Reactive Systems—Finite Element Analysis

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This paper outlines the equations which govern the nonisothermal flow of reactive fluids, and describes the means by which finite element analysis can be used to solve these equations for the sort of arbitrary boundary conditions encountered in industrial practice. The performance of the computer code is illustrated by several trial problems, selected more for their value in providing insight to polymer processing flows than as practical production problems. Although a good deal remains to be learned as to the performance and proper use of this numerical technique, it is undeniably useful in providing better understanding of today's complicated polymer processing problems.

Finite element analysis offers great promise for reducing the empiricism often found in polymer processing design, since it is well suited for modeling the complicated boundary conditions and material properties encountered in industrial practice. Although the method is now well accepted in structural stress analysis, its use in fluid transport situations is less widespread. We have sought to exploit some of the many advantages of the finite element method in polymer fluid processing analysis, and this paper describes some of our work in chemorheology.

Reactive flows have several advantages in polymer processing in comparison with more traditional melt-flow techniques. Perhaps the most significant of these is the energy savings which result from the elimination of the several melting stages necessary in such technologies as extrusion or injection molding. However, these advantages are offset to some degree by the complexity of the process, which renders the empirical approach to process development difficult in the extreme. The flow velocities in such processes are governed by the fluid viscosity, which is a strong

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function of temperature and molecular weight. The temperature in turn is affected by the viscous dissipation and the heat released or consumed by the reaction, and the reaction rate is also a strong function of temperature. All of these variables interact and change in such a way as to make an intuitive grasp of the process almost impossible, and there is obviously an advantage to being able to provide some sort of mathematical or numerical simulation of the process.

The finite element scheme to be described below is very useful for obtaining numerical solutions for reactive flows with arbitrary boundaries, and such a technique is well suited for detailed analysis of real industrial processes. However, we argue that the greatest value of the method may not be in these detailed calculations, but in the degree to which the method can enhance the process designer's intuition. For this latter purpose, it is often sufficient to run only very small and inexpensive trial problems; these can elucidate the manner in which the various problem parameters interact, so that the designer develops a much improved "feel" for the problem. It is likely that most real advances in processing technology will continue to be made more by Edisonian innovation than by detailed mathematical calculations. But since today's processes have become so complicated, such a technique as the finite element method can be a powerful adjunct to intelligent intuition.

Theoretical background

The equations which govern the nonisothermal flow of a reactive fluid are derived in several texts on transport phenomena and polymer processing (e.g. refs. 1,2). Regarding velocity, temperature, and concentration of unreacted species as the fundamental variables, the governing equations can be written as:

$$\rho[\partial u/\partial t + u\bullet\nabla u] = -\nabla p + \eta\nabla^2 u$$
$$\rho c[\partial T/\partial t + u\bullet\nabla T] = Q + k\nabla^2 T$$
$$[\partial C/\partial t + u\bullet\nabla C] = R + D\nabla^2 C$$

(A list of nomenclature is attached.) The similarity of these equations is clear. In all cases, the time rate of change of the transported variable (velocity, temperature, or concentration) is balanced by the convective or flow transport terms (e.g. $u\bullet\nabla C$), the diffusive transport (e.g. $D\nabla^2 C$), and a generation term (e.g. R).

The analyst seeks expressions for the space- and time-dependent velocities, temperatures and concentrations which satisfy these equations and also the problem's boundary conditions. It is generally the boundary conditions which make real problems intractable: even if one were able to describe the boundaries mathematically, the resulting expressions would not likely be amenable to closed-form solution. In addition, many of the

"constants" in the above equations are often nonlinear functions of the problem variables. In reactive polymer processing, one might encounter such expressions as the following:

$$\eta = \eta_0 \dot{\gamma}^{n-1} \exp[E_1/R_gT] \exp(\beta p) (mw^{3.4})$$
$$Q = (\eta/2)(\dot{\gamma}:\dot{\gamma}) + R(\Delta H)$$
$$R = -k_m \exp(E_2/R_gT) C^m$$

It is clear that all of these expressions, taken together, constitute a mathematical situation which must be approached with caution. Even though it is not overly difficult to incorporate them into a numerical scheme, which we have done, it is important to proceed slowly enough to develop the proper experience in the computer code's behavior before tackling full-blown problems.

