

**AC 2008-2010: UNDERGRADUATE ENGINEERING PROGRAM IN
NANOMATERIALS, MACROMOLECULES AND INTERFACES**

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Undergraduate Engineering Program in Nanoparticles, Macromolecules and Interfaces

Abstract

A coursework sequence for chemical engineering undergraduates is offered by the Colloids, Polymers and Surfaces (CPS) Program at Carnegie Mellon University to provide education about technology applications in nanomaterials, macromolecules and interfaces. This program has developed and improved over the last 30 years for two main reasons: continued interest from industry to hire graduates with this background and the sustained expertise and commitment of faculty in these research areas. The coursework includes the physical chemistry of colloids and polymers coupled with an intensive lab experience that covers classical physical characterization methods. The lab experience also includes exposure to examples of relevant products and processes used in industry. Recently, the program was expanded to a minor in Colloids, Polymers and Surfaces (CPS) and is available to all engineering majors in the college of engineering at Carnegie Mellon. A short review of the program content will be presented. Assessment of the program will include input from employers and graduates of the program. This paper describes how a novel program to enhance undergraduate education in engineering developed because of an alliance that was formed between industry and the research university.

History of the Program

An elective undergraduate four course sequence in Colloids, Polymers and Surfaces (CPS) was initiated for chemical engineering students in 1978 at Carnegie Mellon University. It followed logically from the introduction of a graduate program in 1972 that granted a Master of Science degree on these topics. In 2003, the coursework sequence was offered to all engineering undergraduates at Carnegie Mellon, with the purpose of providing these topics to an increasing audience of students interested in engineering applications of nanomaterials and macromolecules. This paper describes how the development of a Master's program resulted in a minor for engineering undergraduates that is relevant to industrial technology.

The CPS graduate program developed because the late Dr. Howard Gerhart, then vice president for R&D at PPG Industries and later adjunct professor of chemical engineering at Carnegie Mellon University, took the lead in approaching Carnegie Mellon with specifics of his company's needs in basic training and continuing education for technical employees. His requirements fit well with existing planning by the polymer research group of the chemistry department to launch a graduate curriculum in polymers and by the chemical engineering department to introduce colloid and surface science as a focus for graduate study. The result was a new interdisciplinary graduate program titled "Colloids, Polymers and Surfaces", beginning with lecture courses in 1972 and hands-on laboratory training added in 1974. On the academic side it was a cooperative effort under the direction of Professor D. Fennell Evans, employing personnel and physical resources of both the chemistry and chemical engineering departments. Input of R&D supervisors from eight local industries came from the Advisory Board, who participated in major policy decisions and periodic reviews, and encouraged qualified employees

to take advantage of this unique educational opportunity, with tuition underwritten entirely or in part by the employer.

Program Content and Philosophy

The rationale for combining the three areas of colloid, polymer and surface science in a single curriculum addresses problems not of traditional industries alone but of emerging high technologies in medical, biological and interfacial science.

Surface chemistry deals with interactions at boundaries where two phases meet. Equilibrium states as well as kinetic events at such interfaces depend upon the phenomena of surface tension, adsorption and desorption, condensation and evaporation, and the like.

Colloid chemistry deals with materials dispersed in a continuous medium in units of size from 10^{-7} to 10^{-4} cm (10^8 Å to 10^4 Å). Colloidal units in dispersions may be single particles containing many molecules (as condensed solids or liquids), or aggregates of many molecules in thermodynamic equilibrium (as micellar surfactants) or the subunits may actually be joined by covalent bonds (as macromolecules or polymers of natural or synthetic origin).

What colloidal systems have in common, and what links them to surface chemistry, are the peculiar properties that follow from the presence of a material boundary or discontinuity of submicroscopic scale, and the relatively enormous extent of that boundary, i.e. the high ratio of surface to mass that prevails when matter is finely subdivided. Some of the interesting properties of colloidal dispersions are enhanced physical and chemical reactivity, scattering of light, hydrodynamic properties, osmotic and electrical phenomena. Polymer physical chemistry, a historical offshoot of colloid chemistry, employs many of the same methods of experimentation that are useful for colloids in general. There is certain cohesion in the common intellectual framework of thermodynamics and statistical mechanics, useful in attacking most problems confronting researchers in colloids, polymers and surfaces. Exclusion of any one of the three areas removes at the same time a substantial zone of overlap wherein lie some of today's most exciting and difficult challenges.

