A Generalized Flow Theory

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Synopsis

A generalized flow theory is put forward which is derived from a review of accepted types of stress–response curves. The theory is summarized in a single flow curve of universal shape from which all types of liquid flow can be interpreted. This "generalized flow curve" can be applied to polymer melts in particular, but there is no reason why it should not equally apply to solutions, dispersions, suspensions, emulsions, or pure liquids. The generalized flow curve is exactly analogous to the typical fully developed load–deformation curve which applies to tough plastics in the solid state. A molecular interpretation of the processes involved in producing the flow phenomena implicit in the various portions of the generalized flow curve is put forward. The evidence on which the theory is based is reviewed. Some fundamental implications are discussed.

INTRODUCTION

Various types of flow behavior in the liquid state have been described which are very different from the Newtonian condition. These flow types include those known as the pseudoplastic, the dilatant, the plastic, the Bingham, and the Ostwald type of flow. Hitherto these types have been regarded as classificatory groups which characterize materials as far as their response to an applied shear rate is concerned. It will be seen that the flow types cannot be separated, but form part of a general response pattern which may be summarized in a generalized flow curve. The generalized flow curve can be derived intuitively from the structural changes which may be assumed to occur during nonturbulent flow as the shear rate is increased. Some of the transitions involved are quite well known, but the various flow regimes and the transitions from one flow regime to another have not hitherto been put together so as to embrace the entire region of nonturbulent flow. The evidence now available proves that the generalization which is possible in the solid state and which is exemplified in the solid state by plots of true stress versus strain of tough plastics under suitable environmental conditions is equally applicable to liquids in general and to polymer melts in particular.

THE GENERALIZED FLOW CURVE

The generalized flow curve is shown in Figure 1a, side by side with a fully developed tensile load–deformation curve for a typical tough material in the
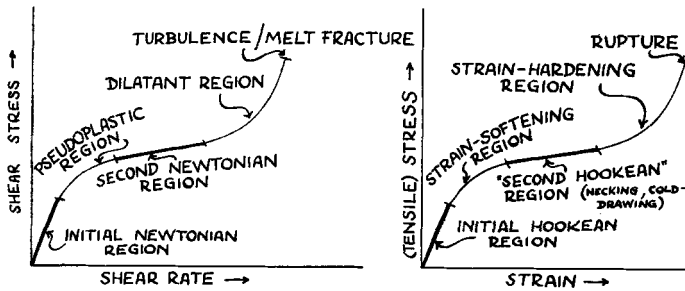
Fig. 1. (a) Generalized flow curve; (b) typical fully developed stress–strain curve as found in tough plastics under appropriate conditions. The conventional stress has been converted to the true stress.

solid state after converting the conventional stress into the true stress. This conversion can be effected if a continuous record of the changes in the cross-sectional area during, say, a tensile test is made.

It will be seen that the shape of the two curves is absolutely identical, that the various regions into which they divide have the same physical significance, and that it is therefore tempting to regard the solid and liquid states as extremes of a generalized fluid state which embraces the mechanical behavior of all materials. This line of thought is being pursued and its outcome will be published in due course. It should be pointed out, however, at this stage, that, since all deformation and flow processes under dynamic as well as static conditions involve strictly definable volume elements, one may regard all these processes as mechanical responses in the widest sense, irrespective of whether the particular force field employed to produce those responses is conventionally mechanical, electromagnetic, optical, acoustic, etc.

It is now necessary to see how the different established flow types fit into the concept of the generalized flow curve.

ANALYSIS OF ESTABLISHED FLOW TYPES IN TERMS OF THE GENERALIZED FLOW CURVE

The following flow types are being considered: Newtonian, pseudoplastic, dilatant, plastic, Bingham, and Ostwald. These are represented in Figure 2.

Newtonian Type

This represents the behavior of any liquid which is subjected to a shear rate between zero and some finite value beyond which the deviations from linearity cannot be experimentally demonstrated. This does not mean that the deviations from linearity do not exist, it merely means that turbulent flow conditions occur before deviation from Newtonian behavior has a chance to manifest itself. Indeed, it is an essential postulate of the generalized flow theory that deviation from Newtonian behavior would
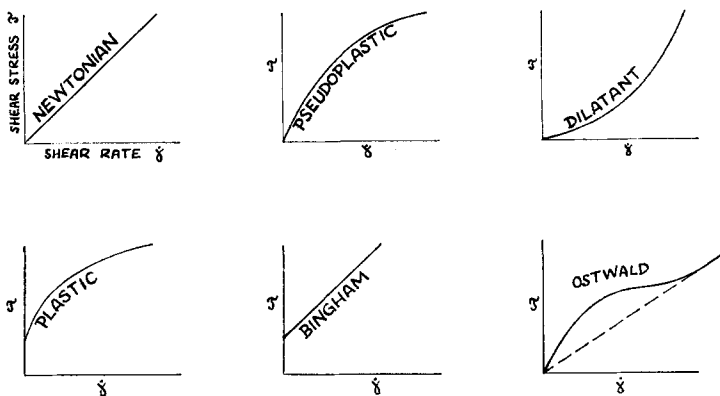
Figure 2.

