

Temperature Effect on Polymer Mechanochemistry

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Synopsis

The influence of temperature is a fundamental variable for the mechanochemical processes of high polymers. However, it is generally recognized that the effect of temperature in this process is not always direct, as in normal chemical reactions, but is mainly indirect involving change in the properties (principally elastic and viscous), in the physical state of the system, and consequently in the mechanism of rupture. The negative temperature coefficient has been considered a prime criterion of a mechanochemical reaction by many researchers. Recently, it has been suggested that the negative temperature coefficient is really due to the viscous heating during polymer deformation and the low thermal conductivity of polymers.

The aim of this paper is to reevaluate the role of temperature on mechanically induced reactions of polymers. In light of evidences published in the last 30 years, the dependence of mechanochemical reaction on temperature must involve the overlapping of the following factors: 1) the usual positive dependence of rate on temperature, as predicted by Arrhenius equation; 2) the true experimental temperature, which depends on viscous heating and on thermostating efficiency; and 3) the breaking tension at the center of the polymer chain which is inversely dependent on temperature, i.e., greater at the higher viscosity and the slower relaxation at the lower temperatures, this last factor being dominant in determining the characteristic negative temperature coefficient for polymer mechanochemistry.

INTRODUCTION

The influence of temperature is a fundamental variable for the mechanochemical processes of high polymers. However, it is generally recognized that the effect of temperature in this process is not always direct, as in normal chemical reactions which increase in rate with temperature (Arrhenius equation), but is mainly indirect, involving change in the properties (principally elastic and viscous), change in the physical state of the system, and consequently changes in the mechanism of rupture. The negative temperature coefficient has been considered a prime criterion of a mechanochemical reaction¹⁻⁶ and has indeed been found and detailed by many researchers in different reaction conditions and using different equipment.⁷⁻³¹ Recently, Alberghini and Sukanek³² have suggested that the negative temperature coefficient is only an apparent accident and is really due to the viscous heating during polymer deformation and the low thermal conductivity of polymers. Their conclusion seems to be in serious doubt. They have not considered all the major experimental evidence in the literature, which supports the concept of a negative coefficient of temperature for mechanochemical processes. The aim of this paper is to re-evaluate the role of temperature on mechanically induced reaction of polymers in light of evidence published in the last 30 years.

EFFECT OF TEMPERATURE ON MECHANOCHEMICAL PROCESSES

Primarily, temperature determines the physical state of the system, whether it is glassy, crystalline, or an elastic or fluid, depending on composition. The softening of polymer systems on raising the temperature results in the imposition of less shear energy at a given shear rate and, consequently, in a reduction in reaction and a higher critical molecular weight below which rupture will not occur. The rate of energy input is proportional to the viscosity times the square of shear rate or the shear rate times stresses. Thus, results compared at the same shear stress are generally similar. At lower temperatures, thermal motion is reduced, the relaxation processes are slower, and the disentangling process longer. As a result of these effects, reaction rate in mechanically induced degradation is higher at lower temperatures.

Secondly, the experimental temperatures (and the presence of air or oxygen) can determine the mechanism of bond rupture, i.e., oxidative-mechanical, thermal-mechanical or purely mechanical oxidative, or thermal.

As postulated by Bestul,³³ the probability that a chain bond will get the activation energy for rupture is the sum of the thermal and mechanical energy contributions. At lower temperatures, the thermal contribution is negligible, while the opposite is true at higher temperatures.

Thirdly, temperature can influence the secondary reactions after radical formation by chain scission.

SURVEY OF EXPERIMENTS

The influence of temperature on mechanochemical processes has been investigated by many workers, using a variety of polymers and methods.

Milling

Vibromilling is a basic method of mechanochemistry which is usually performed in polymers in the solid state. If there is no phase change over the temperature range investigated, the influence of temperature on the milling reaction (molecular weight decreases) is relatively small.^{10,34} According to De Vries, Royalance, and Williams,³⁵ the number of broken bonds is essentially independent of T up to T_g . Above T_g , the number drops off rapidly. These features are certainly consistent with conventional chemical reactions. Moreover, typical negative coefficients have been reported for many cases.¹⁰⁻¹² Temperature also influences strongly the specific surface of dispersed particles.^{9,36,37}

Interesting experiments have also been performed by Hess and co-workers.^{38,39} They found a zero temperature coefficient on milling polystyrene. They calculated, by the number of broken bonds, the number of particle collisions, and the energy developed by each collision, that molecular weight decrease arose from a mechanical mechanism and not by local hot spot caused by viscous heating. Only 0.0128% of the applied energy is spent in breaking the bonds. The calculation of the temperature increase due to impact showed that the temperature reached during milling is not sufficient to promote thermal degradation. In a second set of experiments, they discovered that mechanochemical products from cellulose were different from those by thermal degradation, although the intrinsic viscosity decrease was similar in both processes.

