 10^9$ dynes/cm.². The theoretical value of n according to the Rouse-Bueche theory is 0.5.

All of these parameters are clearly indicated in Figure 1.

Plots of $\log [K(T)/K(T_i)]$ vs. $T - T_i$ are nearly linear in the region where $T = T_i$. A plot of this type is shown for polyisobutylene in Figure 2. The slope of this plot at $T = T_i$ is defined as p , which we take to be another characteristic parameter. The WLF equation predicts p to be 0.338.

Values of characteristic parameters for several amorphous polymers are given in Table I.

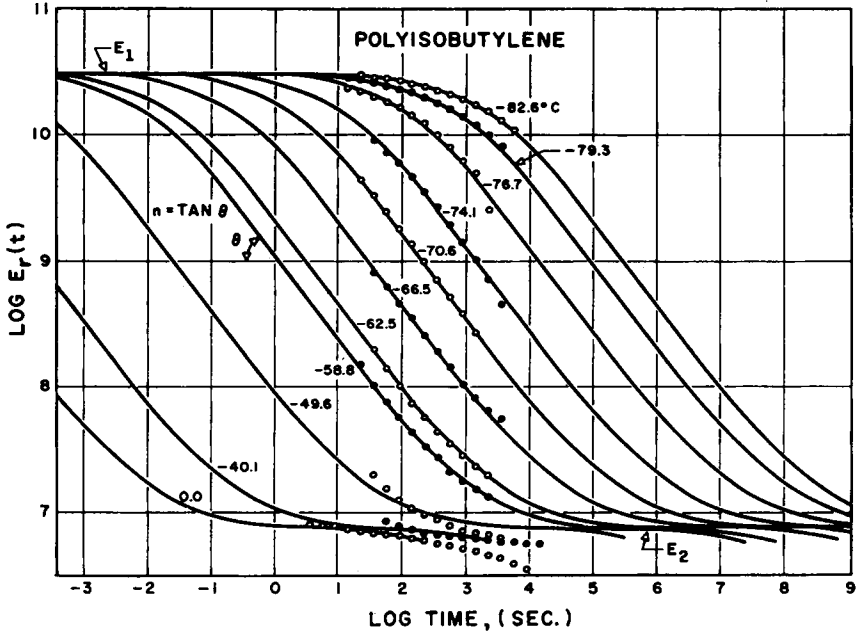


Figure 1.

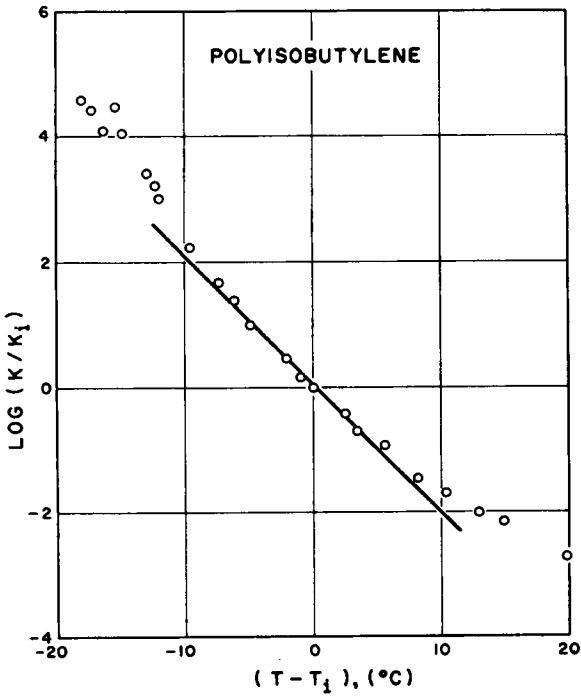


Figure 2.

TABLE I
Characteristic Parameters for Stress Relaxation Master Curves

	E_1 $\times 10^{10}$	E_2 $\times 10^7$	$T_i, ^\circ\text{C.}$	n	p	np
Linear polymers						
Polyisobutylene	3.02	0.759	-64.4	0.75	0.21	0.15
Polystyrene	2.00	0.339	93.1	0.87	0.26	0.22
Polymethyl methacrylate	2.82	2.51	113.3	0.54	0.33	0.18
Natural rubber (unvulcd.)	2.63	1.00	-66.9	1.23	0.31	0.38
Slightly crosslinked polymers						
Natural rubber (vulcd.)	2.46	1.82	-63.6	1.10	0.28	0.31
Butadiene/styrene (weight ratios)						
75/25	1.74	2.76	-50.8	0.71	0.34	0.24
60/40	1.86	5.50	-33.7	0.50	0.32	0.16
50/50	1.62	3.63	-18.4	0.53	0.31	0.16
30/70	0.912	1.82	13.6	0.54	0.28	0.15

MODULUS-TEMPERATURE CURVES

A very convenient type of viscoelastic measurement is the measurement of torsional (shear) modulus at a fixed time as a function of temperature.² We shall choose 10 sec. as our fixed time of measurement. For purposes of more direct comparison with stress relaxation data measured in tension we shall always multiply the 10 sec. shear modulus G by 3.

