The Effect of Viscous Heating on the Observed Temperature Dependence of Mechanochemical Reactions

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Synopsis

The temperature dependence of mechanochemical reactions of high polymers is investigated in light of viscous dissipation in the flow field. The viscosity of the polymer melt is assumed to depend exponentially upon temperature, and the power-law model is used to describe the shear stress–shear rate relationship. Using equations previously reported in in the literature for the temperature profile generated in capillary flow, evidence that such an experimental system operates under decidedly nonisothermal conditions is presented. These equations, together with the classical Arrhenius equation for the temperature dependence of chemical reactions, predict that the average reaction rate in a capillary decreases, passes through a minimum, and increases as the capillary wall temperature is increased. Good agreement exists between the temperature at the minimum rate found in this work and that found experimentally for polystyrene, natural rubber, and polyisobutylene.

INTRODUCTION

It has long been realized that mechanochemical reactions differ from the usual types of chemical reactions in one important, and striking, manner: as the temperature *increases*, the rate of mechanochemical reactions appears to *decrease*. The purpose of this work is to show that this peculiar temperature dependence can be accounted for in a relatively straightforward way. This is done by using the classical Arrhenius dependence of rate on temperature, which predicts that the rate increases with temperature, and by recognizing that the temperature which the polymer sample senses under shear is neither uniform nor equal to the external temperature which is measured.

The quantitative evidence upon which this hypothesis is based will be presented only for reactions taking place in a capillary rheometer, although the analysis is not limited to this system.

History of the Negative Temperature Coefficient

In 1938, Busse published his studies on the mastication of natural rubber.[1] His article contained a plot, shown here as Figure 1, of the mastication efficiency versus mastication temperature. The minimum in this curve
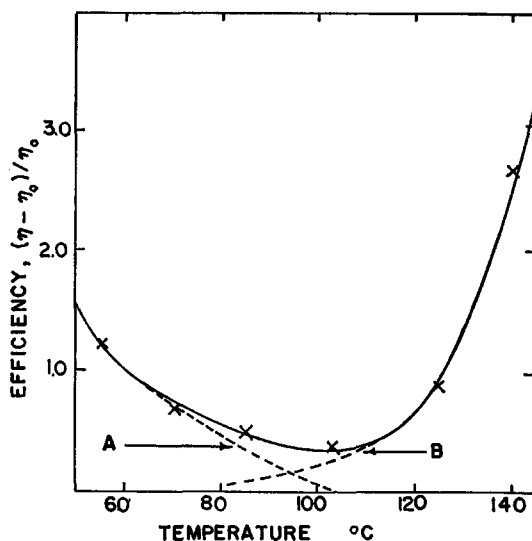
Fig. 1. Efficiency of rubber mastication with temperature.   After Busse.[1]

indicated a temperature at which bond breakage is effected with minimum efficiency.   Theorists, intrigued by the peculiar shape of this curve, were, and still are, unable to provide a single, comprehensive explanation for this anomalous behavior.

Kauzman and Eyring[2] in 1940 postulated that large molecules, caused to flow by high shear fields, undergo bond rupture due to mechanical forces alone.   This led to a dual-mechanism hypothesis to explain Busse's studies, attributing each portion of the curve in Figure 1 to a separate and distinct phenomenon.   According to this theory, at low temperatures, large stresses are developed in the fluid owing to its high viscosity, causing mechanical bond rupture.   Since the viscosity decreases with temperature, the degree of degradation is reduced as the shear strain is relieved at the molecular level.   This part of the theory is used to account for curve A of Figure 1 and explain the "negative temperature coefficient" which this curve indicates.

The right portion of Figure 1, curve B, is assumed to be the result of oxygen attack and follows the well-known Arrhenius equation for the temperature dependence of chemical reactions.   For natural rubber at and above 115°C, this oxidative mechanism is said to be predominantly responsible for cleavage.

This dual theory was supported by Piper and Scott[3] in 1947, who attributed curve A to mechanical effects and curve B to thermal-oxidative scission.   The investigation of Pike and Watson[4] added even more weight to Kauzman and Eyring's explanation of the peculiar temperature behavior of curve A in Figure 1.   This work seems to have firmly established the concept of the negative temperature coefficient in the minds of future investigators.

The results of experiments on the mastication of several synthetic polymers in the rubbery state were published by Ceresa and Watson[5] in 1959. They showed that polystyrene, poly(methyl methacrylate), poly(vinyl acetate), and poly(vinyl chloride) all exhibit the negative temperature coefficient of degradation over some temperature range.

From 1959 to the present, similar results have been found by a large number of workers for a wide variety of polymeric systems. The existence of the negative temperature coefficient seems to be unquestionably documented. In a recent review of mechanochemistry, Casale, Porter, and Johnson[6] state flatly: "The negative temperature coefficient is a prime criterion of a mechanochemical reaction."

The case for this paradoxical temperature behavior is not yet closed. Indeed, the entire concept of a degradation mechanism based upon mechanical forces alone in viscous flow should remain open to question. To prove this assertion, a theory will be presented which utilizes the concepts of viscous heating and temperature-dependent viscosity.

The analysis of mechanochemical reactions to be presented here is not the usual one based on molecular physical chemistry. Rather, these reactions are viewed simply as chemical ones, with the typical temperature dependence of such reactions. The purpose of the present work is to determine whether such a simple chemical mechanism is consistent with the observed behavior, not to develop a kinetic mechanism for the reaction at the molecular level. Such a distinction should be kept in mind. This investigation deals only with the temperature dependence of the rate equation. Other factors, including the site of the chemical reaction along the polymer chain and the concentration-dependent term in the rate expression, are not treated.

