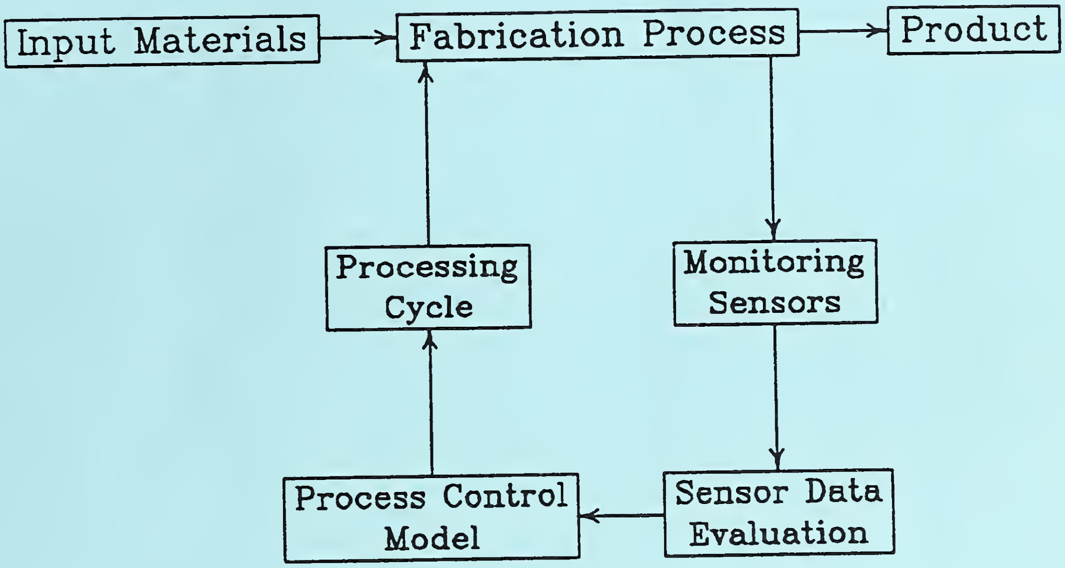
NISTIR 4514

Assessment of the State-of-the-art for Process Monitoring Sensors for Polymer Composites



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U.S. DEPARTMENT OF COMMERCE
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SUMMARY

A variety of techniques have been applied to monitoring the changes that occur in the resin during composite processing. This report identifies and analyzes those techniques that have the most promise for on-line application, namely: ultrasonic, dielectric, spectroscopic, and optical techniques. All these methods have advantages and disadvantages, and the best technique for a given application will depend strongly on the materials and processes involved.

This report discusses these on-line monitoring techniques and compares them in the areas of measurement speed, sampling volume, sensitivity to different resins, effects of fiber type, resistance to the manufacturing environment, interpretation of the data, adaptability for other uses, and temperature capabilities. The most important comparison, however, concerns the research and development work that is needed to achieve the full potential of each technique in applications on the factory floor. Dielectric and ultrasonic methods have an advantage in this connection because commercial equipment designed for process monitoring is already available. The various spectroscopic and optical methods are generally in an earlier stage of development. The great potential inherent in these latter methods, however, makes it highly desirable to actively pursue their developments as well.

Although each of the monitoring techniques has its own research and development needs, the most important technical and scientific issues are common to all. From a technological standpoint, the major short term need is to build more rugged and reliable equipment that can withstand the harsh manufacturing environment. Even commercially available systems would benefit from such improvements, particularly in the sensors, electrical connections, and/or electronics, so process monitoring can be used with more confidence on the factory floor. It is also important to develop better systems for operating in electrically noisy environments and with "impure" industrial-grade resins. Solutions to these technical problems are critical to progress in this field, and considerable effort will be required to solve them, but the approach is straightforward.

The scientific issues are equally important and more difficult to resolve. The two major issues are interpretation of the sensor output, and correlation of the resulting data to process control information through processing models.

A wide range of correlations have been developed between the various process monitoring measurements and a variety of material parameters such as viscosity, degree of cure, and mechanical properties. The basis for these correlations is almost exclusively empirical comparisons between laboratory data. Very few studies have attempted to develop a fundamental understanding of the correlations. As a result, such correlations must be used with care since they are generally resin specific, and their ranges of applicability and validity are unknown. Unfortunately, reports in the literature are not always careful to state these limitations clearly, and consequently, the erroneous conclusion is made that the

measurement provides a direct measurement of a property, like viscosity. This may lead the industrial user to push the correlations too far. The resulting problems could cause users to reject the whole idea of process control, and that would be extremely unfortunate. Consequently, there is an urgent need for more research on interpretation of sensor output in terms of materials properties.

The second scientific issue is how to translate the data from the sensors to process control information. As mentioned above, the outputs from the four techniques have been related to useful parameters such as viscosity, and degree of cure, for specific cases, and additional research should improve such correlations significantly. What remains then is to couple the sensor measurements with the appropriate processing models to provide process control information. This coupling is a challenging task because the problems span many disciplines, but the rewards are substantial since the results will form the basis for real-time process control. A number of laboratories are engaged in research on processing models, but these studies generally do not take full advantage of the potential of monitoring sensors.

The future for process control is very bright. Many programs are currently underway. Despite the critical role that sensors play in this field, however, the development, interpretation, and implementation of sensors have not received sufficient attention. Consequently, research and development on sensors is badly needed. Moreover, it could leverage the work performed in projects addressing other aspects of the process control area and thereby play a vital role. The scientific questions outlined above are particularly appropriate since the results will have maximum impact on the development of on-line monitoring techniques.

INTRODUCTION

1.1 PURPOSE

This report reviews the state-of-the-art for sensors applicable to on-line composite process monitoring. The review covers techniques that are currently used as well as those that are in the development stage. The objective is to evaluate each method, determine its promise for commercial applications, and discuss what is needed for the sensor to reach its full potential including both developments in hardware and improvements in technical understanding.

1.2 SCOPE

In preparing this report, the scientific literature for all process monitoring techniques was surveyed to identify those methods with the most promise for on-line process monitoring. The techniques identified fell into four categories: ultrasonics, dielectrics, optics, and spectroscopic methods. Because of this potential, an in-depth review of was performed for each category. The information came from personal knowledge of the authors, comprehensive literature searches, mail and telephone surveys of industry representatives and researchers with expertise in these areas, and visits to typical industrial locations. The review covered the time period through the end of 1989. The results of this effort are described in the remainder of this report.

In addition to process monitoring sensors, the future for on-line process control relies on developments in two other areas: processing models and control technology. In most cases, the two most important control parameters are temperature and pressure, and thus, sensors to measure these properties are important. As a result, a brief review of temperature and pressure sensors as well as a description of the current status of process modeling were included in a separate section of the report. In addition, the introduction contains comments on the industrial relevance of process monitoring, a brief discussion of off-line measurement techniques, and some comments on major industrial and governmental programs on process control. All of these latter topics, however, are outside the main thrust of this report which focuses on process sensors so it is not the intent here to cover them comprehensively, but rather to provide sufficient information to illustrate how they will contribute to the ultimate goal of on-line process control.

Throughout this report certain commercial materials and equipment are identified. This is done to specify adequately what is available but does not imply recommendation or endorsement, nor does in imply necessarily that the items are the best available for the purpose.

1.3 INDUSTRIAL RELEVANCE

In discussing process monitoring with representatives from various industries, a number of concerns and themes were expressed. These comments are presented in this section.

The most important observation was that the driving force for implementation of process control is the need to improve the efficiency and reliability of processing, and thereby increase the competitiveness of the United States composites industry. Although composites are attractive to many industries due to their high strength and stiffness per unit weight, the labor intensive nature of the manufacturing process greatly hinders the widespread use of these materials.

The inability to measure changes in chemical and physical properties as they occur during processing hinders the development of efficient processing cycles and thus the incorporation of new resin systems into products. A processing cycle is the predetermined program of temperatures, pressures, flow rates, etc. that are used to produce the part. Many processing cycles are developed on a "trial and error" basis which can lead to problems. Often a general cycle is chosen. This is seldom optimal and cannot deal with the batch-to-batch variations caused by factors such as variations in starting materials, differences in humidity, and limited shelf lives of the resins. These problems can result in highly variable parts, unpredictable part yield, high cost, and inefficient use of resin systems.

In addition to general manufacturing concerns, different industries have their particular needs. The automotive manufacturers want composites that can penetrate markets through large volume productions (rapid processing) with low rejection rates and thus low costs. Automotive cycle times can be of the order of minutes. Materials such as vinyl ester/styrene/peroxide systems are often used to provide these short cure times. Injection rates can be as high as 20 lbs. per minute (9.1 Kg/min.) and processing temperatures are 250°F (121°C) or more. The processor's major concerns are to reduce cycle time, improve part quality, and to increase cost effectiveness. Sensors which are consumed during processing, such as embedded sensors, must be inexpensive if they are to impact high volume applications.

The aerospace industry is developing higher temperature resins such as polyimides, but do not have process sensors that can operate at those high temperatures. This industry desires a better understanding of what is happening to the whole part, not just a section. The cost of embedded sensors is not as critical here since manufacturing costs are higher and performance is often the major consideration. The effects of embedded sensors on performance properties, however, are a concern, as is the need to tailor the sensors to meet industries needs, rather than requiring adjustments in processing to accommodate the requirements of the sensor. Another important concern is that an autoclave run can involve 1 to 120 parts being cured at once. Questions arise as to how sensors can be used most effectively in such situations.

The electronics people have processing concerns similar to the aerospace industry, but with some important differences. Printed circuit boards are composites, and the dielectric constant is a key property. As a result, dielectric monitoring is important, and there is a need for high temperature sensors. Processing conditions can reach 716°F (380°C) and 1700 psi (11.7 MPa). Another concern that is important to the electronics manufacturers, and other industries as well, is the electrically noisy nature of the manufacturing environment. Sensors must be adapted to work in such situations.

Once a proper sensor is developed or selected, the output must be related to properties, such as viscosity and degree of cure, that provide information useful for on-line process control. With the exception of some types of spectroscopy, which measure concentrations of reacting species, none of the on-line techniques provide a direct measure of such properties. As a result, the data from the on-line measurements must be related to the required information, and currently, this is achieved by empirical correlations.

It is appropriate, at this point, to say a few words about what correlations are most useful. This is not a simple question, however, because the answer varies considerably depending upon the material and fabrication technique involved. Viscosity is perhaps the most useful property because it controls flow. Sensor data that is related to viscosity will allow the operator to estimate what is happening inside a mold, press, or autoclave, and to influence events such as consolidation by changing processing variables, i.e. temperature, pressure, etc. Once gelation or solidification occurs, however, viscosity is no longer useful, and yet important changes in the material will still occur. For thermosets, the degree of cure, or an equivalent property, is valuable since it indicates when the fabrication is complete or has reached the stage where the part can be removed for post-processing in different equipment. This can decrease both turnaround time and cost.

Correlations for viscosity or degree of cure are quite common since these parameters often provide the most useful information for understanding a process and implementing process control. Nevertheless, there are a variety of other parameters that can be very useful to estimate with an appropriate correlation. One example is the elastic modulus since it can help to predict residual stress and give some indication of overall part quality. Information on morphology and crystallinity (where appropriate) can also be useful for indicating quality and performance, particularly for thermoplastics. Measurements related to flaws and voids are valuable when failure behavior is a key element of part performance. Other useful properties can also be estimated, but this list illustrates the variety that is available.

With this type of information and suitable processing models which relate the determined quantities to process control variables, a manufacturer can process each batch individually. The operators will be able to adjust the processing cycle to respond to changes that were caused by differences in humidity, variations in starting materials, and limitations in material shelf life. If something goes wrong during processing, a sensor will alert the operator to cancel the run, or adjust the process to compensate for the problems. With continued development, this procedure can become increasingly automated. The result is real-time on-line process control, the ultimate goal in many cases.

1.4 OFF-LINE TECHNIQUES

Though this report deals with on-line process sensors, off-line techniques are the most widely used methods today. These sensors are, and will continue to be, very useful for the evaluation and calibration of on-line methods. They often provide the data for the empirical correlations mentioned above.

Another use for off-line methods is in developing processing cycles and for improving the scientific understanding of the changes that occur during processing. Until recently, the composites industry developed processing cycles based largely on empirical experience with fabrication. Significant amounts of time, effort, and money were expended in "trial and error" testing to generate a cycle for each particular resin and curing agent system. This seldom produces an optimum result, and any switch to newer and potentially better resin systems required starting over again.

In recent years, the use of off-line measurement methods such as viscosity and differential scanning calorimetry (DSC) to augment practical processing knowledge has significantly shortened and improved the development of processing cycles. Although not a substitute for on-line measurements, off-line data can be quite helpful, and so a brief summary of such techniques will be given here.

1.4.1 Viscosity

Viscosity is one of the most important variables in composite processing. A variety of viscometers can be used to measure the change in steady-flow viscosity as a function of time at a fixed temperature or for a given temperature history. Steady flow viscosity is useful, however, only prior to gelation (or solidification), and even near gelation, it is doubtful that steady flow is achieved. Consequently, in this range, the numbers represent only a lower bound on viscosity. Thermosets usually begin with molecular weights sufficiently low that the viscosity is not dependent on shear rate in the flow rate range of interest. As the material approaches gelation, however, shear rate effects can become a problem. Thermoplastics may also exhibit shear rate effects. This complicates the interpretation of the data. Nevertheless, large changes in viscosity can clearly be identified.

Another useful experiment is small amplitude oscillation which measures a dynamic viscosity. Such tests can follow changes throughout the entire processing cycle. They also provide information on elastic properties. Only a single frequency is measured, however, so care must be exercised in interpreting the data for process cycle development.

An important consideration for viscosity measurements, and in fact for all off-line methods, is that the laboratory results can differ from the behavior observed in production. Differences in factors such as thermal mass and humidity are certainly important in this regard. Another major difference can be the absence of fibers in some laboratory test samples. It is well known that characteristics like reaction rates can change in the presence of surfaces, and there is a very large amount of fiber surface area in a composite. Fibers can cause other complications as well. For example, some viscosity experiments have been performed with fibers present, but the flow fields become quite complex, and the interpretation of results is questionable.

Despite all of these complications, viscosity tests remain a very useful off-line tool. The major reason is that the changes during processing are very large, and consequently, even approximate results are quite helpful.

1.4.2 Differential Scanning Calorimetry

A second parameter that is of interest for process control, at least for thermosets, is the degree of cure. Differential scanning calorimetry (DSC) can be used to characterize the heat evolved by the chemical reactions during cure. In many systems, it is not possible to obtain reaction of all possible reaction sites, so the degree of cure is defined relative to the maximum level of cure that can be obtained under some defined set of conditions. DSC data can then be used to follow the degree of cure relative to this maximum. A detailed description of the required procedure has been published in the literature (Chang, 1988B). The sample size for DSC tests is normally quite small so care must be exercised to obtain a typical specimen. Fibers can be present in the sample, but this reduces the measured changes in proportion to the volume fraction of fibers present. For those reactions where the total heat generated is small, this can significantly limit accuracy.

DSC has also been used to study crystallinity and crystallization kinetics in partially crystalline thermoplastics (Chang, 1988). Crystallinity plays a major role in determining the properties of thermoplastic resins, and thus control of crystallinity is important.

Relating the results of DSC tests to behavior in actual processing is a challenge since the size scale is so different. With the use of models, however, many of the factors such as thermal mass can be taken into account.

1.4.3 Mechanical Testing Techniques

Another measurement type that has been used extensively for off-line studies is mechanical characterization. The most common experiment involves impregnating a fiber braid (Gillham, 1977, 1986, and 1988) or cloth strip (Goldfarb, 1979; and Lee, 1982) with resin and measuring the elastic and loss properties of this system in free or forced oscillation. If chosen properly, the properties of the uncoated braid or cloth do not change as a function of time and temperature, so any variations in behavior for the system when these variables are varied, can be attributed to the resin. A disadvantage of the technique is that the absolute values of the mechanical properties for the resin cannot be determined because the geometry is so complex. For processing, however, the relative values and changes with time and temperature often provide the most useful information.

One example of the scientific insight that can be obtained with this approach is the time-temperature-transformation (TTT) diagram (Enns, 1982). A TTT diagram is constructed by observing the cure behavior of a resin at various temperatures and noting the cure times when there are changes of state, namely, gelation and vitrification. The cure time corresponding to these changes is then plotted in a temperature vs. cure time coordinate system. If all of the gelation points and all of the vitrification points are joined to form two contours, the result is a graph which indicates the regions of temperature and time where the material is in a given state. This information is extremely useful for understanding the cure behavior of a material and for developing appropriate processing cycles.

A number of other mechanical property tests have been used to study cure in thermosets. Examples include strain impulse technique (Ferris, 1984), resonance vibration tests (Jang, 1987), squeeze flow tests (Tungare, 1987), and dynamic mechanical tests of various types (Chambon, 1987; Gotro, 1987; Scott, 1987; Senich, 1979; Zukas, 1984). All provide useful information.

1.4.4 Other Techniques

Another major off-line technique is spectroscopy. This measurement method is particularly useful for thermosets because it provides a tool that can directly follow specific cure chemistries. Like DSC, spectroscopy techniques can provide kinetics data, but it also provides a great deal more information, so the primary cure reaction and other side reactions can be identified and analyzed. A number of geometries and procedures have been used with good success (Moacanin, 1982; Young, 1984).

A variety of other methods have been discussed in the literature. They include thermally stimulated discharge measurements (Affrossman, 1985), chemiluminescence (George, 1985), pyrolysis-gas chromatography (Nakagawa, 1988), and mass spectroscopy (Smith, 1984). Each provides some insight into the changes that occur during processing.

1.5 MAJOR INDUSTRY AND GOVERNMENT PROGRAMS

The final topic to be mentioned in the introduction concerns major industry and government programs investigating real-time process control (Abrams, 1987; Kau, 1987; Roberts, 1987). There are many such programs in industry, particularly aerospace but other sectors as well. A few examples include: Alcoa, Boeing, Ford, General Dynamics, General Electric, IBM, Lockheed, McDonnell Douglas, Rockwell, Sikorsky, United Technologies, and Westinghouse. A number of government agencies also have major in-house and/or contract programs on this topic. There are major thrusts by the Air Force, NASA, and the National Institute of Standards and Technology. NSF, DARPA, the Office of Naval Research, the Army Research Office, and the Army's Materials Technology Laboratory also have at least some projects on composite process control. Through contracts and subcontracts, many universities are involved in these programs as well.

The major thrust in many of these programs is to implement the existing sensor technology into on-line process control. As a result, there is a heavy emphasis on process model development, and evaluation of fabricated parts. Where these programs involve specific subprojects that deal with the science and technology of sensors, the subproject is covered in the subsequent sections of this report under the appropriate measurement technology. The more general aspects of the large programs, however, is beyond the scope of this report and will not be covered in detail.

It is worth noting, however, that these programs provide a key technology, i.e. control models. These models take the sensor data and explicitly or implicitly relate this information to material properties, such as viscosity or degree of cure, which define the state of the material at any point in the processing. The models then predict the best ways to change the processing parameters throughout the remainder of the processing cycle in order to reach the desired end point. A discussion of current approaches to this problem including those based on an expert systems programming is contained in the Chapter on Process Control and Modeling.

The important point to be made here is that significantly improved results can be obtained if more and better information is provided to the model by the sensors. It does not make sense to handicap an elaborate and sophisticated modeling system with poor sensor data. The development and implementation of process monitoring sensors are therefore as critical to the goal of on-line process control as is modeling. Sensor research and development, however, has generally not received the emphasis they deserve, and this reinforces the need for and importance of the topic in this report.

1.6 **REFERENCES**

Abrams, F. L., "Expert System Process Controller for Advanced Composites," p. 117 in Automotive Challenges and Plastics Response: Automotive Plastics," (SPE, 1987).

Affrossman, S., and Pethrich, R. A., "Thermally Stimulated Discharge Measurements as a Nondestructive Test Method for the Characterization of Cure in Thermosetting Resins - Epoxy Systems," p. 329 in Proc. Adhesives, Sealants and Encapsulants Conference, Vol. 2, Stress Analysis. Test Methods, (Plastics and Rubber Inst., London, 1985).

Chambon, F., and Winter, H., "Linear Viscoelasticity at the Gel Point of a Crosslinking PDMS with Imbalanced Stoichiometry," J. Rheol., 31, 683 (1987).

Chang, S. S., "Multiple Melting Peaks of Poly(Aryl Ether Ether Ketone)," Polym. Comm., 29, 138 (1988A).

Chang, S. S., "Heat of Reaction and Curing of Epoxy Resins," J. Thermal Anal., 34, 135 (1988B).

Enns, J. B., and Gillham, J. K., "The Time-Temperature-Transformation (TTT) Diagram: Modeling the Cure Behavior of Thermosets, Org. Coatings & Plastics Prep., 47, 575 (1982).

Ferris, R. J., "Impulse Approach to Linear Viscoelasticity," J. Rheol., 28, 347 (1984).

George, G. A., and Schweinsberg, "Simple Chemiluminescence Method for Monitoring Viscosity Changes during the Cure of Epoxy Resins," p. 374 in Proc. Inter. Symp. on Characterization and Analysis of Polymers, (Royal Australian Chem. Inst., Australia, 1985).

Gillham, J. K., "Polymer Characterization using an Automated Torsion Pendulum: Formation and Properties of Network Polymeric Materials," Org. Coatings and Plastics Prep., 38, 221 (1977).

Gillham, J. K., "Cure and Properties of Thermosetting Polymers," p. 1 in Structural Adhesives: Developments in Resins and Primers," Ed. Kinloch, A. J., (Elsevier, 1986).

Gillham, J. K., and Enns, J. B., "Torsional Braid Analysis (TBA): A Technique for Characterizing the Cure and Properties of Thermosetting Systems," Polym. Mat. Sci. Eng. Prep., 59, 851 (1988).

Goldfarb, I. J., and Lee, C. Y. C., "Torsional Impregnated Cloth Analysis (TICA): Thermal Mechanical Behavior of Partially Cured Epoxy Resins," Org. Coatings and Plastics Prep., 41, 393 (1979).

Gotro, J., and Yandrasits, M., "Cure Monitoring using Dielectric and Dynamic Mechanical Analysis," p. 1039 in Proc. 45th ANTEC Conf., (SPE, Brookfield, 1987).

Jang, B. Z., Shelby, D., Hsieh, H. B., and Lin, T. L., "Vibration-based Nondestructive Evaluation (NDE) Technique for Cure Monitoring and Damage Assessment in Composites," p. 265 in Proc. 19th International SAMPE Technical Conf., (SAMPE, Covina, 1987).

Kau, W. J., and Matson, M. W., and Russell, J. P., "Automated Fabrication of Graphite-Epoxy Composites," p. 1152 in Proc. 32nd SAMPE Symposium, (SAMPE, Covina, 1987).

Lee, C., "Dynamic Mechanical Properties of an Acetylene-Terminated Quinoxaline System under Air/Nitrogen Cure," J. Appl. Polym. Sci., 27, 407 (1982).

Moacanin, J., Cizmecioglu, M., Tsay, F., and Gupta, A., "Spectroscopic Monitoring of Chemistry and Chain Mobility in the TGDDM-DDS System during Cure," Org. Coatings and Plastics Prep., 47, 587 (1982).

Nakagawa, H., Wakatsuka, S. Tsuge, S. and Koyama, T., "Studies on Curing Process of Epoxy Resins by High-Resolution Pyrolysis-Gas Chromatography," Polym. J., 20(1), 9 (1988).

Roberts, R. W., "Automated Composites Cure Control Implementation, A Cure Modeling Approach to Automation," SAMPE J., Sept./Oct., 28 (1987).

Scott, K. W., "Application of the Vibrating Needle Curemeter to Liquid Polymer Cures," Europ. Adhes. Sealants, 3, 28 (1987).

Senich, G. A., MacKnight, W. J., and Schneider, N. S., "Dynamic Mechanical Study of the Curing Reaction of two Epoxy Resins," Polym. Eng. Sci., 19, 313 (1979).

Smith, A. C., "Application of Mass Spectroscopy Technique to Autoclave Curing of Materials," p 1083 in Review of Progress in Quantitative NDE, Vol. 3B, Ed. Thompson, D. O., and Chimeni, D. E., (Plenum Press, New York, 1984).

Tungare, A. V., Martin, G. C., and Gotro, J. T., "Rheological Analysis of the Cure Behavior of Epoxy Resins,", p. 330 in Proc. 45th ANTEC Conf., (SPE, Brookfield, 1987).

Young, P. R., and Chang, A. C., "Prepreg Cure Monitoring using Diffuse Reflectance-FTIR," SAMPE Tech. Conf., 16, 136 (1984).

Zukas, W. X., Schneider, N. S., and MacKnight, W. J., "Dielectric and Dynamic Mechanical Monitoring of Epoxy Resin Cure," Polym. Prep., 25, 205 (1984).

ELECTRICAL MEASUREMENTS

Fred Mopsik

2.1 SUMMARY

Electrical measurements of capacitance and conductance, or equivalently dielectric constant and loss, has many advantages for cure monitoring. The measurable parameters can be directly related to molecular structure and mobilities. The actual measurement techniques have had a long history of development as they have intrinsic interest in many areas outside cure monitoring, both in electrical and electronic engineering and in the study of molecular properties. The actual sensor can be quite flexible, as well, since all that is necessary is for the resin to be placed in an electric field maintained between two separated metal electrodes.

Much work has already been done to implement the use of electrical measurements for cure monitoring. Many studies have been made of curing systems showing large, well defined changes in conductance during cure with changes being observable even after the resin is nominally cured. The initial response has been shown to be due to ionic conductance with relaxation processes associated with the resin dipoles becoming observable at audio frequencies at the end of the cure.

In addition to the resin studies, several commercial systems specifically targeted for cure monitoring have appeared on the market. They include both parallel plate geometry as well as comb electrodes that depend on fringing fields. Since the measurement requires only the determination of a conductance and a capacitance, however, many designs are possible.

The main problems that still have to be addressed include sensor designs that are compatible with the finished part. Since the connection with bulk mechanical properties is not direct, calibration is required where this is the primary concern. Optimal measurement frequency regimes still have to be established from estimated rates of change for the cure process. Also, the connections to the sensor and the general measuring system must be made compatible with the production environment, both in terms of electrical noise and length of leads. Finally, while sensor materials, especially the electrode material, must be carefully chosen, for the purposes of cure monitoring this last point is not expected to be a major problem.

2.2 INTRODUCTION

Dielectric constant and loss are known to be material parameters that are sensitive to the state of a material. They can change over a wide span of values and, from their very nature, have the potential for direct and simple incorporation with electronic instrumentation.

Furthermore, since these are frequency dependent properties, time scales can be conveniently chosen.

The main complications from applying electrical measurements arise from the general temperature dependence of activated constants, inherent long range interactions of electric fields and the possible interaction with the chemistry of the system. The first complication, which is also present with other material parameters such as viscosity and viscoelastic relaxation, may be either avoided by suitable data reduction or possibly be used to provide extra information. The last two, which are often manifested by electrode dependant behavior, anomalously large parameter values, and sensitivity to both external surroundings and the presence of nearby conductors, are the main problems that have to be overcome in the application of electrical measurements to cure monitoring.

2.3 **BASIC THEORY**

2.3.1 Static Fields

The use of electrical measurements for cure monitoring arises from the definition of the dielectric constant, ϵ. For a pair of conductors in a vacuum with a charge Q transferred between them, a capacitance, C_g, can be defined as

$$C_g = Q/V$$

where V is the potential needed to produce the charge transfer. If a medium completely replaces the vacuum, then the capacitance and entire field pattern will be scaled by a dielectric constant ϵ, such that

$$\epsilon = C/C_g \tag{2.1}$$

For a constant field, ϵ must always be greater than one (Landau, 1960).

For a constant charge Q, this means that the field between the conductors is reduced by the same ratio, ϵ. This reduction in field can then be associated with another field, the polarization, **P**, which can be shown to have units of dipole moment/unit volume(Landau, 1960). It is the association of the polarization field, **P**, with molecular properties that provides the basis for much of the application of dielectric measurements to cure monitoring.

For normal organic materials at microwave frequencies and below, there are two main sources that contribute to the polarization **P**. One source that is always present is the induced polarization from distortions of the molecules in the presence of an applied electric field. The distortion produces a dipole moment proportional to the field at the molecule, **F**, with a constant of proportionality, α. This moment requires no reorientation of the molecule and occurs on time scales that correspond to frequencies in the infrared or higher. For most organic materials that have only polarizability contributions to ϵ, ϵ is approximately equal to 2 and varies mainly with the density. To a good level of accuracy, the relation between α and ϵ is given by the Clausius-Mossotti equation

$$\frac{\epsilon - 1}{\epsilon + 2} V = N\alpha \qquad (2.2)$$

where V is the molar volume, and N is Avogadro's number.

For most molecules, there is another contribution to **P**. Molecular asymmetries lead to electronic asymmetries and, as a result, the molecule has a permanent dipole moment $\boldsymbol{\mu}$. If the molecule can reorient with the field at times faster than the field is changing, then, at equilibrium, the molecular dipoles will have an average orientation that is not random but parallel to the applied field. This orientation leads to a net polarization and contributes to ϵ. Typical values for μ can lead to values of ϵ much higher than 2 (Froehlich, 1949; Boetcher, 1950). If bond rotations allow, the individual sections can respond on time scales representative of those smaller sections rather than the molecule as a whole (Cole, 1952).

At equilibrium, with respect to cure monitoring, perhaps the most relevant development is the Froehlich-Kirkwood-Onsager equation

$$\epsilon - \epsilon_{\infty} = \frac{3\epsilon}{2\epsilon + \epsilon_{\infty}} \left[\frac{\epsilon_{\infty} + 2}{3}\right]^2 \frac{4\pi N\mu^2}{3kT} g \qquad (2.3)$$

In this equation ϵ is the equilibrium dielectric constant, ϵ_{∞} is the limiting high frequency value, μ is the molecular dipole moment as measured in the gas phase, and g is the correlation factor between any given dipole μ_i and its neighbors $\mu_{j,}$ $\Sigma_j \{<\mu_i \cdot \mu_j>/<\mu_i \cdot \mu_i>\}$, where < > represents the average over all molecules and all allowed orientations. This correlation factor measures the average orientation of the neighboring dipoles relative to any reference dipole. For random, independent orientations, $g = 1$. For water molecules with hydrogen bonds between neighboring oxygen and hydrogen atoms and free rotation about the bonds, $g = 4$. For most materials with large values of g and μ, the maximum value for ϵ is several hundred. If $g \approx 1$, then for any reasonable value of μ, ϵ is below 100.

2.3.2 Dynamic Fields

It is the requirement for reorientation that leads to the main applications of dielectrics for cure monitoring. When the resin components have not yet reacted and formed a network, then the molecules are mobile and can reorient rapidly. As the cure progresses, mobility is reduced and the time required for reorientation is increased. If the reduction of mobility is reduced greatly enough, then the dipoles cannot respond to the field at all, even if they are present. In this case, only the polarizability terms can contribute.

While molecular response is most easily modeled in the time domain, the results are most easily seen experimentally in the frequency domain. Fortunately the connection is quite straight-forward. If the field is suddenly increased by a unit amount, then the molecular dipoles will reach equilibrium with a function $\phi(t/\tau)$, where τ is a scaling parameter that sets the time scale for ϕ. For simple molecular models, ϕ can be an exponential function of time. For most materials, especially polymers, ϕ can be represented as a integral sum of exponentials over a wide range of τ. For all cases, the frequency response of ϵ must be represented as a complex quantity ϵ^* and can be related to the Laplace transform of the time derivative of ϕ,

$$\epsilon^* - \epsilon_\infty = (\epsilon_s - \epsilon_\infty) \int_0^\infty e^{-st} (d\phi/dt) dt \tag{2.4}$$

where ϵ_s is the limiting low frequency dielectric constant, ϵ_∞ is the limiting high frequency value and s is the complex valued transformation variable.

In the above equation, the complex variable s can be replaced with the imaginary angular frequency $i\omega$ if the integral is taken in the limit of the real part of s approaching zero from positive values. When this is done, the imaginary part of ϵ^*, ϵ'', which corresponds to dielectric loss, has a maximum at an inverse frequency corresponding to the time scale of ϕ and the real part of ϵ^*, ϵ', varies from a low value at high frequencies to a high value at low frequencies centered about the maximum in ϵ''.

Two observations must be made about the above development. One is that to be strictly correct, the molecular function ϕ is properly Φ, the macroscopic polarization relaxation function. However, the difference is not great, especially for most homogeneous substances and can be ignored for this discussion (Glarum, 1960, Cole, 1965, Fatuzzo, 1967). The other is that the above development carries through in the presence of a limiting zero-frequency or DC conductance. When a conductivity term is present, it can be shown that the frequency response is given by

$$\epsilon^* = \epsilon' - i(\epsilon'' + \epsilon_0\sigma/\omega) \tag{2.5}$$

where ϵ_0 is the permeability of free space and σ is the conductivity.

It should be noted that a measurement can determine only ϵ' and the sum of the conductivity term and the dielectric loss. Any separation of this sum must be done on the basis of models. Only if the measurements extend over a very wide range of frequencies can one attempt a separation of relaxation response from the conductivity response. Furthermore, while conductance does not contribute to the dispersion of the real part of ϵ^*, there can be an underlying dispersion so that ϵ' is slowly changing even while ϵ'' has only a measurable $1/\omega$ dependence.

2.4 MEASUREMENT TECHNIQUES

2.4.1 Frequency Domain

The basic theory of frequency domain measurements directly derives from the previous discussion. If one has a material completely filling the space between two conductors or electrodes, then for a given frequency ω, one can measure between the two conductors an equivalent parallel capacitance C_m and conductance G_m with an admittance Y defined as

$$Y = G_m + i\omega\, C_m, \tag{2.6}$$

and then ϵ^* can be defined as

$$\epsilon^* = C_m / C_g - iG_m / \omega C_g, \tag{2.7}$$

where C_g is measured in the absence of any dielectric between the conductors.

For simple geometries, C_g can actually be calculated from electrode geometries. For the case of parallel plates where the electrode area, A, is large compared to the spacing, d, $C_g = \epsilon_0 A/d$. Similar formulas can be derived for other simple systems such as coaxial cylinders. For practical applications C_g often is directly measured. For many other applications, where only relative changes are needed or the reduced loss $\tan\delta = \epsilon''/\epsilon'$ is sufficient, then C_g need not be determined or only estimated to set the experimental scale.

2.4.2 Measurement Circuits

2.4.2.1 Bridges

The classic method for measuring Y at low frequencies is the bridge circuit. The bridge balance can be defined in terms of the admittance Y; the parallel combination of C and G; C and the dissipation factor $\tan\delta$; the series impedance, $Z = 1/Y$; the series combination of C and R; or finally C and $Q = 1/\tan\delta$. Traditional circuits include the Schering, Wheatstone and Maxwell Bridges. Regardless of the balance condition definition, all other conditions are easily obtained by simple transformations.

A refinement on traditional bridge techniques was best implemented with the introduction of the transformer bridge (Cole, 1949). In this system, the two arms of a tightly coupled transformer secondary form the ratio arms of the bridge. The magnetic coupling between the two arms ensures that the voltages at the ends of these arms is equal and opposite. A reference circuit of a parallel capacitance and conductance in the third arm and the unknown in the forth complete the circuit. The detector is connected between the junction of the reference with the unknown and the center tap of the transformer arms which is connected to ground. With this arrangement, only the direct admittance between the transformer arms and the detector is measured and any stray admittances to ground are not. Strays to ground on the detector leads only shunt the detector and do not affect the balance. Admittances on the transformer arms also are ignored as any load imbalance between the arms is canceled by the magnetic coupling between them and hence the applied voltage across both the sample and reference must remain the same. This circuit has been the basis for several commercial bridges with extremely high precision.

The transformer bridge is the prototype for the guarded, three-terminal measurement. Instead of just two reference conductor surfaces, there are now three, one connected to the transformer, one connected to the detector and one connected to ground. At balance, the detector input must be at ground potential. Therefore, no current can flow between the detector and ground. If the low electrode in a parallel plate capacitor is surrounded with a guard ring connected to ground, any leakage currents resulting from the applied voltage on the high electrode must be intercepted by the guard ring and not interfere with the measurement. At low frequencies, which are of great importance in cure monitoring, this can become very important.

Bridges are also the basis for many measuring devices that are commercially produced. There are now many automated instruments that use bridge type measurement systems with direct readout and computer interfaces. They typically have accuracies up to 0.1%. These devices often have only spot frequency coverage. In common with most bridge circuits, this coverage is often limited to the audio frequency range. This limit is inherent in the design as a result of effective impedance levels, saturation effects or residuals that degrade the performance at the frequency range extremes.

2.4.2.2 Other Techniques

Any system that maintains a known voltage on one electrode and approaches ground potential on the other becomes a three-terminal measurement. For use at low frequencies, the Harris bridge (Harris, 1967), employing operational amplifiers for ratio arms as well as that of Berberian and Cole (Berberian, 1969), are good examples of such schemes. They extend the range of usable frequencies below the 100 Hz limit set by transformer coupling. Such bridges are limited only by amplifier stability, sensitivity considerations and, ultimately, by the time it takes to traverse a cycle.

There are also methods that are direct reading rather than dependent on a bridge balance. One is to use a defined potential on one side of the sample and a zero input voltage current detector on the other. Then, if a phase-sensitive detector is used to extract the in- and out-of-phase components of the current passing through the sample, both the capacitance and loss can be computed. This method has been used in a commercial instrument (Schlumberger Solartron). It has also been used specifically for cure monitoring to follow the conductance during cure of epoxy resins. A block diagram is shown in Figure 2.1. The limits for such methods are the time it takes to traverse a single cycle as well as the phase stability of the phase-sensitive detector, which is typically 0.1%.

Still another type is the impedance analyzer. This instrumentation often can cover a wider frequency range than most as it can be made to use transmission line components. These instruments, which can cover wide frequency ranges often up to the microwave region, are automated and again capable of being interfaced with computers. Their main limitation is that they are most accurate where the sample impedance is near that of a typical transmission line, which is the order of 100 ohms. Especially near the end of the cure cycle, where the loss and frequency used are low, this condition may be hard to satisfy with reasonable sized samples.

There are many other schemes that have been used to measure dielectric constant and loss, but they typically work better at high frequencies. As will be discussed later, better sensitivity to cure is often found at lower frequencies and so these methods will not be discussed in this review.

2.4.3 Time Domain

As was mentioned previously, there is a close connection between the response of a dielectric to constant frequency and the response of a dielectric to the application of a step voltage. The connection is through the Laplace transform. While a detailed derivation will not be given, the only requirements are that the transform conditions are met, namely that

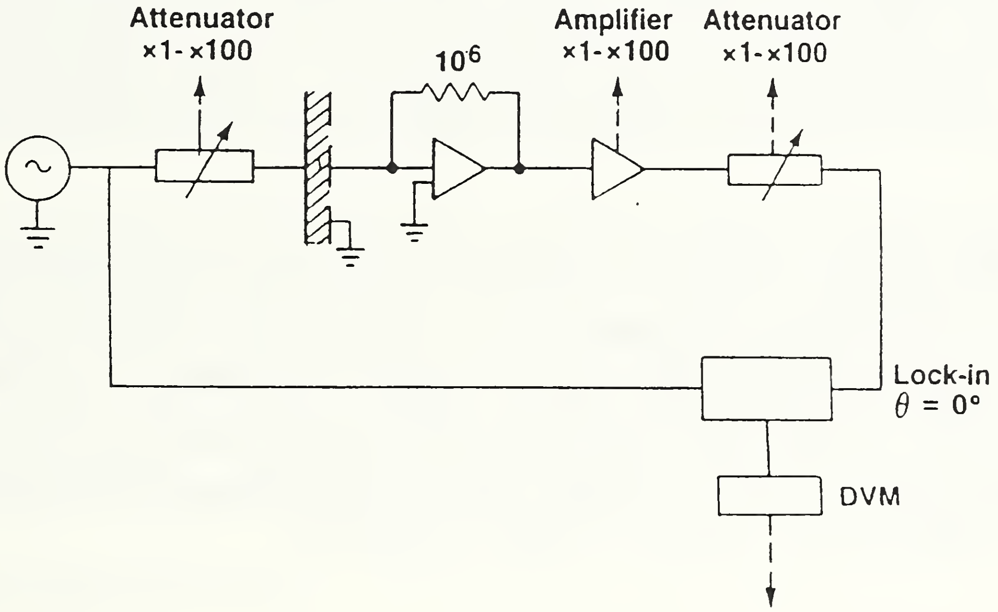

Figure 2.1 The three-terminal AC conductance system. The arrows indicate connection to the computer system. The low impedance generator and zero input voltage current detector prevent shunt admittances to ground on the sample leads from being measured.

there is no prior excitation in the observable past, and that a dielectric constant is meaningful. This knowledge has existed for a long time (Cole, 1942) and several attempts had been made to implement the scheme (Davidson, 1951). Until recently, however, implementation in a quantitative sense was not possible. The first relatively modern attempt at a true time-domain instrument was made by Hyde (Hyde, 1970). This used digital logic as well as non-linear time sampling. However, this instrumentation still lacked accuracy and sensitivity to small losses. A similar attempt by Johnson *et al.* (Johnson, 1975) a little later had similar limitations. Both developments did show, nevertheless, that the method had great potential and was extremely effective in covering a wide frequency range at audio and subaudio frequencies.

The assumed limitations of time-domain instrumentation were shown to be not valid by the Time-Domain Spectrometer developed by F. I. Mopsik (Mopsik, 1984). This instrument has high sensitivity ($\tan \delta \geq 10^{-6}$) and high accuracy (0.05% of full scale). With the development of modern integrated circuits and computer circuits, it was able to overcome earlier deficiencies. This applies not only to the acquisition of the time-domain signal, but also to the computation of the numerical transform so that the transformation preserved the original accuracy of the measured signal. A block diagram is shown in Figure 2.2.

This instrument is a true three-terminal device. It employs a precision low output-impedance generator at the high electrode and a zero input-voltage charge detector at the low electrode. It can measure the frequency spectrum from 10 kHz down to frequencies as low as 10^{-4} Hz for a voltage step of 3000 sec duration. This is only one-third of a cycle for the lowest frequency. This relation is maintained for shorter measurement times so that it takes only 30 sec to cover the six decades from 10 kHz to 0.01 Hz. It is this wide frequency range that gives time-domain measurements their great advantage over frequency-domain measurements.

The main limitation on time-domain measurements is the rapidity with which they can be repeated. The transform assumes that there is no prior excitation. In practice, this limit is met by a delay of five times the measurement time. More practical limitations arise from very high conductances which can affect the instrumentation. Only just so much charge can be transferred before a charge amplifier saturates. Offsets in the amplifiers can create large drifts. Furthermore, until now, the computation of the transform took enough time to act as a limit to the repetition rate. With more recent circuits and computers, it is believed that even these limitations can be relaxed by an order of magnitude.

