INTEGRATING KINETICS CHARACTERIZATION AND MATERIALS PROCESSING IN THE LAB EXPERIENCE

DENNIS J. MICHAUD, RAJEEV L. GOROWARA, ROY L. MCCULLOUGH
University of Delaware • Newark, DE 19716

At the University of Delaware, we have developed an integrated sequence of two undergraduate laboratory experiments (spanning the junior and senior years) in which the students investigate different aspects of batch process design. The design task assigned to the students is to identify adequate processing conditions to produce a quality one-inch-thick composite laminate within a limited time frame. Thick-sectioned thermoset composites can be difficult to process correctly due to the exothermic nature of the polymerizing resin and the low thermal conductivity of the laminate.

The Resin Transfer Molding (RTM) process incorporates a number of core chemical engineering concepts within a laboratory exercise while at the same time introducing students to the manufacture and properties of composite materials. A numerical cure simulation of the RTM process,[1] developed within the Center for Composite Materials at the University of Delaware, is used during each lab's design component to evaluate different processing scenarios. Figure 1 outlines the important features of the two experiments and illustrates the manner in which they are integrated.

In the first experiment, the juniors characterize the resin's polymerization kinetics and heat of reaction using differential scanning calorimetry (DSC). Using an empirical nonlinear kinetic model for the thermosetting resin,[2] the data is correlated to establish the model parameters needed by the process simulation. The simulation is then used for a preliminary design of the processing conditions required to successfully produce a one-inch-thick composite laminate within a two-hour processing window. The sensitivity of their design to kinetic parameter variability is also investigated.

The senior composite laboratory experience continues the simulation-based sensitivity analysis of the RTM process by including variations of the simulation's heat transfer model parameters. The students implement their initial design, producing a ten-inch-square composite laminate with a one-inch through-thickness. Density, void fraction, and mechanical tests of the laminate help students evaluate the success (or failure) of their experiment. By comparing measurements from thermocouples embedded within the composite and those predicted by the simulation, the students make modifications to the simulation's model parameters (heat transfer and kinetic) to improve the simulation's accuracy.

Armed with an improved process simulation and more knowledge of the process, the students then generate a new set of processing conditions and again implement it experimentally, producing a new (and hopefully improved) composite laminate. The students then use a combined evaluation of the simulation's model parameters and their process-

Dennis J. Michaud *is currently Lecturer of Chemical Engineering at the University of Delaware. He received his BS from Northeastern University and was awarded a PhD in Chemical Engineering at the University of Delaware in 2000 for his work in the optimization and control of thick-sectioned RTM composite processing.*
Rajeev L. Gorowara *received his PhD in Chemical Engineering under the direction of Professor McCullough at the University of Delaware in 2001, focusing on interphase formation in glass-fiber vinyl-ester composites. He received his BS and MS from Ohio State University. He is currently a Consulting Engineer in the DuPont Engineering Particle Science and Technology Group.*
Roy L. McCullough *was Professor of Chemical Engineering at the University of Delaware until his death in December of 2001. He received his undergraduate chemistry training at Baylor University and was awarded a PhD in Chemistry by the University of New Mexico in 1960. He published numerous technical papers and organized symposia in the areas of polymer science and composite materials.*

ing experience to propose a final design in their written report.

THICK-SECTIONED COMPOSITE MANUFACTURING

The specific problem given to students concerns the manufacture of thick (greater than one-half inch through-thickness) composite materials via RTM. This nontraditional subject matter allows students to apply classroom knowledge of kinetics and transport phenomena while also introducing process control and the limitations of mathematical models. Processing thick-sectioned composites is challenging due to the exothermic nature of the reacting resin and the heat transfer limitations of the polymer and glass fiber composite.[1,3] Unfavorable processing conditions of the composite part can lead to poor part quality, including cases where the laminate cracks internally due to residual stresses within the part.

