# A Course Sequence in

# POLYMER PROCESSING

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THE POLYMER INDUSTRY is a very rapidly growing segment of the economy and one that employs a large fraction of chemical engineering graduates from both undergraduate and graduate programs. Education has been slow to respond to this need. Until recently education in polymers was limited to one or at most two courses that were usually entitled, "Polymer Science" or "Polymer Engineering" and were primarily survey courses. This has been changing rapidly and courses are now being listed by various colleges that indicate that quantitative instruction in polymer topics is becoming available.

At VPI&SU, a series of quantitative polymer courses that are designed for the first year graduate student has been developed within the chemical engineering department. This series has been undergoing development for over three years and student response has been very enthusiastic. The response is due in part to the rather unique philosophical approach taken in designing the courses.

The courses were not developed as survey courses as is the case with most courses in polymers. Rather, primary consideration was given to the problems commonly faced by the chemical engineer involved in polymer activities; particularly, to the types of problems most likely to be solved by sound application of chemical engineering principles. Aspects of polymer science that are critically important in the solution of engineering problems were also considered to be legitimate topics. Finally, virtually all material includes quantitative discussions, including quantitative solutions of a variety of problems.

On this basis, a three quarter sequence of three credit hour courses has been developed. These courses can be taken in sequence or as a two course program concentrating on thermoplastics or thermosets. Most chemical engineering students interested in polymers pursue the three quarter sequence, but most students from other



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disciplines select the two quarter sequence on thermosets.

#### A QUANTITATIVE APPROACH

The primary objective of the sequence is to help the student develop a basic level of competency in handling problems involved in polymer reactor design, film and fiber extrusion, extruder design, injection molding, polymer foaming, thermoset formulation, reinforced plastic design, and thermoset performance. These problems are mostly of a processing nature and a large number of chemical engineers are engaged in studying them. Obviously, students will not have developed a high level of competence in any one topic by completing the sequence, but they will have had a quantitative introduction to the topics that can serve as a sound basis for further course work or individual study.

Material that is basic to a quantitative approach to polymer processing problems is presented in the first course of the sequence, which is considered a prerequisite for the other two courses. The topics include polymer characterization, thermal analysis, crystallization, non-Newtonian flow models, diffusion, thermal conductivity, polymerization kinetics, linear viscoelasticity, and polymer solutions. These topics can be divided into three groups as follows:

#### 1. POLYMER SCIENCE

- a. Characterization—Molecular weight, molecular weight distribution, radii of gyration, virial coefficients, branching
- b. Thermal Analysis—Transitions, thermodynamic quantities, decomposition
- c. Crystallization—Avrami equation, crystal structure
- d. Linear Viscoelasticity—Models, superposition
- e. Solution—Three parameter models, theta solvents.

#### 2. TRANSPORT

- a. Non-Newtonian Flow—Flow models and data fitting, effect of temperature, elongational viscosity
- b. Diffusion—Effects of polymer structure, non-Fickian behavior
- c. Thermal Conductivity—Effects of structure, conduction in melts

### 3. POLYMER KINETICS

- a. Step and Free Radical Polymerization— Basic models, kinetics, probable distributions
- b. Ionic Polymerization—Basic models, kinetics, applications
- c. Co-Polymerization—Selectivity and concontrol, random vs. block co-polymers.

Approximately equal time is spent on each group of topics and the student must complete sets of quantitative problems concerned with these topics. There is no one text available that is suitable for the course; instead, a set of informal notes compiled from the literature and the listed references has been prepared and are distributed to the students. Students also make extensive use of the references.

Obviously, the basic course is too broad to develop a high level of competency in any one topic, but that is not the object. The objective is to prepare the student for more concentrated study on selected topics in advanced courses or independent studies while training the student to analyze polymer problems quantitatively. Even so, the students are capable of calculating characterization quantities from basic data, of modeling fluids, of modeling reactions, and they are aware of the problems inherent in the procedures used.