Nonisothermal Effects in Degradation Experiments

The physical properties of high polymers make it extremely difficult to perform shear experiments under isothermal conditions. Extremely high viscosity and low thermal conductivity conspire to produce significant viscous heating, even in the smallest of samples.

Frictional heating exists to some degree in all deformations of materials. For many fluids, both Newtonian and non-Newtonian, at low shear rates, the effects of viscous heating are inconsequential. The frictional heating phenomena, however, can be of great importance in the processing and fabrication of most polymeric materials. For example, Tadmor and Klein[7] have shown that the heat generated by this mechanism can be as much as 50% and more of the total heat required for melting in screw extrusion. Bolen and Colwell[8] and McKelvey[9] have also demonstrated the importance of viscous heating in dispersive mixing.

On the basis of this circumstantial evidence, it is surprising to find no analysis of the effects of viscous heating on the mechanism of mechanochemical reactions. If chemical reactions do take place under shear, the novice would intuitively expect them to have the same temperature de-

pendence as any other reaction. As the temperature increases, the chemical bonds should become more and more energetic, requiring less energy input to break the bond. Experimental evidence, however, appears to prove intuition wrong, at least for this class of reactions. Whether the same result still holds when the additional factor of viscous heating is included is the question to which this paper is addressed.

Probably one of the most important reasons why the problem of viscous heating has been ignored by mechanochemical experimenters is the extremely complex shear fields generated in the apparatus originally used to study the reactions. Most of the early work was done in devices such as the ball mill or Banbury mixer for which a quantitative analysis of the fluid flow is almost impossible. Although the shear rates are high and the heat generated can be significant, early workers in the field thermostated the exterior of the device and thereby tried to keep heat effects to a minimum.

With the advent of more modern experimental tools, such as the capillary rheometer and the Couette viscometer, mechanochemists have been able to quantify their results to an extent never before possible. These devices offer a great advantage over the ones previously mentioned in at least one respect: they generate well-defined shear fields. This advantage offers the opportunity to predict the effects of viscous dissipation.

Fluid mechanicians have been interested in the temperature profiles generated by such simple shear flows for several decades. Brinkman[10] and Bird[11] obtained solutions for temperature profiles in cases where viscous heating is important but where the temperature profile plays no part in determining the flow field. For many fluids, however, and most especially for polymeric materials, the viscosity is a very sensitive function of temperature. Hausenblas[12] presented velocity and temperature profiles for the flow of fluids with a hyperbolic dependence of viscosity on temperature.

The experiments of Bolen and Colwell demonstrated another interesting feature of flows with viscous heating: the existence of a maximum shear stress. As the shear rate is increased, the shear stress increases, passes through a maximum, and then starts to decrease. Hausenblas' solutions do not show this feature. However, if the viscosity is assumed to be an exponential function of temperature, the resulting equations do indeed predict the existence of a maximum shear stress. Kearsley[13] solved the equations for a Newtonian fluid with an exponential dependence of viscosity on temperature in capillary flow. Martin[14] investigated the case of a power-law fluid in the same flow system. Finally, Sukanek[15] showed that the temperature and velocity profiles for capillary flow are unique in the Brinkman number, which is a measure of the heat generated by dissipation to that removed by conduction. Sukanek and Laurence[16] have also solved the capillary flow problem with temperature-dependent thermal conductivity as well as viscosity, and they discuss many of the implications of the results. The plane and circular Couette flows of both Newtonian and power-law fluids with viscous heating and temperature-dependent viscosity were examined by Gavis and Laurence.[17,18] All of the above works show that

significant amounts of heat can be generated in simple shear flows. This has been demonstrated by Gerrard and Philippoff,[19] who studied, experimentally and theoretically, the capillary flow problem with an adiabatic wall and showed that in such a system temperature gradients across the capillary can exceed 150°F for a low-viscosity liquid.

Outline of the Present Work

In the present work, the effects of the heat generated by viscous dissipation on the rate of a chemical reaction in capillary flow are studied. The primary purpose is to determine how the external temperature, i.e., the temperature at the boundary of the experimental apparatus, influences the rate of reaction.

In the following section, the equations governing the variation of rate with external temperature are derived and solved. The next section gives the results of these calculations and discusses the implications of viscous heating on polymer degradation. The conclusion of the present study, together with a review of its limitations, are given thereafter. Finally, some recommendations for future studies of mechanochemical reactions are suggested in the concluding section.

MATHEMATICAL DEVELOPMENT

The Temperature Profile

The development of equations presented here is restricted to the case of capillary flow. Couette flows may be treated in a similar manner, the appropriate profiles having been developed by Gavis and Laurence.

Following Sukanek, these assumptions concerning the fluid are made:

1. Non-Newtonian flow behavior may be described by the familiar power-law relationship. The constitutive equation for such a fluid is[20]

$$\boldsymbol{\tau} = 2^{(1+n)/2} m \ (\mathbf{d}:\mathbf{d})^{-(1-n)/2} \mathbf{d} \tag{1}$$

where $\boldsymbol{\tau}$ is the shear stress; $\mathbf{d}$, the deformation rate; m, the consistency and n, the flow behavior index.

2. The consistency is an exponential function of temperature, and can be represented by an equation of the form:

$$m = m_0 \exp \ [-\ \beta \ (T \ - \ T_0)/T_0] \tag{2}$$

where β is an empirical constant and m_0 is the consistency at temperature T_0. This model predicts with good accuracy the consistency variation with temperature over a reasonable range for most polymeric systems. In reality, n is also a function of temperature, but not so sensitive as m. In this work, n is assumed constant.

