総合論文

Memory Effect and Extrudate Swell*

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The first part of this paper describes an interpretation of extrudate swell with an emphasis on the following aspects: (1) The material behavior in the entrance zone leading to capillary is in transient and not in steady state. (2) The material behavior is predominantly in elongation and not in shear. (3) The deformational memory introduced in this zone is carried into capillary. (4) The material behavior in capillary is the steady state flow with accompanying memory mentioned in (3). (5) The memory is dissipated (relaxation) during the flow. (6) The remaining memory results in extrudate swell after material exit from capillary. (7) Even with a long capillary, the memory does not dissipate completely, because the steady state flow itself maintains certain memory. (8) The extrudate swell is time-dependent and not instantaneous. (9) It is like a creep-recovery. (10) The extrudate swell is related to the normal stresses in the flow through capillary.

The second part of the paper describes various subjects, which are required for the fundamental understanding of the memory behavior and extrudate swell in particular. (11) The deformation associated with extrudate swell is nonlinear. Therefore, a theoretical treatment of nonlinear viscoelasticity is needed. (12) Because the material behavior involves both shear and elongation, the relationship between them must be established. (13) A quantitative description of deformational memory is needed. (14) In the transient behavior a memory is being built and at the same time a part of memory is lost. A "balance sheet" of the memory at any instant of time must be available. (15) Stress relaxation accompanying steady state flow must be elucidated. A use of stress relaxation measurement is proposed as a quantitative means of describing the "memory balance".

Key words: Extrudate Swell / Deformational Memory / Stress Relaxation / Non-linear Viscoelasticity / Transient Behavior

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1. INTRODUCTION

In the late 50's and early 60's there were many significant developments in the world of rheology. One of them concerns the memory effect and extrudate swell. With the development of the popular use of thermoplastics, the swelling of extrudate became an important industrial problem and recognized as a memory effect.

Since then much progress has been made for understanding the mechanisms involved in extrudate swelling, but even today there is a lack of means to predict the extent of swelling. This makes a control of the extrudate swelling difficult.

In the first part of this paper I intend to bring the discussion from 25 years ago to the present. However, it is not intended to be a review. This is primarily a presentation of my viewpoints regarding the memory behavior. In the second part more recent analysis of memory behavior will be presented.

2. BACKGROUND OF STUDIES IN EARLY 60's

A rapid growth of plastics industry in early 60's brought about various processing problems. One of them was the swelling of extrudate in the extrusion. This was particularly an important problem with polyethylenes, which gave a large degree of swelling and thus more variability in swelling, necessitated control. One of the examples was a high speed blow-molding of bottles¹.

Two pioneering works were those of Arai and his co-workers² and of Bagley and his coworkers³. Although the phenomenon of the extrudate swelling had been recognized since late nineteenth century, first by Barus⁴, the above two works distinguish themselves with a number of respects; (i) both papers treated extrusion of polymer melts, particularly polyethylenes; (ii) they treated the extrudate swelling as the elastic phenomenon, which is related to the energy loss at the entrance to the capillary⁵; (iii) Bagley and his coworkers recognized the extrudate swelling to be the memory effect with acknowledgement given to the earlier work of Arai⁶.

However, in their treatment of the phenomenon they did not accept the interpretation that the extrudate swelling is related to the normal stress⁷. Neither did they relate the extrudate swell to the viscoelastic behavior of the material, which is represented with a variety of viscoelastic functions⁸. Those were the days when the three major areas of rheology existed, by and large, separately; they were the study of (i) steady state flows of liquids, (ii) viscoelasticity and (iii) continuum mechanics. In addition, (iv) the molecular mechanisms of the flow of polymeric liquids were not well understood.

3. NAKAJIMA AND SHIDA'S INTERPRETATION⁹

When these authors began their investigation, they immediately recognized that the phenomenon of extrudate swelling is much more complicated than the previous workers had visualized. At the same time these authors knew that a systematic interpretation can be developed by combining the previously mentioned four areas of rheology. Such a systematic frame-work, however, required assumptions and approximations, because the phenomenon is very complex. These were described in detail in their original publication⁹. However, in this presentation the highlights of the development will be recalled.

3.1 Overall Picture of Polymer Melt-Flow

The first attempt of Nakajima and Shida was to develop an overall picture of polymer melt behavior encompassing the flow in the barrel leading to the capillary entrance, the flow through the capillary, and the exit-phenomenon as the extrudate swelling. By that time, it was known that polymer melt establishes "wine glass-shaped" flow lines in the barrel, smoothly leading into the entrance of capillary¹⁰. Then, it was obvious to them that the material behavior in the entrance region of the barrel is neither in a laminar shear nor in the steady state, which were the assumptions of previous works^{2,3}. Two new viewpoints were advanced: one was that on an average, the deformation at the entrance is elongational and the other, that it is a transient behavior. In the transient state, the memory is progressively built, as the material is elongated with a finite rate. Two approximations are made in this treatment; one is to ignore the shear contribution to the overall elongational flow. The other is to ignore the effect of the eddies formed in the corner, when the entrance angle is large⁹, e.g., 180°. The latter approximation was adopted by measuring the entrance pressure-losses with 90° included-angle dies.