become manifest if nonturbulent flow conditions at high enough shear rates could be experimentally realized.

Pseudoplastic Type

This represents the behavior of any liquid which is subjected to a shear rate from zero upward and which shows a convex curvature with respect to the shear rate coordinate.

It is well known that at extremely low shear rates the slope of the curve is constant and that there exists some very low but finite and sometimes experimentally determinable threshold shear rate beyond which deviation from linearity commences. The slope of the linear portion of the curve is known as the limiting viscosity at zero shear rate or the Newtonian viscosity. A better term is first (or initial) Newtonian viscosity. Beyond the low-shear-rate region characterized by the initial Newtonian regime the material is shear-softened, a phenomenon which has its precise counterpart in the solid state where it is known as strain-softening.

Continuing into the pseudoplastic portion proper it has frequently been shown that an upper threshold point can be reached beyond which no further reduction in viscosity occurs. The curve then enters a second linear region of proportionality, the slope of which is the second Newtonian viscosity. Some workers have termed this the viscosity at infinite shear rate, but it will presently be evident that this latter terminology is incorrect.

Pseudoplastic systems are common in polymer melt rheology, and the existence of first and second Newtonian regions has long been recognized. It need hardly be said that the second Newtonian region can only be experimentally demonstrated if nonturbulent flow conditions can be maintained beyond the upper threshold of pseudoplastic behavior.

Dilatant Type

This type is less common among plastics under ordinary conditions, but it can be found in heavily filled (crowded) systems and in some PVC

pastes. The dilatant type represents the entire generalized flow curve in which the initial Newtonian and pseudoplastic regions have, however, degenerated to a vanishingly small portion of the curve as a whole. The initial Newtonian and pseudoplastic regions therefore tend to coincide with the origin and are not experimentally demonstrable. In some cases of dilatancy a linear region may be discerned before the curvature (concave with respect to the shear rate coordinate) appears. In other cases no distinctly linear portion can be seen at the low-shear end. It is reasonable to argue that where a low-shear linear region is apparent in a dilatant liquid this represents the second Newtonian viscosity, and that in the absence of a low-shear linear region the second Newtonian region has also become vanishingly small, just like the first Newtonian and pseudoplastic regions which preceded it.

Plastic Type

It is by no means certain that this flow type does in fact exist. But if it does, then the generalized flow curve can readily account for it on the assumption that the initial Newtonian viscosity coincides with the shear stress coordinate. This is equivalent to saying that the liquid is characterized by an initial Newtonian viscosity of infinity, since the low-shear portion of the curve coincides with the shear stress coordinate up to a point where a certain "yield stress" is reached. Beyond this point the same arguments hold which were used in the pseudoplastic type.

Bingham Type

The Bingham type is not common among plastics, but it has been observed in a number of crowded disperse systems, notably those involving clay and other mineral slurries containing a high volume fraction of disperse phase. The Bingham flow curve is readily derived from the generalized flow curve if it is assumed, as in the plastic type described in the preceding subsection, that the initial Newtonian viscosity is infinity, and by postulating additionally that the pseudoplastic region has degenerated to vanishing point so that the curvature characteristic for the pseudoplastic type disappears. Again, we have a "yield stress" which characterizes the departure from the initial Newtonian viscosity which in this case, as in the plastic type, is infinity. The linear portion which, in view of the degeneracy of the intervening pseudoplastic region, follows the initial Newtonian region directly is, of course, the second Newtonian region.

Ostwald Type

A flow curve of this type has been described by Ostwald,[1] who described it as being pseudoplastic and who claimed that a true Newtonian region follows the pseudoplastic region and that that region possessed linearity which extrapolated to the origin. The writer believes that the extrapolation to the origin is fortuitous and insignificant and that the linearity itself is spurious. If there is a second Newtonian region in the Ostwald curve it is

degenerate and is represented by the point of inflection of the plot. The region which Ostwald claims to be Newtonian at high shear rates is in fact the dilatant region which starts with the curvature towards the shear rate axis and then flattens out into a quasi-linear function which is asymptotic to the dilatancy parabola.