Two polymers have been tested over a broad range of temperatures. For the case of polyisobutylene,³³ mechanical degradation shows the typical negative coefficient; the maximum temperature of shear stability above which oxidative degradation becomes relevant is 140°C. For the case of vibromilling of poly-(methyl methacrylate), degradation occurs most prominently in the glassy state.⁷ Preliminary tests have shown that in pure heating, degradation occurs mainly at higher temperatures (above 170°C).

Mastication

It has long been known that natural rubber mastication efficiency passes through a minimum³¹ at a temperature of approximately 115°C. Curve A in Figure 1 is due to mechanical degradation of rubber; curve B is caused by oxidative degradation.¹³ Using radical acceptors other than oxygen, it is possible to avoid the overlap of the two degradation mechanisms. No degradation is detectable in the absence of oxygen up to 140°C.^{13,40} Figure 2 shows clearly the negative coefficient and absence of a temperature for minimum degradation coefficient. In a different set of experiments, natural rubber has been masticated in oxygen and nitrogen plus a radical acceptor.¹⁶ The difference in the extent

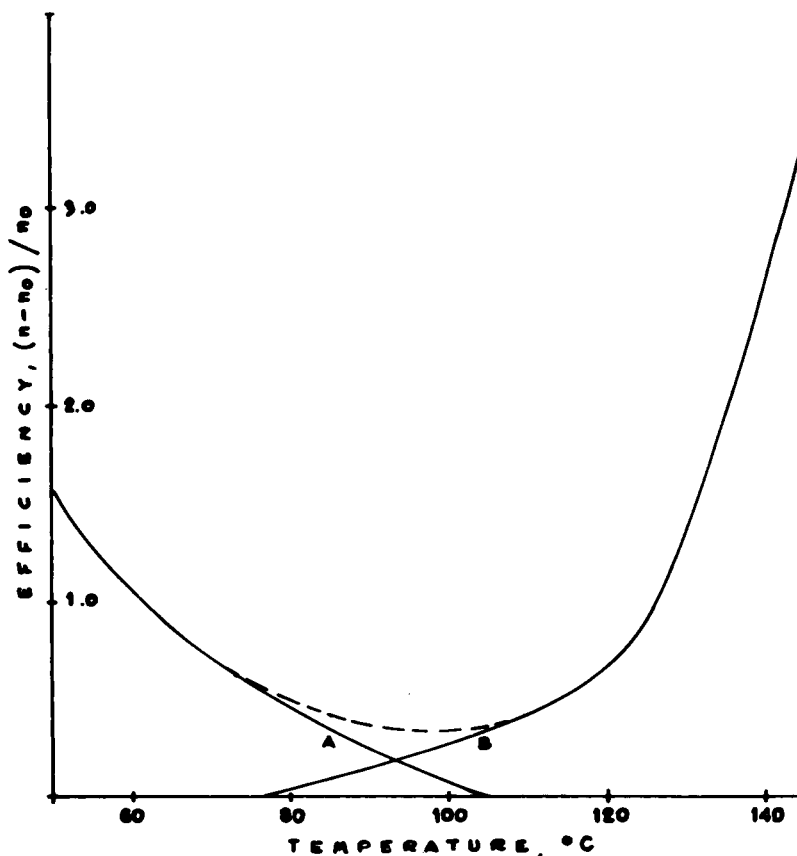


Fig. 1. Efficiency of natural rubber mastication at different temperatures. Reprinted from *J. Polym. Sci.*, 9, 229 (1952).