The primary design problem for thick-sectioned composite is to identify an acceptable temperature trajectory (or "cure cycle") that balances

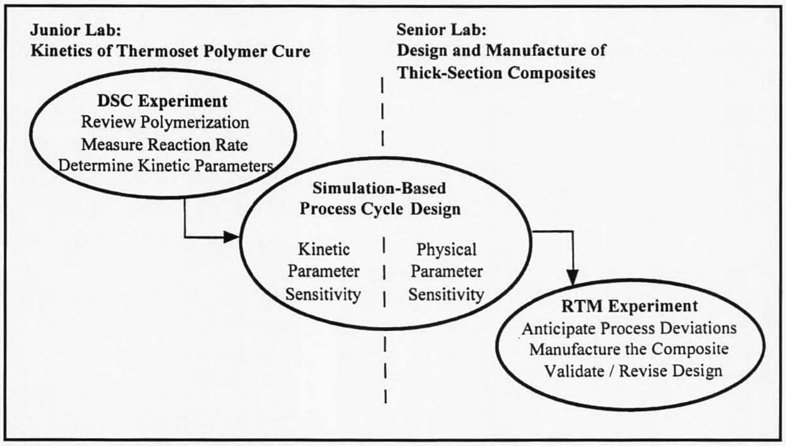

Figure 1. *Schematic of integrated undergraduate laboratory experiments.*

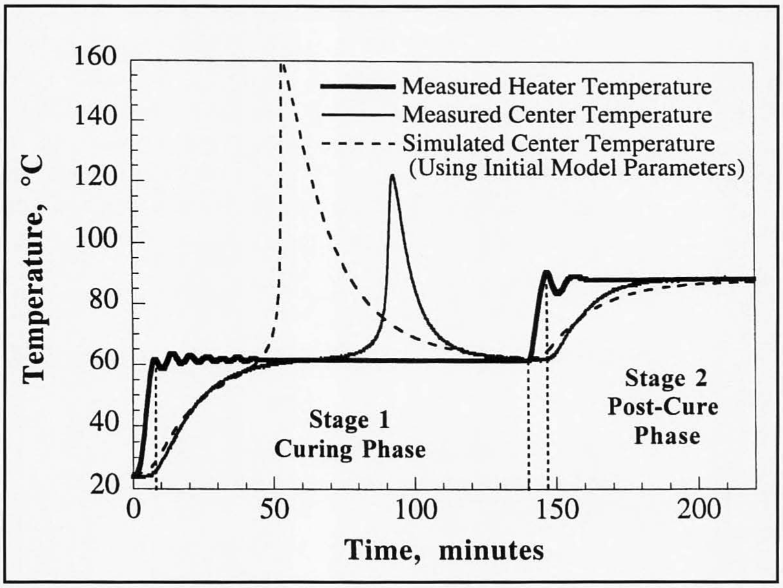

Figure 2. *Example cure cycle and corresponding internal composite temperature.*

the heat necessary to initiate the polymerization reaction (cure) with the heat transfer limitations of the composite once the reaction begins, while also maintaining a processing time that is economically feasible. The example cure cycle presented in Figure 2 shows experimentally measured heater and composite (measured at the center of a one-inch-thick laminate) temperatures. The cure cycle is broken up into different stages, each with a specific heater set-point.

For the experiment shown in Figure 2, the first set-point was 62°C and the second set-point for the post-cure was 90°C. Due to the low thermal conductivity of the composite, almost 60 minutes of processing is required for the center of the composite to reach the heater set-point, but once the resin at the center begins to cure, the heat generated from the reaction quickly raises the composite's temperature and drives the polymerization reaction to completion. A lower temperature curing stage reduces the temperature gradient within the part as well as residual stresses, but also increases processing time. Since the surface temperature of the composite remains much closer to the heater set-point, a post-cure is generally required to ensure the surfaces of the composite are adequately cured for removal of the part from the mold.

LABORATORY FORMAT AND EDUCATIONAL OBJECTIVES

At Delaware, the undergraduate chemical engineering laboratory is a two-course sequence, taken in the spring of the junior year and the fall of the senior year. Initially, all students attend five background lectures in laboratory safety, measurement techniques, statistics, report writing, and oral presentation.