Both of these assumptions are, of course, fairly restrictive. However, they do predict the behavior of real substances over fairly wide ranges of shear rate and temperature, and do not place stringent limitations on the applicability of the analysis.

Other assumptions of Sukanek's work include:

3. The flow system is at steady state.

4. Fourier's law can be used to describe the heat conduction process.

5. All physical properties, save consistency, are constant.

6. The wall temperature is a constant.

Using eqs. (1) and (2), the temperature profile (in dimensionless form) in capillary flow is found to be [15]

$$\theta = 2 \ln\left[\frac{C - \alpha}{c - \alpha x^{1/2\alpha}}\right] \tag{3}$$

where θ is the dimensionless temperature, β $(T - T_0)/nT_0$; x is the dimensionless radial distance, r/R; $\alpha = n/(6n + 2)$; and $C = -2(\alpha/K)$ $(P/2)^{2/n}$. The velocity profile is

$$U = \left(\frac{P}{2}\right)^{1/n} (C - \alpha)^2 \int_x^1 \frac{y^{1/n}\, dy}{[C - \alpha y^{1/2\alpha}]^2} \tag{4}$$

where U is the dimensionless axial velocity, v/V, with V the average velocity, and y is a dummy variable of integration.

The values of K and P are given by the equations

$$Br = \frac{1}{\alpha}\left(\frac{Br}{K}\right)^{n/(n+1)} - 2\left(\frac{Br}{K}\right)^{(n-1)/(n+1)}$$

$$K = \left(\frac{P}{2}\right)^{(n+1)/n} Br$$

where Br is the Brinkman $(\beta m_0 V^{n+1})/(nkT_0 R^{n-1})$; k is the thermal conductivity; T_0 is the wall temperature; and R is the capillary radius.

For Newtonian fluids $(n = 1)$, the temperature and velocity profiles take on a particularly simple form

$$\theta = 2 \ln\left[\frac{2 + Br}{2 + Brx^4}\right] \tag{5}$$

$$U = (2 + Br)\left\{\frac{1}{2 + Br} - \frac{x^2}{2 + Brx^4} + \frac{1}{\sqrt{2Br}} \tan^{-1}\left[\frac{\sqrt{2Br}\,(1 - x^2)}{2 + Brx^2}\right]\right\}. \tag{6}$$

Rate Equation Based on a Thermal Mechanism

To pursue the present hypothesis, namely that the rate equation for degradation is of the same form as that for any chemical reaction, a very simplified type of rate expression is assumed:

$$r = kf(c) \tag{7}$$

where r is the rate of formation (or disappearance) of some species by the reaction, k is the rate constant, and $f(c)$ is some arbitrary function of the concentration of the reacting species. This function, $f(c)$, is assumed to be constant across the capillary.

The purpose here is not to perform the usual kinetic study of the reaction rate to determine the mechanism and extent of conversion, but rather, merely to see what effect the wall temperature has on the rate itself. Therefore, assuming the usual Arrhenius temperature dependence of chemical reactions,

$$k = k_0 \exp{[- E/RT]} \tag{8}$$

where k_0 is the frequency factor, R is the gas constant, and E is the activation energy for reaction, eq. (7) can be rearranged to give

$$\phi \equiv \frac{r}{k_0 f(c)} = e^{-E/RT}. \tag{9}$$

This parameter ϕ is seen to be a measure of the effect of temperature on the rate of reaction.

Since the temperature changes continuously across the capillary, ϕ is a local value. To find the average rate, ϕ must be integrated across the cross section. For capillary flow, this average value is

$$2\psi \equiv \phi_{\mathrm{AV}} = \frac{\displaystyle\int_0^{2\pi}\int_0^1 x\phi(x)dxd\theta}{\displaystyle\int_0^{2\pi}\int_0^1 xdxd\theta} \tag{10}$$

Using eq. (9) and integrating the denominator

$$\psi = \int_0^1 x \exp{[- E/RT(x)]}dx. \tag{11}$$

The temperature variation has already been determined. Hence, from eq. (3) and the definition of θ,

$$\psi = \int_0^1 x \exp\left\{- (E/R)\left[T_0\left(1 + \frac{2n}{\beta}\ln\left[\frac{C - \alpha}{C - \alpha x^{1/2\alpha}}\right]\right)\right]^{-1}\right\} dx \tag{12}$$

A plot of ψ versus T_0 will now reveal how the average reaction rate in a capillary depends upon the temperature at the wall of the capillary. If the rate increases continuously with T_0, the concept of a negative temperature coefficient for mechanochemical reactions, as well as the concept of mechanically induced reactions, will be supported. On the other hand, if ψ passes through a minimum as T_0 increases, the idea of a separate, mechanically induced reaction mechanism would seem to warrant further scrutiny.

