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The Application of Nutting's Equation to the Viscoelastic Behavior of Certain Polymeric Systems

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The Nutting equation $\epsilon = \psi \times \sigma^{\beta} \times t^{n}$, where ϵ=strain, σ=stress, t=time, and ψ, β, and n are material constants, is applicable to a large number of polymeric systems, such as plasticized polyvinyl chloride, styrene-butadiene copolymers, polystyrene. It has been shown that the material constant n is closely related to the damping coefficient as obtained from dynamic mechanical measurements The temperature dependence of n and δ (damping coefficient) are about the same; and, in some cases, there exists a simple quantitative relationship between the two constants. A mathematical derivation of the relationship between n and δ is given and a physical interpretation of the dimensional changes in the Nutting equation, in terms of complex moduli, is presented. Furthermore, it is shown that, in the case of styrene-butadiene copolymer, n varies with the differences in gel content and gel structure.

INTRODUCTION

THE phenomena of creep, stress relaxation, and recovery are observable in metals, crystals, glasses (organic or inorganic), rubbers, etc. The viscoelastic behavior of solid organic polymers only differs from that of other material in that large variations in these properties can be brought about by relatively small changes in temperature and/or composition. A theoretical interpretation of these phenomena, in terms of molecular processes, requires, first of all, a satisfactory mathematical representation of the large number of available experimental data. Two methods have been suggested to obtain useful parameters to characterize the deformation processes. One might be termed the analytical approach:[1] The over-all deformation process is separated into two or three processes, as shown in Eq. (1). The integral approach does not attempt such a separation and is based on a relationship first suggested by Nutting,[2] as shown in Eq. (2).

$$\epsilon/\sigma = 1/E_0 + 1/E_i(1 - \exp(-t/r_i)) + (1/\eta)t. \quad (1)*$$
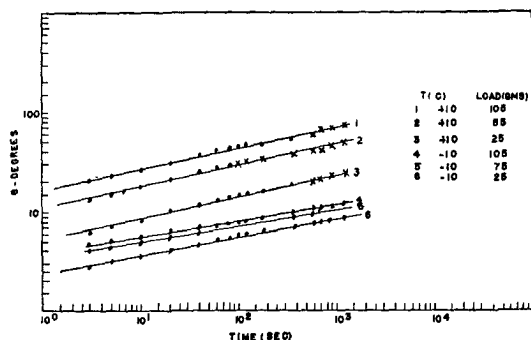
$$\epsilon = \psi \sigma^{\beta} t^{n}. \quad (2)*$$

FIG. 1. Deformation-time curves for a polyvinyl chloride-plasticizer composition at two different temperatures and three different shear stresses.

[1] T. Alfrey, Jr., *Mechanical Behavior of High Polymers* (Interscience Publishers, Inc., New York, 1948).
[2] P. Nutting, Proc. Am. Soc. Testing Materials **XXI**, 1162 (1921).

* ϵ=strain, σ=stress, t=time, E_0 and E_i=moduli, η=viscosity, ψ, β, and n=constants.

During the last few years the analytical method has been used extensively in the characterization of the viscoelastic behavior of polymeric systems. As more and more experimental data became available, it was necessary to abandon the inherent simplicity of this method by the introduction of a relaxation spectrum. This necessity not only limits the usefulness of this method to characterize the viscoelastic behavior by a small number of intrinsic parameters, but it has also raised new questions relating to the physical interpretation of such a spectrum. The integral method, based on the Nutting equation, has been given relatively scant attention in the polymer field, although it has been used extensively to characterize deformation processes of such varied materials as metals, asphalts, and baking dough. The general objections raised in opposition to the use of this method have been: (a) that the time dependence of the viscoelastic deformations cannot always be expressed by a single constant; (b) that the variation of the exponent "n" between 0 and 1 leads to varying dimensions in the material constant ψ; (c) that the constant "n" is an arbitrary quantity which cannot be related to other quantities of the material. In the following it will be shown that these
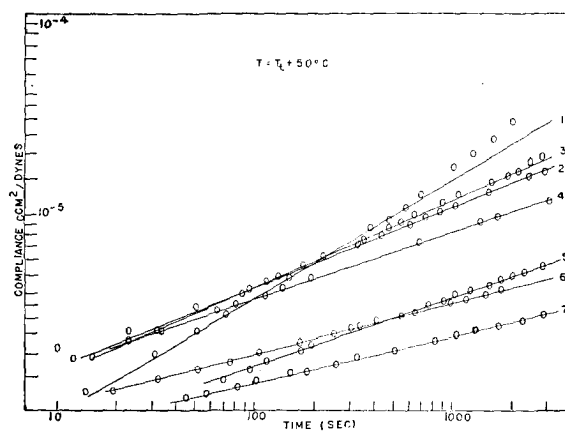

