A Course in

POLYMER PROCESSING

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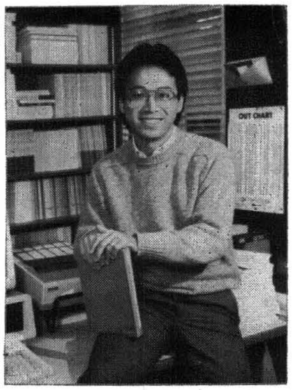
A SHORT PAPER describing a new course in polymer processing at Berkeley was written four years ago [1]. Since then this special-topics course has acquired a regular course stature and Berkeley has changed from a quarter to a semester system. With the additional five weeks of instruction and the accumulated experience of past offerings, this course has evolved significantly to embody new features and emphases.

The original goal was to introduce the basic concepts in polymer rheology and processing to entering graduate students. Much effort was devoted to developing a full appreciation of the behavior of polymers as a special class of material and to nurture the ability to set up equations of continuity as well as motion to describe the various processes under consideration. Classic textbooks by Middleman [2], Bird *et al* [3, 4]), and Dealy [5], remained as major references. The course, however, was re-structured to accommodate both the original and the newly emerged objectives. It began with an introduction to the fundamentals, where general transport equations, kinematics and dynamics, boundary and initial conditions, and simple and combined model flows were analyzed. Descriptions of polymer rheological properties by constitutive equations followed the introduction, enabling predictions by these transport equations for materials with increasing degrees of rheological complexity. Both the kinetic network and reptation theories were discussed to provide the class with some familiarity of contemporary models.

The overall aim was to dispel a certain mystique surrounding polymers, viscoelasticity, and the related processes. In addition, the students were given a first-hand opportunity to observe and practice the development of systematic approaches to process modeling.



David S. Soong received his BS in chemistry from the National Taiwan University in 1973. He began graduate study in chemical engineering at the University of California, Berkeley, in 1975, and received his MS in 1977 and his PhD in 1978. Since 1979 he has been a member of the chemical engineering faculty at Berkeley. In 1984 he received the Dreyfus Teacher-Scholar Award in recognition of his performance and promise in teaching and research. His current research interests lie in polymer rheology and processing, polymer applications in microelectronics and microsensors, thermodynamics and kinetics of polymer phase separation, and polymerization reaction engineering.

Rheometrical techniques and rheological measurements were also included in recent versions. The bulk of the course dealt with traditional processes such as extrusion, calendering, fiber spinning, injection molding, and polymerization reaction engineering. Hence, much of the original content was retained. The lengthened instructional period allowed examination of coating and mixing as well. The overall aim was to dispel a certain mystique surrounding polymers, viscoelasticity, and the related processes. In addition, the students were given a first-hand opportunity to observe and practice the development of systematic approaches to process modeling.

NEW DEVELOPMENTS

Knowledge accumulated in the first two-thirds of the course became invaluable in the undertaking of new subjects in emerging technology: polymer applications in microelectronics. The decision to incorporate this new segment was based partly on the geographical proximity of the Berkeley campus to the Silicon Valley. Berkeley graduates constitute a significant portion of the manpower resources for this industry. In addition, polymers play a major role in achieving our current state-of-the-art in microelectronics. They are not only found in final products such as housing of components, packaging of integrated circuits and intermetallic dielectric layers, but are also employed extensively in critical processing steps, exemplified by resists in microlithography. Comprehension of the salient and the subtle issues of such a plethora of usages dictates a firm grasp of the basic principles of polymers, which the students were expected to have already acquired, at least partially, by this point in the course.

Integration of this new segment seemed superficially difficult since few students were adequately prepared and therefore had to learn the rudiments of the field rapidly. My experience suggested that our students possessed an amazing ability to assimilate the information presented once they were sufficiently motivated. The effort was great. Nonetheless, they were rewarded by the realization that most established rules, equations, and correlations remained valid in the miniature world of microelectronics. Furthermore, the students emerged from this course having gained a certain familiarity with the current status, future trends, and central issues of polymer applications in microelectronics.