Time-dependent liquids have not so far been mentioned. The question arises, however, as to whether the generalized flow curve can also cover time-dependent hysteresis effects. It is not intended to discuss thixotropy and rheopexy here, but it must be said that the generalized flow curve applies in the first place at shear accelerations which are low enough to maintain flow curve equilibrium and so avoid the complications of hysteresis. In general one may well say that all liquids have time-dependent hysteresis, but the time scale of those liquids which are not normally considered to be time-dependent is so small that it escapes experimental recognition.

CAUSES FOR CHANGES IN FLOW REGIME

In the following the flow mechanism believed to be involved and the changes during transitions are explained on a molecular basis.

Random Ground State

This applies to a molten polymer with a blank shear history or, more precisely, to a melt in which Brownian chain randomness and random entanglement of chain segments have been attained after a long rest period during which any prior strain-induced memory effects have become obliterated.

If vanishingly small shear rates are applied to a melt in this condition, then the random ground state will remain undisturbed and the slope of the flow curve will remain constant so long as the shear rate increase fails to affect the overall molecular configuration. The random ground state thus coincides with the region of initial Newtonian linearity.

Structural Breakdown

By this is meant a breakdown in the random ground state structure and not a lower degree of order in the system. Indeed, the breakdown of the random ground state structure is accompanied by the build-up of a shear-oriented structure.

When the shear rate reaches the threshold value at which the random ground state is beginning to be disturbed, the molecules arrange themselves increasingly in such a manner as to present the least resistance to flow. In the case of polymer chains this will obviously tend towards a conformation favoring alignment along the flow lines created by the shear field. With polymers this process commences already at very low shear rates, but in the case of liquids of smaller molecular chain length where entanglements are less likely to occur or cannot possibly occur the alignment may

take the form of an end-on arrangement. With simple liquids very high shear rates may be necessary to secure end-on alignment of the small molecules, and since at such high shear rates turbulence is bound to supervene, the regions beyond the first Newtonian region are not experimentally accessible.

In high molecular weight materials, on the other hand, the least disturbance will tend to cause alignment so that the ground state structure is virtually confined to the rest condition. The moment at which the random ground state structure begins to break down and a shear-oriented structure begins to build up in its stead is the point of transition from the initial Newtonian to the pseudoplastic condition. The discontinuity in flow regime is clearly seen in the log–log plot provided by the power law. In this presentation the power index changes abruptly from a value of unity to one which is less than unity.

Second Newtonian Region

If random ground state structure is progressively broken down and a shear-oriented structure is created in its stead which offers reduced resistance to the force field, it is clear that this process must terminate when it is complete. If this process characterizes the pseudoplastic region, then the moment at which all ground state structure has been sheared out and the maximum possible alignment along the flow lines has been attained is characteristic for the inception of the second Newtonian region. On a molecular level this means that further increases in shear rate will only bring about proportional increases in shear stress because the molecular chains, having aligned themselves to the maximum degree, have no means of further conforming to the shear field. We have thus reached a limiting viscosity which is often, (but incorrectly!), referred to as the viscosity at infinite shear rate. Linearity in the curve is reattained, but the slope can obviously not be extrapolated to the origin. This is the second Newtonian region. In the log–log plot which represents the power law, the transition from the pseudoplastic to the second Newtonian regime is characterized by a return to unity of the power index. Although the log–log slope of the first and second Newtonian regions are both the same (unity), the second Newtonian region differs from the first in that the line cannot pass through the origin but must give a positive intercept with the shear rate coordinate on extrapolation.

Dilatant Region

When very high shear rates are operating on a polymer melt the chain segments of the polymer molecules, aligned along the stream lines to the greatest extent possible, will begin to exert a frictional force on their neighbors. This will modify the flow pattern which will however not necessarily become turbulent. Secondary flow patterns may be created which will alter the dimensions and the shape of the flow units. The new shapes are pictured as micro whorls or flow nuclei which will tend to flow in

"balled-up" fashion and so present more resistance to flow than the aligned segments did in the second Newtonian region which preceded the new state of the system. When the balled-up flow nuclei attain large dimensions (as they may well do in high polymer melts), flow may become virtually impossible altogether. The flow curve will then become asymptotic to the shear stress axis. On the other hand, the balled-up flow nuclei may attain a limiting diameter. If flow is then still possible, the flow curve will tend to become asymptotic to the straightening extrapolated curvature of the dilatancy parabola. In the log–log plot which represents the power law, the transition from the second Newtonian to the dilatant regime is characterized by a discontinuous change in the slope of the power index from unity to some value in excess of unity.