The material behavior in the capillary was treated as the steady state shear flow upon which an elongational stress relaxation was superposed. They did not know if any one had conducted this type of experiment. However, they were aware of a steady shear experiment, upon which a shear oscillatory deformation was superposed¹¹.

Since the memory is that of the elongational deformation,

Fig. 1 Telescopic flow and absence of extrudate swell.

the recovery of memory is expected to be the reverse, i.e., the extrudate swelling. Because the elongational contribution had not been recognized previously, there had been a puzzle as to why a telescopic elastic deformation (from the laminar shear flow in a capillary) could result in an expansion of diameter¹²⁾ (Figure 1).

The occurrence of the stress relaxation means the dissipation of memory with the flow time. This explains the decrease of magnitude in swelling with the increasing L/D of the capillary, (L/D) being proportional to the flow time at a fixed shear rate.

Also, while the elongationally deformed material is confined in the capillary and while the stress resulting from the said deformation is not completely relaxed, such a stress acts against the capillary wall in such a way that, if given a chance, it would expand the diameter and contract the length. This recognizes the fact that the extrudate swelling is related to the normal stress effect. Although such an interpretation was not new for the extrudate swelling subsequent to the steady state flow⁶⁾¹³⁾, this was the first time that the normal stress effect was associated with the transient memory of the deformation at the entrance.

If the above interpretation had been sufficient for the material behavior, the extrudate swelling must have diminished to zero after a sufficiently long flow time. On the contrary, as the capillary (L/D) was increased, there was a finite degree of extrudate swelling, which was of appreciable magnitude with polyethylene, for example⁹⁾. As mentioned before, the swelling of the extrudate exiting from the steady shear flow through a capillary was treated as the normal stress effect⁷⁾¹³⁾. The examples were polymer solutions and jellied gasoline. This interpretation had not been applied to a much higher viscosity fluid such as polyethylene melt. Naka-

jima and Shida recognized that the same interpretation was applicable to the swelling of polymer-melt extrudate. This is based on their interpretation of a mechanism of polymer chain motion under the steady state shear flow, Figure 2.

When polymer chains are subjected to simple shear motion, the chain as a whole moves along the flow line. However, segments of the chains are required to undergo complicated motions involving all directions. The latter motions have normal components. Having the material confined in a capillary, these normal motions exert normal stresses against the capillary wall¹⁴⁾. Therefore, even in the steady state shear flow, an "elongational" memory is present, resulting in certain magnitude of extrudate swelling. This steady state memory is introduced during the build-up of the previously discussed transient memory; the situation is somewhat analogous to the stress overshoot phenomenon, although in the latter the excess memory is built under a constant deformation rate whereas in the present case it is under a varying deformation rate.

Having established the overall picture of polymer melt-flow through a capillary, the next step is on how to extract quantitative information from the experimental data. Without this the quantitative prediction of the extrudate swelling is not possible. However, even today, many problems remain to be solved.

4. PROBLEMS INVOLVED IN QUANTITATIVE PREDICTION

Here, I shall attempt to highlight practical problems in predicting the extrudate swelling.

4.1 Transient Behavior at the Entrance

In order to describe the material behavior fully, the flow lines and velocity profiles must be known. This means an experiment for the above purpose must be performed for each shear rate of the flow in the capillary and for each given geometry of the entrance. This requires rather an extensive experiment. Usually this part of the investigation is by-passed; instead the whole phenomenon is treated as the "entrance pressure loss", which is found from the experimental data by the "Bagley correction"⁵⁾. In addition to ignoring the details of flow and deformational pattern, this approach presents a difficult problem. The most difficult problem is to separate the entrance loss into viscous and elastic contributions. Arai and Aoyama²⁾ treated the flow at the entrance as if it were an extension of the steady laminar shear flow in the capillary and assumed the viscous contribution to be a constant value, equivalent to the Couette's correction for Newtonian liquids. Bagley and his coworkers³⁾ also made a similar treatment, i.e., assumed a constant value of Couette's correction, except that the constant was evaluated by extrapolating from the plot of the experimental data. However, there is no reason to assume the Couette's correction to be independent of shear

Fig. 2 Movements of polymer chain in shear and elongational field.

rate for non-Newtonian liquids like polymer melt. Nakajima and Shida⁹⁾ attempted to estimate the elastic contribution from the observed value of the extrudate swell for the zero-length capillary. In order to do this, the magnitude of swelling was converted to strain, a Hookian elasticity was assumed and a modulus was estimated from the experimental data of memory-decay rate. In addition to the approximate nature of the treatment, this approach does not offer predictive capability. Recent work by Meinecke and Yau¹⁵⁾ ignores the viscous contribution to the entrance loss. In summary, a new approach must be developed to describe the build-up of the memory and a partial loss of memory at the entrance region. This will be described later.

