

Entropy and Melt Fracture

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Synopsis

The onset of a well-known flow instability commonly called "melt fracture" has remained one of the fundamental unsolved problems of polymer rheology. This work attempts to explain this phenomenon via a criterion based upon limitations to configurational entropy as dictated by the second law of thermodynamics. It is shown that the molecular orientation resulting from a sustained stress-deformation rate field may be sufficient to affect the entropy balance of the system to the point of violation of the second law. The flow field then spontaneously changes, producing the condition called melt fracture, in a manner such as to prevent the violation of this law. Other theories on the mechanism of melt fracture are discussed in the context of the above criterion.

INTRODUCTION

Melt fracture is a rather drastic energy-absorbing change in a normal laminar flow field. In a sense, it is like the onset of turbulence; but unlike turbulence, its onset does not appear correlatable with any generalized Reynolds number. Also, it is a phenomenon unique to macromolecular fluids, since it appears never to have been observed with Newtonian fluids. Its magnitude as measured by amount of surface irregularity tends to increase with increasing capillary diameter and cone inlet angle and to decrease with increasing L/D ratio.¹ The various mechanisms proposed in the literature to explain melt fracture have been reviewed by Pearson,² and the reader is referred to this article for a complete background. Only certain important existing theories will be discussed here for purposes of comparison.

It appears reasonably certain that melt fracture is the result of some form of tube flow instability.² A few flow field stabilities can be predicted from a mathematical stability analysis of the governing equations.^{3,4} For example, the laminar-turbulent transition for flows in channels and tubes and the onset of the Taylor laminar secondary flow instability can be estimated by looking for mathematical instabilities in the governing momentum equations. Bénard convection⁵ cells correspond to a thermal instability in the combined energy and momentum equations. Recently, Serrin,⁶ Davis and von Kerczek,⁷ Gurtin,⁸ and others have developed a stability theory based upon an energy criterion for stability alone. Pearson and Petrie⁹ have attempted to mathematically analyze the stability of non-Newtonian tube flows using a variety of constitutive equations.

Experimentally, melt fracture has been studied by numerous investigators.⁹⁻²⁵ The onset of this phenomenon appears to be able to occur almost anywhere within the flow in a capillary system, with "inlet," "land," and "exit" fracture points having been observed.^{1,10,19} Once the flow field has changed into a "fractured" state, it appears never to spontaneously reverse back to the normal laminar state further downstream, except possible in systems with very large L/D ratios. Further, no one appears ever to have observed the onset of melt fracture in initially turbulent non-Newtonian flows or in Newtonian flows of any type. It normally occurs in small diameter, low Reynolds number, high shear rate, non-Newtonian flows.

THE FIRST LAW OF THERMODYNAMICS: THE CONSERVATION OF ENERGY

The first law of thermodynamics and the conservation of energy statement are not identical concepts as is sometimes implied. The first law is simply an energy balance on an arbitrary system, which word form is

$$\left\{ \begin{array}{l} \text{Net Energy} \\ \text{into the} \\ \text{System} \end{array} \right\} + \left\{ \begin{array}{l} \text{Net Energy} \\ \text{Produced by the} \\ \text{System} \end{array} \right\} = \left\{ \begin{array}{l} \text{Net Energy} \\ \text{Gain by} \\ \text{the System} \end{array} \right\} \quad (1)$$

Whereas the conservation of energy states that

$$\left\{ \begin{array}{l} \text{Net Production} \\ \text{of Energy by} \\ \text{the System} \end{array} \right\} = 0 \quad (2)$$

and eqs. (1) and (2) combined give the normal Clausius statement of the first law. The "balance" concept for an entity is a remarkably primitive and powerful tool of physical analysis. It is completely general and universally valid.