Computer Model

We have sought to develop a finite element code which is able to predict polymer fluid velocities, stresses, temperatures, and degrees of chemical conversion in a variety of flow geometries and for a variety of fluid material properties. Space limitations prohibit our listing here the full derivation of the finite element equations from the above differential equations, but there exist several well developed means by which this may be done. The reader is directed to standard texts (3,4) for a more complete description, and we will just state here that we employ the Galerkin method of weighted residuals, together with isoparametric mapping and interpolation, to replace the differentials by integrals which can be evaluated numerically over small subregions ("elements"). The results of these numerical integrations are then assembled into a set of simultaneous algebraic equations which can be solved numerically.

The salient features of our code can be listed briefly as follows: (1) Velocity, temperature, and chemical conversion are taken as nodal unknowns, so that coupled incompressible viscous flow and diffusive-convective heat and mass transport may be modeled. (2) Incompressibility is enforced by a "penalty" formulation employing selective reduced integration. This approach requires the use of double precision arithmetic with a concommitant reduction in the amount of available core, but it has several programming advantages which usually outweigh this drawback. (3) The code is developed primarily for plane and axisymmetric flows. We have coded a three-dimensional capability, but generally feel that the expense of running three-dimensional problems is not justified for most of our modeling research. (4) The code includes several models for the effect of shear rate, temperature, pressure, and chemical conversion on the fluid viscosity. These nonlinear models have not yet been researched extensively, however, and the exploration of the interative schemes needed for their proper use constitutes a major goal for

future research. We have also coded a capability for viscoelastic fluid effects (ref. 5), but currently feel that this difficult aspect of polymer flow is being researched satisfactorily by other workers. (5) Convective transport of heat or chemical species can be handled either by a conventional Galerkin treatment or by the convenient but still controversial "optimal upwinding" approach. (6) The code can treat transient problems by means a two-point "theta-method" time-stepping algorithm. The dynamic algorithm is also useful in nonlinear problems, in which the final fluid state may be approached dynamically from an estimated initial state. (7) The code is capable of a variety of iterative treatments of nonlinear problems, including Newton-Raphson iteration and incremental load methods.

Some additional discussion is warranted concerning the treatment of convective effects beyond what has been mentioned in item (5) above. Momentum convection ($\rho u \bullet \nabla u$) is generally negligible in comparison with the viscous terms due to the high viscosities of polymer fluids, but the convective terms tend to dominate the energy and mass transport equations due to the generally low thermal and mass diffusivities. The programming of the convective terms presents no special problems in the Galerkin approach beyond the need to store and solve unsymmetric matrices, but it is well known that the presence of strong convective terms tends to create oscillations in the final solutions which can be large enough to destroy their value. This instability is related to the tendency of convection to produce large downstream gradients which the finite element grid cannot resolve. A largely ad hoc procedure known as "upwinding" has been used in both finite element and finite difference work which seems to alleviate this problem by providing a greater numerical weight to the upstream portion of the element. Hughes (6) has published a very convenient means of upwinding, in which the sampling points in the numerical integration scheme are simply moved upstream an appropriate distance. We have made extensive use of the Hughes upwinding technique, but the reader is cautioned that this method is regarded as controversial by many workers. A provocative paper by Gresho (7) details many of the possible pitfalls in upwinding, and states a strong preference for grid refinement as the appropriate cure for convection-induced instabilities.

Selected Numerical Result

The operation of the numerical model will be illustrated by means of three computer experiments, chosen more for their value in visualizing reactive flow than as detailed numerical simulations of real industrial processes. Simple fluid property models will be used in which material parameters such as viscosity and reaction order are not allowed to vary during the process, although real situations are often much more complicated than this. The numerical model does have the capability of performing

a variety of iterative schemes to model real situations in which nonlinear and time-varying fluid properties are present, but such complicated simulaions are often not as revealing as simple trial problems, at least in the earlier stages of research.