The second course involves study of a number of polymer processes—die design, single screw extruder design, fiber and film extrusion, molding and foaming. The descriptive material is presented as selected outside reading so that time in the classroom can be used for quantitative discussions.

The problems studied include:

- Die Design—Flow through tubes, annuli, and diverging sections, flow between flat plates
- Extruder Design—Design of metering, plasticating, and feed sections
- Fiber Extrusion—Melt and dry spinning by analyses of Ziabicki and of Kase and Matsuo
- Molding—Analysis of filling and cooling cycles, approximations for injection molding short shot, melting and cooling in rotational casting
- Foaming—Dynamics of phase growth, principles of solvent blowing
- Films—Stresses and orientation in blown and drawn films.

Several of these topics are in an advanced state of treatment while treatment of others is still developing. Lectures and discussions are based on notes prepared from treatments available in the open literature or in monographs. For example, study of extruder screw design is based on work presented in Tadmor and Klein's excellent monograph, "Engineering Principles of Plasticating Extrusion". On the other hand, very little has appeared on the analysis of the rotomolding cycle; however, approximations can be made by application of non-steady state heat transfer analysis.

In every case, the similarity of treatment of polymer processing problems and of typical chemical processing problems is stressed. The student

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realizes that sound engineering process analysis can be used effectively in the study of polymer processing and that polymer processing need not be considered to be a very specialized engineering study. He quickly learns to approach these problems as typical chemical engineering problems and rapidly develops confidence in his ability to model them. The resulting attitude of the students toward the topics permits the instructor to effectively proceed at a more rapid rate.

Quantitative problems have been developed for most of the topics. These are graded in difficulty, but almost all must be solved by numerical methods. The students write their own computer program, if solution by numerical methods is required; however, the logic to be used is usually given as part of the problem statement. Data on physical properties is usually given as taken from the literature: the student is expected to model the effect of process variables on the property as required for the problem. Calculation of the filament area, temperature, and velocity for melt spinning; calculation of the temperature and pressure profiles for an extruder screw as a function of screw speed and discharge pressure; and estimation of packing pressure and cooling cycle time for injection molding are typical of the type and scope of major problem assignments.

Normally, four of these major problems are assigned to the students during the course. In addition, one or more minor problems are assigned each week. Obviously most of the class time is devoted to discussions of applications. Usually, only the assumptions made in a development are discussed in class. This is as it should be. After all, it is presumed that graduate students can read and comprehend.

#### THERMOSETS STUDY

The third course is a study of thermosets, and the approach is somewhat different. Except for limited general study of cross-linking, the course consists of a study of the effects of chemical formulation on gelation, cure, and properties of some of the major types of the thermosets. These include unsaturated polyesters, urethane foams, epoxies, rubber, and formaldehyde cured resins. For purposes of study, a few standard formulations of each type of thermoset are discussed in detail and principles for variations in properties with respect to change in formulation are developed, if possible. For example, a polyester formulation of one mole phthalic anhydride, one mole fumaric acid, two moles propylene glycol, and two moles styrene with a standard promoted peroxide catalyst system is studied as a performance standard. Effects of changes in this basic formulation on properties are then developed in as logical a manner as possible.

In addition to a study of basic formulation principles, methods of fabrication are discussed and reasons for special formulation requirements due to fabrication methods are developed. When appropriate, principles developed earlier are applied, such as copolymerization selectivity relations for cross-linking of polyesters by vinyl resins.

Problem assignments consist of suggesting formulations for particular applications with reasoned justification for the formulation selected, specifying changes in formulation to accomplish changes in specific properties, and of performing example analyses of property evaluation methods such as viscoelastic moduli spectra. While not as satisfying from a chemical engineering point of view as the types of analyses used in the second course of the sequence, the processes of analysis are typical of current practice. From the viewpoint of instruction, relating various formulations to a standard for each resin has proven to be a useful vehicle for establishing order in the subject matter.