FIG. 2. Deformation-time curves for different styrene-butadiene copolymers. T_t=temperature of maximum damping.

objections are not particularly valid and that the Nutting equation not only gives a simple characterization of the viscoelastic behavior of polymers but promises to result in a better understanding of the molecular mechanism responsible for this type of deformation process.

THE TIME DEPENDENCE OF VISCOELASTIC DEFORMATIONS

According to the Nutting equation the strain, at constant stress, is proportional to t^n where n is assumed to be a constant at a given temperature. Figures 1, 2, and 3 show some results obtained on various polymer systems and it can be seen that the relationship is of the form given by the Nutting equation. (Many more creep curves have been analyzed by this procedure and found to give a linear relationship between log strain and log time; see also the papers by Hahn and Gardik,[3] and Scott, Blair, and Copper.[4]) It should also be pointed out that the data in Figs. 1, 2, and 3 were obtained on different instruments.

Other investigators[5,6] have reported data which give a linear relationship between the strain and the logarithm of time. For small strains such a relationship follows from the Nutting equation by expanding the logarithm of strain into a power series. There are, however, experimental data which cannot be represented by a single constant n, as is shown in Fig. 4. Usually such data can be approximated quite well by two curves of constant "n" of which one curve will have a slope equal or rather close to one. Systems exhibiting this kind of viscoelastic behavior possess a semipermanent network.[7] The quantity "n" which characterizes the nature of the time dependent deformation process can only remain constant if the molecular processes remain unchanged during the time of the test. If they change, "n" must change by necessity. The fact that "n" does not always remain constant during a long-time creep test should, therefore, not be used as an argument against the applicability of the Nutting equation to systems in which the network points, or crosslinks, are not of permanent kind.

There can be no doubt, therefore, that the Nutting equation can be applied to characterize quantitatively the creep behavior of a large number of polymeric compositions. The determination of the parameter characteristics of the material—particularly n, but also ψ and β—is simple and more readily accomplished than by the use of the analytical approach. One other point is worth emphasis: Using the analytical approach one frequently calculates a viscosity term from the linear portion of the deformation-time curve. Quite often such a calculation is carried out on curves having an "n"
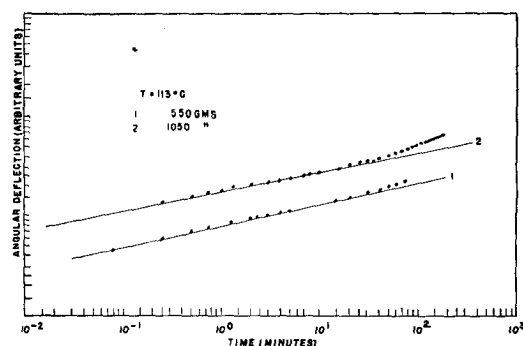

Fig. 3. Deformation time curves for polystyrene at two different shear stresses.

considerably smaller than one. As a viscosity, by definition, can only be determined when $n=1$ it is obvious that such data are completely misleading. In general one finds that temperature coefficients of viscosities obtained from such data are unusually high[8] which, in turn, has led to a considerable amount of speculation concerning the origin of such a high "apparent" activation energy of viscous flow of polymers. This difficulty disappears when one accepts as viscosity values only such data which, on a $\log\epsilon-\log t$ plot, have a slope of not less than about 0.9.

