MODELLING OF ORIENTATION DEVELOPMENT IN WELDING FLOWS OF MACROMOLECULAR FLUIDS

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ABSTRACT

Molecular orientation near weld interfaces is studied for macromolecular fluids. Individual material elements are tracked along their path lines in welding flows, using approximate solutions for the flow field. Measures of molecular orientation are the normal stress difference and probability of finding molecular strands in a given direction $\underline{u}$. The stress and the probability function are both determined as memory integrals over the strain history of material elements near the weld interface. Numerical interpolation gave the strain tensor components in the tracking procedure. The memory integrals had also to be determined numerically (Romberg integration).

INTRODUCTION

Welding flows occur in almost all the commercially important polymer processing operations. Examples are flow in multigated injection molds or flow past a streaker plate in a pipe extrusion die. Welding flows have in common that the stream of molten polymer is divided by obstacles and recombined downstream. Separate flow fronts of molten polymers meet and form weld interfaces inside the material. These interfaces would vanish instantaneously in a low molecular weight material. In a polymeric material, however, the macromolecules near the weld interface require long time to diffuse across the interface and to adopt a random configuration. The diffusion process depends on molecular weight of polymer chains, contact time, and the molecular orientation which was generated in the welding flow, i.e. during the formation of the weld interface.

The welding process has been studied by two groups: One large group of researchers was interested in engineering properties of welded samples and their dependence on processing conditions, see Malguarnera (ref. 1) and Turner (ref. 2). The microstructure near weld interfaces was found to be very inhomogeneous, especially with partially crystalline polymers (ref. 3).

The second group considered the diffusion process across a polymer - polymer interface. Prager and Tirrell (ref. 4) base their analysis on the reptation picture of polymer dynamics due to de Gennes (ref. 5). They predict the number

of chain segments per unit area crossing the interface as a function of time, t, and molecular weight, M. The total crossing density was found to be proportional to $t^{1/2} M^{-3/2}$, if the initial contact is made between surfaces which already have been equilibrated against a gas phase. Alternatively, if the contacting surfaces contain many chain ends, they predict the crossing density to be proportional to $t^{1/4} M^{-1/4}$ at short times. The comparison of their theory to the crack-healing experiments of Jud, Kausch and Williams (ref. 6) and Wool and O'Connor (ref. 7) supports an exponent of $1/4$ for the healing time.

The diffusion studies assume a random initial orientation of the macromolecules. Our calculations, however, show that the macromolecules are highly oriented at a newly formed interface. This will make it necessary to reconsider the diffusion studies and to take initial orientation into account. It can be speculated that the diffusion of a macromolecule in an oriented matrix (surrounding molecules) is highly anisotropic with a higher diffusion coefficient in the direction of orientation.

STRESS, ORIENTATION DISTRIBUTION FUNCTION, STRAIN HISTORY

The stress is chosen as a macroscopic measure of molecular orientation in a material element at the weld interface. The probability of finding molecular chain segments parallel as compared to normal to the interface is a microscopic measure of molecular orientation. The stress is calculated here with a memory integral constitutive equation (ref. 8-12) and the probability function is determined as the orientational distribution function of Curtiss and Bird (ref. 13). Both depend on the strain history of material elements in the welding flow.

Stress

Stress calculations with integral constitutive equations are based on the knowledge of the strain history of material elements. A well tested integral constitutive equation (ref. 9-11) is used:

$$\underline{\sigma}(t) = -p(t)\underline{1} + \int_{-\infty}^{t} m(t',t)\underline{c}^{-1}(t',t)dt' \tag{1}$$

where $\underline{\sigma}(t)$ is the stress at time t, p the isotropic pressure contribution, $\underline{c}^{-1}(t',t)$ the relative Finger strain tensor between time t' and t, and $m(t',t)$ the memory functional, which can be separated as product of strain functional and time function (ref. 11).

Orientation Distribution Function

The probability density of molecular segments at time t oriented in direction of the unit vector $\underline{u}$ is described by the orientation distribution function (Curtiss and Bird, ref. 13)

$$f(\underline{u},e,t) = \frac{1}{4\pi} \int_{-\infty}^{t} p(e,t-t')[\underline{\underline{C}}:\underline{u}\,\underline{u}]^{-3/2}\, dt' \tag{2}$$

with
$$p(e,t-t') = \frac{4\pi}{\lambda} \sum_{\alpha,\text{odd}} \alpha(\sin\pi\alpha e)\exp\left(\frac{-\pi^2\alpha^2(t-t')}{\lambda}\right) \tag{3}$$

$$\lambda = \pi^2 T_d \tag{4}$$

e is the fractional distance along the macromolecule and T_d is the largest relaxation time. The orientation distribution function can be averaged over the length of the molecules

$$\overline{f} = \int_0^1 f(\underline{u},e,t)de \tag{5}$$

This function was calculated for strain histories of welding flows.