The educational focus of CPS core courses is first to teach theoretical chemical and physical concepts that account for the properties of macromolecules and nanoparticles, including the critical role of surface phenomena. This is accomplished with two physical chemistry lecture courses, one covering colloids and surfaces and the other macromolecules followed by two lab courses in characterization techniques.

The Physical Chemistry of Colloids and Surfaces lecture course includes topics such as thermodynamics of surfaces; adsorption at gas, liquid, and solid interfaces; capillarity; wetting, spreading, lubrication and adhesion; properties of monolayers and thin films; preparation and characterization of colloids; colloidal stability, flocculation kinetics, micelles/association colloids, electrokinetic phenomena and emulsions.^{1,2} The Physical Chemistry of Macromolecules lecture course covers methods for synthesis, processing and testing of polymers

that are currently used in industry including topics such as physical, chemical and mechanical properties, their relationship to chain structure and molecular weight, glass transition temperature, rubber elasticity and polymer rheology.^{3,4}

Applications of the theoretical principles covered in lecture courses to the characterization and manipulation of complex systems, which confront industry in everyday production, development and trouble-shooting, are the tools which students gain from this experience. The requirement of a full year of laboratory training is not meant to turn out accomplished technicians but to reinforce, extend and make tangible the theory which has been learned. It has the further practical value of showing students what can be learned from the appropriate design and choice of investigational tools with full appreciation of both the power and the limitations of available modern methods.

CPS Laboratory Experience

Students describe the CPS laboratory exercises as “hands-on-theory”, a union of theoretical framework and experimental technique. Each experiment is designed to explore aspects of the principles covered in the lecture courses. Colloids, polymers, and surfaces are evaluated and characterized using state-of-the-art instruments.

The initial set of classical experiments was developed over 30 years ago by the late Emerita Professor Ethel Casassa and Rosemary Frollini to complement topics covered in the physical chemistry courses; these continue to serve the program well and have been adapted over the years to involve new equipment, new techniques, and current applications. Experiments are added to the curriculum with the acquisition of instruments which reflect current and expanded research expertise by the faculty.

Presently, two semesters of laboratory courses are offered to undergraduates: Experimental Colloid and Surface Science and Experimental Polymer Science. A brief description of the experiments comprising each follows.

Experimental Colloid and Surface Science Experiments

- Surface Tension Determinations by the Dipping Ring Method
Pure liquids, solutions, and liquid-liquid interfaces are studied. Topics include surface free energy, surface excess, intermolecular forces, and the influence of solutes on surface tension.
- Contact Angle Determination by the Sessile Drop Method
Equilibrium contact angle of liquids and critical surface tension of wetting of polymer surfaces are related to adhesion, detergency, surface energy, spreading, and non-ideal surfaces.
- Critical Micelle Concentration of a Surfactant Solution

Abrupt changes in physical properties of a solution series are used to determine the critical micelle concentration of an ionic surfactant. Experimental methods include dye solubilization, conductance, surface tension, and foaming behavior.