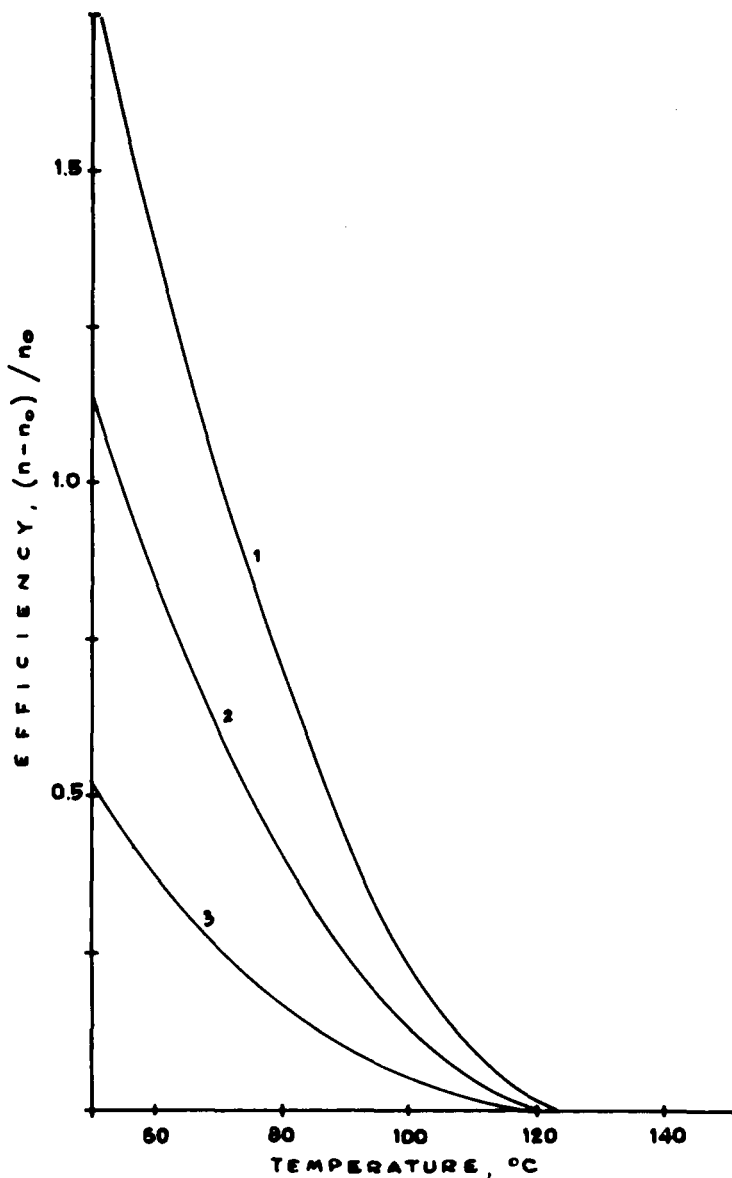


Fig. 2. Efficiency of natural rubber mastication under nitrogen with radical acceptors of different reactivity: (1) thiophenol; (2) benzoquinone; (3) azobenzene. Reprinted from *J. Polym. Sci.*, **9**, 229 (1952).

of degradation increases by increasing the temperature, though the absolute extent of degradation decreases by increasing the temperature for both cases, as expected. If, however, an antioxidant which easily reacts with RO_2 radicals is added, the extent of degradation in oxygen is closely similar to that in nitrogen.

Chemical evidence for the shear dependence of hot mastication has also been reported.⁴⁰ In contrast to oxidized rubber, hot masticated samples follow the viscosity-molecular weight relationship predicted for nonrandom scission. The mechanochemical processes of rubber mastication and the role of oxygen have been discussed by Kuzminskii and co-workers⁴¹⁻⁴⁴ using selective radical sta-