THE SECOND LAW OF THERMODYNAMICS: ENTROPY IS NOT CONSERVED

The balance statement can be applied to any concept, even entropy:

$$\left\{ \begin{array}{l} \text{Net Entropy} \\ \text{into the} \\ \text{System} \end{array} \right\} + \left\{ \begin{array}{l} \text{Net Entropy} \\ \text{Produced by the} \\ \text{System} \end{array} \right\} = \left\{ \begin{array}{l} \text{Net Entropy} \\ \text{Gain by} \\ \text{the System} \end{array} \right\} \quad (3)$$

However, this balance is *not* a statement of the second law of thermodynamics. Entropy is *not* a conserved quantity, it can be produced and destroyed by a system. The second law states that the net entropy production must be positive definite for every real process (it can be zero only for a reversible process), i.e.;

$$\left\{ \begin{array}{l} \text{Net Entropy} \\ \text{Production by a} \\ \text{Real System} \end{array} \right\} > 0. \quad (4)$$

Thus, the second law corresponds more to the conservation of energy statement, whereas the first law is just a balance statement which incorporates the conservation principle.

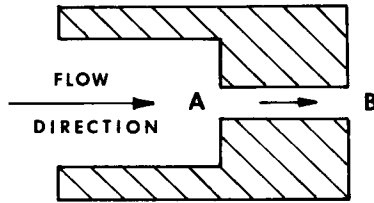


Fig. 1. Schematic diagram of flow through a capillary.

Since entropy is not conserved, the entropy balance does not reduce to a simpler form (except for reversible processes, which do not occur in reality). And since the entropy production is almost always unknown, the entropy balance (which is a scalar equation) is relatively useless for calculating anything except the entropy production itself. Consequently, the second law statement currently enjoys relatively little engineering utility since a balance statement cannot generally be used to solve for a system unknown (such as heat transfer rate or mass flow rate) unless again, of course, the often impractical assumption of reversibility is made. Equation (4) can be used to check gross effects, such as whether or not a certain system will operate in a certain way; but because of the inequality, it does not yield specific quantitative information.

The entropy balance can be developed into a mathematical equation in the following manner: During some time interval dt , let δS_T be the net entropy transported into the system, δS_P , be the net entropy produced by the system (note $\delta S_P \geq 0$) and dS_G be the net gain in entropy of the system. (We let $\delta()$ denote an inexact differential and $d()$ denote an exact differential, e.g., see ref. 26). Thus, over time interval dt , eq. (3) takes the form

$$\delta S_T + \delta S_P = \delta S_G. \tag{5}$$

Dividing eq. (5) by the time interval dt gives the "rate" form of the balance equation:

$$\dot{S}_T + \dot{S}_P = \dot{S}_G \tag{6}$$

where $\dot{S}_T = \delta S_T/dt$, and so forth. The second law now takes the following form:

$$\dot{S}_P \geq 0. \tag{7}$$

Consider now a simple flow system in the absence of magnetic and electric field effects and chemical reactions such as shown in Figure 1 with a single inlet (a) and a single exit (b). It can be shown²⁶ that in such a system, entropy can only be transported across the system boundary by two modes: heat transfer and mass transfer. Thus,

$$\dot{S}_T = \int_{c.s.} \frac{q}{T} dA + \dot{m}(s_a - s_b) \tag{8}$$

where $\int_{c.s.} \frac{q}{T} dA$ is a surface integral over the system boundary; q is the boundary heat flux (\dot{Q}/Area); T is the absolute temperature at the system

boundary (the integral reduces to \dot{Q}/T for an isothermal boundary with a constant heat flux); s_a and s_b are the average specific entropies at the entrance and exit cross sections, respectively; and \dot{m} is the mass flow rate (the same at the exit as it is at the entrance by virtue of the conservation of mass).

Now, in a steady flow situation, there is no net gain or loss of entropy by the system; thus, eq. (6) reduces to (the literature contains more complex entropy production equations, e.g., ref. 27, p. 599, from which one could possibly glean additional relevant information)

$$\int_{c.s.} \frac{q}{T} dA + \dot{m}(s_a - s_b) + \dot{S}_P = 0$$

or

$$\dot{S}_P = \dot{m}(s_b - s_a) - \int_{c.s.} \frac{q}{T} dA \geq 0. \quad (9)$$

We adopt a sign convention such that heat transfer into the system is positive.