- Surface Area of a Powder by Gas Adsorption
Specific surface area of a fine powder is determined by measuring the low temperature adsorption of nitrogen at the gas-solid interface and then constructing a Brunauer, Emmett, & Teller (BET) isotherm.
- Surface Area of a Porous Solid by Adsorption from Solution
Equilibrium concentrations of a series of acidic solutions are measured by computer-assisted titration and used to construct a Langmuir isotherm. Topics include solution equilibrium, monolayer formation, chemisorption, and effects of temperature, adsorbent size and structure.
- Adsorptive Bubble Separation
A bubble fractionation column produces a concentration gradient due to differences in surface activities of the solution components. After concentrations of samples from along the column are determined spectrophotometrically, thermodynamic and transport properties are studied. Other topics include surface excess, monolayer evaluation, and surface activity at the gas-liquid and gas-solid interfaces relative to flotation and separation.
- Colloid Stability
Electrical repulsion of charge-bearing particles is studied in a river-water treatment simulation. Clay dispersions are treated with varying concentrations of electrolytes and polyelectrolytes. The effect of concentration on inducing flocculation leads to a study of the electric-double layer theories of Debye-Huckel, Gouy-Chapman, Stern, Van der Waals attraction, the DLVO theory of stability, and the Schultz-Hardy theory of the effect of electric charge on interparticle repulsion. The compression of the double layer of adsorption and neutralization or bridging by polymers is observed by turbidimetry.
- Coefficient of Friction
Static and kinetic coefficients of friction are measured by ASTM methods using an Instron Tensile Tester with specially designed adapters. Topics include the four laws of friction, boundary and hydrodynamic lubrication, adhesion, slip-stick motion and the frictional properties of elastomers.
- Particle Size Characterization
Polystyrene particles are examined with a Coulter Counter to determine average particle diameter, size distribution, and polydispersity.
- Scanning Tunneling Microscopy
An instructional Scanning Tunneling Microscope is used to study surface topography of gold and graphite coatings. Individual crystals are isolated and sized, and the carbon-carbon bond length in graphite is determined.

Additional demonstrations include electrophoretic migration of colloidal particles and the Tyndall Effect in colloidal dispersions.

Experimental Polymer Science Experiments

- Mechanical Properties of Polymers
ASTM test methods are used with an Instron Tensile tester to determine tensile properties of polymer films and elastomers including tear propagation, stress-strain relations, Young's modulus, and tensile strength. Cold-drawing, stress crazing, and stress relaxation and recovery are observed, and polymer films are examined with polarized light for indications of internal ordering and stresses.
- Adhesives Testing
Appropriateness of adhesives of various applications is determined by ASTM methods using an Instron Tensile Tester. Topics include surface preparation, application method, curing conditions, spreading and contact angle, and comparative bond strength.
- Thermal Analysis of Polymers
A Differential Scanning Calorimeter (DSC) is used to study thermal events in polymer samples, specifically melting point and glass transition temperature. Topics include effect of molecular weight on T_g , changes in heat capacity and effect of molecular orientation on melt temperature.
- Size Exclusion Chromatography
Gel Permeation Chromatography (GPC) data is evaluated to calculate number and weight average molecular weight and to construction molecular weight distribution curves. The polydispersity ratio, viscosity average molecular weight, and intrinsic viscosity of the polymer in toluene are also calculated.
- Dilute Solution Viscosity of Polymer Solutions
Making use of Poiseuille's Law, students calculate the viscosity of dilute polymer solutions using data from a capillary viscometer. Using the Mark-Houwink-Sakurada equation, the molecular weight of the polymer is determined. Variations of the chemical structure of the polymer chains and the statistical occurrence of head-to-head linkages among head-to-tail linkages between monomer units are studied after oxidative cleavage of the polymer (PVOH) and the effect of solvent choice on viscosity is examined.
- Injection Molding of Thermoplastic Polymers
A Laboratory Mixing Molder is used to mold polymer specimens for tensile testing. Elastic modulus, yield stress, and tensile strength are evaluated.
- Swelling and Elastic Modulus of Cross-linked Rubber
Two types of stress deformation of vulcanized rubber are measured: swelling by solvent and elongation under load. The information is used to characterize the cross-linked

polymer in terms of two related parameters: average chain length between points in the network and the bulk modulus of elasticity. The Flory-Huggins equation is used to determine crosslink density and the Mooney-Rivlin equation is used to calculate the elastic modulus.

