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# Cold Flow in High-Impact Polystyrene

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## Synopsis

Eyring's theory of viscous flow has been applied to some mechanical properties of rubber-modified polystyrenes. Yield strengths as a function of orientation, temperature, and rate of strain have been shown to be consistent with the theory. The temperature of transition from ductile to brittle fracture as a function of orientation has also been measured and found to be consistent with theoretical predictions.


## INTRODUCTION

Only recently has the suggestion been made that rubber-modified polystyrenes achieve their resistance to impact in any way other than by calling upon the rubber to glue together minute fragments of a glassy matrix. Newman and Strella[1] have recently suggested that cold drawing in the glassy matrix is the mechanism by which high-impact polystyrenes achieve their desired property. A counterproposal was then made by Bucknall and Smith,[2] in which they postulated the generation of myriad craze planes. Since it is known that craze planes are matter-filled,[3,4] presumably with oriented threads, both of the above mechanisms propose a flow of the hard matrix material.

It is known that the rubbery inclusions in high-impact polystyrenes do not of themselves contribute significantly to the observed mechanical strengths.[1] Thus, their role must be something other than tensile reinforcement. The most striking feature of high-impact polystyrene is its high elongation relative to unmodified material, and it would seem reasonable to try to define the role of the rubber particles with respect to this property. In light of the mechanism proposed by Bucknall and Smith,[2] we can associate at least one craze plane with each particle. Based on the material content of a polystyrene craze as measured by Kambour,[4] one can calculate an extension of the craze matter of some 70%. Thus, an overall extension of 30% is well within reason as long as the small crazes maintain their integrity. Thus for the purposes of this paper we will ignore the force contribution of the rubbery inclusion but consider them as nuclei around which the cold-flow process occurs.

If we accept the idea of flow in the hard matrix then we should be able to derive an equation governing the mechanical behavior of these materials. Eyring's theory of viscous flow[5] has already been applied to the cold drawing of polycarbonates[6] with reasonable success. Therefore, it would be appropriate to try the same theory in the present case. Eyring's theory presents the additional benefit of facilitating the inclusion of orientation in the analysis.

Since most of the experimental work described here was performed under cantilever impact conditions, we must inquire as to the effect of this technique on the interpretation of the data. A cantilever experiment imposes a stress gradient on the sample in two dimensions with a maximum stress at the surface of the sample at the fixed support diminishing in both directions. If we consider the yield strength to be the force at the onset of craze formation, then it is possible to calculate the maximum stress condition from standard cantilever theory. The assumption here is that the sample behaves elastically up to the point of craze formation.

In dealing with orientation phenomena the use of a cantilever test is actually an advantage since we are dealing mainly with the conditions which exist at the sample skin. Hence even such a nonuniformly oriented material as an injection-molded sample may be treated, provided we have a reasonable estimate of skin orientation.

## THEORY

Eyring's theory of viscous flow can be represented by eq. (1):[7]

$$V_0 = 2aK\ (kT/h)\ \exp\left\{-\Delta\tilde{G}^{\ddagger}/RT\right\}\ \sinh\ (aF/2\delta nkT) \qquad (1)$$

where $V_0$ is the net material flow velocity, $a$ is the distance a flow unit must move to the next lattice site, $K$ is the rate theory transmission coefficient, $k$ is Boltzmann's constant, $T$ is absolute temperature, $h$ is Planck's constant, $\Delta\tilde{G}^{\ddagger}$ is the Gibbs free energy of activation for flow, $R$ is the gas constant, $F$ is tensile force, and $\delta$ is the distance between layers of flow units. The equation as given provides three tests of flow behavior provided independence for the proper variable can be achieved. In particular, from eq. (1) we can derive the functional dependence of force on velocity, force on temperature, and velocity on temperature. The first two tests can be reasonably achieved by measuring yield forces as a function of temperature and velocity. The third test was not attempted, due to velocity limitations of the pendulum.