THE TEMPERATURE DEPENDENCE OF "n" AND "ψ"

It was pointed out some time ago[9] that the shape of the creep curve of plasticized polyvinyl chloride compositions varied in a systematic manner with the temperature; similar conclusions could also be drawn from creep experiments made by Conant and Liska[10] on various rubbers. These observations suggested a more careful investigation of the temperature dependence of parameters of the Nutting equation. For this reason, the creep of two plasticized polyvinyl chloride compositions was investigated in detail over a wide temperature range. Some of the experimental data are shown in Fig. 1 and the values of n and ψ at all tem-
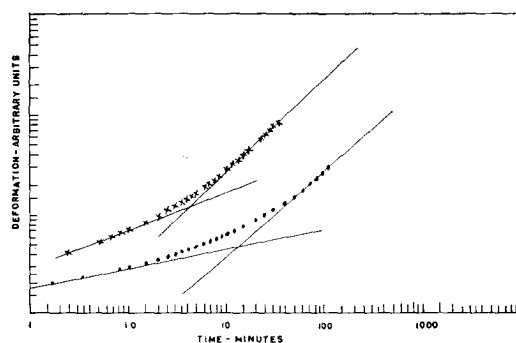

Fig. 4. Deformation-time curves for polystyrene.

[3] S. H. Hahn and I. Gardik, Rubber Chem. and Tech. 14, 433 (1941).
[4] Scott, Blair, and Copper, J. Soc. Chem. Ind. 60, 190 (1941).
[5] W. Brenschede, Kolloid Z. 104, 1 (1943).
[6] Conant, Hall, and Lyons, J. Appl. Phys. 21, 499 (1950).
[7] L. E. Nielsen and R. Buchdahl, J. Colloid Sci. 5, 282 (1950).

[8] G. J. Dienes, Meeting of Soc. of Rheology, New York, New York, November, 1950.
[9] Nielsen, Buchdahl, and Levreault, J. Appl. Phys. 21, 607 (1950).
[10] F. S. Conant and J. W. Liska, J. Appl. Phys. 15, 767 (1944).

TABLE I. n, ψ, and E''/E' as a function of temperature.

Temp. (°C)	PVC+0.417ϕ, DOP			PVC+0.378ϕ, TCP		
	n	ψ^a	E''/E'	n	ψ	E''/E'
50	0.080	2.5	0.095	0.085	3.6	0.127
40	0.075	1.4	0.133	0.087	3.0	0.143
30	0.115	1.1	0.209	0.133	1.5	0.318
20	0.158	0.64	0.30	0.355	0.25	0.66
10	0.220	0.43	0.41	0.25	0.066	0.45
0	0.266	0.17	0.44	0.11	0.0082	0.175
−10	0.175	⋯	0.24	0.047	0.016	⋯
−20	0.113	0.12	0.155	0.027	0.010	⋯
−30	0.090	0.03	0.150	0.026	0.006	⋯
−40	0.073	0.02	⋯	⋯	⋯	
−50	0.060	0.018	⋯	0.024	0.005	⋯

^{a} ψ in arbitrary units.

peratures are given in Table I (see also Fig. 5). The results obtained are in complete agreement with data given by Bilmes[11] for polyvinyl chloride samples of unknown composition and one is justified, therefore, to consider the relationship between n and T and ψ and T applicable to polymer compositions of this kind irrespective of the particular plasticizer or polymer used. It was also found that "n" was independent of stress within the range of stresses used in these experiments. The accuracy of the ψ-value is considerably less than the accuracy of n because a double extrapolation is necessary to obtain ψ, whereas n is obtained directly from the $\log\epsilon - \log t$ curve. As β is rather close to unity for these materials the creep behavior over an extended time interval is completely characterized by the two
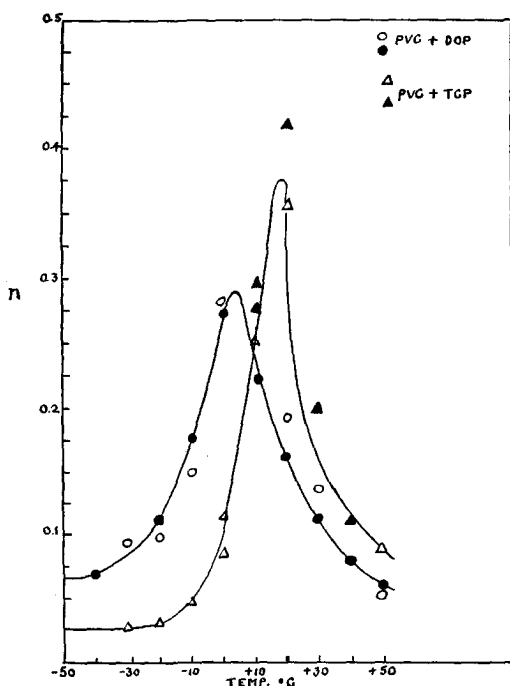

FIG. 5. n as a function of temperature for two plasticized polyvinyl chloride compositions (see Table I; ○, ▲ are calculated from the dissipation factors, see reference 12).

