

Experimental and Theoretical Study of the Extrusion of Two-Phase Molten Polymer Systems

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Synopsis

An experimental and theoretical study of two-phase flow of molten polymers has been carried out. The theoretical analyses apply the theory of nonlinear viscoelastic fluids to consider stress and velocity profiles and interface shape in stratified flow between parallel plates and in a tube. The second normal stress difference is predicted to influence interface shape. Experimental studies have been made of stratified two-phase flow of a low viscosity but elastic low-density polyethylene and a high-viscosity polystyrene in a capillary rheometer. In the stratified flow experiment, velocity fields and interface shape in the reservoir approaching capillary die and the emerging extrudate were investigated, the former being observed through visual experiments. The emerging extrudates possessed convex polystyrene surfaces at the interface. A strong tendency toward the collection of bubbles near the capillary entry was found. We have made an experimental study of the extrusion of disperse mixtures of polystyrene and different polyolefins. The morphology of the disperse two-phase emerging extrudates has been investigated.

INTRODUCTION

Investigations of mechanically mixed two-phase blends of molten polymers date at least forty years back to the period when polystyrene, butadiene-styrene, and butadiene-acrylonitrile copolymers were first becoming commercial materials and their blends with natural rubber and gutta percha were studied.¹ These investigations even seem to go back to Farbenfabriken Bayer's pioneering pre-World War I synthetic rubber program.² It is well known that blends (indeed even ternary and quaternary systems) maintain a key role in the elastomer industry.³ Probably the first two-phase polymer systems to play an important role in the plastics industry were the ABS resins and the high-impact polystyrenes which are created during their polymerization as opposed to mechanical mixing.⁴ However, while these two-phase polymer systems hold their own, mechanically mixed composites play an increasing role in today's plastics industry.⁵ The mechanical mixing of two polymer phases to obtain improved fiber properties seems to have long been under consideration, but attention was first focused on such materials by Allied Chemical's development of a *biconstituent* fiber from blending polyester and polyamide.⁶

There is a second type of two-phase polymer system of importance, one involving two stratified continuous phases as opposed to one phase dispersed in a second. This is of special significance to the fiber industry, for the cooling of two different semicylindrical polymer phases along the length of the fiber leads to a buckling of the filament to form a so-called *crimped* fiber. As shown by Horio and Kondo,⁷ this sort of two-phase structure exists in wool and leads to its crimping characteristics. The first man-made fiber based on these principles, developed about 1950 by American Viscose, was described in a paper by Sisson and Morehead.⁹ This work, which led to a generic patent, involved creating what are now called *bicomponent* fibers from two different viscose solutions which flow from adjacent chambers in a spinneret reservoir into the same capillary. The first truly synthetic bicomponent fiber was a two-phase acrylic fiber devised by du Pont.⁹⁻¹¹ This company later marketed a bicomponent nylon fiber based upon the same principles.¹⁰⁻¹² Several companies now manufacture bicomponent fibers.

Little work of a fundamental nature seems to have been done on the flow characteristics of two-phase polymer melt systems. There has been considerable effort given to the understanding of stratified¹³⁻¹⁹ and annular flow¹⁴ of two Newtonian liquids. The disperse two-phase flow of dilute suspensions of Newtonian liquid drops in a Newtonian liquid matrix has similarly received consideration.^{20,21} In these studies laminar velocity profiles and pressure drops were derived in the stratified and annular flow problems and increase in emulsion viscosity and drop distortion in the dispersed flow problem.

As mentioned, there has been little direct effort to understand (as opposed to developing new products and processes) two-phase flow of molten polymer systems. No study of the characteristics of stratified flow has appeared, though Slattery²² several years ago did publish an analysis of annular two-phase viscoelastic flow. Li^{23,24} has published a pair of papers regarding hydrodynamic interfacial instabilities in two-phase stratified viscoelastic flow. Recently, Professor C. D. Han communicated to the author that he was engaged in experimental studies of pressure distribution in stratified two-phase flow through a slit die. One of the earliest studies of disperse two-phase flow of molten polymers was published by Spencer and Wiley²⁵ and later extended by Mohr and his colleagues,²⁶ who envisaged mixing occurring through the deformation and increase in interfacial surface caused by the shearing action in the melt. In recent years, one of us (J.L.W.) has described the mechanics of development of the morphology of rubber blends during processing. Hayashida, Takahashi, and Matsui²⁸ and Maxwell and his colleagues²⁹⁻³¹ have undertaken fundamental studies of the structure of disperse two-phase molten plastic systems. More recently, further work in this area has been carried out by Van Oene³² and by Han,³³ the former being concerned with the mechanism leading to observed morphologies and the latter, with the rheological properties.

In this paper we present an experimental and theoretical study of two-phase flow of molten polymers. An especially extensive study of stratified two-phase flow has been attempted. Stress and velocity fields and the nature of interface shape have been considered. Visual observations of flow patterns have been made. In a sense, these researches represent an extension of our experimental studies of flow patterns in homogeneous one-phase polymer melts.³⁴⁻³⁶

STRATIFIED SYSTEMS

Theoretical

General

In this section, we will consider the stress and velocity fields arising in continuous two-phase flow of polymer melts. We basically presume that the melts behave as isotropic viscoelastic fluids, i.e., the stress is a hereditary function of the deformation history of an initially isotropic material. Recent literature³⁷⁻³⁹ has emphasized utilization of single integral theories of the form

$$\boldsymbol{\sigma} = -p \mathbf{I} + \boldsymbol{\tau} = -p \mathbf{I} + \int_{-\infty}^t [\alpha_1(t-s) \mathbf{e} + \alpha_2(t-s) \mathbf{e}^2] ds \quad (1)$$

where $\boldsymbol{\sigma}$ is the stress tensor, p is the pressure, \mathbf{I} is the unit tensor, $\boldsymbol{\tau}$ is the extra-stress, \mathbf{e} is a Finger strain tensor measured from time t to past time s , and $\alpha_1(t)$ and $\alpha_2(t)$ are relaxation functions dependent upon the variants of \mathbf{e} or the rate of deformation tensor. The work of Chen and Bogue³⁹ is most important here, for it shows the quantitative applicability of nonlinear viscoelasticity to polymer melts. For smooth flows, the strain tensor may be expressed in a Taylor series about the instantaneous state^{38,40-42} and the stress tensor may be written^{41,38}

$$\boldsymbol{\sigma} = -p \mathbf{I} + \sum_j \mathbf{M}_j \quad (2)$$

where the \mathbf{M}_j are polynomials of order j in the acceleration tensors

$$\begin{aligned} \mathbf{B}_1 &= \nabla \mathbf{V} + (\nabla \mathbf{V})^T \\ \mathbf{B}_{n+1} &= \frac{D\mathbf{B}_n}{Dt} - \nabla \mathbf{V} \mathbf{B}_n - \mathbf{B}_n \nabla \mathbf{V} \end{aligned} \quad (3)$$

where \mathbf{V} is the velocity vector. For long-duration flows, the coefficients become constants.^{42,43} For rectilinear flows,

$$V_1 = V_1(x_2, x_3), \quad (4)$$

equation (2) reduces to

$$\boldsymbol{\sigma} = -p \mathbf{I} + \mu \mathbf{B}_1 - (1/2) \beta_1 \mathbf{B}_2 + \beta_2 [\mathbf{B}_1^2 + 1/2 \mathbf{B}_2]. \quad (5)$$