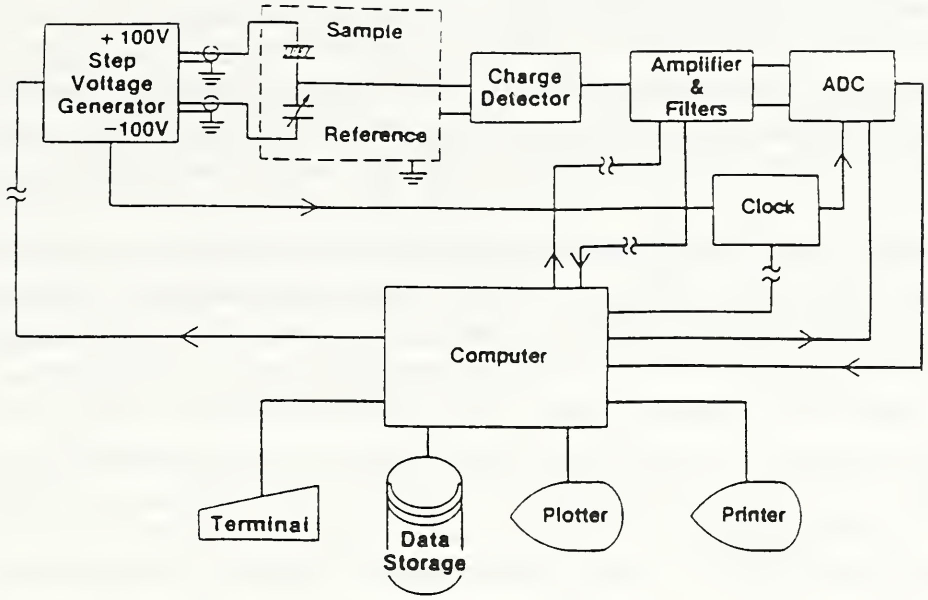

Figure 2.2 Block Diagram of the Dieclectric Spectrometer. The breaks in the data lines represent optical isolators with the directions shown by arrows.

There has been some controversy as just what is measured in the time domain. While the derivation has been made in terms of a pure sample, if one recasts the derivation of the transform relation from dielectrics to ordinary electrical circuits, it will be seen that the only requirement is a defined admittance connected between the high and low terminals. This is the same requirement for all frequency-domain measurements.

Another is the clear requirement that the sample not change significantly over the course of the measurement. Any drift in a capacitance will be transformed into an equivalent loss. While it is commonly assumed that a bridge can be balanced dynamically to correct for a drifting sample, it can be demonstrated that this is not true. In particular, if an ideal phase-detector is used so that both phases can be tracked at the same time, it can be demonstrated that the bridge balance will give exactly the same value of admittance as that found from the transform. These last two concerns, which affect all electrical measurements, will be shown later to affect the use of electrical measurements for cure monitoring.

2.4.4 Sample Holders (Sensors)

As indicated earlier, dielectric constant and loss are defined in terms of the scaling of the electric field when a material completely replaces the vacuum between a pair of conductors. The better this condition is approached, the more accurate and reliable the measurement becomes. Note that this has included any region of space where any significant electrical field exists between the conductors. Since shape plays no role in this consideration, this must include the leads from the electrodes to the measuring circuit.

If the measurement is defined as a three-terminal set, then the sample need only occupy all space in which there are field lines between the electrodes. Since any field line to the third terminal is not part of the measuring circuit, the dielectric can safely end where only such components of the field are present. For ordinary liquids, this is easily accomplished and absolute measurements of ϵ are possible (ASTM D924). Since ϵ-1 for air $\approx 5 \times 10^{-4}$, the ratio of the filled cell to the empty cell suffices to good accuracy.

Usually such liquid cells form completely enclosed systems in which the container becomes the guard as well as acting as a shield to keep out interference. For solids, the resulting complex shapes are not suitable. The most common design for solids is the guarded parallel plate construction in which on one side there is a large high electrode and on the other a smaller low electrode with a guard ring surrounding it separated by a small gap. If the guard gap is small enough, then the field lines remain essentially parallel between the high and low electrodes. Then the area becomes well defined with the boundary near the center of the guard gap. If the thickness is known, the capacitance becomes determined (Lauritzen, 1964). For an ordinary solid in which the electrodes are solid pieces of metal, the main error is the inevitable air gap between the specimen and the electrodes from surface roughness. This limitation can be overcome by the two fluid technique (ASTM D150) or by depositing electrodes on the solid.

Another problem with solids is that, since the solid can not be easily deformed, there is almost always an interface in a region with significant field. For some materials, including epoxies, there can be a layer at a surface with different properties than the bulk material. Usually such layers tend to be more conductive due to component exclusion and contamination. This conductance can become dominant as the observational frequency becomes lower. If there is an adherent guard ring completely surrounding one of the electrodes and the material in the gap is like the bulk sample, then leakage currents will not affect the measurement. For cure monitoring in epoxy resin systems, where the use of low frequencies can be important, leakage effects must be always be thought of. Possible configurations are shown in Figure 2.3.

The last consideration is the presence of an inhomogeneous sample. A common cause of such layers is from the electrochemical reactions that can take place at the electrodes in the presence of ionic conductivity. If the electrodes do not form reversible half cells with the ions present, then there can be a charge build-up at the electrode and most of the applied potential can drop across the blocking layer. Since this layer is thin and can accommodate a large amount of charge, this results in a very large apparent dielectric constant. The extent of the problem increases with the amount of ions present and the lower the frequency since the charge layer has time to form. It also depends very strongly on exactly which ions are present and the exact nature of the electrode material. Some materials such as platinum are traditionally used to minimize the problem while others, such as aluminum and tantalum form such layers so easily that they actually are used as capacitors. While electrode polarization effects do decline with frequency, the frequency dependence is not understood

(Johnson, 1951) and can become significant in the frequency range needed. Typically, polarization affects the measurement of capacitance more strongly than the conductance.

Often, in the presence of large sample conductance, to keep the system parameters within range of what is measurable an insulating layer of known thickness is placed between the sample and one or both electrodes. This is also done to try to avoid the electrochemical problems just discussed. Unfortunately, the applied field is then mainly across the blocking layer and sensitivity to the desired material parameters is rapidly lost. Also the ions present commonly seem to affect the blocking layer so that its properties are modified. In such cases, computing the desired values can be misleading. Also, composite layers can vitiate guarding schemes and lead to other interface problems.

As will be discussed later, epoxy resin systems undergoing cure are the kind of system where interface and surface phenomena must be accounted for. This is a general feature of all electrical measurements where there can be equipotential surfaces. From Coulomb's Law, the long range nature of electric forces leads to Gauss' Theorem, in which the electric field in the interior of a body is completely determined by the surface charges. Any change in the surface conditions can then lead to very large changes in the apparent behavior of the material.

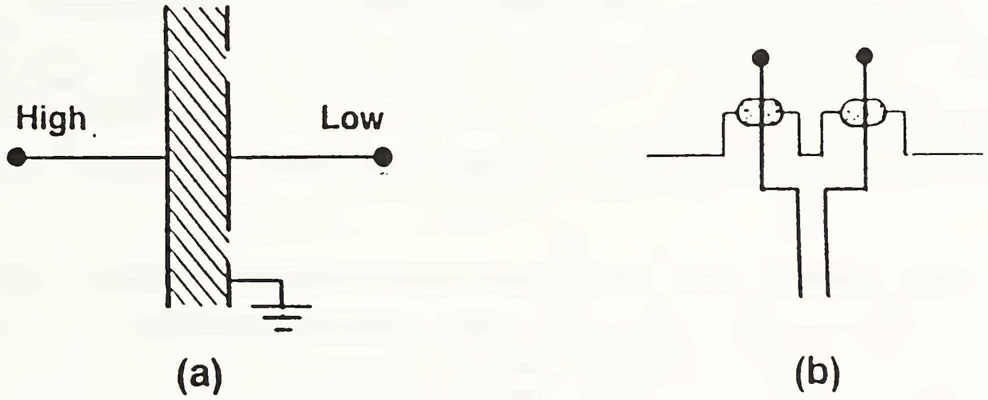

Figure 2.3 (a) A typical guarded electrode configuration. The guard, surrounding the low electrode at the right, along with the shields on the leads connecting the measuring electrode is connected to ground and is not in the measuring circuit. (b) An equivalent electrode configuration to (a). The electrode penetrates a shielded container with the feed-through insulation recessed. The container is grounded and acts as the guard.

2.5 **CURE MONITORING**

2.5.1 Relaxation Effects

The starting materials for epoxy resins, epoxides and curing agents such as acid anhydrides and amines are relatively small molecules with large dipole moments associated with the active parts of the molecules. If the starting monomers are in the liquid state, then the molecules have no preferred orientation and the dipoles can achieve equilibrium with an applied electric field on time scales characteristic of molecular reorientation times. For low viscosity liquids these times correspond to frequencies in the microwave or high radio frequency part of the spectrum. The change in relaxation time with temperature correlates well with the change in viscosity (Denney, 1959). The size of the moving entities is approximately the same size for both phenomena as so this relation is expected to be present.

This connection, however, is not exact. The original theoretical treatment by P. Debye (Debye, 1929), aside from problems from an incorrect internal field, associated an exponential time behavior with rotational diffusion and the Stokes-Einstein law to derive relaxation times. These times were shown quickly to be often too long and so a "microscopic viscosity" was introduced. This concept has proven hard to maintain in a consistent manner and is not used very often to explain relaxation behavior.

Another problem with this model is the lack of agreement with an exponential decay even in liquids of small molecules (Cole, 1941, Davidson, 1950). The observed width of the loss peak as a function of frequency is often much broader than that predicted by an exponential and cannot be explained by rotation of part of the dipole around a molecular bond. While this type of motion can give rise to broadening of the loss or even another loss peak, it cannot explain most behavior. As the molecules get longer, such phenomena can start to come into play (Mopsik, 1966), but nonexponential behavior is inherent to the process.

For the cure of epoxies, as the cure progresses, the important consideration is that, as the resin cross-links, the relaxation times will increase in a manner similar to viscosity. For relaxation to occur there must be molecular rearrangements just as they are required for viscosity. Since dipolar relaxation is a rotational motion while viscosity is a displacement motion, while the trends must be similar, there can easily be differences. This is best illustrated by the presence of rotator phases (Smythe, 1955) or ferroelectric polymers such as polyvinylidene fluoride that switch in the crystalline state (Bur, 1986) as extreme cases where reorientation can take place without any corresponding translation motion.

During cure, since a network is being formed, these extreme cases are not expected to occur. The main relaxation loss peak should move to lower and lower frequencies as the cure progresses so that in the cured state motion is frozen out and most of the dipole moment cannot contribute to ϵ. If one held the frequency constant one would at first observe a high value for ϵ' and a low value for ϵ''. As the cure progressed and the molecular relaxation time corresponded to the measuring frequency then ϵ' would be decreasing as the cure progressed and ϵ'' would pass through a maximum (Mopsik, 1989). At the end of the cure, ϵ' would have a low value and the loss would again be low. Just as important is the fact that any change in the dipole moment from possible curing reactions is small. This can be best seen by comparing the gas phase values of μ for ethylene oxide and ether and ethanol (Nelson, 1967). There may be bigger differences in the dipole-dipole correlation factor, g, but there is no empirical way to find out. Given the normal spacing of functional groups in the monomers, however, great changes would not be expected.

From a great amount of work that has been done on polymeric systems (McCrum, 1967), it is very well established that dielectric relaxation parallels mechanical relaxations such as that in shear or tension. While there may be relatively small shifts in the frequency of maximum loss and differences in the magnitude of the dispersion, for a given material as a function of temperature, mechanical and dielectric relaxations change in a very similar manner. Either can be used to monitor changes in the other to a good approximation.

It must not be assumed that all molecular motion has been lost after cure. Epoxy resins have a value for ϵ of 3.5 at audio frequencies while this value must decline to approximately 2 at high enough frequencies where only polarizability terms can contribute. Also, in this laboratory, relaxations at very low frequencies ($\approx$ 0.0001 Hz) have been found to slowly move to lower frequencies for long periods of time after cure when the material is a brittle solid. This can occur as dipole moments are localized, for groups such as amino or ether or epoxide, about molecular bonds. Relatively small scale motions can reorient some of the dipole even if it is attached to a rigid network.

2.5.2 Conductance Effects

Not only dipolar relaxation but also ionic conductivity can contribute to the measured loss in a dielectric measurement. As was indicated previously, a pure conductance contributes a term proportional to $1/\omega$. At low frequencies, a conductivity term can easily dominate any contribution for dipolar relaxation. This is a very important consideration since the starting materials used in resin systems tend to be conductive. This conductivity is not only from impurities that can be dissolved in the polar materials, but also from spontaneous ionization. Amines, for example, are well known sources of ions. Acid anhydrides can form ionizable organic acids and supply H^+ ions. Furthermore, most of the curing reactions are thought to be ionic in nature so that ions can be formed during the course of the curing reaction (May, 1973).

What makes the conductivity contribution even more important, is the fact that to ensure that the mechanical properties are good enough, low frequencies are needed to ensure that there are no relaxations present which would make the resin too rubbery. Thus it is to be expected that at least during a part of the cure, prior to and, in some cases, even during gelation, conductivity will dominate the dielectric response. The conductance of ions is determined by the product of the ionic concentrations and the ionic mobilities, summed over all species present. In turn, ionic mobility is dependent on the solvent and the particular ionic species. To the extent that ionic mobility tracks the fluid viscosity, the conductance of the resin during cure tracks the viscosity of the curing system.

The earliest connection of conductance with viscosity was by Walden (Walden, 1973) who found that the product of viscosity and conductance for a given concentration of ions tends to be a constant. Walden's Rule can be explained by assuming that ions follow a Stokes Law for spheres moving in a viscous medium (Harned, 1958). Walden's Rule has been known from the very beginning to be most accurate in the limit of large ions moving in a fluid of small molecules. As the ions become comparable to the size of the solvent molecules, mobilities becomes larger and deviations occur. Also, again, if ions such as H^+ and OH^- are present in protonic solvents, mobilities are abnormally large. These observations have important consequences for cure monitoring.

While most of the conductance has been claimed to be due to salt (Fava, 1968; Senturia, 1986), this clearly cannot be the case for carefully purified materials that have been measured. What is more important, as the resin gels and forms a solid, is that the ions are much smaller than the cross-link spacing and so the ion mobility must be controlled by motions on a scale much smaller than those required for macroscopic motion. Therefore, as the cure progresses, departures from a strict relation with macroscopic viscosity must occur.

Ultimately the limit to which conductance can be used to follow cure must be set by any finite level of conductivity of the cured resin. The development of the Time-Domain Dielectric Spectrometer has permitted a closer look at this. While for many low loss polymers, no true conductance can be found at temperatures below 100°C, ordinary epoxy composites such as circuit board do. Solids can and do have true conductances since even a solid can permit enough local motion to allow small molecule diffusion. Except in unusual cases, however, this conductance is much smaller than for an equivalent liquid.

If audio or lower frequencies are used, what is seen at first is conductivity induced loss, which will follows the cure time and temperature in a manner similar to the reciprocal of viscosity (see Figures 2.4 and 2.5). As gelation occurs and the network starts to form, the conductance will decrease to some limiting value characteristic for the solid at the observation temperature. If the conductance decreases fast enough, at constant frequency, it is possible, in some systems, to see contributions from dispersion mechanisms moving through the measurement frequency (see Figure 2.5). At final cure, the loss may be controlled by either residual dipolar losses or conductance depending on the experimental parameters. Examples of this behavior are shown in Figures 2.4 and 2.5. For loss spectra at low frequencies, 10^{-3} Hz or below, the contribution from dipolar motion becomes smaller than that due to ionic conductance, and the DC conductivity can actually be estimated. The presence of this conductivity is indicated by the appearance of an upsweep towards the right end of the data in the complex plane plots of Figures 2.6 and 2.7.

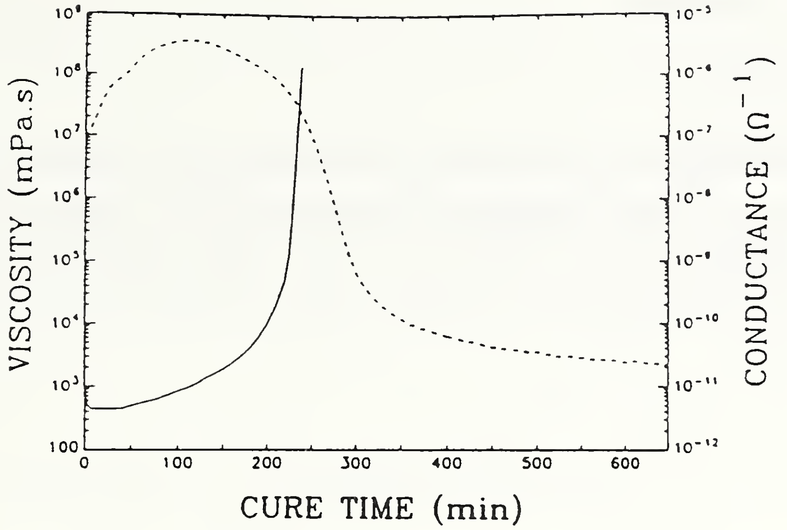

Figure 2.4 The dashed line is the AC conductance vs. time for an epoxy (diglycidyl ether of bisphenol-A) cured with ethyl methyl imidazole at 50°C. The frequency used was 50 Hz. The solid line is shear viscosity taken at low shear rate and terminated at the instrumental limit.

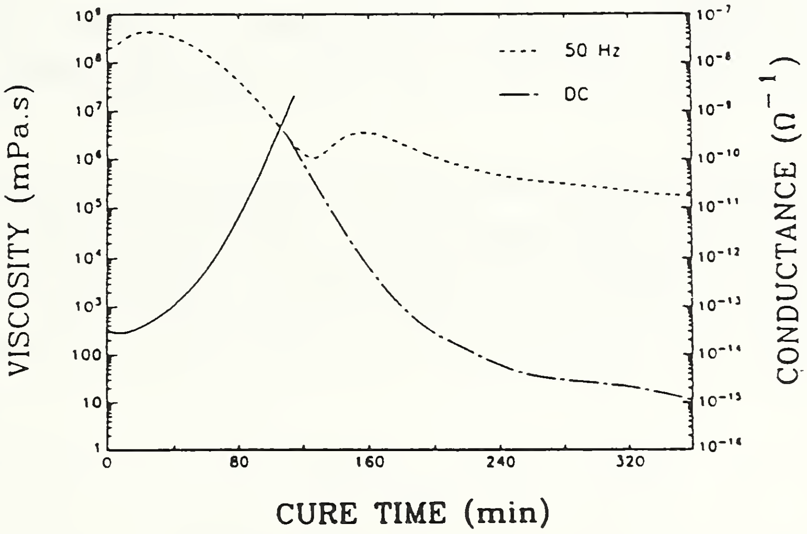

Figure 2.5 The dashed line is AC conductance vs. time for an epoxy (diglycidyl ether of bisphenol-A) cured with bis-(para-aminocyclohexyl)methane at 45°C. The frequency used was 50 Hz. The broken line is the estimated DC conductance obtained by measuring the loss spectrum over a range of frequencies and estimating the DC conductance with plots such as Figure 2.7. The solid curve shows the shear viscosity measured at a low shear rate and terminated at the instrumental limit.

2.6 IMPLEMENTATION

2.6.1 Instrumentation

The instrumentation for performing cure monitoring by dielectric loss is well developed. There are enough commercial instruments on the market, all capable of being interfaced to a computer, so that further work in this area, specifically for cure monitoring, is not needed. The instrumentation of choice will be set more by considerations of the

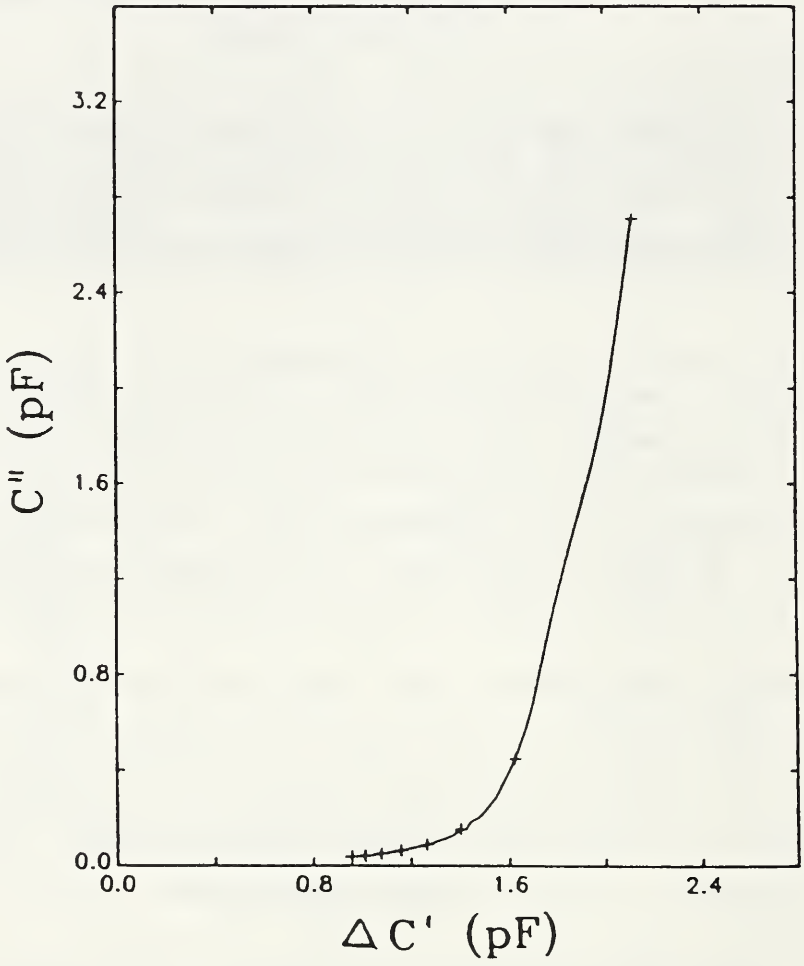

Figure 2.6 The loss spectrum, $C^* = \epsilon^* C_g$, taken after 24 hr. for the sample measured at 50°C in Figure 2.4 plotted in the complex plane. The real axis has been arbitrarily displaced. Frequency decreases from left to right. The plotted points represent the frequency decades from 10^4 to 10^{-3} Hz. The upsweep seen is due to conductance.

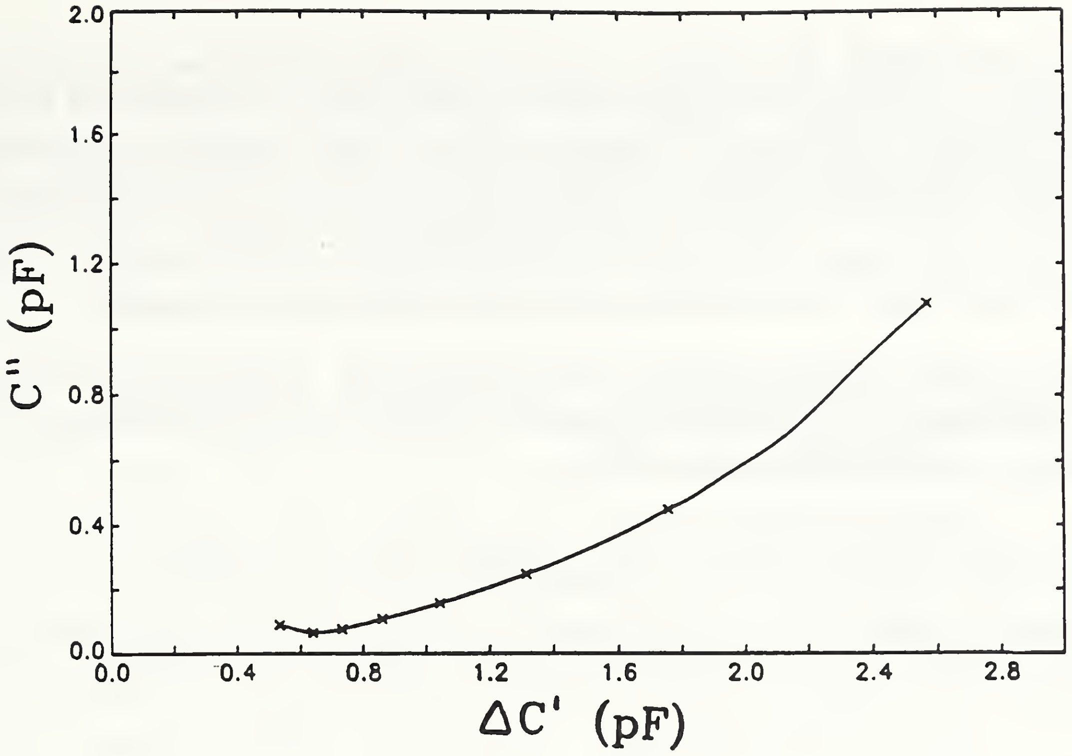

Figure 2.7 The loss spectrum taken at 300 min in the cure shown in Figure 2.5. The frequency decades are shown as the plotted points and decreases left to right from 20^4 to 10^{-1} Hz. The real axis is arbitrarily displaced. The upsweep seen after $\Delta C' = 2.0$ was used to estimate the DC limiting conductance with the aid of 24°C data where results at 50°C were not available.

sampling electrodes, what the material to be monitored is and what the equivalent sampling frequencies have to be rather than availability. This instrumentation could be either frequency or time domain depending on implementation, convenience and needed experimental coverage. In all cases, the system should be chosen to ensure that the extremes in the measurement conditions are well covered for the given system and electrode configuration.

2.6.2 Electrodes (Sensors)

Ultimately, the problem of cure monitoring is the development of a suitable electrode system for performing the measurement. This problem includes defining the measuring path, desired admittance levels, available sample volume, electrode interactions, measurement interferences and interaction with the finished part.

As mentioned earlier, the classic measurement configurations are parallel plates, preferably with guard rings and coaxial cylinders. They have the great advantage of calculable cell constants, enclosed sample space and the potential for high accuracy measurements. For curing systems that adhere to the electrodes, they do not offer the easy possibility of disassembly. For research and quality control applications, they are probably the best choice. At NIST, guarded electrode sets made from circuit board with bare copper, and the leads brought out the rear through plate-through holes, provided an inexpensive, reproducible and artifact-free means to measure cures on the research level (Mopsik, 1984). They have also been used extensively in the past (May, 1976, Dragataki, 1976). While the sample thickness may vary during cure, the resulting error from these changes are small compared to the changes in the electrical properties occurring during the cure.

More recently, alternate schemes have been proposed. One is the comb electrode, originally fabricated on a silicon chip (Sheppard, 1981) and one by Kranbuehl that also uses electrodes from one side (Kranbuehl, 1987A).

The comb electrode essentially uses a fringing field to do sampling from one side. This system has the advantage of only contacting the sample from one side. While it is small, it is still the order of 1 cm across and can cause problems if not removed from the finished part. It does, of course, measure only at the surface. These electrodes normally have blocking layers on them, leading to enhanced electrode polarization effects as manifest by values of ϵ' that are unrealistically large. There is also a dominant interface present at the sample sensor boundary that could lead to misleading results. There are also problems with sensitivity at the extremes of the cure due to the nonlinear response of the circuit (Senturia, 1982). Finally, there is the temperature limits set by the silicon substrate. This last restriction has been removed with passive electrodes, but it is not yet possible to assess the limitations that might be introduced with this system (Micromet, 1989). Another reported problem is a possible separation of the resin from the electrode near the end of cure (Sanjana, 1986b, Bidstrup, 1986) which affects the apparent measured parameters.

Sensors from Micromet and from Kranbuehl have both been used at temperatures approaching 400°C. The sensors used at these temperatures are passive electrode systems and even include the reintroduction of a parallel plate cell from Micromet.

From the development given above, any system of electrodes, of any size and aspect ratio could be used if the connecting end is sufficiently guarded. This could be accomplished by recessing the feed-throughs in a grounded metal structure for a three-terminal measurement. Thin wires suitably spaced could be used. As long as the resin completely fills the space between the wires, the electrode shape is irrelevant. It is probable that no one electrode system will be adequate for every application.

The questions that must be addressed in a practical system is to what extent an electrode set will interfere with the use of a part. If the electrodes remain behind, they may degrade the performance of the part. On the other hand, they may be useful to monitor degradation of the resin over the lifetime of the piece. If they are removed, the removal of the electrodes or just their presence could affect performance. The location of the electrodes may not be sufficiently representative of the bulk to be of much help.

All these concerns are not limited to electrical measurements but must be addressed by any method that employs a localized sensor. These include not only cure monitors but any others that follow variables that need not be uniform. In particular, it should be noted that one of the major problems in temperature control is the establishment of a valid reference point since a thermometer is usually a point sensor.

2.6.3 Relation to Cure

At least as problematic as the development of a proper electrode set is the connection with the cure cycle. As shown by a set of simultaneous measurements of parts of the same batch of sample (Mopsik, 1989), the 50 Hz conductance easily follows the cure as accurately as other techniques such as viscosity (Figure 2.8), ultrasonic attenuation (Figure 2.9), the reaction exotherm as monitored by DSC (Figure 2.10), and even fluorescence spectroscopy (Figure 2.11). While the shape of the curve is not exactly the same, since there is no exact one-to-one correspondence between the measured properties, this should not be surprising. What is more important is that the relation to the stage of cure is clear and easy to follow.

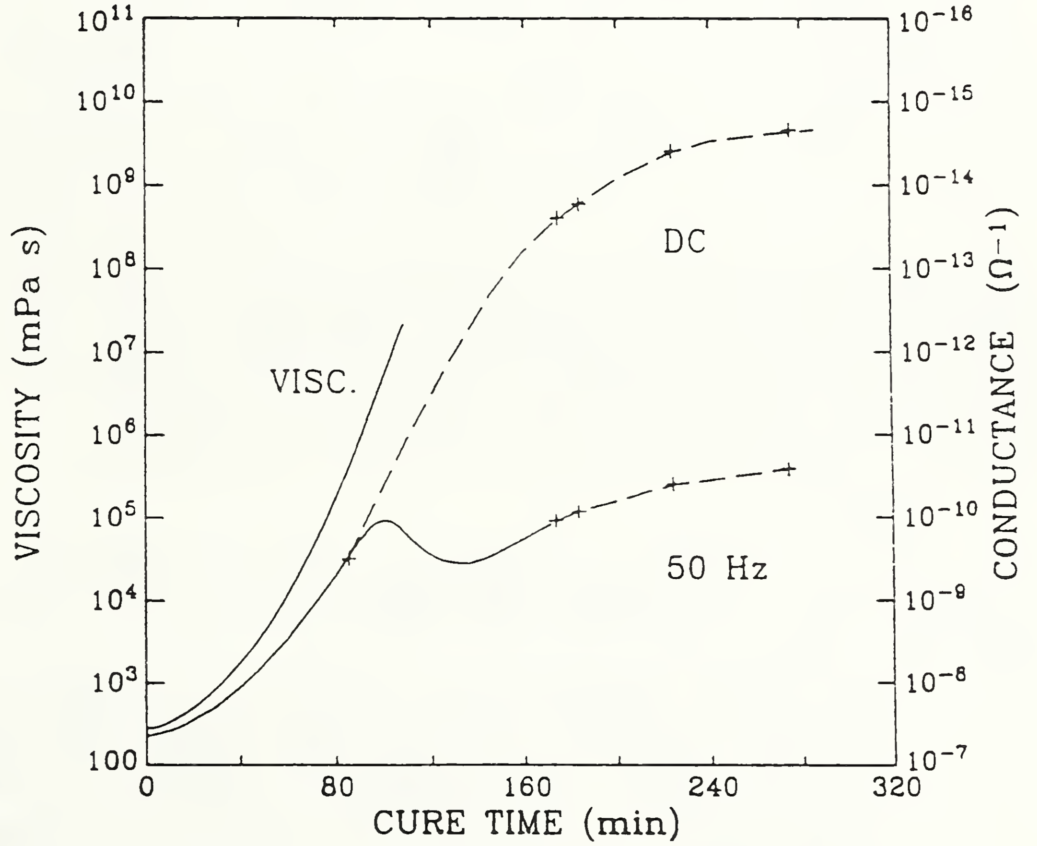

Figure 2.8 Plot of conductance (DC and 50 Hz) and low shear-rate viscosity (VISC.) for the sample used in Figure 2.5. The conductance scale runs from the top to bottom so the viscosity can be compared with the reciprocal of conductance. The data are shifted along the time axis to compensate for differences in heat-up times for the two experiments.

If the viscosity is compared with the reciprocal of conductance as in Figure 2.8 (and Figure 2.4), it is clear that the way they both change with cure prior to gelation is quite similar. A direct proportionality between the two is not observed, however. Not only does conductance begin to level off while viscosity increases rapidly prior to gelation, but even before this, the changes in viscosity are significantly larger than the changes is conductance. In fact, the differences are even larger than shown, since at high values of viscosity, not enough time was available for the flow to reach equilibrium due to the evolution of the cure. When this occurs, the measured values represent only a lower limit on the actual steady-state viscosity. The lack of a direct proportionality for this thermoset system is in keeping with the discussion earlier in this report.

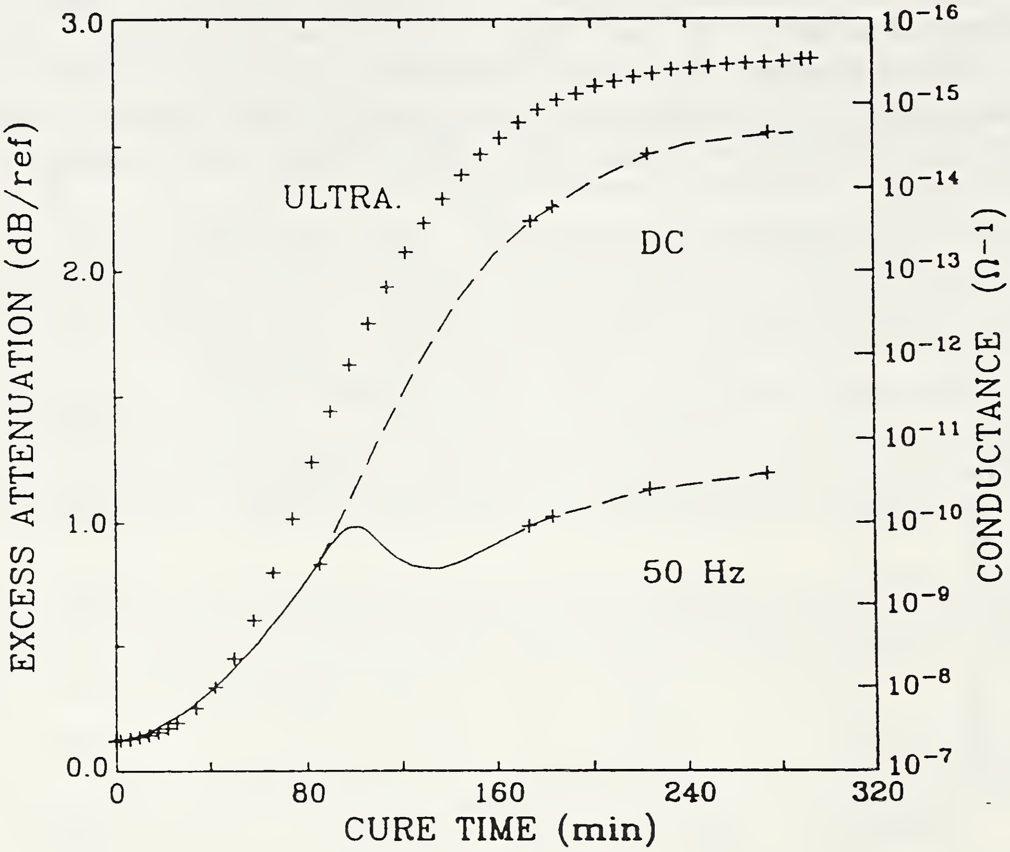

Figure 2.9 Plot of conductance (DC and 50 Hz) and ultrasonic attenuation data (ULTRA.) measured with the shear mode reflection technique at 5 MHz (see section on Wave Propagation Techniques) for the sample used in Figure 2.5. After the first 30% of the cure, the attenuation results provide a direct measure of shear modulus. The conductance scale runs from the top to bottom so the attenuation can be compared with the reciprocal of conductance. The data are shifted along the time axis to compensate for differences in heat-up times for the two experiments.

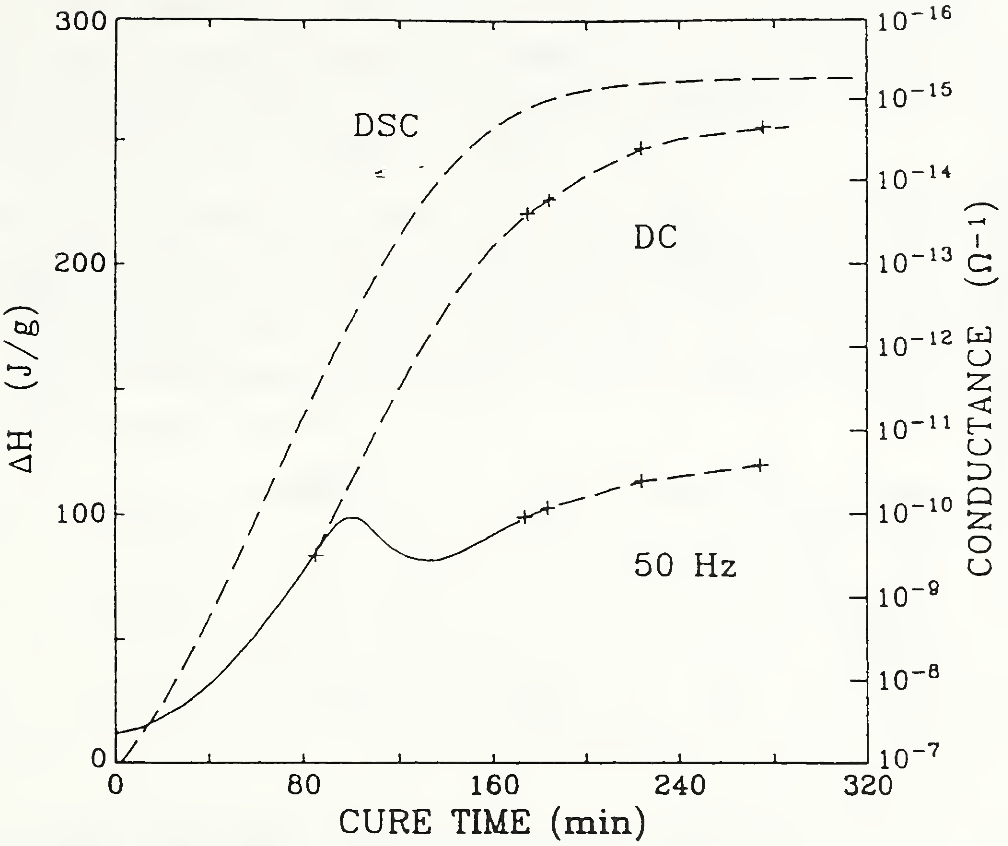

Figure 2.10 Plot of conductance (DC and 50 Hz) and exotherm (DSC) mesured with DSC for the sample used in Figure 2.5 The conductance scale runs from the top to bottom so the exotherm can be compared with the reciprocal of conductance. The data are shifted along the time axis to compensate for differences in heat-up times for the two experiments.

Cure monitoring data for many materials have already been reported in the literature. Epoxy resins have received the most studied as they are extensively used in composite system. The measurements have included not only the neat resin (Chang, 1987, Bidstrup, 1986, Sanjana, 1981) but also composites (Sanjana, 1986A). Other materials, such as polyimide (Kranbuehl, 1986A), PEEK (Kranbuehl, 1987B) and polysulfone (Kranbuehl, 1986B), have also been studied. Just as importantly, comparisons have been made between dielectics results and data from alternative measurement techniques such as torsion braid (Zukas, 1984; Kranbuehl, 1987C). In a very careful set of simultaneous measurements on controlled samples, a five different techniques have been compared to dielectrics (Chang, 1987; Mopsik, 1989). The results demonstrated that under the proper conditions electrical measurements can see the entire cure, including not only the gelation but also post-cure aging, at least as well as other techniques.

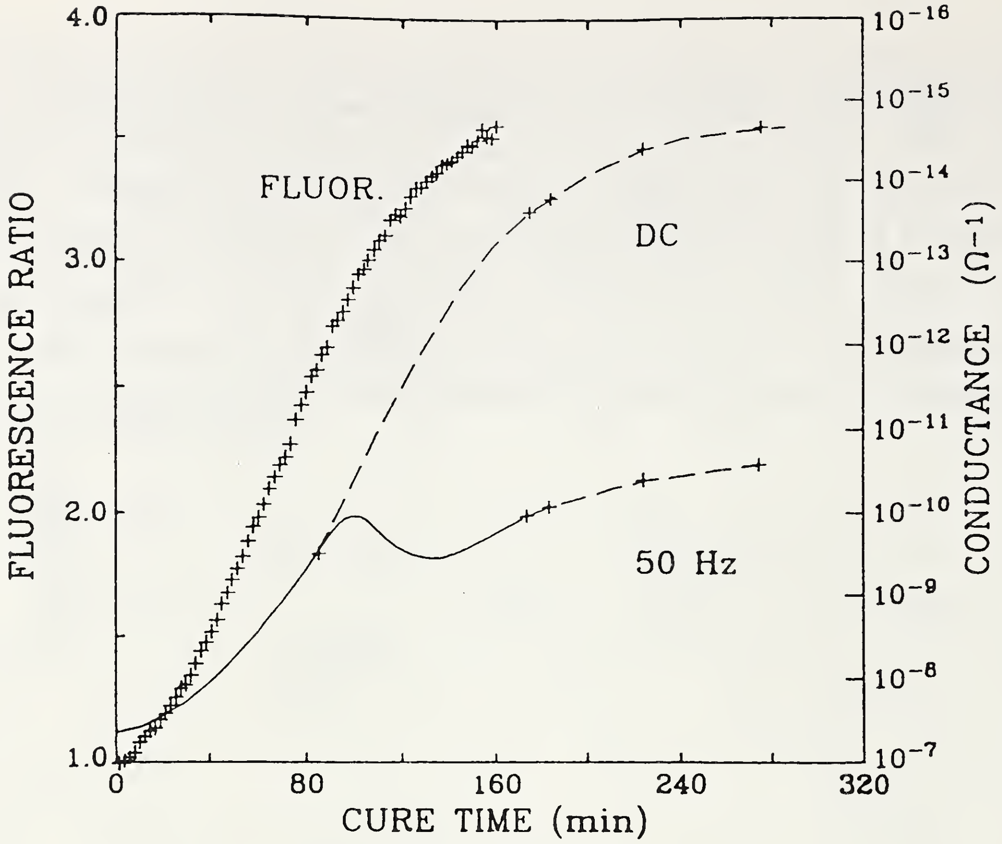

Figure 2.11 Plot of conductance (DC and 50 Hz) and fluorescence ratio (FLUOR.) measured by spectroscopy (see section on Optical and Spectroscopic Techniques) for the sample used in Figure 2.5. The conductance scale runs from the top to bottom so the exotherm can be compared with the reciprocal of conductance. The data are shiften along the time axis to compensate for differences in heat-up times for the twc experiments.