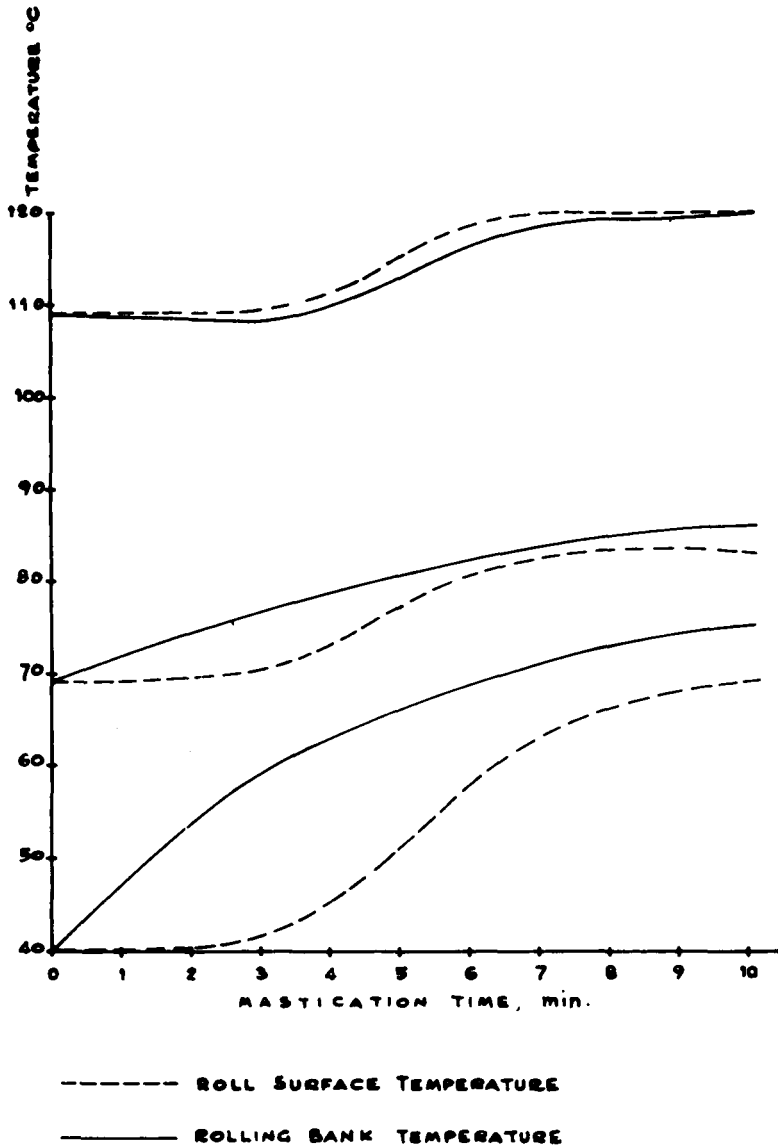


Fig. 3. Roll surface and rolling bank temperatures as function of mastication time at different cooling fluid temperatures.³²

bilizers. Recently,²⁴ an experiment has been performed in order to measure accurately the temperature increase during natural rubber cold mastication. A fluid was circulated inside the rolls at constant temperatures (of 40°, 70°, and 100°C). The temperature of the roll surface and of the rolling bank at five different points was measured by thermocouples. The results are summarized in Figure 3. The temperature increase is higher at lower temperatures, but the bulk temperatures are in the same order as the cooling fluid. By changing the temperature of the circulating fluid, it is possible to control precisely the bulk polymer temperature. The Mooney viscosity after mastication was, respectively, 42, 58, and 86, in agreement with previous results.

Similar results have also been reported for EPDM rubbers.^{18,19} The intrinsic viscosity change with mastication temperature shows three different regions: the first (for the range of 20–65°C) where the viscosity change is inversely proportional to temperature (negative temperature coefficient for reaction); a second one (65–155°C) for which the viscosity change is very small; and a terminal range (155–250°C) where the intrinsic viscosity decrease rapidly with increasing temperature. The case for the negative temperature coefficient during mastication in the rubbery state is similarly well documented for a number of polymers.^{14,15} Moreover, the above behavior is consistent with Bueche's theory on mechanical degradation of high polymers.⁴⁵

Extrusion and Injection

A conclusion concerning overlapping mechanisms, similar to that for natural rubber mastication, has been reached by Porter and co-workers^{46,47} in their study of polystyrene capillary extrusion.

By the number of ruptured bonds and by the mechanical energy required to cut a mole of bonds at different temperatures, they found the maximum stability for polystyrene may be near 180°C. Below this temperature, mechanical reactions dominate and at higher temperature, a thermo-oxidative reaction aided by mechanical forces. They also developed a new experimental technique ("solvent coring") to evaluate the molecular weight and its distribution on a point-to-point basis across the extrudate.⁴⁸ Only a little difference has been found across the extrudate, in any case, degradation is a maximum on the outside where the stress is highest and temperature lowest. These general results have been substantiated by other investigators using different polymers and equipment.^{49–53} The deduction from their results is that, though at the processing conditions the nature of degradation is basically thermal, there is a distinct reduction in temperature needed for reaction, provided by the mechanical energy stored by shear within the polymer chain.