EVIDENCE FOR THE GENERALIZED FLOW THEORY

Analogy with Solid-State Deformation

This has already been dealt with above.

Existence of an Initial and a Second Newtonian Viscosity

These two Newtonian regions are well recognized and generally accepted as such. The reader is referred to Wright and Crouse,[2] where the first and second Newtonian regions are used for flow reference.

Experimental Observation of Dilatancy in Polymer Melts

Experimental evidence for the existence of dilatancy in polymer melts at very high shear rates has recently been provided as a result of the studies of Galt and Maxwell[3] and of van der Vegt and Smit.[4]

Evidence from the Work of Galt and Maxwell. These workers studied the flow of polyethylene melts by direct visual and photographic observation, using a particle tracer technique like Clegg[5] had done before them. Galt and Maxwell clearly demonstrated the existence of shear discontinuities at the wall of the capillary rheometer which they used. The zones where the shear discontinuities occurred could extend to as much as about one-sixth of a channel radius towards the axis. More importantly, the boundary between the "wall zone" and the cylindrical zone within it showed an abrupt transition in the velocity profile and hence the viscosity profile. Moreover, the transition in the velocity profile became more pronounced and extended more deeply towards the channel axis the more the severity of the shear conditions was increased. Galt and Maxwell attributed the annular region at the wall to "the highly elastic behaviour, of polymer melts that do not flow continuously. The highly elastic melt elements are created by long chain branching which causes the generation of molecular clusters." In other words, Galt and Maxwell detected an element of dilatancy in polyethylene melts which have hitherto been regarded as typically pseudoplastic materials. Moreover, they detected

this dilatancy precisely where it is most likely to occur, namely, in the wall region of the die channel where the shear conditions are most severe. The fact that they were actually able to observe this is not only due to the tracer technique but also to the experimental geometry of the system which constrained the highly pressurized flow while at the same time preventing it from becoming turbulent.

Evidence from the Work of van der Vegt and Smit. These workers also studied polymer melts in capillary rheometers, including polypropylene, polyethylene, cis-1,4-polybutadiene, and cis-1,4-polyisoprene. They were thus dealing with typical plastics as well as unvulcanized elastomers. The melts were subjected to varying shearing conditions. Van der Vegt and Smit observed that at high shear rate conditions the apparent melt viscosity increased sharply with shear rate and that this viscosity increase may be so great as to completely inhibit flow. The same effect was also observed by others[6] on PVC and polystyrene. Van der Vegt and Smit suggested that the observed viscosity increase is due to shear-induced orientation crystallization in the melt, and the most striking feature of this concept is that this manifestation of crystallinity is possible in polymers which are normally considered amorphous as well as to those which possess substantial crystallinity at submelt temperatures. The assumption of melt crystallinity was confirmed by the x-ray diffraction patterns of the contents of the rheometer capillaries after quenching. It was clearly seen that a highly oriented crystalline structure is present during flow at high shear rates, while at lower shear rates the crystallization is random and isotropic and at even lower ones it is altogether absent. Since crystallization in the melt is comparable to orientation crystallization in highly stretched rubber vulcanizates we incidentally obtained a further significant feature of correspondence between the "liquid" and "solid" states. The effect of shear-rate-induced orientation crystallization in the melt cannot be connected with the pressures necessary to produce those high shear rates since these pressures, as van der Vegt and Smit point out, are quite moderate—of the order of 100 kg./cm.^{2} at 165°C. for polypropylene. Far greater pressures are required to cause genuine pressure-induced viscosity increases of the Bridgman type.

Galt and Maxwell's "molecular clusters" and van der Vegt and Smit's "crystallites" in the melt are obviously identical, and they represent, in fact, the balled-up flow nuclei, the existence of which was postulated as an essential requirement for a satisfactory molecular interpretation of the generalized flow curve.

DISCUSSION

The evidence given in the preceding section proves that the generalized flow theory and the generalized flow curve which characterizes it, as well as the molecular interpretation of the mechanisms involved in the various flow regions and transitions between those regions, are basically correct.

The generalized flow theory can be used to explain satisfactorily certain disturbance phenomena in the calendering, extrusion, and injection-molding processes, especially the phenomenon of "sharkskin" and melt fracture in extrudates.