The current state of the art for electrical measurements with respect to evaluating the degree of cure is about the same as for other techniques. There have been many measurements made to show that cure can be followed a relatively straightforward manner. The measured parameters vary with each system but so does the cure itself. The results are temperature dependent although the changes during cure can be much larger than the temperature changes. Furthermore, any measurement that relates to a mobility, including viscosity behaves similarly so that this problem is not unique to electrical parameters. Since a cure cycle must be evaluated in terms of the desired properties of the finished part, cure monitoring must be eventually tied to what is optimal.

2.6.4 Other Considerations

The most difficult problem for electrical measurements is the presence of the composite fibers. If they are good insulators, matching approximately the properties of the resin matrix, then they would not significantly change the results found for pure resin systems. Much more difficult is the presence of carbon fibers as in many high-performance composites. These fibers are so conductive that they are the equivalent of metal. If the fibers form a continuous path between the electrodes, they effectively short out the measurement and render it useless. At the frequencies and current levels employed in cure monitoring such fibers cannot support any potential across them.

Clearly cure monitoring with electrodes requires either an electrode system that excludes any carbon fibers or is used in an area where the fibers do not exist. A sensor that has its electrodes embedded in an absorbent material that excludes fibers is a possibility. Another is to use sensors in any absorbent material used on the outside of the prepreg. In all cases, this is a major engineering challenge since not only must the fibers be excluded, but the resin must be properly sampled.

Another problem is the selection of the proper measurement frequency. The conductance can be followed more deeply into the cure with low frequencies. However, the more rapidly the system is changing, the higher the optimal frequency will be. As mentioned before, in step response measurements, any drift in the parameters can easily be seen as an error. If the capacitance is increasing linearly with time, then there is an apparent conductance. However, what is not usually appreciated is that a constant frequency bridge will give exactly the same result. While a pure capacitance exhibits no loss, an increase in its value absorbs energy from the surroundings and to the surroundings this is the same as a loss. Clearly, one measurement frequency will not do, especially in rapidly curing systems. If too low a frequency is used, not only will the result not be correct, but it will be rate dependent.

The problem of a suitable measurement frequency is one that will depend on the speed of the reaction. Most instrumentation can cover a relatively wide band of frequencies compared to most reaction rates, so that this issue is mainly one to be aware of rather than a major impediment.

Still in its infancy is the incorporation of the data into a usable scheme for feedback control of the curing process. There have been several investigations into this aspect (Minoda, 1985; Kranbuehl, 1986C) but much remains to be done. The main modeling has been on observing the logarithmic slope of the conductance and the reaction onset (Day, 1986A, 1986B). For some resin systems, especially the fast, autocatalytic ones, feedback control may just not be feasible (Chang,1988).

What is certainly capable of implementation at the current time is the use of cure cycle monitoring for quality control on the resin. For such purposes, there need not be any constraints on the electrode system and disposable parallel plate electrodes can be easily used. Changes in the cure curve due to resin aging in prepreg or other forms should be readily detectable.

2.7 REFERENCES

ASTM D150.

ASTM D924

Berberian, J. G., and Cole, R. H.,Rev. Sci. Instrum., 40, 811 (1969).

Bidstrup, W. W., Sheppard, N. F., and Senturia, S. D., Polym. Eng. Sci., 26, 358 (1986).

Boetcher, J. E., "Theory of Electrical Polarization", (Elsevier Publishing Co., Amsterdam, 1950).

Chang, S. S., Mopsik, F. I., and Hunston, D. L., 19th Int. SAMPE Tech. Conf., 253, (1987).

Chang, S. S., Hunston, D. L., and Mopsik, F. I., "Cure Monitoring for Thermoset Resins", Proc. 4th Ann. Conf. Adv. Comp. (ASM Int.), 90, (1988).

Bur, A. J., Barnes, J. D., and Wahlstrand, K. S., J. Appl. Phys., 59, 2345 (1986).

Cole, K. S., and Cole, R. H., J. Chem. Phys. 9, 341 (1941).

Cole, K. S. and Cole, R. H., J. Chem. Phys. 10, 98 (1942).

Cole, R. H., and Gross, Jr., P. M., Rev. Sci. Instrum., 20, 252 (1949).

Cole, R. H., and Davidson, D. W., J. Chem. Phys. 20, 1389 (1952).

Cole, R. H., J. Chem. Phys., 42, 637 (1965).

Davidson, D. W., and Cole, R. H., J. Chem. Phys., 18, 1417 (1950).

Davidson, D. W., Auty, R. P., and Cole, R. H., Rev. Sci. Instrum., 22, 678 (1951).

Day, D. R., Int. SAMPE Symp. Exhib. 33 (Mater.--Pathway Future), 594-602, (1988A).

Day. D. R., "Thermoset Process Control Using Microdielectric Sensors", Proc. 4th Ann. Conf. Adv. Comp. (ASM Int.), 83 (1988B).

P. Debye, "Polar Molecules", (Chemical Catalog Co., New York, 1929).

Denney, D. J., J. Chem. Phys., 30, 159 (1959).

Dragataki, L. D., Sanjana, Z. N., Insul./Circuits, 24, 27 (1978).

Fatuzzo, E., and Mason, P. R., Proc. Phys. Soc., 90, 729 (1967).

Fava, R. A., and Horsfield, A. E., Brit. J. Appl. Phys. (J. Phys. D), Ser. 2, 1, 117 (1968).

Froehlich, H., "Theory of Dielectrics", (Oxford, London, 1949).

Glarum, S. H., J. Chem. Phys., 33, 1371 (1960).

Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions", 3^d ed., (Rheinhold Publishing Co., New York, 1958).

Harris, W. P., 1966 Ann. Rept. Conf. Elec. Insul. Diel. Phenom., NAS-NRC Publ. 1484, (1967).

Hyde, P. J., Proc. IEE 117, 1891 (1970).

Johnson, J. F., and Cole, R. H., J. Am. Chem. Soc., 73, 4536 (1951).

Johnson, G. E., Anderson, E. W., Link, G. C., and McCall, D. W., Am. Chem. Soc., Div. Org. Coat. Plast. Chem. Pap. 35, 1, 404 (1975).

Kranbuehl, D. E., Delos, S. E., and Jue, P. K., Polymer 27, 11, (1986A).

Kranbuehl, D. E., Delos, S., Yi, E., Mayer, J., Jarrie, T., Winfree, W., and Hou, T., Polym. Eng. Sci. 26, 338 (1986B).

Kranbuehl, D. E., Delos, S. E., Hoff, M. S., Whitham, M. E., and Weller, L. W., Advan. Compos., Proc. Conf., 2nd, 61-7, ASM: Metals Park, Ohio (1986C).

Kranbuehl, D. E., Delos, S., Yi, E., Mayer, J., Jarrie, T., Winfree, W., and Hou, T., Polym. Eng. Sci. 26, 338 (1986D).

Kranbuehl, D. E., U.S. Patent US 4710550A, U.S. Ser. No. 729459 (1987A).

Kranbuehl, D., Delos, S., Hoff, M., Weller, L., Hagerty, P., and Sealy, J., Polym. Mater. Sci. Eng. 56, 163 (1987B).

Kranbuehl, D. E., Delos, S. E., Hoff, M. S., and Weller, P., 32^d Int. SAMPE Symp., Exhib., 338 (1987C).

Landau, L. D., and Lifshitz, E. M., "Electrodynamics of Continuous Media", (Addison Wesley Publishing Co., Reading, MA 1960).

Lauritzen, J. I., 1963 Ann. Rept. Conf. Elec. Insul., NAS-NRC Publ. 1141, 67 (1964).

May, C. A., and Tanaka, Y., eds., "Epoxy Resins, Chemistry and Technology", (Marcel Dekker, New York, 1973).

May, C. A., Proc. 21st SAMPE Symp. 21, 803 (1976).

McCrum, N. G., Read, B. E., and Williams, G. "Anelastic and Dielectric Effects in Polymeric Solids", (John Wiley and Sons, London, 1967).

Micromet Brochure, 1989.

Minoda, Y., Sakatani, Y., Yamaguchi, Y., Niizeki, M., and Saigoku, H., ASTM Spec. Publ., 864(Recent Adv. Compos. U.S. Jpn.), 489-501 (1985).

Mopsik, F. I., and Cole, R. H., J. Chem. Phys. 44, 1015 (1966).

Mopsik, F. I., Rev. Sci. Instrum. 55, 79, (1984).

Mopsik, F. I., Chang, S. S., and Hunston, D. L., Materials Eval., in press (1989).

Nelson, R. D., Lide, Jr., D. R., and Maryott, A. A., "Selected Values of Electric Dipole Moments in the Gas Phase", NSRDS-NBS **10**, (1967).

Sanjana, Z. N., and Selby, R. L., IEEE Trans. Elec. Insul. **EI-16**, 496 (1981).

Sanjana, Z. N., Polym. Eng. Sci. 26, 373 (1986A).

Sanjana, Z. N., "Use of Microdielectrometry in Monitoring the Cure of Carbon-Epoxy Prepreg", Report 86-9B7-CURES-R1, (1986B).

Senturia, S. D., Sheppard, N. F., Lee, H. L., Jr., and Day, D. R., J. Adhes. 15, 69 (1982).

Senturia, S. D., and Sheppard, N. F., Adv. Polym. Sci. (Epoxy Resin Comp. 4) 80, 1 (1986).

Sheppard, N. F., Garvelick, S. L., Day, D. R., and Senturia, S. D., Proc. 26th SAMPE Symp. 26, 65 (1981).

Smythe, C. P., " Dielectric Behavior and Structure", (McGraw Hill Book Co., New York, 1955).

Walden, P., and Ulich, H., Z. Physik. Chem., 107, 219, (1923).

Zukas, W. X., Schneider, N. S., and MacKnight, W. J., Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 25, 205 (1984).

WAVE PROPAGATION TECHNIQUES

Donald Hunston

3.1 SUMMARY

Information on changes in mechanical properties during cure can be extremely valuable since properties such as viscosity play a direct role in the success of part fabrication. The only mechanical tests with the potential for on-line process monitoring are wave propagation methods. A wide range of frequencies can be employed, but sonics and ultrasonics are most common. Such techniques have been used for many years to examine materials and are a common tool for post-processing inspection of composite parts. As a result, there are many people with experience and expertise in this field, and much of the equipment is readily available and relatively inexpensive. Moreover, significant efforts have been made to develop equipment that is rugged enough to be used under harsh conditions in an industrial environment. Although modifications will certainly be necessary for the particular application of process monitoring, this background is an important advantage. The past experience with post-processing inspection also gives industry fabrication people confidence in the results for identifying certain types of processing related defects, for example flaws and voids. This confidence and familiarity would be of great benefit in overcoming the resistance to introduce wave propagation sensors into actual fabrication equipment.

Another advantage of these techniques is that many different kinds of waves and different measurement geometries can be used, and each provides unique information. For example, many experiments have employed ultrasonics to characterize voids, porosity, and fiber volume fraction in composite parts. The potential exists to determine these same features during fabrication. In addition, processing characteristics, such as viscosity, moduli, glass transition temperature, degree of cure, etc., have been empirically correlated to wave propagation experiments made during processing.

Although wave propagation methods have many advantages, there are also a number of barriers and challenges. These methods are sensitive to a wide variety of features, but the current capability to distinguish these features and analyze the signal when multiple features are present is quite limited. Most experiments performed today use the simplest possible test method even though more sophisticated implementations are possible. This significantly limits the information that can be obtained and the analysis that is possible. Consequently, there is a need to more fully utilize and develop the potential of wave propagation methods and explore advancements in signal analysis technology. Improvements in the theoretical analysis of wave propagation in a curing system is also needed to help provide a scientific foundation for the interpretation of the data.

Wave propagation methods measure average properties over a volume of material that has a significant size. This can be an advantage or a disadvantage depending on the particular situation. Good contact between the sensor and the sample is essential, but is not always easily obtained. Analysis of the data often requires other information such as temperature and sample dimensions which must be measured separately. Finally, the current sensors have a limited upper temperature capability, and this must be extended.

A related measurement technique is acoustic emission (AE) where the waves are generated by internal events such as crack formation. AE has been used successfully to monitor certain events that occur during processing. This technique is at a very early stage of development, however, and additional research is needed to clarify the full potential of this method.

3.2 INTRODUCTION

Mechanical properties tests provide a valuable tool for process monitoring because they play a direct role in the success of part fabrication. For example, in autoclave curing, the resin flow largely determines consolidation, and resin flow depends on viscosity and the local pressure fields. Another example is residual stress which depends on modulus and local deformations such as cure shrinkage. Of all the mechanical tests, viscosity measurements, both steady flow and dynamic, are probably the most widely used in the laboratory since they can be of great help in developing cure schedules for new resins. Also widely used are forced or free oscillation experiments on resin coated cloth, fibers, or braids. These tests have provided some of the most important insights for processing science. Unfortunately, none of these methods are easily adapted to on-line monitoring. In this connection, the best candidates are the wave propagation techniques.

In such tests an oscillatory disturbance (or wave) is generated in the sample, and the propagation characteristics of the wave are determined. These characteristics depend on the material properties of the sample, and as they change during processing, the corresponding changes in the wave propagation are monitored. The range of frequencies that can be used is quite large. Although most studies have focused on ultrasonics (low MHz frequencies), experiments can also be conducted in the sonic range (KHz frequencies). In fact the potential extends to even lower and higher frequencies, but the required equipment for such measurements is not so readily available and complications can arise when the wavelengths become very large or very small. In this report, the term ultrasonics will be used to discuss wave propagation techniques, however, the discussion really applies to both sonic and ultrasonics frequencies.

The purpose of this chapter is to conduct a careful examination of these methods. The discussion will be divided into three sections. First, the Basic Theory will be presented with two subsections: a brief discussion of Material Properties, and an outline of the basic concepts of Wave Propagation. Second, a major section will consider the application of ultrasonics to On-line Process Monitoring. Three subsections will address: Hardware and Application Considerations, Interpretation of Results, and Future Trends. Finally a few brief comments will be made on Acoustic Emission.

Acoustic Emission is a measurement method closely related to ultrasonics tests. This measurement involves monitoring disturbances that are generated by the sample itself. The formation of cracks, for example, produces a wave motion which can often be detected. If sufficient information is obtained and the knowledge base is adequate, the nature of the event which caused the disturbance can be characterized and, in some cases, even identified. This technique is normally applied to the examination of parts that are actually in use. The information obtained is employed to determine features such as the level of damage. Recently, however, the application of this method to the monitoring of events during processing and subsequent cool down has begun to be examined. A brief discussion of this approach will be given at the end of this chapter.

3.3 **BASIC THEORY**

3.3.1 Material Properties

Since the propagation of a wave through a material depends on the properties of that material, it is useful to consider the area of materials properties before examining wave propagation. The basic tool for analyzing the response of a material to a stress is the fact that any arbitrary deformation can be viewed as a unique combination of three basic motion types: (1) rotation and translation, (2) compression or dilatation, and (3) shear strain. The first type involves motions where there is no change in size or shape. This is usually not of interest so subsequent discussions will focus on the other two. The second type is defined as deformations that change the size (volume) of the specimen but do not alter its shape. These motions are characterized with the compressibility or bulk modulus. The third type of motion involves deformations that change the shape of the sample but not its volume. These motions are characterized by the shear modulus. Since any deformation can be split into a unique combination of these three types of motion, the material's response can be completely characterized by parameters (or moduli) which describe the stress-strain relationships in each case.

3.3.1.1 Linear Elastic Solids

Since the motion present in wave propagation normally involves very small amplitude deformations, the behavior can usually be described as linear. For an elastic solid this means the compressibility and shear are characterized by a linear relationship between stress and strain with the proportionality constants being the bulk modulus, K, and the shear modulus, G. In shear for example the shear stress, σ, is proportional to the shear strain, γ.

$$\sigma = G\gamma \tag{3.1}$$

In such materials the modulus values depend only on temperature.

3.3.1.2 Linear Viscous Fluids

For many substances the linear elastic model provides an approximate but adequate description of the material's behavior. With polymers or polymer containing material systems such as organic matrix composites, this is generally not the case, and thus a more general model is needed. Often a linear viscoelastic equation can be employed. In this case the material's response involves both elastic and viscous components. The viscous component can be understood by first considering a linear viscous material (fluid). Here the stress is directly proportional to the rate of strain with the proportionality constants being the viscosity. Both shear viscosity, η, and bulk viscosity, η_v, are needed to characterize the material, but since fluids almost always flow by shear unless forced to do otherwise, it is the former that is usually meant when the term viscosity is used. Consequently, in shear

$$\sigma = \eta \frac{d\gamma}{dt} \qquad (3.2)$$

3.3.1.3 Linear Viscoelastic Materials

With a linear viscoelastic material subjected to sinusoidal oscillation, the response can be characterized by using the same equations as for a linear elastic or linear viscous system but allowing the material constants to be complex numbers. The real part and imaginary part of the complex number makes it possible to combine the elastic and viscous components of the material response as indicted below. In the discussion that follows, the material behavior will be illustrated using shear deformations, but an equivalent set of relationships exist for compression-dilatation, and they could be used to illustrate the points just as well.

The dynamic shear modulus, G^*, involves a real part (G') which is termed the shear storage modulus and quantifies the elastic component of the response, and an imaginary part (G'') which is called the shear loss modulus and measures the viscous component of the response.

$$G^* = G' + i\,G'' \qquad (3.3)$$

The dynamic shear viscosity, η^*, is defined in a similar way except that a negative sign is included, and, unlike with the modulus, here the real part corresponds to the viscous response while the imaginary part relates to the elastic response.

$$\eta^* = \eta' - i\,\eta'' \qquad (3.4)$$

The steady-flow, zero shear-rate viscosity, η_o, is the limit of η' at zero frequency.

In a propagating wave the oscillating strain at any point in the material is represented by

$$\gamma = \gamma_o e^{i \omega t} \tag{3.5}$$

where γ_o is the amplitude, ω is the angular frequency, and t is the time. By the proper manipulations of equations (3.1) to (3.5), the relationship between the dynamic shear viscosity and the dynamic shear modulus can be obtained.

$$\eta' = \frac{G''}{\omega} \tag{3.6}$$

$$\eta'' = \frac{G'}{\omega} \tag{3.7}$$

3.3.1.4 Frequency and Temperature Dependence

For a linear viscoelastic system the response not only involves both elastic and viscous components but also depends on the test frequency (or time scale). The dynamic moduli and viscosities therefore are functions of both temperature and frequency. For a simple viscoelastic material the frequency dependence can be described as a transition from elastic like behavior at higher frequencies (and lower temperatures) to more viscous like behavior at lower frequencies (and higher temperatures). This is illustrated in Figure 3.1 which shows the shear storage modulus, G′, for three types of materials. The simplest response (Curve A) is a direct transition from solid-like, elastic behavior (high modulus, G′) to fluid-like, viscous behavior (G′ = 0). For materials with molecular weights high enough to have entanglements, a rubbery plateau is present between the elastic and viscous regions (Curve B). Finally, in a chemically cross-linked system, the material can never really flow because the covalent bonds prevent it. Consequently, although high temperatures and low frequencies will give sufficient molecular mobility to have a rubbery plateau, this region persists at all low frequencies (Curve C).

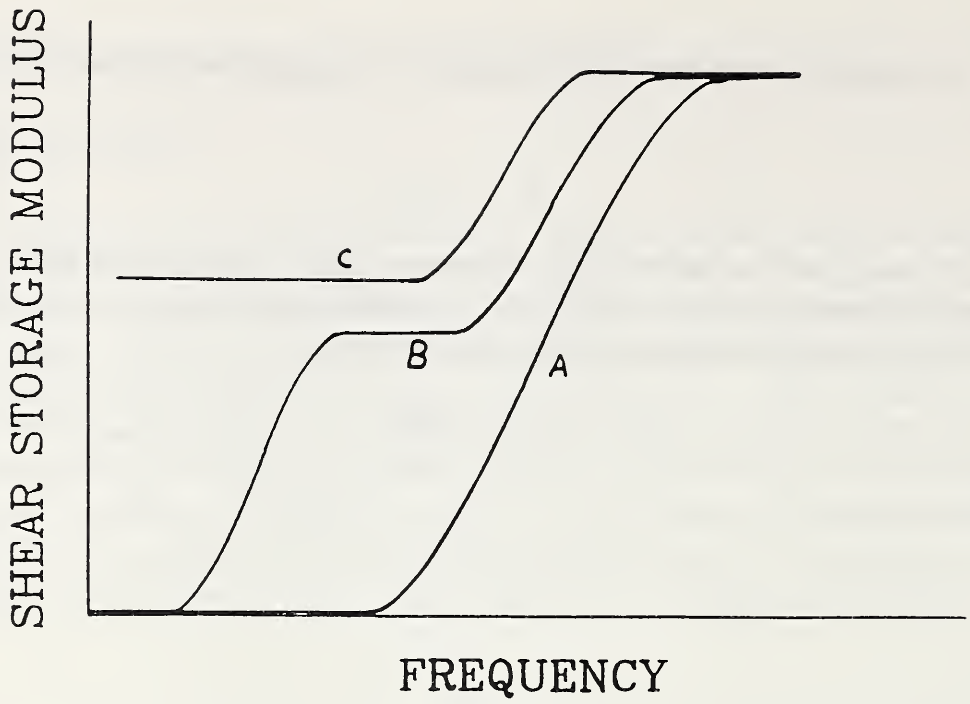

Figure 3.1 Typical curves for dynamic mechanical properties as a function of test frequency of polymers: Curve A represents a low molecular weight material, Curve B represents a material with molecular weight high enough to produce entanglements and therefore a rubbery plateau, and Curve C represents a crosslinked system.

3.3.1.5 Characteristic Time

The meaning of "higher" and "lower" in the paragraph above depends on the material. It is helpful in this regard to describe the behavior with a characteristic time, τ, which is defined as the value of $1/\omega$ at the midpoint of the transition. It should be noted that a quantitative description of a viscoelastic material usually requires a distribution of characteristic (or relaxation) times for even the simplest systems. Consequently, in the discussion here, the term, characteristic time, will be used in a figurative sense and is meant to include both simple one-characteristic-time descriptions that are highly approximate but can be useful, and more sophisticated descriptions involving a distribution of relaxation times. A final point worth noting is that Curve B has two characteristic times: one between rigid solid and rubber and the other between rubber and fluid. For the discussion here, however, it is usually the former that is of interest.

3.3.1.6 Changes During Processing

A material like a low molecular weight polymer behaves as a fluid under normal laboratory test conditions, i.e., frequencies in a range like 1000 Hz to 0.001 Hz. Consequently, the characteristic time must be significantly shorter than 0.001 seconds. At sufficiently high frequencies, however, it will respond as a solid. In contrast, a high molecular weight polymer has a characteristic time that is very long since the material will normally behave as a solid. In processing, the key is to change the characteristic time so that the material will behave as a liquid and solid at the appropriate times. In fact, the most important change in the mechanical behavior during processing is the shifting of the mechanical property curves (such as those in Figure 3.1) horizontally by changing the characteristic time. Increasing the temperature lowers τ while increasing molecular weight raises it.

When processing a thermoplastic, either Curve A or B is appropriate depending on the molecular weight. The value of τ is quite high initially since the material is a solid under normal conditions. During processing, the temperature is increased, which lowers τ, thereby shifting the curve horizontally to the right. The curve must be shifted sufficiently to result in fluid behavior at a time scale (frequency) appropriate for processing. When the sample is cooled, the curve shifts back to its original position or a slightly altered position. In contrast, the starting material for a thermoset is low molecular weight and will usually have a simple transition (Curve A) and a very low value of τ. Increasing the temperature, first lowers τ slightly, but as the reactions increase the molecular weight, the curve undergoes a dramatic shift to the left. At some point a rubbery plateau may form as the molecular weight reaches the entanglement point (Curve B). Eventually, cross-linking produces a curve similar to Curve C with a large value of τ corresponding to a glassy solid.

In addition to the horizontal shifts, processing can produce changes in the shapes of the curves and shifts in the plateau levels. For example, in partially crystalline thermoplastics, changes in crystallinity can alter the curves. These changes, however, are usually much less pronounced than the horizontal shifts.

3.3.1.7 Challenges for Process Monitoring

This discussion illustrates a major concern in the use of ultrasonics for process monitoring. The measurements are made at high frequencies, while the properties such as flow that controls processing often involve longer time scales (low frequencies). The challenge, therefore, is to gain insight into the low frequency behavior from the measurement of high frequency data. In simple terms, this means estimating the horizontal shift of the curve from measurements made at high frequencies. Obviously, this can be done most accurately when the transition region is not too far away from the measurement frequency. In this range (ω near $1/\tau$) even small shifts in the curve (changes in τ) produce large changes in G' since a region of the curve with a large slope is involved. In the early stages of cure for a thermoset, this condition may be met. In many other cases, however, the measurement frequency corresponds to a point near or on the elastic plateau. For such conditions, the measurements must reflect the more subtle changes, i.e., alterations in the shape of the curves or changes in the plateau levels since purely horizontal shifts would have little effect on the value of G'. These secondary changes are often more difficult to measure and interpret, but fortunately, experiments have shown that such data can be quite useful. As will be seen later, excellent correlations with properties such as viscosity can often be achieved even though the correlations are strictly empirical.

3.3.2 Wave Propagation

Before investigating the information gained by wave propagation experiments, it is useful to examine the types of deformations involved. For a homogeneous material with distant boundaries, two types of waves are possible: shear waves where the motion of any point in the material is perpendicular to the direction in which the wave's energy is propagating, and longitudinal waves where the motion in the material is parallel to the direction of propagation. Normal sound waves, for example, are longitudinal waves. The motion in shear waves is governed by the dynamic shear modulus while longitudinal waves involve the dynamic longitudinal modulus, L^*. The latter motion involves a combination of deformations, and thus both shear and bulk moduli are needed

$$L^* = K^* + \frac{4G^*}{3} \tag{3.8}$$

3.3.2.1 Characterizing the Wave Motion

In analyzing wave propagation in a linear viscoelastic material, the equations are identical to those for an elastic solid except that the modulus is complex. This results in a wave which is damped; i.e., the amplitude decreases with distance propagated away from the source. If U is the displacement of a point in the material for a wave propagation in the x direction, then

$$U = U_o e^{-mx} e^{i \omega t} \tag{3.9}$$

where U_o is the initial amplitude (at $x = 0$), and m is the complex propagation constant. The propagation constant is defined as

$$m = \alpha + i\beta \tag{3.10}$$

where α indicates the attenuation and β is related to the wave length. These are the quantities usually measured in an experiment.

The amplitude attenuation coefficient, α, is defined as the natural log of the amplitude ratio at points separated by a unit distance in the direction of propagation.

$$\alpha = \ln\frac{|\ U(x)\ |}{|U(x-1)|} \tag{3.11}$$

The wave length, λ, is the distance over which the angular part of U (i.e. ωt - ßx) changes by one cycle (or 2π) at fixed time.

$$(\omega t-\beta x) - (\omega t-\beta[x+\lambda]) = 2\pi \tag{3.12}$$

so

$$\beta\lambda = 2\pi \tag{3.13}$$

Since,

$$\lambda = \frac{2\pi V}{\omega} \tag{3.14}$$

where V is the propagation velocity, then

$$\beta = \frac{\omega}{V} \tag{3.15}$$

Consequently, β is the usual propagation constant for a linear elastic solid.

The equation for this simple example of a wave propagating in the positive x direction in a linear viscoelastic material is

$$[M]^{*}\frac{\partial^2 U}{\partial x^2} = \rho\frac{\partial^2 U}{\partial t^2} \tag{3.16}$$

where ρ is the density and $[M]^*$ represents the complex modulus appropriate for the type of wave involved (usually either L^* or G^*). Substituting for U in equation (3.16) gives the relationship between the propagation constant and the modulus.

$$(m)^2 = -\frac{\omega^2\rho}{[M]^{*}} \tag{3.17}$$

3.3.2.2 Relationship between Dynamic Moduli and Measurements

Experiments are normally designed to measure attenuation and velocity, thus providing α and ß. The modulus can be expressed in terms of α and ß by solving equation (3.17) to give

$$[M]' = \omega^2\rho \frac{(\beta^2-\alpha^2)}{(\beta^2+\alpha^2)} \tag{3.18}$$

and

$$[M]'' = \omega^2\rho \frac{2\beta\alpha}{(\beta^2+\alpha^2)} \tag{3.19}$$

Since both components of the modulus must be positive, the limits on α are

$$0 \leq \alpha \leq \beta \tag{3.20}$$

The important point to note here is that these relationships are quite complex in a viscoelastic material. Consequently, as a general rule, both α and ß must be evaluated to determine either part of the complex modulus. The only exceptions are the extremes where the material is primarily elastic so $\alpha = 0$

$$[M]' = \frac{\omega^2\rho}{\beta^2} = \rho V^2 \tag{3.21}$$

or primarily viscous so $\alpha =$ ß and

$$[M]'' = \frac{\omega^2\rho}{2\beta^2} = \frac{\rho V^2}{2} \tag{3.22}$$

The former condition is not as unusual as might be thought since the measurements are made at high frequencies, and as indicated in Figure 3.1, the behavior here can be quite elastic even if the lower frequency behavior is not (i.e. $1/\tau$ is less than the measurement frequency but still relatively high). The latter condition is probably unusual in processing since the starting materials generally have high enough molecular weights that the measurement frequency does not meet the requirement for viscous behavior, i.e. that the frequency must be much less than $1/\tau$.

Even if both parts of the modulus are determined (Figure 3.2), however, the question from a processing point of view is how to relate the high frequency modulus to parameters important in fabrication. To date, most efforts to address this problem have involved simple

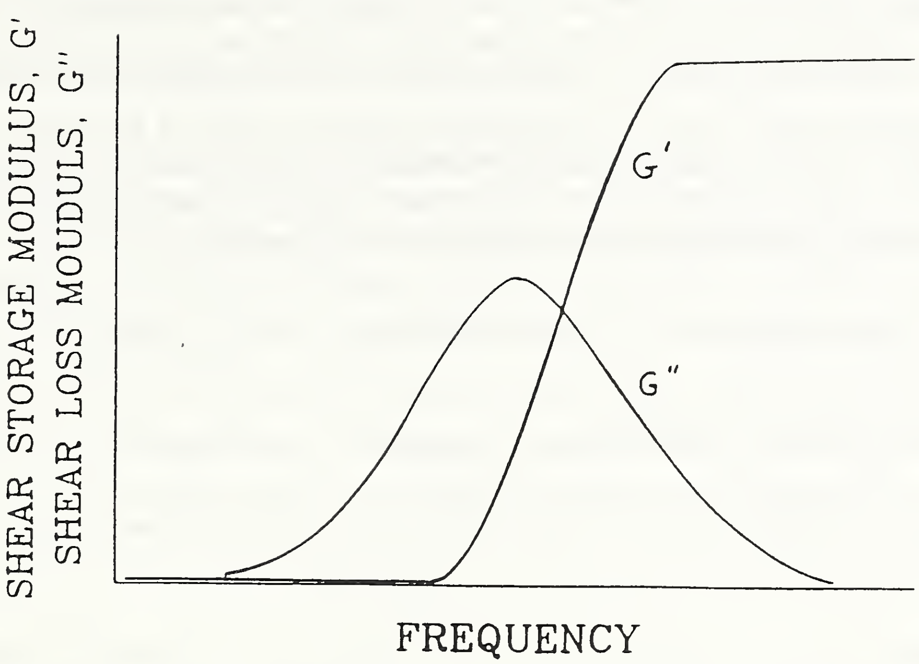

Figure 3.2 Typical curves for the shear storage modulus and the shear loss modulus shown as a function of frequency for a simple low molecular weight polymer.

empirical correlations. Although very useful, such correlations must be used carefully since the limits on their validity are unknown. A few studies have tried to develop models to establish a more fundamental basis for the correlations, but clearly, this is an area where more research is needed.

3.4 **ON-LINE PROCESS MONITORING**

3.4.1 Hardware and Application Considerations

3.4.1.1 Direct Measurement Methods

In order to employ ultrasonics as a process monitoring tool, it is necessary to excite a wave in the sample and monitor its propagation. The simplest approach, which will be termed the direct measurement method in this report, involves mounting transducers on both sides of the sample and using one to generate the signal while the other acts as a receiver. Since the wave will reflect back and forth between interfaces, discontinuities, etc., a pulse technique is often used to separate the signals from the various reflection paths. The sending transducer generates a short burst of mechanical motion and is then turned off. The receiving transducer monitors the pulse each time it reaches the sample-receiver interface. A series of pulses is usually detected, and the transit time (time between generation and detection) can be used to determine the reflection path involved. When the motion has been completely attenuated by the various loss mechanisms, another pulse is generated by the sending transducer. In such a system, the same transducer can be used to both generate and monitor the pulse, if the attenuation is low enough that the pulse can be measured after traveling through the sample and reflecting back from the opposite side.

The velocity and attenuation of the propagating wave can be calculated by measuring the transit time, signal amplitude, and distance over which the pulse traveled. Appropriate corrections must be made for the changes introduced by conversion between the electronic signal and mechanical motion, reflections from interfaces or discontinuities, and other complications. A discussion of these effects is beyond the scope of this report. Suffice it to say here that much has been done in addressing these problems by procedures such as calibration and the use of optical (non-contact) sensors.

Another important consideration is the form of the pulse used to excite the transducer. A spike is often used, and this generates a complex mechanical motion involving a distribution of frequencies. Separating the response of the sample to the different frequencies is very difficult in this case, so only an average response is obtained. As will be discussed in the next section of the report, much can be learned from the frequency dependence of the response. Consequently, a much better approach is to excite the transducer with a pulse of sine waves at a fixed frequency. The pulse should contain a sufficient number of cycles to cause the predominant response to be at that frequency. In this way, different frequencies can be used and the resulting responses analyzed.

Although the measurement methods outlined above are the most direct, there are several limitations. First, the sample geometry may make it difficult to obtain a simple transit path of sufficient length to make the measurement possible. Second, it may be difficult to make and maintain intimate contact between the transducer and the sample. Third, the sample attenuation may be too high to propagate the pulse the required distance. These difficulties can be encountered with both longitudinal and shear waves, but the second and third are particularly important for shear. The motion involved in shear requires excellent coupling between the transducer and the sample. This is often difficult to obtain, particularly when the sample shrinks during processing. In addition, the attenuation of shear waves in a liquid or soft solid is very high, so the early phases of cure simply cannot be followed using shear waves in the way described above.

Most studies using the direct measurement method have employed longitudinal waves, but some have utilized shear waves. Shear waves have the advantage that the propagation characteristics depend on only the dynamic shear modulus, while longitudinal waves depend on both the dynamic shear and dynamic bulk moduli. The problems mentioned above, however, often make longitudinal experiments considerably easier to perform. Ideally, one would like to utilize both types of waves to obtain the maximum information possible.

3.4.1.2 Interface Waves and Reflection Techniques

As a result of the limitations for the direct measurement method, a variety of other techniques have been developed. These methods involve alternate ways to do the measurement and/or wave motions other than the two basic types, i.e., longitudinal and shear. In general, such techniques employ either a wave guide or an interface to control the wave propagation. A wave guide is a geometric shape, for example a plate or cylinder, that acts as a carrier for the wave.

Two examples of interface methods have appeared in the cure monitoring literature. The first involves the reflection of shear waves at the interface between the sample and a substrate which is pressed against the sample (Chang, 1987 and 1988; Cohen-Tenoudji, 1985; Fanconi, 1986 and 1987; Hunston, 1983; Senich, 1984). If the displacement in the wave is parallel to the interface, only shear waves will be present. The angle of incidence (between the wave propagation direction and the interface) controls the sensitivity of the technique. Most studies have found that the least sensitive mode (normal incidence) is the most useful. The reflection of the wave produces a similar shear wave in the sample. Even if the attenuation in the sample is too high to measure this wave directly, the reflection back into the substrate can be monitored. Certain characteristics of the reflected wave depends on the mismatch in mechanical properties between the sample and the substrate. When the sample is present, there is a decrease in amplitude and a shift in the phase for the reflected wave relative to a reflection from the substrate air interface. By measuring these quantities, the dynamic shear modulus of the sample can be determined and followed during processing.

Experiments of this type have been conducted for a number of laboratory systems. The phase angle measurement, however, is very sensitive to temperature and requires temperature control that is generally impossible to achieve in realistic processing situations. Consequently, the technique is normally used in a more empirical way by simply monitoring the attenuation changes. As the sample cures, the attenuation increases as illustrated in Figure 3.3 (Chang, 1987). During the latter stages of cure, the material's response at ultrasonic frequencies is primarily elastic, and thus, the attenuation provides a direct measurement of the shear storage modulus.

A second example of interface testing involves one of the geometries available in a commercial cure monitoring system manufactured by Applied Polymer Technology (Applied Polymer Technology, 1989). In this system, the sensor uses two transducers placed side by side and separated by a few millimeters. When placed against the sample, one transducer is excited and generates a wave that travels along the surface of the sample and is detected by the second transducer. The amplitude and velocity of this surface wave can be measured and followed as the sample cures. The technique has the advantage that it works even when the attenuation in the sample is high. On the other hand, the measurement detects changes in

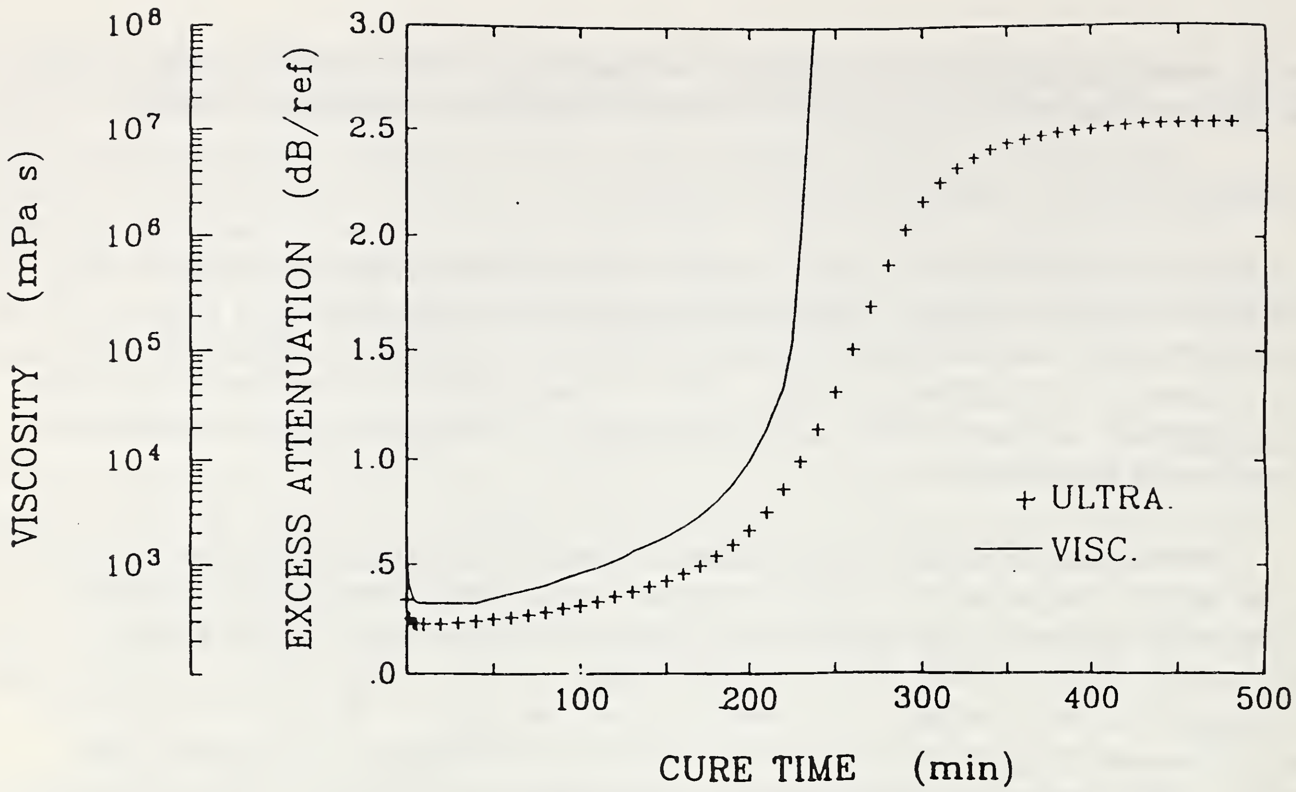

Figure 3.3 A comparison is made between the attenuation measured in the shear wave reflection technique and the measured viscosity as a function of reaction time for an epoxy (diglycidyl ether of bisphenol-A) cured with ethyl methyl imidazole. The attentuation is adjusted by subtracting the attenuation when no sample is present.

only a very small volume of materials so care must be exercised in the placement of the probe and the interpretation of the results. Another disadvantage of this technique is that the exact details of the wave motion have not been explored, and so it is impossible to say exactly what properties of the sample are being measured. As a result, this technique, like many other methods, is used to follow cure in a qualitative way. In some cases empirical correlations with parameters like viscosity can be established, and these can be very valuable if used carefully.

3.4.1.3 Wave Guide Methods

In the area of wave guides two geometries have been used to monitor processing. Just as in the shear wave reflection technique, these methods usually operate based on the mismatch in mechanical properties between the sample and the wave guide material. When this mismatch is great, the wave's energy largely remains in the wave guide so the attenuation is low and velocity is high. As the mismatch decreases, more of the energy is lost into the sample, and the apparent attenuation of the wave in the guide goes up.

Moreover the interaction between the wave and the sample often results in a decrease in the speed of the wave in the guide. As the mismatch becomes greater, the wave speed decreases. This is, of course, a simple description, and more complex behavior is often observed in practice, but it provides feeling for the types of things that can happen.

The most extensively studied wave guide technique (Advanced Material, 1987; Harrold, 1986A, 1986B, 1987, 1988, and in press; Harruff, 1988; Sun, 1987) employs a large fiber (approximately 1 mm in diameter). An acoustic wave is transmitted down the length of the fiber which is inserted through the sample. As the sample cures, the apparent attenuation of the wave increases first and then decreases with further cure. The velocity of the wave can also be measured and exhibits a significant decrease near the point where the attenuation shows a peak. An analytic expression relating the velocity and attenuation of the wave in the fiber to the moduli of the sample has not been developed, so as with the other techniques, the focus is on establishing empirical correlations with cure parameters.

The other wave guide geometry is a plate. A number of different versions of this approach have been developed using different geometries and different types (or modes) of wave propagation. The simplest example employs a pure shear wave (Hunston, 1983 and 1985; Martin, 1989; Ricco, 1987). This technique is the limiting case for the shear wave reflection method in that the angle of incidence between the direction of wave propagation and the interface is zero. The technique has a very high sensitivity and can examine liquids with viscosities of 0.01 centiPoise or less. This is useful for some systems, but it can also become a problem in the latter phases of cure for many materials when the attenuation becomes too high for accurate measurements. As with the reflection technique, this monitoring method has the advantage that there is a known analytical relationship between the measured velocity and attenuation of the wave in the plate and the dynamic shear modulus of the sample. It also has the same limitation, however, in that the changes in velocity during cure are very small, and measurement requires temperature control that is difficult to achieve in real processing environments. Consequently, empirical correlations are again the usual approach.