RESULTS AND DISCUSSION
The Magnitude of Temperature Variations

For concreteness in the present discussion, physical properties corresponding to real polymeric materials will be considered. Unfortunately, there have not been many degradation experiments reported in the literature in a well-defined capillary or Couette flow, the only systems for which the temperature profiles have been determined at this time.
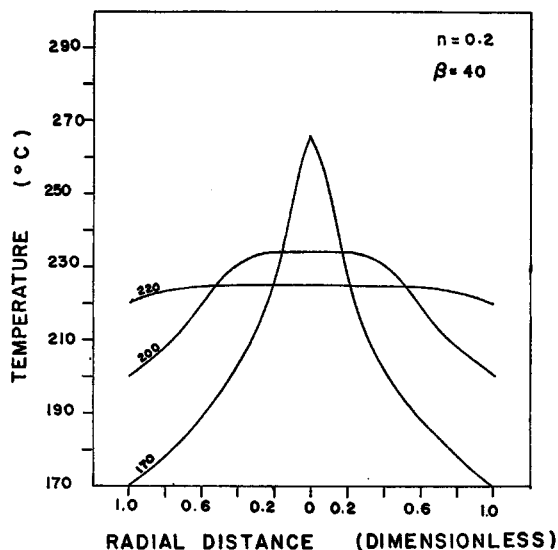
Fig. 2. Temperature profiles for power-law fluid. The power-law index n is 0.20 and $\beta = 40$.

One exception is the recent paper of Arisawa and Porter,[21] which presents data on the degradation of polystyrene during extrusion. An Instron capillary rheometer was used to establish known shear conditions at various temperatures. Capillaries of 0.020 and 0.030 in. in diameter were used, with L/D ratios on the order of 50 to 60, large enough to minimize entrance effects. The walls of the capillary were electrically heated and thermostated to remain at constant temperature. As is usual in experiments of this type, the small capillary diameter was assumed to ensure an isothermal system.

When the equations in the section on the temperature profile are applied to the system studied by Arisawa and Porter, the analysis predicts temperature profiles of the shape shown in Figure 2 for various values of the capillary wall temperature. The physical properties for polystyrene used in these calculations are given in Table I. The parameter β, which is the measure of the temperature sensitivity of the viscosity, is very important in this analysis. The values of β shown in Table I were found from temperature–viscosity data reported in the literature[23,24,27] and seem to represent a reasonable range for the polymers under discussion.

The effects of viscous heating are far more significant at low capillary wall temperatures than at the higher temperatures. The flow is decidedly nonisothermal, and huge temperature gradients can be established across the capillary radius. The profiles in Figure 2 were determined by assuming a power-law index n of 0.2. This is indicative of strong non-Newtonian behavior and is often a reasonable value for high polymers at high shear rates.

TABLE I

Physical and System Properties

A. Polystyrene[a]

k^{22} = 1.2 × 10⁴ g cal/sec³ °K

m^{21} = 2 × 10⁵ p at 497°K

$\beta^{23,24}$ = 30, 40 for T in °K

V = 10 cm/sec

D = 0.05 cm

E^{25} = 55,000 cal/mole

B. Rubber

k^{26} = 1.3 × 10⁴ g cal/sec³ °K

m^{23} = 1.37 × 10⁷ p at 353°K

β^{23} = 10, 15 for T in °K

V = 1 cm/sec

D = 0.05 cm

E^{25} = 56,000 cal/mole

C. Polyisobutylene

k = 1.2 × 10⁴ g cal/sec³ °K

m^{27} = 2.24 × 10⁹ p at T = 344.5°K

β^{27} = 15, 20 for T in °K

V = 0.1 cm/sec

D = 0.05 cm

E^{25} = 49,000 cal/mole

[a] The superscripts appearing in this table refer to the references, listed at the end of this paper, where the physical properties were obtained.

Another limit to the problem may be illustrated by using a value of n = 1.0, indicative of purely Newtonian flow behavior. The temperature profiles for this case are shown in Figure 3. The same values as were used in Figure 2 for all other physical properties were used here. For a Newtonian fluid, viscous heating is seen to be even more pronounced.

Note that in either case, Newtonian or power law, the maximum temperature in the capillary is achieved at the *lowest* wall temperature. This point is brought out more clearly in Figure 4, where the maximum (centerline) and bulk temperatures are plotted against the wall temperature for the Newtonian case. The bulk or cup-mixing temperature, T_b, is defined by

$$T_b = \frac{\int_0^{2\pi} \int_0^R v(r)\ T(r)\ rdrd\theta}{\int_0^{2\pi} \int_0^R v(r)\ rdrd\theta}.\qquad(13)$$

In terms of the dimensionless variables θ and U, this is

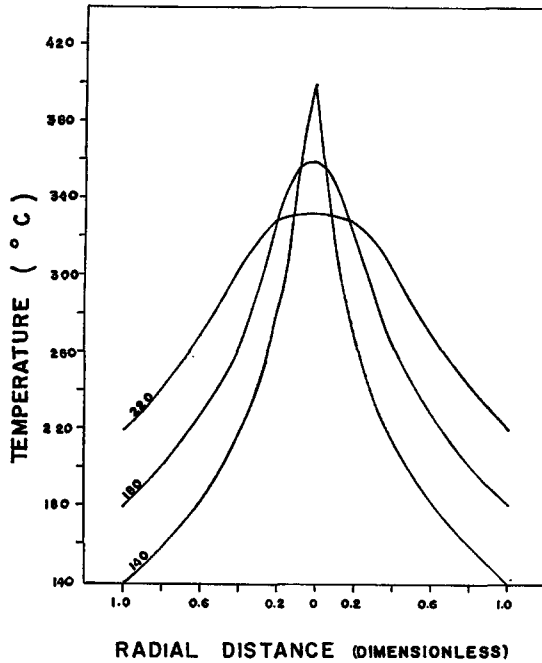$$\theta_b = \frac{\beta}{n}\frac{T_b - T_0}{T_0} = 2\int_0^1 U(x)\ \theta(x)\ x\ dx.\qquad(14)$$

Fig. 3. Temperature profiles for a Newtonian fluid; $\beta = 40$.