Subsequent to a brief survey, a few topics were selected for detailed examination (Table 1). These represented areas where a chemical engineer is expected to make the most contributions. They also dovetailed the rest of the course naturally. We began with resist processing. Spin-coating of resist films on semi-conductor substrates is accomplished by dispensing a fixed amount of a polymer solution onto a wafer. The wafer is then rotationally accelerated to a pre-set speed. Centrifugal force causes the fluid to flow radially outward, reducing the thickness of the layer. Simultaneously, evaporation of the solvent continually changes the fluid composition, and thereby its rheological properties. Clearly, coupled momentum and mass transport are essential for the accurate description of this process. Exposure of the deposited film to photons or energetic particles induces chemical modifications and/or structural alterations. The energy absorption profiles are then translated into iso-structural contours. Such knowledge provides a starting point for the prediction of the outcome of resist dissolution (wet development). To this end, a model for polymer dissolution is given. The glassy film is first converted into a swollen gel by the incoming solvent, whereupon entangled coils disengage from the network into the developer. The problem is thus described by two moving boundaries. Stress-induced Case II diffusion governs the kinetics of glass-gel interface, whereas polymer dissociation at the gel solvent interface is characteristic of a reptation type process. Only through this sort of systematic examination of the resist development can the process dependence on the developer strength, system temperature, molecular weights of both the exposed and unexposed areas, and the thermomechanical history (*e.g.*, in the baking or the annealing period prior to the development) be understood.

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TABLE 1
Selected Topics of Polymer Processing In Microelectronics Fabrication

MICROLITHOGRAPHY
- **Spin-coating**
- **Exposure**
- **Film dissolution (resist development)**
- **Baking**

PACKAGING (Encapsulation of Integrated Circuits)
- **Reaction Injection Molding**
- **Diffusion in Polymers**
- **Heat Conduction**
- **Stress Field Due to Mismatched Thermal Expansion**
- **Interfacial Adhesion**

Polymers have also found increased uses as intermetallic dielectrics and encapsulants for integrated circuits and their hybrids. Here, a variety of engineering considerations are relevant. First, reaction injection molding of mixtures such as epoxy with a high solid loading is employed for chip packaging. This process epitomized the range of rheology, transport, and reaction problems discussed in the course. Constitutive equations for suspensions, heat transfer through composites, reactive fluid flow, and highly non-linear reaction kinetics were mere examples of the complexity of this process. Next, the packaging material must possess adequate barrier properties against moisture penetration. This necessity entailed a review of mass transfer in polymer composites. Efficient thermal management to dissipate the great power consumed by the encapsulated chips required a good understanding of heat conduction in composites. Approaches to analyze stress fields induced by mismatched thermal expansion coefficients of the polymers and the substrates were yet another subject for discussion. Finally, interfacial adhesion between polymers and dissimilar surfaces stimulated much classroom interaction.

SELECTED TERM PROBLEMS

A list of open-ended term problems was given at the beginning of the class, from which every member chose one for an in-depth study. Through weekly lectures and office visits, the students had ample opportunities to interact with the instructor and to receive guidance in a literature search and theoretical analysis of these problems. Time was set aside at the end for students to present their work to the class. This proved to be an effective incentive for diligent learning, which led (in some cases) to innovative ideas. The problems covered a wide range of topics, both in conventional polymer processing and microelectronics applications. A central theme was followed in each development; any reasonable attempt at the solution required the judicious use of conservation equations and polymer principles. Some example problems are discussed in the following paragraphs.

Recently, a sliding cylinder rheometer (SCR) was constructed for use with an existing materials test system (MTS) in my laboratory to measure fast transient and steady-state responses of viscoelastic fluids [6]. This MTS-SCR combination exploited the versatility and capability of the MTS programmable drive and its stiff load train. The sample confining surfaces of the SCR were assumed to be perfectly concentric in order for ideal simple shearing to be obeyed. Effects of axis tilting and eccentricity on the time-dependent as well as the steady-state rheological properties were investigated by a student with the use of a constitutive equation based on the kinetic network approach [7]. This project generated useful sensitivity plots, allowing the tolerance level for instrument misalignment to be delineated.

A second problem was modeling fiber spinning of viscoelastic fluids, in particular those described by the classic Maxwell model and some recent kinetic network theories. Heat transfer into the surrounding cross-flow air caused a notable spinline temperature variation. Hence, temperature-dependent parameters were used in modeling fluid flow in the momentum conservation equation. Air drag, inertia, gravity, and draw-down were all considered. This exercise highlighted the differences between continuum and structured-fluid models.