Other modes of wave propagation in a plate have been employed including Lamb waves and Leaky Lamb waves (Adler, 1986; Rokhlin, 1987). These techniques work quite well for certain systems. The procedure is similar to that described for the other methods in that the velocity and attenuation of the wave in the plate are correlated with cure parameters. Although the motion in these waves is often complex and the cure monitoring geometry has usually not been analyzed, experiments have established useful empirical correlations.

3.4.1.4 Application to Adhesives and Composites

It is worth noting at this point that wave guide methods have also been applied to the study of adhesive joint both during and after fabrication (Hunston, 1985; Pike, 1982; Rokhlin, 1984 and 1987). The changes that occur during hardening of an adhesive are closely related to the transformations that occur in composite process monitoring. The materials are quite similar; interfaces are present in both cases; and thin layers of resin are often involved. With both adhesives and composites, the fabrication generally occurs with the sample in contact with molds, tools (shape controlling plates used with composites), or adherends that can act as a plate wave guide when properly adapted. As a result, the plate wave guide approach can be a convenient method to monitor fabrication of both adhesives and composites.

3.4.2 Interpretation of Results

Once the measurements have been made, the next major issue is the interpretation of the results. Many studies have addressed this area, and a useful way to summarize this work is a list of parameters that have been correlated to ultrasonic cure data. Table 3.1 lists both the parameters and corresponding references. With only a few exceptions the papers cited include only those studies that focus on cure or processing. There is, of course, a voluminous literature concerning the use of ultrasonics as a nondestructive evaluation (NDE) tool for post processing inspection. A brief summary of the results and benefits of this work will be described later in this section, but no attempt will be made to furnish a complete review of this area since that is clearly beyond the scope of this report.

The parameters listed in Table 3.1 are divided into 3 categories: those related to geometry features, material parameters, or performance. This provides a useful order in which to discuss the results.

3.4.2.1 Geometry Parameters by Direct Measurement Methods

The most highly developed use of ultrasonics is NDE of post processing inspection of parts for flaws, voids, and defects. Both the equipment involved, and the theory required, have received extensive study. For example, theories have been developed for the scattering of an ultrasonic signal from inclusions of various sizes, shapes, concentrations, orientations, etc. Moreover, the effects of changing wave parameters such as frequency have been analyzed. Experiments were then performed to confirm these theories with independent measurements of the flaws, voids, defects, etc. As a result, there is often a firm theoretical basis for the correlations between geometry features and ultrasonics results. For example, tests of the frequency dependence can be used to distinguish and analyze defect characteristics.

Flaws, Voids, and Defects: The most common experiment associated with the NDE approach involves through-transmission tests, but both reflection and scattering measurements are also possible. In through transmission a wave (usually longitudinal) is generated on one side of the sample and detected on the other. Velocity and attenuation are the measured quantities. In the reflection technique the same transducer is used to generate motion and receive signals reflected back from voids, flaws, and other defects. Both the intensity of the reflected signal, and the transit time are recorded. The scattering technique is similar to the through-transmission experiment, except that the receiving transducer is not directly opposite the sending transducer but placed at an angle to the direction of wave propagation. These techniques have been classified in the previous section as the direct measurement methods.

With through transmission, the amplitude of the received signal is reduced when there is a defect in the path. The degree of attenuation is effected by the defect's size, shape, orientation, etc., so information about the defect can be obtained by analyzing the signal. Although measurements can be made with fixed transducers, it is common procedure to

TABLE 3.1 PARAMETERS CORRELATED WITH ULTRASONICS

Category	Parameter	References
Geometry	Flaws, delaminations, etc.	Advanced Materials, 1987 Harrold, in press Rokhlin, 1987
	Porosity	Hsu, 1988 Lamm. 1989
	Fiber volume fraction	Tornberg, 1988
	Fiber orientation	Lamm, 1989 Saliba, 1989
Material	Viscosity	Bujard, 1987 Chang, 1987 and 1988 Cohen-Tenoudji, 1985 Elsley, 1986 Fanconi, 1986 and 1987 Harrold, 1986A and 1986B Martin, 1989 Ricco, 1987 Saliba, 1989 Tittmann, 1985 Tuegel, 1986
	Mechanical Properties	Adler, 1986 Advanced Materials, 1987 Harrold, 1986B Rokhlin, 1986 and 1987

Category	Parameter	References
Material (Cont.)	Degree of Cure	Advanced Materials, 1987 Alig, 1987 and 1988 Chang, 1987 and 1988 Fanconi, 1986 and 1987 Harrold, 1987 and in press Harruff, 1988 Kryovich, 1984 Lindrose, 1978 Parker, 1986 Rokhlin, 1986 Saliba, 1989 Sun, 1987 Thomas, 1988 Tuegel, 1986 Winfree, 1985 and 1986 Woo, 1987
	Gel Point	Alig, 1987 and 1988 Harrold, 1987
	Glass Transition Temp. Network Structure	Alig, 1987 and 1988
Performance	Various	Lamm, 1989 Pike, 1982 Tuegel, 1986

move the transducers across the sample surface in a raster pattern to produce a map of the defects. This is called a C-scan. The scattering technique generally gives information that is similar but not identical. As a result, scattering measurements can help provide additional data on the defect's characteristics. This approach may also be more sensitive to certain types of flaws than the through-transmission technique. The third variation involves measuring reflections. The amplitude of the reflected signal provides information about the defect that is similar to that obtained with the other methods, but the transit time measurement gives a direct indication of the depth of the defect in the sample.

It is worth noting that in most applications only one of these approaches is used despite the fact that the information obtained with the different methods is quite complimentary. By combining all three techniques, a much more detailed analysis is possible, and thus this should be strongly encouraged.

Porosity, fiber volume fraction, and orientation: Through transmission has also been used to estimate porosity in composites (Hsu, 1987; Lamm, 1989). The attenuation increases as the porosity levels become greater. Fiber volume fraction is another parameter that has been estimated by through transmission ultrasonics (Tornberg, 1988). In fact, a commercial instrument is currently available based on this idea (Test, Inc., 1989). Finally, through transmission can be used to estimate fiber orientation provided the patterns are relatively simple (Lamm, 1989; Saliba, 1989).

The success of the above procedures relies on the extensive work in the NDE field. As a result, these tests can accurately analyze simple systems, i.e., materials with only one feature to characterize. The current challenge is to extend these methods to complex situations such as the evaluation of a number of overlapping defects at different levels in the material. New approaches are available which show considerable promise to help in this area. These will be discussed in the section on Future Trends.

From the viewpoint of this report, the important question is the adaptation of this technology to the field of process monitoring. As indicated in Table 3.1, much has already been accomplished. There is still important challenges to be solved. The biggest difficulty is interpreting the data since the systems will always be quite complex in that both geometry parameters and material parameters must be analyzed simultaneously. The strong foundation established in the NDE work, however, will be of great help.

3.4.2.2 Geometry Factors by Interface and Wave Guide Methods

In addition to the direct measurement methods discussed above, both wave guide and interface techniques have been correlated with geometry parameters. For example, the shear wave reflection technique has been applied to study systems where the substrate-sample bond partially failed during cure (Hunston, 1985). In this experiment the attenuation of the reflected wave, which normally increases during cure, exhibited the normal behavior initially and then decreased as the interface bond failed. This was easily seen in the ultrasonic data although direct observation of the sample gave no indication of a problem. When the sample was removed, however, the difference in interface strength was clearly evident. In another study, the results from the fiber wave guide geometry were correlated with voids such as would be formed during cure (Harrold, in press). Again, excellent correlations were obtained provided the complicating effects of other factors were minimized. Unlike the NDE techniques, however, neither the interface method nor the wave guide technique has an appropriate mathematical analysis for the effects of geometry parameters. Consequently, the range of conditions over which the correlations are valid remains uncertain.

3.4.2.3 Material Parameters

The second category of correlations with cure monitoring results is material parameters. These parameters fall into two general classes: those that can, in principle, be related to ultrasonic results with an appropriate mathematical analysis, and those that require the use of a constitutive equation and a cure model to go beyond simple empirical correlations. It should be noted that even when a mathematical analysis is possible, it often has not been performed for the specific system used for process monitoring. Moreover, very little work has been done with constitutive equations and cure models. As a result many of the correlations that have been developed must be used very carefully since their range of validity is unknown.

Moduli and Viscosities: The most obvious correlation is between the ultrasonic results and the corresponding high frequency moduli. As detailed in the theory section, the mathematical relationships are well established for the direct measurement methods. With the wave guide and interface methods, mathematical analysis should be possible, but with the exception of shear waves, most of these situations have not been analyzed. Clearly, this is a fertile area for research. Unfortunately, even if the high frequency elastic properties are determined, these are of limited direct use for process control. To go beyond the high frequency elastic moduli requires additional assumptions. As mentioned in the theory section, even to estimate the low frequency moduli, a constitutive relationship (i.e. Figure 3.1) is required.

A good example of this is viscosity. Viscosity data is very useful for process control, and many ultrasonic experiments have been correlated to this parameter. For example, Figure 3.3 shows both viscosity results and attenuation data obtained with the shear wave reflection technique on a curing system (Chang, 1987). As can be seen in this Figure, the correlation prior to gelation is quite good. Similar correlations have been obtained with other types of ultrasonic experiments as well.

Several studies have tried to develop an analytical relationship between viscosity and ultrasonic data during cure (Elsley, 1986; Hahn, 1983; Tuegel, 1986). The procedure involves a process similar to the following. First, the ultrasonics data is converted to moduli, and the frequency dependence of the moduli is estimated with a constitutive equation. This equation will involve parameters such as the characteristic time described in the theory section. By using this equation the high frequency moduli can be used to estimate the low frequency moduli which are then converted to viscosity. This conversion is straight forward if the moduli are shear, but additional assumptions are required if they are not. To predict the behavior during cure, the characteristic time is related to molecular weight, and a kinetic cure model is used to describe the growth of molecular weight with time. Each of these steps involves assumptions and simplifications. As a result, the relationships are not simple and must be used with great care. For example, note that in Figure 3.3 the viscosity changes by 6 orders of magnitude while the attenuation changes by only a factor of 2. Consequently, any errors or uncertainty in the estimation of attenuation will give large differences in the prediction of viscosity.

Other Material Properties: As indicated in Table 3.1, a wide variety of other material parameters have been empirically correlated with ultrasonic cure data. Very few studies have attempted to develop analytical relationships between these properties and ultrasonics.

Clearly this is an important area for new research. It can be hypothesized, however, that more reliable correlations are likely with mechanical properties than with parameters such as network structure where the connection to ultrasonics is indirect and complex at best.

To illustrate the type of studies that have been published in this area, two examples are instructive. The first involves the fiber wave guide (Harrold, 1987). As mentioned earlier, the expected result is for the attenuation to increase and the velocity to decrease for the wave in the fiber as the sample cures. The experiments, however, show that the attenuation actually goes through a peak during processing, and the velocity shows the most significant change at approximately the same time. The authors observe that the peak in attenuation and rapid change in velocity corresponded to the gelation point in the sample.

The second example involves a correlation between the extent of reaction and attenuation data obtained with the shear wave reflection technique (Chang, 1987). An epoxy system was studied with both ultrasonics and differential scanning calorimetry (DSC). DSC measures the heat generated by the cure reaction and is therefore a direct measure of the extent of reaction. Figure 3.4 shows a comparison of the results from DSC and ultrasonics. The correlation is very good.

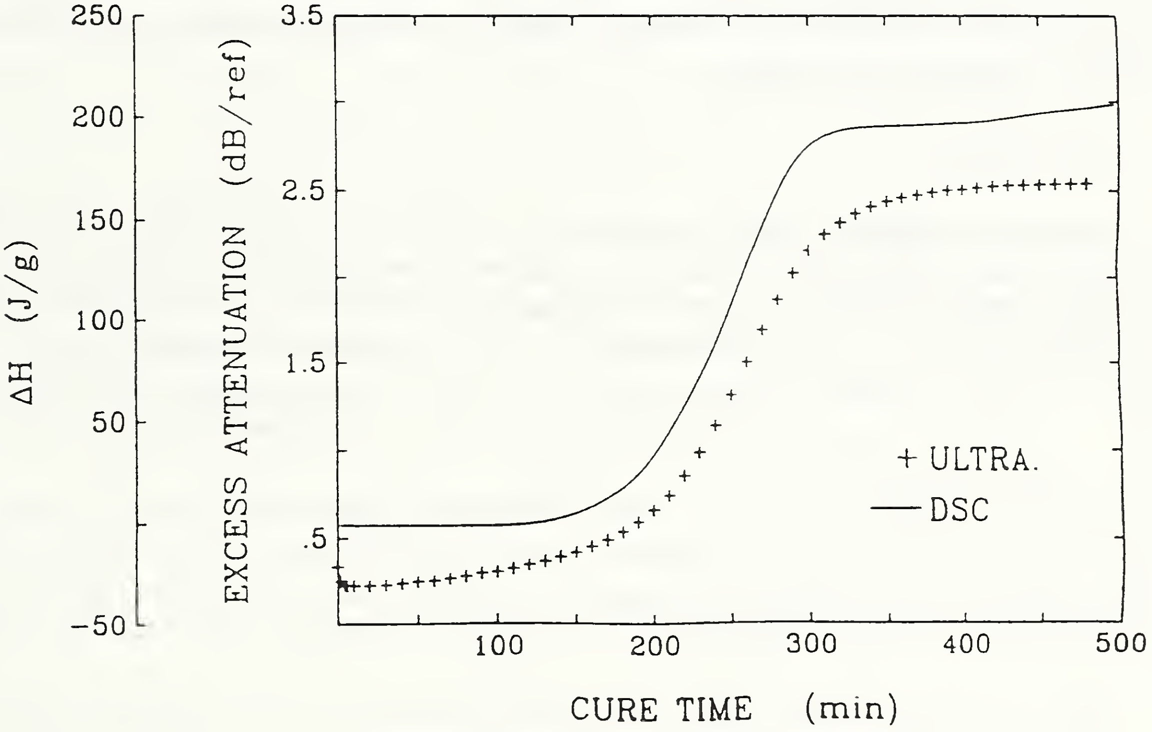

Figure 3.4 A comparison is made between ultrasonic data for the shear wave reflection technique and the heat generated during the reaction as measured by DSC. The sample is an epoxy (diglycidyl ether of bisphenol-A) cured with ethyl methyl imidazole. The attenuation is adjusted by subtracting the attenuation when no sample is present.

Such correlations can be very useful in converting ultrasonic data into quantities that provide direct information for process control. Nevertheless, these relationships must be used with care when a theoretical foundation has not been established. Unfortunately, the literature contains examples of exaggerated claims or insufficient warnings regarding the lack of knowledge concerning the range of validity for some correlations. This could lead to very unfortunate consequences. If industry uses the correlations outside their range of validity and have problems, many fabricators may discard the whole idea of process monitoring.

3.4.2.4 Performance

A few studies have tried to correlate ultrasonic cure data directly with some measure of performance (Pike, 1982; Tuegel, 1986; Lamm, 1989). Usually, the processing conditions are varied in some way, process monitoring data are recorded, and the finished parts tested. Correlations are then developed between the monitoring data and the test results. This is certainly the most direct approach and, if performed in a systematic way, can produce rapid results. In the short term, this can be quite useful. From a longer range perspective, however, such work must be coupled with more basic studies because only in this way can a scientific understanding be developed. Without such an understanding, the limits and reliability of the correlations will be uncertain, and it will be difficult to convince fabricators to use a correlation that can not guarantee a high degree of success. In addition, it will be hazardous to extrapolate outside the range of conditions actually tested, and testing all conditions is simply not possible.

3.4.3 Future Trends

There are a number of ongoing trends which could significantly advance the potential of ultrasonics. Most current applications use ultrasonics in the simplest possible way. Often only a single parameter, either velocity or attenuation, is obtained. Clearly, much of the potential information from ultrasonic methods is lost. As mentioned earlier, the real challenge is to handle complex systems where the response from multiple features must be analyzed. As a result, any lost information can be critical. What is required is a more aggressive use of ultrasonic methods. For example, the normal through transmission technique can be used to measure both transit time (or velocity) and attenuation for reflected signals, as well as the through transmission signals. In addition, multiple frequency tests can be used to generate data that helps distinguish between features such as flaws, fibers, and porosity, since their frequency dependencies are different (Rokhlin, 1986; Lamm, 1989).

Another approach to aggressive use of ultrasonics is to employ multiple modes of wave propagation. Several studies have combined both longitudinal and shear waves to provide additional information (Lindrose, 1978; Lamm, 1989). There have also been significant advances in signal analysis techniques. Such techniques can help both to separate noise from signal and to deconvolute signals which contain overlapping contributions from more than one feature. More research to fully utilize these advances is needed.

A final development that offers promise is the use of other monitoring techniques to help evaluate and calibrate ultrasonics results (Chang, 1987 and 1988; Cohen-Tenoudji, 1985; Fanconi, 1986 and 1987; Harruff, 1988; Saliba, 1987; Senich, 1984). Studies have correlated ultrasonic data with results from differential scanning calorimetry, several optical methods, and a variety of electrical techniques. Figure 3.5, for example, shows a number of comparisons of this type. The information gained in such studies not only helps to enhance the understanding of ultrasonics but also provides data for testing cure models. The development of improved constitutive equations and cure models is another critical area for future research, since this is required to gain a scientific basis for the correlations that are being made. This is vital to improve the reliability of monitoring methods. Finally, an integrated approach is needed since development in these areas compliment each other. With such an approach, significant progress can be made.

3.5 ACOUSTIC EMISSION

3.5.1 Background

Before closing the chapter on wave propagation, a few comments on acoustic emission (AE) are in order. In this technique, sensors are used to monitor any disturbances which are propagating through the material and are produced internally by a source such as the formation of a microcrack. To help stimulate these sources, the sample may be subjected to mechanical loads, thermal energy, or other stresses. The disturbances are then analyzed to determine as much as possible about the original source or sources. The simplest detection scheme is to measure the number of "events," where an event is defined as a displacement that reaches the sensor and has an energy or amplitude above a certain preset minimum. Consequently, a single source may produce one or more than one event. A more sophisticated detection method characterizes a disturbance by measuring the peak amplitude, total energy, rise time (the time required for the initial rise in signal intensity), duration, and/or other features of each event. Finally, in the most detailed detection method, the complete wave form of the disturbance can be recorded.

The key to AE is the so called inversion problem. Inversion is the characterization of the source of a disturbance from the signals measured by the sensor. To accomplish this, a number of factors which affect the received signal must be considered. First, there is the relationship between the source and the initial wave form of the disturbance. Second, the material can alter this wave form as it propagates to the sensor. Third, the coupling between the material and the sensor can affect the signal. Finally, the sensor and its electronics may change the wave form. Numerous improvements and calibration techniques have been developed to help simplify the analysis of these effects, but composites are very complex materials, and therefore, success with the inversion problem has been limited. Clearly, the more information that can be obtained, the better are the chances to define the source.

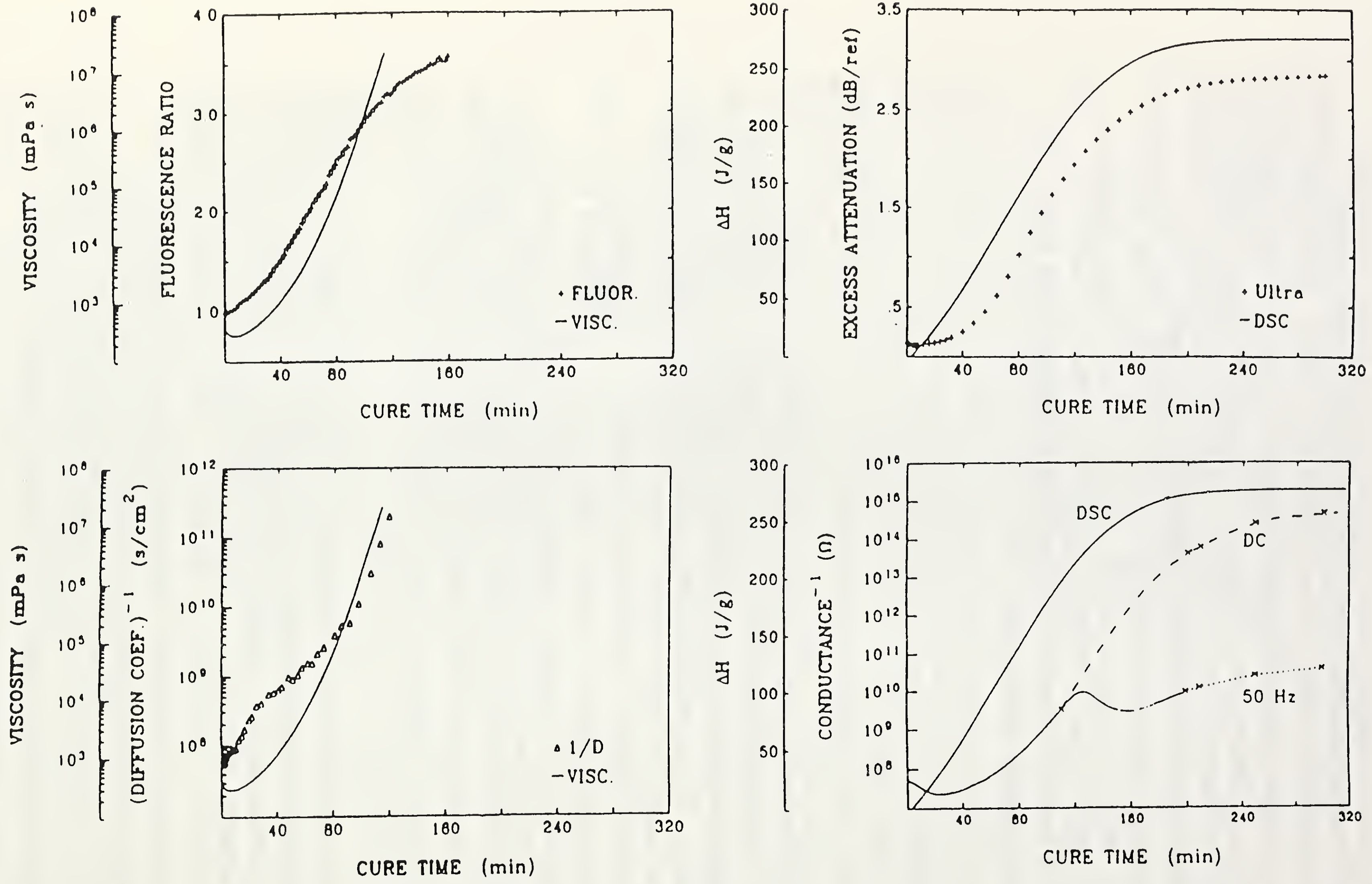

Figure 3.5 A comparison is made for data from six different cure monitoring techniques for an epoxy (diglycidyl ether of bisphenol-A) reacted with bis- (para-aminocyclohexy)methane. See other sections of this report for details on the fluorescence and electrical measurements. The upper left plot shows steady shear viscosity and fluorescence ratio data. The lower left plot compares the viscosity data with results for diffusion constant obtained with photo bleaching experiments using fluorescence. The plots on the right show DSC data compared with results from ultrasonic (top) and dielectric (bottom) experiments.

One approach that is being developed is the use of multiple sensors in an array. These sensors are distributed over the sample so that some will be close to the source. This improves sensitivity, and minimizes the changes in the wave form associated with propagation through the material. In addition, the arrival time at various sensors can be used to locate the position of the source while comparisons of the wave forms can help determine the effects of propagation through the material. The result is a significant improvement in the usefulness of AE.

The primary application of AE is the assessment of damage acquired through in-service use. Two major reviews of this technique (Hamstad, 1983 and 1985) were published some years ago, while a recent note in Advanced Composites (1988) indicates the current interest in AE by both manufacturers and equipment companies. These references also mention the application of AE to process monitoring. Although the work in this area is quite limited, some examples (Hinton 1986; Houghton 1979; Shuford 1985; St. Germain 1989) will illustrate the current state of the technology.

3.5.2 Process Monitoring During Cool Down

The most obvious application is in the cool down period following the completion of composite consolidation. In this case, the formation of cracks due to stresses resulting from differences in thermal expansion coefficients for the resin and the fibers can be a major event. These stresses can be quite large and complex since the fibers can have different axial and radial expansion coefficients. The interpretation of the results from such experiments is helped by the fact that the source (i.e. formation of cracks) is similar to that in the classic use of AE for damage assessment.

An example of the use of AE to monitor the cool down for E-glass-epoxy composites is the work at the Army's Materials and Mechanics Research Center (Hinton 1986; Houghton 1979; Shuford 1985). They found that a fast cool-down led to large and frequent AE bursts while slow cool-down resulted in small and infrequent AE activity. The high level of AE correlated with tests indicating a lower degree of residual stresses in the fast cooled specimens. This is consistent with the idea that more microcracks are formed by the rapid cooling, and these microcracks relieve the residual stresses. In addition, these studies found that the level of AE events was much greater below a critical temperature. It was suggested that this corresponded to the temperature at which the material becomes glassy, and this should be related to the glass transition temperature. Finally, the studies observed that AE levels were much greater for Kevlar-epoxy composites than glass-epoxy samples. This was attributed to the fact that Kevlar actually has a negative thermal expansion coefficient in the axial direction so the difference between the fiber and the matrix was even greater than for the glass-epoxy composites. The poor interface bonding with Kevlar may also have been a factor.

More recently, St. Germain and Wai conducted AE experiments during the fabrication of an actual part. As in the previous studies, these authors examined the effects of cool down following cure. They found results similar to those cited above but were able to provide more direct evidence to support their conclusions. By using visual and acoustic nondestructive evaluation techniques, they were able to establish a clear correlation between AE signals and void formation. As in the previous work, the strongest AE signals were found to occur below a critical temperature. In this case, however, the glass transition temperature was measured and found to be just above the temperature where most AE events occurred. Based on their results, St. Germain and Wai concluded that AE can be a useful tool in monitoring quality in a part during fabrication.

3.5.3 Process Monitoring During Heat-up

The scientists at the Army's Materials and Mechanics Research Center have also investigated the use of AE during the cure of glass-epoxy composites using a two-step cure cycle. They found that the AE activity increased with increasing temperature during the early part of the cure. There was an even more significant increase in AE signals during the second temperature step. It was suggested that the early activity was caused by outgassing of the resin, and the latter activity by cure shrinkage in the resin. The independent verification of this conclusion was less convincing, however. The work has also attempted to develop interpretations for the AE activity by combining AE results with data from other process monitoring techniques. Unfortunately, the studies in this area are quite limited, and more work is needed to clarify some of the issues.

3.5.4 Conclusions

Based on the current literature, it can be concluded that AE shows promise as a monitoring technique. At the present time, however, the results are very limited, and more work is needed to judge the ultimate potential of this method. Two final points should be made. First, the events, such as void formation, that produce AE are often the same events that must be avoided through process control. Consequently, the AE signal may come too late for the process to be modified. On the other hand, the same sensors and electronics that are used for AE can be used for some of the wave propagation measurements discussed in the previous section of this chapter. Consequently, adding AE measurements may involve minimal additional effort.

3.6 **REFERENCES**

References of Wave Propagation Methods

Adler, L., Rose, W. R., Rokhlin, S. I., and Nagy, P. B., "Lamb Wave and Leaky Lamb Wave Characterization of Fiber Reinforced Composites," p. 263 in Advanced Composites: the Latest Developments, (ASM, Metals Park, 1986).

Adv. Mater., "Embedded Wave Guides Monitor Composite Cures and Stresses," 8(23), 2 (1987).

Alig, I., Haeusler, K. G., and Unger, S., "Gel Point Determination in Polymers," Patent, Aug. 25, 1987.

Alig, I., Haeusler, K. G., Taenzer, W., and Unger, S., "Monitoring of Crosslinking and Characterization of Modified Epoxy Resins by Ultrasonic Techniques," Acta Polym., 39, 269 (1988).

Applied Polymer Technology, Escondido, CA, Technical Literature, 1989.

Bujard, M., Tittmann, B. R., Ahlberg, L. A., and Cohen-Tenoudji, F., "Dynamic Viscosity Measurement of fluids Employing Resonance Characteristics of a Piezoelectric Element Vibrating in the Shear Mode," p. 1267 in Review of Progress in Quantitative NDE, Vol. 6B, Ed. Thompson, D. O. and Chimenti, D. E., (Plenum Press, New York, 1987).

Chang, S. S., Mopsik, F. I., and Hunston, D. L., "Correlation of Cure Monitoring Techniques," Proc. 19th Intl. SAMPE Tech. Conf., 19, 253 (1987).

Chang, S. S., Hunston, D. L., and Mopsik, F. I., "Cure Monitoring Techniques for Thermoset Resins," P. 91 in How to Apply Advanced Composites Technology, Advanced Composites Conference and Exhibition, ASM, 1988.

Cohen-Tenoudji, F., Pardee, W. J., Tittmann, B. R., Ahlberg, L. A., and Elsley, R. K., "Ultrasonic Monitoring of Thermally Curing Resins with the Use of Shear Wave Reflectivity," p. 535 in Proc. IEEE Ultrasonics Symposium, Vol. I, Oct. 16, 1985.

Elsley, R. K., Pardee, W. J., Buckley, M. J., Cohen-Tenoudji, F., and Fertig, K. W., "Advanced Concepts in the Control of Autoclave Cure of Composites," p. 1015 in Review of Progress in Quantitative NDE, Vol. 5B, Ed. Thompson, D. O. and Chimenti, D. E., (Plenum Press, New York, 1986).

Fanconi, B. M., Wang, F. W., Hunston, D. L., and Mopsik, F., "Cure Monitoring for Polymer Matrix Composites," p. 275 in Materials Characterization for Systems Performance and Reliability, McCauley and Weiss, Eds. (Plenum Pub. Corp., New York, 1986).

Fanconi, B. M., Wang, F. W., and Hunston, D. L., "Comparisons among Process Monitoring Techniques," p. 1100 in Proc. ANTEC 87, SPE, May 4, 1987.

Hahn, H. T., "Application of Ultrasonic Technique to Cure Characterization of Epoxies," p. 315 in Nondestructive Methods for Material Property Determination, Ed. Ruud, C. O., and Green, R. E. (Plenum Press, New York, 1983).

Harrold, R. T., and Sanjana, Z. N., "Acoustic Wave Guide Monitoring of the Cure and Structural Integrity of Composite Materials," Polym. Eng. Sci., 26(5), 367 (1986A).

Harrold, R. T., and Sanjana, Z. N., "Theoretical and Practical Aspects of Acoustic Wave Guide Cure Monitoring of Composites and Materials," Proc. 31st International SAMPE Symposium, 31, 1713 (1986B).

Harrold, R. T., and Sanjana, Z. N., "Non-Destructive Evaluation of the Curing of Resin and Prepreg Using Acoustic Wave Guide Sensors," p. 1277 in Review of Progress in Quantitative NDE, Vol. 6B, Ed. Thompson, D. O. and Chimenti, D. E., (Plenum Press, New York, 1987).

Harrold, R. T., and Sanjana, Z. N., "Acoustic Characterization of Curing Process using Wave Guides Embedded Within Polymers," p. 1549 in Review of Progress in Quantitative NDE, Vol. 7B, Ed. Thompson, D. O. and Chimenti, D. E., (Plenum Press, New York, 1988).

Harrold, R. T., and Sanjana, Z. N., "Cure Monitoring of Composites using Multiple Acoustic Wave Guides," Review of Progress in Quantitative NDE, Vol. 8, Ed. Thompson, D. O. and Chimenti, D. E., (Plenum Press, New York, in press).

Harruff, P. W., Levy, R. L., Harrold, R. T., Sanjana, Z. N., and Schwab, S., "Composite Curing Process Nondestructive Evaluation, Final Report, Sep. 1985 - Dec. 1987," Report No. AD-A197834 AFWAL-TR-88-4707-2, June 1988.

Hsu, David K., "Porosity Evaluation in Composite Laminates by of Ultrasound," Proc. AUTOCOM 87, Paper IQ87-354, SME, 1987.

Hunston, D. L., "Cure Monitoring of Thermoset Polymers by an Ultrasonics Technique," p. 1711 in Review of Progress in Quantitative NDE, Vol. 2B, Ed. Thompson, D. O. and Chimenti, D. E., (Plenum Press, New York, 1983).

Hunston, D. L., Koutsky, J. A., and Weisshaus, H. "Measuring Rheological Changes in Adhesives During Bond Formation and Cure," Proc. Adhesion Society Meeting, Feb. 24, 1985.

Krylovich, V. I., Ermolenko, I. N., Alekseeko, V. I., Dubkova, V. I., Logvinovich, P. N., and Lyubliner, I. P., "Ultrasonic Method of Monitoring the Setting of an Epoxy Composition," Ultrason., 14(4), 126 (1984).

Lamm, F., et al, United Technologies, personal communication, 1989.

Lindrose, A. M., "Ultrasonic Wave and Moduli Changes in a Curing Epoxy Resin," Experimental Mechanics, 227 (1978).

Martin, S. J., Ricco, A. J., and Taylor, P. A., "Viscosity Sensor Utilizing Horizontally Polarized Shear Waves," unpublished manuscript, 1989.

Parker, F. R., and Winfree, W. P., "Acoustic Characterization of Composite Cure," p. 1063 in Review of Progress in Quantitative NDE, Vol. 5B, Ed. Thompson, D. O. and Chimenti, D. E., (Plenum Press, New York, 1986).

Pike, R. A., and Williams, R. S., "Ultrasonic Assessment of Cure Rate Effects in Bonded Honeycomb Structures," Org. Coatings and Plastics Prep., 47, 115 (1982).

Ricco, A. J., and Martin, S. J., "Acoustic Wave Viscosity Sensor," Appl. Phys. Lett., 50(21), 1447 (1987).

Rokhlin, S. I., "Adhesive Joint Characterization by Ultrasonic Surface and Interface Waves," p. 307 in Adhesive Joints: Formation, Characterization, and Testing," Vol. 2, Ed. Mittal, K. L., (Plenum Press, New York, 1984).

Rokhlin, S. I., Lewis, K., Graff, K. F., and Adler, L., "Application of Spectral Analysis Techniques for the Study of Curing Reactions in Epoxy Resins," p. 1047 in Review of Progress in Quantitative NDE, Vol. 5B, Ed. Thompson, D. O. and Chimenti, D. E., (Plenum Press, New York, 1986).

Rokhlin, S. I., "Adhesive Joint Evaluation by Ultrasonic Interface and Lamb Waves," p. 290 in Materials Analysis by Ultrasonics: Metals, Ceramics, Composites, (Noyes Data Corp., New Jersey, 1987).

Saliba, S. S., Saliba, T. E., and Lanzafame, J. F., "Acoustic Monitoring of Composite Materials During Cure," 34th International SAMPE Symposium, May 8, 1989.

Senich, G. A., Flynn, J. H., Phillips, J. C., and Weisshaus, H., Cure Kinetics Measurements on Polymer Composite Matrix Materials, Polymer Preprints, 25(2), 211 (1984).

Sun, K. J., and Winfree, W. P., "Propagation of Acoustic Waves in a Copper Wire Embedded in a Curing Epoxy," p. 439, in Proc. IEEE Ultrasonics Symposium, Oct. 14, 1987.

TEST Inc., San Diego, CA, Technical Literature, 1989.

Thomas, L. J., "Use of Marginal Oscillator for Acoustic Monitoring of Cure of Epoxy Resin," p. 1555 in Review of Progress in Quantitative NDE, Vol. 7B, Ed. Thompson, D. O. and Chimenti, D. E., (Plenum Press, New York, 1988).

Tittmann, B. R., Ahlberg, L. A., Bulau, J. R., and Cohen-Tenoudji, F., "Ultrasonic NDE of Non-Newtonian Fluids for Material Processing," p. 1027 in Review of Progress in Quantitative NDE, Vol. 4B, Ed. Thompson, D. O. and Chimenti, D. E., (Plenum Press, New York, 1985).

Tornberg, N. E., "A Novel Ultrasonic Technique for the Nondestructive Determination and Mapping of Fiber/Resin Ratio of Advanced Composites," p. 1738 in Proc. 33rd International SAMPE Symposium, March 7, 1988.

Tuegel, E. J., and Hahn, H. T., "Ultrasonic Characterization of Epoxy Resins: Constitutive Modeling," Progress Report, Office of Naval Research (N00014-85-K-0795), Oct. 1986.

Winfree, W. P., and Parker, F. R., "Ultrasonic Characterization of Changes in Viscoelastic Properties of Epoxy during Cure," p. 1203 in Review of Progress in Quantitative NDE, Vol 4B, Ed. Thompson, D. O. and Chimenti, D. E., (Plenum Press, New York, 1985).

Winfree, W. P., and Parker, F. R., "Measurement of the Degree of Cure in Epoxies with Ultrasonic Velocity," p. 1055 in Review of Progress in Quantitative NDE, Vol. 5B, Ed. Thompson, D. O. and Chimenti, D. E., (Plenum Press, New York, 1986).

Woo, E. M., and Seferis, J. C., "Thermal Sonic Analysis of Polymer Matrixes and Composites," J. Compos. Mater., 21(3), 262 (1987).

References for Acoustic Emission

Advanced Composites, "Prefailure Warning System Contracted," November/December, 22, 1988.

Hamstad, M. A., "Quality Control and Nondestructive Evaluation Techniques for Composites - Part VI: Acoustic Emission - A State-of-the-Art Review," AVRADCOM Report No. TR 83-F-7, 1983.

Hamstad, M. A., "A Review: Acoustic Emission, a Tool for Composite-Materials Studies," Experimental Mechanics, March, 7, 1986.

Hinton, Y. L., Shuford, R. J., and Houghton, W. W., "Acoustic Emission During Cure of Fiber Reinforced Composites," Proceedings of the Critical Review: Techniques for the Characterization of Composite Materials, AMMRC MS 82-3, May 1982, p. 25.

Houghton, W. W., Shuford, R. J., and Sprouse, J. F., "Acoustic Emission as an Aid for Investigating Composite Manufacturing Processes," 11th National SAMPE Technical Conference, 131 (1979).

Shuford, R. J., Hinton, Y. L., Murray, T. J., and Brockelman, R. H., "Advanced NDE Techniques for Composites," Proceedings Conference on Composites in Manufacturing 4, SME, January 1985, p. EM85-113.

St. Germain, S. A., and Wai, M. P., "Utilization of Acoustic Emission to Monitor Integrity of a Composite Structure During Autoclave Cure," 34th International SAMPE Symposium, 2141 (1989).

OPTICAL AND SPECTROSCOPIC TECHNIQUES

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4.1 SUMMARY

Spectroscopic techniques provide the most direct measure of the degree of cure since these methods directly sense the chemical state of the reactants. Remote sensing with spectroscopic techniques as well as several other optical methods described herein may be achieved through optical fibers. Although most cure monitoring work has not been concerned with remote sensing applications, there have been a few promising reports of the use of optic fibers for cure monitoring and an extensive literature on optical fiber sensors for other chemical and physical properties. These other applications of optical fibers illustrate approaches to their use for cure monitoring. The stability of optical fibers over the temperature and pressure ranges of thermoset cure combined with the predictable response of spectroscopic methods to temperature and pressure add to their attractiveness to monitor cure. Furthermore, data acquisition and analysis times for all optical and spectroscopic techniques are well within requirements for remote sensing with feedback control.

Electronic and vibrational spectroscopy have been applied in laboratory studies of the degree of cure of thermosets. The most versatile and potentially useful of the spectroscopic techniques utilizes fluorescence probes which are sensitive not to the chemical state of the reactants, but to the resin viscosity. These probe molecules, added to the resin in extremely dilute concentrations, have been shown to have high sensitivity from inception of cure to gelation, and somewhat lower sensitivity from gelation to vitrification. In other applications, electronic state absorption and fluorescence spectroscopies have been used to monitor cure of specific resin systems through direct observation of reactive species. Chemiluminescence, which results from combination of free radicals produced by oxidation, has been applied as well, but the general applicability has not been shown to date.

The recent availability of infrared transmitting optical fibers opens up the use of vibrational spectroscopy which directly measures concentrations of chemical species involved in cure processes. Thus, the wealth of infrared spectroscopic data in the literature may be exploited in cure monitoring applications.

Optical methods involve measurement of effects of curing resins, i.e. changes in refractive index, on the light transmission properties of optical fibers. These methods also require an optic fiber specific to the resin system to be sensed.

Although no commercial systems exploiting optical and spectroscopic techniques for cure monitoring are available at present, and unlikely in the near term, it appears that technical barriers to their exploitation could be removed in the 3 to 5 year time frame. With the exception of those methods specific to particular resin systems all the optical and spectroscopic methods are usable over a wide range of temperatures and pressures. As the more promising techniques essentially measure viscosity an accurate measurement of temperature would also have to be made.

4.2 INTRODUCTION

Spectroscopic techniques provide the most direct measure of the degree of cure since these methods directly sense the chemical state rather than a bulk property, such as sonic velocity, which is only remotely related to chemical structure. Indeed, the infrared band assigned to a vibration of the epoxide group, whose concentration decreases during polymerization of epoxies, is routinely used to measure the degree of cure in laboratory studies (Lee, 1967).

Several types of spectroscopy have been utilized to the determination of the cure state by probing the electronic (Fanconi, 1986, 1987A, 1987B; Levy, 1983A, 1983B, 1984; Sung, 1985, 1986; Wang, 1985, 1986, 1987A, 1987B) (UV-Vis), vibrational (Lee, 1967; Garton, 1984; Wu, 1983; Young, 1989) (infrared and Raman), or nuclear (Havens, 1983) (nuclear magnetic resonance) properties of molecules. These spectroscopies share in common the sensitivity of transition frequencies and intensities to the chemical bonding state of molecules. Discussion are limited to electronic and vibrational spectroscopies since at the present stage of development it seems unlikely that nuclear magnetic resonance (NMR) will have an application for on-line monitoring the degree of cure. The increase in NMR linewidth with molecular rigidity limits the applications at high degrees of cure. Nonetheless, NMR may be used to characterize in-coming materials, such as prepregs, where sufficient molecular mobility exists to produce high quality NMR spectra.

The other spectroscopy types mentioned above have potential for remote sensing through the use of optical fiber waveguides (Andrade, 1985; Boisde, 1984; Dahne, 1984; Giallorenzi, 1978; Hirschfield, 1983; Lew, 1984; Maugh, 1982; Munkholm, 1986; Newby, 1984, 1986; Peterson, 1984; Rockhold, 1983; Schirmer, 1988; Schwab, 1984; Tromberg, 1984; Weyer, 1987). The combination of optical fibers and sensing elements are referred to as fiber optic sensors (FOS). Although line-of-sight access to the sample in the manufacturing environment may suffice for surface interrogation by optical spectroscopic techniques, optical fibers clearly offer the most versatile means of remote sensing. Indeed, the optical fiber may be imbedded in the curing specimen to probe the state of cure in the interior of a composite structure (Fanconi, 1986).