4.2 Memory Dissipation in Steady Flow

The memory dissipation during the flow through capillary which is observed as a decrease of the extrudate swell, usually follows an exponential decay²⁾⁹⁾. Therefore, from the observed data, the first order rate constant, may be obtained⁹⁾. As a reciprocal of the rate constant a single relaxation time may be calculated⁹⁾. However, there is no a priori reason to believe that the single relaxation time is responsible for the memory dissipation, because polymer melt possesses, in general, a spectrum of relaxation times⁹⁾. In addition, the above approach does not offer a predictive capability. Meinecke and Yau treated the phenomenon as the relaxation occurring quite independently from the steady state flow. Also, they assumed that the introduction of the memory occurs instantaneously at the inlet of the capillary. With these simplifications they successfully used the stress relaxation data calculated from dynamic measurement to predict the decrease of extrudate swelling with the flow time¹⁵⁾. However, more accurate treatment requires two modifications; one is the introduction of the memory, which is not instantaneous but takes a finite time as the flow line converges and the polymer melt is deformed at the entrance region of the barrel. The other modification is for a possibility that the relaxation superposed on the steady state flow may not be the same as the relaxation in the absence of flow.

4.3 Recovery of Memory as Extrudate Swelling

The process of swelling is time-dependent; this is clearly indicated in the photograph where the profile of extrudate is shown. With an extrusion grade of polyethylene, about 50% of the total recovery, i. e., swelling, takes place within a few seconds⁹⁾. This is often regarded as an instantaneous occurrence. However, in the blow-molding of bottles, for example, the mold closes within this initial period of the recovery. For the fundamental study of the memory recovery, the time dependence must be recognized. With the polyethylenes it was shown that a full recovery of memory takes place 15 minutes to almost an hour⁹⁾, Figure 3.

Nakajima and Shida, although recognizing the time-dependent nature of the extrudate swelling, treated it as if it were

Fig. 3 Recovery of memory observed as extrudate swelling.

a recovery of an elastic network, ignoring viscous effect⁹⁾. A number of researchers who followed this work also used this approximation¹⁵⁻¹⁷⁾¹⁹⁾. When the recovery is relatively fast, or more specifically when the material is in rubbery state, the viscous response is so much smaller than elastic response that the latter may be neglected for the approximation. However, for the fundamental study of the memory and for the extrudate swelling which takes 15 minutes or more for the full recovery, the viscous contribution may not be ignored. A more precise approach would be a treatment like a creep recovery⁹⁾. Combining with the memory dissipation during the flow through capillary, the material behavior is like a recovery after partial stress relaxation²⁰⁾²¹⁾.

4.4 Overall Description of the Memory Behavior

Summarizing the memory behavior of extrudate swelling, the material behavior at the three stages may be described as follows: at the entrance region of the barrel the deformation is imposed with a finite and variable rate of strain, which is dictated by the flow line and by the velocity profile. This is where the memory is introduced. Since the material spends a finite time here, a part of this memory dissipates before it enters capillary. During the flow through capillary the material behavior is like a stress relaxation superposed on the steady laminar flow. The memory dissipates through the relaxation process towards certain limiting value, which is an "equilibrium memory" in the steady flow. The latter memory is associated with a "deformation" created by polymer chain motions in the normal direction during flow. Finally, after exiting capillary, the remaining memory recovers in a manner of creep recovery. Therefore, during the recovery process, a portion of memory is lost. The loss may be relatively small and negligible if the material is in the rubbery state.

5. FUNDAMENTAL INVESTIGATION OF MEMORY BEHAVIOR

The extrudate swelling, an example of the memory behav-

Fig. 4 Complex modulus, stress-strain master curve, and ultimate properties of sample B.

ior, points to a need for investigating several important areas of rheology: They are (1) treatment of large deformation and non-linear behavior, (2) relation between elongation and shear, (3) transient behavior leading to steady state, and (4) a method for "printing" a memory being carried by a material at a given instant of time. From a practical point of view the above investigation must include polymer melts, elastomers as well as those consisting of polymer blends and filled compositions. With the increase of the complexity of the material composition the complexity in the rheological treatment also increases. Here, I chose only polymer melts and gum elastomers as examples excluding any mixed compositions.