Nonreactive entry flow. Figure 1 shows the streamlines for a 4:1 entry flow. Here a grid of 100 four-node linear elements was used to model the upper symmetric half of a plane capillary, and a fully-developed Poiseuille velocity was imposed on the reservoir entry as a boundary condition. The streamlines are identical with published experimental and numerical results, although the grid used here was not intended to be fine enough to capture the weak recirculation which develops in the stagnant corner of the reservoir.

The temperature contours for convectionless flow are shown in figure 2, which shows a hot region at the entrance of the capillary due to the combination of high viscous energy dissipation there and its distance from cool boundaries to which heat may be conducted. These isotherms are normalized on the maximum centerline temperature expected for Poiseuille flow in the capillary.

The importance of thermal convection relative to conduction is given approximately by the Peclet number $Pe = UL\rho c/k$, where U and L are a characteristic velocity and length. Figure 3 plots the variation of temperature along the centerline for various values of the Peclet number, and it can be seen that the effect of increased thermal convection is to sweep the cooler upstream flow particles into the capillary, with a resulting lowering of the temperatures overall and a shift downstream of the hot spot near the throat. The relatively coarse grid used in this problem produced unstable Galerkin results for Peclet numbers higher than approximately ten, and the higher degrees of thermal convection were computed using the upwinding formulation. Further tests with refined grids should be completed to assess the accuracy of the upwinded solutions, although the plots in figure 3 appear reasonable.

One-dimensional reactive flow. As a preliminary trial problem in our computations of reactive flow, we have studied a simple situation in which a fluid obeying first-order chemical kinetics moves at constant velocity and temperature in the positive x direction. Here only the mass-transport equation is operative, and it takes the simple form:

$$u(dC/dx) = -KC + D(d^2C/dx^2)$$

This equation is solved easily, and for nonzero values of the diffusion coefficient D two boundary values for C must be specified. One of these is the initial concentration at the inlet, and the other requires a consideration of the outlet conditions. Here several possibilities exist, and we have studied the case in which

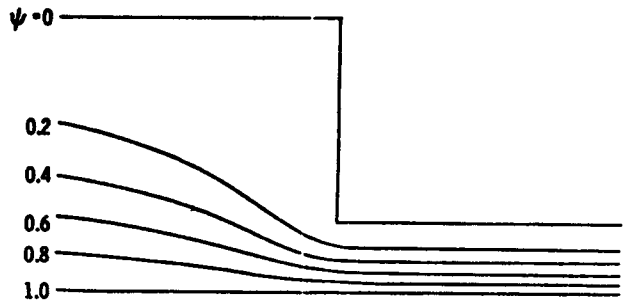

Figure 1. Streamlines for nonreactive 4:1 entry flow, Newtonian fluid with imposed Poiseuille flow at inlet.

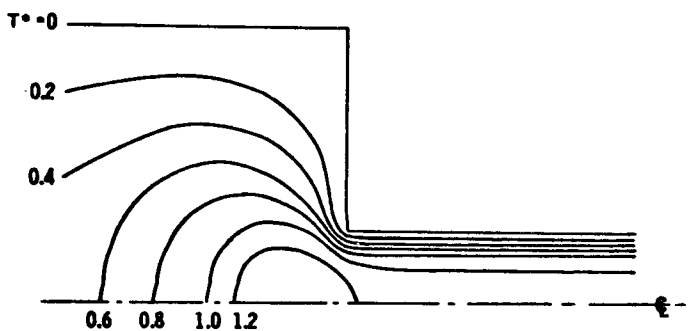

Figure 2. Contours of constant temperature for convectionless entry flow, with heat generation by viscous dissipation only.

the concentration of the outlet reservoir is allowed to rise to meet that supplied by the flow; this is equivalent to specifying a zero concentration gradient at the outlet. For the case of negligible diffusion (D→0), the second-order term vanishes from the above equation and the downstream boundary condition cannot be specified. The solution is then a simple exponential, in which the reactive species vanish according to first-order kinetics as they are carried downstream at constant velocity.