In the junior course, student groups go through three experimental cycles, with each cycle centering around a design problem using information gathered during a laboratory experiment. Over a four-week period, the students must learn about the problem, perform the experiment, analyze the data, prepare a preliminary data report, revise the data analysis, and complete the design problem in a final report.

In the first week of a cycle, the students prepare for the lab by reviewing the experiment and laboratory procedures with the teaching assistant (TA). They prepare an experimental proposal, and during the graded pre-lab conference they present it to the supervising faculty member, who must be convinced that valuable "research facility" time should be spent on the problem. The students must also show an understanding of the safety issues involved.

In the second week the students perform the experiment under the guidance of the TA, and in the third week they conclude the data analysis and preliminary data report. The students then use their lab data during the fourth week for the design problem and present the final report for the cycle to the faculty member.

At the conclusion of the course, the individual groups orally present one of their experiments to their colleagues and faculty and then critique their videotaped performance. The format of the senior-year course is very similar in approach, but has only two experiment cycles. A longer six-week sequence allows the students to return to the lab after their first experiment and either extend or correct their experimental data.

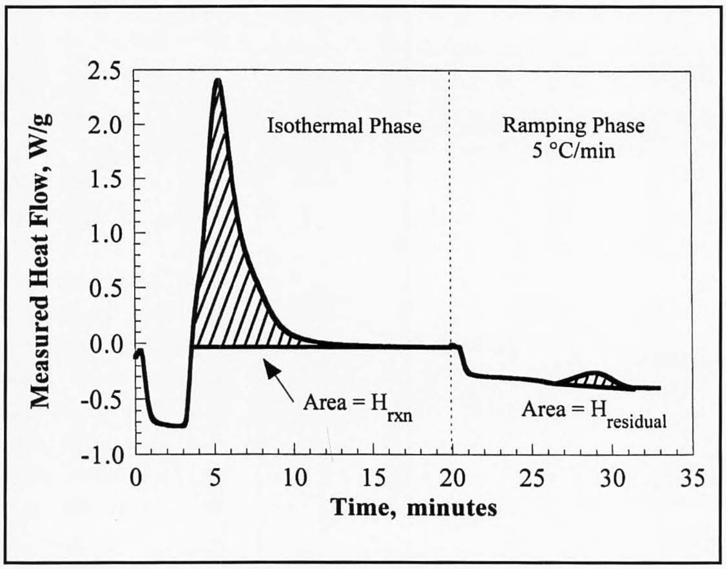

Figure 3. *Example heat flow of a differential scanning calorimetry (DSC) experiment.*

The integrated lab format allows us to address the entire hierarchy of educational objectives outlined by Bloom and colleagues in their famous taxonomy.[4] These objectives include analysis, synthesis, and evaluation, referred to as "higher-level skills" by Felder, *et al.*[5] The fundamental objectives of knowledge, comprehension, and application are referred to as "lower-level skills."

We agree with Miller, *et al.*,[6] that the engineering laboratory is an ideal setting to help students become better engineering practitioners and to enhance their higher-level thinking skills. Since the time of Professor Robert Pigford, it has been the tradition at the University of Delaware to focus the chemical engineering laboratories not only on the determination of experimental data, but also on a design problem using that data. In the terms of Bloom's taxonomy, the higher-level objectives are not only *analysis,* but also the *synthesis* of this new information into an engineering design. We find the design problem's requirements to be an excellent motivation for the laboratory experiments, and that the *synthesis* step reinforces the need to succeed in the lower-level skills.

We add the integrated lab to this tradition, as it creates a situation that stresses *evaluation*, based on the student's own depth of experience: *evaluation* of the validity of experimental data in comparison to the other groups; *evaluation* of their process design in the second experiment; and (after revising their process model based on the second experiment) *evaluation* of their ability to evaluate. The supervising professor focuses on the higher-level skills, guiding students in analyzing their data, using it in the synthesis of a new process design, and evaluating that design in the process experiment.

The TA tends to focus on the lower-level skills: *knowledge* of polymerization kinetics and composites processing; *comprehension* of the experimental methods; and *application* of that knowledge to extract model parameters from the experimental data.