Solution State

Most of the investigators,^{25,26,28–30,33,54,55} with the exception of Klimov and Zarundii,⁵⁶ and Ram and Kadim,⁵⁷ found a negative temperature dependence (in terms of equilibrium molecular weight and rate of degradation). Ram and Kadim, however, found in all the experiments but one that the final viscosity is slightly lower at the lower temperatures.

The NBS researchers²⁵ calculated the energy required for degradation at different temperatures. They found a value of 325,000 kcal/mole of broken bonds, 400,000 and 480,000, respectively at 30–50°C, and 60° and 80°C. The increase in energy requirement at higher temperature represents a negative temperature coefficient for degradation and is claimed to be support of the mechanical mechanism.

TEMPERATURE DEPENDENCE OF MECHANOCHEMICAL REACTIONS OF POLYMERS

The temperature dependence of mechanochemistry has been rediscussed³² in light of viscous heating during processing. The general idea is that it is very diffi-

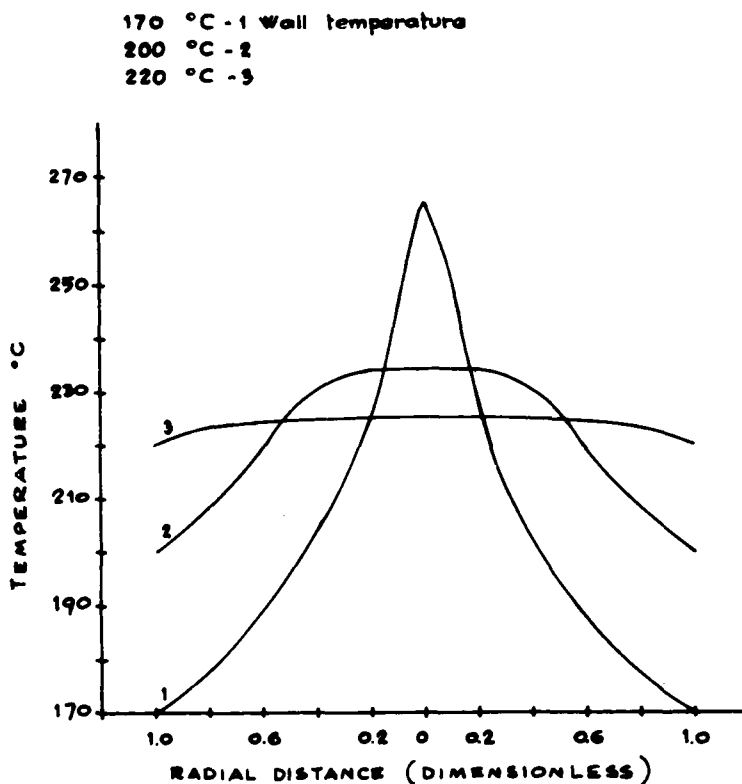


Fig. 4. Temperatures profiles for power-law fluid during capillary extrusion at different capillary wall temperatures. Reprinted from *J. Appl. Polym. Sci.*, **16**, 1701 (1972).

cult to perform shear experiments under isothermal conditions because of high polymer viscosity and low thermal conductivity. The actual temperature of the process may thus be much higher than that at which the experiment was planned. Consequently, the rate equation for mechanical degradation might follow the usual Arrhenius temperature dependence for chemical reactions.

The extrusion process of molten polystyrene performed by Porter⁴⁶ has been analyzed in detail. The temperature profile in the system studied by Porter has been calculated. The effects of viscous heating are far more significant at low capillary wall temperature (Fig. 4), and huge gradients purportedly exist across the capillary radius. The authors calculated, also, that, as the wall temperature increases, not only the maximum but also the bulk temperatures decrease, pass through a maximum, and then approach the wall temperature. As a consequence, the average reaction rate will pass also through a minimum. The shape of the curve as a function of temperature is similar to that of Figure 1 (Fig. 5). The minimum is very close to the minimum determined experimentally by Whitlock and Porter. Similar calculations have been performed for prior experiments on natural rubber and polyisobutylene. The curves were again U-shaped with a minimum for natural rubber between 65° and 100°C and 116°–130°C for polyisobutylene.