Developments over the last decade in the communication industry have led to a variety of special components such as connectors, multiple couplers, and input-output optics for manipulating light in waveguides (Giallorenzi, 1978). Although designed specifically for communication-quality fibers, many of these components can also be used with other optical fibers, such as infrared transmitting fibers. Communication quality optical fibers are readily adaptable to remote sensing with visible radiation, whereas other regions of the electromagnetic spectrum, i.e. infrared, require special fibers.

Prior to a discussion of research and development activities in fiber optic sensors (FOS), the various spectroscopies, the quantities measured and their relationships to chemical degree of cure, and principles of optical waveguides are reviewed. Emphasis is placed on aspects deemed important to the further application of spectroscopic methods to remote sensing the degree of cure. Although the majority of the investigations involve only laboratory studies on neat resin, the following issues are addressed to the extent possible.

- sensitivity throughout the cure range
- measurement and data processing time
- sampling considerations
- sensitivity to the manufacturing environment and temperature
- application to various resin systems
- capability for on-line, real time measurements

Next, applications of FOS to monitoring the state of cure as well as related developments are reviewed.

4.3 MEASUREMENT TECHNIQUES

4.3.1 Vibrational Spectroscopy

As indicated in the Introduction, infrared (IR) spectroscopy has been widely used in laboratory studies of thermoset cure (Lee, 1967). Adaptation of IR to the production environment has been stymied, however, by the lack of robust fibers which transmit infrared radiation. Raman spectroscopy, another form of vibrational spectroscopy, which involves the inelastic scattering of light by molecular vibrations or phonons, may be easier to implement in remote sensing since visible light, readily transmitted by optic fibers, carries the spectral information. Both IR and Raman spectroscopies measure vibrational frequencies and intensities sensitive to chemical bonding and molecular conformation. To probe the state of cure, primarily interest will be in types and concentrations of certain chemical bonds.

The frequencies of molecular vibrations occur in the range 10-4000 cm^{-1}, where cm^{-1} is the reciprocal wavelength, $\hat{\nu}$, and is related to frequency, ν, by the speed of light, c, $\hat{\nu} = \nu/c$. Owing to the nonharmonic effects, molecules also absorb radiation of frequencies which are multiples or sums of the frequencies of fundamental vibrations. These transitions, termed overtones (multiples of the fundamental vibrations) or combinations (sums of the fundamental vibrations), are of interest since the frequencies lie in the range 3000-10000 cm^{-1} for which several different materials are sufficiently transparent and robust for optical fibers (Fredericks, 1987; Schirmer, 1988). Transitions in the region 4000-10000 cm^{-1}, termed the near infrared (NIR), absorb more weakly than those of the fundamentals since absorption probabilities depend on the small anharmonic character of the fundamental vibrations. Nonetheless, owing to simplifications in instrumentation and the availability of optical fibers, NIR spectroscopy shows promise as a cure monitoring technique.

4.3.1.1 Infrared

The typical application of infrared spectroscopy measures absorption of a beam transmitted through the specimen, although reflectance, emission, photoacoustic detection, and combinations of reflectance and absorption have been employed in unusual sampling cases. Researchers reported the use of two different sampling schemes to conduct remotely infrared absorption measurements of cure (Weyer, 1987). One scheme positions the sample in a gap between two infrared transmitting optic fibers, and measures the amount of light absorbed in the gap. In the second technique, the sample absorbs radiation from the evanescent wave of the guided light, and the intensity decrease of the transmitted light is measured.

Developments in IR instrumentation also facilitate adaptation of IR to cure monitoring. The most important development involves using interferometers rather than dispersive instruments based on gratings or prisms (Fanconi, 1984). Interferometers, combined with highly monochromatic laser light sources and powerful computers, have made this technique, called Fourier Transform IR, FT-IR, far superior to conventional dispersive IR spectroscopy. Improvements in frequency accuracy result from the use of lasers to calibrate mirror positions in interferometers and gains in sensitivity (signal-to-noise) result mainly from the high throughput of interferometers compared to the slit dependent bandwidth of dispersive instruments. Conventional instrumentation may still have application to cure monitoring, however, particularly when a single IR band is interrogated (Lee, 1967).

4.3.1.2 Raman

Raman spectroscopy measures the intensity and frequency shifts of inelastically scattered light. The frequency shifts equal the vibrational frequencies of the molecule and the intensities relate to changes in the polarizability tensor caused by the vibrating molecule. Raman and infrared spectroscopy complement one another, since infrared intensities are related to the change in the dipole moment caused by the molecular vibration.

Frequently, the Raman spectra of organic substances are obscured by luminescence from species which undergo electronic excitations at the Raman excitation frequency. Conventional Raman scattering is an exceeding weak effect in that typically only one in 10^7 photons is inelastically scattered. By contrast, the fluorescence yield may be very high, approaching one photon of emitted light for every photon absorbed light.

Typically, lasers operating in the visible region of the electromagnetic spectrum are used in Raman spectroscopy, owing to their monochromaticity, high intensity, and also the high sensitivity of detectors in the visible range. Although most organic compounds do not absorb in the visible region, the high efficiency of the fluorescence process compared to the Raman effect means that fluorescent impurities, in even exceedingly small concentrations, may interfere with the observation of Raman scattered photons (Peticolas, 1971).

The low sensitivity of Raman spectroscopy can be overcome by excitation with radiation at or near an electronic state absorption. In this case, a significant enhancement of the Raman intensity of those vibrational modes coupled to the electronic transition occurs. This technique has been applied to organic molecules which absorb in the visible region (Bloor, 1976). Another approach which circumvents the fluorescence problem involves excitation at frequencies in the near infrared, far from electronic absorptions which may give rise to fluorescence (Fujiwara, 1986). One weakness of this technique is that the Raman scattering efficiency is proportional to the fourth power of the frequency, so that lowering the excitation frequency also lowers the scattering probability. To overcome this difficulty together with the lower detector sensitivity in the near infrared, several researchers employed interferometers and Fourier transform spectroscopy (Hirschfield, 1986).

Reports of evanescently generated Raman scattering appeared in the literature (Schwab, 1984), and one may conclude that similar approaches may be applicable to cure monitoring. However, few laboratory studies of cure by Raman spectroscopy have been reported and more basic work to identify appropriate vibrational modes to follow the cure of thermosetting resins needs to be done before one can truly assess the potential of Raman spectroscopy for cure monitoring.

4.3.2 UV-Vis Spectroscopy

4.3.2.1 Absorption

Ultraviolet and visible absorption spectroscopies also have been explored, in some cases rather successfully, to monitor the degree of cure (Sung, 1986). These spectroscopies, together with fluorescence spectroscopy, probe the electronic states of molecules. Since chemical bonds are broken and formed in the curing process, the electronic states of the reacting species undergo changes which affect electronic absorption and fluorescence spectra. Most electronic transitions of organic molecules occur in regions of the electromagnetic spectrum inaccessible with conventional instrumentation. In fact, carbon-carbon single bond electronic excitations lie in the vacuum ultraviolet region, $<$ 200nm, which require, as the name implies, conducting experiments in a vacuum, and also using special sources and detectors. However, carbon-carbon double bonds and other carbon single bonds absorb in regions accessible by conventional instrumentation. Compared to the infrared, the UV-Vis region is of limited usefulness in the determination of types and concentrations in multicomponent systems. This arises because the ratio of typical spectral width to the overall frequency range is 1 to 400 in the infrared, but only 1 to 10 in the usual UV-Vis spectral range. Thus, electronic absorption bands tend to overlap making resolution of spectral contributions from specific species difficult, if not impossible.

4.3.2.2 Fluorescence

Fluorescence spectroscopy may be the most versatile UV-Vis technique in that fluorescence appears against a low intensity background whereas absorption removes only a few percent of the photons impinging on the sample, hence one measures small changes in large signals. Furthermore, fluorescence processes can be very efficient, that is, nearly every photon absorbed results in an emitted photon. For these reasons, fluorescence is commonly observed from species diluted to one part per million. This observation suggests that molecules whose fluorescence characteristics are sensitive to the degree of cure may be used as probes. Indeed, much work has been reported on just this application (Fanconi, 1986, 1987A, 1987B; Levy, 1983A, 1983B, 1984; Sung, 1985, 1986; Wang, 1985, 1986, 1987A).

4.3.2.3 Chemiluminescence

Chemiluminescence is another type of emission spectroscopy which has been applied to monitor the cure of epoxies (George, 1986). Chemiluminescence refers to light emitted as a consequence of chemical reactions, usually involving oxidation. In polymers, chemiluminescence is thought to result from recombination of free radicals produced during free radical auto-oxidation. Two free radicals are involved in the recombination process and the reaction rate is controlled by the free radical diffusion constant. Since the diffusion constant is related to medium viscosity the chemiluminescence intensity should relate to the degree of cure.

4.4 OPTICAL FIBERS

Thus far, the discussion has focussed on spectroscopic measurements performed in the laboratory. However, to be useful in process monitoring the technique must be adaptable to the manufacturing environment and provide real time measurement. Although line-of-sight access to the sample in the manufacturing environment may suffice for surface interrogation by Raman and fluorescence spectroscopies, optical fibers provide a more versatile method of transmitting radiation to a site within a production facility and of retrieving the modulated light and transmitting it to the detection system. Light delivered by optical fibers can probe either the surface of the sample, or the interior of the sample by embedding the fiber.

4.4.1 Waveguides

Optical fibers transmit light by total internal reflection (Giallorenzi, 1978). Light focussed onto the entrance face (normal to the fiber axis) intersects the fiber-medium interface at an angle determined by Snell's law. What happens to the light at the interface depends on the refractive indices of the fiber and the medium as well as the angle of incidence at the interface. If the refractive index of the medium is lower than that of the fiber an angle of incidence exists beyond which no net energy flows into the rarer medium.

Light propagating in the fiber at angles of incidence greater than this angle, termed the critical angle, are guided by the fiber. The electric field amplitude of the guided wave decays exponentially in the lower index medium with the exponent dependent on the refractive indices of the fiber and medium, the angle of incidence at the interface, as well as the wavelength of light (Rockhold, 1983). Evanescent wave refers to the electric field in the rarer medium and the penetration depth defines the distance over which its amplitude decreases to 1/e of the value at the interface. If the lower refractive index medium interacts with evanescent wave by absorption or scattering, the amplitude of the evanescent wave diminishes and the guided beam loses intensity.

4.4.2 Commercial Fibers

Commercial optical fibers designed for optical communication are attractive for cure monitoring owing to availability of not only fibers but associated fiber couplers, manipulation devices, optical components, and related instrumentation (Giallorenzi, 1978). Communication fibers consist of glass silica cores surrounded by lower index cladding, generally a silicone polymer, which protects the fiber and maintains a constant and lower refractive index. Another layer of material, for example, polyethylene, surrounds the cladding to provide further protection. The refractive index profile within the silica core may also be designed to improve transmission properties. Step index fibers refer to a constant refractive index in the silica core and a step in the refractive index at the silicone cladding. Graded index fibers have a decreasing index from the fiber axis to the cladding.

Most communication fibers are multimode fibers, that is, light rays of many angles of incidence at the fiber-cladding interface will propagate through the fiber. These fibers are characteristically greater than 50 microns in diameter. A characteristic of multimode fibers is that they do not preserve the polarization of light. Another type of fiber transmits only a single mode, that is, light of one angle of incidence (Jeunhomme, 1983). Single mode fibers preserve the polarization of the transmitted light, an important feature of sensor designs in which the phase and polarization of the transmitted light depend on physical properties of the environment. The core diameters of single mode fibers are much smaller than those of multimode fibers and a glass cladding surrounds the core to better define the propagating mode. The design of a single mode fiber is specific to the wavelength of light propagated.

4.4.3 Remote Sensors

Researchers have utilized three different properties of optical fibers in the design of cure monitoring probes. One design uses the fiber to transmit the probing radiation to the sampling site situated at the fiber terminus which may be at the surface of the specimen, or in the interior (Schwab, 1988). The light exits the fiber in a cone defined by the numerical aperture of the fiber, and probes material lying in this cone. Optical elements may be placed at the fiber terminus to concentrate the light, i.e. lens, or to direct the light through the sampling volume into another, or the same fiber for transmission to the detection system. In this design, the fiber cladding remains on the fiber to ensure that the probing radiation reaches the fiber terminus. In another design, the cladding is stripped from the embedded fiber, and the evanescent wave probes the medium (Fanconi, 1986; Young, 1989). If the medium absorbs at the frequency of the propagated light, then the transmitted light intensity decreases. This is equivalent to attenuated total reflection which is widely used in infrared spectroscopy to measure infrared absorption of opaque materials or surface layers since the penetration depth of the evanescent wave is of the order of 100 nanometer (Levy, 1984). A third design uses the dependence of the guided light on the refractive index difference between fiber and medium to monitor characteristics of the medium (Afromowitz, 1988, 1989). This type operates more like a switch, that is, it senses when a particular condition has been achieved, rather than a continuous measurement of a property.

4.5 **CURE MONITORING**

4.5.1 Vibrational Spectroscopy

4.5.1.1 Mid Infrared Spectroscopy

A number of laboratory studies of thermoset cure exploited the ability of mid-infrared spectroscopy to determine the type and concentrations of chemical bonds (Lee, 1967; Wu, 1983; Compton, 1988; Young, 1989). From this information the kinetics of cure can be determined in most cases since it is usually possible to identify infrared bands associated with the various reactants and products of the crosslinking chemistry. The limited reported work (Compton, 1988; Young, 1989) applying vibrational spectroscopy to remote sensing the degree of cure underscores the need to develop inexpensive and robust optic fibers for the mid infrared spectral region, and to a lesser extent, for the near infrared. Nonetheless, recent reports encourage further studies, particularly in mid-infrared spectroscopic methods. Compton, et al. (1988) and Young, et al. (1989) reported the use of an infrared transmitting chalcogenide fiber to monitor conversion of poly(amide acid) to polyimide resins and transformation of prepreg to graphite composites. A schematic of their experimental arrangement which utilized attenuated total reflection in the mid infrared (1250 cm^{-1} to 3250 cm^{-1}) as the sensor is shown in Figure 4.1. A 0.1mm O.D. fiber with an arsenic germanium selenide core of 120 microns and silicone polymer cladding transmits IR in the frequency range 1200-3000 cm^{-1} a distance of about 3 meters. Absorption of evanescent light by the silicone polymer greatly reduces the spectral range accessible by this technique. Nonetheless, a 3-6 cm length of the fiber, stripped of cladding and exposed to the sample produced sufficient spectral data to monitor cure as shown by the plot of the absorbance of the 1710 cm^{-1} imide band as a function of cure temperature, shown in Figure 4.2.

In this preliminary work, (Compton, 1988; Young, 1989) a high quality Fourier Transform Infrared instrument was used in conjunction with an IR microscope and high-sensitivity mercury, cadmium, telluride detector. To produce an infrared spectrum with this instrumentation required a measurement time of about one minute and a similar time

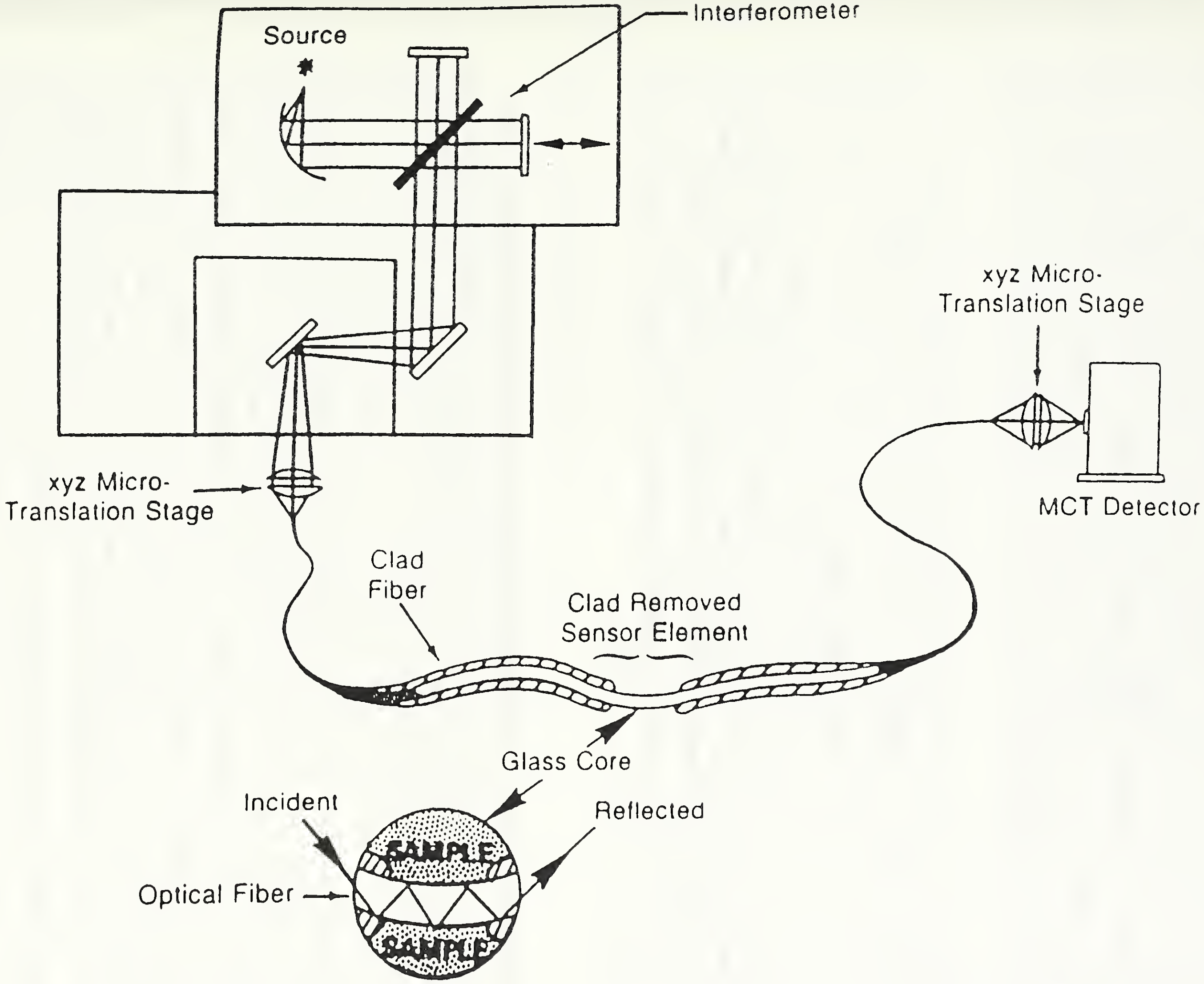

Figure 4.1 Schematic of experimental arrangement of an infrared fiber optic sensor. A Fourier transform interferometer processes the optical throughput of the infrared transmitting fiber, a portion of which is stripped of cladding and exposed to the sample. (After Young, P.R., Druy, M.A., Stevenson, W.A., and Compton, D.A.C., SAMPE J. 25 (2), 11 (1988).)

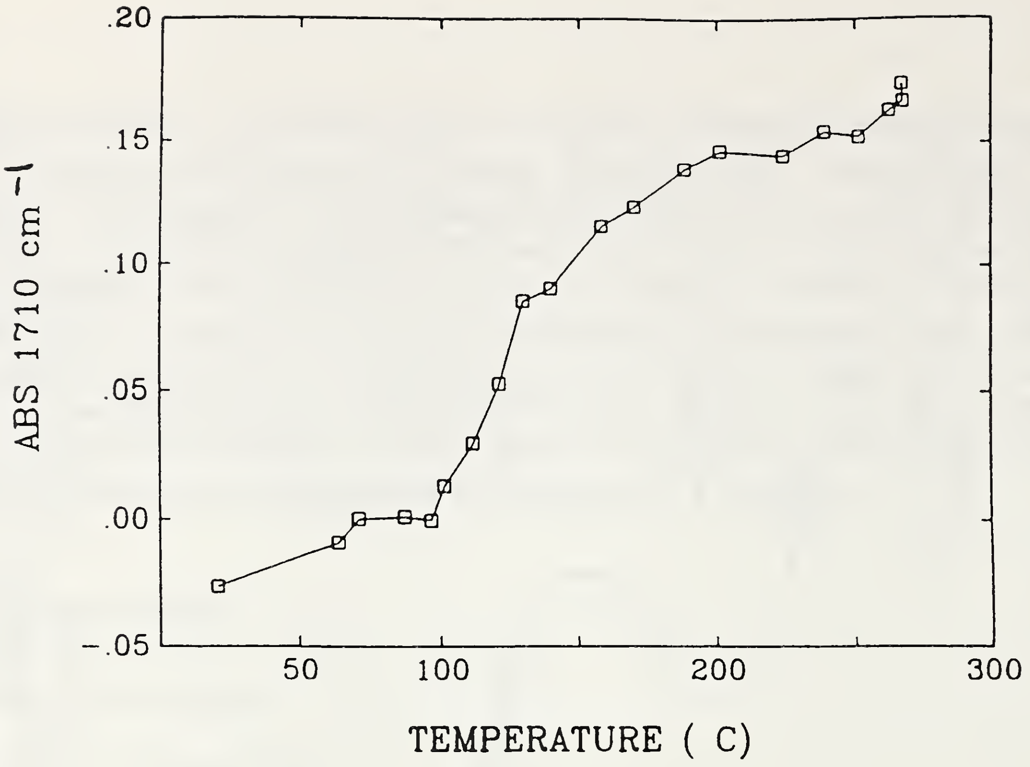

Figure 4.2 Cure curve of polyimide-graphite prepreg PMR-15 presented as the absorbance of the imide 1710 cm-1 band vs. cure temperature. Data were taken from spectra ratioed against the 206° spectrum. (After Young, P.R., Druy, M.A., Stevenson, W.A., Compton, D.A.C., SAMPE J., 25 (2), 11 (1989).)

interval to transform the interferogram to an absorption spectrum. In the latter stages of cure the spectral changes diminish and additional measurement time may be required to maintain the same sensitivity. Nonetheless, mid-infrared FOS show considerable promise for yielding on-line real time measurements of the degree of cure.

Imbedding an array of mid-infrared sensors should give an image of the state of cure throughout the specimen. Questions of cost and possible detrimental effects of the infrared fibers on post-processing performance may limit the number of fibers that can be embedded, and subsequently the extent to which the cure profile can be established. The chalcogenide fibers appear to have sufficient thermal stability as this application (Compton, 1988; Young, 1989) exposed the embedded fiber to temperatures in excess of 275°C. It remains to be shown whether low cost IR components have sufficient sensitivity to replace the expensive instrumentation used in this study. The brittleness, toxicity, and expense of IR transmitting fibers need to be addressed before complete assessment of this approach.

4.5.1.2 Near Infrared Spectroscopy

The potential of near infrared spectroscopy, NIR, to monitor cure has advanced to a greater extent in terms of practical optical fibers and instrumentation (Stinson, 1989). NIR transmitting fibers are less costly, more durable and less toxic than mid-infrared transmitting fibers. Similar to mid-infrared transmitting fibers, the NIR fibers display good thermal stability through the temperature range of interest.

A number of companies market systems for conducting measurements via optical fibers in the NIR (Stinson, 1989). Although commercial developments have been targeted to other process monitoring applications, (Stinson, 1989) the technology appears applicable to cure monitoring once cure dependent spectral features in the NIR have been identified for the particular resin of interest. Both silica fibers with transmission to about 2100 nm and fluoride fibers with transmission to about 4000 nm have been used to conduct the NIR radiation to the sampling volume (Fredericks, 1987; Schirmer, 1988; Weyer, 1987). The fluoride fibers are both more expensive and fragile than standard silica fibers.

Since common organic resins, such as epoxies, absorb in the NIR remote sensing via NIR should be adaptable to cure monitoring. Indeed, one would anticipate that sensitivity throughout cure range, measurement and data processing time, sampling considerations, application to various resin systems, and capability for on-line real time measurements would be similar to expectations of mid-infrared spectroscopy. NIR has the advantage that optical waveguides for the NIR are developed to a much greater extent than those which transmit in the mid-IR. These waveguides are also cheaper and more robust than those suitable to mid-IR. A disadvantage is that less is known about assignments of transitions in the NIR so that the theoretical basis of the observables is not as firmly established.

4.5.1.3 Raman Spectroscopy

Although no reports of the application of Raman spectroscopy to cure monitoring appear in the literature, this technique may offer advantages over infrared absorption or attenuated total internal reflection techniques. Raman spectroscopy measures frequencies and Raman scattering probabilities of fundamental vibrations, much the same as mid-infrared measures fundamental frequencies and transition probabilities. Furthermore, Raman spectra can be generated with visible light which means that commercial optical fibers can be used to conduct the excitation light to the sampling site and to transmit the Raman scattered light to the detection system (Schwab, 1984). However, the low efficiency of the Raman process requires the use of high intensity sources, sophisticated monochromators to reject elastically scattered light and high sensitivity photon detectors and associated electronics. Also, fluorescence, whether from the material under study or from impurities present at dilute concentrations, can mask the Raman scattered light. One solution to the fluorescence (Fujiwara, 1986) problem employs light sources in the near infrared to reduce fluorescence and Fourier Transform interferometers to increase signal-to-noise (Hirschfield, 1986). Excitation by near infrared light greatly diminishes the fluorescence since the frequency of the light is well removed from that of electronic transitions.

Raman spectra should display the same sensitivity to cure as infrared spectra and be equally adaptable to various resin systems provided that the fluorescence does not interfere. The sampling schemes for Raman spectroscopy are much more versatile than infrared, however, and similar to fluorescence spectroscopy. Evanescent wave Raman spectroscopy has been reported (Schwab, 1984) in addition to the more conventional sampling arrangements of 0, 90 and 180 degree scattering geometries. Evanescent wave refers to the electric field in the lower refractive index medium of propagating electromagnetic field in the higher index medium.

Although Raman scattering is extremely weak, measurement times are comparable, or even superior to infrared requirements because laser sources for visible light excited Raman spectroscopy are more intense and detectors are more sensitive than those for the infrared. In addition, cure monitoring may require measurement of a single band which could be scanned in a few seconds in a Raman experiment. FTIR loses some of its sensitivity advantages in these cases since entire spectra are produced per unit measurement time. Intensified diode array detectors are now available to simultaneously record a Raman spectral region of 500 cm^{-1}, or more. The instrumentation of either conventional Raman or FT-Raman is complex and expensive, however.

The Raman intensity of a vibrational mode of frequency ν varies with temperature as $(1 - \exp(-hc\nu/kT))^{-1}$, where h is Planck's constant, k is the Boltzmann constant and T is the temperature. This relationship between Raman intensity and temperature is well-established and spectral data are easily corrected to account for differences in temperature.

4.5.2 UV-Vis Spectroscopy

4.5.2.1 Absorption and Fluorescence of Reactive Species

UV-Vis spectroscopy has been adapted to remote sensing of various processes, for example, biological functions, (Andrade, 1985; Dahne, 1984; Newby, 1984, 1986; Peterson, 1984; Rockhold, 1983) chemical mixing, (Fitch, 1985; Wang, 1989) addition of colorants to polymers, (Fitch, 1985) as well as to cure monitoring. (Fanconi, 1986, 1987A, 1987B; Levy, 1983A, 1983B, 1984; Sung, 1985, 1986; Wang, 1985, 1986, 1987A). Some other efforts are also of interest, in particular those involving the use of optical fibers. An example is the work of Andrade and coworkers (Andrade, 1985; Newby, 1984, 1986) who employed optic fibers to measure absorption and fluorescence of biological molecules. Their sensor were designed for evanescent excitation and detection of either the fiber-medium interface region or the surface layer formed by chemically bonding a chemical reagent to the fiber surface. The probe consisted of a multimode fiber with the cladding removed from the distal end to form a sensing element of a few centimeters in length. A black epoxy coated the end of the fiber to diminish the signal arising from excitation at the fiber terminus. These researchers showed that the fluorescence signal produced by their sensor design depended linearly on the exposed fiber length, as predicted for evanescently excited fluorescence (Newby, 1984).

Application of UV-Vis spectroscopy to cure monitoring exploited the absorption and fluorescence of reactive species (Levy, 1984; Sung, 1985, 1986) as well as absorption and fluorescence of probe molecules (Fanconi, 1986, 1987A, 1987B; Levy, 1983A, 1983B; Wang, 1985, 1986, 1987A). The former approach is resin system specific, whereas the latter is applicable to a variety of resin systems, although different probes may have to be used.

Sung, et al. (1985, 1986) observed that the absorption spectrum of the probe p,p'-diamino azobenzene changed with the degree of substitution at the amino nitrogens which corresponded to the formation of the chemical network. A small amount of this probe was added to an epoxy cured with 4,4' diamino diphenyl sulfone, DDS, which had a similar cure chemistry to that of the probe. Through spectral deconvolution, the extent of reaction of the probe molecule was determined and owing to the chemical similarity with the curing agent, the kinetics of the cure was deduced. Figure 4.3 shows the cure curves at three temperatures for diglycidyl ether of bisphenol-A, DGEBA, and the DDS amine hardener. Sung, et al. (1986) have also shown that the fluorescence spectrum of the same probe molecule can be deconvoluted to reveal cure kinetics. This probe is resin specific since to monitor cure by either absorption or fluorescence measurements requires similar reactivity of the probe and curing agent.

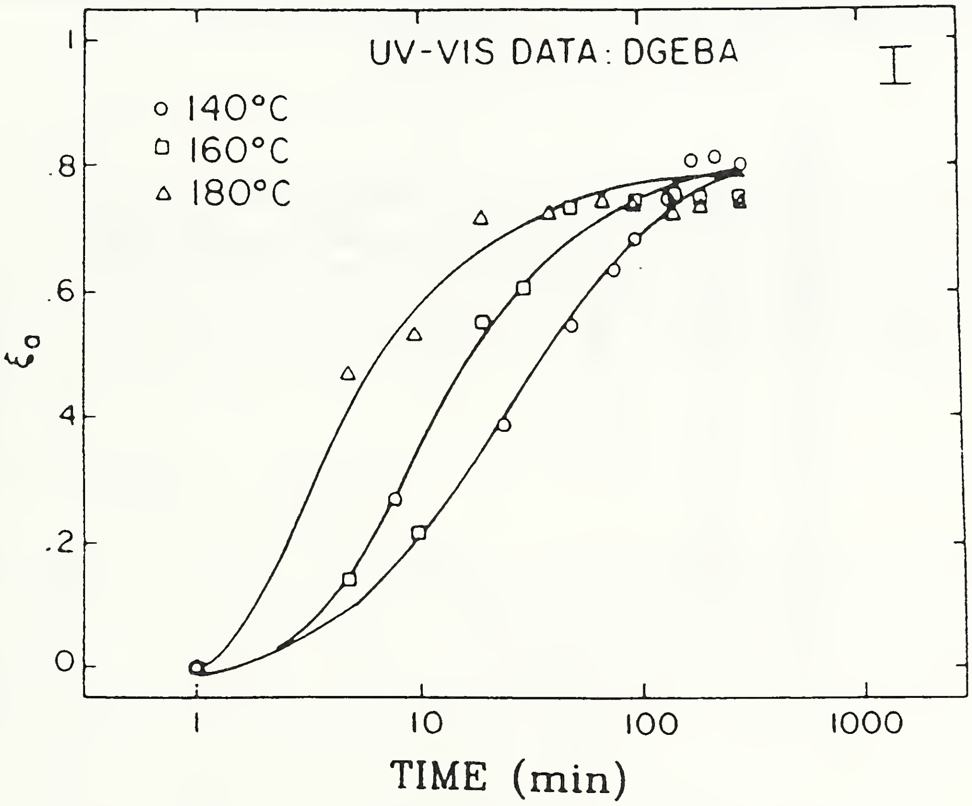

Figure 4.3 Cure curves of diglycidyl ether of bisphenol-A with curing agent diamino diphenyl sulfone investigated by an azochromophore label technique. Extent of amine reaction is plotted against time for systems cured at three temepratures. (After Sung, C.S.P., Pyun, E. and Sun, H.-L., Macromolecules, 19, 2922 (1986).)

Although optical fibers were not employed by Sung, et al. (Sung, 1985, 1986) it appears that either of their spectroscopic measurement procedures could be carried out by either terminal (distal) or evanescent sensors. Owing to the required similarity in the chemical reactivity of the curing agent and probe p,p′-diamino azobenzene it is likely that this type of probe would only be useful in epoxies cured at low temperatures. For reasons given in the discussion on Raman spectroscopy, measurement and data processing times are within the requirements for cure monitoring. Even if deconvolution of complex spectral bands are performed to reveal cure kinetics the data processing times appear to be sufficiently short to give real time results.

Certain epoxies and polyimides exhibit natural fluorescence which is sensitive to the degree of cure. Levy (1984) showed that the fluorescence spectrum of the resin tetraglycidyl- diaminodiphenyl methane displays sensitivity to the degree of cure and Wang et al. (1989) have demonstrated that the conversion of poly(amide acid) to polyimide can be measured by fluorescence. Figures 4.4 and 4.5 display cure data obtained with self-fluorescence, one an example of a low temperature system, and the other a high temperature resin. Sensitivity of the method decreases in the latter stages of cure and both of these studies are resin specific, however. Through the use of FOS the self-fluorescence approach has capabilities for sensing the state of cure throughout the sample.

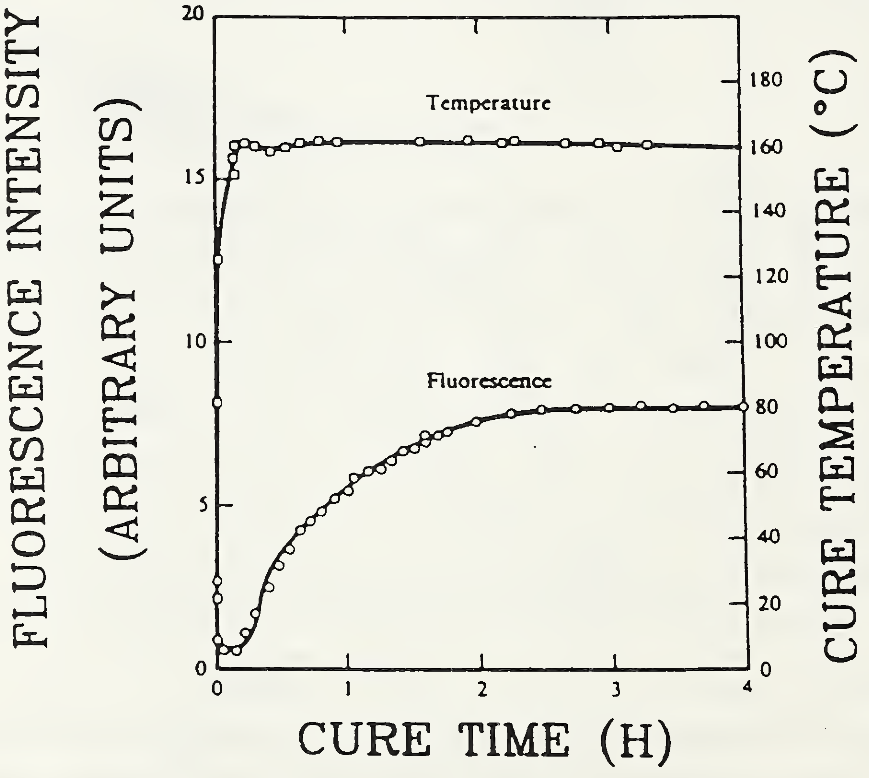

Figure 4.4 Cure curve obtained from self-fluorescence of tetraglycidyl diamino diphenyl sulfone system. (After Levy, R.L., Polym. Mat. Sci. & Eng., 50, 124 (1984).)

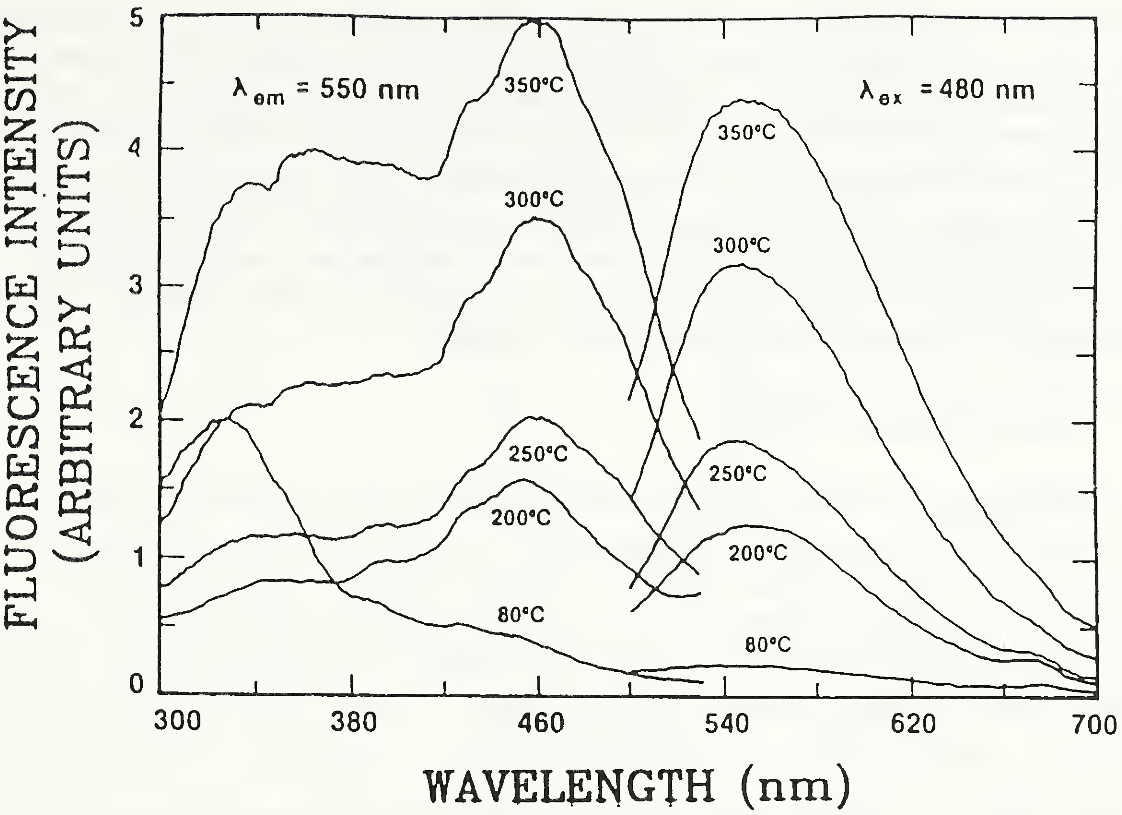

Figure 4.5 Excitation and emission spectra of poly(amide-acid) film after heating. The increased fluorescence at 550nm reflects conversion to polyimide. (After Wang, F.W., Bur, A.J., Lowry, R.E. and Fanconi, B.M., in Advances in Chemistry Polymer Characterization by Interdisciplinary Approaches. Ed. by Clara D. Carver, Plenum Press, 1989.

4.5.2.2 Fluorescent Probes

Most applications of UV-Vis spectroscopy to cure monitoring utilize fluorescent probes which do not directly participate in the chemistry (Fanconi, 1986, 1987A, 1987B; Levy, 1983A, 1983B; Wang, 1986, 1987A). These approaches are based on a technique first used by Loufty (1981) to follow the polymerization of linear polymers. The technique involves the use of probe molecules whose fluorescence spectra display sensitivity to the viscosity of the solvent. Owing to the high spectral sensitivity of fluorescent molecules, probe concentrations of the order of 10^{-5} M are used. It is unlikely that at this concentration the probe molecules would have any effect on bulk properties of the composite with the possible exception of color, if the probe molecule absorbs in the visible region.

The sensitivity of fluorescence probes to viscosity arises from the dependence of internal rotation on the local viscosity, or as sometimes called, microviscosity (Loufty, 1982B). An electronically excited molecule returns to the ground electronic state either by giving off radiation (fluorescence or phosphorescence) or by transferring the electronic excitation into vibrational of rotational degrees of freedom (nonradiative). Nonradiative transition probabilities depend on molecular mobility, in particular, internal rotations. A molecule constrained by its environment so as to limit internal rotations exhibits increased fluorescence since nonradiative pathways are restricted. The connection to viscosity is made through free volume, on which viscosity depends exponentially. The probability of internal rotation depends linearly on free volume, and as a consequence, there should be a logarithmic relationship between fluorescence and viscosity. Indeed, this has been observed experimentally, although not in all cases (Law, 1980).

4.5.2.3 Excimer Forming Probes

One example in which the fluorescence decreases with increasing viscosity occurs with excimer-forming molecules (Fanconi, 1986). An excimer refers to electronic excitation shared by two or more molecular species. Excimer formation results when two chromophores, the portions of the molecules which are electronically excited, are situated such that the electronic excitation of one chromophore is shared with the other through transition dipole coupling. Emission from the excimer state occurs at a lower frequency than that from the excited monomer. An example of an excimer-forming molecule is 1,3-bis-(1-pyrene)propane whose fluorescence spectrum is shown in Figure 4.6. In the absence of excimer formation, excitation of the pyrene chromophore produces the emission spectrum centered at 390nm. If within the lifetime of the excited electronic state of pyrene the two pyrene moieties adopt the conformation in which the two planar pyrene rings are face-to-face then the electronic excitation is shared and emission occurs at 490nm rather than at 390nm. An electronically excited molecule undergoes internal rotations among its various configurations, with the probability of transition among the conformations dependent on the microviscosity. Thus, the higher the viscosity, the weaker the excimer fluorescence. Self-calibration is an attractive feature of excimer probes in that the monomer fluorescence intensity serves as an internal standard to which the excimer fluorescence is ratioed to produce a result independent of measurement conditions.

The excimer-type probes were used by Fanconi et al. (1987b) to monitor the cure of epoxy resins; an example is the cure curve for diglycidyl ether of bisphenol-A, DGEBA, and amine hardener, 4,4′-methylene-bis-(cyclohexylamine), PACM, given in Figure 4.7. The ratio of the fluorescence of the monomer to excimer is plotted against cure time. The initial decrease in the intensity ratio corresponds to the decrease in viscosity with rise in temperature and the rapid increase in the intensity ratio is attributed to network formation. The subsequent decrease of the intensity ratio is attributed to photochemical reactions involving the probe molecule.