Figure 4 shows the computed and exact predictions for reactive group concentration as a function of distance along the channel. The Galerkin values are nearly exact, but it is clear that upwinding leads to erroneous results in the small-diffusion case. The upwinding has introduced an artificially high diffusivity and a zero concentration gradient at the outlet, and such artifacts must be considered as possibilities when upwinding is used.

Two-dimensional nonisothermal reactive flow. Figure 5 shows the contours of constant conversion for a two-dimensional analog of the flow discussed in the previous section. Here again, a simple uncoupled problem is treated in which the material parameters are taken to be independent of the solution variables, and in which the velocity conditions are prescribed. The concentration is taken to have a fixed value at the inlet and a zero gradient at the outlet, as before. The two-dimensionality of the problem is contained in two features: the velocity is taken to be parabolic, ranging from a maximum at the centerline to zero at the walls (a Poiseuille flow); and now diffusive heat and mass transport can occur in both the x and y direction. For the low diffusivities shown, mass diffusion in the x direction is negligible, as was demonstrated in the previous section. However, the concentration gradients in the y direction are substantial, so that diffusive transport in that direction is appreciable even at D = 0.01. At D = 0.001, even the y-diffusion is negligible, so the concentration contours simply represent a fluid which moves in the x-direction while reacting by first-order kinetics. The concentrations along the centerline are then identical with the D = 0.01 curve of figure 4.

Figure 6 shows the contours of constant temperature which result from this flow (with D = .001), where the temperature boundary conditions were set to zero at the entry and along the top and bottom surfaces. The temperature gradient at the outlet was allowed to become zero, similar to the concentration gradient. The results obtained for the temperature field are of course dependent on the values chosen for fluid properties. To avoid using space here for a detailed discussion of the dimensional analysis used for selecting these parameters, we will state simply that in figure 6 the viscous dissipation and reaction heat make approximately equal contributions to the internal heating (Brinkman and Damkoehler numbers both equal to three).

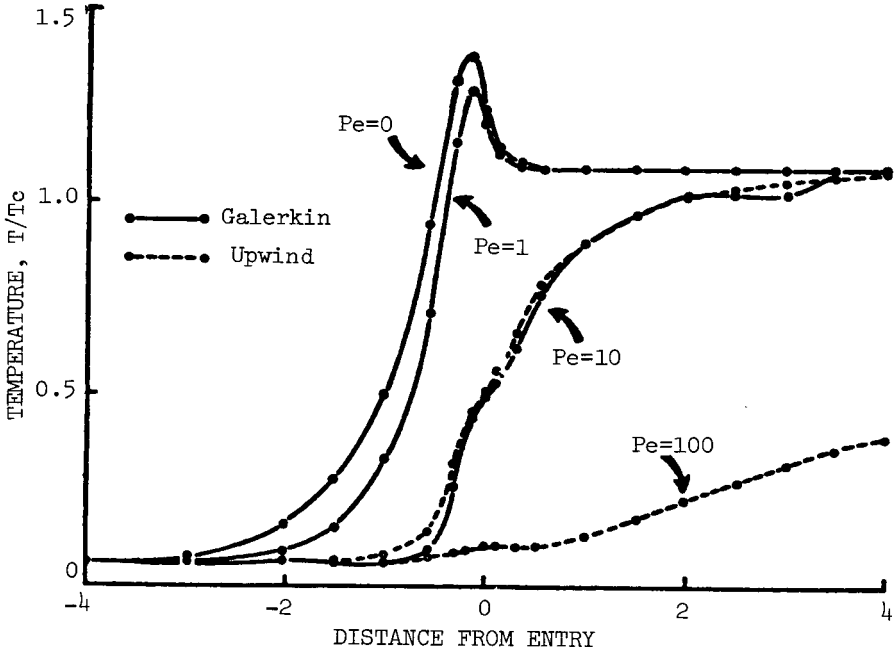

Figure 3. Entry flow centerline temperatures at various Peclet numbers.