While viscous heating can have a great significance on the polymer processing, considerable experimental evidence against this speculation exists.

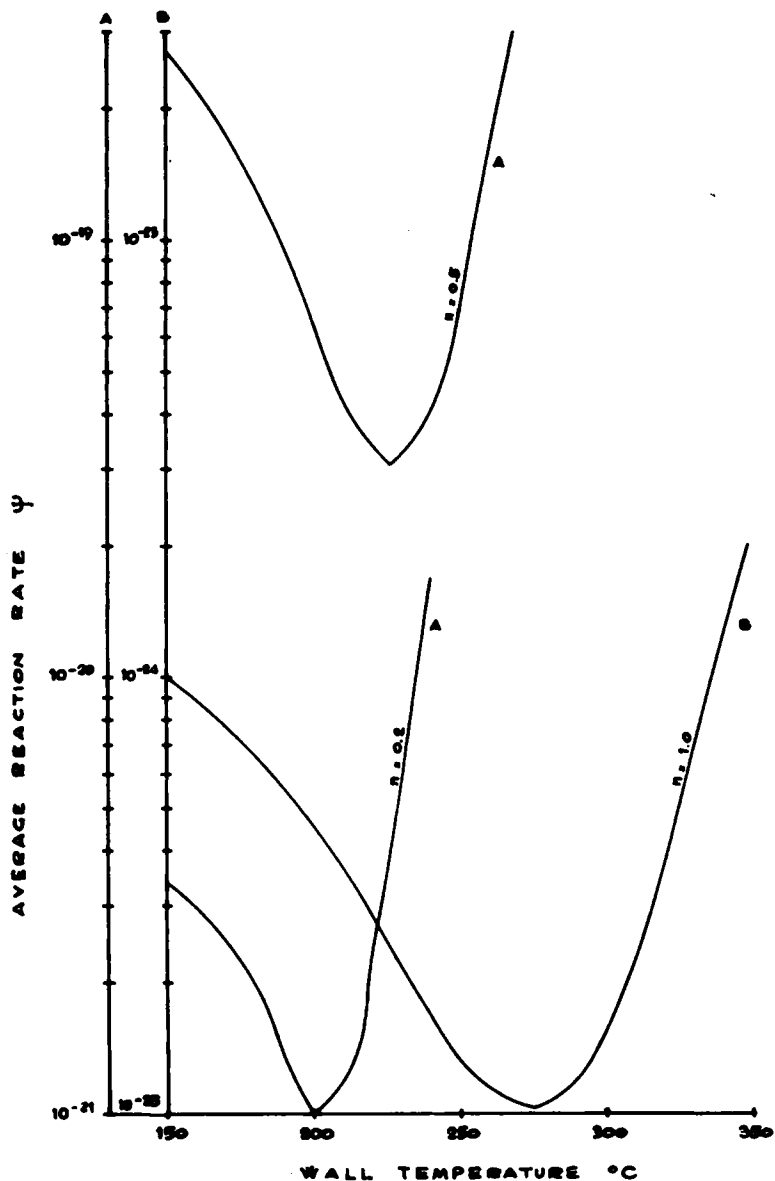


Fig. 5. Average degradation rate over capillary cross section vs. wall temperature. Data for polystyrene from ref. 32; n is the flow behavior index. Reprinted from *J. Appl. Polym. Sci.*, **16**, 1701 (1972).

Contrary are:

1. The observed and calculated increase of temperature in the ball milling experiments of Hess, who attacked this problem 30 years ago.^{38,39}
2. The temperature study of Watson,⁴⁰ who claimed that it is possible to maintain the rubber temperature during mastication within a few degrees, and by Casale and Croci²⁴ (see Fig. 3).
3. Importantly, the results in inert atmosphere, which show that there is no degradation in rubber mastication in a region above 140°C¹³ (see Fig. 2) and that obtained during mastication of natural rubber in oxygen and in nitrogen at