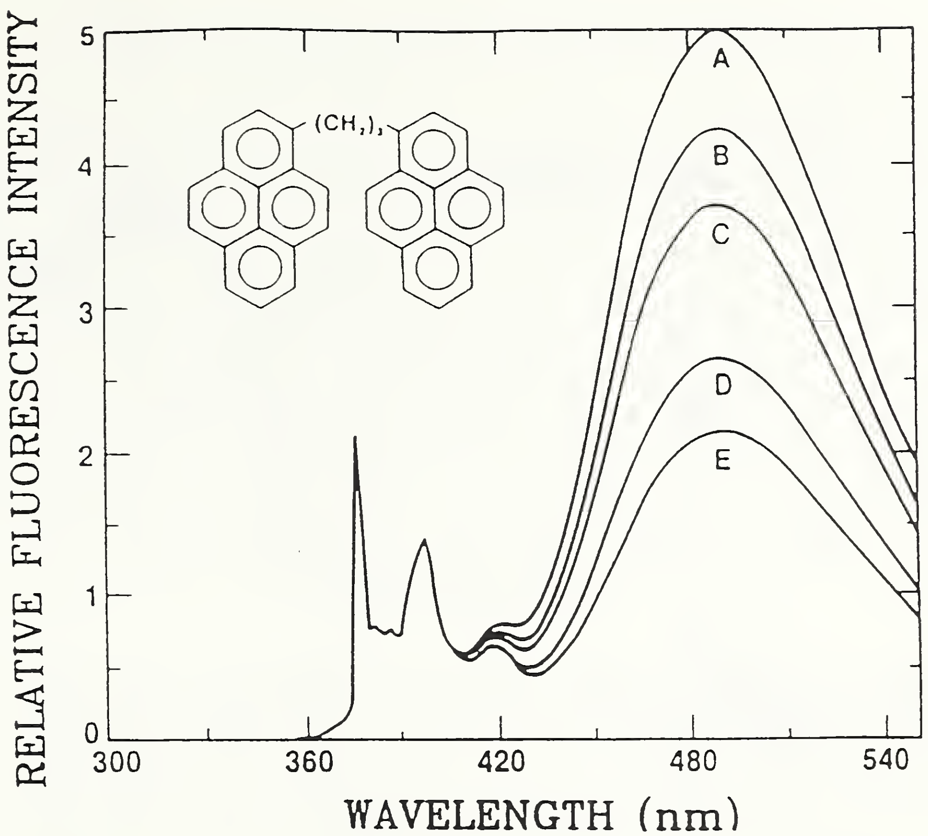

Figure 4.6 Dependence of the fluorescence spectrum of excimer-forming probe 1,3-bis-(1-pyrene) propane on the solvent viscosity. All spectra are normalized to constant monomer intensity. The viscosity increases by a factor of 10 from A to E. (After Fanconi, B., Wang, F., Hunston, D. and Mopsik, F., in Materials Characterization for Systems Performance and Reliability, McCauley, J.W. and Weiss, V., Eds., p. 275, Plenum Press, 1986.)

4.5.2.4 Comparison of Fluorescent Probes to Laboratory Techniques of Cure Monitoring

Owing to the limited range of sensitivity of the excimer probe Wang et al. (1986) used a second dye system consisting of a pair of molecules which fluoresce at different frequencies. One dye of the pair exhibited a fluorescence intensity dependent on viscosity and the other a viscosity independent fluorescence intensity. The cure curve of the epoxy system DGEBA/PACM obtained with this dye pair, shown in Figure 4.8, displays the rapid rise seen in Figure 4.7 followed by a more gradual increase in the latter stages of cure. The cure curve of Figure 4.8 has been compared to those obtained on the same resin by ultrasonics, dielectrics, differential scanning calorimetry, and viscometry (Fanconi, 1987A). The overall shape of the cure curves, given in Figure 4.9, are similar, although variations are evident. These variations are not surprising given that different physical processes underlie these methods. It would appear that a combination of several techniques may provide the optimal description of the cure process.

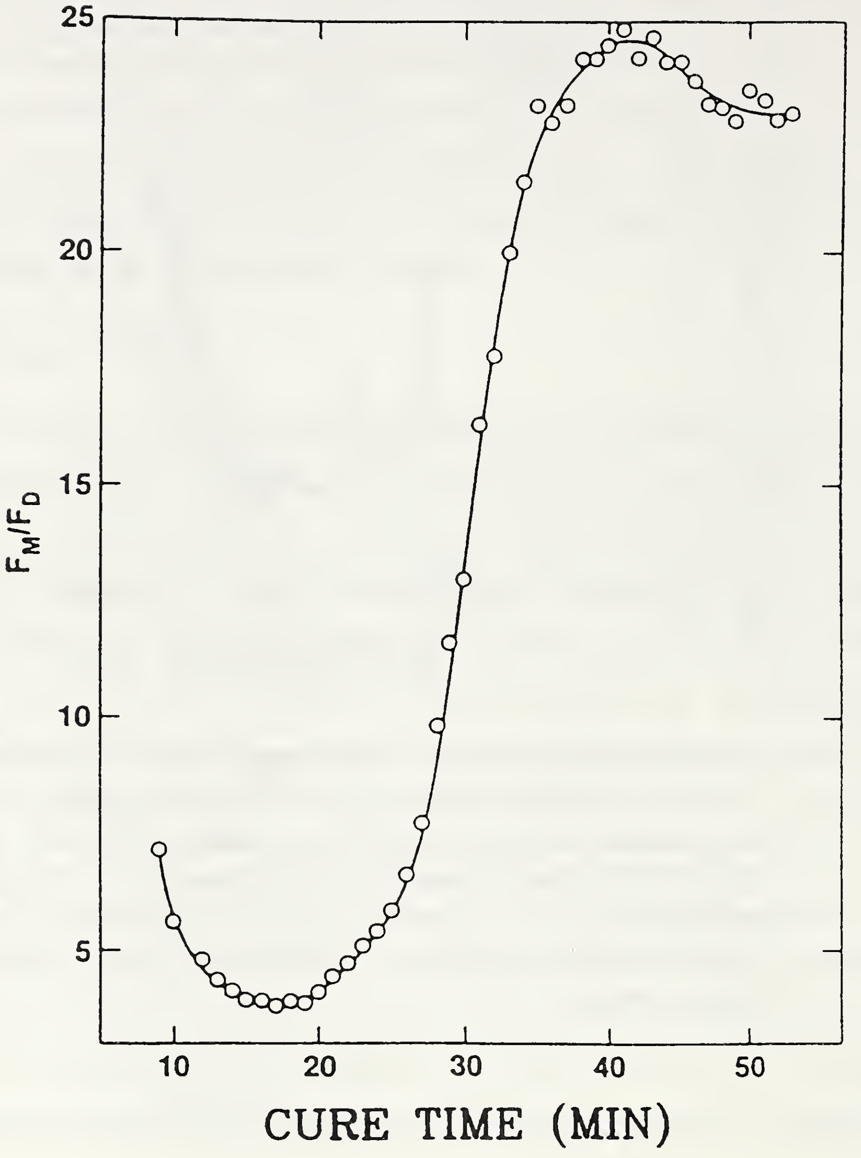

Figure 4.7 Cure curve of an epoxy rein system, diglycidyl ether of bisphenol-A and amine hardener, 4,4′-methylene-bis-(cyclohexylamine), monitored by the ratio of the monomer fluorescence intensity, F_m, to excimer fluorescence intensity, F_d, of the excimer-forming probe, 1,3-bis-(1-pyrene) propane. (After Fanconi, B., Wang, F., Lowry, R., in Review of Progress in Quantitative Nondestructive Evaluation, Vol. 6B, Thompson, D.O. and Cleminti, D.E., Eds., p. 1287, Plenum Press, 1987.)

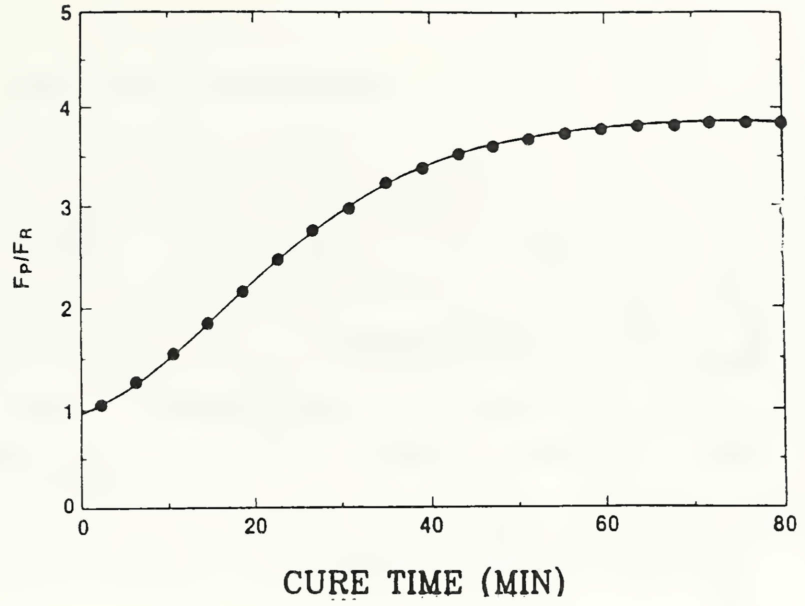

Figure 4.8 Cure curve of an epoxy resin system, diglycidyl ether of bisphenol-A and amine hardener, 4,4′-methylene-bis-(cyclohexylamine), obtained by ratioing the fluorescence intensity of the viscosity sensitive probe, 1-(4-dimethylaminophenyl-6-phenyl-1,3,5-hexatriene to that of the viscosity insensitive probe 9,10-diphenyl anthracene. (After Wang, F.W., Lowry, R.E. and Fanconi, B.M., Polymer, 27, 1529 (1986).)

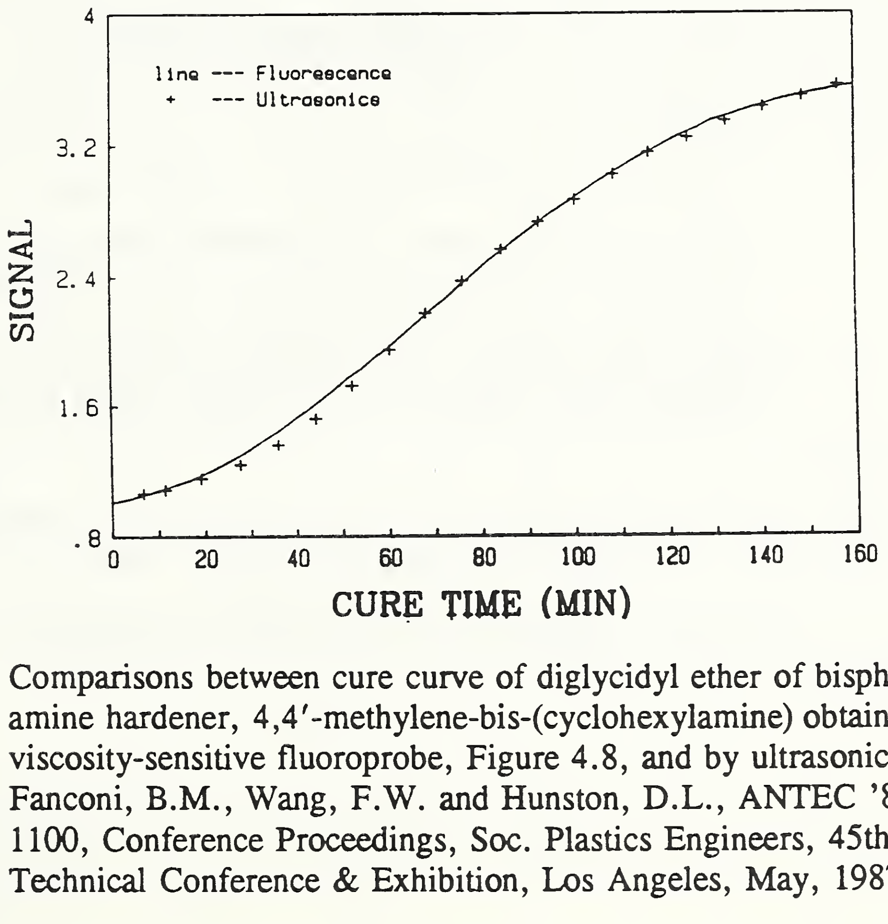

Figure 4.9 Comparisons between cure curve of diglycidyl ether of bisphenol-A and amine hardener, 4,4′-methylene-bis-(cyclohexylamine) obtained by viscosity-sensitive fluoroprobe, Figure 4.8, and by ultrasonics. (After Fanconi, B.M., Wang, F.W. and Hunston, D.L., ANTEC '87, p. 1100, Conference Proceedings, Soc. Plastics Engineers, 45th Annual Technical Conference & Exhibition, Los Angeles, May, 1987.)

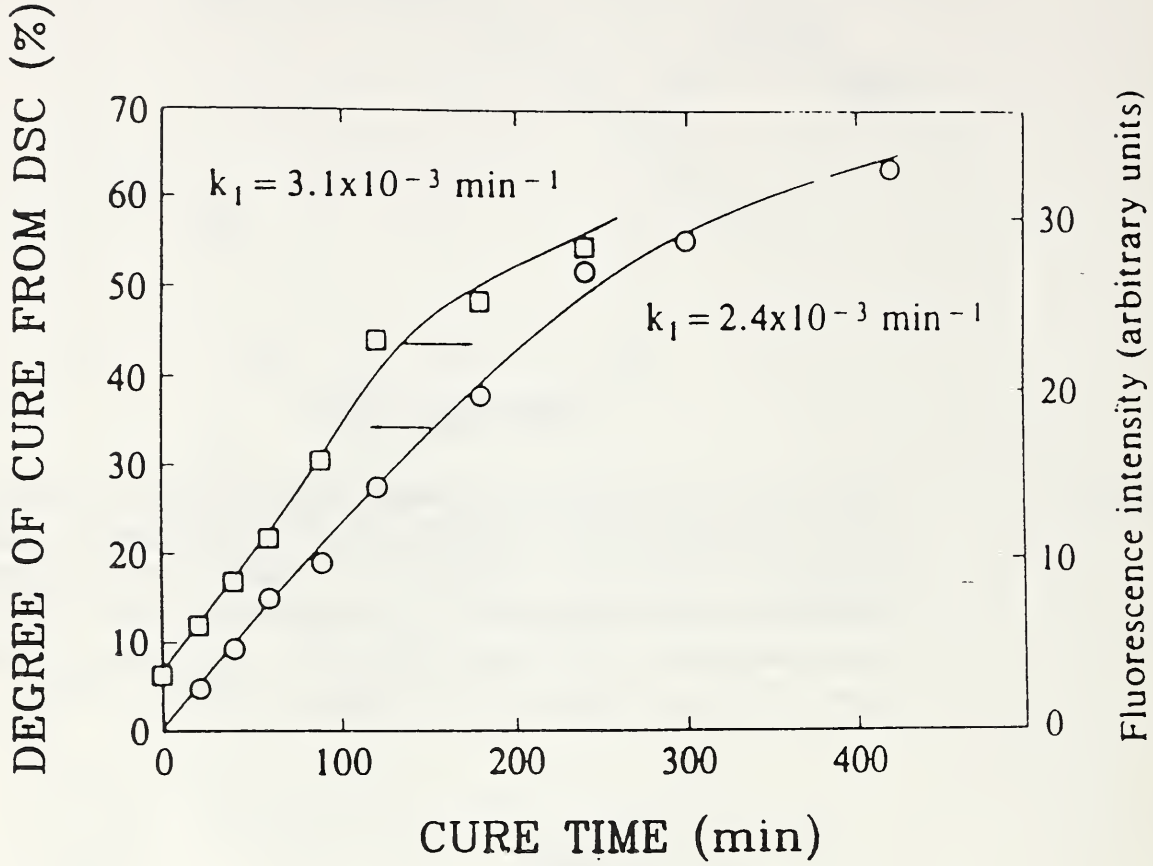

Figure 4.10 Cure curve of the epoxy TGDDM/DDS determined by intensity of fluoroprobe p-(N,N-dialkylamino)benzylidene malononitrile and comparisons with cure behavior determined by DSC. (After Levy, R.L. and Ames, D.P., in Adhesive Chemistry Developments and Trends, L.-H. Lee, Ed., Plenum Press, New York (1983).

Levy and Ames (1983A) used the fluorescence probe, p-(N,N-dialkylamino) benzylidene malononitrile for monitoring epoxy cure kinetics. The plot of increase in the probe's fluorescence intensity with cure time closely followed that obtained from DSC as shown in Figure 4.10. A probe concentration of 0.5% was used without an internal standard, however.

4.5.2.5 Fluorescent Recovery After Photobleaching

Another application of fluorescence spectroscopy to cure monitoring exploits the connection between resin viscosity and diffusion coefficients of photosensitive low molecular weight molecules (Wang, 1987B). In this method, termed fluorescence recovery after photobleaching, FRAP, a laser beam is focussed through a microscope onto the curing sample which contains a small amount of a photosensitive dye dissolved in the resin. The intense beam initiates photochemical reactions in the probe molecules such that fluorescence ceases within the small volume of material illuminated by the focussed light. Subsequently, a second beam of intensity too low to cause further photochemical reactions bathes the bleached area and the rise in fluorescence as probe molecules diffusion into the bleached region is measured. From the growth in fluorescence intensity with time and the size of the exposed region the diffusion coefficient of the probe molecule is determined.

Wang et al. (1987B) employed the FRAP technique to monitor the cure of the epoxy system DGEBA/PACM as a function of time and temperature. Figure 4.11 shows the logarithm of the translational diffusion coefficient of the photobleachable probe 1,1′-dihexyl-3,3,3′,3′-tetramethylindocarbocyanine perchlorate as a function of cure time at cure temperatures of 45°C, 60°C, and 75°C. In all cases the diffusion coefficient increased slightly as the resin temperature was raised from room temperature to the cure temperature owing to the decrease in viscosity with increasing temperature. As crosslinking proceeded, the viscosity increased because of the growth in molecular weight, and this was reflected by the decrease in the translational diffusion coefficient. This linear decrease changes abruptly upon vitrification of the resin. The cure data of Figure 4.11 compares favorably with that obtained by other techniques as shown in Figure 4.12. An advantage of the FRAP method is the sensitivity to cure beyond gelation. We see in Figure 4.8 that viscosity sensitive probe molecules exhibit a slow rise in fluorescence at the latter stages of cure.

4.5.2.6 Chemiluminescence

Another type of emission spectroscopy which has been used to follow the cure of epoxies (George, 1986) is chemiluminescence which refers to light emitted as a consequence of chemical reactions involving recombination of free radicals produces during free radical auto-oxidation. Two free radicals are involved in the recombination process and the reaction rate is controlled by the free radical diffusion constant which relates to the medium viscosity in a manner similar to that discussed above for the FRAP technique.

The functional relationship for the emitted light intensity is given as

$$I = \phi D [R \cdot]^2 \tag{4.1}$$

where I is the emitted light intensity, ϕ is the quantum efficiency of the process, D is the diffusion coefficient, and $[R \cdot]$ is the free radical concentration. The medium viscosity affects ϕ in a manner similar to that previously discussed for fluorescence probes of viscosity. Although the quantum efficiency, ϕ, increases with increasing viscosity whereas the diffusion constant, D, decreases, there is a net result on the luminescence intensity. According to Loufty (1982A), ϕ varies as the x-power of viscosity where x is between 0.3 and 0.6. The diffusion coefficient varies inversely with viscosity, η, so that the above equation assumes the form

$$I = C\,\eta^{x-1}\,[R\cdot]^2 \tag{4.2}$$

and if [R•] is constant during cure the luminescence intensity should decrease with degree of cure.

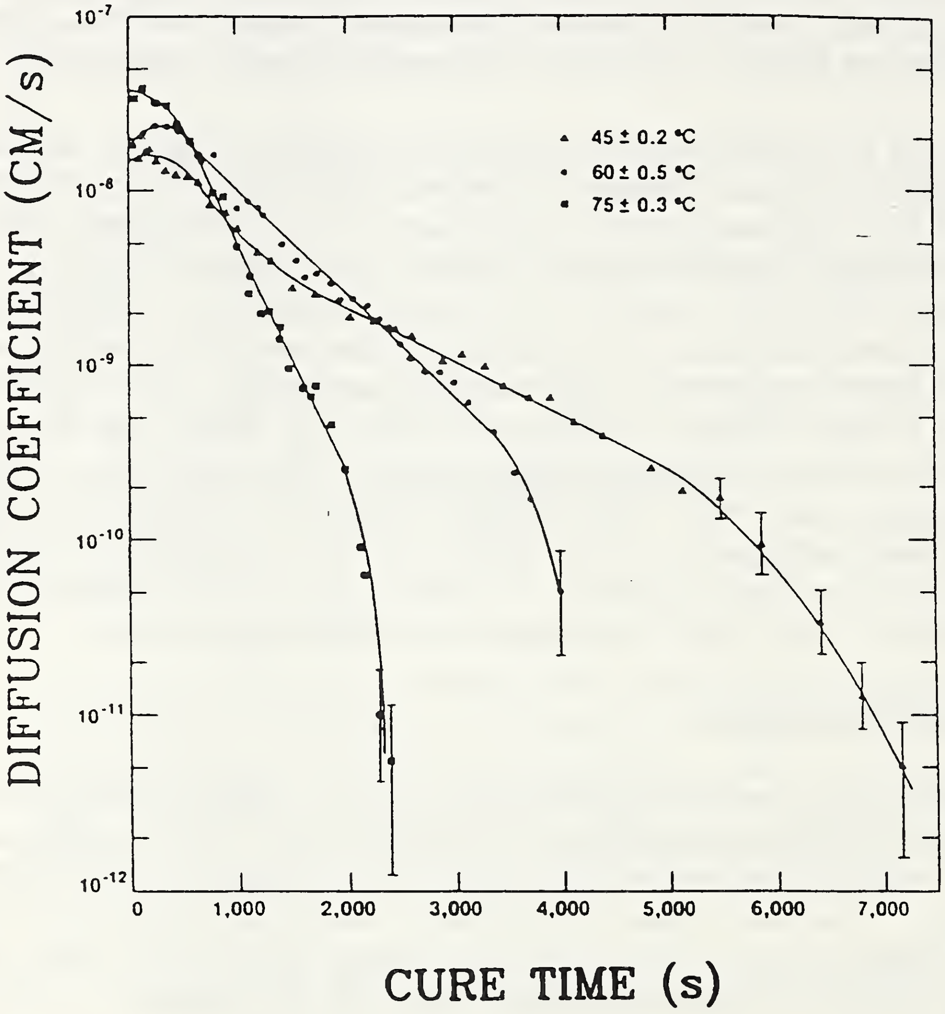

Figure 4.11 Diffusion coefficient of the photobleachable probe 1,1′-dihexyl-3,3,3′,3′-tetramethylindocarbocyanine perchlorate in the stoichiometric mixture of diglycidyl ether of bisphenol-A and amine hardener, 4,4′-methylene-bis-(cyclohexylamine) measured by fluorescence recovery after photobleaching. (After Wang, F.W., and Wu, E.-S., Polym. Comm. 28, 73 (1987).)

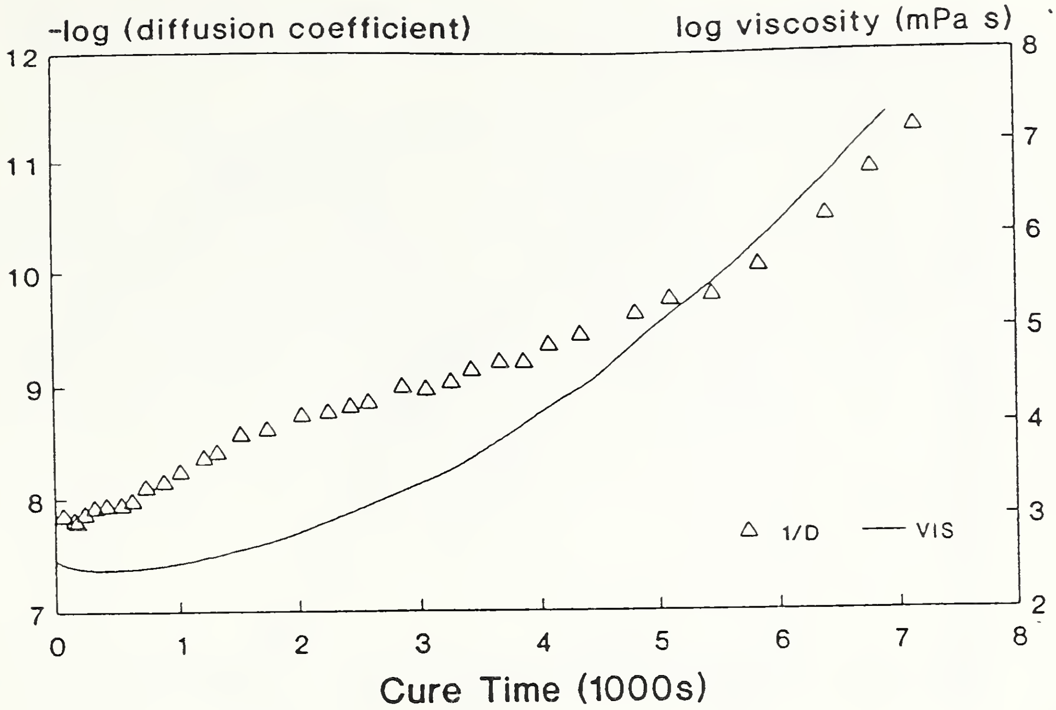

Figure 4.12 Comparison of cure curve of epoxy resin system, diglycidyl ether of bisphenol-A and amine hardener, 4,4′-methylene-bis-(cyclohexylamine), obtained by FRAP and viscometry. (After Fanconi, B.M., Wang, F.W., and Hunston, D.L., ANTEC '87, p. 1100, Conference Proceedings, Soc. Plastics Engineers, 45th Annual Technical Conference & Exhibition, Los Angeles, May, 1987.)

Epoxy resins cured with amines have been observed to be luminescent prior to, during and subsequent to cure (George, 1986). The cure curves of an epoxy system cured with two different concentrations of the amine hardener 4,4′-diamino diphenyl sulfone, DDS, shown in Figure 4.13, exhibit a break corresponding to the time of gelation. The overall shape of these curves is similar to that seen in the fluorescence recovery after photobleaching (FRAP), Figure 4.11. This is not surprising since the quantities measured by the two techniques depend on ϕ and the diffusion coefficient in a similar fashion. It should be noted, however, that whereas fluorescence requires excitation by light, chemiluminescence does not. An inherent problem in the use of equations (4.1, 4.2) to monitor the degree of cure is the required knowledge of the functional dependence of the concentration of free radicals on degree of cure. Changes in free radical concentrations with degree of cure could easily mask effects due to viscosity.

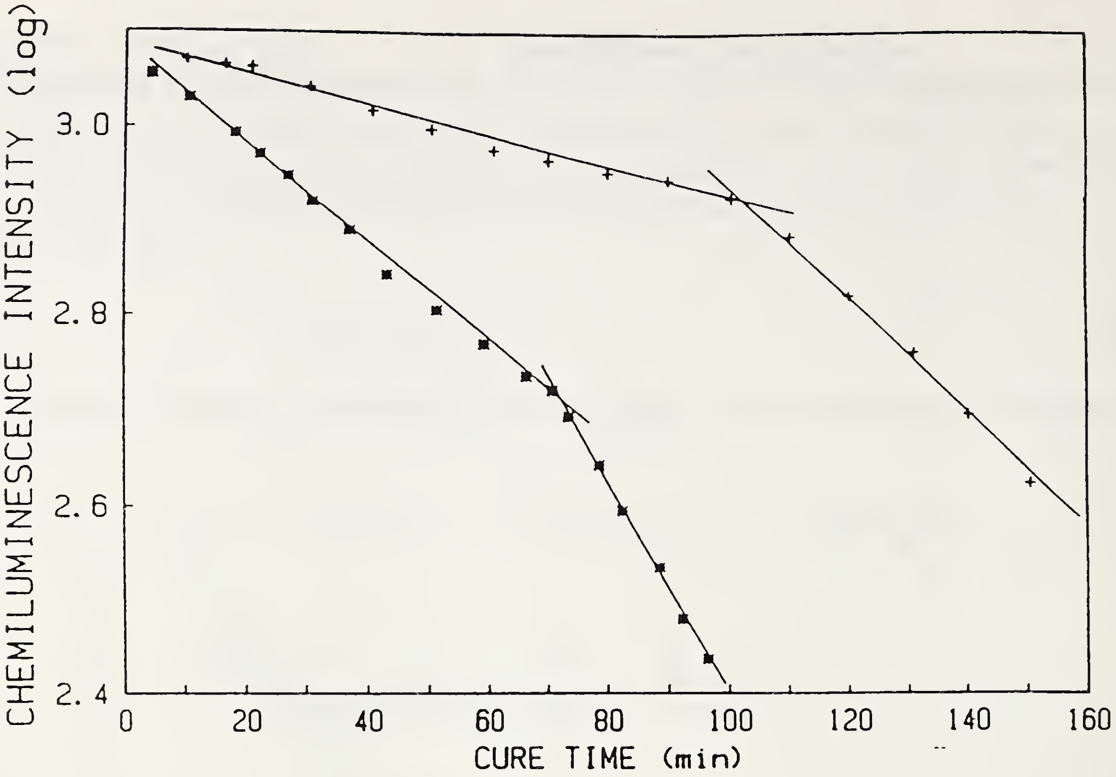

Figure 4.13 The changes in the intensity of chemiluminescence during cure of an epoxy (tetraglycidyl 4,4′ diamino diphenyl methane) cured at 135°C with 27% DDS (4,4′ diamino diphenyl sulfone) (+) and 37% DDS (*). (After George, G.A., 1986.)

George (1986) proposed a transient chemiluminescence technique which overcomes the calibration difficulties of the steady-state method. In this measurement scheme, free radicals are produced in the sample by a short exposure to UV light. The decay of the resultant chemiluminescence is measured and the half-life of the decay is taken as a measure of degree of cure as shown in Figure 4.14. A limitation of this technique is that the time interval between measurements must be sufficiently long for determinations of the half-life in the decay of the chemiluminescence. Figure 4.14 shows the degree of cure curves of epoxies cured with two different concentrations of DDS as determined by this technique. It has not been demonstrated that light intensity levels from chemiluminescence are sufficiently high to permit use of optic fibers or that repeated exposures to UV radiation does not adversely affect properties and performance of the composites. It should be borne in mind that the chemical basis of chemiluminescence involves scission of polymer molecules and that mechanical and other engineering properties of polymers are adversely affected by degradation of molecular weight. George concludes of this method that "further research into the use of the technique under industrial processing conditions is required to determine if it a viable alternative ....". Clearly, the same can be said of all the optical and spectroscopic techniques.

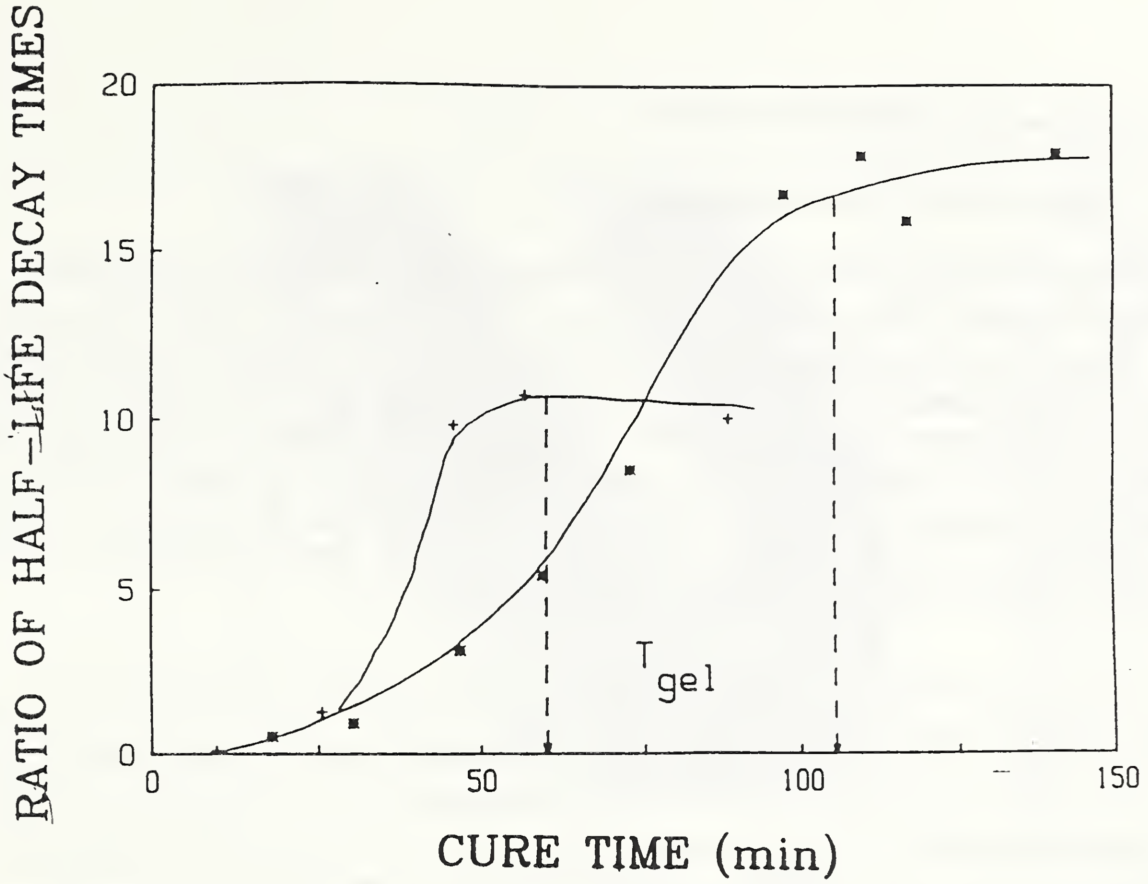

Figure 4.14 Change in the chemiluminescence half-life τ/τ as a function of cure time at 135°C for epoxy (tetraglycidyl 4,4′ diamino diphenyl methane) cured with 27% DDS (4,4′ diamino diphenyl sulfone) (*) and 37% DDS (+). The gel time from thermal analysis is marked T_{gel}. (After George, G.A., Materials Forum, 9, 224 (1986).)

4.5.2.7 Current Status of Fluorescent Probes for Cure Monitoring

Both research groups (Levy, 1983A; Fanconi, 1986) applying viscosity sensitive fluorescence probes purified the epoxy resin systems prior to use, and this points to a limitation of the method. Commercial resins tend to fluoresce due to the presence of impurities. For this reason, the fluorescence probes considered thus far likely would not be commercially viable. Nonetheless, an optical probe of resin viscosity would be extremely useful in that viscosity is the critical materials property in the various processes occurring in the manufacture of composites. Through optical fibers there is, in principle, a method of remote sensing.

4.5.3 Spectroscopic Optical Fiber Sensors

4.5.3.1 Measurement of Resin Properties

Remote sensing of the degree of cure through the use of optical fibers shows considerable promise. The work of Andrade et al. (1985) on biochemical sensing with optical fibers has been mentioned. A design similar to that of Andrade was developed independently by Fanconi, et al. (1986) to explore the adaptation of fiber optics to cure monitoring of polymer composites. In this design, shown in Figure 4.15, the optic fiber replaces one of the reinforcement fibers, and the entire length of the embedded fiber is stripped of the cladding to form the sensing element. Laser light is coupled into one end of the embedded fiber and the fluorescent light collected by the fiber is transmitted to either end of the fiber where it can be directed into the detection system.

The evanescent type sensor restricts applications to resin systems with lower refractive indices than that of the waveguide. High refractive index optical fibers are needed since the refractive index of epoxies is about 1.5 whereas that of ordinary glass fibers is 1.46. A further complication may arise from fluorescence of the waveguide material, a frequent manifestation of the higher index glasses. One way to overcome this problem is to use probe molecules which fluoresce at lower frequencies than the fiber fluorescence. In any case, identification of the optimal probe-optic fiber combinations requires further research.

The distal type optic fiber probe does not require a higher refractive index optic fiber since the lower index cladding remains on the fiber to ensure wave guiding. Schwab and Levy (1988) utilized this fiber design in cure monitoring. Evanescent and distal type sensors differ in the geometry of the sampling volume. The distal type monitors a volume of material in the shape of a cone at the fiber terminus, if the fiber end incorporates no optical elements. The evanescent type, on the other hand, senses a volume of material in the shape of a cylinder surrounding the fiber along its entire exposed length. Thus, the distal type functions as a localized sensor, much the same as microdielectric sensors. The evanescent type, on the other hand, can sense a localized region by removing the cladding from a small portion of the embedded fiber, or a much larger region by removing the cladding from the entire length of the embedded fiber. A much lower signal would result from a localized evanescent type sensor since the electric field amplitude and fiber collection efficiency are lower than for the distal type sensor.

Another difference between the two designs has to do with the proximity of the sampling volume to the fiber surface, being closer in the case of the evanescent type sensor since the penetration depth is of the order of tens of nanometers. This difference may be important in the determination of interfacial properties in fiber reinforced materials, and in particular, the cure of the resin near an interface compared to cure in the bulk (Wang, 1987). Localized sensors, such as microdielectric probes, tend to insulate the resin from the

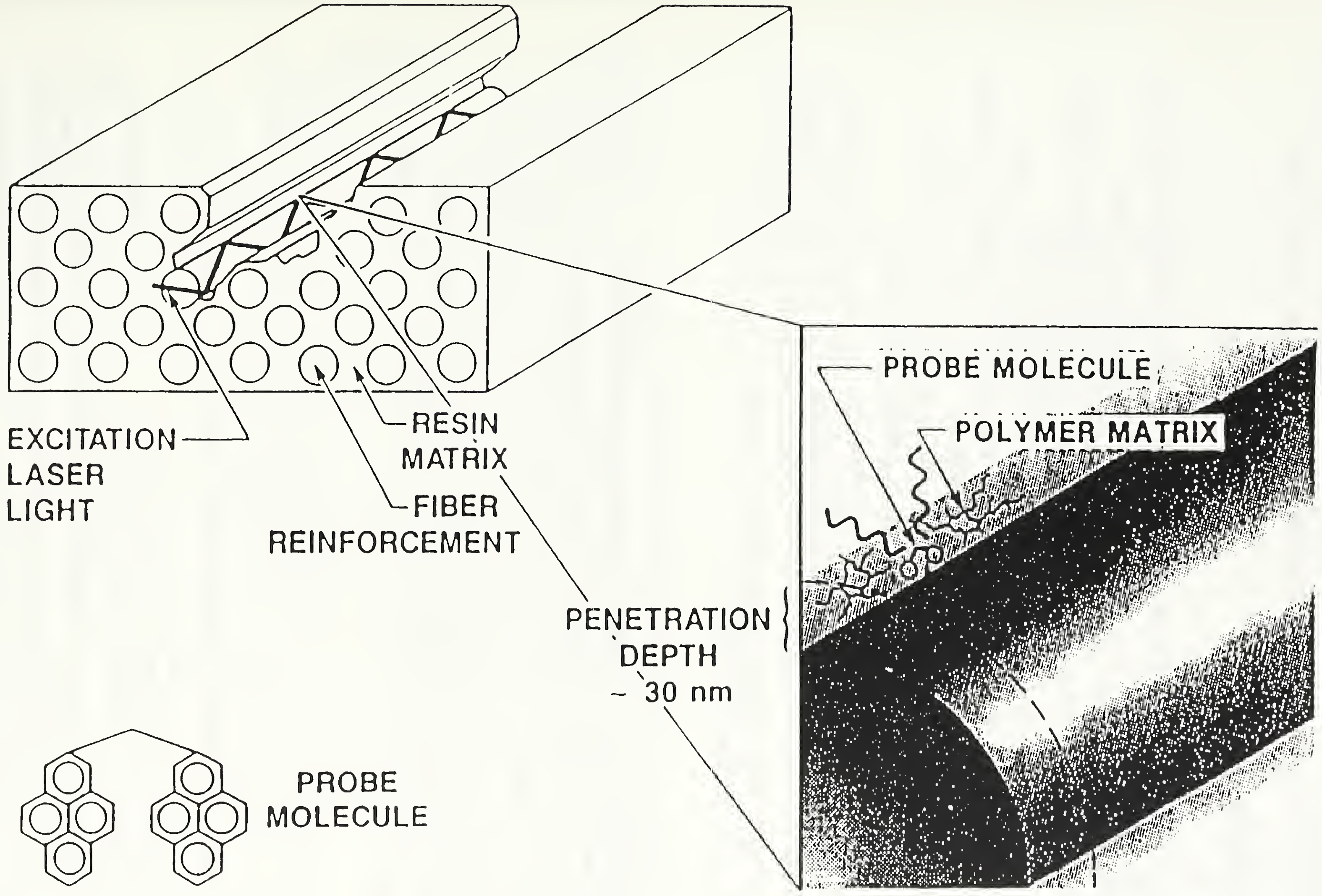

Figure 4.15 Experimental scheme employing optical fibers to deliver excitation light into the interior of a thick composite part, and to retrieve a portion of the signal from a fluoroprobe for transmission to the detector. (After Fanconi, B., Wang, F., Hunston, D. and Mopsik, F., in Materials Charcterization for Systems Performance and Reliability, McCauley, J.W. and Weiss, V., Eds., p. 275, Plenum Press, 1986.)

reinforcement. Further, laboratory techniques measure bulk properties and typically on neat resins rather than composites. Evanescent spectroscopy provides a means to determine resin characteristics in the interfacial region of the resin and a fiber, albeit an optical fiber.

4.5.3.2 Fiber-Attached Probes

Thus far, the discussion has focussed on measurement of some property of the resin either directly, or through use of a molecular probe dispersed in the resin. Other applications of fiber optic sensors involve chemical attachment of reactive species (reagents) to the fiber surface (Dahne, 1984; Munkholm, 1986). These reagents operate spectroscopically, such as a color indicator of pH, or through a refractive index effect. Dahne et al. (1984) applied evanescent type waveguides to the detection of antibody-antigen reactions at a solid-liquid interface by immobilizing the antibody to the surface of the waveguide. Fluorescence spectroscopy was used to determine concentrations of species at the fiber surface. In another application, Munkholm et al. (1986) incorporated fluoresceinamine, a pH sensitive fluoroprobe, into an acrylamide-methylenebis (acryamide) copolymer which was chemically attached to a glass fiber surface. The polymer increased the surface area and number of sites for attachment of the fluoroprobe resulting in improved sensitivity. This work showed that sufficient quantities of indicator materials can be chemically attached to an optical fiber sensor.

The technique of covalently bonding an indicator to the fiber surface for monitoring the degree of cure has not been pursued to date. An overriding consideration is restricted diffusion, particularly in the latter stages of cure. In order for a surface-attached indicator to function properly, the chemical reactants must readily diffuse to and from the optical fiber surface. The high mobility of hydrogen ion suggests the use of a pH sensitive fluoroprobe for crosslinking systems in which pH measurements indicate the extent of the chemical reaction. A pH sensitive fluoroprobe covalently attached to the fiber surface would presumably form a sensor with superior sensitivity to one in which the reactive probe were dissolved in the bulk resin.

The sensitivity of a fluoroprobe for microviscosity may also be improved by labeling a polymer with the fluorescent group and then chemically bonding the polymer to the fiber. Wang et al. (1984) used the fluorescent probe, 1,3- bis(1-pyrene)propane, to monitor polymerization of poly(methylmethacrylate), PMMA either by dissolving the probe in the solvent, or by chemically attaching the chromophone, pyrene, to PMMA to form a probe polymer. The data presented in Figure 4.16 indicated a similar response when the probe was chemically linked to the polymer as when dissolved in the reactants. This result suggests that a surface-bound polymer fluoroprobe may also exhibit a similar response to microviscosity as a probe dissolved in the resin. A possible spinoff of attaching a labeled polymer to the fiber surface may be to change the refractive index at the surface to the extent that conventional glass fibers could be used with epoxies and other high index matrix resins.