If we consider the variables $a$ and $\delta$ to measure the shape of the flow unit in Eyring's theory we have a possible handle by which to evaluate the influence of orientation on some of the mechanical properties of high impact polystyrenes. Let us assume that the flow unit deforms under constant volume conditions in the same ratios as the bulk material. Thus, if the bulk material has a one-dimensional extension ratio $\epsilon$, the deformed parameters of the flow unit will be the following,

$$a(\text{oriented}) = \epsilon a\ (\text{unoriented})$$

$$\delta\ (\text{oriented}) = (1/\epsilon)^{1/2}\delta\ (\text{unoriented})$$

Since $a$ and $\delta$ are usually assumed to be equal in liquids,[7] we will choose the same condition for the unoriented state of the glassy polymer. Further, since $a\delta^2 = 1/n$, we have the following equation:

$$V_0 = 2\epsilon(1/n)^{1/3}K\ (kT/h)\exp\{-\Delta\tilde{G}^{\ddagger}/RT\}\ \exp\{\epsilon^{3/2}F/2nkT\} \qquad (2)$$

The hyperbolic sine term can be replaced with the exponential because of the large values of the argument ($\epsilon^{3/2}F/2nkT$) which are involved.

Equation (2) provides three additional tests which may be used to check the feasibility of both the cold flow hypothesis and the orientation hypothesis. Force as a function of orientation is one obvious test; temperature as a function of orientation will be used in relation to fracture mode, which will be discussed more fully later. The third test (velocity versus orientation) was not tried, again due to the limited range of the pendulum.

In attempting to apply Eyring's theory it will be useful to consider in some detail the model being invoked. High-impact polystyrenes are dispersions of discrete soft particles in a glassy matrix. Under applied stress these soft particles behave as stress concentration points or nuclei for craze formation. Thus, the mechanism for initiation of crazes is obvious. The mechanism of craze growth is quite another matter; Spurr and Niegisch[3] consider it to be a highly localized yielding or a special ductile flow. This is the mechanism which will be invoked here as a basis for considering multiple craze formation to be an activated flow process.

## EXPERIMENTAL

With the exception of the data of Strella[11] all measurements were made on an ABS material containing 13.5% rubber. The material was molded into impact bars under a variety of molding conditions to control orientation (Table I). The samples were then broken under impact conditions by

TABLE I
Orientation of Molded Bars

| Temperature, °F. | Ram pressure $\times 10^{-3}$, psi | Core orientation | Skin orientation |
|---|---|---|---|
| 585 | 6 | 1.05 | 1.09 |
| 585 | 9 | 1.06 | 1.11 |
| 535 | 6 | 1.11 | 1.14 |
| 535 | 9 | 1.13 | 1.19 |
| 535 | 12 | 1.09 | 1.15 |
| 485 | 9 | 1.12 | 1.20 |
| 485 | 12 | 1.15 | 1.25 |
| 485 | 15 | 1.18 | 1.30 |
| 435 | 12 | 1.17 | 1.30 |
| 435 | 18 | 1.26 | 1.51 |
| 385 | 18 | 1.33 | 1.69 |
| 385 | Compression | 1.0 | 1.0 |

using an instrumented pendulum and temperature control system previously described.[8] The arm speed was maintained at 20 ft./sec.

## Cantilever Impact Test

The cantilever impact test is a simple test to run, and, because of the speed with which it can be performed, it lends itself to greatly simplified testing procedures, particularly when temperature is a variable.[3] Another unique feature of the cantilever test is that the mechanics of bending place the point of maximum tensile stress at the surface of the sample. The main objection to surface-based measurements is that surfaces are prone to mechanical imperfections which markedly reduce the apparent strength of the material. However, Balazs and Cheesbro[9] have shown that the introduction of notches and holes into rubber-modified polystyrenes does not reduce tensile strengths; rather, their data indicate a slight increase in strength. Consequently, evaluation of data from the cantilever test can and should be based on the conditions at the point of maximum stress, i.e., the surface. It was this consideration which suggested that injection-molded test samples would be suitable, even though orientation is a variable quantity throughout an injection-molded piece.[10]