The teaching approach used in the sequence of courses has proven to be quite effective. It relates material presented in other required graduate courses to polymer problems and prepared the student for further independent study or research. Since nine quarter hours amounts to one-fifth of the total requirement for a M.S. degree, which is nearly one-half of the elective hours usually taken, this is usually all the time an M.S. student can afford to devote to the subject. Therefore, the polymer courses necessarily contain a broad range of topics; however, scope is not expanded at the expense of completeness. Under these restrictions, good performance requires a high level of motivation, but motivation has not proved to be a problem, because the interest of the student in the topic is very high.

Perhaps the best measure is the performance of students in subsequent courses, research, and employment. Students have proved their ability to use modern methods of polymer analysis without further instruction, and their organization and development of research projects has been sound. Some have taken more advanced courses and performed very well. Finally, several former students who have entered the polymer field have reported that they were prepared for their assignments and have succeeded in handling them very capably. There are no entirely suitable texts for the courses and few problems for assignments are available. About one and one-half to two manyears has been spent in collecting and collating lecture material, preparing notes, and designing problems for assignments. Problem preparation has proven to be the most difficult task, but problems are an absolutely essential part of the instruction. Even though the instructional burden has been heavy, the success of the courses has made it worthwhile. Ideally, the sequence should be taught by two or more instructors who are specialists in particular topics and who co-operate to preserve the continuity of the sequence. This is our next objective.  $\Box$ 

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# ECONOMICS OF THE CHEMICAL PROCESSING INDUSTRIES: Wei

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are the major cost elements and reduction possibilities, is there security of raw material supply;

(c) **Environmental impact:** what nuisance is created during manufacturing, use or transportation, what are the harmful effects and do they outweigh the benefits, can the bad effects be controlled and at what cost.

A term paper on a company must include:

- (a) Function: what business is the company in, who are the customers and are they likely to prosper in the future, does it have a mix of products to render it less vulnerable to market changes;
- (b) **Dynamism:** is the company an aggressive growth oriented company, making unique chemicals for outstanding profit margin, or a mature company making bulk commodity chemicals for low markup; is innovation of new products, processes and markets an important activity;
- (c) **Past Record:** what is the last ten years' record of sale, profit, earning per share, stock price; how does this company compare with a competitor company and with the chemical industry; how does its growth rate compare with the Gross National Product and population;
- (d) **Strengths and Weaknesses:** is this company in possession of special skills or unusual assets, what are its weak points,

what can a good chemical engineer accomplish here;

(e) **Threats and Opportunities:** what are the external forces that can materially affect this company, and cause it to prosper or to decline.

Topics of the term papers prepared by the students include:

- Air Products and Chemicals, Atlantic Richfield, Foster Wheeler, Joseph Schlitz, Smith-Kline-French;
- Petroleum in Nigeria, titanium dioxide in South Africa, fertilizer in Brazil;
- urea, acrylic fibers, lead alkyls, nylon 66.

Selected term papers were presented orally in class, where a jury of fellow students would rate the talks according to organization, comprehensive coverage, analysis, and clarity of presentation.

The course was given twice, to classes numbering 26 and 30. The classes were divided roughly in equal parts of seniors, full time graduate students, and extension graduate students. There were also a handful of students from chemistry, electrical engineering and civil engineering. Student rating at the end of the course ranged from very good to excellent. The rating on the usefulness and interest in the course is 4.3 out of a possible 5.0. 95% of the class would recommend this course to friends. We are planning to continue to offer this course in the Spring term, with continuous updating of topics and reading materials.  $\Box$  vance of the macroscopic approach. In the two years since publication, except for the excellent application of its tenets by Dr. Odum and his associates, signs of use of the macroscopic approach are few. Understanding of these recent papers (examples below<sup>1-4</sup>) is predicated largely on the reader's knowledge of the methodology and symbolism developed in the book.

There is little doubt, however, that the macroscopic approach will gain additional adherents and increasing use. So, with Professor Odum, I enjoin you to learn how to use the macroscope and apply it in the search for a better understanding of the large-scale interrelationships among living things and the environment; being mindful that societal objectives are a critical driving force in the environment and must be incorporated into the macroscopic analysis in most cases.  $\Box$ 

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