Strain History

The strain tensor $\underline{\underline{C}}(t',t,\underline{x})$ defines the strain history of a material element which at time t is positioned at $\underline{x}$. The strain history will be determined from a velocity field (for determination of the velocity field see next section) by a path line tracking procedure (ref. 14). In this tracking procedure, the deformation of an infinitesimal material element is calculated from the length change and the relative angle change of three independent material vectors which deform affinely with the material element. The path line tracking procedure is especially successful for numerical calculations in which the velocity field is given as a table of discrete values and not as an explicit function.

APPROXIMATE KINEMATICS OF WELDING FLOWS

In this study, we assume that the kinematics of Newtonian fluids in plane creeping flow around a cylinder gives a good approximation for the welding flow of the first kind, see fig. 1. Similarly, we assume that the Newtonian velocity field near an advancing front in a narrow slit gives a good approximation

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for welding flow of the second kind, see fig. 2. Even if this is a far reaching assumption (which we plan to improve on), the strain histories of material elements in welding flows of non-Newtonian fluids are qualitatively the same as in the corresponding Newtonian flow. The assumption is a very good one for polymeric liquids which exhibit second order behavior (ref. 15).
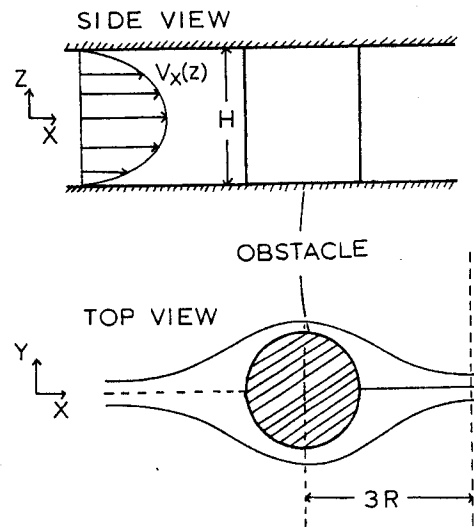

Fig. 1. Welding flow of the first kind. The stream divider is chosen here as a cylinder across a slit cavity. The molecular orientation is calculated in a cross section downstream of the cylinder.
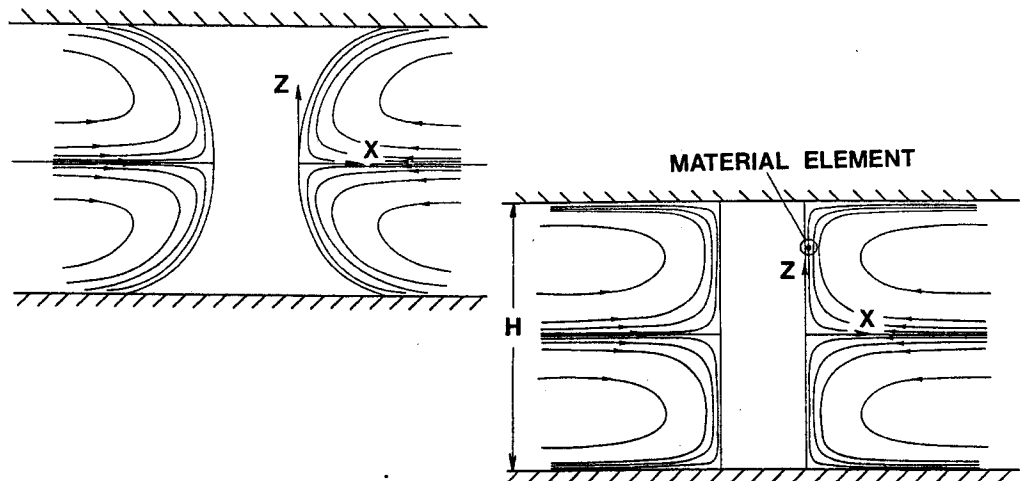

Fig. 2. Welding flow of the second kind. The flow fronts are impinging in a plane cavity of width H. The upper picture shows a sketch of stream lines for flow with curved free surfaces. The lower picture gives calculated stream lines with the assumption that the flow fronts are flat.