The bulk temperature is a convenient average temperature to use in the present discussion. It is the temperature that would be measured if the throughput from the capillary were collected and thoroughly mixed.

Figure 4 shows that as the wall temperature increases, the maximum and bulk temperatures decrease, pass through a minimum, and then approach the wall temperature. The temperature which the fluid senses is not equal to the wall temperature; and hence the wall temperature is not an accurate measure, at lower values, of the temperature in the interior of the capillary.

Figure 4 is based on a Newtonian fluid. However, the results will be qualitatively the same for a power-law fluid.

Porter and Arisawa performed several experiments in an effort to gauge the extent of degradation induced by purely thermal effects. They found rapid and extensive degradation of material held in an oven at 250°C, both in air and under nitrogen. Figure 2 shows that even under the mildest shear conditions ($n = 0.2$), a significant fraction of material will achieve a temperature which is above 250°C for all wall temperatures below 180°C. This suggests that the degradation mechanism which is operative at low temperatures may be triggered thermally and not by mechanical forces.

Calculations Based on a Purely Thermal Mechanism

The results reported by Arisawa and Porter on the effect of temperature on degradation are analogous to those found in the mastication of natural
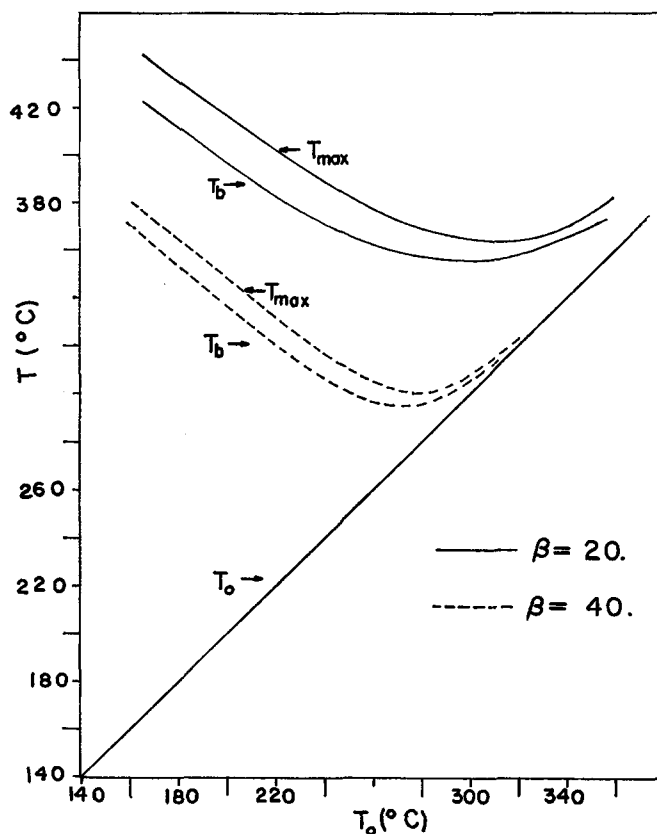
Fig. 4. Variation of maximum and bulk temperatures with wall temperature for a Newtonian fluid.

rubber, i.e., there is some temperature at which degradation is minimized. For polystyrene, that temperature was found to be in the neighborhood of 180°C. Arisawa and Porter allude to the bimechanistic theory mentioned above to explain this behavior.

It has been demonstrated that the system can be decidedly nonisothermal. To pursue the hypothesis that a single degradative mechanism, purely thermal in nature, might also explain the negative temperature coefficient, the average rate must be calculated. This is easily done, since the integration of eq. (12) can be performed numerically.

A computer program was written to evaluate this average rate for various values of the capillary wall temperature T_0. For definiteness, the value of E chosen is the same as the activation energy for thermal degradation.[25] This value is probably not correct in the present case, but the actual value is unimportant in this application. The results of these calculations, for the parameters given in Table I for polystyrene, are shown in Figures 5 and 6 for various values of the parameter n and values of β of 30 and 40, re-
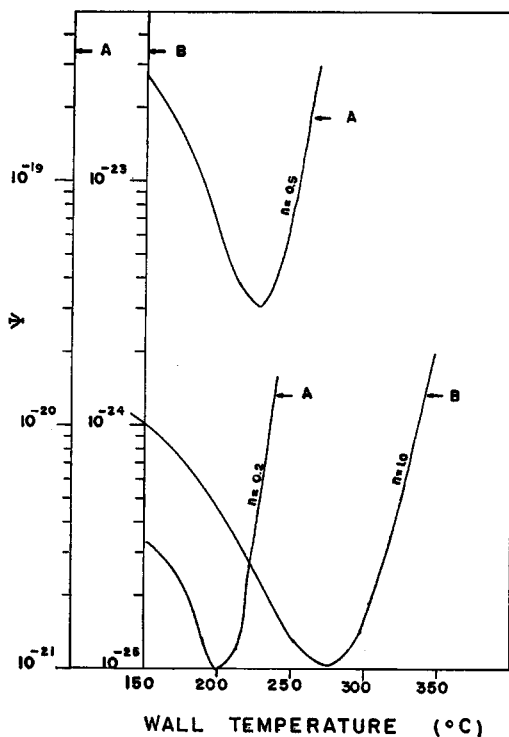
Fig. 5. Average reaction rate over capillary cross section vs. wall temperature. Data for polystyrene; $\beta = 30$.

spectively. The actual magnitude of the average rate is unimportant in the present study, since only the temperature dependence is of interest. These values, are, however, included in the graphs for completeness. Although they seem very small, it should be remembered that in the usual mechanochemical experiments very few bonds are broken.