Equation (2) can also be reduced to a group of semiempirical equations which could be useful in predicting generalized behavior of rubber modified polystyrenes. Reduction of eq. (2) is facilitated by the extreme insensitivity of those factors in the exponential term on the pre-exponential factors. Equations (3) show the general relationships to be expected in the four cases described in this paper.

$$F \approx C_1 T + C_2 \tag{3a}$$

$$F \approx C_1/s\epsilon^{3/2} \tag{3b}$$

$$F = C_1 \ln V_0 + C_2 \tag{3c}$$

$$T \approx C_1\epsilon^{3/2} + C_2 \tag{3d}$$

Here, $s$ is the stress concentration factor.

## Evaluation of Factors in Equation (2)

The factors in eq. (2) can be divided into three categories: (*1*) universal constants ($K$, $k$, $h$, and $R$); (*2*) sample parameters ($n$ and $\Delta\tilde{G}^{\ddagger}$), (*3*) test values ($V_0$, $T$, $\epsilon$, and $F$). In group *1*, $K$ was chosen to be $^1/_2$ in keeping with the usual rate theory value.

In group *2*, $n$ could not be evaluated outside the context of the theory; therefore it was necessary to use it as an adjustable parameter, keeping in mind the necessity of having a value which reflects the molecular character of the flow. On the other hand, $\Delta\tilde{G}^{\ddagger}$ can be estimated on the basis of independent measurements. In small molecule viscosities it has been found that $\Delta\tilde{G}^\ddagger = \Delta\tilde{U}/2.45$,[7] where $\Delta\tilde{U}$ is the energy (not enthalpy) of vaporization. In high polymer parlance the same intermolecular binding energy is evaluated in the cohesive energy density (CED); therefore we substituted

$$\Delta\tilde{G}^\ddagger = (\mathrm{CED}/2.45)\ (N/n)$$

where $N$ is the number of flow units per cubic centimeter.

Group 3 at first glance seems to be straightforward in its interpretation, but this is definitely not the case. The temperature is probably the least equivocal of the factors in this group, but even here the high-speed nature of the test necessitates an assumption regarding the actual temperatures involved. The initial temperature is probably good for yield strength values, since very little work is involved in achieving yield conditions and it is distributed over a relatively large volume of material. The fracture mode determination is another matter. However, here it was necessary to evaluate another parameter (effective force) which negates any meaning of modified temperature factors.

The velocity ($V_0$) is interpretable provided a mechanism is known for the overall elongation. Based on the considerations put forth in the introduction we can postulate three mechanisms of drawing. The first mechanism would be a general drawing of the whole matrix, second would be a simultaneous generation of a large number of crazes, and third would be a consecutive generation of craze planes.

Based on cantilever theory for elastic members[12] we can derive for mechanisms one and two the equation:

$$V_0 = 3Vd\ \Delta x/2l^2 \tag{4}$$

where $\Delta x$ is the distance unit on which flow velocity would be based, $V$ is the pendulum arm speed, $d$ is the cantilever sample width, and $l$ is the active length of the cantilever sample. For a general cold flow, $\Delta x$ would be the length of the flow unit (i.e., $\epsilon(1/n)^{1/3}$), whereas for the simultaneous generation of multiple crazes $\Delta x$ would be the average distance between craze planes in the direction of the applied strain.

For the case of consecutive craze formation, the velocity $V_0$ is derived assuming that each craze experiences the full rate of material flow. Here the velocity is just the pendulum velocity $V$ corrected by a lever arm factor, viz.,

$$V_0 = dV/2l \tag{5}$$

Regardless of the actual mechanism of cold flow, this latter relationship should be used in fracture mode interpretations.