This leads to the following stress components:

$$\begin{vmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{vmatrix} = - \begin{vmatrix} p & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & p \end{vmatrix} + \begin{vmatrix} \beta_1(\Gamma_2^2 + \Gamma_3^2) & \mu\Gamma_2 & \mu\Gamma_3 \\ \mu\Gamma_2 & \beta_2\Gamma_2^2 & \beta_2\Gamma_2\Gamma_3 \\ \mu\Gamma_3 & \beta_2\Gamma_2\Gamma_3 & \beta_2\Gamma_3^2 \end{vmatrix} \quad (6)$$

where Γ_2 is $\partial V_1/\partial x_2$ and Γ_3 is $\partial V_1/\partial x_3$, and μ , β_1 , and β_2 depend upon $\sqrt{\Gamma_2^2 + \Gamma_3^2}$.

We will now look at the detailed stress and velocity fields in two geometries. First, we will look at stratified flow between parallel plates, because of its simplicity and the fact that it readily yields to mathematical analysis. The results may be qualitatively applied to other geometries. Secondly, we will look at the more important case of stratified flow in a tube.

Stratified Flow Between Parallel Plates (Fig. 1)

Let us first restrict ourselves for heuristic purposes to one-dimensional motion in a Cartesian coordinate frame and consider the parallel flow of two different viscoelastic fluids between two parallel plates separated by a distance H . We set the coordinate system in the surface of the lower of the two plates containing the fluids. Let B be the lower layer of fluid of thickness Δ and A be the upper layer of fluid of thickness $H - \Delta$. The stress in each of the fluids may immediately be found from eq. (6) by setting

$$\Gamma_2 = \Gamma \quad \Gamma_3 = 0. \quad (7)$$

The equations of motion take the form

$$0 = -\frac{\partial p}{\partial x_1} + \frac{\partial \tau_{12}}{\partial x_2} = -\frac{\partial p}{\partial x_1} + \frac{\partial}{\partial x_2} \left(\mu \frac{\partial V_1}{\partial x_2} \right) \quad (8a)$$

$$0 = -\frac{\partial p}{\partial x_2} + \frac{\partial \tau_{22}}{\partial x_2} = -\frac{\partial p}{\partial x_2} + \frac{\partial}{\partial x_2} \left[\beta_2 \left(\frac{\partial V_1}{\partial x_2} \right)^2 \right] \quad (8b)$$

where different values of μ and β_2 will exist for each phase. At the interface we must have

$$\sigma_{12A}(x_1, \Delta) = \sigma_{12B}(x_1, \Delta) \quad \text{or} \quad \mu_A \left(\frac{\partial V_1}{\partial x_2} \right) (x_1, \Delta) = \mu_B \left(\frac{\partial V_1}{\partial x_2} \right) (x_1, \Delta) \quad (9a)$$

$$\begin{aligned} \sigma_{22A}(x_1, \Delta) = \sigma_{22B}(x_1, \Delta) \quad \text{or} \quad p_A(x_2, \Delta) - \beta_{2A} \left(\frac{\partial V_1}{\partial x_2} \right)^2 (x_2, \Delta) \\ = p_B(x_2, \Delta) - \beta_{2B} \left(\frac{\partial V_1}{\partial x_2} \right)^2 (x_2, \Delta). \end{aligned} \quad (9b)$$

Let us first investigate the implications of the x_2 component. As eq. (8b) also means that σ_{22} will be constant throughout each of the phases, it follows that the wall pressures or negative stresses ($-\sigma_{22}$) which will be

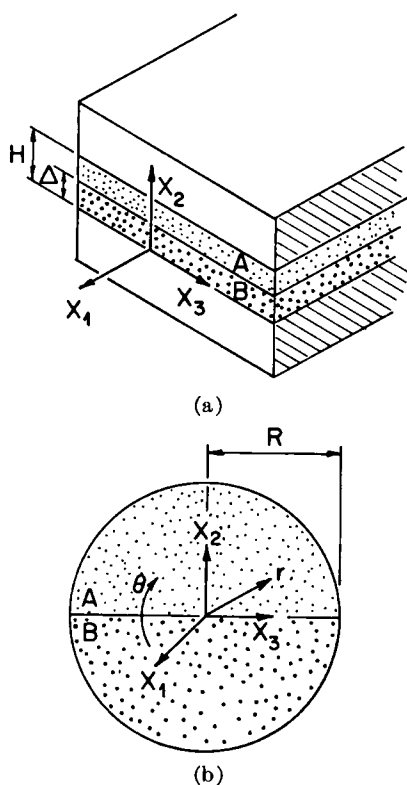


Fig. 1. Two-phase flow systems considered: (a) flow between parallel plates (Cartesian coordinates); (b) flow in a tube (Cartesian and cylindrical coordinates).

read by, say, flush-mounted transducers are the same on both plates at the same axial position. However, the pressures p_A and p_B will vary with x_2 in such a way as to maintain this constancy while allowing for changes in the rheological extra stress with shear rate.