In a system such as shown in Figure 1, the flow of a macromolecular material from (a) to (b) will tend to increase the net molecular orientation partially owing to the increase in magnitude of the uniform stress field and partially owing to the increase of surface area to volume ratio resulting in interfacial configurational effects. The fundamental work of Boltzmann and others in statistical thermodynamics has shown that any molecular orientation whatsoever corresponds to a state of *lower* entropy than that of a purely random totally disoriented molecular state.^{26,27} Then clearly, for a system such as that shown in Figure 1, the entropy at (b) can easily be *less* than the entropy at (a), and $s_b - s_a$ will be negative. Brownian motion of the molecules themselves will tend to randomize the system; and if the flow is slow enough, this effect may dominate with the result of no net orientation, and thus no difficulties with the second law. However for fast flows of very large macromolecules, the orientation effect could be very pronounced, yet eq. (9) must not be violated. Equation (9) will allow for a net entropy reduction if there is heat transfer *out* of the system; but there can be no net orientation effects if the system is well insulated or if heat is actually transferred *into* the system.

What happens to the flow as the Brownian motion has less and less success in keeping the macromolecules disorientated as the stress field continues to increase? Since eq. (9) cannot be violated, only two possible alternatives exist: (1) The macromolecules break into smaller molecules which are more susceptible to Brownian forces; or (2) the main flow field itself changes in such a way as to reduce or eliminate molecular orientation. The first we call molecular degradation; the second we call melt fracture. This clearly explains why melt fracture is never observed with Newtonian (or low molecular weight) fluids, but is observed with pure polymers and polymer solutions.

THE SECOND LAW AND THE ONSET OF MELT FRACTURE

Since eq. (9) allows for heat flow either into or out of the fluid, and since entropy is a monotonic function of temperature, the following conditions serve to define unique flow situations.

Case 1. $q < 0$ and $T_b - T_a \leq 0$; the fluid loses heat to the capillary, and the temperature remains constant or decreases. Here, the last term in eq. (9) is positive, and \dot{S}_P will be positive until the first term dominates over the second. In this case, $s_b < s_a$ (due mainly to orientation effects), and the entropy production will become negative when the mass flow rate exceeds the critical value:

$$\dot{m}_c = \left(\frac{1}{s_b - s_a} \right) \int_{c.s.} \frac{q}{T} dA. \quad (10)$$

This critical mass flow rate defines the onset of melt fracture for this case.

Case 2. $q < 0$ and $T_b - T_a > 0$; the fluid loses heat, but more heat is generated internally than is dissipated and the fluid temperature rises. In this case, two possibilities exist. The last term in eq. (9) is still positive, but the increase in fluid temperature and the resulting increase in Brownian activity may prevent sufficient molecular orientation from taking place; thus, s_b may not become less than s_a . If this happens, melt fracture, as defined here, is impossible since \dot{S}_P will always be positive. Secondly, if the temperature does not effect the entropy enough to prevent an increase in orientation at the exit over the inlet, melt fracture will occur at the critical flow rate defined in eq. (10).

Case 3. $q \geq 0$ and $T_b - T_a \leq 0$; the fluid is either insulated, or else heat is added through the capillary walls and the fluid temperature either decreases or is constant. Here, the last term in eq. (9) is negative, and thus it is impossible for s_b to be less than s_a without violation of the second law. However, as the flow rate increases from zero with no temperature increase in the fluid, s_b continually decreases because of molecular orientation with increasing shear field magnitude. Again, melt fracture begins at the critical mass flow rate given by eq. (10), but the conditions defining this case appear to be somewhat unrealistic in practice.²⁸

Case 4. $q \geq 0$ and $T_b - T_a > 0$; the fluid is either insulated, or else heat is added through the capillary walls and the fluid temperature increases from inlet to exit. Here again, the last term in eq. (9) is negative, and again it is impossible for s_b to be less than s_a . However, this is perfectly normal since the rising temperature can conceivably override the shear field effect on the entropy. Thus, generally, it appears that melt fracture does not normally occur in this case, but it is not impossible for it to occur here.