The force $F$ is simply obtained from cantilever theory[12] as

$$F = 6Wl/bd^2 \tag{6}$$

where $W$ is the measured force from the pendulum test, and $b$ and $d$ are cantilever sample thickness and width, respectively.

One more factor which must be included is the stress-concentrating effect of the rubber inclusions and the reduced cross section of the load-bearing matrix; thus

$$F = 6sWl/\bar{A}bd^2 \tag{7}$$

where $\bar{A}$ is the fractional cross-sectional area of glassy material in the sample. On taking the stress concentration for a spherical void in an infinite matrix, a value for $s$ of 2.1 can be obtained.[13]

The orientation $\epsilon$ was measured directly for all injection-molding conditions. Since the initial mechanical response in all cases occurs at the skin, the skin orientation was used as the independent variable. This measurement was achieved by slicing the edges from injection-molded bars (see Fig. 1) and annealing for 3 hr. at 120°C. $\epsilon$ was then calculated from the retraction of the central bar and the curvature generated on the edges.

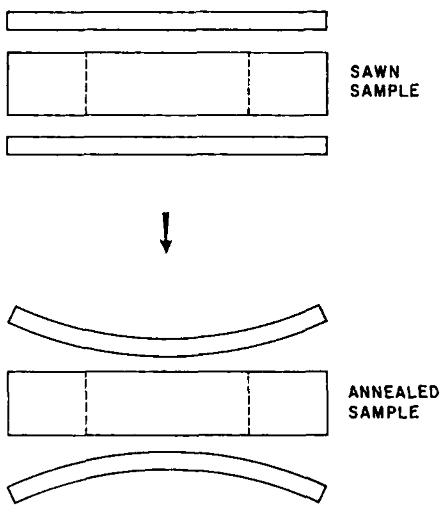


Fig. 1. Measurement of orientation in injection-molded samples.

## RESULTS

As mentioned in the previous section there are three possible mechanisms from which one might attempt to analyze the behavior of rubber-modified polystyrene. Unfortunately the only criterion available in this treatment by which to judge the merit of the three mechanisms is the order of magnitude of $n$. The criterion completely fails to discriminate among the possibilities. The value of $n$ changes by less than a factor of three even though the calculated local flow velocity for the three mechanisms is as widely divergent as seven orders of magnitude.

With a pendulum arm speed of 20 ft./sec., the values of $V_0$ for consecutive craze formation, simultaneous craze formation, and general flow are 1.7 $\times$ $10^2$, 6 $\times$ $10^{-2}$, and 1.8 $\times$ $10^{-5}$ cm./sec., respectively. For the data for

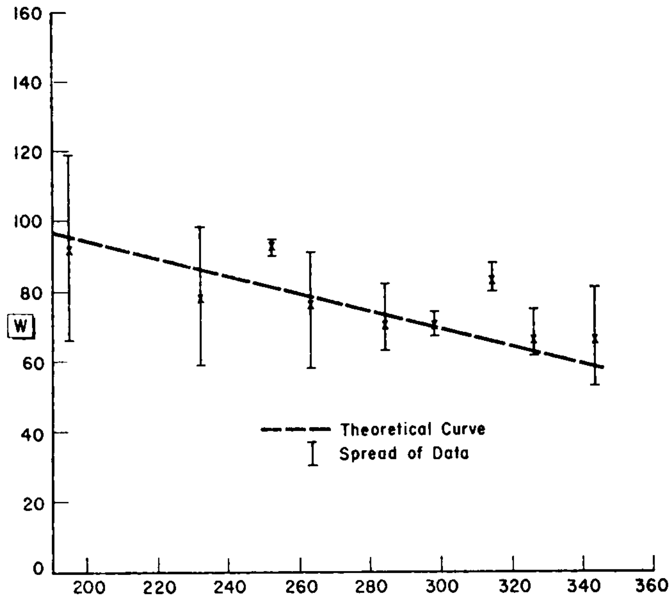


Fig. 2. Yield force on cantilever test samples as a function of temperature; $\epsilon = 1.0$.

yield strength at 25°C. and $\epsilon = 1.0$, the above velocities give values for $n$ of $3.5 \times 10^{21}$, $1.6 \times 10^{21}$, and $1.3 \times 10^{21}$ units/cc., which correspond to flow units containing 5, 11, and 13 carbon atoms. Thus, any one of the mechanisms would provide an intuitively reasonable flow unit.