- Gel Rheology
A cone and plate viscometer is used to study flow properties of dilute dispersions. Viscosity is measured as a function of shear rate for a variety of Newtonian and non-Newtonian solutions and gels.
- Capillary Rheology
Data from a capillary extrusion rheometer is used to study melt properties of polymers and to calculate melt viscosity, the non-Newtonian flow index and wall shear rates. Diameters of extrudate are measured to compare die swell with shear rates and varying capillary diameter. Surfaces are observed for distortion as an indication of melt fracture.
- Static and Dynamic Light Scattering
A light scattering photometer with a laser light source is used to study molecular weight distributions and average particle diameter and particle size distribution of dilute polymer solutions.
- Membrane Osmometry
The colligative property of osmotic pressure and solution thermodynamics are used to determine polymer molecular weight.
- Emulsion Polymerization
In perhaps the ultimate CPS experiment, polyethylacrylate is produced by the free-radical polymerization of ethylacrylate in an emulsion system. Polymerization takes place within micelles in an aqueous solution. The colloidal latex is precipitated and the product is dried and evaluated. Heat evolution during the reaction, is monitored by a computer controlled temperature probe.

Demonstrations for the Polymer Science Laboratory course include interfacial polymerization reactions (polyester and Nylon 6,10), polycondensation reaction (production of a polyurethane foam), super absorbing polymers and their application to consumer products, food thickening agents (xanthan and alginate gums), preparation and properties of network polymers, oil spill remediation simulation.

Most of the lab exercises contain topics that are explored more than once during the course. Concepts are combined to present a more complete characterization. Multiple interactions, non-ideal conditions, non-homogeneity and experimental limitations present the students with “real world” deviations from the theoretical ideal giving them an appreciation of what the research and technology development entails.

Assessment from Students, Alumni and Corporate Scientists and Engineers

Since, 1978, 342 undergraduate chemical engineers have elected this four course sequence, which comprises 10-25% of each chemical engineering graduating class at Carnegie Mellon. Once the minor was instituted in 2003, an average of 8 students elected the minor per year and all of these 40 students graduated the year their minor was granted. The BS graduates work in industries that manufacture, for example, coatings, paints, pigments, surfactants, nanomaterials, polymers, food, personal care products, cosmetics and biomaterials; approximately 20% of the students that received the minor entered graduate school working toward a PhD after graduation.

The initial eighteen students that enrolled in the CPS courses were surveyed regarding the course sequence offered in the 1978-79 academic year as seniors prior to graduation. Highlights of the survey focused on two main questions: “Do you think your chances of employment were affected by your exposure to the CPS Program?” and general comments about the program. With regard to employment, 15 of the 18 students responded and 87% of respondents felt that exposure to the program positively affected their employment opportunities. Other general comments were:

- Provided examples of practical applications and valuable hands-on experience
- CPS topics good to discuss in an interview
- Made me feel more knowledgeable about the chemical industry
- Made me feel more confident about job application process
- Some employers feel you are more qualified while others feel you are over-qualified

The above group of alumni was then surveyed one year after receiving the BS degree with CPS specialization to determine usefulness of the coursework experience in their industrial job. All respondents said the CPS background was very helpful in job hunting and that both theoretical and applied CPS knowledge was useful in their present positions. When asked if CPS contributed to interest or satisfaction derived from their present work, the some of the following responses were:

- “Gives me a fuller understanding of many of the surfactant and surface energy problems we encounter”
- “My knowledge has put me on an equal level with my (more experienced) co-employees who work on polymers, plasticizers and detergents”
- “CPS knowledge has provided me with a vocabulary that I otherwise would have no exposure to, and has allowed me to see a potential area for my career development that I hope to pursue with further education”
- “It made adjustment on the job easier—I could pick up things more quickly and became more effective faster.”
- “I know when I get a test result back what it means and how to interpret data”
- “I’ve found applications to industry based on material I learned through CPS...I don’t think I would have realized or appreciated without that study”.

We continue to receive similar comments from today's recent alumni confirming the importance and relevance of their exposure to the topics presented in the CPS program and the very positive and significant effect the experience has had on their careers.