[11] L. Bilmes, J. Soc. Chem. Ind. **63**, 182 (1944).

constants n and ψ. The analytical method, on the other hand, requires a very much larger number of constants to describe adequately the viscoelastic behavior of these materials.

THE RELATIONSHIP OF "n" AND "ψ" TO OTHER PHYSICAL QUANTITIES

The shape of the $n-T$ curve and also the dependence of ψ on T are qualitatively very similar to the curves of the damping or dissipation factor and of the dynamic modulus as a function of temperature.[9] At the temperature of maximum damping the constant "n" goes through a maximum and on either side of the maximum "n" decreases to fairly small values. Furthermore, the width of the two curves ($n-T$ and $E''/E'-T$) are also related as can be seen from Fig. 5; a broad dissipation maximum yields a broad maximum for the $n-T$ curve. This striking qualitative similarity between the two independent physical parameters n and E''/E' suggests very strongly that a quantitative relationship should be obtainable without reference to specific molecular models. Indeed, a quantitative relationship can be readily obtained starting from an equation given by Zener[12] and combining it with the Nutting equation. Zener showed that the following equation relates the dissipation coefficient to the stress relaxation function:

$$E''/E' \doteq -\pi/2(d \ln\sigma/d \ln t), \qquad (3)$$

where E' and E'' are the real and imaginary part of the complex modulus E^* ($E^* = E' + iE''$). This relationship only presupposes the validity of the Boltzmann superposition principle. If the further assumption is made that the stress relaxation function $\sigma(t)$ and the creep function $\epsilon(t)$ obey the relation

$$\epsilon(t) = 1/\sigma(t), \qquad (4)$$

then

$$\frac{d \ln\sigma}{d \ln t} = -\frac{d \ln\epsilon}{d \ln t}. \qquad (5)$$

Equation (3) can then be written as

$$\frac{E''}{E'} \doteq \frac{\pi}{2}\frac{d \ln\epsilon}{d \ln t}. \qquad (6)$$

Putting Eq. (1) into logarithmic form and differentiating with respect to time gives

$$d \ln\epsilon/d \ln t = n. \qquad (7)$$

Combining (7) and (6) gives the desired relationship between n and the dynamic dissipation factor

$$n \doteq 2E''/\pi E'. \qquad (8)$$

How closely this relationship agrees with the experimental data can be seen from Fig. 5 where the dissipa-

[12] C. Zener, *Elasticity and Anelasticity of Metals* (The University of Chicago Press, Chicago), p. 54; also T. S. Kê, Phys. Rev. **71**, 533 (1947).

tion factors—given in Table I—have been converted into n values. (The dynamic dissipation factors have been reported previously;[9] for the tricresyl phosphate-polyvinyl chloride compositions E''/E' has been corrected to take into account small differences in plasticizer concentration between the specimens used in creep and dissipation factor measurements.) Similarly, a close correlation can be obtained between the dynamic shear modulus (E^*) and the 5 or 10 second modulus calculated from a creep curve, as can be seen from Fig. 6.† This means then that the constant ψ of the Nutting equation is proportional to the reciprocal dynamic modulus for these and similar polymeric compositions. It is possible, therefore, to calculate with reasonable accuracy the complete creep curve from dynamic mechanical data or vice versa, provided the relationships given above are fulfilled.

It was pointed out above that the product of creep function and the stress relaxation function must be equal to one, in order for Eq. (8) to hold. It has been shown that this is at least approximately so for many polymeric compositions.[13,14] However, this condition does not hold in all cases: The creep of polystyrene above its second order transition temperature is an example of this (see also Fig. 4). Whenever the creep function contains a large amount of nonrecoverable deformation, Eq. (8) can only be valid for that part of the creep function which is identical with the stress-relaxation or recovery function.[14]

THE DIMENSIONAL ANALYSIS OF THE NUTTING EQUATION

One of the most serious objections to the Nutting equation is based on the fact that the use of the fractional and variable exponent n results in the constant ψ having variable dimensions, as the dimensions of ϵ, σ, and t are fixed. Although Scott Blair[15] has argued that the use of constants of variable dimensions is justified from various points of view, it would be most desirable to give a satisfactory explanation of this fact within the framework of classical physics which requires that the dimensions of physical parameters remain constant. Using the complex dynamic modulus E^* it is possible to understand the variations in dimensions of ψ.