For any of the above values for $n$ the theoretical curves of Figures 2 and 3 can be calculated. Yield strength versus temperature for $\epsilon = 1.0$ shows very good agreement. Yield strength versus orientation is not nearly so good; however, two influences have not been included in the theoretical treatment. The first of these is rubber particle distortion.[14] It would be expected that under injection-molding conditions the rubber particles would be deformed into prolate spheroids with a resultant lowering of the stress-concentration factor. The main effect here is to increase the observed average force at high orientations. The second factor is the thermal history of the samples. The molding conditions given in Table I show that the low orientation samples were prepared at relatively high temperatures. In addition, relatively rapid thermal cycling was used to freeze in the orientation achieved. The high temperatures and rapid cycling cause a change in the free volume of the matrix material, which change diminishes with decreasing molding temperature. This effect could account for the lowering of yield forces at low degrees of orientation through a change in the size of the average flow unit.

Figure 4 is a graphical representation of the fracture mode observed in the material. The change in fracture mode was assessed by observing the stress–time curves obtained from the pendulum. The transition from

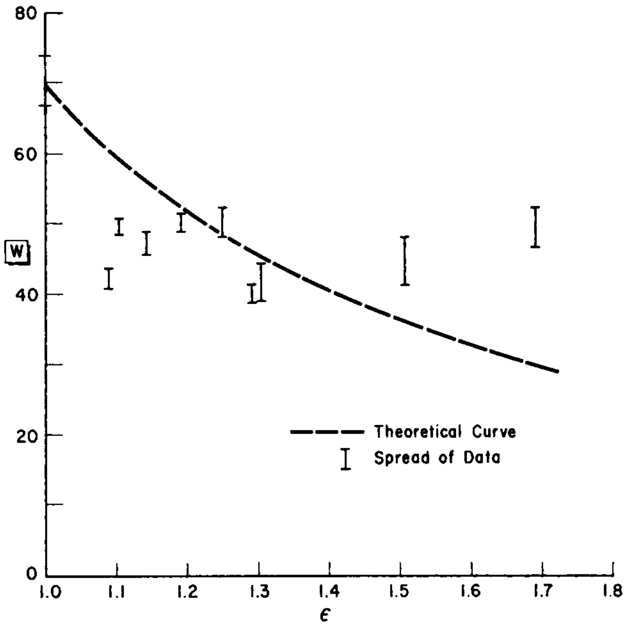


Fig. 3. Yield force on cantilever test samples as a function of skin orientation; $T$ = 298°C.

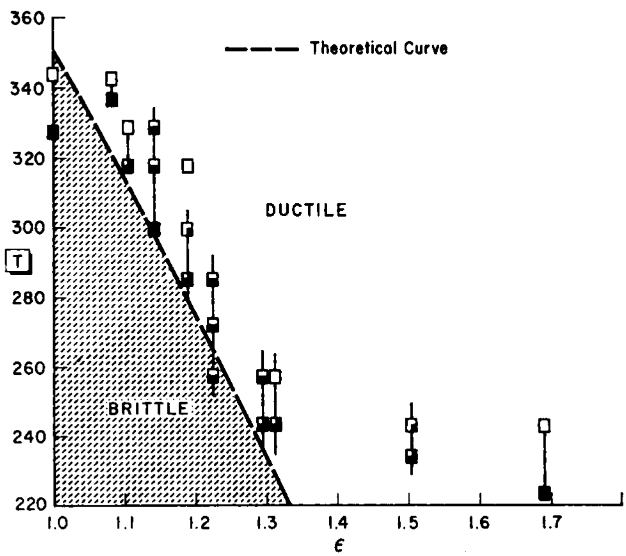


Fig. 4. Fracture mode behavior of injection-molded test samples. The fractional shading of each square indicates the fraction of samples which failed in a brittle manner under impact conditions.