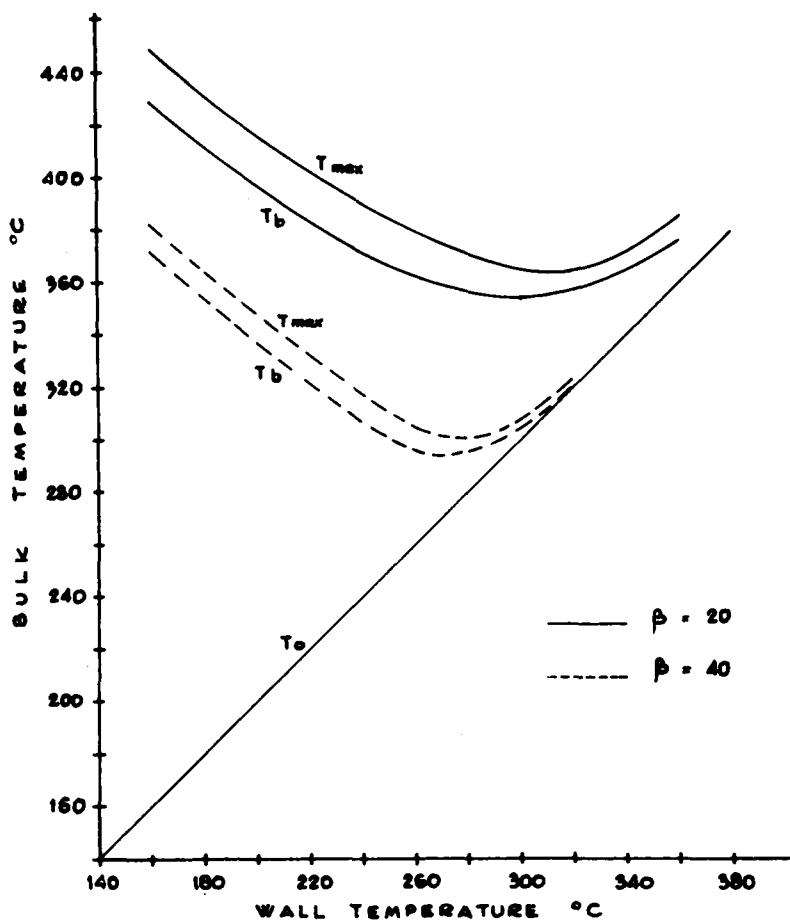


Fig. 6. Variation of maximum and bulk temperatures during extrusion at different capillary wall temperatures (T_0) for a Newtonian fluid³²; β is an empirical constant. Reprinted from *Appl. Polym. Sci.*, 16, 1701 (1972).

different temperatures.¹⁶ The agreement between the minimum degradation temperature calculated and observed for natural rubber is thus fortuitous, as in mastication the mass of the material is homogeneous for continuous revolving, and this is not the case with capillary extrusion. Beside, convection plays a different role in capillary and mastication experiments.

4. The Baranwal results in EPDM mastication, who found a difference of about 135°C between the lower experimental temperature and the minimum temperature for degradation. This last temperature falls in a region where, according to the calculations of Alberghini and Sukanek, there is no temperature increase due to viscous heating.

5. If such a huge gradient will take place during mastication, vulcanization would occur during milling.

6. The experiment by Whitlock and Porter⁴⁸ which shows that maximum degradation in capillary experiments is on the outside, not on the inside of the extrudate, as predicted by reference 32.

7. Very importantly (and independent of mechanochemical reactions) if the prediction of Alberghini and Sukanek were true, the viscosity of polystyrene