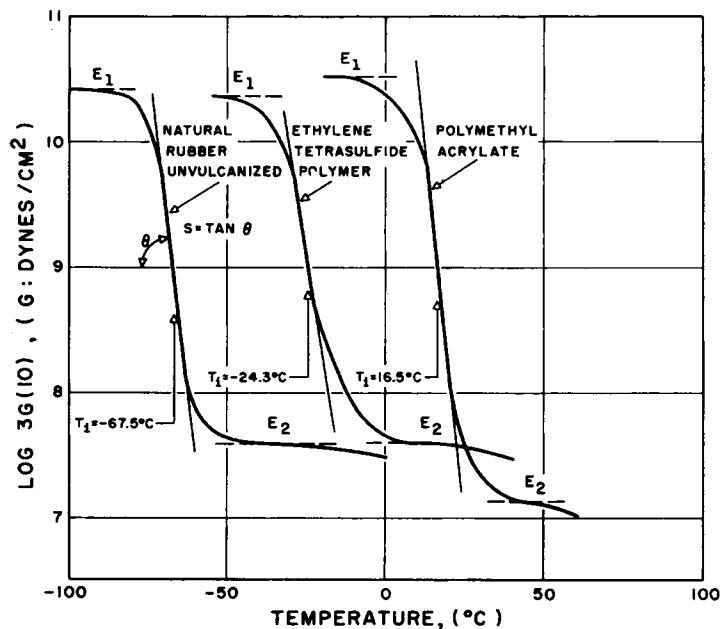


Figure 3.

For modulus values below 10^9 dynes/cm.² the relationship $E = 3G$ is very nearly exact. For modulus values much above 10^9 dynes/cm.², this is only an approximate relation, which may be in error by as much as 50%. The exact relation between E and G depends on the Poisson ratio.

Plots of $\log 3G(10)$ vs. temperature T are shown for various amorphous polymers (in their transition region) in Figure 3. It is easy to obtain $3G_1$ and E_2 from such a plot. For definiteness we say $3G_1$ is the value of $3G(10)$ at $T_i - 30^\circ\text{C}$. E_2 is the value of $3G(10)$ selected at the point in the rubbery plateau region where the slope of $\log 3G(10)$ vs. T is a minimum. Another characteristic parameter s may be defined from the log modulus vs. T curve. This is defined as the negative slope of $\log 3G(10)$ vs. T at $T = T_i$, i.e., at $3G(10) = 10^9$ dynes/cm.².

In principle, s should equal np as seen below.

In the neighborhood of 10^9 dynes/cm.² the relaxation master curve is given by

$$\begin{aligned}\log E_r(t) &= 9 - n \log [t/K(T)] & (1) \\ &= 9 - n \log t + n \log K(T) \\ &= 9 - n \log t + n \log K(T_i) - np(T - T_i)\end{aligned}$$

Setting $t = 10$ sec. in the above equation we obtain

$$\log E_r(10) = 9 - np(T - T_i) \quad (2)$$

TABLE II
Characteristic Parameters for Modulus-Temperature Curves by Torsion

Polymer	$3G_1$ $\times 10^{10}$,	$E_2 \times 10^7$	T_i	s
Linear polymers				
Polyisobutylene	3.39	0.892	-62.3	0.132
Natural rubber (unvulcd.)	2.51	3.98	-67.5	0.218
Polystyrene	1.82	0.47	101.0	0.212
Polymethyl acrylate	3.16	1.35	16.5	0.230
Polymethyl methacrylate	1.35	1.86	107.1	0.136
Polybutyl acrylate	1.51	0.562	-51.9	0.218
Polybutyl methacrylate	0.89	1.12	31.3	0.141
<i>cis</i> -Polybutadiene	2.00	1.07	-106.2	0.192
Ethylene tetrasulfide polymer	2.19	3.81	-24.3	0.153
Atactic polypropylene	1.70	2.51	-16.1	0.168
Ethylene propylene copolymer (2:1 mole ratio)	1.23	7.08	-58.8	0.160
Slightly crosslinked polymers				
Natural rubber (vulcd.)	3.39	4.27	-56.6	0.203
Tetrahydrofuran polymer	3.17	10.0	-73.1	0.146
Butadiene/styrene 75/25	2.09	4.57	-48.3	0.162

For polyisobutylene the value np obtained from stress relaxation data correlates quite well with s obtained from torsional modulus vs. temperature curves. For other polymers the agreement is not so good.