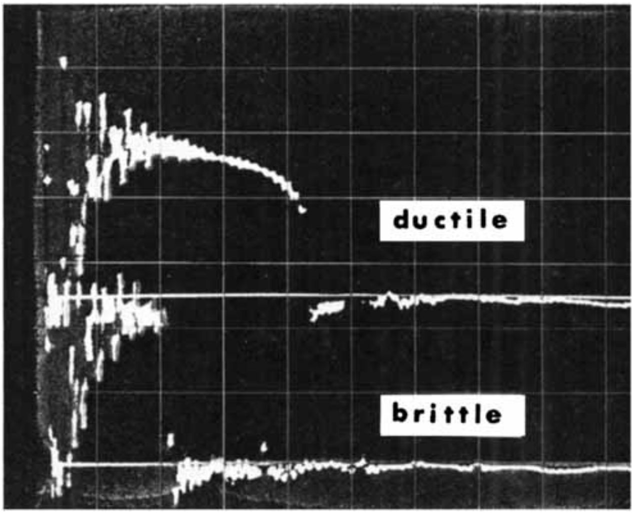


Fig. 5. Stress–time curves from impact tests demonstrating failure behavior.

ductile to brittle failure is reasonably sharp so that interpretation of the curves was minimal. It was assumed the transition would occur when the calculated flow velocity became less than the imposed velocity. In calculating the theoretical curve it was necessary to fit the data by adjusting $F$, since no value of the stress concentration factor was available from theory. The data were fit by a single value of $F$ with surprisingly good agreement.

In many of the samples tested for fracture mode a single crack propagation mechanism was observed, either slow (ductile) or fast (brittle). Figure 5 shows the results for one sample which apparently exhibited both mechanisms, as shown by the rounded shoulder and subsequent rapid force drop. This is particularly pertinent, since it suggests that under these particular conditions the more highly oriented skin facilitated ductile failure, in contrast to the brittle behavior of the core which is known to have a lower degree of orientation.

In attempting to use Strella's data[11] it was found that the parameter $A$ was unavailable; however this should remain constant for any given material and the functional relationship, $F = C_1 \ln V_0 + C_2$, should still obtain. Figure 6 shows this relationship, and the logarithmic nature of the response is evident.

## DISCUSSION

Throughout the course of this presentation it has been tacitly assumed that the mechanical properties of the rubbery inclusions did not contribute to the measured properties. It was shown by Newman and Strella[1] that in a typical composite material the contribution of the rubber phase to total impact strength is around 10%. Therefore, the analyses probably are no more inaccurate than 10% or so from this one source. When the temperature and velocity of the test conditions bring the rubber phase near its glass transition then there may be a marked change in response which will not agree with predictions. This is suggested in Figure 4 at low temperatures. At still lower temperatures the question becomes academic, since the system no longer shows a yield point nor in any way exhibits impact-resistant behavior.

It would appear from eq. (2) and the succeeding discussion that a great many adjustable parameters are involved. In a sense this is true, since some of the tests which can be derived from eq. (2) require data which are not readily attainable. For example, in the fracture mode experiment there is no direct measurement of the effective force at failure; hence the assumption of constancy was made, and a value for $F$ was calculated which best fit the data. In the case of the cantilever yield force experiment, all parameters except $n$ were readily available. Thus it was only necessary to fit the data at one point (25°C., $\epsilon = 1.0$) to achieve the functional agreement shown in Figures 2 and 3.

## CONCLUSIONS

Eyring's theory of viscous flow provides a convenient model from which to predict mechanical behavior patterns of rubber-modified polystyrenes.