Let us assume that the creep function $\epsilon(t)$ is given by the following equation (assuming $\beta = 1$)

$$\epsilon = \frac{\sigma}{E^*} = \frac{\sigma}{E' + iE''}. \tag{9}$$

It can be shown that $E'' = \omega\eta = 2\pi\eta/t$. Inserting this

† The modulus scales in Fig. 6 are shifted slightly because the time scale in the two experiments is not the same; however, the shapes of the curves are almost identical over an extended temperature region.

[13] H. Leaderman, *Elastic and Creep Properties of Filamentous Materials* (Textile Foundation, Washington, 1943).
[14] Buchdahl, Nielsen, and Merz, J. Polymer Sci. **6**, 404 (1951).
[15] G. E. Scott Blair, *A Survey of General and Applied Rheology* (Pitman Publishing Corporation, New York, 1944), p. 145.

expression into (9) gives

$$\epsilon = \frac{\sigma}{E' + (2\pi\eta)/t} = \frac{\sigma t}{E't + 2\pi\eta}. \tag{9a}$$

As long as $E'' \ll E'$, the second term in the denominator can be neglected with respect to the first one and one obtains

$$\epsilon \simeq \sigma/E'. \tag{10}$$

This is the one limiting case of the Nutting equation corresponding to t^0 and $\psi \simeq 1/E'$. If $E'' \gg E'$ the first term in the denominator can be neglected, one obtains

$$\epsilon = \sigma t/2\pi\eta. \tag{11}$$

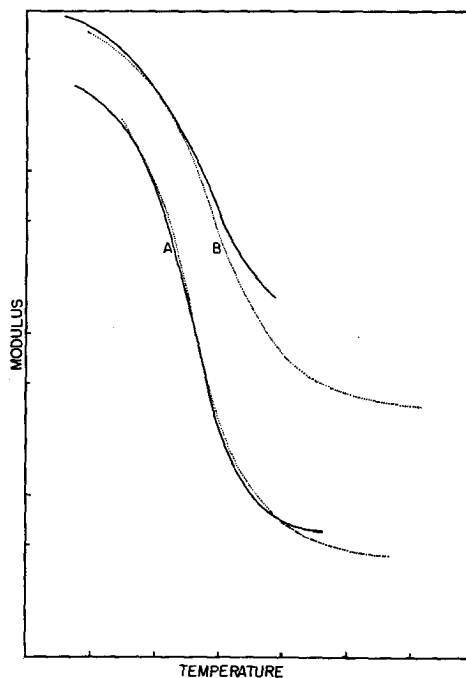This is the other limiting case of the Nutting equation

FIG. 6. Comparison between dynamic modulus and 5 second creep modulus.

corresponding to t^1 and $\psi \simeq 1/2\pi\eta$. In many cases—as for example in the transition region of all polymeric substances—E'' cannot be neglected with respect to E', or vice versa. One must, therefore, retain in the intermediate range, when n lies between 0 and 1, the complex modulus. The intensity of E^* is given by $|E| = (E'^2 + E''^2)^{\frac{1}{2}}$ whereas the contribution of time (t) to $|E|$ is proportional to $\sin\phi$ which is equal to E''/E^* (see Fig. 7). It will be recognized that the limiting cases of $\sin\phi = \{^0_1\}$ correspond to the limiting cases of the Nutting equation. Equation (9) in terms of real quantities takes the form (always assuming $\beta = 1$)

$$\epsilon \simeq \frac{\sigma t^{\sin\phi}}{(E'^2 + E''^2)^{\frac{1}{2}}} = \frac{\sigma t^{E''/E^*}}{(E'^2 + E''^2)^{\frac{1}{2}}}. \tag{12}$$
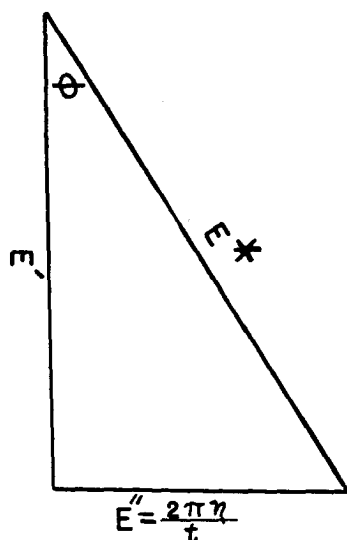
FIG. 7. Relationship between E^*, E', and E''.