KINETICS OF THERMOSET POLYMER CURE *(JUNIOR YEAR)*

The junior-level composite laboratory experiment requires that the students evaluate the resin's kinetic parameters necessary to predict the resin curing behavior within a thick-sectioned composite and to develop a preliminary design of the processing conditions for a one-inch-thick composite laminate. The students investigate the resin-curing process of pure (neat) resin samples using differential scanning calorimetry (DSC), which accurately measures the heat evolved from the reaction and the reaction temperature.[7] They are challenged to consistently prepare the small (8 to 12 mg) resin samples and to interpret the DSC's baseline and endpoint data. The DSC is used to measure the isothermal heat release rate, dQ/dt, which is related to the polymerization reaction rate, $d\alpha/dt$, by

$$\frac{\partial \alpha}{\partial t} = \frac{1}{H_{ult}} \frac{dQ}{dt} \tag{1}$$

and the extent of ploymerization (cure), α

$$\alpha(t) = \frac{1}{H_{ult}} \int_{t_0}^{t} \left(\frac{dQ}{dt} \right) dt \tag{2}$$

where H_{ult} is the total heat of reaction given by

$$H_{ult} = H_{rxn} + H_{residual} = \int_{t_0}^{t_{f,isothermal}} \left(\frac{dQ}{dt} \right) dt + \int_{t_{f,isothermal}}^{t_\infty} \left(\frac{dQ}{dt} \right) dt \tag{3}$$

H_{ult} is determined by summing the heat measured during the isothermal cure of the resin with the residual heat measured at the conclusion of an isothermal run. Using Figure 3 of experimentally measured heat flows as an example, the value of H_{rxn} is evaluated from t_0 = 3.2 minutes (when the DSC pan is added to the cell) to the final isothermal time point, $t_{f,isothermal}$, of 20 minutes. The temperature of the DSC cell is then ramped at 5°C/min until no residual heat is observed.

For the students to simulate resin cure in an actual part, they need to be able to describe the reaction in a non-isothermal cure. The kinetics of the free-radical polymerization can be described using the popular autocatalytic model[2,8] shown in Eq. (4), which gives the reaction rate, $d\alpha/dt$, as a function of the fractional extent of cure, α, the maximum extent of cure, α_{max}, and an overall reaction order of 2

$$\frac{d\alpha}{dt} = k \cdot \alpha^m (\alpha_{max} - \alpha)^{2-m} \tag{4}$$

and

$$\alpha(t) = \frac{\alpha_{max}}{1 + [(1-m)\alpha_{max} \cdot k \cdot t]^{1/(m-1)}} \tag{5}$$

An Arrhenius expression is used to account for the temperature dependence of the rate constant, k

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{6}$$

For the incomplete curing case in which vitrification occurs before complete reaction, the maximum extent of cure, α_{max}, for an isothermal curing temperature is less than one, and a linear relationship may be used to approximate the effect of temperature, T, on α_{max}.

$$\alpha_{max} = a_0 + a_1 \cdot T \qquad \text{for} \qquad \alpha_{max} < 1 \tag{7}$$

We have used the resin Derakane 411-C50 (Dow Chemical), a free-radical polymerizing resin that is 50 wt% DGEBA-based vinyl ester and 50 wt% styrene, since we use it in other projects.[1,9] Alternative resin systems can easily be implemented, however. We have also used a variety of initiators and accelerators to alter the kinetic performance of the resin.

From heat rate and time data, the students estimate the resin's kinetic parameters (H_{ult}, A, E_a, m, a_0, and a_1) required by the cure simulation. We recommend that the students first determine H_{ult}, then $\alpha_{max}(T)$, and then k(T) and m at each cure temperature, using nonlinear regression. We make available for their use KaleidaGraph (Synergy Software), which allows curve fits of nonlinear functions. To help ensure reasonable curve fitting results, we ask the students to use their derived kinetic model to predict the extent of cure (α) as a function of time and compare that to the experimental extent of cure data.