The velocity field and flow rate pressure drop relationship may be obtained by solving eqs. (8a) and (9a). Generally, the non-Newtonian viscosity of the melts will make eq. (8a) nonlinear and will necessitate obtaining numerical solutions. Indeed, this is the case even for a power law fluid. An analytical solution may be obtained if we presume that the viscosities μ_A and μ_B are constants, say η_A and η_B . No slip boundary conditions at the plate surfaces and interface are presumed. The velocity profiles in the two phases are (compare Russell and Charles¹⁴)

$$V_A = \frac{P}{2\eta_A} \left[H^2 - y^2 - 2\Delta(H - y) \right] - \left(\frac{\tau_i}{\eta_A} \right) [H - y] \quad (10a)$$

$$V_B = \frac{P}{2\eta_B} \left[2\Delta y - y^2 \right] + \left(\frac{\tau_i}{\eta_B} \right) y \quad (10b)$$

where P is the pressure gradient $-\partial p_A/\partial x_1$ or $-\partial p_B/\partial x_1$, and τ_i is the interfacial stress. The interfacial shear stress and velocity are

$$\tau_i = \tau_{12}(x_1, \Delta) = \frac{P}{2} \left[\frac{\frac{\Delta^2}{\eta_B} - \frac{(H - \Delta)^2}{\eta_A}}{\frac{\Delta - H}{\eta_A} - \frac{\Delta}{\eta_B}} \right] \quad (10c)$$

$$V_i = \frac{P}{\eta_B} \Delta^2 + \frac{\Delta}{\eta_B} \tau_{12}(x_1, \Delta). \quad (10d)$$

Stratified Flow in a Tube (Fig. 1)

This problem could be formulated in either Cartesian or cylindrical coordinates. Choosing Cartesian coordinates and accepting again what would seem to be the reasonable hypothesis of rectilinear flow, eq. (4), the shear stress tensor takes the form of eq. (6). Here, 1 represents the direction of the flow, 2 and 3 represent the directions perpendicular to flow. There are three components of the equations of motion:

$$0 = -\frac{\partial p}{\partial x_1} + \frac{\partial}{\partial x_2} [\mu \Gamma_2] + \frac{\partial}{\partial x_3} [\mu \Gamma_3] \quad (11a)$$

$$0 = -\frac{\partial p}{\partial x_2} + \frac{\partial}{\partial x_2} [\beta_2 \Gamma_2^2] + \frac{\partial}{\partial x_3} [\beta_2 \Gamma_2 \Gamma_3] \quad (11b)$$

$$0 = -\frac{\partial p}{\partial x_3} + \frac{\partial}{\partial x_3} [\beta_2 \Gamma_3^2] + \frac{\partial}{\partial x_2} [\beta_2 \Gamma_2 \Gamma_3] \quad (11c)$$

When we considered flow between parallel plates, symmetry considerations dictated that there would be only two independent components of the equations of motion. The component in the direction of flow would be solved to give the velocity field and that in the direction parallel to flow, to give the pressure distribution across the cross section. However, no such simplification is valid here, and three independent components are in general obtained. Equations (11b) and (11c) may be combined to give

$$0 = \frac{\partial^2}{\partial x_2 \partial x_3} [\beta_2 (\Gamma_2^2 - \Gamma_3^2)] + \left(\frac{\partial^2}{\partial x_3^2} - \frac{\partial^2}{\partial x_2^2} \right) \beta_2 \Gamma_2 \Gamma_3. \quad (12)$$

Equations (11a) and (12) represent two simultaneous equations for the velocity profile. These may only be satisfied if (1) certain severe requirements are placed on the rheological properties, in particular that β_2 be zero or proportional to μ , or (2) certain symmetry conditions exist, in particular either all derivatives in one direction, say x_3 , are zero, or derivatives in the x_2 and x_3 directions are equal, including $\Gamma_2 = \Gamma_3$.^{44,45} These geometric restrictions are equivalent to flow between parallel plates or a symmetric velocity profile in a tube. The latter of these cases may be simulated by two-phase flow in a tube if the viscosities of the two phases μ_A and μ_B are

equal. An angularly symmetric velocity profile will then exist, and eq. (12) will be satisfied. A second case is of interest. If one phase is much more viscous than the second, angular symmetry will be approached in the more viscous phase, for the flow in this phase will resemble flow through a trough where a half-parabola velocity profile has been shown to exist.^{46,47} In the cases where eq. (12) cannot be satisfied, secondary circulating flows superposed on the rectilinear flow pattern will probably exist. Secondary circulating flows superposed on rectilinear flow have been predicted theoretically⁴⁸⁻⁵⁰ and observed experimentally^{51,52} in the flow of polymer solutions through noncircular ducts where eqs. (11) and (12) also arise. The superposed secondary flows in the two-phase problem should exist in each of the four quadrants of the tube cross section with the diameter perpendicular to the interface and bisecting each phase acting as a line of symmetry. These secondary flows would not arise until the fourth-order approximation, i.e., a fourth-order fluid (compare Langlois and Rivlin⁴⁹), and their intensity would be a complex function of the difference in viscosity functions of the two phases. Pressure variations around the perimeter of the tube should also exist in a manner similar to what is found for noncirculating conduits.^{51,53}

The circulating secondary flows described in the above paragraph will certainly be small in magnitude, and the total amount of angular movement will be small in a normal die. Indeed, Han⁵⁴ has not observed these flows in studies of polymer melts in rectangular dies of moderate length. Certainly, the simultaneous solution of eq. (11a) for the fluids on both sides of the interface will be an excellent approximation. If one chooses a suitable Ellis-like non-Newtonian viscosity function,³⁸ eq. (11a) becomes

$$0 = -\frac{\partial p}{\partial x_1} + \frac{\partial}{\partial x_2} \left[\frac{\eta \Gamma_2}{1 + \Lambda [\Gamma_2^2 + \Gamma_3^2]^{(1-n)/2}} \right] + \frac{\partial}{\partial x_3} \left[\frac{\eta \Gamma_3}{1 + \Lambda [\Gamma_2^2 + \Gamma_3^2]^{(1-n)/2}} \right] \quad (13)$$

with boundary conditions of equal interfacial stresses and velocities and no slip at the wall. Even if we presume a flat interface, computation of the velocity profile can be seen to be a most difficult numerical problem to solve.

We now come to the problem of interface shape. As a starting point, let us presume that we do have a flat interface and let us try to compute the forces which will tend to make the interface curve. If we proceed now in cylindrical coordinates, the net stress difference at an arbitrary interface position pushing phase A into phase B will be

$$[\sigma_{\theta\theta}(x_1, r, \theta = 0^\circ)] = [\tau_{\theta\theta}(x_1, r, 0^\circ) - p(x_1, r, 0^\circ)] \quad (14a)$$

where the bold-face brackets refer to a *jump* across the interface,⁵⁵ in particular

$$[A] = A^B - A^A. \quad (14b)$$

Let us now consider the pressure and stress distribution in one of the phases. The radial variation of pressure in cylindrical coordinates (x_1, r, θ) is given by

$$0 = -\frac{\partial p}{\partial r} + \frac{\partial \tau_{rr}}{\partial r} + \frac{1}{r} \frac{\partial \tau_{r\theta}}{\partial \theta} + \frac{\tau_{rr} - \tau_{\theta\theta}}{r} \quad (15)$$

where we have neglected derivatives of τ in the x_1 direction. Integration of eq. (15) and substitution into eq. (14a) yields

$$\sigma_{\theta\theta}(x_1, r, \theta = 0^\circ) = (\tau_{\theta\theta} - \tau_{rr}) + \int_0^r \left\{ (\tau_{\theta\theta} - \tau_{rr}) - \left(\frac{\partial \tau_{r\theta}}{\partial \theta} \right)_{\theta=0} \right\} d \ln r + C. \quad (16)$$