Student assessment of the CPS lab courses from faculty course evaluations conducted by the university each semester are available from 1978 and 1988- 2007. From the 20 years worth of data, we find that students enrolled in the lab courses rated the overall courses with an average value of 4.4 on a 5.0 scale, where 5.0 is the highest possible score of excellent. These data represent responses from 195 students of the 342 total students, which comprise 57% of all students taking the courses in the past 30 years, a clear demonstration of the usefulness of these courses from the student perspective. Note that the course evaluations are not mandatory; students are encouraged to provide a response, but there is no method for insuring that the student evaluates the course.

Industrial scientists and engineers familiar with the program were polled in 1998 regarding their opinion of the CPS Program. This was a group of industrial scientists and engineers, including some CPS Advisory Board members and some alumni from industrial corporations; both groups had hired students from our program. Their comments are summarized below:

- "...our products and manufacturing technology must remain at the forefront of technology. To this end, world class skills and training are essential. We feel that the Carnegie Mellon CPS Program can produce people with these skills."
- "The technological area of CPS is very useful in the metals industry...These characteristics translate directly to the bottom line in terms of product success in the marketplace."
- "In any manufacturing industry that is related to paper making, printing inks, photography, xerography, thermal printing, magnetic recording, polymeric film or sheets, filled plastics, protective finishes and paints, ceramics, electronics and semiconductors...there should be some staff...with professional training that includes competence in colloid and surface science and polymer chemistry."
- "It is critical that the USA provide ...knowledge to students that can then be available to US companies that are now competing in a world market. The CPS Program is a much needed area of education"
- "As a recognized academic leader in this area (the CPS Program) is educating students that will provide competitive advantage to the American chemical industry for years to come."
- "...without a doubt, the training I received in CPS at Carnegie Mellon has helped me the most in my career...the training your students receive ...makes them better able to compete and contribute immediately...CPS training is applicable to a number of our businesses..."
- "Our competitors include international polymer manufacturers....the material covered in existing CPS courses....will be essential to increasing the international competitiveness of the US water soluble polymer industry...."
- "The CPS Program at Carnegie Mellon is regarded within (our technical) community as one of the top programs in the nation..."
- "Education is the underlying key....the CPS Program fills an educational gap in ...an important area of science."
- "...through the CPS Program at Carnegie Mellon, students are better prepared to handle the challenges...this program is an invaluable asset..."

Comments similar to those above are currently provided by many alumni that return to our campus on a regular basis to recruit new graduates; they often specifically express interest in graduates with a CPS background.

The success and industrial relevance of the CPS course sequence prompted the formation of a CPS minor, instituted in the College of Engineering at Carnegie Mellon in 2003. It consists of five courses: a thermodynamics course, two courses in the Physical Chemistry of Colloids/Surfaces and Polymers and the two lab courses described previously; the minor is available to all engineering students.

This program exemplifies how industry and the research university can combine to form novel programs that enhance undergraduate education in engineering. As applications for nanomaterials and macromolecules continue to grow, 30 years after the program's inception, we observe that CPS courses for both graduate and undergraduate students at Carnegie Mellon are elected by a continually more diverse group of students that come from the Departments of Chemical Engineering, Chemistry, Physics, Civil & Environmental Engineering, Materials Science and Engineering, Biomedical Engineering and Mechanical Engineering. This demonstrates the continued importance of these multidisciplinary topics to many areas of science and technology.

Acknowledgement

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Bibliography

1. Hiemenz, Paul C., and Rajagopalan, R. Principles of Colloid and Surface Chemistry, 3rd edition. New York: Marcel Dekker Inc., 1997.
2. Evans, D.F. and Wennerstrom, H. The Colloidal Domain: Where Physics, Chemistry, Biology and Technology Meet (Advances in Interfacial Engineering). New York: Wiley-VCH Publishers, 1999.
3. Rosen, Stephen L. Fundamental Principles of Polymeric Materials (Society of Plastics Engineers Monographs), second edition. New York: John Wiley & Sons, 1993.
4. Coleman, M.M., and Painter, P.C. Fundamentals of Polymer Science, 2nd edition. Boca Raton, Florida: CRC Press, 1998.