Obviously, in all cases, the curve shape is similar to the classic plot published by Busse in 1938. The average rate first decreases, passes through a minimum, and then increases again as the wall temperature increases. It is also important to note that the temperature for which degradation proceeds at the minimum rate is predicted to lie between 200°C and 230°C for non-Newtonian flow behavior ($n = 0.2$ and 0.5). The experiments of Arisawa and Porter show a minimum at 184°C, but this measurement was bracketed by other runs at 164°C and 204°C. The minimum has not been precisely defined experimentally.

The surprisingly close correspondence between the present theoretical calculations and experimental findings raises the question of whether these results are universally true or whether they are merely an accidental result of the system parameters which have been chosen. In an attempt to answer this question, two more numerical experiments were run, with physical parameters which describe the behavior of two other real polymeric
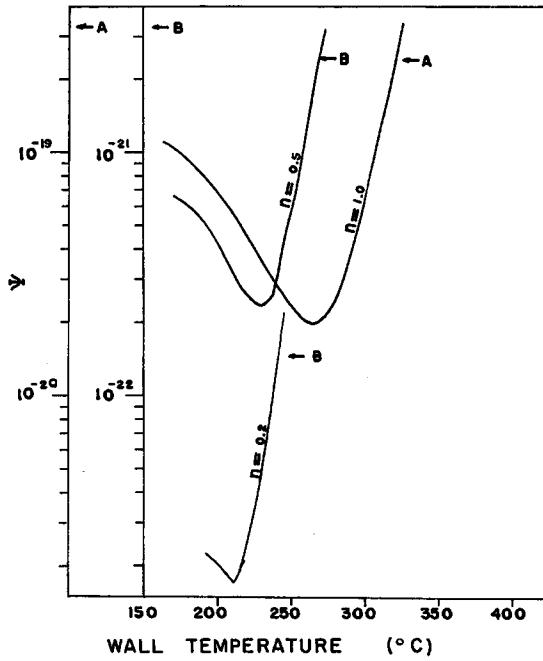
Fig. 6. Average reaction rate over capillary cross section vs. wall temperature.   Data for polystyrene; $\beta = 40$.
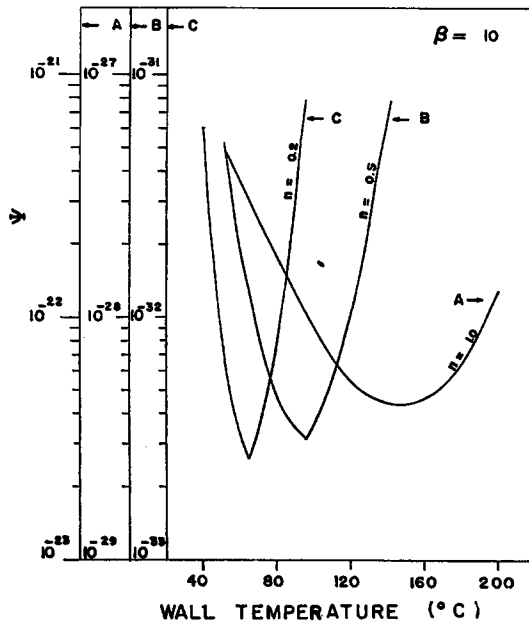

Fig. 7. Average reaction rate over capillary cross section vs. wall temperature.   Data for natural rubber; $\beta = 10$.
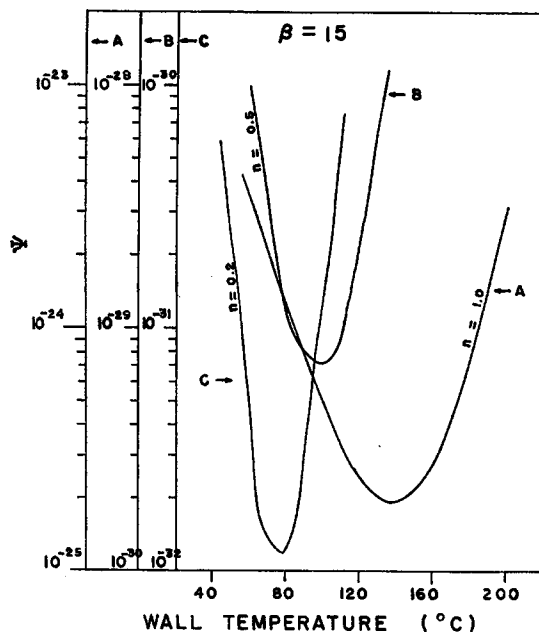
Fig. 8. Average reaction rate over capillary cross section vs. wall temperature. Data for natural rubber; $\beta = 15$.

systems, natural rubber and polyisobutylene. The values of these parameters are also given in Table I.

The results for natural rubber are shown in Figures 7 and 8, corresponding to values of β of 10 and 15, respectively. Again, the curve shape is the same as that in Figure 1. The rate is a minimum for the non-Newtonian behavior (n = 0.2, 0.5) at temperatures between 65°C and 100°C. Experiments on rubber mastication show a minimum degradation efficiency in the neighborhood of 115°C, although, as can be seen from Figure 1, the minimum is quite broad and begins at approximately 80°C. The close correspondence between the present predictions and experimental findings is indeed surprising in this case, given the vast difference between the shear field experienced in a rubber masticator and that assumed here.