Another problem where simultaneous transport equations must be invoked to find the solution was the process of microsphere formation. These miniature containers are designed for use as laser fusion targets when filled with mixtures of deuterium and tritium. Two important steps occur here. Volatile-containing droplets emerging from a nozzle with imposed oscillation first undergo a spontaneous blowing process, driven by the evaporation of volatile solvent which pushes the polymeric shell outward. These hollow particles then enter a refinement zone where a centering process takes place to eliminate eccentricity between the shell internal and external surfaces. The confined vapor partially permeates to the surroundings, allowing shrinkage of the microspheres in this zone to the desired final dimensions and sphericity. Biaxial extensional flow dominates the rheology of microsphere expansion, whereas detailed dynamics of radial flow results in improved concentricity and sphericity. The effects of viscoelasticity on the rate and stress associated with microsphere expansion have been studied using the Newtonian and Maxwell constitutive equations. Simple analytic results to describe microsphere refinement have been obtained for conditions representative of the centering process where Newtonian behavior prevails. A manuscript based on this effort has been drafted for future publication.

Several term papers eventually inspired the development of full-scale research programs. One such project was the wafer spin-coating process. Predictions for both Newtonian and nonNewtonian fluids were made, and later compared with experimental data. Resist dissolutions was the subject of another fruitful term project. Here, numerical techniques were established to monitor the movement of two boundaries. Realistic constitutive equations for both solvent diffusion and polymer reptation were employed in the simulation. The model qualitatively predicted the anticipated trends, when the polymer molecular weight, its glass transition temperature, solvent size, and polymer-solvent compatibility were individually adjusted. In addition, the effect of the rate of cooling following annealing (baking) was carefully examined. The analysis was based on the varying free volume fraction trapped in the glassy film upon cooling. Effects of physical aging below glass transition were also included. An ongoing experimental and theoretical project originated out of this effort. Non-isothermal polymerization in tubular reactors and CSTR's in series, rheology of fiber suspensions in polymeric matrices, and transient temperature profiles of local spots irradiated with laser pulses were additional examples, which led to certain past as well as current research activities.

Besides maturing into full-fledged research projects, major results of previous class efforts were disseminated in later offerings. Some problem statements were modified so that current students could build upon earlier findings and study unexplored features. Hence, although successive classes were handed revised sets of problems, the basic theme remained the same. One thing is certain. The course in polymer processing at Berkeley continues to evolve and yet remains a rewarding experience for the instructor.

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REVIEW: Liquid Filtration

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cludes examining them in more detail by referring to the original work.

After reading the book and observing the number of papers that have been written, it appears that a coherent filtration theory that connects the very practical aspects of filter media selection, predictive rather than reproductive filter design, and optimal operation has eluded this significant research effort on a unit operation that is common to a wide segment of the chemical process industries. □

ChE book reviews

MOMENTUM, HEAT, AND MASS TRANSFER
by C. O. Bennett and J. E. Myers
Third Edition, McGraw Hill, Inc. (1982), pp. 832

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How should transfer operations be taught? The answer to this question determines the choice of textbooks for such a course. The unit operations approach was effectively advocated in a number of textbooks which appeared in the 1950s. This was in line with the earlier evolution of the subject area. The development of a unified transport theory profoundly affected the teaching of transport phenomena at the graduate level and also led to a critical evaluation of how transfer operations were being taught to undergraduates. As a consequence, textbooks emphasizing the fundamentals and providing a connection between transport theory and unit operations were conceived. One of the prominent outcomes was *Momentum, Heat, and Mass Transfer* by Bennett and Myers, first published in 1962.

The publication of the Third Edition of *Momentum, Heat, and Mass Transfer* is a measure of the favorable reception the book has received, since its first appearance, for its approach to teaching transport processes. The Third Edition of the book is essentially identical to the Second Edition. The principal change is the introduction of SI units in a larger number of problems. Further, in each chapter, two or three additional exercise problems have been introduced. However, the added problems are similar to those already existing and they provide an instructor with a larger quantity rather than a larger variety of problems to choose from.

Momentum, Heat, and Mass Transfer by Bennett and Myers is written primarily as a textbook. The material is arranged in three main sections dealing with the three transfer operations. The early chapters in each section deal with fundamental transport theory. Each section includes a discussion of relevant design equations

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