Now, if fluids of the same viscosity characteristics exist on both sides of the interface, laminar shearing motion will exist throughout. Equation (6) may be applied with Γ_3 set equal to zero and the (x_1, r, θ) directions equated to (1,2,3). It follows that

$$\sigma_{\theta\theta}(x_1, r, 0^\circ) = -\beta_2 \Gamma^2 - \int_0^r \beta_2 \Gamma^2 d \ln r + C. \quad (17)$$

At $r = 0$, Γ will be zero so that C will be $\sigma_{\theta\theta}(x_1, 0, 0^\circ)$ and

$$\sigma_{\theta\theta}(x_1, r, 0^\circ) = \sigma_{\theta\theta}(x_1, 0, 0^\circ) - \beta_2 \Gamma^2 - \int_0^r \beta_2 \Gamma^2 d \ln r. \quad (18)$$

As the second normal stress difference is found by most investigators to be negative,^{47,56,57} we shall take β_2 to be negative. It follows then that

$$\sigma_{\theta\theta}(x_1, r, 0^\circ) > \sigma_{\theta\theta}(x_1, 0, 0^\circ) \quad \text{or} \quad p(x_1, r, 0^\circ) < p(x_1, 0, 0^\circ) \quad (19)$$

where p is $-\sigma_{\theta\theta}$ and there will be a tendency for the interface to protrude at small r . (Remember that this tendency would be due to negative $\sigma_{\theta\theta}$.)

Let us now consider the force balance across the interface:

$$[p(x_1, 0, \theta = 0^\circ) - p(x_1, r, \theta = 0^\circ)] = - \left[\beta_2 \Gamma^2 + \int_0^r \beta_2 \Gamma^2 d \ln r \right]. \quad (20)$$

If we take $|\beta_{2A}|$ to be greater in magnitude than $|\beta_{2B}|$, then the bracketed term on the left hand of eq. (20) will be less than zero. Equating p across the interface at some radius r , yields

$$[p(x_1, 0, \theta = 0^\circ)] > 0, \quad (21)$$

and the fluid with the greater absolute second normal stress difference will tend to protrude into the other fluid. The convex fluid will be the one with the larger $|\beta_2|$, and the fluid on the concave side of the interface will be the possessor of the smaller $|\beta_2|$.

It should also be mentioned that surface tension is not included in the above analysis.* Our arguments should be valid when

$$\frac{\text{surface tension}}{\text{radius of curvature}} \ll [\beta_2 \Gamma^2].$$

This interpretation is similar to that given by Tanner⁴⁷ for the shape of the interface of a viscoelastic fluid moving down a trough.

The analysis of the above paragraphs suggests a qualitative form of the interface but it does not yield a quantitative steady-state shape. Certainly this shape may be derived using the methods of Wineman and Pipkin. This type of analysis is being studied by our group. However, one must be wary of the meaning of such a result, for the residence time of stratified flow of two melts in a spinneret is small, and certainly this steady-state shape is not able to develop in a typical short die.

For the case where the fluid viscosities are different, the problem is more complex and laminar shear flow no longer exists. The velocity field even in Newtonian fluids becomes complicated. In experimental studies of Newtonian fluids moving down a trough, flat interfaces have been observed.⁴⁷ Interfaces in two-phase stratified flow of oil and water in conduits have been found to possess little stability and to be readily disturbed to give waves.¹⁹ Generally, the oil interface has been found to be convex and the water interface concave with the relative convexity of the oil interface increasing with flow rate.¹⁹ The water tends to coat a greater portion of the conduit circumference than the oil. The mechanism for this would seem to involve both surface tension and viscosity differences. One would also suspect that there is in many cases no unique solution of the two-phase stratified flow problem in Newtonian fluids. What we mean is that the Navier-Stokes equations may be simultaneously satisfied in both phases and interfacial stress conditions, satisfied with more than one type of interface shape. This would lead to an instability. Our intuition is that we may have a stability problem with the two-phase system tending toward a low dissipation configuration, one in which the water encapsulates the oil. Yih⁵⁸ has given an analysis of viscosity stratification instabilities in Newtonian fluids. With polymer melts, one must consider also normal stress differences and other viscoelastic manifestations. Indeed, one must retreat from eqs. (5) and (6) to eq. (1) to compute the stress field. If two chemically similar melts of differing molecular weight are considered, both the viscosity difference and normal stress differences would tend to make the lower molecular weight melt encapsulate the other. The Yih instability problem has been studied for viscoelastic fluids by Li,^{23,24} but its applications are not immediately apparent.

* *Note added in proof:* It is not difficult to calculate the shape of the interface between two liquids in a horizontal tube as caused by surface tension. This has been done by one of us (JLW) with B.-L. Lee using the methods of Collins and Cook (*Trans. Faraday Soc.*, 55, 1602 (1959)) and Buff (*Handbuch der Physik*, Vol X, Springer Verlag, Berlin, 1960).

Experimental

Procedure

We carried out an experimental study and made color motion pictures of flow patterns in stratified tubular flow. Copies of the film are available by writing to one of us (J.L.W.). The basic experimental procedure was similar to that used in our studies of die entry flow of single polymer systems.³⁴ A heater-surrounded glass extension possessed a window through which the interior of the capillary could be observed. Extruded polymer rod was purchased from Cadillac Plastics. The rods were machined down to the size of the inside diameter of the Instron rheometer barrel. They were then cut approximately in half, and one half was ground almost exactly to be a right half-cylinder. Small holes were drilled every inch along the length of each rod and were filled with colored extruded filament of the same polymer. Two half-cylinder rods of different polymers were placed together to make a full cylinder which was then inserted into the Instron barrel. The system was then heated to the operating temperature of interest and extrusion was begun. Flow patterns were observed through the window.

Materials

Our experiments were limited to one binary polymer system, namely low-density polyethylene and atactic polystyrene at 180°C. The non-Newtonian viscosity of these melts was measured in the Instron capillary rheometer. It is plotted as a function of shear rate as shown in Figure 2. The ratio of entrance pressure drop to shear stress, which is a sort of Weissenberg number^{34,36} measuring relative melt elasticity, is also plotted in Figure 2. The rheological measurements were made by T. F. Ballenger in conjunction with an earlier research project.