Comparing cases 1-4 above suggests a meaningful experiment. If the inlet and exit entropies could be held constant, melt fracture should occur at a lower mass flow rate when heat is added to the fluid from an external source. The problems of measuring and maintaining a given entropic value in a polymeric system are, however, considerable.

This approach to melt fracture easily explains the effect of inlet geometry on the onset of melt fracture. In the normal experimental situations (case 1 or case 2 above), the heat flow is out of the fluid, and thus the onset of melt fracture corresponds to the critical mass flow rate given by eq. (10). In the case of a 180° entry angle, the entering entropy s_a is greater than that of, say, a 20° entry angle because the shear field (and thus the molecular orientation) is higher with the smaller entry angle. Then, for decreasing s_a , eq. (10) predicts a larger mass flow rate at the onset of melt fracture.

That molecular orientation actually exists in the capillary is demonstrated by the flowing birefringence work on dilute polymer solutions by Eirich²⁸ and on polymer melts by Dexter and Miller³⁰ and others³¹ (the very existence of flowing birefringence implies molecular orientation³²). Further, Furu-kawa et al.³³ have shown that increasing the melt draw ratio outside the capillary increases the molecular orientation within the final filament. Schreiber et al.³⁴ have suggested a molecular orientation mechanism based upon the observations of macroscopic deformable particles suspended in sheared fluids. These particles tend to migrate toward a region of low shear gradient via presumably hydrodynamic forces.³⁵ Han³⁶ has recently shown with flowing birefringence that as a melt exits a capillary it carries with it a residual elastic stress (and thus orientation) which gives rise to a nonzero exit pressure.

CROCCO'S THEOREM

As an example of the influence of entropy on a flow, consider Crocco's theorem. Crocco³⁷ has shown that in a nonviscous fluid without body forces, vorticity can be produced in a steady flow only through some phenomenon which will generate gradients of entropy or stagnation enthalpy. If we somehow had a nonviscous flow of orienting macromolecules, we could invoke Crocco's theorem and say that, since an entropy gradient existed in our flow, we should expect some vorticity to be generated. The swirling, or helical-like, flow in melt fracture establishes that it has developed an axial vorticity component, whereas normal laminar capillary flow has only an angular vorticity component. There is, in fact, a great deal of similarity between the observations of the characteristics of melt fracture and the known hydrodynamic effects of vorticity.

The vorticity equation for a general incompressible fluid with conservative body forces has the form

$$\frac{D\bar{w}}{Dt} = (\bar{w} \cdot \nabla) \mathbf{V} + \frac{1}{\rho} \bar{\nabla} \times (\bar{\nabla} \cdot \sigma) \quad (11)$$

where $\bar{w} = \bar{\nabla} \times \bar{V}$ is the vorticity vector, σ is the deviatoric stress tensor, and \bar{V} is the velocity vector. The last term in eq. (11) represents the diffusion of vorticity through the fluid by means of the stress field which allows vortex lines to cross stream lines. Thus, the stress field, which is the macroscopic manifestation of the macromolecular orientation, also influences the vorticity directly.

THE STORED ELASTIC ENERGY THEORY

There exists a large literature, apparently begun by Weissenberg and Herzog³⁸ in 1928, which revolves around the concept of elastic strain energy stored in a flowing medium. In the 1930's, Eisenschitz and Philippoff³⁹ and Philippoff⁴⁰ and others began to establish this concept experimentally. In the late 1940's and early 1950's, Weissenberg⁴¹ and Mooney⁴² established the concept of an elastic recoverable shear strain in shear flows. In the mid-1950's, Roberts,⁴³ Lodge,⁴⁴ and Philippoff^{45,46} discovered the relationships between flowing birefringence and stress fields, and Philippoff, Gaskins, and Brodnyan⁴⁷⁻⁴⁹ related flowing birefringence to the recoverable shear strain field. In the late 1950's and early 1960's, Philippoff and Gaskins⁵⁰ and Bagley^{51,52} correlated the capillary elastic-end correction factor with the recoverable shear strain with an equation of the form

$$e = n + Sr/2 \quad (12)$$

where e is the Bagley end-correction factor, n is the Couette correction factor and, Sr is the recoverable shear strain. More recently, Balmer⁵³ has developed the relationship between the Bagley end-correction factor and the fluid properties for an Oldroyd rate-type fluid.