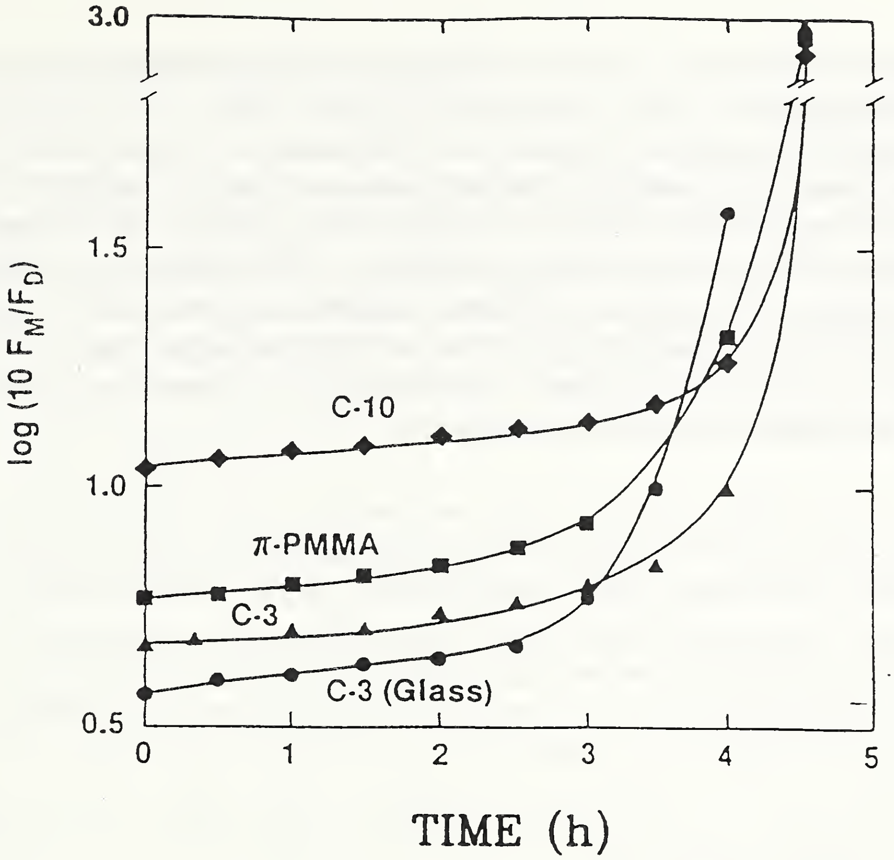

Figure 4.16 Fluorescence response of excimer-forming probes in polymerizing poly(methylmethacrylate). (After Wang, F.W., Lowry, R.E. and Grant, W.H., Polymer, 25, 690 (1984).

The other fluorescence type technique discussed, FRAP, uses a microscope to focus the laser light into a small volume of dye-labelled resin. Additional research needs to address whether fiber optics can be used to define the bleached region, either by evanescent excitation or through illumination at the distal end of the fiber.

4.5.4 Non-Spectroscopic Fiber Optic Sensors

4.5.4.1 Refraction Index Changes Measured by Interferometry

Most fiber optic sensors currently in use are based on refractive index rather than spectroscopic measurements, and some of these sensor designs may be relevant to cure monitoring. Refractive index sensors fall into two categories, one involves measurement of the effect of the environment (temperature, pressure, stress, strain, etc.) on the fiber itself, (Claus, 1984) and the other on refractive index changes in the medium surrounding the fiber (Afromowitz, 1988, 1989; Claus, 1984; Graindorge, 1985; Karahara, 1983). Very small changes in the refractive index of the fiber induced by the environment are measured either by interferometry which compares the retardation of the beam passing through the fiber under environmental influence to a reference fiber, or by polarimetry in which the state of polarization of the propagating light is determined (Hecht, 1987). Both of these methods require single mode fibers to preserve phase and polarization and sophisticated detection equipment. Nonetheless, the interferometric technique was used to determine temperature distributions and internal strain in graphite epoxies (Reddy, 1987). The photoelastic effect provides a measure of strain under certain assumptions. Densification of curing thermosets and differences in thermal expansion coefficients between resin and reinforcements would likely produce strain in an embedded optical fiber which could conceivably serve as an indication of degree of cure, although other variables, such as fiber type, content, layup, thermal history, are likely to affect internal strain.

Changes in the refractive index of the medium may also be detected with optical fiber sensors through measurement of either polarization or intensity of the transmitted light (Jeunhomme, 1983; Afromowitz, 1988, 1989; Fanconi, 1989). Optical fiber polarimeters use a special optical fiber which is birefringent, by either stress or shape birefringent, and propagates light polarized along two mutually perpendicular directions (Jeunhomme, 1983). By removing the cladding from the waveguide surface on only one side, that is, normal to one of the axes of the elliptical fiber cross-section, the state of polarization of the propagated light will be affected by the medium and the magnitude of the effect will be proportional to the refractive index difference. Polarimeter based fiber optic sensors are attractive because they contain their own reference state.

4.5.4.2 Refractive Index Changes Measured by Transmitted Light Intensity

The intensity of the propagated light provides another measure of the refractive index of the medium which is especially sensitive when the refractive index of the medium nearly equals that of the fiber (Afromowitz, 1988, 1989). This results from the criterion for waveguiding that the index of the resin be less than that of the waveguide. Two applications of the refractive index criterion for waveguiding have been proposed to monitor the cure of composites (Afromowitz, 1988, 1989; Fanconi, 1989). Afromowitz (1988) reported the design of an optic fiber polymer cure sensor which incorporates a fiber section made from the totally cured resin. Optical fibers of silica were glued onto either end of the resin fiber and the assembly embedded in the prepreg of the partially cured resin. The partially cured resin possesses a lower refractive index than the cured resin which results in propagation of the light through the resin fiber section. As the resin cures, however, its refractive index approaches that of the fiber section and waveguiding ceases. Experiments showed that this sensor is sensitive over the entire range of cure owing to the range of angles of incidence displayed by the guided light. The effect of cure is to change the critical angle which affects the number of modes propagated. The results obtained on an epoxy cure carried out at two temperatures indicated that temperature affects the refractive index mismatch between cured and partially cured resin. This effect is superimposed on the effect of cure which dominates the transmitted light intensity. Although in principle this method is self-calibrating, there are factors, such as fiber bends, which can impact the results. Research continues on this sensor design.

4.5.4.3 Applications of Refractive Index Sensors

Fanconi (1989) proposed optical fiber sensors based on propagated light intensity for monitoring the consolidation of reinforcement plies of composite laminates. In this design, an optic fiber sensor of refractive index less than that of the resin is placed between plies prior to consolidation. As long as the sensor is surrounded by air or other volatiles all light propagates the fiber. As resin wets the fiber, it affects the light rays impinging at the interface where the resin contacts the fiber such that total internal reflection is replaced by refraction. The transmitted intensity degrades as more and more of the fiber surface comes in contact with the resin. The limiting transmitted intensity is proportional to the fraction of fiber surface in contact with voids.

The fluoroprobe fiber optic sensor could also be used to monitor consolidation provided that the fluorescence of the probe is independent of viscosity (Fanconi, 1989). Whereas internal standards are needed for fluoroprobes this is not the case for refractive index sensors since once the intensity reaches a constant value further consolidation is unlikely. To relate this intensity to void content, however, would require some type of internal standard.

Other applications of refractive index measurements of the medium have been characterization of the flow of inhomogeneous materials (Graindorge, 1985) and chemical sensing (Karahara, 1983). The first application is similar to the proposed application to consolidation (Graindorge, 1985). In the other application a sensor was developed to monitor oils in water (Karahara, 1983). An optical fiber was stripped of its cladding and coated by an organophilic compound which preserved the refractive index condition for waveguiding. The normal total internal reflection is degraded by adsorption of hydrocarbons in the organophilic coating, owing to changes in the refractive index at the surface of the fiber, and the variation in output signal can be related to the concentration of hydrocarbons in the water.

4.6 REFERENCES

Afromowitz, M.A., "Fiber Optic Polymer Cure Sensor", J. Lightwave Tech. 6, 1591 (1988).

Afromowitz, M.A., and Lam, K.-Y., "Fiber Optic Sensor for Thermoset Composites", Review of Progress in Quantitative Nondestructive Evaluation, Vol. 8, Thompson, D.O. and Clementi, D.E., Eds, Plenum Press, (1989).

Andrade, J.D., Vanwagenen, R.A., Gregonis, D.E., Newby, K., and Lin, J.-N. "Remote Fiber-Optic Biosensors Based on Evanescent-Excited Fluoro-Immunoassay: Concepts & Progress", IEEE Transactions on Electronic Devices, ED-32, 1175 (1985).

Bloor, D., Preston, F.H., Ando, D.J., and Batchelder, D.N., "Resonant Raman Scattering from Diacetylene Polymers", in Structural Studies of Macromolecules by Spectroscopic Methods, ed. by K.J. Ivin, John Wiley & Sons, New York, 1976.

Boisde, G., and Perez, J.J., "Remote Spectrometry with Optic Fibers, Ten Year of Development and Prospects for On-Line Control", Conference Proceedings of the 2nd International Conference on Optical Fiber Sensors, 1984. Conference Proceedings.

Claus, R.O., and Wade, J.C., "Distribution Strain Measurement in a Rectangular Plate Using an Array of Optical Fiber Sensors", J. Nondestructive Evaluation, 4, 23 (1984).

Compton, D.A., Hill, S.L., Wright, N.A., Druy, M.A., Piche, J., Stevenson, W.A., and Vidrine, D.W., "*In-Situ* FT-IR Analyses of a Composite Cure Reaction Using a Mid-Infrared Transmitting Optical Fiber," Appl. Spectros., 42, 972 (1988).

Dahne, C., Sutherland, R.M., Place, J.F., and Ringrose, A.S., "Detection of Antibody-Antigen Reactions at a Glass-Liquid Interface: A Novel Fiber-Optic Sensor Concept", 2nd International Conference on Optical Fiber Sensors, 1984, 75 (1984).

Fanconi, B.M., "Fourier Transform Infrared Spectroscopy of Polymers-Theory and Application", Journal of Testing & Evaluation, 12, 33 (1984).

Fanconi, B., Wang, F., Hunston, D., and Mopsik, F., "Cure Monitoring for Polymer Matrix Composites", Materials Characterization for Systems Performance and Reliability, McCauley, J.W. and Weiss, V., Eds.,p. 275, Plenum Press, 1986.

Fanconi, B.M., Wang, F.W., and Hunston, D.L., "Comparisons Among Process Monitoring Techniques", ANTEC'87, p.1100, Conference Proceedings, Soc. Plastics Engineers, 45th Annual Technical Conference & Exhibit, Los Angeles, May, 1987A.

Fanconi, B., Wang, F., and Lowry, R., "Process Monitoring of Polymer Matrix Composites Using Fluorescence Probes", Review of Progress in Quantitative Nondestructive Evaluation, Vol. 6B, Thompson, D.O. and Clementi, D.E., Eds, p.1287, Plenum Press, 1987B.

Fanconi, B.M., "Monitoring Consolidation of Reinforcement Plies in Polymer Matrix Laminates", SAMPE Journal, 25, 35, 1989.

Fitch, P., and Gargus, A.G., "Remote UV-Vis-NIR Spectroscopy using Fiber Optic Chemical Sensing", American Laboratory, December, 1985.

Fredericks, P.M., Samson, P.J., and Stuart, A.D., "Characterization of Optical Fibers using a Modified FT-IR Spectrometer", Appl. Spectrosc. 41, 327 (1987).

Fujiwara, M., Hamaguchi, H., and Tasumi, M., "Measurements of Spontaneous Raman Scattering with Nd:YAG 1064-nm Laser Light", Appl. Spectrosc., 40, 137 (1986).

Garton, A., "The Crosslinking of Epoxy Resins at Interfaces. I. Germanium, Germanium Dioxide, and Silane-treated Germanium", J. Polym. Sci., Polym. Phys. Ed., 22, 1495 (1984).

George, G. A., "New Approaches to the Characterization of the Cure of Epoxy Resins for Advanced Composite Materials", Materials Forum, 9, 224 (1986).

Giallorenzi, T.G., "Optical Communications Research and Technology: Fiber Optics", Proc. IEEE, 66, 744 (1978).

Graindorge, Ph, LeBoudec, G. Meyet, D., and Arditty, H.J. "High Bandwidth Two-Phase Flow Void Fraction Fiber Optic Sensor", SPIE 586, 211 (1985).

Havens, J.R., and Koenig, J.L., "Applications of High-resolution Carbon-13 Nuclear Magnetic Resonance Spectroscopy to Solid Polymers", Appl. Spectrosc. 37, 226 (1983).

Hecht, J. "Fiber Optics Turns to Sensing", High Technology, pg.. 49, July/August (1987).

Hirschfeld, T., Deaton, T., Milanovich, F., and Klainer, S., "Feasibility of Using Fiber Optics for Monitoring Groundwater Contaminants", Optical Engineering, 22, 527 (1983).

Hirschfeld, T., and Chase, B., "FT-Raman Spectroscopy: Development and Justification", Appl. Spectrosc. 40, 133 (1986).

Jeunhomme, L.B., Single Mode Fiber Optics, Marcel Dekker, Inc., New York (1983).

Kawahara, F.K., Fiutem, R.A., Silvus, H.S., Newman, F.M., and Frazar, J.H., "Development of a Novel Method for Monitoring Oils in Water", Analytical Chemica Acta, 151, 315 (1983).

Law, K.Y., "Fluorescence Probe for Microenvironments: anomalous Viscosity Dependence of the Fluorescence Quantum Yield of p-N,N-Dialkylamino benzylidenemalononitrile in 1-Alkanols", Chem. Phys. Ltrs., 75, 545 (1980).

Lee, H., and Neville, K., Handbook of Epoxy Resins, Ch. 6, McGraw-Hill, New York, 1967.

Levy, R.L., and Ames, D.P., "Monitoring Epoxy Cure Kinetics with a Viscosity Dependent Fluorescent Probe", Adhesive Chemistry Developments and Trends", L.-H. Lee, ed.,Plenum Press, New York (1983A).

Levy, R.L. and Ames, D.P., "Monitoring Epoxy Cure Kinetics with a Viscosity Dependent Fluorescence Probe", Proc. Org. Coat. Appl. Poly. Sci., 48, 116 (1983B).

Levy, R. L., "Viscosity-Dependent Self-Probe Fluorescence of an Epoxy", Polym. Mat. Sci. & Eng., 50, 124 (1984).

Lew, A., Depeursinge, C., Cochet, F., Berthou, H., and Parriaux, O., "Single Mode Fiber Evanescent Wave Spectroscopy", 2nd International Conference on Optical Fiber Sensors, 1984, 71 (1984).

Loufty, R.O., "High-Conversion of Polymerization Fluorescence Probes. 1. Polymerization of Methyl Methacrylate", Macromolecules, 14, 270 (1981).

Loufty, R.O., "Fluorescence Probes for Polymerization Reactions: Bulk Polymerization of Styrene, n-Butyl Methacrylate, Ethyl Methacrylate, and Ethyl Acrylate," J. Polym. Sci., Polym. Phys. Ed. 20, 825 (1982A).

Loufty, R.O., and Arnold, B.A., "Effect of Viscosity and Temperature on Torsional Relaxation of Molecular Rotors", J. Phys. Chem., 86, 4205 (1982B).

Maugh, T.H. "Remote Spectrometry with Fiber Optics", Science, 218, 875 (1982).

Munkholm, C., Walt, D.R., Milanovich, F.P., and Klainer, S.M., "Polymer Modification of Fiber Optic Chemical Sensors as a Method of Enhancing Fluorescence Signal for pH Measurement", Anal. Chem., 58, 1430 (1986).

Newby, K., Reichert, W.M., Andrade, J.D., and Benner, R.E. "Remote Spectroscopic Sensing of Chemical Adsorption Using a Single Multimode Optical Fiber", Applied Optics, 23, 1812 (1984).

Newby, K., Andrade, J.D., Benner, R.E., and Reichert, W.M., "Remote Sensing of Protein Adsorption Using Single Optical Fiber", J. Colloid & Interface Sci., 111, 280 (1986).

Peterson, J.I., and Vurek, G.G. "Fiber-Optic Sensors for Biomedical Applications", Science, 123 April, 1984.

Peticolas, W.L., Small, E.W., and Fanconi, B.M., "Characterization of Biological Molecules by Laser Light Scattering" in Polymer Characterization: Interdisciplinary Approaches, Ed. by Clara D. Carver, Plenum Press, 1971.

Reddy, M., Bennett, K.D., and Claus, R.O., "Imbedded Optical Sensor of Differential Strain in Composites", Review of Progress in Quantitative Nondestructive Evaluation, Vol. 6B, Thompson, D.O. and Clementi, D.E., Eds, p. 1241, Plenum Press, 1987.

Rockhold, S.A., Quinn, R.D., Van Wagenen, R. A., Andrade, J.D., and Reichert, M., "Total Internal Reflection Fluorescence (TIRF) as a Quantitative Probe of Protein Adsorption", J. Electroanal. Chem., 150, 261 (1983).

Schirmer, R.E., and Gargus, A.G., "Monitoring Polymer Processing Through Fiber Optics", American Laboratory, p. 87, November 1988.

Schwab, S.D., and McCreery, R.L., Versatile, "Efficient Raman Sampling with Fiber Optics", Anal. Chem., 56, 2199 (1984).

Schwab, S.D., and Levy, R., "Advances in the Development of the Fluorescence Optrode Cure Sensor (FOCS)", Polym. Matls. Sci. & Eng., 59, 591 (1988).

Stinson, S.C., "Advances Made in Applying IR Sensors to Process Control", C&EN, p. 30, January 9, 1989.

Sung, C.S.P., Chin, I.J., and Yu, W.-C., "A Novel Fluorescence Technique for Monitoring Cure Reactions in Epoxy Networks", Macromolecules, 18, 1510 (1985).

Sung, C.S.P., Pyun, E., and Sun, H.-L., Characterization of Epoxy Cure by UV Visible and Fluorescence Spectroscopy:Azochromphoric Labeling Approach", Macromolecules, 19, 2922 (1986).

Tromberg, B.J., Eastham, J.F., and Sepaniak, M.J., "Optical Fiber Fluoroprobe for Biological Measurements", Appl. Spectrosc. 38, 38 (1984).

Wang, F.W., Lowry, R.E., and Grant, W.H., "Novel Excimer Fluorescence Method for Monitoring Polymerization: 1. Polymerization of Methyl Methacrylate," Polymer, 25, 690 (1984).

Wang, F.W., Lowry, R.E., and Fanconi, B.M., "Cure Monitoring of Epoxy Resins by Fluorescence Spectroscopy", Proc. ACS Div. of Polym. Matls.: Sci. & Eng. 53, 180 (1985).

Wang, F.W., Lowry, R.E., and Fanconi, B.M., "Novel Fluorescence Method for Cure Monitoring of Epoxy Resins", Polymer, 27, 1529 (1986).

Wang, F.W., and Fanconi, B.M., "In-Situ Characterization of the Interface of Glass Reinforced Composites", NBSIR 87-3581, June, 1987A.

Wang, F.W., and Wu, E.-S.,"Cure Monitoring of Epoxy Resins by Fluorescence Recovery after Photobleaching," Polym. Comm. 28, 73 (1987B).

Wang, F.W., Bur, A.J., Lowry, R.E., and Fanconi, B.M., "Fluorescence Monitoring of Polymer Processing",in Advances in Chemistry Polymer Characterization by Interdisciplinary Approaches, Ed. by Clara D. Carver, Plenum Press, 1989.

Weyer, L.G., Becker, K.J., and Leach, H.B., "Remote Sensing Fiber Optic Probe NIR Spectroscopy Coupled with Chemometric Data Treatment", Appl. Spectros. 41, 786 (1987).

Wu, W.-L., and Fanconi, B.M., "Post-Curing of Dental Restorative Resins", Polymer Eng. & Sci., 23, 704 (1983).

Young, P.R., Druy, M.A., Stevenson, W. A., and Compton, D.A.C., "In Situ Composite Cure Monitoring Using Infrared Transmitting Optical Fibers", SAMPE Journal, 25(2), 11 (1989).

PROCESS CONTROL AND MODELING

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and Donald Hunston

5.1 INTRODUCTION

Two additional topics are important to the development of on-line process control. First, any control system in the future will not only need the information provided by on-line real-time sensors such as those described in the previous sections of this Report, but also data for temperature and pressure. Consequently, sensors for these two parameters are also needed. Second, process modeling is directly relevant to the process control problem. Two categories of models are worth discussing: process simulation and process control. The former are very useful to help understand a process and develop a processing cycle. As a results, they have received a great deal of study during the last decade. Process control models, on the other hand, are in an earlier stage of development at least for composites. Moreover, these models can be proprietary so much less information is currently available in this area. Although a complete discussion of these topics is beyond the scope of this Report, a brief presentation will be given here for each.

5.2 CONVENTIONAL TEMPERATURE AND PRESSURE SENSORS

Conventional temperature and pressure sensors have been treated recently by several authors. Some of the topics discussed by Benedict (1984) are: liquid-in-glass thermometers, resistance thermometry, thermoelectric thermometry, optical pyrometry, calibration of temperature sensors, temperature measurement in moving fluids, installation effects on temperature sensors, transient temperature measurement, pressure standards, principles of conventional pressure transducers, pressure measurement in moving fluids, and transient pressure measurement. McGee's (1988) treatment on temperature measurement includes not only conventional sensors but also a chapter on novel methods for temperature measurement. Such measurements were also treated recently by Leigh (1988) and Schooley (1986). In addition, Jones' Instrument Technology (1985) contains chapters on measurement of pressure and temperature.

Hashemian and Petersen (1988) analyzed the accuracies of industrial temperature measurements made with thermocouples and resistance temperature detectors or RTDs. They concluded that achievable overall accuracies for industrial temperature measurement systems based on thermocouples and RTDs are in the range of 0.1 to 1.0°C, with RTDs at the more accurate end. Mangum (1984) reported the results of an investigation of the stability of small industrial platinum resistance thermometers (IPRTs) upon heat treatment and handling. Ninety-four IPRTs, including models obtained from five different manufacturers, were studied. Most of the IPRTs exhibited calibration drifts and also effects due to the presence of moisture or strain. Comparisons were made of the relative stability of the products of the five companies. Finally, Demorest (1985) reviewed the appropriate application of mechanical and electromechanical sensors for pressure measurements, as well as transmitters and transducers.

5.3 OPTICAL FIBER TEMPERATURE AND PRESSURE SENSORS

The advantages of optical fiber sensors include their insulating properties, the intrinsic safety of a passive medium, the immunity from electrical interference, their low weight, and the ease of installation provided by their flexible geometry. These unique advantages over conventional sensors are particularly important in environments that are thermally or electromagnetically harsh.

5.3.1 Intensity Modulation

Berthold (1988) defined an intensity modulated optical fiber sensor as a sensor where the variable to be sensed or measured causes a change in light intensity at one or more optical wavelengths. After suitable wavelength filtering, the change in light intensity is converted to an electrical signal by a photodetector. The intensity modulated optical fiber sensors offer the virtues of simplicity, reliability, and low cost. Berthold (1988) recently reviewed commercially available intensity modulated optical fiber sensors for industrial applications and listed manufacturers and sensing methods for each specific variables to be sensed. The measurement parameters discussed are temperature, pressure, position/proximity/displacement, flow, and liquid level.

Intensity modulated optical fiber sensors can suffer from serious errors unless methods are employed to compensate for variation in light source intensity, losses in optical fibers and connectors, and variations in detector sensitivities. Methods to overcome these potential sources of errors have been described by Medlock (1987) and by Ulrich (1987). Ulrich analyzed the method of spectral encoding from a system point of view. Medlock (1987) gave examples of referencing methods based on the use of digital devices, two wavelength system (Spooner, 1985) and the use of a single wavelength in a balanced bridge system (Culshaw, 1983).

5.3.2 Temperature

Examples of temperature sensors based on the temperature dependent variation of the transmission, fluorescence or Planck radiation emitted by a black body were described by Glenn (1987). The sensing element can be a separate component or it can be a section of the fiber itself. The examples include fiber sensors based on the transmission of Nd or Eu doped fibers, the fluorescence of Nd doped glass, and the black body radiation from a sapphire rod-fiber that has a metallic coating on a small portion of its tip. Brenci (1984) described a thermochromic transducer optical fiber temperature sensor employing two spectral transmission channels. Varshneya (1986) designed and developed a fiber optic temperature probe system that is based on selective two-color radiation measurement emitted by a particle. The system was used to measure in-situ the temperature-time history of individual coal particles at the temperature range of 250 to 1200°C.

5.3.3 Pressure

Simple pressure sensors based on displacement devices attached to a membrane have been developed for industrial (Tallman, 1980) and medical measurements (Matsumoto, 1978; Krarstein, 1983). In Matsumoto's device, a pressure-sensitive watertight membrane, located in a side hole of the catheter tip, is attached to a cantilever mirror. Any pressure on the membrane presses down the cantilever plate; the mirror changes its position relative to the cross section of the fiber bundle and hence alters the amount of the back reflected light. Another mechanical optical fiber transducer (Lawson, 1983) relies on the effect of the change in diaphragm curvature (rather than displacement) on the intensity of the reflected light from a diaphragm. Jones and Spooner (1983) described an optical fiber pressure sensor in which light intensity is modulated by displacement of a pair of holographic gratings relative to each other in a direction perpendicular to the rulings. Hfk and Jonsson (1984) described a pressure sensor based on the change of the fluorescence decay rate of Nd doped glass with pressure.

5.4 PROCESS MODELING: Autoclave Compression Molding

As indicated in the introduction, there are a number of major industry and government programs addressing the question of processing models. A good indication of the current state-of-the-art in this area, however, can be obtained from publications in the recent literature.

5.4.1 Introduction: The Cure Cycle

The first process modeling area to be considered is the Autoclave/Vacuum Degassing molding process which is a procedure for producing high performance laminate composites. In this process, composite structures using thermosetting resins are formed by laying up individual uncured resin-fiber prepreg plies in a prescribed orientation to form a laminate, then curing this structure in a mold of the desired shape by applying heat and pressure. Heat is applied to initiate and control the chemical reaction, and to reduce the resin viscosity so that the material will readily flow. Pressure is applied to squeeze out excess resin, compact the plies, and minimize void content.

The temperature and pressure levels that are applied as a function of time determine the processing cycle (or cure cycle). The economy of the process and the final properties of the cured part depend a great deal upon the cure cycle that is chosen. An optimum cycle has the following characteristics (Springer, 1986)

a) the resin content of the final part is uniform

b) the part is uniformly and completely cured

c) void content in the part is minimized

d) the part does not experience any undesirable exotherms

e) the part is produced in the shortest time possible
while still satisfying a) - d).

The characteristics of the optimal cure cycle depend upon the material properties of the resin and fiber, and also, upon the geometry of the mold in which the composite is formed. Therefore, it is quite useful to have available models which describe this process so that new processes can be readily designed without having to resort to trial and error procedures. Such models are also useful for on-line process control as long as the time-scale for obtaining model predictions is short compared to the time-scale of the process (Springer, 1986).

5.4.2 Elements of Autoclave Modeling

The elements that go into a complete model of this process can be divided into two distinct areas. The first area is the modeling of the cure cycle. This involves describing the heat transfer, chemical reaction and flow consolidation which occur during curing due to the applied temperature and pressure. The second area can be called post-cure modeling. These models are used to predict mechanical properties of the cured part which result due to the applied cure cycle.

5.4.2.1 Modeling of the Cure Cycle

When heat and pressure are applied to the mold, the resin in the laminate begins to flow and react. In order to achieve an optimal cycle, the most important goals are to compact all the plies in the laminate before the material gels, and to accomplish this in the shortest time possible. For fixed values of the applied temperature, applied pressure, mold geometry and fiber properties, the ability to achieve these goals depends mostly upon three variables: the temperature in the composite, the resin viscosity, and the degree of cure.

The viscosity is the main variable which determines how fast the material will flow out of the laminate. Low viscosities are desirable in order to achieve fast and complete compaction of the plies. In thermosetting systems, the viscosity is low when the temperature is high and the degree of cure is low. Thus, the optimal applied temperature is one that keeps the viscosity as low as possible, while still maintaining adequate control of the chemical reaction. A reaction that is too fast (due to too high an applied temperature) can lead to several undesirable features. The greatest danger is that the material will gel before all the plies have compacted. The part will then be filled with voids and resin-rich areas, and thus have poor mechanical properties. Another danger is reaction runaway which can occur if the applied temperature is too high and the heat transfer between the mold and the surroundings is poor. This can lead to non-uniform cure and thermal degradation.

Models for simulating the cure cycle must be able to predict the temperature, resin viscosity, and degree of cure as a function of time and position, and the flow of resin out of the system as a function of time. Such models require, as input, values for the applied pressure and temperature, the mold geometry, and the material properties of the resin and fiber.

5.4.2.2 Post-Cure Modeling

The important variables to predict in post-cure modeling are defined by Loos and Springer (1983) as the residual stress in the part, the number and volume of voids in the part, and the mechanical strength and modulus of the part. This information can be used to evaluate the ability of a cure cycle to produce an acceptable part and provide feedback for helping to work towards an optimum cycle. It should be noted, however, that the prediction of ultimate properties such as strength is quite difficult, particularly if the loading is such that the failure is not fiber dominated. Consequently, the models must be used carefully in this area.

5.4.3 Literature Survey

One of the most complete models of autoclave compression molding is that of Loos and Springer (1983). This model, described in detail in Springer (1986), consists of five submodels for describing the thermochemical effects, flow consolidation, residual stresses, void formation, and strength and modulus. This model has been implemented on a user-friendly computer program called CURE, and is available by writing to Springer at the Department of Aeronautics and Astronautics at Stanford University (Loos and Springer, 1983).

The strength of the Springer-Loos model is that it can be used to predict many aspects of the curing process ranging from heat transfer and chemical reaction during processing to strength and modulus of the final part. The basic inputs for this program are the mold geometry, the material properties, the applied temperature and pressure, and the vacuum bag pressure as a function of time. Among the outputs are the temperature, pressure, degree of cure, and resin viscosity in the part as a function of position and time, and the number of compacted prepreg plies as a function of time (Springer, 1986).

While the Springer-Loos model is a relatively complete description of the autoclave process, there are now other models available which exhibit improved predictive capability over some of the various submodels that make up the Springer-Loos formulation. This is especially true in the case of their resin flow submodel. Therefore, some other "cure models", which in the context of the entire process are properly called submodels, are discussed below.

5.4.3.1 Thermochemical Models

There are two major needs in developing thermochemical models for cure monitoring. The first is the need for expressions for the rate of reaction (or degree of cure) and the heat of reaction as a function of time and temperature. The second is the need for an expression for the viscosity as a function as temperature and degree of cure. A discussion of how one goes about establishing such relationships is discussed in Lee, Loos and Springer (1982). The basic approach is to regress experimental data into suitable analytical expressions. Such expressions are, of course, material dependent to some extent. However, it has been found that for many thermosetting systems similar expressions can be used for different cases, with different values of some adjustable parameters (Kamal, 1987A and 1987B). Considering possible kinetic models for the reactions can be quite helpful in selecting appropriate equations.

A suitable expression for viscosity in epoxy resin systems has been presented by Schmitt et al. (1989). Other references for viscosity models are Tajima et al. (1986), Tajima et al. (1983), Dusi et al. (1982), and Roller et al. (1975).

5.4.3.2 Resin Flow Models

One of the early resin flow models is the one developed by Springer (1982). In this model, the laminate is considered to be a layer of porous sheets (which lack deformability) in which there exists pressure gradients in the horizontal and vertical directions. The flow in the vertical direction is modeled using Darcy's law, while the flow in the horizontal direction is accounted for in a heuristic manner. Although the Springer model is able to predict flow in both the horizontal and vertical directions, it suffers from two major shortcomings. First, it is assumed that all of the applied pressure is borne only by the resin. This can lead to major over predictions of the resin flow rate when the degree of ply compaction is large. Second, the flow in the horizontal and vertical directions is decoupled. This can lead to errors in the predictions of pressure.

Other models, similar in nature to the Springer model, are those presented by Kardos et al. (1983), Williams et al. (1984), and Halpin, Kardos and Dudukovic (1983). These models, however, offer no major improvements over the Springer model. Another major approach is that developed by Lindt (1982), but the evidence indicates that the models cited above, which are based on Darcy's Law, are more accurate (Dave et al., 1987).

The model developed by Gutowski et al. (1987A) considers the laminate to be an elastic, deformable porous medium in which the flow in all direction is governed by Darcy's law. This model offers several improvements over previous models of flow consolidation. First of all, it accounts for the pressure borne by the fibers due to their elastic deformation. Second, it couples the modeling of the flow in both horizontal and vertical directions. Third, it allows prediction of the time-dependent pressure profiles in the horizontal and vertical planes. Experimental measurements showing the validity of their approach are presented in Gutowski et al., (1987B).

A similar resin flow model is that developed by Dave et al. (1987). They use the theory of consolidation and flow in a porous medium developed by Teraghi (1923) and Biot (1941, 1955, and 1956). The only major difference between the flow model developed by Dave et al. (1987) and those of Gutowski et al. (1987A) is the description of the change of permeability with compaction. Either of these models represent the most accurate description of flow in a porous medium to date for treatments applied to composite systems.

5.4.3.3 Post-Cure Modeling

The philosophy of post-cure modeling is not to try to obtain exact numbers, but rather order-of-magnitude estimates which give an idea as to whether or not the cure is proceeding in an acceptable manner (Tucker, 1987). Few good approaches are available for estimating residual stresses in autoclave compression molded parts (Tucker, 1987). Useful models also exist for other important post-cure modeling variables. This is a difficult area, however, and there is much potential for future work.

A model for the residual stress and modulus in autoclave compression molded parts has been formulated by Tsai and Hahn (1980). The principles upon which this model has been established are accepted (Jones, 1980) and used in practice (e.g., Loos and Springer, 1983). Another approach, which may have some application to autoclave compression molding, is that used by Shaffer and Levitsky (see, Shaffer and Levitsky, 1974; Levitsky and Shaffer, 1974; Levitsky and Shaffer, 1975).

A model for void size and pressure in autoclave composites has been formulated by Loos and Springer (1983). This model tracks void evolution for voids of known position and initial location. A discussion of void formation is given in Kardos, Dudukovic, McKague, and Lehman, (1983). Void formation can be minimized by applying very high pressures right before gelling (Brown and McKague, 1982). Loos and Springer (1983) have discussed how this can be applied in the context of modeling to obtain parts with minimal void content.

5.5 **PROCESS MODELING: Resin Transfer Molding**

5.5.1 Introduction

A second important area for process modeling is resin transfer molding (RTM). RTM is a versatile process for producing fiber-reinforced plastic (composite) structures ranging from small, low-performance articles with simple shape to very large, high-performance articles of complex shape (Johnson, 1987; Babbington et al., 1988). In the basic process, catalyzed resin is pumped into a mold which has been prefilled with some type of fiber reinforcement. The resin wets out the fiber, fills the mold, and cures. When the part has gained sufficient green strength it is demolded and the process is repeated for the next part. Post curing in an oven can be used to complete cure if necessary.

The mold filling stage of RTM can be described as the non-isothermal flow of a chemically reacting fluid in a porous medium. The most important issues are:

1) How does the liquid spread as it is pumped into the mold?
   Does the mold completely fill, or are there dry spots?
   Where should the mold be vented to allow air being displaced by the incoming fuid to escape?

2) How high are the pressures generated during mold filling?

3) How should the control variables be set so that the mold is completely filled before the material begins to gel?

The goal of modeling is to answer these types of questions, and hence, come up with an efficient and economical process.

5.5.2 Elements of RTM Modeling

The most important variables affecting RTM mold filling are the resin viscosity and the permeability of the porous material. Because the liquid is reacting as it flows, the viscosity changes as it goes through the mold. Initially, the viscosity decreases because the mold is heated, but eventually the viscosity increases due to the polymerization. One of the goals of mold filling is to completely fill the mold before the viscosity begins to increase due to the gain in molecular weight. This is necessary because RTM is very often carried out with materials that cure very close to the gel point. If the mold is not filled before this rise several undesirable things can result, such as, incomplete mold filling and/or mold warpage due to the generation of high pressures. In fact, because of this many molds are filled at significantly below the cure temperature and then when the mold is filled, heat is applied to the mold to promote rapid cure.

The most important variables to take into account when describing the viscosity in mold filling are the temperature and the degree of cure. Viscoelastic or shear thinning effects are probably not significant since the mold is completely filled before significant crosslinking has taken place and the starting resins are generally Newtonian. However, non-Newtonian behavior will be very important if the resin is highly filled, which is often the case. Thus, the effect of filler must definitely be taken into account.

Issues such as heat transfer and chemical reaction are handled in the manner standard for thermosetting resin systems in other operations such as RIM (see e.g., Kamal and Ryan, 1987A and 1987B). The important models are a rate expression, data on the heat of reaction, and an expression for the viscosity as a function of the temperature and degree of cure.

5.5.3 Literature Survey: Mold Filling

Resin transfer molding studies have, thus far, been limited to mold filling experiments and simulation. This is because the reaction kinetics and heat transfer problems encountered for RTM systems are very similar to those encountered in other thermoset processes such as RIM and autoclave compression molding.

Because RTM mold filling involves the flow of fluid through a porous media, the flow is usually modeled using averaged balance equations and Darcy's law (Greenkorn, 1983). Adams et al. (1988) have developed an approximate analytical solution for the advancement of a flow front through an infinite, initially dry medium. However, while this solution provides insight, it cannot be used to model real processes where the material encounters walls and other obstructions to the flow path. Therefore, such problems must be solved numerically.

Numerical flow modeling studies of RTM filling have been carried out by Bruschke and Advani (1988), Coulter, Smith and Guceri (1987), and Martin and Son (1986). All three of these studies solve exactly the same equations, but for different flow situations and with different numerical schemes. Experimental results are presented as well. Excellent agreement between model and experiment are obtained in all cases.

Based on these results, it seems that the Darcy's law approach for describing the fluid flow through the porous fiber filler works very well. Thus, the coupling of such models with accurate thermochemical models, should ultimately allow for a very accurate description of the RTM mold filling process.

5.6 **PROCESS MODELING: Compression Modeling**

5.6.1 Introduction

The Compression Molding process is the most highly developed way for incorporating fibers into plastics to form composite structures (Johnson, 1988). While it is sometimes used for molding thermoplastic materials, most often it is used with sheet molding compounds (SMC), which are mixtures of glass fibers and thermoset resin, thickened with magnesium oxide. Because of the close association of compression molding with this material, the process is commonly called by the acronym, the SMC process.

In a typical compression molding cure cycle, there are three main stages. In the first stage, a "charge" of SMC or some other material is placed in the mold. The placement and shape of the initial charge is very important, since it is the primary factor affecting the subsequent flow (Tucker, 1987). Typically, the charge covers 30-80% of the mold. Heat and pressure are then applied. The pressure squeezes the material and causes it to flow until the mold is filled, and the heat causes the material to cure. Since the mold filling step is generally very fast, almost no cure takes place during this time. Therefore, this is usually taken to be the second stage of the process. Stage three is taken to be the final curing stage.

5.6.2 Elements of Modeling Compression Molding

In the modeling of the cure cycle there are two critical issues, cycle time and fiber orientation. The cycle time is important for economic reasons: too slow a cycle time leads to an unprofitable process. The orientation of the fibers is induced by the flow of the charge. This orientation can greatly effect the mechanical properties of the final part. Therefore, as is the case in other thermoset molding processes, the important elements in modeling the cure cycle are fluid flow, heat transfer, and chemical reaction. Stages one and two of this process are dominated by flow, stage three by heat transfer and chemical reaction.

5.6.3 Literature Survey

5.6.3.1 Flow Modeling

Two major approaches have been used to model mold filling in compression molding. The first is the Hele-Shaw model. The formulation and assumptions that lie behind this model are discussed in Tucker (1987). The equations and the flow geometries that they are solved for are sufficiently complex as to require numerical solution. Several methods have been tried. A finite difference scheme has been developed by Silva-Nieto, Fisher and Birley (1980). This approach is interesting because they start with a filled mold and integrate backward in time to calculate an initial charge shape (recall, the primary factor affecting flow is the placement and shape of the original charge). The finite element method has also been used. Numerical calculations are presented in Tucker and Folgar (1983), and Lee, Folgar and Tucker (1984). While the model used by these authors gives excellent with experiment, the element stretching scheme that they employ breaks down if the geometry becomes to complex. An alternative finite element scheme that overcomes such difficulties has been developed by Brown (1983). In this approach, the geometry is covered with elements at the start and calculations are only performed in elements that are full. Preliminary results based on this approach show promise and are presented in Tucker (1987).

Another major approach to modeling compression mold filling is that developed by Barone and Caulk (1979). In this model, the flow kinematics are assumed to those of lubricated squeezing (Chatraei, Macosko, and Winter, 1980). Recently, these same authors have developed a modification of this approach (Barone and Caulk, 1986). The modified model incorporates elements of both the Hele-Shaw and the initial lubricated squeezing approach. Preliminary calculations show excellent agreement with experiment (Tucker, 1987).

5.6.3.2 Fiber Orientation

As the charge is compressed and flows to fill the mold, the fibers in the mixture tend to obtain a preferential orientation in the direction of flow. The flow-induced structure that is generated can significantly effect the mechanical properties of the final part. Therefore, it is desirable to be able to predict the flow-induced fiber orientation, or even optimize this effect.

In order to model fiber orientation, two things are needed: accurate modeling of the flow field as the material is squeezed and a model which predicts fiber orientation as a function of the kinematics. There are three main models currently being used to predict fiber orientation in compression molded parts. The classical model of Jeffery (1922) is valid for dilute systems. A model for concentrated systems has been developed by Folgar and Tucker (1984). A more recent model, which is valid for mildly concentrated materials is that of Advani and Tucker (1987). These models are able to predict fiber orientation in flow provided the kinematics of the flow are known. Therefore, the approach used so far has been to simulate the fluid mechanics of the mold filling based on the flow models discussed above in section 5.6.3.1, and then, using these kinematics, calculate the flow induced fiber orientation. The major studies utilizing this approach are by Givler, Crochet, and Pipes (1983A), Givler (1983B), Jackson, Folgar, and Tucker (1985), Jackson, Advani and Tucker (1986), and Advani and Tucker (1988).

One weakness of the approach above is that although the fiber orientation itself effects the rheology in actual flow systems, this has not been accounted for in any of the mold filling simulations. Thus, this remains an area of future work. A review of work done to study the rheology of fiber filled suspensions is given in Advani (1989).

5.6.3.3 Heat Transfer and Chemical Reaction

Heat transfer models of the compression molding process usually consider the balance between the heat given off by the reaction and conduction in the thickness direction. The effect of convection in the initial mold filling stage and conduction in the plane are usually ignored. Such assumptions are generally valid since the mold filling step is fast (as mentioned above), and the parts made by this process are usually quite thin.