5.1 Treatment of Large Deformation and Nonlinear Behavior

In order to take advantage of the linear viscoelasticity

Fig. 5 Comparison of viscosities calculated from tensile measurements to dynamic shear viscosities for Sample C.

Fig. 6 Comparison of viscosities calculated from tensile measurements to dynamic shear viscosities for Sample I.

theory, a basic question is whether nonlinear behavior can be linearized or not. For polymer melts and gum elastomers the nonlinearity concerns primarily the large deformation behavior. With a polyethylene melt the non-Newtonian steady state viscosity, the stress-growth under steady deformation rates leading towards the steady state and the dynamic oscillatory motion superposed onto the steady state flow were all successfully treated with a concept of the shear-rate dependent relaxation spectrum²²⁾²³⁾. With EP (D)M elastomers a similar linearization may be applicable²⁴⁾. On the other hand, with acrylonitrile-butadiene copolymer elastomers a strain-time correspondence principle is the effective tool for linearization²⁵⁾.

There are many other attempts for linearization or otherwise to treat nonlinear behavior. However, this paper is not intended to be the review of the subject.

5.2 Relation Between Elongation and Shear

The extrudate swelling is a good example of the co-existence of elongation and shear deformation. In many cases the material behavior in elongation and shear are different²⁶⁾. However, if appropriate means are available for linearization, then, elongational modulus and shear modulus are related with a factor of three. With some gum elastomers for which the strain-time correspondence principle is applicable, such a relation exists between elongation and shear²⁷⁾²⁸⁾, (Figures 4, 5 and 6).

5.3 Transient Behavior Leading to Steady State

When a steady deformation rate is imposed on a viscoelastic material, the corresponding stress does not reach steady state immediately. Instead, it takes a finite time for a stress to grow. This transient behavior leading into steady state is somewhat similar to the material in the entrance region from the barrel to capillary, although the former is simpler in many respects. For the linear viscoelastic material the treatment of this behavior is well established²¹⁾. For some polymer melts the shear-rate dependent relaxation spectrum enables quantitative treatment of this behavior²²⁻²³⁾. With nonlinear behavior of some gum elastomers the strain-time correspondence principle and subsequent linearization were shown to be satisfactory treatments²⁴⁾²⁵⁾ (Figure 7).

Fig. 7 Complex viscosity observed with oscillatory measurements (—) and that calculated from stress-rise data, $\dot{\epsilon} = (\circ)$ 0.025, $(\triangle)$ 0.040, $(\times)$ 0.078; BN-2 sample at 100°C.

5.4 Analysis of Transient and Steady State Memory

In general, while a material is being deformed, a memory is being built. However, with viscoelastic material the memory dissipates even while it is being built. Therefore, at any instant the memory possessed by the material is a balance of what was built and what was lost. The analysis of such memory behavior is intriguing. The memory behavior of gum elastomers was examined under a constant shear deformation

Fig. 8 Stress-relaxation curves after a constant rate of deformation, from stress overshoot and after cessation of steady state flow; EP sample and $\dot{\epsilon} = 0.395 \text{ s}^{-1}$.

Fig. 9 Stress relaxation from stress overshoot presented as a modulus-time curve; EP sample and $\dot{\epsilon} = 0.395 \text{ s}^{-1}$.

Fig. 10 Stress-relaxation curves after a constant rate of deformation and after cessation of steady state flow; BN-1 sample and $\dot{\epsilon} = 0.025 \text{ s}^{-1}$.

rate; the stress relaxation measurements were conducted by interrupting at any state of initial stress growth, stress overshoot or steady state flow. The manner of stress-relaxation is a manifestation of the memory retained by the material just prior to the relaxation measurement. When the relaxation behavior is either linearly viscoelastic or being linearized, this

Fig. 11 Stress relaxation after a constant rate of deformation and from very close to steady state flow; BN-1 sample and $\dot{\epsilon} = 0.025 \text{ s}^{-1}$.

curve may be compared to the linear stress relaxation curve after an "instantaneous" deformation. The difference between the two curves provides the data indicating the lost part of the memory²⁹⁾ (Figures 8, 9, 10, 11).

6. POSTSCRIPT

In the industrial processes of molding and shaping, the material often undergoes a variety of deformational events in succession. At each event a memory is introduced in the material. As soon as the memory is introduced, however, a forgetting process begins. The manner of the gain and the loss of memory depends on not only the inherent nature of the material but also the way by which the material is treated. This presents a fascinating subject for investigation. The analysis of extrudate swell is a good example for the study.

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