If flow discontinuities exist at the die inlet and along the channel walls which are due to local differences in the shear conditions, then one may expect dilatant volume elements to arise at certain critically severe shear conditions. These volume elements which van der Vegt and Smit have shown to be shear-induced orientation crystallites occurring in the melt may be expected to cause intermittent blockages and surges in the melt flow. At first, when the critical shear level for the onset of melt crystallinity is barely exceeded, the blockages and surges may be mild, but as the shear conditions become more severe the short periodicity in the disturbance will become longer and longer, and eventually gross extrudate distortion without periodicity will indicate that melt fracture has occurred. The same processes occurring at the die wall give rise to "slip-stick" effects which are thought to be responsible for sharkskin extrudates. It is thus possible to say that both melt fracture- and slip-stick-induced defects are due to shear-rate-induced orientation crystallization in polymer melts. Moreover, this type of crystallization can occur in polymers which are either crystalline or amorphous in the conventional sense. Die inlet melt fracture effects can be healed by virtue of the fact that the crystallization process is reversible within a finite relaxation time, and if the die length is sufficient and hence the melt dwell time long enough for relaxation to occur then the fractured melt can recover uniformity as it passes through the die. The concomitant pressure drop along the die channel also renders the shear conditions progressively milder towards the die exit, so that wall effects will likewise tend to disappear. Finally, the practice of heating the die tip will assist in producing defect-free extrudate by reducing the melt viscosity and thus creating less severe shear conditions.

References

1. See, e.g., in M. Reiner, *Deformation, Strain and Flow*, H. K. Lewis, 1960, p. 223.
2. W. A. Wright and W. W. Crouse, *A.S.L.E. Trans.*, **8,** 184 (1965).
3. J. Galt and B. Maxwell, *Mod. Plastics*, **42,** 115 (Dec. 1964).
4. A. K. van der Vegt and P. P. A. Smit, paper presented at Conference on Advances in Polymer Technology, London, September 1966.
5. P. L. Clegg, in *The Rheology of Elastomers*, P. Mason and N. Wookey, Eds., Proceedings of the Welwyn Garden City Conference 1957, Pergamon, New York, p. 174.
6. E. Atkinson, discussion contribution following the reading of the paper by A. K. van der Vegt and P. P. A. Smit (see ref. 4).

Résumé

Une théorie généralisée de l'écoulement est avancée qui est dérivée d'une revue des types acceptés des courbes de réponse à la tension. La théorie est résumée en une courbe d'écoulement simple de forme universelle au départ de laquelle tous les types d'écoulement liquide peuvent être interprétés. Cette courbe généralisée d'écoulement peut être appliquée à des polymères fondus en particulier, mais il n'y a aucun motif pourlequel elle

ne serait pas également applicable à des solutions, dispersions, de suspension, émulsions, ou liquides purs. La courbe généralisée d'écoulement est exactement analogue a une courbe de déformation sous une charge développée typique qui s'applique à des plastiques durs à l'état solide. L'interprétation moléculaire des processus qui se passent en produisant des phénomènes d'écoulement dans les différentes parties de la courbe généralisée d'écoulement est avancée. Une évidence sur laquelle la théorie est basée est passée en revue. Certaines applications fondamentales sont soumises à discussion.

Zusammenfassung

Eine verallgemeinerte, aus einer Zusammenfassung der bekannten Typen von Spannungsverhaltenskurven abgeleitete Fliesstheorie wird aufgestellt. Die Theorie führt zu einer einzigen Fliesskurve von universeller Gestalt, mit welcher alle Typen des Flüssigkeitsfliessens interpretiert werden können. Diese "verallgemeinerte Fliesskurve" kann mit Vorteil auf Polymerschmelzen angewendet werden, es besteht aber kein Grund, sie nicht in gleicher Weise auf Lösungen, Dispersionen, Suspensionen, Emulsionen oder reine Flüssigkeiten anzuwenden. Die verallgemeinerte Fliesskurve ist völlig analog der typischen, voll entwickelten Belastungs-Deformationskurve, welche für zähe plastische Stoffe im festen Zustand gilt. Eine molekulare Deutung der für die Fliesserscheinungen in den verschiedenen Teilen der verallgemeinerten Fliesskurve verantwortlichen Prozesse wird gegeben. Das der Theorie zu Grunde liegende Tatsachenmaterial wird zusammengestellt. Einige grundlegende Folgerungen werden diskutiert.