Weld Interface Downstream of a Circular Cylinder (first kind)

The flow around a circular cylinder is approximated with a velocity field

$$\underline{w}(x,y,z) = \underline{v}(x,y)[1 - (2z/H)^2] \tag{6}$$

where $\underline{v}$ is given by steady plane creeping flow of a Newtonian fluid around a circular cylinder. The stream function of plane flow is given (ref. 16) as:

$$\psi \sim (\Delta_1 + \sum_{n=3}^{\infty} a_n \Delta_1^n)(r \ln r - \frac{1}{2}r + \frac{1}{2r})\sin\theta \tag{7}$$

$$\Delta_1 = \left[\ln \frac{3.703}{Re}\right]^{-1}$$

$$a_3 = -0.87$$

where r is the radial distance, Re is the Reynolds number.

The stream lines of a Newtonian fluid are symetric for the upstream and downstream part of the flow. Non-Newtonian fluids exhibit stream lines which are non symmetric (ref. 17). For both fluids, however, the material elements near the weld interface have a flow history of compression in the stagnation flow immediately upstream of the cylinder, of shear when flowing around the cylinder (near the wall), and then a history of stretching when being accelerated to the velocity of the bulk of the flow.

Weld Interface Between Impinging Flow Fronts (second kind)

The kinematics is, again, determined in an approximate solution. The velocity field in an advancing flow front of a Newtonian fluid in a narrow slit has been calculated by Bhattacharji and Savic (ref. 18) and by Castro and Macosko (ref. 19). The difficulty of the free surface flow is circumvented by assuming a flat flow front, see Fig. 2, and with the origin located at the flow front. The stream function is

$$\psi = \frac{\overline{v}_x z}{2} \left[1 - (\frac{2z}{H})^2\right]\left[1-\exp(\frac{-5x}{H})1.45 \sin(0.76+ \frac{2x}{H})\right] \tag{8}$$

$$+ \overline{v}_x z \left[1 - (\frac{2z}{H})^4\right] 0.53 \exp(\frac{-5x}{H}) \sin(\frac{2x}{H})$$

where $\overline{v}_x$ = average velocity in x-direction, H = width.

With the flat front approximation, the meeting of the impinging fronts is obviously modelled by just stopping the flow. A material element at the weld interface has a strain history which is given by the "steady" flow. In reality, the formation of the weld interface is more complex since the flow front is curved (ref. 20), and it becomes flat as the two fronts meet. Additional stretching will occur in the corners near the wall. This influence of curvature of the flow front is neglected in this study.

CALCULATED RESULTS

The molecular orientation near newly formed weld interfaces was found to be very pronounced. Parameters for the relaxation behavior of macromolecular materials were taken from the literature: a relaxation spectrum for a low density polyethylene (Laun, ref. 10) was used for the stress calculations and a longest relaxation time $T_d = 10^3$s was used for the calculation of the orientation distribution function.

For welding flow of the <u>first</u> kind, the molecular orientation was calculated in the cross section three radii downstream of a stream divider of radius R. Figure 3 gives the first normal stress difference as a measure of molecular orientation and fig. 4 gives the difference of the orientation distribution function in x-direction and in y-direction. Both calculations based on the same flow field (shear rate $\dot{\gamma}=0.5s^{-1}$ at the cylinder wall, halfways between the stagnation points; R = 1cm). We found that the orientation is the highest at the weld interface and that the oriented region has a thickness of over two radii on each side of the weld interface.
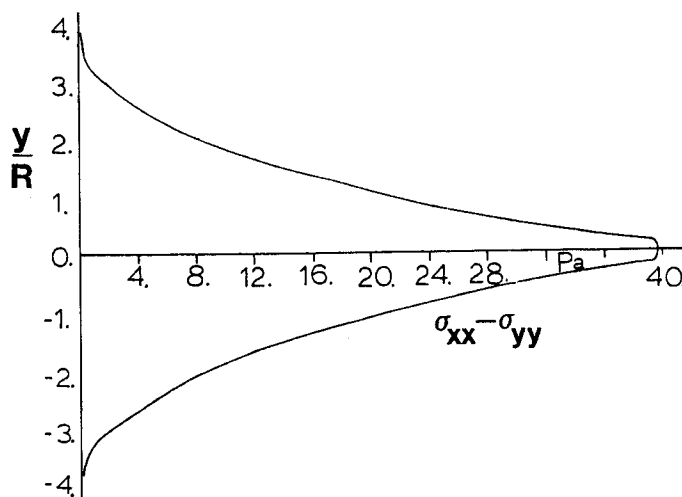