The students estimate the error for some of the parameters based on the nonlinear regression fitting of the data, and the error for the others is determined by propagation of experimental measurement errors. The melting of a standard Indium sample is used to estimate error in the DSC heat flow and temperature measurements.

The Resin Transfer Molding (RTM) process incorporates a number of core chemical engineering concepts within a laboratory exercise while at the same time introducing students to the manufacture and properties of composite materials.

Once the students submit their preliminary data reports, the data from all of the groups (including previous cycles) is circulated via memos in order to provide a larger estimate of variability from the pooled data. This gives the students an introduction to the statistical treatment of data, including the use of significance testing (*i.e.,* t-test) to determine if their data is within the norm. There is generally a lot of variability between groups, and this exercise gives the students an appreciation of these statistical techniques as well as refining the data they will need during the design component. The students are asked to use these estimates as bounds for the sensitivity analysis on the simulation parameters.

SIMULATION-BASED PROCESS CYCLE DESIGN *(INTEGRATED DESIGN PROBLEM)*

As part of the junior lab, the students are introducted to simulation-based batch-process cycle design, focusing primarily on the effects of the resin's kinetic parameters. The RTM process cure simulations are provided via a course homepage.* Before their prelab meeting, the students use a fast, but imperfect, neural net version of the simulation to explore the dynamics of the system and get a "feel" for their design problem. Once they have experimentally determined the resin's kinetic parameters, they use the more accurate finite difference cure simulation[1] for their design.

We define the problem of cure-cycle design as the proper selection of the composite's time-temperature cycle (similar to Figure 2), within the limits of available equipment, to make a high-quality part while completing the cure process in as short a period of time as possible to reduce the production cost. We define a successful cure cycle in terms of several quality criteria, such as achieving an acceptable degree of cure while minimizing void content, thermal degradation, and residual stresses.

* *<http://www.che.udel.edu/cheg445/composite/>*

The students are informed of the different process parameters that must be controlled to meet the product design limits. For example, void formation is affected by the vaporization of styrene, and therefore the students must calculate this temperature limit at process pressures (approximately 20 psig). To avoid thermal degradation, the student's proposed temperature cycle should minimize the peak temperature observed in the center of the composite. To minimize residual stresses, the students should ensure that the composite cures inside/out once the resin's gel-point is reached. The resin shrinks 8% during cure, and significant curing on the outside of the composite before the center begins to cure results in large internal stresses (and possible delaminations) once the resin at the center begins to polymerize.

In terms of minimizing processing time, the students are given the goal of curing the composite ($\alpha_{surface} > 0.75$) in less than 2 hours. The juniors present their proposed design in their final report for the DSC experiment. In their senior year, they again visit the simulation-based design problem, but with a new emphasis on the material properties of the composite (resin content, composite density, thermal conductivity, etc.), heat transfer coefficients within the mold, and the effect of fibers on the kinetic behavior of the resin.

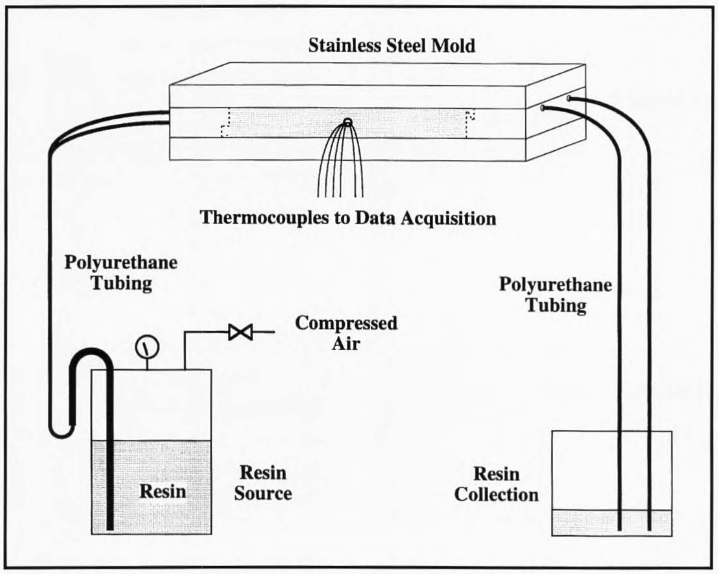

Figure 4. Diagram of resin transfer molding (RTM) equipment.