Finally, the curves calculated for polyisobutylene are shown in Figure 9 for $\beta = 15$, and in Figure 10 for $\beta = 20$. Once more, the curves are of the same shape as the others, with the minimum degradation rate occurring for temperatures between 116°C and 130°C. Baramboim[28] reports experiments on the milling of polyisobutylene and shows the minimum occurring at a temperature of 140°C, bracketed by temperatures of 100°C and 210°C. Pohl and Gogos[29] and Pohl and Lund[30] also investigated the degradation of this polymer under shear, the former in a biconical rheometer, the latter in a capillary device, but their temperatures were too low (less than 110°C) to observe the turn-around in rate. In the temperature
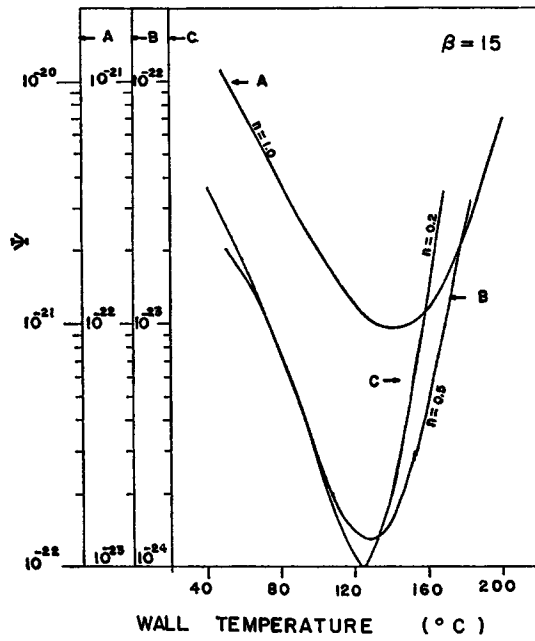
Fig. 9. Average reaction rate over capillary cross section vs. wall temperature.   Data for polyisobutylene; $\beta = 15$.
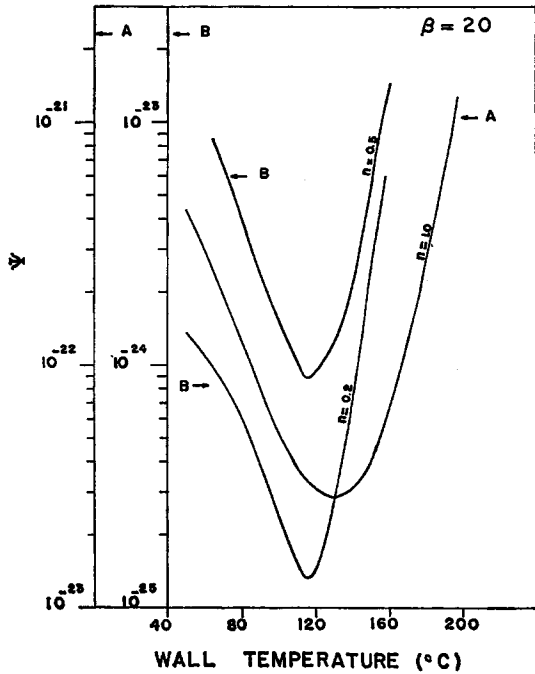

Fig. 10. Average reaction rate over capillary cross section vs. wall temperature.   Data for polyisobutylene; $\beta = 20$.

TABLE II
Temperatures Corresponding to Minimum Rate

A. Polystyrene—Experimental value lies between 164°C and 204°C

$\beta = 30$		$\beta = 40$	
n	T, °C	n	T, °C
1.0	276	1.0	265
0.5	227	0.5	230
0.2	200	0.2	210

B. Natural rubber—Experimental value lies between 80°C and 115°

$\beta = 10$		$\beta = 15$	
n	T, °C	n	T, °C
1.0	148	1.0	136
0.5	95	0.5	100
0.2	65	0.2	76

C. Polyisobutylene—Experimental value lies between 100°C and 210°C

$\beta = 15$		$\beta = 20$	
n	T, °C	n	T, °C
1.0	140	1.0	130
0.5	130	0.5	116
0.2	124	0.2	116

region they dealt with, the rate of reaction decreased continuously as the wall temperature increased.

These results are summarized in Table II.

CONCLUSIONS

General Observations on the Theory

The calculations presented above lend strong support to the hypothesis that degradation in viscous, polymeric flow is thermally induced. They show that certain experimental systems cannot be considered isothermal; consequently, rate data obtained from these experiments are suspect. The argument is enhanced by the fact that the analysis shows good correspondence with experimental data for three separate polymers. It is interesting, at this point, to note the work of Regel' et al.[31] which showed that the volatile products evolved from polymers under mechanical stress are almost identical to those formed by thermal degradation. Indeed, these authors state: "Both mechanical breakdown and thermal degradation are based on common elementary events...caused by thermal fluctuations."

From the calculations presented here, it seems plausible that the "negative temperature coefficient" is nothing more than an experimental artifact. If the rate of degradation is understood to increase monotonically with fluid temperature, a bimechanistic theory is unnecessary to explain

the observed behavior. A single mechanism, based upon common chemical kinetics, will suffice. Indeed, in this light, evidence of chain rupture in fluids caused by mechanical stress at the molecular level becomes extremely slim.

The present theory of the temperature dependence of mechanochemical reactions is not conclusively proven, for this can only be done by experiments. This work does show, however, how the primary characteristic of mechanochemical reactions can be accounted for in a reasonable manner, using the classical theory of the temperature dependence of reactions.

The present theory is not only limited to polymer melts, which have been treated exclusively in this work, but may also be extended to degradation in solution. Although it might appear that viscous heating is not important in solution, it should be remembered that these degradation experiments are usually carried out at very high shear rates[32,33] compared to experiments with polymer melts.