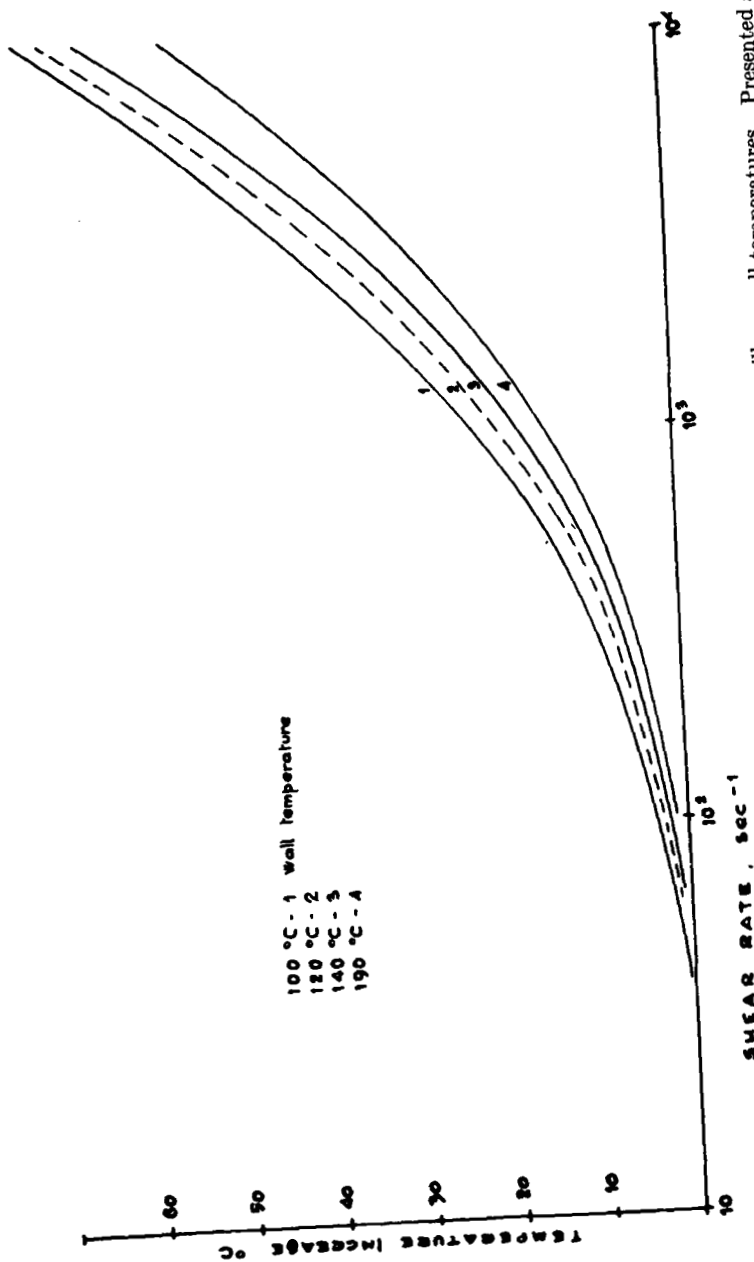


Fig. 7. Temperature increase during EPDM rubber extrusion as a function of shear rate, at different capillary wall temperatures. Presented at the 2nd Symposium of the Italian Society of Rheology, Siena, Italy, May 10-12, 1973.

measured by capillary experiments (without taking in account the prediction of temperature increase for correcting data) must also pass through a minimum (see Fig. 6, where the predicted bulk viscosity is reported as a function of wall temperature). It is well known that this is not the case.⁵⁸ The above concept, of course, applies to viscosity data on all polymers reported in literature.

8. As regards capillary experiments, recent measurements have been performed to control the temperature increase due to viscous heating using a special capillary, of low thermal conductivity. It has been reported that the increase of temperature (ΔT) increases on increasing the wall temperature at constant shear stress and decreases at constant shear rate. ΔT , however, is independent of the bulk temperature at constant $\tau_w \cdot \dot{\gamma}_w$, i.e., at constant rate of energy input. In any case, the measured temperatures are all in the same order of the initial temperature. (Fig. 7). Moreover, using conventional metal capillaries, ΔT 's are much lower due to the high thermal capacity and conductivity.⁵⁹

9. The same behavior has been found on solution experiments, though the temperature influence is not so strong as in bulk experiments.

10. The differences between degradation products after mechanical and thermal degradation found in certain experiments.^{1,39,40}

CONCLUSIONS

The heat generation calculations may well, in themselves, be valid, predicting tremendous temperature increase. However, heat transfer mechanism other than conduction such as convection may not have been considered and may be difficult to do precisely and in details.

In conclusion, then, the dependence of mechanochemical reaction on temperature must involve the overlapping of factors, as predicted by theories of Bueche⁴⁵ and Bestul.³³ These include:

1. The usual positive dependence of rate on temperature, as predicted by Arrhenius equation.
2. The true experimental temperature, which depends on viscous heating and on thermostating efficiency.
3. The breaking tension at the center of the polymer chain which is inversely dependent on temperature, i.e., greater at the higher viscosity and the slower relaxation at lower temperature, this last factor being dominant in determining the characteristic negative temperature coefficient for polymer mechanochemistry.

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