DESIGN AND MANUFACTURE OF THICK-SECTIONED RTM COMPOSITES *(SENIOR YEAR)*

After an introduction to composite processing in the junior lab, the seniors are given an opportunity to manufacture a composite laminate. While they previously only investigated the kinetic behavior of neat resins, they soon discover that the heterogeneous nature of composite materials, as well as other manufacturing realities, can complicate a situation.

One of the challenges they find with manufacturing thick-sectioned composites is that extrapolating kinetic data down to the lower temperatures necessary for thick-sectioned cure can result in significant error.[1] Other complications include the change in the resin's kinetic behavior in the presence of fibers and the effect of inhibitors within the resin system that are not currently modeled by the simulation. Lastly, the students are responsible for measuring and/or estimating the physical properties of the composite and the mold environment (*e.g.*, volume fraction of the resin, composite density and thermal conductivity, and effective heat transfer coefficients). The students are given the pure component properties for the resin and glass fibers for their calculations. Heat capacity of the composite is estimated using the "rule of mixtures," and its thermal conductivity can be predicted using a number of techniques.[10,11]

The seniors begin their composite laboratory sequence with a tour of the composite manufacturing equipment and an overview of the experimental procedure and safety issues. The experimental RTM equipment is shown in Figure 4. Using their experience from the junior lab, students use the on-line simulation to identify the cure cycle they will implement experimentally. The simulation is also used to analyze the effect of possible model parameter variations on the cure cycle (*i.e.*, sensitivity analysis).

The lab begins with the students filling the stainless steel mold with a predetermined volume fraction of glass fiber reinforcement. The particular fiber reinforcement has varied over the years to include woven sheets, random mats, and stitched layers of different fabric types, which can affect the resulting volume fraction of resin and the composite's thermal conductivity. During the placement of the fibers, six J-type thermocouples are placed between the fabric layers to provide internal temperature data during manufacturing. The entire mold assembly is placed within a heat press to seal the mold components and to provide the heat necessary to cure the composite. The catalyzed resin, contained within a pressurized pot, is injected into the room-temperature mold until no air bubbles are seen exiting from the mold. Once the mold has been filled with resin, the flow of resin is stopped and the cure cycle is begun.

As discussed earlier, the cure cycle is defined by the temperature set-point of the heat press. A representative cure cycle for a one-inch-thick composite laminate is shown in Figure 2. LabView® is used to observe and collect the internal composite temperatures during processing. When the observed temperatures do not match those generated by the simulation, the students are challenged with modifying the cure cycle on-line according to insights from their sensitivity analysis.

Once the cure cycle is completed and the mold is cooled, the composite is removed from the mold and cut into test samples. The students estimate the composite's quality according to ASTM standards for density (D792), void fraction (D2584/D2734), and short-beam shear strength (D2344).

Although some material and heat transfer model parameters of the composite and the mold can be measured, a few of them (*e.g.,* thermal conductivity and the simulation's boundary condition) must be estimated by the students in order to improve the accuracy of the cure simulation. By comparing the simulated composite temperatures with those measured at the beginning of the cure cycle when no resin cure has occurred, the students identify which of the estimated heat transfer model parameters is most likely responsible for the mismatch, and they can then estimate new values. Likewise, the students compare simulated composite temperatures to those measured during the curing phase of the resin to identify possible changes in kinetic parameters due to lower processing temperatures and the effect of fibers.

As is shown in Figure 2, the numerical simulation generally underpredicts the length of time necessary to cure the composite when the default model parameters are used (neat resin kinetics and predicted heat transfer parameters). Since there are a number of parameters within the simulation that can be altered to improve the fit of the simulated temperature profile, the students must defend their choices by using knowledge they have gained about the system and by performing a sensitivity analysis.