Because the heat transfer models are so simple, the ability to obtain good agreement with experiment depends a great deal upon having an accurate model for the chemical reaction (Tucker, 1987). A number of models are currently in use. The model of Kamal and Sourour (1976) is fairly simple and fits cure data for unsaturated polyester resins very well. A more detailed model for thermoset cure kinetics has been developed by Stevenson (1980; 1981). A simplification of Stevenson's model has been derived by Lee (1981). Such models and numerical solutions are presented in Barone and Caulk (1979), Lee (1981), and Stevenson (1981).

5.7 CURRENT STATE OF COMMERCIAL COMPUTER SIMULATION PROGRAMS FOR POLYMER PROCESSING

The advances in process modeling have led to the development of commercial computer programs to describe and optimize a process. In most cases these programs are designed for polymers rather than composites, but predictions of flow fields in polymers are sometimes very useful as a first step in composites modeling. Consequently, a few brief comments on the state-of-the-art in this area will be presented here.

Due to recent innovations in the technology of computer hardware and software, simulations can now be used as an engineering tool to expedite, analyze, or optimize many facets of complex polymer processes. The commercial software packages currently available consist of user-friendly CAD/CAM programs (such as MOLDFLOW®, C-FLOW® and POLYFLOW®). In conjunction with numerical methods, these packages permit the analysis of response to changes in material properties, process conditions, mold geometry, etc. in minutes, not weeks. Simulations can be performed on the computer, and problems observed and corrected on screen. This saves both time and money. These developments of computer simulations have been almost exclusively focused on the mold filling behavior of thermoplastic materials. Application to thermosetting systems has not received the same attention due to inadequacies in material characterization and in process models that incorporate chemical reaction.

Future directions for commercial programs can be illustrated by recent work of Vespoli and Marken (1987 and 1988). They treat the reaction injection molding process and predict fill patterns, viscosity effects, and curing behavior. These simulations only predict flow front conditions, and thus, the effects of reaction on flow viscosity, heat transfer, and degree of cure elsewhere in the mold are still unknown. Furthermore, the models assume isothermal wall condition, while in fact, some heat transfer from the chemical reaction is expected to raise the mold temperature. Consequently, these results can only be used as a general guideline to optimize RIM mold design and processing. Further developments in this area are clearly coming in the future.

5.8 PROCESS CONTROL MODELS

The models described in the previous section are best characterized as process simulation or prediction. In their normal form, they are not designed for on-line control. Nevertheless, one approach to the control problems is through simulation programs. There are two possible routes. First, an effort can be made to invert the model. Normally such a model take the starting conditions and the processing cycle and predict what will happen. An inverted model would use the desired end point and the current state of the system to predict the processing cycle needed to get from one to the other. Inverting a model in this way, however, has generally proved to be a very difficult task. Consequently, a second route has been tried using an iterative procedure. In this method, the current state of the part is input to the model and a variety of processing cycles are tried in an effort to reach the desired end point. The most successful cycle is then chosen.

The procedures described above have two disadvantages. First, they require sophisticated programs and a great deal of knowledge about the materials and events that occur during processing. Second, the programs often require significant amounts of computing time at each evaluation point in the process. This can be a major handicap for real-time control.

As a result, a second approach has been tried in recent years. It uses artificial intelligence programming methods (Abrams, 1987). In this procedure, the process is first divided into a series of stages. A list of rules is then formulated for each stage based on the knowledge and intuition of "experts.". These rules indicate how the control parameters should be changed based on data provided by the sensors. They also indicate what conditions are required for successful completion of each stage in the processing cycle. When one stage is completed, the program moves on and invokes the set of rules for the next stage. One advantage of this approach is that a program can be developed without a detailed knowledge of all the events that occur in the part during processing although, obviously, a better knowledge base will produce a superior set of rules. Moreover, the quality and quantity of data available from sensors and the level of understanding as to what this data means has a significant impact on the success of the procedure. Programs based on this approach to process control are just beginning to appear and are still fairly simple. Nevertheless, the early results show considerable promise.

5.9 REFERENCES

Pressure and Temperature References

Benedict, R. P., Fundamentals of Temperature, Pressure, and Flow Measurements, 3rd Edition, (John Wiley & Sons, New York, 1984).

Berthold, J. W., "Fiber Optic Intensity Sensors: Commercial Hardware for Industrial Applications," Photonics Spectra, December, 1988.

Brenci, M., Conforti, R., Falciaci, R., Mignani, A. G., and Scheggi, A. M., "Thermochronic Transducer Optical Fiber Temperature Sensor," in Proceedings of the 2nd International Conference on Optical Fiber Sensors, OFS '84, Stuttgart, VDE-Verlag, 1984.

Culshaw, B., J. Physics E., 16 (10), 978 (1983).

Demorest, Jr., W. J., "Pressure Measurement," Chemical Engineering, September, 56, 1985.

Glenn, W. H., "Fiber Optic Temperature Sensors," Optical Fiber Sensor, p. 185, Chester, A. N., Martellucci, S. and Verga Sheggi, A. M., Eds., (Martinus Nijhoff, Dordrecht, Boston, Lancaster, 1987).

Hashemian, H. M. and Petersen, K. M., "Accuracy of Industrial Temperature Measurement," Advances in Instrumentation, 43 (3), 943 (1988).

Hök, B., and Jonsson, L., "Pressure Sensor with Fluorescence Decay As Information Carrier," p. 391, Conference Proceedings, 2nd International Conference on Optical Fiber Sensors, Sept. 5-7, 1984, Liederhalle Stuttgart VDE - Verlag, GmbH Berlin, Offenbach the International Society for Optical Engineering SPIE-Vol. 514, 1984.

Jones, B. E., and Spooner, R. C., "Optical Sensor with Fibre Optic Links:A Shutter Modulator, SPIE, 376, 29-36 (1983).

Krarstein, B., et al. J. Urology, 130, 504 (1983).

Lawson, C. M., and Tekippe, V. J., Opt. Lett. 8, 286(5) (1983).

Leigh, J. R., Temperature Measurement and Control, Peter Peregrinus, Ltd. on behalf of the Institution of Electrical Engineers, 1988.

Mangum, B. W., "Stability of Small Industrial Platinum Resistance Thermometers," Journal of Research of the NBS, 89 (4), 305 (1984).

Matsumoto, H., et al. J. Med. Eng. Tech., 2, 239 (1978).

McGee, Thomas D., Principles and Methods of Temperature Measurement, (John Wiley & Sons, New York, 1988).

Measurement of Temperature and Chemical Composition, B. E. Noltingk, Ed., Jones' Instrument Technology, Volume 2, Fourth Edition, (Butterworths, London; Boston, 1985).

Mechanical Measurements, B. E. Noltingk, Ed., Jones' Instrument Technology, Volume 1, Fourth Edition, (Butterworths, London; Boston, 1985).

Medlock, R. S., "Fibre Optic Intensity Modulated Sensors," in Optical Fiber Sensors, Chester, A. N., Martelluccia, S. and Verga Scheggi, A. M., Eds., (Martinus Nijhoff, Dordrecht, Boston, Lancaster, 1987).

Schooley, James F., Thermometry, CRC Press, Inc., 1986.

Spooner, R. C., "Fibre Optics in Physical and Chemical Sensors," IMC Conf., Harrogate, Nov., 1985.

Tallman, C. R., Wingate, F. P., and Ballard, E. O., ISA Trans., 19, 49 (1980).

Ulrich, R., "Theory of Spectral Encoding For Fiber-Optic Sensors," in Optical Fiber Sensors, Chester, A. N., Martellucci, S. and Verga Sheggi, A. M., Eds., (Martinus Nijhoff, Dordrecht, Boston, Lancaster, 1987).

Varshneya, D., and Berthold, J. W., "Fiber Optic Non-Contact Temperature Probe System," SPIE, 718, 142 (1986).

Process Modeling and Control

Abrams, F. L., "Expert system Process Controller for Advanced Composites," p. 117 in Automotive Challenges and Plastics Response: Automotive Plastics," (SPE, 1987).

Adams, K. L., Russell, W. B., and Rebenfeld, L., "Radial Penetration of a Viscous Liquid into a Planar Anisotropic Porous Medium," International Journal of Multiphase Flow, 14(2), 203- 215 (1988).

Advani, S. G., and Tucker III, C. L., "The Use of Tensors to Describe and Predict Fiber Orientation in Short Fiber Composites," Journal of Rheology, 31(8), 751-784 (1987).

Advani, S. G., and Tucker III, C. L., "A Numerical Simulation to Predict Fiber Orientation in Thin Compression Moldings," SPE Tech. Paper, 34, 687-691 (1988).

Advani, S. G., "Flow Behavior in Molding Short Fiber Composites," to appear in the Encyclopedia of Composites, 1989.

Babbington, D., Barron, J., Enbos, J., Ramsey, R., and Preuss, W., "Evolution of RTM With Vinyl Ester Resins," in How To Apply Advanced Composites Technology," Proceedings of the Fourth Annual Conference on Advanced Composites, ASM International, 1988.

Barone, M. R., and Caulk, D. A., International Journal of Heat and Mass Transfer, 22, 1021 (1980).

Barone, M. R., and Caulk, D. A., Journal of Applied Mechanics, 53, 361 (1986).

Biot, M. A., J. Appl. Phys., 12, 155 (1941).

Biot, M. A., J. Appl. Phys., 26, 182 (1955).

Biot, M. A., J. Appl. Phys., 27, 459 (1956).

Brown, G. G., and McKague, E. L., "Processing Science of Epoxy Resin Composites," Technical Orientation, General Dynamics, Convair Division, San Diego, CA, August, 1982.

Brown, P. F., M.S. Thesis, Department of Mechanical and Industrial Engineering, Univeristy of Illinois at Urbana-Champaign, Urbana, Illinois, 1983.

Bruschke, M. V., and Advani, S. G., "A Numerical Simulation of the Resin Transfer Mold Filling Process," Soc. of Plast. Engineers, 47th Annual Tech. Conf., Conf. Proceedings, New York, pp. 1769-1773, 1989.

Chatraei, S. , Macosko, C. W., and Winter, H. H., Journal of Rheology, 27, 387 (1981).

Coulter, J. P., Smith, B. F., and Guceri, S. I., "Experimental and Numerical Analysis of Resin Impregnation During the Manufacturing of Composite Materials," in Proc. 2nd Tech. Conf. Am. Soc. Comp. Mat. 209-217 (1987).

Dave, R., Kardos, J. L., and Dudukovic, M. P., "A Model for Resin Flow During Composite Processing: Part 1 - General Mathematical Development", Polymer Composites, 8(1), 29-38 (1987).

Dusi, M. R., May, C. A., and Seferis, J. C., Org. Coat. and Appl. Poly. Sci. Proc., A.C.S., 47, 635 (1982).

Eduljee, R. F., Gillespie Jr., J. W., and Pipes, R. B., "Design Methodology for the Molding of Short Fiber Composites", in Proc. 2nd Tech. Conf. Am. Soc. Comp. Mat., pp 199-208, 1987.

Folgar, F. P., and Tucker, C. L., "Orientation Behavior of Fibers in Concentrated Suspensions," J. Reinf. Plas. Compos., 3, 98- 119 (1984).

Greenkorn, R. A., "Single-fluid Flow Through Porous Media," Ch. 11 of Handbook of Fluid in Motion, Cheremisinoff, N.P. and Gupta, R., Eds., (Ann Arbor Science, Ann Arbor, MI 1983).

Givler, R. C., Crochet, M. J., and Pipes, R. B., "Numerical Prediction of Fiber Orientation in Dilute Suspensions," J. Composite Mat., 17, 330-343 (1983A).

Givler, R. C., "A Numerical Technique for the Prediction of Short Fiber Orientation Resulting from the Suspension Flow," in Transport Phenomena in Material Processing, Chen, , M. M., Mazumdar, J. and Tucker, C. L., Eds., pp 99-103, (ASME, New York, 1983B).

Gutowski, T. G., Morigaki, T., and Cai, Z., "The Consolidation of Laminate Composites," J. of Composite Mat., 21, 172- 188 (see Givler 1983A, February 1987A).

Gutowski, T. G., Cai, Z., Bauer, S., Boucher, D., Kingery, J., and Wineman, S., "Consolidation Experiments for Laminate Composites," 21, 650-669 (June 1987B).

Halpin, J., Kardos, J. L., and Dudukovic, M. P., "Processing Science: An Approach for Prepreg Composite Systems," Pure and Appl. Chem., 55(5) (1983).

Jackson, W. C., Folgar, F., and Tucker, C. L., "Prediction and Control of Fiber Orientation in Molded Parts," in Polymer Blends and Composites in Multiphase Systems, Han, C. D., Ed., Adv. Chem. Ser. No. 206, p. 279, (ACS, Washington, 1984).

Jackson, W. C., Advani, S. G., and Tucker, C. L., "Predicting the Orientation of Short Fibers in Thin Compression Moldings," J. of Composite Mat., 20, 539-557 (1986).

Jeffery, G. B., "The Motion of Ellipsoidal Particles Immersed in a Viscous Fluid," Proc. Roy. Soc., A102, 162 (1922).

Johnson, C. F., "Compression Molding," in Engineered Materials Handbook, Volume 1, Composites, (ASM International, 1987A).

Johnson, C. F., "Resin Transfer Molding," in Engineered Materials Handbook, Volume 1, Composites, (ASM International, 1987B).

Jones, R. M., Mechanics of Composite Materials, (McGraw-Hill, 1980).

Kamal, M. R., and S. Sourour, Polym. Eng. and Sci., 13, 41 (1976).

Kamal, M. R., and Ryan, M. E., "Thermoset Injection Molding," in Injection and Compression Molding Fundamentals," Isayev, A. I., Ed., (Marcel Dekker, New York, 1987A).

Kamal, M. R., and Ryan, M. E., "Thermoset Injection Molding," in Injection and Compression Molding Fundamentals, pp 329-376, Isayev, A. I., Ed., (Marcel-Dekker, New York, 1987B).

Kardos, J. L., Dudukovic, H. P., McKague, E. L., and Lehman, M. W., "Void Formation and Transport during Composite Laminate Processing," in Composite Materials, Quality Assurance and Processing, Browning, C. E., Ed., pp 96-109, (ASTM STP 797, 1983).

Lee, L. J., Polym. Eng. and Sci., 21, 483 (1981).

Lee, W. I., Loos, A. C., and Springer, G. S., "Heat of Reaction, Degree of Cure, and Viscosity of Hercules 3501-6 Resin," J. of Composite Mat.," 16, 510-520 (1982).

Lee, C.-C., Folgar, F., and Tucker, C. L., J. Eng. Industry, 106, 114 (1984).

Levitsky, M., and Shaffer, B. W., J. Appl. Mech., 41, 647 (1974).

Levitsky, M., and Shaffer, B. W., J. Appl. Mech., 42, 651 (1975).

Loos, A. C., and Springer, G. S., "Curing of Epoxy Matrix Composites," J. of Composite Mat., 17, 135-169, (1983).

Martin, G. Q., and Son, J. S., "Fluid Mechanics of Mold Filling for Fiber Reinforced Plastics," Proceedings of the ASM/ESD Second Conference on Advanced Composites," pp. 149-157, 1986.

Molnar, J. A., Trevino, L., and Lee, L. J., "Mold Filling in Structural RIM and Resin Transfer Molding," 44th Annual Conference, Composites Institute, The Society of the Plastics Industry, Inc., pp. 1-10, Session 20-A, February, 1989.

Roller, M. B., Polym. Eng. Sci., 15, 406 (1975).

Schmitt, G., Wiley, J., and Gotro, J., "Viscosity Modeling During Epoxy Resin Cure," Polym. Eng. and Sci., 29(5), (1989).

Shaffer, B. W., and Levitsky, M., J. Appl. Mech., 41, 652 (1974).

Silva-Nieto, R. J., Fisher, B. C., and Virley, A. W., Polymer Composites, 1, 14 (1980).

Sourour, S., and Kamal, M. R., Thermochim. Acta, 14, 41 (1976).

Springer, G. S., "Resin Flow During the Cure of Fiber Reinforced Composites," J. of Composite Mat., 16, 400-409 (1982).

Springer, G. S., "Modeling The Cure Process Of Composites," 31st International SAMPE Symposium, 776-787, April, 1987.

Stevenson, J. F., SPE Tech. Papers, 26, 452 (1980).

Stevenson, J. F., Polymer Process Engineering, 1, 203 (1983- 1984).

Tajima, Y. A., and Crozier, D., Polym. Eng. Sci., 23, 1 (1983).

Tajima, Y. A., and Crozier, D. G., Polym. Eng. Sci., 26, 427 (1986).

Terzaghi, K., Akad. wiss. Wien, Mathem. Nuturw. Kl., Abt. IIa, 132 (1923).

Tsai, S. W., and Hahn, H. T., Introduction To Composite Materials, (Technomic Publishing Co., Westport, CT, 1980).

Tucker, III, C. L., and Folgar, F., Polym. Eng. and Sci., 23, 69 (1983).

Tucker III, C. L., "Compression Molding fof Polymers," Ch. 7 of Injection and Compression Molding Fundementals, Isayev, A. I., Ed., (Marcel Dekker, New York, 1987).

Williams, J., Donnellan, T., and Trabocco, R., 16th National SAMPE Technical Conference, (October 1984).

Computer Simulation

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Vespoli, N. P., and Marken, C. C., paper presented at the 1987 Annual AIChE Meeting, N.Y., New York (November 1987).

Vespoli, N. P., and Marken, C. C., paper presented at the 31st SPI Polyurethane Conf., Philadelphia (October 1988).

CONCLUSIONS

6.1 GENERAL COMMENTS

A wide variety of techniques have been developed to study the changes that occur in the resin during composite processing. This report focuses on those techniques which have the highest potential for on-line monitoring applications, namely: ultrasonic, dielectric, spectroscopic, and optical methods. All these techniques have advantages and disadvantages so the best technique for a given application will depend strongly on the materials and processes involved, i.e. autoclave molding, compression molding, resin transfer molding, pultrusion, etc. To help in this selection process, a comparison of the techniques is given in the next section.

On-line sensors that measure temperature and pressure already exist and are constantly being improved. These sensors will always be useful and necessary since they measure two of the most important parameters that can be controlled during processing. Appropriate feedback information is essential. Temperature and pressure information is not very useful, however, for evaluating the nature of the changes that are occurring in the resin, and such data is required to determine how the temperature, pressure, etc. should be controlled. Data for this purpose can be provided by ultrasonics, dielectrics, spectroscopy, and optical data since such results can be related to parameters such as viscosity, degree of cure, etc. When coupled with the appropriate processing model, this information forms the basis for real-time process control.

The following discussion reviews the current state of development for these techniques and their potential for on-line implementation. The techniques are compared in eight specific areas: speed, sampling volume, sensitivity for different resins, effects of different fibers, measurement considerations, temperature range, problems with use in a manufacturing environment, and interpretation of the data. The potential for implementation on the factory floor is then considered for each technique. Finally, the research and development needed to fully exploit these methods are explored.

6.2 COMPARISON OF TECHNIQUES

Comparisons among the techniques are made below is based on the current state of the technology. Comparisons in those areas where the level of development is highest are presented first while those where more work is needed appear at the end. A summary of results from these comparisons is given in Tables 6.1.

6.2.1 Measurement and Data Processing Time

All four techniques--ultrasonics, dielectrics, spectroscopy, and optical methods--can provide data in the time-scale required for real-time monitoring. As a result they are rated as excellent in this category (Table 6.1). One constraint for ultrasonics and dielectrics is that the measurements are limited to a single intermediate frequency or a small range of high frequencies unless the rates of change in resin properties are quite slow. Near the end of cure, however, the rate will be low, and thus low frequency dielectrics measurements can be made. Such measurements can be very useful in this range.

6.2.2 Sampling Volume

A second important issue is whether the techniques measures local or global regions in the resin. The answer is not simple because some of the techniques can be utilized as either a local or global sensor. Spectroscopy tends to be the most localized method while ultrasonics is the most global, with other optical methods and dielectrics falling in between. Ultrasonics can also be used to measure relatively localized regions using interface and wave guide methods.

Global measurements have the advantage that the results will not be skewed by non-typical local events. Local probes can be used to make a global mapping of properties by using multiple sensors; however, embedded probes may cause stress concentrations which degrade the performance of the part. In some cases, local measurements can be advantageous. For example, evanescent spectroscopy performed using optical fibers provides a means to determine resin characteristics in the interfacial region of the resin near the probe fiber. Such interfacial characteristics can be important. Another advantage of local measurement techniques is that sampling may be confined to specific regions where changes in thermal conditions during processing are not optimal. For example, embedded sensors can probe the center of a thick part. These regions are often the most critical to assuring the quality of the manufactured item.

6.2.3 Application to Various Resin Systems

In discussing the applicability of the various techniques to different materials, it is useful to consider thermoset and thermoplastic resins separately. Although the primary focus in this report is on thermoset systems, some important comments can be made concerning thermoplastics. Generalizations about different resin systems are difficult to make because there are many special situations, but a useful approach is to focus on what are probably the most important resin parameters: degree of cure and viscosity for thermosets and viscosity for thermoplastics. In examining the sensitivity of a technique two factors must be considered: the magnitude of the changes that must be measured and the rates at which the changes occur. When the rates are very slow, accurate measurements can be complicated by effects such as instrument drift.

Table 6.1: COMPARISON OF TECHNIQUES: TODAY'S TECHNOLOGY

Consideration	Dielectrics	Ultrasonics	Optical and Spectroscopic
Speed	E[1]	E	E
Sampling Volume	Local	Global-Local	Very Local
Resin Type			
Thermoset	VG	VG	VG
Thermoplastic	VG	G	F[2]
Fiber Type	VG-G[3]	VG	VG
Sampling Considerations			
Internal Properties	Embedded Sensor Required	VG	Embedded Sensor Required
Multi-use Embedded Sensor	F[4]	P	G[5]
Temperature Range	Commercial at all Temp. but High Temp. Data Limited	Commerical at Low and Medium Temp. but not High Temp.	All Temp. but not commercial
Manufacturing Environment	G	G+	F
Interpretation of Data	G	G	G-E[6]

[1] E-excellent, VG-very good, G-good, F-fair, and P-poor.
[2] Possible advantages for specific properties.
[3] Good rating indicates limit imposed by conducting fibers.
[4] Potential for improvement with continued research and miniaturization of sensors.
[5] Rating ranges from very good to fair depending on size of optical fiber.
[6] Excellent rating refers to techniques that provide a direct measure of chemistry.

For thermosets, both degree of cure and viscosity are important so a technique sensitive to either or both can be useful. Comparisons among the techniques indicate a wide range of sensitivities. Measurements of conductance (dielectrics) may change by many orders of magnitude during cure while some types of fluorescence (spectroscopic) measurements could change by only a factor of 2 or 3 with the same system. Moreover, some measurements may be more sensitive in certain parts of the cure than other techniques. For example, ultrasonics, high- or intermediate-frequency dielectrics, and fluorescence spectroscopy measure very localized motions which might be expected to exhibit only small changes at high degrees of cure. One might expect these measurements to be less sensitive than, for example, low frequency dielectric measurements in the final stages of processing. Some experimental results do suggest that the sensitivity of fluorescence spectroscopy may be limited in this range. There can be specific situations where data at the end of the cure is critical, but usually this is not the case. As a general rule, therefore, the available experimental data indicate that all of the techniques have adequate sensitivity for good measurements throughout the cure range of interest. The reason is that thermosets exhibit very large changes in both viscosity and degree of cure during processing so high sensitivity is not usually necessary. As a result, all of the techniques are rated as very good in this category (Table 6.1).

With thermoplastics the situation is quite different. First, there is no change in degree of cure so those techniques which are sensitive only to changes in the chemistry, for example certain spectroscopy methods, are not useful. In addition, viscosity, which is probably the most important parameter for a thermoplastic, usually changes much less than it does in a thermoset systems. Consequently, high sensitivity is important. As a result, in this category (Table 6.1) dielectrics is rated very good since conductance has a high sensitivity and ultrasonics is rated as good. Those spectroscopic techniques which measure changes in the chemistry must be rated as poor, while fluorescence techniques which can be correlated with viscosity are rated as fair since their sensitivity is limited.

There are several reasons for urging caution in comparing monitoring techniques in this category. First the magnitude of the changes that are measured during processing depend not only on the technique but how it is implemented. For example, through transmission ultrasonics may show only modest changes during processing of a particular material while an ultrasonic wave guide method may exhibit very large changes for the same system. In addition, properties other than degree of cure and viscosity can have an impact. For example, fiber wetting and degree of crystallinity are important in processing of thermoplastics, and spectroscopic techniques may provide the best method to assess these parameters. As a result there may be particular instances where a technique can be useful even though it would not be a good choice in general.

One final point about resin is that there are some systems where direct process control is not feasible because the reactions are too fast for controls to be effective, for example, certain autocatalytic cures. Nevertheless, the information gained in the fabrication of one part can be used to adjust the process for the next part so monitoring techniques can still be quite useful.

6.2.4 Fiber Type

In addition to the resin type, the nature of the fiber must be considered. Fortunately, ultrasonics, spectroscopy, and optical techniques are relatively unaffected by the fiber. Moreover, only electrically conducting fibers, such as carbon fibers, affect dielectric measurements. Because of the conductivity in carbon fibers, the dielectric sensors must be shielded to prevent shorting. A number of methods have been developed for doing this, but it does limit the geometries that are possible. As a result, ultrasonics, spectroscopic, and optical methods are rated very good in this category (Table 6.1). Dielectrics is rated very good except for systems with conducting fibers where the rating is reduced to good.

6.2.5 Measurement Considerations

There are a number of issues related to measurement considerations that require comment. With ultrasonics, the sample dimensions must be known to analyze the data, and, in addition, intimate contact must be maintained between the transducer and the sample. With dielectrics, the sensor system must be chosen so that the extremes in the measurement are within the detectable range. The goal should be to develop a suitable electrode system for performing the measurement in the desired environment. Finally, evaluation of the data from ultrasonic, dielectric, and fluorescence spectroscopy generally requires a knowledge of the temperature so a separate measurement must be made with an independent sensor for temperature.

One of the most significant differences among the monitoring techniques is the ability to measure internal properties of the sample without inclusion of an embedded sensor. Ultrasonics when used in the through transition or scattering mode measures properties along the entire length of the wave propagation path. Consequently, the internal properties of the material strongly influence the results. The data can therefore be used to estimate internal properties without embedded sensors. On the other hand, certain ultrasonic wave guide methods do involve embedded sensors. These sensors can be large and often represent a significant disturbance to the sample. Dielectric measurements can penetrate thin samples, but in most cases the thicknesses are too large and the material measured is limited to the area very close to the sensor. Spectroscopic and optical methods also interrogate material near the sensor. As a result, these latter methods can probe the interior of the sample only through the use of embedded sensors. The ability to sense internal properties without embedded sensors is a major advantage for the ultrasonic methods of through transmission and scattering.

There are three approaches that have been used to address this limitation of embedded sensors. First, models have been employed to estimate the internal properties from measured data at the surface. This approach is handicapped by limitations in the models. Second, sensors have been embedded in a part of the sample which can be cut off after the fabrication is finished. Unfortunately, this means the sensors are usually located far away from the most critical regions in the sample. Finally, miniaturized sensors have been developed to minimize the impact of the embedded probe on the part's performance. Dielectric probes consisting of electrodes on a thin strip of polyimide film are small but still have significant perturbation to the sample since they can act as stress concentrators. Spectroscopic and optical techniques have used optical fibers that range in size from 200 μm, which can cause a significant disruption in the sample, to 10 μm where the perturbation is minimal. Unfortunately, not all techniques can use the smaller fibers.

In an effort to counterbalance the detrimental effects of embedded sensors, a number of studies have attempted to find ways to use these sensors during the lifetime of the part to detect damage and assess the state of the material in other ways. Such multiuse applications can increase the viability of these methods. As a result, a brief discussion of the potential applications is given here.

The most versatile embedded sensors are based on fiber optics. They can be placed in critical areas where the formation of cracks and delaminations might be expected to break the fiber. This will decrease or destroy the ability of the fiber to transmit light, and thus a simple monitoring device can detect such damage during the life of the part. Optical fibers can also be employed to measure stress and strain near the fiber. By placing fibers in the proper areas, very valuable information about the part performance can be obtained. Another application is to conduct fluorescence spectroscopy using probes that are sensitive to local polarity. Absorption of water changes local polarity, and thus this technique might be used to detect and perhaps quantify moisture absorption. Moisture can have a detrimental effect on a composite, particularly when near the fiber-matrix interface. Certain fluorescence probe molecules may be sensitive to free volume, and if so, they could be used to monitor physical aging. Finally, spectroscopy can follow chemistry, and thus fiber optic spectroscopic might be used to characterize degradation and other chemical changes.

Embedded dielectric probes could also provide useful information during the lifetime of a part by measuring changes in the dielectric relaxation spectrum. As a polymer ages, the spectrum can be expected to change. Chemical degradation often increases the dielectric loss levels due to the introduction of large dipole moment species caused by oxidation. Ions can form which can be detected as changes in conductance at low frequencies. Absorption of water would also effect the dielectric behavior, and this could be used to monitor moisture effects.

Ultrasonic wave sensors are less likely to be considered for use as embedded probes for post processing monitors of properties for several reasons. First, through transmission and scattering techniques are used instead for process monitoring. Second, after completion of fabrication the sensitivity of wave guide methods is often low because it is difficult to propagate sufficient wave energy through the wave guide since much of the energy is lost into the sample. If wave guide sensors were to be used, however, the information provided would be very useful since mechanical property data are obtained.

In rating the techniques for their potential with multiuse embedded sensors, the critical issue is the size of the sensor since this governs the degree to which the sensor can perturb the performance of the sample. Ultrasonics is rated as poor, but it must be noted that embedded probes are not required for ultrasonic measurements so this is not a real limitation. Dielectrics is rated as fair although smaller sensors may be developed in the future. Spectroscopic and optical methods are rated as very good to fair depending on the size of the fiber used.

6.2.6 Temperature Range of Sensors

Commercial equipment for ultrasonic is currently available and can easily make measurements at 135°C (275°F) and with some effort at 205°C (400°F). For temperatures up to 371°C (700°F), the sensors with this equipment will not work and must be modified to isolate the transducer from the high temperature region with a delay rod or something similar. This is common practice in other areas so it should not be a limitation in the future. In addition, other types of wave generation procedures such as non-contact excitation and monitoring with lasers might be adapted for process monitoring. Commercially available dielectric sensors can easily operate at 135°C and 205°C. To handle 371°C, the probes must use passive electrodes, i.e. no electronic circuitry on the sensor. Current commercial sensors often use local electronics for signal processing and amplification to minimize noise. Passive electrodes are easily made, however, and electric noise problems can be addressed in other ways. Although passive sensors are available commercially, data on and experience with high temperature materials is limited. Optical fibers are stable over the complete temperature range under discussion. This stability and the predictability in the response of spectroscopic methods to temperature and pressure changes add to the attractiveness of fiber optic cure sensors and monitors. Commercial equipment with demonstrated performance for process monitoring is not yet available, however.

6.2.7 Sensitivity to the Manufacturing Environment

As indicated above, commercial measurement systems for process monitoring are currently available for ultrasonics, and dielectrics. Nevertheless, the equipment for all techniques would benefit from improvements to make them more robust and reliable in the harsh environment of the factory floor. Areas for improvement include the sensors, electronics, and connecting circuitry. Fiber optic methods may need the most improvement since this method is the newest technology, while ultrasonics may be in the best position because of past work developing nondestructive evaluation equipment. Adaptation of infrared spectroscopy to production has been stymied by the lack of robust fibers which transmit infrared radiation. The brittleness, toxicity, and expense of IR transmitting fibers need to be addressed before complete assessment of this approach is possible.

In summary, all of the techniques need development in this area, and this is an important topic for future research and development. Ultrasonics and dielectrics are only rated as good in this category (Table 6.1) with a slight plus for ultrasonics. Optical and spectroscopic techniques are rated as fair.

6.2.8 Interpretation of Results

For a process monitoring sensor to be useful, the output data must be converted to parameters that can be input to process control models. Consequently, a wide range of correlations have been developed between the various process monitoring measurements and a variety of material parameters such as viscosity, degree of cure, mechanical properties, etc. The basis for these correlations is almost exclusively laboratory data rather than results obtained in a production environment. Moreover, it should be noted that very few studies have examined these relationships to develop a fundamental basis for the correlations. The two major exceptions are the determination of high frequency mechanical properties by ultrasonics and the monitoring of chemical changes during cure with spectroscopy. Most of the remaining relationships fall into the category of empirical correlations. As a result, they must be used with care since they are generally resin specific and their range of validity is uncertain. Unfortunately, the reports in the literature are not always careful to state these limitations clearly, and as a result, the impression can be left that a direct measurement of a property, like viscosity, is made. In a few cases, the claims that are made are completely incorrect. This situation is one of the most important concerns identified in this report because there can be major problems when the correlations are pushed too far. Such problems can cause industrial users to reject the whole idea of process control, and that would be extremely unfortunate.

The most common empirical relationship is with viscosity, and although none of the techniques really measures viscosity, the correlations are generally quite good. The range over which the viscosity and the monitoring data change is often quite different, and thus a quantitative correlation may involve large uncertainties. Fortunately, the most useful information for process control is often features that can be clearly identified, at least approximately, such as the point of minimum viscosity. Another important relationship is with the degree of cure. Data for many techniques suggest a very useful correlation. The formation of voids has also been related to process monitoring results with some success. These are only a few of the parameters that have been examined.

The value of obtaining a variety of correlations is the fact that no single property change controls fabrication. For example, early in the process, viscosity variations are critical to achieve proper flow and consolidation. Then as solidification begins, the elastic and creep properties become important to minimize residual stresses. For thermosets, the measurement of cure state is vital to determine when initial processing and post processing are complete. Finally, in the latter stages, the detection of voids and flaws is extremely useful.

The process monitoring correlations that have been developed to date work best when only a single property is involved. In real part fabrication, however, many properties are changing simultaneously. An important challenge, therefore, to improve the ability to analyze complex systems where many properties are important, for example, identifying the degree of cure when voids are also present. This require a much deeper understanding of the monitoring techniques and the resin systems as well as improved processing models. More work in this area is clearly needed. Because correlations have been used successfully, all techniques are rated good in this category (Table 6.1), and spectroscopic measurements which can be directly related to chemistry are rated excellent.

6.3 TIME FRAME FOR ON-LINE APPLICATION IN FACTORY PRODUCTION

A final important comparison for the monitoring techniques is the estimated time frame for on-line application in a production environment assuming an active development program is pursued.

6.3.1 Current Situation

Dielectric and ultrasonic techniques have a clear advantage at present since equipment designed for process monitoring is commercially available. This is generally not true for spectroscopy and optical methods.

A comparison between ultrasonics and dielectrics gives a slight advantage to the latter, at present, because much more laboratory data is available for a variety of material systems, and experiments have been performed in both autoclaves and presses. It should be added, however, that the particular processing method and material system involved may be even more important in deciding which method is best. Moreover, both methods would benefit from further development to increase ruggedness and reliability for routine on-line measurement in a factory environment. Other technological concerns are the need to determine how best to mount or attach the sensors in the production equipment and the need to generate the empirical data base required to effectively utilize the information gained by the sensor. Since this knowledge is very limited and almost totally empirical at present, the current emphasis must be on process monitoring for quality control, and only the simplest forms of process control. Nevertheless, this still represents a major advance.

6.3.2 Near Future

At the current level of research and development, it is unlikely that the full potential of spectroscopic and other optical techniques will be realized in the near future, although they will certainly be much closer to commercialization. A few methods, such as fluorescence probes for specific processing applications, may have reached commercialization. For the most part then, ultrasonics and dielectrics will continue to have an advantage. In comparing these two methods for the near future, the wide variety of ultrasonics methods that can be used and the acceptance of the method based on past experience with nondestructive evaluation may give ultrasonics a slight advantage. Nevertheless, the application will continue to play a major role in determining the method of choice.

Although the technological problems mentioned above will continue to be a concern, considerable progress should have been made to address them for all of the sensor techniques. Consequently, the emphasis will shift to the needs in the scientific area, i.e. what do the measurements mean in terms of events in the resin. For example, a more scientific basis for the relationships between the measured quantities and parameters such as viscosity, and degree of cure must be sought. Such information is critical for significant gains to be achieved in real process control.

6.3.3 Longer Range Outlook

When viewed in a longer range time frame, spectroscopic and other optical techniques could become competitive with other monitoring methods if sufficient investments in research and development are made. Progress in infrared transmitting optical fibers may be driven by other applications as well, and this would benefit cure sensor development. Although the spectroscopic and other optical methods are last to be developed, they have an advantage relative to the other techniques that make them very important. They provide a direct measure of chemistry, and this is the most useful information for input to processing models and ultimately for process control. Indeed, the development of spectroscopic techniques, along with parallel advances in process modeling, will permit correlations to be established. These correlations will be based on molecular models that account for the complex chemical and physical changes associated with cure.

The scientific concerns discussed above will be even more important in the future since major advances will have been made in process control models. To take full advantages of these advances, improved sensor technology will be required.

6.4 **FUTURE WORK**

As indicated above, there are both technological and scientific issues that must be addressed to achieve the full potential of process monitoring. The major technological issue is the building of rugged systems that can withstand the manufacturing environment. Even commercially available equipment would benefit from such improvements, particularly in the sensors, electrical connections, and/or electronics, so process monitoring can be used with more confidence in the harsh conditions on the factory floor. It is also important to develop better systems for operating in electrically noisy environments and with "impure" industrial-grade resins. Solutions to these technical problems are critical to progress in this field and considerable effort will be required to solve them, but the approach is straightforward.

The scientific issues are equally important and perhaps more difficult to resolve. The two major issues are interpretation of the sensor output, and correlation of the resulting data to process control parameters through processing models.

A wide range of correlations have been developed between the various process monitoring measurements and a variety of material parameters such as viscosity, degree of cure, and mechanical properties. The basis for these correlations is almost exclusively empirical comparisons between laboratory data. Very few studies have attempted to develop a fundamental understanding of the correlations. As a result, correlations must be used with care since they are generally resin specific, and their ranges of applicability and validity are unknown. Unfortunately, reports in the literature are not always careful to state these limitations clearly, and consequently, the erroneous conclusion is made that the measurement provides a direct measurement of a property, like viscosity. This can lead the industrial user to push the correlations too far. The resulting problems may cause users to reject the whole idea of process control, and that would be extremely unfortunate. Consequently, there is an urgent need for more research on interpretation of sensor output in terms of materials properties.

The second scientific issue is how to translate the output from the sensors to process control information. As mentioned above, output from each of the four techniques has been related to useful parameters such as viscosity, and degree of cure, for specific cases, and additional research should improve such correlations significantly. What remains then is to couple the sensor measurements with the appropriate processing models to provide process control information. This coupling is a challenging task because the problems span many disciplines, but the rewards are substantial since the results will form the basis for real-time process control. A number of laboratories are engaged in research on processing models, but these studies generally do not take full advantage of the potential of monitoring sensors.

In addition to these issues which are common to all the measurement techniques, there are a number of problem areas specific to each methods. These are briefly summarized below.

6.4.1 Dielectric Techniques

The main challenge for dielectric techniques is the need to integrate the sensors with the manufacturing process. For embedded sensors, this involves either reducing the size of the sensor or establishing a geometry that is compatible with both the manufacturing environment and the demands of the part. This compatibility must be made for both the operating environment, such as the levels of electrical noise, vibration, temperature, and pressure, as well as the measurement resolution as set by the available instrumentation. The sensor parameters must be chosen so that the desired sensitivity is maintained throughout the phases of the cure that are important to successful fabrication. For carbon fiber based composites, better methods for reliable exclusion of the fibers must be developed. In addition to the sensor itself, an improved understanding of the dielectric properties of the composite materials is required to assist in the interpretation of the data during and after processing. Scientific studies must be made to increase basic knowledge and develop reliable correlations with parameters important in processing for specific systems. Finally measurement dependencies such as that on frequency must be better investigated so that proper optimization can be made with respect to both measuring speed and sensitivity.

6.4.2 Ultrasonic Techniques

For ultrasonic methods the important challenges include the development and use of advanced signal processing techniques to extract more information from the data. Methods must be devised to extend the upper use temperature of ultrasonic sensors. Implementation of sensors in the manufacturing process must include methods to obtain and maintain good contact between the sensor and the sample. More theoretical work is needed to analyze wave propagation in systems undergoing reactions and processing. This should be complimented with experimental studies such as correlations with results from other monitoring techniques. Research should also investigate the more aggressive use of ultrasonics which includes exploiting data from multiple frequencies and a variety of wave propagation modes. Finally, acoustic emission should be investigated for its potential as a cure monitoring technique.

6.4.3 Spectroscopic and Optical Techniques

Implementation of fiber optic sensors requires a broad range of instrument development to achieve on-line capabilities as well as research activities particularly focussed on the optical fibers. The size and cost of optical components must be reduced while durability must be increased. New light sources and detectors are require. The fibers must be improved in durability and reduced in size. Robust fibers transparent at longer wavelengths are needed for infrared spectroscopy while higher refractive index fibers are needed for fluorescence experiments. Better ways are needed to couple the fiber to the source and detector. Finally new probe molecules must be found and a better understanding of the science behind the experiments must be developed.

6.4.4 Concluding Comments

The future for process control is very bright. Many programs are currently underway. Despite the critical role that sensors play in this field, however, the development, interpretation, and implementation of sensors have not receiving sufficient attention. Consequently, research and development on sensors is badly needed. Moreover, it could leverage the work performed in projects addressing other aspects of the process control area and thereby play a vital role. The scientific questions outlined above are particularly appropriate since the results will have maximum impact on the development of on-line monitoring techniques.

APPENDIX

The following companies were visited:

- Ford Motor Company
- Sikorsky Aircraft
- United Technologies Corporation

The following companies were contacted by telephone or letter:

- Advanced Controls, Inc.
- Applied Polymer Technology
- AT&T
- Automated Intelligence,Inc.
- Control Technology, Inc.
- Dravo Automation Sciences, Inc.
- EFCO Incorporated
- G. E. Aircraft Engine Business Group
- General Motors Corporation
- IBM
- Litton Industrial Automation, Inc.
- Pultrusion Technologies
- Rockwell International
- Southwest Research Institute
- Texas Instruments, Inc.
- W. R. Grace/Emerson & Cuming

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This report surveys the scientific literature for all process monitoring techniques and identifies four types of measurements that show the most promise for on-line, real-time process monitoring. These are ultrasonics, dielectrics, optics, and spectroscopic methods. The four types are reviewed in depth and compared with each other in the areas of measurement speed, sampling volume, sensitivity to different resins, effects of fiber type, resistance to the manufacturing environment, interpretation of the data, adaptability for other uses, and temperature capabilities. In addition, brief reviews are provided on temperature and pressure sensors, and process modeling, since the future for on-line process control relies on developments in these areas as well. Industrial needs and opportunities, off-line measurement techniques, and major industrial and governmental programs on process control are commented upon.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

acoustic emission; cure monitoring; dielectrics; fiber optics; pressure sensors; process modeling; sensors; spectroscopy; temperature sensors; ultrasonics.

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