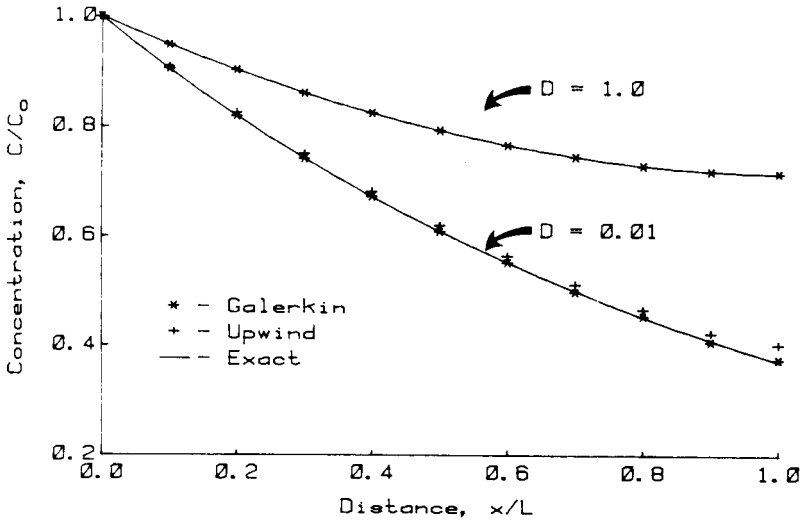

Figure 4. Degree of conversion along channel in one-dimensional reactive flow.

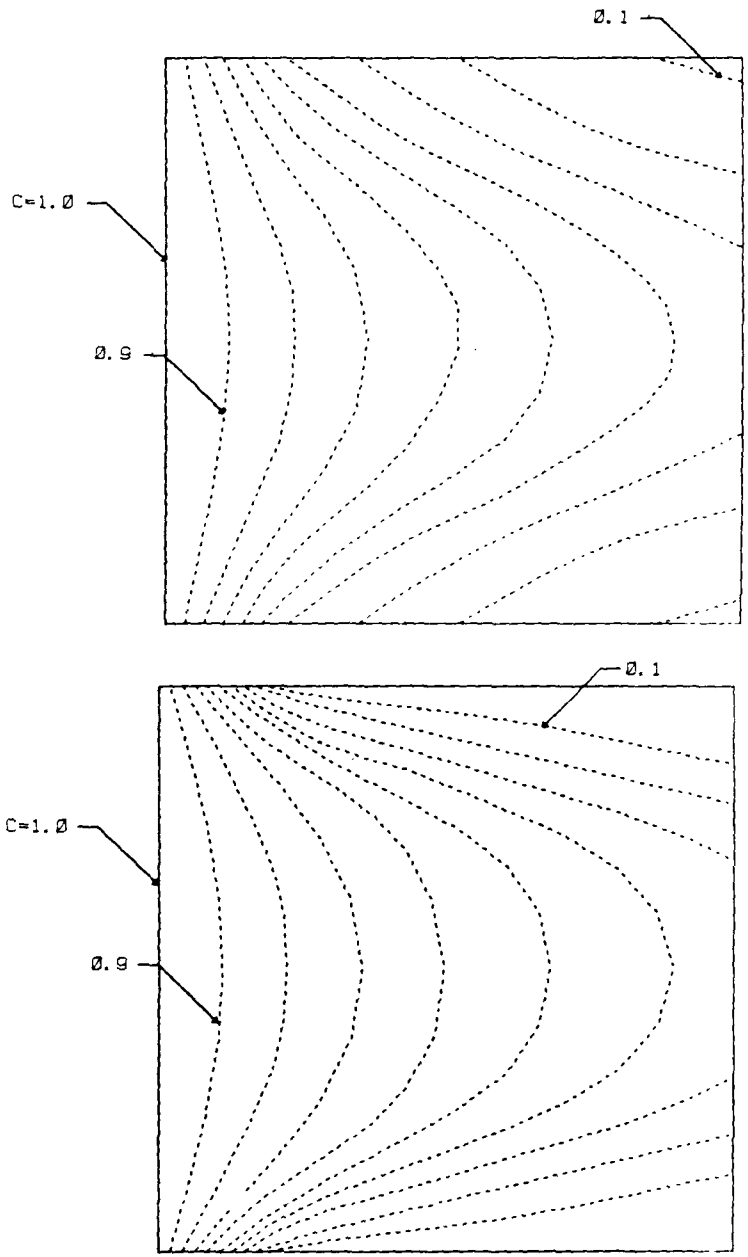

Figure 5. Isoconversion contours in two-dimensional reactive flow at two different mass diffusivities, Galerkin calculations.