As no objection can be raised against Eq. (9) on the basis of dimensional analysis, Eq. (12) should be dimensionally correct also since [time] is still partly tied up in the denominator to balance out the exponent in the numerator in either equation.

Comparing (12) with (2), it follows that

$$n \simeq E''/|E^*| \tag{13}$$

and

$$\psi \simeq \frac{1}{(E'^2 + E''^2)^{\frac{1}{2}}}. \tag{14}$$

Two equations (8) and (13) have been given to relate "n" with dynamic mechanical quantities. There is a significant difference between the two expressions: $E''/(E^*)$ varies between 0 and 1 whereas E''/E' varies between 0 and ∞. Equation (8) should not be used to calculate n for large values of E''/E' because no experimental data are known where n becomes larger than one (it certainly never does approach infinity). Using $E''/(E^*)$ to calculate n does not give a good quantitative agreement with the data given in Table I and Fig. 5. In evaluating a large number of creep curves, it was found that n never exceeded 0.7 unless the deformation was predominantly a purely viscous one, $n \rightarrow 1$. It seems reasonable, therefore, to introduce a limiting upper value for the parameter n which in combination with $E''/(E^*)$ gives satisfactory agreement with experimental data.

$$\epsilon \simeq \frac{\sigma t^{2E''/\pi|E^*|}}{(E'^2 + E''^2)^{\frac{1}{2}}}, \tag{15}$$

where $n = 2E''/\pi|E^*|$. This expression for n is the same as derived above on the basis of Zener's equation except that E' is replaced by $|E^*|$.

THE COEFFICIENT β AND THE EFFECT OF STRESS ON n

The Nutting equation contains a coefficient β which so far has been assumed to be equal to one. In reality deviations from the value $\beta = 1$ are quite frequent; for the polyvinyl chloride composition given above the average value of β is about 0.80 and does not seem to vary in a systematic manner with temperature. For polystyrene the compliance $\{\epsilon(t)/\sigma = J(t)\}$ is also a function of the stress (14). It is well known that in the study of flow curves ($d\epsilon/dt =$ constant) one observes very frequently a shear dependence which is characteristic of non-newtonian fluids. In recent publications[16] Scheele and collaborators have tried to show that β goes through a maximum in the transition region similar to n; except that in the latter case β approaches a value of one at either side of the maximum. It is, however, questionable that creep data below the second-order transition temperature can be correctly represented by a constant creep rate in view of the data presented in this paper. (According to the Nutting equation $(d\epsilon/dt) \sim nt^{n-1}$ which implies a variable rate of shear unless $n \sim 1$; see also the paper by A. Smekal.[17]) The stress dependence of the creep rate has been studied by Findley[18] and Sauer[19] for polystyrene at temperatures well below the second order transition temperature. The results obtained by these investigators show that β varies between 0.5 and 1.3 depending on the stress; the problem is very similar in its complexity to phenomena of strain-hardening in metals.

Very little is known about the stress dependence of n or $E''/(E^*)$. Unpublished data obtained by one of us (L.N.) indicates that on the low temperature side of the transition the dissipation coefficient is rather insensitive to stress variations at low stress levels. However, in the transition region the dissipation factor increases with increasing stress rather markedly. One would, therefore, expect an analogous behavior for n. However, such data as are available are not precise enough to determine with certainty whether or not this is so, although on the basis of Sauer's data[19] at room temperature and tensile creep measurements in the transition region at large and small stresses it would appear that the analogy carries over.