Another feature of mechanochemical reactions not excluded by the present theory is the belief of many experimenters that there exists a critical molecular weight below which the polymer will degrade no further.[5,32] Since such a phenomenon is not thermal in nature, it could be accounted for by the concentration-dependent term in the rate expression, eq. (2). For example, the rate expression might be:

$$r = -k_0\, e^{-E/RT} \left(\frac{1}{M_{n\infty}} - \frac{1}{M_n} \right) \tag{15}$$

where M_n is the number-average molecular weight and $M_{n\infty}$ is its limiting value.

One of the most serious accusations which can be raised against the present theory is that for many polymers, the site of bond breakage differs for thermal degradation as compared to rupture caused by mechanochemical reactions.[34] Thermal degradation of many polymers produces the gaseous monomer, whereas it appears that for many systems, mechanochemical reactions cause the polymer chain to break near the center, producing two chains of lower molecular weight.

However, it should be remembered that the thermal degradation process is extremely complex.[35] The "unzipping" reaction is not the only one which occurs. Bonds also break all along the polymer chain, and it is not unreasonable to expect the radicals which form to react in several different ways. One manner of accounting for the different products of degradation, e.g., lower molecular weight polymer and gaseous monomer, would be by postulating that the two products are the results of reactions with different activation energies. If the reaction producing the gaseous monomer has a higher activation energy than the other reaction, it will not become significant until very high temperatures are reached.

Limitations of the Analysis

The limitations of the present analysis and some of the simplifying assumptions which have been made to make the problem amenable to a

preliminary investigation should be kept in mind, not only to understand these limitations, but also to see what the next step in a theoretical or experimental investigation should be.

The temperature coefficient of viscosity, β, has been assumed constant over the temperature range of interest. This is generally a good approximation, but cannot be considered as rigorously correct. Actually, β varies with temperature and might also depend on shear rate, molecular weight, and molecular weight distribution.

Second, the physical properties of the polymers have been assumed to remain constant throughout the degradation process, although the viscosity is allowed to vary with temperature. However, the viscosity, density, etc., may be expected to change with molecular weight and overall distribution. Although the reactions considered here affect only a small fraction of the material present (Arisawa and Porter found that much less than 1% of the bonds present are cleaved), the molecular weight distribution can change significantly. Hence, a complete analysis of the problem should include this effect.

Another problem associated with the fact that a reaction is taking place is that heat is being generated by the chemical reaction, so that the steady-state temperature profiles would be modified somewhat. This effect, however, can be safely neglected because of the low extent of reaction.

A serious difficulty encountered in analyzing degradation reactions is the multitude of reactions which must be accounted for. Chains may break and recombine by several different mechanisms. Since the diffusion coefficients of polymers are low, some reactions might be diffusion controlled. Since the purpose of this work is to analyze the temperature dependence of the reactions, all of these additional, complicating effects have been ignored.

The determination of the temperature and velocity profiles for capillary flow are based on the assumption that the system is at steady state, i.e., the profiles are fully developed. This assumption is probably valid for the velocity profile, since, because of the very low Reynolds numbers, the profile should become fully developed within a few pipe diameters. However, the question of how long the capillary must be for the temperature profile to become fully developed is unanswered. All investigations which have appeared in the literature are based on the assumption of constant physical properties. However, because of the temperature-dependent viscosity, the determination of the entrance length is a difficult problem. In any case, the results of the present investigation should be at least qualitatively correct, even if it is found that a very large L/D is necessary to ensure a fully developed temperature profile.

The preceding analysis deals only with capillary flow, although similar results can also be expected from systems of different geometries. Calculations similar to those made here could be easily made for Couette flow using the profiles of Gavis and Laurence. The problem of obtaining fully

developed flow, which might be difficult to obtain in a capillary, can be easily solved in a Couette device. Running the instrument for a sufficiently long time would assure approximating equilibrium conditions.

Finally, it should be stressed that a complete kinetic examination of the degradation reactions which take place in a capillary rheometer should include the effects of the velocity profile as well as the influence of the temperature profile on the rate expression. The rheometer cannot be considered a plug flow reactor. Denbigh[36,37] and Aris[38] have analyzed problems of a similar nature and have shown the importance of considering the velocity profile. This point, though extremely important, seems to have been completely overlooked by some authors, who write a rate expression as though dealing with a simple batch reactor.

RECOMMENDATIONS FOR FUTURE WORK

The authors would like to emphasize the need for continuing the fundamental investigations of the flow behavior of macromolecules. In light of the present work, this suggests that a much closer cooperation than has existed before must be initiated among the physical chemist who is interested in the mechanism of polymer degradation, the rheologist who wants to measure the flow properties of high polymers, the reactor design specialist who is concerned with the analysis of chemical reactors, and the fluid mechanician who deals with the determination of the velocity and temperature profiles in complex flow situations.

Specifically, the following criteria should be embodied by subsequent experiments concerned with "mechanically induced" degradation:

1. The physical properties, and most especially the flow properties, of the polymer to be degraded should be accurately established.

2. The experimental apparatus should generate a well-defined shear field which, together with the constitutive equation relating shear stress to temperature and shear rate developed in (1), lends itself to hydrodynamic analysis. Many common viscometric devices are in this category.

3. The experiment should contain some means of determining the temperature profile generated in the fluid to estimate the magnitude of the nonisothermal effects.

4. The data obtained from such an experiment should be analyzed in light of the equations governing the device's performance as a chemical reactor.

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