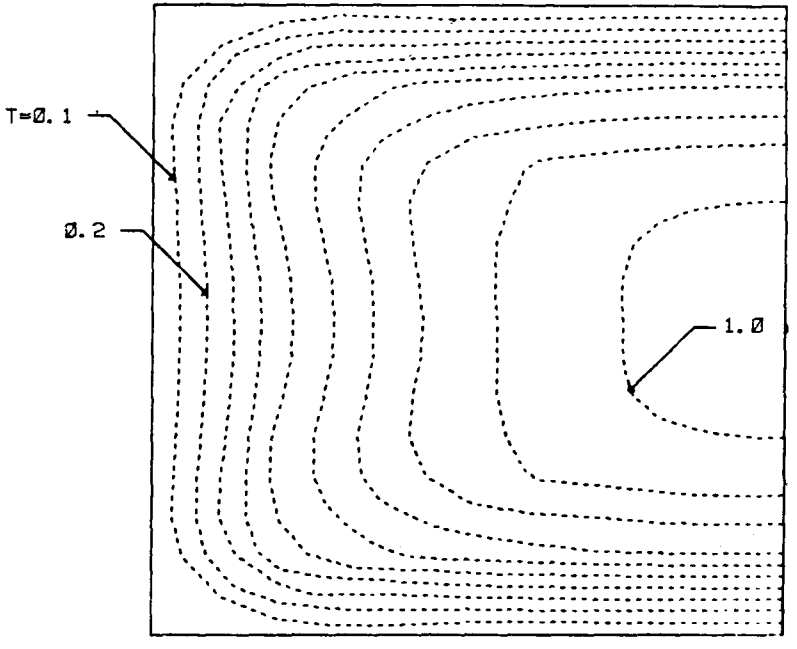

Figure 6. Isothermal contours in two-dimensional reactive flow, Galerkin calculation. Heat generation by viscous dissipation and reaction heating.

Conclusions

The numerical model described above has a significant present ability to simulate a wide range of problems in polymer processing. At the same time, it is small enough to permit easy implementation in even rather small processing facilities, and for quick familiarization by process designers. We feel such a capability would lead to a significant advance in industry capability for process development and optimization.

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Nomenclature

c	specific heat
C	concentration of reactive species
D	diffusion coefficient
E_1	activation energy for viscosity
E_2	activation energy for reaction
k	coefficient of thermal conduction
k_m	reaction rate preexponential factor
K	overall reaction rate
m	reaction order
mw	molecular weight
n	power-law exponent for viscosity
p	pressure
Q	internal heat generation
R	internal species generation
R_g	gas constant
T	temperature
u	velocity or velocity vector
β	factor for pressure dependency
$\dot{\gamma}$	shear rate
η	viscosity
η_0	viscosity coefficient
ρ	density
ΔH	heat of reaction
∇	gradient operator

Literature Cited

1. Bird, R.B., W.E. Stewart, and E.N. Lightfoot: "Transport Phenomena," John Wiley & Sons, Inc., New York, 1960.

2. Middleman, S.: "Fundamentals of Polymer Processing," Mc Graw-Hill Co., New York, 1977.

3. Zienkiewicz, O.C.: "The Finite Element Method," McGraw-Hill Co., London, 1977.

4. Huebner, K.H.: "The Finite Element Method for Engineers," John Wiley & Sons, Inc., New York, 1975.

5. Collins, B.R., S.M. Thesis, MIT, Cambridge, 1981.

6. Hughes, T.R.J., W.K. Liu, and A. Brooks, J. Comp. Physics, vol. 30, pp. 1-59, 1979.

7. Gresho, P.M., and R.L. Lee, Computers and Fluids, vol. 9, pp. 223-253, 1981.

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