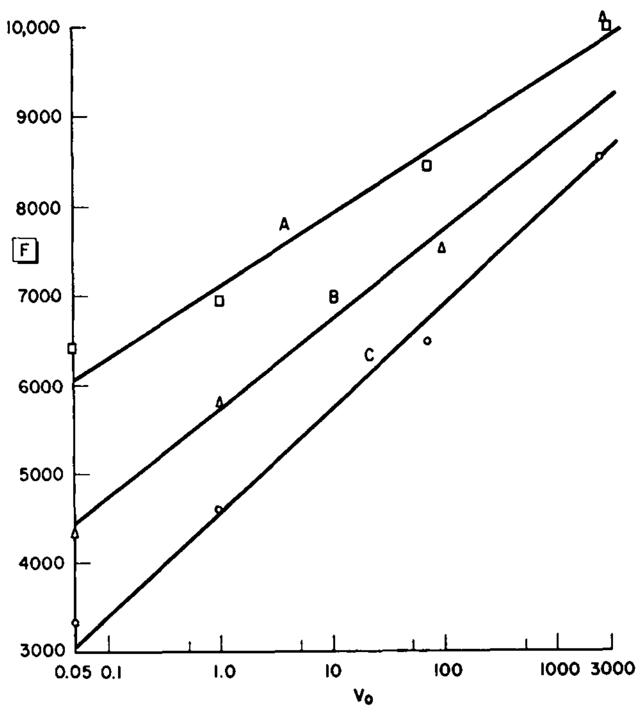


Fig. 6. Yield stress as a function of test velocity. Data from Strella.[11]

TABLE II
Data of Strella[11]

| Sample | Test speed, ft./min. | Yield force, psi |
|---|---|---|
| A | 0.05 | 6,400 |
| | 1.0 | 6,950 |
| | 70.0 | 8,450 |
| | 3000 | 10,000 |
| B | 0.05 | 4,340 |
| | 1.0 | 5,785 |
| | 97.0 | 7,550 |
| | 2900 | 10,000 |
| C | 0.05 | 3,320 |
| | 1.0 | 4,600 |
| | 74.0 | 6,480 |
| | 2500 | 8,550 |

When sufficient information is obtainable, a single arbitrary parameter must be evaluated in order to permit application of the derived equations. Orientation as a parameter can be treated in a fashion which will permit general trends and functional relationships against other mechanical parameters to be established.

No decision can be made as to the detailed mechanism of yield and cold drawing in rubber-modified polystyrenes, but the observed behavior is consistent with predictions based on the assumption of an activated flow process.

While the agreement between theory and experiment has been gratifying, it should be pointed out that the inherently poor precision of measurements of this type allow fairly large variations in some of the assumed parameters. Hence, any quantitative application of the treatment should be handled carefully.

I wish to thank John Wiley and Sons, Inc. for permission to reproduce data from reference 11.

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## Résumé

La théorie de Eyring pour l'écoulement visqueux a été apliquée à certaines propriétés mécaniques de polystyrènes modifiés avec du caoutchouc. Leurs tenacités en fonction de l'orientation, de la température et de la vitesse d'étirement, ont été montrées en accord avec la théorie. La température de transition d'une cassure ductile à une cassure fragile en fonction de l'orientation a également été mesurée et elle est également d'accord avec les prédictions théoriques.

## Zusammenfassung

Die Theorie des viskosen Fliessens von Eyring wurde auf einige mechanische Eigenschaften kautschukmodifizierter Polystyrole angewendet. Die Abhängigkeit der Elastizitätsgrenze von Orientierung, Temperatur und Verformungsgeschwindigkeit stand mit der Theorie in Übereinstimmung. Weiters wurde die Übergangstemperatur vom duktilen zum spröden Bruch als Funktion der Orientierung gemessen und mit den theoretischen Aussagen in Übereinstimmung befunden.

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