Once the students have improved the simulation, they use it to redesign their cure cycle (while understanding that they do not have a perfect model of the system) and use it to manufacture another composite part. The experimental results from this second experiment are then used to further improve the estimate of the simulation's model parameters. Using model parameters derived from both experiments and their newly acquired knowledge of composite processing, the students generate a final cure-cycle design as part of their written report of the lab. This report also includes a sensitivity analysis of their final design and recommendations as to how the simulation and the experiments might be improved in order to better generate an "optimal" cure cycle design that can account for observed batch-to-batch variability.

CONCLUSION

The double sequence of junior and senior laboratory experiments described in this paper has been implemented successfully at the University of Delaware for the past five years. In order to understand the goals of the experiments and complete the design portion, students are required to integrate a number of important engineering concepts, including kinetics, heat and mass transfer, and some process control. Both experiments also provide a good basis for implementing a statistical treatment of the data. Furthermore, the students are introduced (through the simulation-based design component) to the reality of process-model mismatch and the effect of significant process variabilities on their design.

As a whole, each laboratory sequence allows the students to demonstrate many of the outcomes defined within the ABET Engineering Criteria 2000. Unlike many other laboratory experiences, the ability to take a piece of the final product home with them (*e.g.,* a composite paperweight) has been well received by the students. We believe that the integrated concept of this lab and its design aspect in each phase provides an invaluable experience for the students.

ACKNOWLEDGEMENT

The paper is dedicated to the memory of Professor Roy L. McCullough, coauthor, educator, mentor, and friend, who passed away unexpectedly in December of 2001.

REFERENCES

1. Michaud, D.J., A.N. Beris, and P.S. Dhurjati, "Curing Behavior of Thick-Sectioned RTM Composites," *J. of Comp. Mats.,* **32**(14), 1273 (1998)
2. Lam, P.W.K., H.P. Plauman, and T. Tran, "An Improved Kinetic Model for the Autocatalytic Curing of Styrene-Based Thermoset Resins," *J. of Appl. Polymer Sci.,* **41**, 3043 (1990)
3. Ciriscioli, P.R., Q. Wang, and G.S. Springer, "Autoclave Curing: Comparisons of Model and Test Results," *J. of Comp. Mats.,* **26**(1), 90 (1992)
4. Bloom, B.S., ed., *Taxonomy of Educational Objectives,* David McKay Co., New York, NY (1956)
5. Felder, R.M., D.R. Woods, J.E. Stice, and A. Rugarcia, "The Future of Engineering Education: II. Teaching Methods that Work," *Chem. Eng. Ed.,* **34**(1), 26 (2000)
6. Miller, R.L., J.F. Ely, R.M. Baldwin, B.M. Olds, "Higher-Order Thinking in the Unit Operations Laboratory," *Chem. Eng. Ed.,* **32**(2), 146 (1998)
7. Willard, H.H., L.L. Merritt, Jr., J.A. Dean, and F.A. Settle, *Instrumental Methods of Analysis,* 7th ed., John Wiley & Sons, New York, NY (1988)
8. Kamal, M.R., and S. Sourour, "Kinetics and Thermal Characterization of Thermoset Cure," *Polymer Eng. and Sci.,* **13**(1), 59 (1973)
9. Gorowara, R.L., S.H. McKnight, and R.L. McCullough, "Effect of Glass Fiber Sizing Variation on Interphase Degradation in Glass Fiber-Vinyl Ester Composites upon Hygrothermal Exposure," *Composites Part A,* accepted for publication
10. Springer, G.S., and S.W. Tsai, "Thermal Conductivities of Unidirectional Materials," *J. of Comp. Mats.,* **1**, 166 (1967)
11. Farmer, J.D., and E.E. Covert, "Thermal Conductivity of an Anisotropic Thermosetting Advanced Composite During Cure," *Am. Inst. of Aeron. and Astron.:Structures, Structural Dynamics, and Materials,* **5**(56), 2939 (1995) ❐

ERRATA

The phrase "to appear in" in citations 4 and 7 of "Developing Troubleshooting Skills in the Unit Operations Laboratory," by Aziz M. Abu-Khalaf, published in *CEE,* **36**(2), p. 122, (2002), should be omitted.