Observations and Discussion

The general observations were of a two-phase flow from a cylindrical reservoir into a capillary die and are summarized in Figure 3. Still photos from the films are given in Figure 4. In the undisturbed pattern generally observed at low flow rates, two-phase velocity fields are found in the upper portion of the reservoir, which resemble those of eq. (10) for flow in slits and the calculations of various authors mentioned above for Newtonian fluids in tubes.¹⁵⁻¹⁸ The velocity profile, in the low-viscosity polyethylene, as expected, exhibited a maximum, and the gradients in the polystyrene were less steep. In the lower part of the reservoir near the die entrance, we observed stable circulating secondary flows of the type found by Bagley and Birks,⁵⁹ our own group,^{34,35,36} and others in single-phase systems. The observation of two different circulating regions on opposite sides of the interface is a striking sight.

Attempts were made to visually observe the shape of the polyethylene-polystyrene interface in the reservoir. Runs with and without added

colored filaments were utilized. The interface seemed flat at low extrusion rates; at intermediate rates the polyethylene appeared convex, but this is uncertain. Some capillary extrudates were cross-sectioned. These indicate convex polystyrene surfaces. The polyethylene and polystyrene

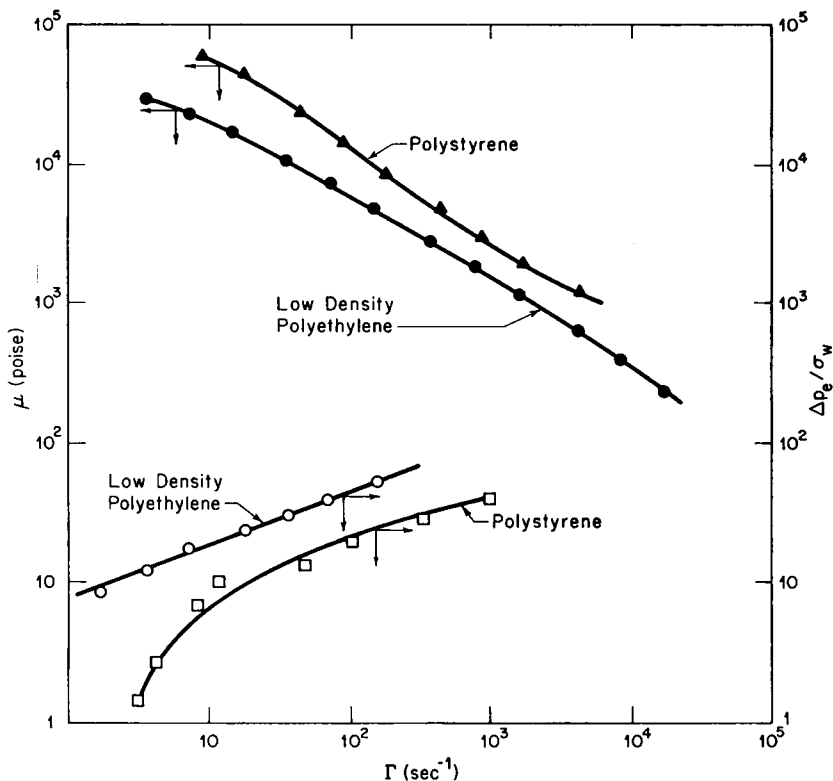


Fig. 2. Rheological properties (non-Newtonian viscosity μ , reduced entrance pressure drop) of the stratified two-phase polymer melt system.

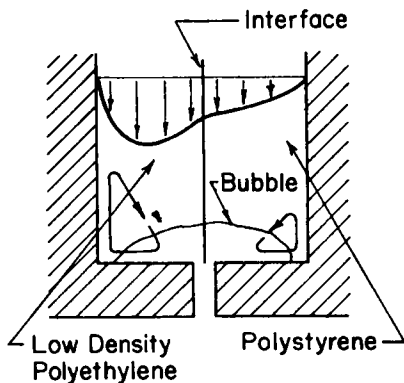


Fig. 3. Sketch summarizing visual observations in stratified two-phase flow experiment.