Fig. 3. The stress distribution calculated at the cross section which is 3 radii downstream of the circular cylinder.
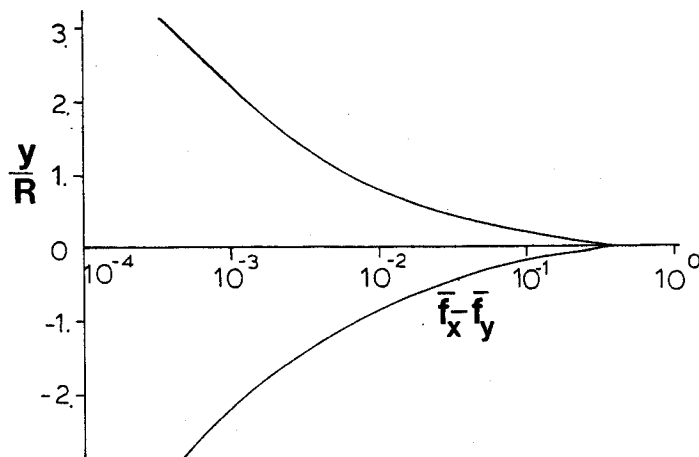
Fig. 4. Orientation distribution function of eq. (5) in the cross section 3 radii downstream of the dividing cylinder.

For the welding flow of the second kind we calculated the strain history of material elements at $2z/H = 0.7$ and different values of the stream function. The stream function value $\psi = 0$ belongs to the interface, and increasing values of ψ denote increasing distance from the interface. Figure 5 shows the calculated strain history of a material element as a function of elapsed time, $t-t'$. Figure 6 compares the development of the principal normal stress difference for material elements on different path lines ψ = const. The same flow conditions (average velocity = 3.5 m/s; slit width = 0.3 cm) were taken for both calculations. The molecular orientation was found to be very pronounced and the rotation of the material element in the flow was found to have a large influence on the orientation development.
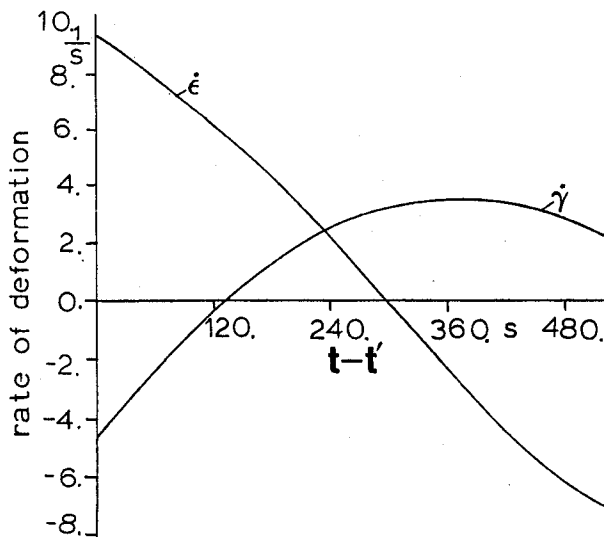

Fig. 5. Strain history of a material element at $2z/H=0.7$ and $\psi=0.0004$: Shear rate $\dot{\gamma}=\partial v_t/\partial x_n$ and extension rate $\dot{\varepsilon}=\partial v_t/\partial x_t$. Subscripts t and n refer to a coordinate system x which translates with the material element and which is locally tangent (subscript t) and normal (subscript n) to the stream line ψ (ref. 14).
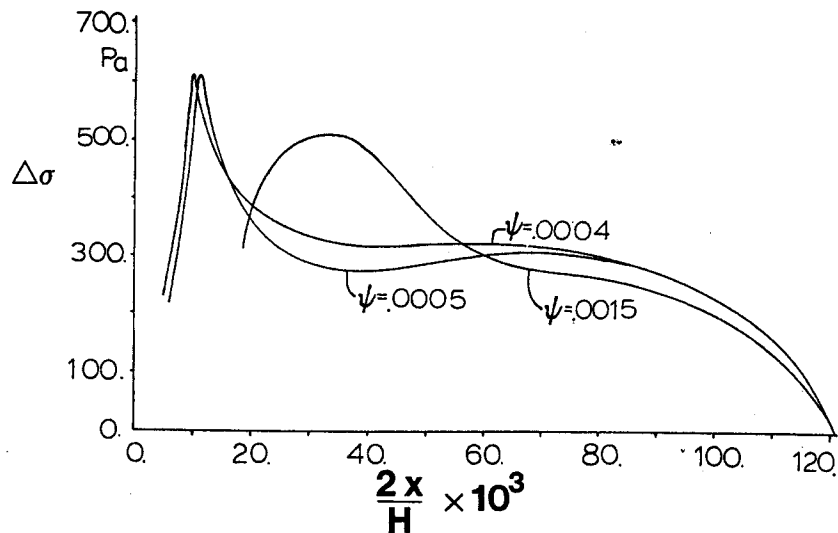
Fig. 6. The normal stress difference at principle coordinate system for material elementsat different position along the path lines ψ = .0004, ψ = .0005 and ψ = .0015. Material data were taken from Laun (ref. 10).

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