THE PHYSICAL INTERPRETATION OF n

Although the details of the relationship between n and the dissipation factor will, most likely, require certain modifications, there can be no doubt about the basic interdependence of these quantities. Kuhn[20] and Tobolsky[21] showed, some time ago, that for materials

[16] Scheele and Timm, Kolloid Z. 116, 129 (1950); Kolloid Z. 120, 103 (1951).
[17] A. Smekal, Kolloid Z. 116, 112 (1951).
[18] W. N. Findley, J. Appl. Phys. 21, 258 (1950).
[19] Sauer, Marion, and Hsiao, J. Appl. Phys. 20, 507 (1949).
[20] Kuhn, Kunzle, and Preissmann, Helv. Chem. Acta 30, 307, 464 (1947).
[21] B. A. Dunell and A. V. Tobolsky, J. Chem. Phys. 17, 1001 (1949).

in the rubbery state the creep and stress relaxation functions can be reasonably well approximated from dynamic mechanical data. The work of Zener and Kê,[13] in particular, has shown that a very good quantitative agreement can be obtained between measured and calculated stress relaxation and creep function in the case of metallic compounds. The results of this investigation show that this relationship between the essential parameter of the creep function (in terms of the Nutting equation) and the dissipation factor remains essentially the same whether a polymeric composition is a rigid high modulus solid, a soft low modulus rubber, or in between these two "states." It is therefore justified to postulate that for solids, in general, the creep function and the dissipation coefficient are manifestations of the same molecular processes. It is understood that transverse or intercrystalline thermal currents[13] which can make a very slight contribution to the dissipation factor will not be effective in the creep function. It follows then that the process or processes responsible for these phenomena should not be interpreted in terms of specific molecular models. For example, the creep function of polyvinyl chloride compositions is the same as that for platinum,[22] although the molecular structure of the two systems is certainly very different. Another example, along the same lines, is the interpretation of creep measurements of styrene-butadiene copolymers in terms of the molecular structure parameters as shown in Table II. A good qualitative correlation between n and the amount of permanent gel content (due to chemical crosslinking) is immediately apparent; n is influenced also by the semipermanent gel-content, as is shown by the data on polystyrene, but this is not measurable by swelling experiments. At first sight it appears reasonable to interpret n in terms of the gel structure of a rubber; however, rubber gels are certainly not the only molecular structures which give these particular creep functions. Therefore, the specific model of a rubber gel—a network consisting of carbon-carbon chains of essentially free rotation and held together at certain points by primary valence forces—should not be used as the basis of a theory of the time dependence of viscoelastic deformation.

[22] R. P. Carreber, J. Appl. Phys. **21**, 1289 (1950).

TABLE II. n and ψ as a function of molecular properties of styrene-butadiene copolymers.

Material	n	ψ (10 sec)	% gel	Swelling index	$[\eta]$ of sol fraction
1	0.600	9.4×10^{-7}	0		0.612
2	0.410	1.6×10^{-6}	0.5–1.0	140	1.530
3	0.432	1.6×10^{-6}	8.2	150	1.774
4	0.347	7.5×10^{-7}	66.6	65.8	0.639
5	0.350	1.7×10^{-6}	52.3	34.8	1.380
6	0.262	1.1×10^{-6}	78.5	27.4	0.328
7	0.242	8×10^{-7}	80.9	25.9	0.578

The dissipation factor measures the ratio of dissipation of energy to the total stored energy when a solid is subject to stress (or strain). The proportionality between the creep function and the dissipation factor means, therefore, that the creep function at any temperature is a measure of energy losses during a deformation process. The deformation of a solid is a cooperative phenomena, in the sense that it involves the simultaneous displacement of a large number of molecules and the degree to which this process takes place as a cooperative phenomena is reflected by the value n or $E''/|E^*|$. The upper limit of n corresponds to a deformation process where all the stored energy is being dissipated into kinetic energy of individual molecules, whereas the lower limit would correspond to a deformation process where no dissipation of energy is possible (perfectly ideal crystal). The parameter "ψ" measures the intensity of the deformation and is therefore primarily determined by the configuration and forces between the molecular units of the material. The dissipation factor $E''/|E^*|$ or n, on the other hand, depends primarily on the state of aggregation, i.e., the size and interaction of domains or clusters—which might or might not be crystalline. A comparison of the temperature dependence of the two parameters—ψ and n—illustrates the point. ψ is either some exponential function of T (when $n \to 1$) or only very slightly dependent on T (when $n \to 0$), whereas the temperature dependence of n is entirely different. It is in a transition region that n changes markedly with temperature; i.e., in regions where the state of aggregation undergoes a profound change.