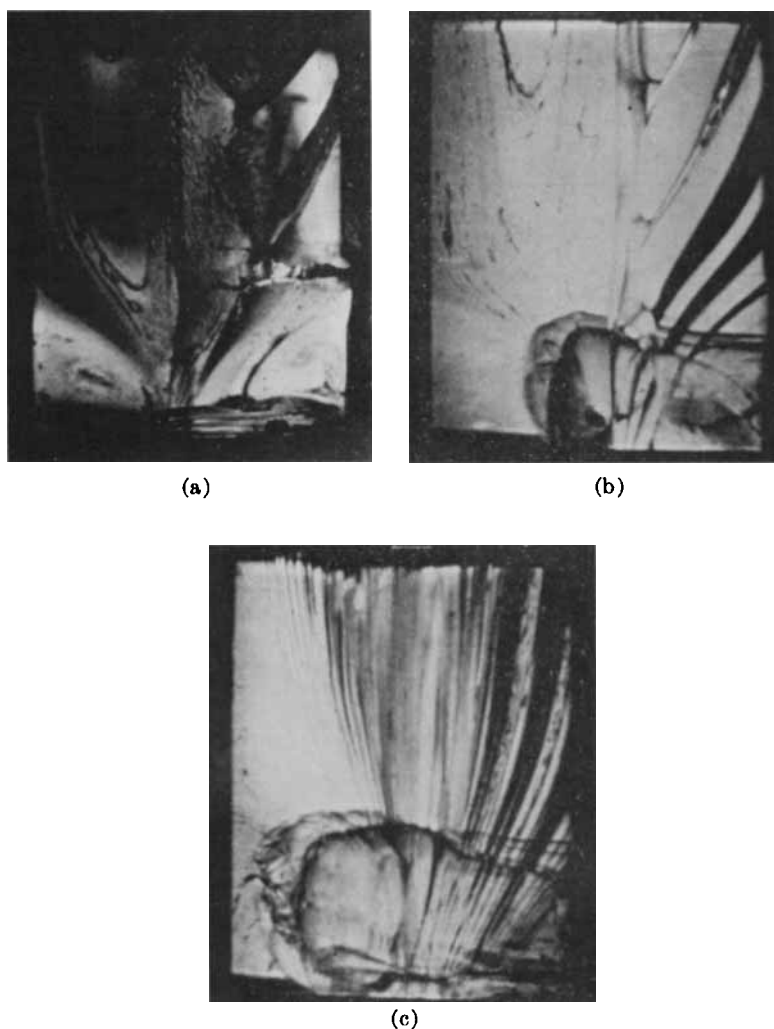


Fig. 4. Flow patterns in the stratified two-phase flow of low-viscosity, low-density polyethylene (left) and high-viscosity polystyrene (right). The velocity profile exhibits a parabolic form including a maximum and two decreasing velocity regions in the lower-viscosity polyethylene. This gives it a higher average velocity than the higher-viscosity polystyrene, which exhibits no maximum. The velocity is the same at the interface. Circulating regions may be seen in the corner of the reservoir for each melt. In Figure 3a, the interface is shown at an oblique angle to the viewer, and the interception of the markers in the polystyrene with the interface may be readily seen. Figure 3b shows an interface parallel with the viewer's line of sight. There also is a large air bubble at the bottom of the reservoir. Figure 3c shows the final phases of the experiment at high extrusion rates. A bubble is sitting at the bottom of the reservoir. Two melt flow instabilities are occurring simultaneously. There is an oscillating flow at the entrance, the type which leads to extrudate distortion. Secondly, there is a fingering into the polyethylene by the polystyrene. The polyethylene has been largely depleted from the reservoir because of its lower viscosity and higher flow rate. The original color film more clearly shows the flow patterns because of the color contrast and motion.

are an interesting pair of polymers to study. On the basis of viscosity differences, an analogy with the oil-water system would suggest that polystyrene is convex. If the second normal stress differences follow the first in value, one would expect on the basis of the arguments of the previous section that the polyethylene is convex.

The extrudate emerging from the spinneret behaves as might be expected for bicomponent fibers. Not far below the spinneret phenomenon surface, it buckles and sometimes contacts and sticks to this steel surface. This is apparently due to both stresses in the filament caused by the differential change in mechanical properties and density with cooling and to the difference in flow rates of the two phases.

At higher extrusion rates, a number of new phenomena arise. First, bubbles collect near the capillary inlet. The source of the bubbles is perhaps small air pockets between the initial polyethylene and polystyrene half-cylinders. The bubble collection near the capillary entrance is apparently the Uebler effect.⁶⁰ At higher rates, the types of instabilities that lead to extrudate distortion are observed. The interface was observed to oscillate back and forth just above the capillary, and the alternating surging of the polyethylene was most visible. At high extrusion rates, another striking occurrence is the breaking of the interface in the upper parts of the reservoir, apparently induced by the depletion of the more rapidly flowing polyethylene. In any case, polystyrene fingering into the polyethylene phase is observed. The depletion effect made the polystyrene interface convex.

DISPERSED SYSTEMS

Rationale

Most of the industrial polymer blends are not of the simple stratified nature discussed in the earlier portions of this paper. Rather, they derive melted blends of pellets and powders or sheared-together bales of elastomers. The morphology of the structures produced seems very complicated. However, one might visualize with Spencer and Wiley²⁵ the thinning out of polymer sheets and filaments during thinning. Eventually, some sort of instability may take place which breaks up the filament or sheet into smaller fragments or droplets. The observations of one of the authors²⁷ on mill blending of elastomers suggests some sort of tearing action. For lower-viscosity polymer melts, the phenomenon might be more akin to hydrodynamic instabilities. Certainly melt elasticity and viscosity will be important, and Weissenberg numbers are involved in the appropriate solutions. Van Oene³² has presented arguments for instability mechanisms in this problem based upon energetic considerations. Here, we will briefly give a progress report on some of the experiments carried out in our laboratories. Similar experiments have been carried out by Starita and Maxwell^{29,30} and by Van Oene.³²

Experimental

Procedure

Our intent has been to carry out a study of the morphology of extrudates produced in extrusion of dispersed two-phase polymer systems. As in the previous experiments of this paper, our basic piece of apparatus was the Instron capillary rheometer. Pellets of two polymers of interest were fed at equal rates (or proportional to the final desired composition) into the Instron barrel at room temperature. The system was heated to the operating temperature and extrusion was carried out through a series of dies with L/D ratios of 14.7, 29.0, and 48.3 and with a diameter of 0.0315 in. Each system was studied at a series of different blend compositions (listed below) and at two capillary-wall shear rates (45 sec^{-1} and 225 sec^{-1}).

Following extrusion, the cooled extrudates were placed in bottles of solvents known to selectively dissolve and thus leach out one of the polymeric constituents. Periods of leaching were up to two weeks. The structure of the remaining polymer fragment was then analyzed by eye and with an optical microscope.

Materials

Several binary systems, each having atactic polystyrene (Dow Styron 666) as one of the components, were studied. The other polymers were (1) low-density polyethylene (Eastman Tenite 800), (2) high-density polyethylene (Eastman Tenite 3340), and (3) isotactic polypropylene (Hercules Profax 6523). Figure 5 contains viscosity-shear rate and shear stress-reduced normal stress ($\tau_{11} - \tau_{22}$)/ τ_{12} data for these materials at 180°C . The rheological data were obtained by I. J. Chen and J. W. Crowder. In each of the polyolefins-polystyrene systems, 50/50, 25/75, and 10/90 ratios were studied at 180°C ; 90/10, 75/25, 50/50, 25/75, and 10/90 ratios for the high-density polyethylene-polystyrene and 50/50 ratio for high-density polyethylene and polypropylene-polystyrene were studied at 230°C . Benzene was used to extract polystyrene from the extrudates.

Observations

Qualitative observations were made (especially with the 230°C extrudates) of the surface features and mechanical properties of the two-phase (polystyrene-polyolefin) filaments. For polyolefin/polystyrene mass ratios ranging down to 25/75, the filaments superficially appeared to be entirely polyolefin. However, closer inspection indicated that the morphology was much closer to a polyolefin sheath surrounding a polystyrene core. The 90% polystyrene filaments seemed superficially to consist entirely of transparent polystyrene. If the various filaments studied were bent, it became apparent that there were two continuous phases of the different materials. Bending would readily fracture the more brittle glassy polystyrene while not affecting the integrity of the polyolefin. Pulling