Bagley⁵¹ argues that the onset of melt fracture corresponds to a critical value of the recoverable shear strain, thus maintaining that the origin of melt fracture lies in the stored elastic energy of the flow. Regardless of the macroscopic rheological model used to explain elastic fluid behavior, it appears quite clear that this "elasticity" is derived on a molecular level from strained primary and secondary atomic bonds and that the shear field in a capillary flow operates in a manner such as to orientate large entangled molecules parallel to the flow direction.

SHEAR FRACTURE THEORY

Spencer and Dillon¹⁰ originally suggested that the onset of melt fracture corresponded to an isoelongated molecular state. Tordella's¹ birefringence work shows that melt fracture begins at the site of maximum elastic strain. Hutton⁵⁴ and Han and Lamonte^{55,56} hold the view that liquid can literally fracture in shear, i.e., that there is a limit to the amount of elastic shear strain that a liquid can withstand, and all energy above this limit that is put into the liquid is converted into new surface free energy.

CRITICAL CONTINUUM PARAMETER THEORY

Since it is clear that the normal Reynolds number is not a critical parameter in predicting the onset of melt fracture,² researchers have been searching for another appropriate dimensionless parameter.

White,^{23,57} by a dimensional analysis technique, has concluded that melt fracture should occur at a critical value of the Weissenberg number. Balmer and Kauzlarich,⁵⁸ on the other hand, show that the momentum equations for a converging power law elastic fluid have a singularity at a Deborah

number equal to unity, and suggest that this indicates the onset of melt fracture. Others² also feel that it is the fluid acceleration in the entry region that is critical and thus are led to a Deborah number of unity as the critical parameter in predicting the onset of melt fracture.

The Deborah number was introduced by Reiner⁵⁸ and has come to mean^{60,61} the ratio of the material time constant t_m (such as the relaxation time) to the process time t_p , and it has the characteristic that it must be less than or equal to unity (the equality corresponds to pure elastic, nondissipative behavior):

$$N_{\text{Deb}} = \frac{t_m}{t_p} \leq 1. \quad (13)$$

At this point in time, a critical continuum parameter theory such as this does not conflict with the configurational entropy criterion presented here. In fact, since eq. (13) must always be obeyed by a material (since it can never respond to a process faster than its natural response time), it can be taken as a restricted statement of the second law. It can be thought of as a "practical" statement of the second law of thermodynamics similar to those of Clausius, Kelvin, and Plank, which dealt with engines and the flow of heat.

CONCLUSIONS

It is proposed that melt fracture may be a direct consequence of the second law of thermodynamics wherein the key parameter is the configurational entropy of the macromolecule. An entropy balance provides an equation which predicts the mass flow rate at the onset of melt fracture in terms of the system heat transfer and entropy change. It is suggested by this theory that melt fracture could occur anywhere in the flow field; at the capillary inlet (inlet fracture), within the capillary (land fracture), or even at the capillary exit* (the limiting case of land fracture). Current macroscopic theories on stored elastic energy or critical Weissenberg or Deborah numbers are found to be compatible with the present configurational entropy theory.

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* There exists a growing literature on a similar instability in the filament downstream from the capillary exit called "draw resonance."²⁴ Since draw resonance starts to occur only in the presence of filament stretching, it is possible that this too is a configurational entropy governed phenomenon wherein the macromolecules are oriented by the stretching process rather than the shearing process in the case of melt fracture.

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