Table II gives values of $3G_1$, E_2 , T_e , and s obtained from modulus-temperature curves. It is interesting to note that the values of s all lie within a quite narrow range (between 0.10 and 0.23). It is expected that this will be found true for most wholly amorphous homopolymers or amorphous compatible copolymers; it is certainly not true for crystalline polymers, for polyblends, or for highly crosslinked polymers.

CHAIN LINKS BETWEEN ENTANGLEMENTS

From the values of E_2 for the linear amorphous polymers presented in Table II, one can calculate the molecular weight between entanglements by the equation

$$E_2 = 3dRT/M_e \quad (3)$$

where d is the density of the polymer, R is the gas constant, T is the absolute temperature at which E_2 is measured, and M_e is the molecular weight between entanglements.

TABLE III
Length between Chain Entanglements for Various Linear Polymers

Linear polymer	$M_e \times 10^4$	No. of links betw. entanglements $\times 10^2$
Polyethylene	0.43	3.10
Polytetrafluoroethylene	0.66	1.32
Polyisobutylene	0.82	2.92
Natural rubber (unvulcd.)	0.287	1.68
Polystyrene	2.15	3.71
Polymethyl acrylate	0.712	1.65
Polymethyl methacrylate	0.619	1.24
Polybutyl acrylate	1.52	2.38
Polybutyl methacrylate	0.805	1.14
<i>cis</i> -Polybutadiene	0.624	4.64
Ethylene tetrasulfide polymer	0.301	1.16
Atactic polypropylene	0.345	1.64
Ethylene propylene copolymer (2:1 mole ratio)	0.127	0.78

From the known molecular weight m per chain link, one can calculate the number of chain links n_e between entanglements by the formula

$$M_e = mn_e \quad (4)$$

Values of n_e are given in Table III.

EMPIRICAL EQUATIONS

Three very simple empirical equations are presented, for the relaxation master curve in the transition region, for the modulus-temperature curve in the transition region, and for $K(T)$ in the transition region.

$$E_n(t) = 10^9 / \{ [t/K(T)]^n + 10^9/E_1 \} + E_2 \quad (5)$$

$$3G(10) = 10^9 / \{ (10^9(T-T_i) + 10^9/E_1) \} + E_2 \quad (6)$$

$$\log K(T)/K(T_i) = -p(T - T_i) \quad (7)$$

Equations (5) and (6) are very far from exact. They do have the virtue of being very simple, they involve the characteristic parameters and no others, and they present the essential behavior of the master curve and modulus-temperature curve.

Appendix. Effect of Rate of Cooling on Modulus-Temperature Curves

We have noted that the modulus-temperature curves are to some extent affected by the rate at which the samples are chilled below T_g . For practical purposes, rubbery samples with a T_g below room temperature are very rapidly chilled in the bath liquid. Samples with a T_g above room temperature may have been quenched more slowly from their liquid or rubbery state to room temperature. The exact value of T_i and the other viscoelastic parameters may depend to some extent upon the rate at which the samples have been quenched to the glassy state.

The partial support of the Office of Naval Research and the Goodyear Tire and Rubber Company are gratefully acknowledged.

References

1. Tobolsky, A. V., *Properties and Structure of Polymers*, Wiley, New York, 1960, Chap. 4.
2. *A.S.T.M. Book of Standards on Rubber Products*, Am. Soc. Testing Mater., 1958, p. 521, Designation D 1043-51; *ibid.*, p. 550, Designation D1053-58 R.

Synopsis

By use of a reference value of modulus equal to 10^9 dynes/cm.² and a reference value of time equal to 10 sec., characteristic viscoelastic parameters are defined from stress relaxation master curves and from modulus-temperature curves. Values of these parameters are tabulated for several linear amorphous polymers and slightly crosslinked amorphous polymers.

Résumé

On se sert d'une valeur de référence du module égale à 10^9 dynes/cm.²; et d'une valeur de référence de temps égale à 10 secondes, pour définir les paramètres caractéristiques de viscoélasticité à partir des courbes étalons de relâchement de tension et des courbes module-température. Les valeurs de ces paramètres sont rassemblées pour différents polymères amorphes linéaires et pour des polymères amorphes légèrement pontés.

Zusammenfassung

Mit einem Modulbezugswert von 10^9 Dyn/cm² und einem Zeitbezugswert von zehn Sekunden werden aus Spannungsrelaxationskurven und Modul-Temperaturkurven charakteristische, viskoelastische Parameter definiert. Werte dieser Parameter werden für einige lineare, amorphe Polymere und für schwach vernetzte amorphe Polymere tabelliert.

Received April 10, 1962