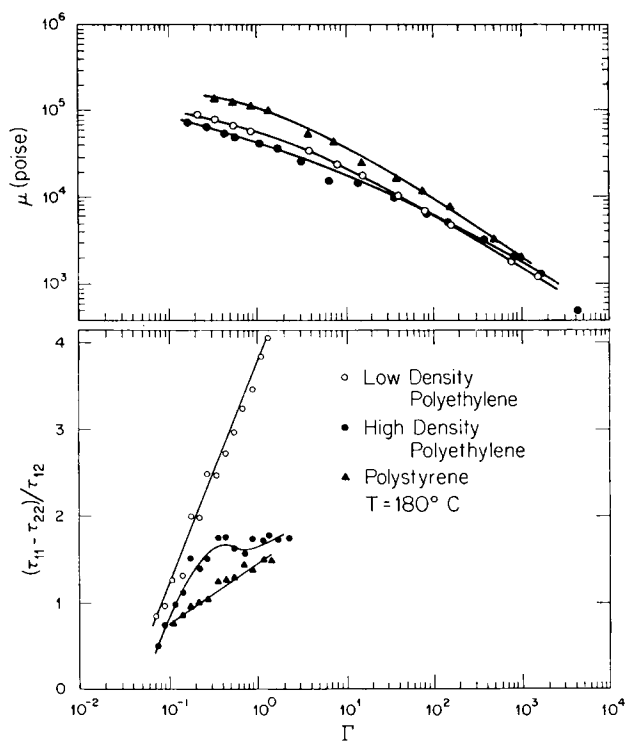


Fig. 5. Rheological properties (non-Newtonian viscosity μ and normal stress ratio, $(\tau_{11} - \tau_{22})/\tau_{12}$) for polymer melts in disperse two-phase flow experiments.

apart those filaments with broken polystyrene phases led to further observations of interest. Generally, necking would develop in a stretched filament and would lead to a break. For the 90/10 low-density polyethylene-polystyrene filament at 230°C, a sausage-like structure evolved on stretching with large-diameter portions being connected by necked-down segments. The large-diameter portions could be seen by closer observation to contain polystyrene fragments. In the case of the bent 90% polystyrene filament, pulling it apart yielded a continuous polyethylene filament located in the center of the internal cross section. The polyethylene filaments could be removed from the polystyrene continuum leaving cylindrical holes.

Measurements were made of the weight loss in benzene as a function of initial weight per cent polystyrene. The averaged values of weight loss, evaluated over several samples of the same apparent initial composition, were an increasing function of the initial polystyrene content. There was considerable scatter in the weight loss data. A careful study of the results suggests a less even composition distribution in the extrudate for the polypropylene and low-density polyethylene than in the high-density polyethylene. This was because the extracts from the former two polymers were

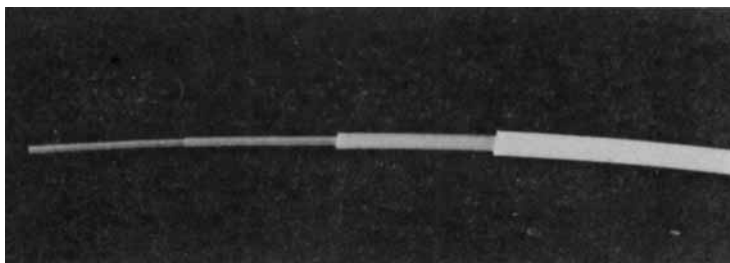


Fig. 6. The above photograph shows the remnant of a 50:50 high-density polyethylene-polystyrene extruded from a 0.0315-in. diameter die ($L/D = 29$) at 45 sec^{-1} after extraction with benzene. The original filament was cut across its cross section with a razor and the inner annuli pushed out.

frequently greater than the superficial polystyrene weight per cent added in the reservoir. An explanation for the low-density polyethylene may be found in that this material is showing the beginnings of extrudate distortion and melt flow instability at this shear rate.^{34,36}

The benzene-extracted filaments were always found to remain as filaments. From visual observations (carried out most extensively at 180°C), the extracted high-density polyethylene filaments remained more regular than the other polyolefins. Indeed in most cases they were found to consist of telescoping layers of polyethylene originally sandwiched with polystyrene. This structure was observed by cutting the remaining filament with a razor blade and pushing out the inner fragment with tweezers. Continuous cylindrical polyethylene filaments were observed within the original filament (Fig. 6). The benzene-extracted low-density polyethylene and polypropylene filaments have similar but less regular structures. The inner telescoping layers are connected to the external layer, and it is impossible to push them out as was done with the high-density polyethylene.

CONCLUSIONS

1. A theoretical analysis of the stress and velocity fields and interface shape has been given for stratified and annular two-phase flow. The velocity field is largely determined by the viscosity of the two phases. Interface shape appears to be influenced by the second normal stress difference coefficient β_2 and differences in melt viscosity and perhaps surface tension.
2. An experimental technique is developed for studying stratified two-phase flow through a cylindrical reservoir and into a capillary die. Experiments were carried out using rheologically characterized low-density polyethylene and polystyrene. Velocity patterns and interface shape were studied. Circulating flow patterns, characteristic of each of the melts were observed on the opposing sides of the interface.
3. Studies of disperse two-phase flow of blends of polystyrene pellets with different polyolefins were carried out in an Instron capillary rheometer.

The extrudate morphologies were determined by benzene extraction. These generally consisted of approximately concentric sandwiched annuli of polyolefin and polystyrene.

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References

1. G. S. Whitby, *Synthetic Rubber*, Wiley, New York, 1954.
2. E. Tornquist, in *Polymer Chemistry of Synthetic Elastomers*, Vol. 1, ed. by J. P. Kennedy and E. Tornquist, Interscience, New York, 1968.
3. E. V. Anderson, *Chem. Eng. News*, **47** (Issue 29), 40, July 14 (1969); E. L. Carpenter, *ibid.*, **48** (Issue 18), 31, April 27 (1970).
4. D. J. Angier and E. M. Fettes, *Rubber Chem. Technol.*, **38**, 1164 (1965); R. N. Howard and J. Mann, *Proc. Roy. Soc. Ser. A*, **282**, 120 (1964).
5. S. M. McDougle, *SPE Antec Tech. Papers*, **13**, 596 (1967); V. E. Malpass, *ibid.*, **15**, 55 (1969); A. E. Tarbox and S. Bonotto, *ibid.*, **14**, 527 (1968).
6. P. V. Papero, E. Kubo, and L. Roldan, *Text. Res. J.*, **27**, 823 (1967); B. T. Hayes, *Chem. Eng. Progr.*, **65** (10), 50 (1969).
7. M. Horio and T. Kondo, *Text. Res. J.*, **23**, 373 (1953); E. H. Mercer, *ibid.*, **23**, 388 (1953).
8. W. E. Sisson and F. F. Morehead, *Text. Res. J.*, **23**, 152 (1953).
9. E. M. Hicks, J. F. Ryan, R. B. Taylor, and R. L. Techninor, *Text. Res. J.*, **30**, 675 (1960).
10. E. M. Hicks, E. A. Tippetts, J. V. Hewett, and R. H. Brand, in *Man-Made Fibers*, Vol. 1, ed. by H. Mark, S. M. Atlas, and E. Cernia, Interscience, New York, 1967.
11. R. A. Buckley and R. J. Phillips, *Chem. Eng. Progr.*, **66** (10), 41 (1969).
12. E. A. Tippetts, *Amer. Dyestuff Rept.*, **54**, 141 (1965).
13. T. W. F. Russell, G. W. Hodgson, and G. W. Govier, *Can. J. Chem. Eng.*, **37**, 9 (1959).
14. T. W. F. Russell and M. E. Charles, *Can. J. Chem. Eng.*, **37**, 18 (1959).
15. M. E. Charles and P. J. Redberger, *Can. J. Chem. Eng.*, **40**, 70 (1962).
16. A. R. Gemmill and N. Epstein, *Can. J. Chem. Eng.*, **46**, 215 (1962).
17. M. E. Charles and L. U. Lilleleht, *Can. J. Chem. Eng.*, **43**, 110 (1965).
18. H. S. Yu and E. M. Sparrow, *A.I.Ch.E. J.*, **33**, 10 (1967).
19. H. S. Yu and E. M. Sparrow, *J. Heat Transf.*, **91C**, 55 (1969).
20. G. I. Taylor, *Proc. Roy. Soc., Ser. A*, **138**, 41 (1932).
21. C. E. Chaffey and H. Brenner, *J. Colloid Interfac. Sci.*, **24**, 258 (1967); B. M. Turner and C. E. Chaffey, *Trans. Soc. Rheol.*, **13**, 411 (1969).
22. J. C. Slattery, *A.I.Ch.E. J.*, **10**, 817 (1964).
23. C.-H. Li, *Phys. Fluids*, **12**, 531 (1969).
24. C.-H. Li, *Phys. Fluids*, **13**, 1701 (1970).
25. R. S. Spencer and R. H. Wiley, *J. Colloid Sci.*, **6**, 133 (1951).

26. W. D. Mohr, in *Processing of Thermoplastic Materials*, ed. by E. C. Bernhardt, Reinhold, New York, 1959.
27. J. L. White, *Rubber Chem. Technol.*, **42**, 257 (1969).
28. K. Hayashida, J. Takahashi, and M. Matsui, *Proc. Fifth Int. Rheol. Congr.*, **4**, 525 (1970).
29. B. Maxwell, Lecture presented at Symposium on Polymer Processing, University of Tennessee, Knoxville, September 1969.
30. J. M. Starita, Ph.D. Dissertation in Chemical Engineering, Princeton University, 1970.
31. A. S. Hill and B. Maxwell, *Polym. Eng. Sci.*, **10**, 289 (1970).
32. H. van Oene, to be published in *J. Colloid Interfac. Sci.*
33. C. D. Han and T. C. Yu, *J. Appl. Polym. Sci.*, **15**, 1163 (1971); *ibid.*, **15**, 2579 (1971); *A.I.Ch.E. J.*, **17**, 1512 (1971).
34. T. F. Ballenger and J. L. White, *J. Appl. Polym. Sci.*, **15**, 1949 (1971).
35. T. F. Ballenger and J. L. White, *Chem. Eng. Sci.*, **25**, 1191 (1970).
36. T. F. Ballenger, I.-J. Chen, J. W. Crowder, D. C. Bogue, and J. L. White, *Trans. Soc. Rheol.*, **15**, 195 (1971).
37. S. Middleman, *The Flow of High Polymers*, Wiley, New York, 1969.
38. D. C. Bogue and J. L. White, *Engineering Analysis of Non-Newtonian Fluids*, NATO Agardograph No. 144, 1970. Available from NTIS, Springfield, Virginia, as Document AD-710-324.
39. I.-J. Chen and D. C. Bogue, *Tran. Soc. Rheol.*, in press.
40. A. E. Green and R. S. Rivlin, *Arch. Rat. Mech. Anal.*, **1**, 1 (1957).
41. J. L. White, *J. Appl. Polym. Sci.*, **8**, 2339 (1964).
42. J. L. White and N. Tokita, *J. Appl. Polym. Sci.*, **11**, 321 (1967).
43. A. B. Metzner, J. L. White, and M. M. Denn, *A.I.Ch.E. J.*, **12**, 863 (1966).
44. J. L. Ericksen, *Quart. Appl. Math.*, **14**, 319 (1956).
45. W. O. Criminale, J. L. Ericksen, and G. L. Filbey, *Arch. Rat. Mech. Anal.*, **1**, 410 (1958).
46. A. S. Wineman and A. C. Pipkin, *Acta Mech.*, **3**, 104 (1966).
47. R. I. Tanner, *Trans. Soc. Rheol.*, **14**, 483 (1970).
48. A. E. Green and R. S. Rivlin, *Quart. Appl. Math.*, **14**, 299 (1956).
49. W. E. Langlois and R. S. Rivlin, *Rend. di Mat.*, **22**, 169 (1963).
50. A. C. Pipkin, *Proc. Fifth Int. Rheol. Congr.*, **1**, 213 (1965).
51. E. A. Kearsley, personal communication.
52. H. Giesekus, *Rheol. Acta*, **4**, 85 (1965).
53. A. C. Pipkin and R. S. Rivlin, *ZAMP*, **14**, 738 (1963).
54. C. D. Han, paper presented at the 42nd Annual Society of Rheology Meeting, Knoxville, October 1971.
55. C. Truesdell and R. A. Toupin, *The Classical Field Theories*, in *Handbuch der Physik*, Vol. III/1, Springer Verlag, Berlin, 1960, pp. 491ff.
56. R. Jackson and A. Kaye, *Brit. J. Appl. Phys.*, **17**, 1355 (1966); N. Adams and A. S. Lodge, *Phil. Trans. Roy. Soc.*, **A256**, 149 (1964); A. Kaye, A. S. Lodge, and D. G. Vale, *Rheol. Acta*, **7**, 368 (1968).
57. R. F. Ginn and A. B. Metzner, *Trans. Soc. Rheol.*, **13**, 429 (1969).
58. C. S. Yih, *J. Fluid Mech.*, **27**, 337 (1967).
59. E. B. Bagley and A. M. Birks, *J. Appl. Phys.*, **31**, 556 (1960).
60. A. B. Metzner, *A.I.Ch.E. J.*, **13**, 316 (1967).

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