COMPOSITE MATERIALS: *QUALITY ASSURANCE AND PROCESSING*

C. E. Browning, *editor*

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COMPOSITE MATERIALS: QUALITY ASSURANCE AND PROCESSING

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Foreword

The Symposium on Producibility and Quality Assurance of Composite Materials was held in St. Louis, Missouri, on 20 October 1981. ASTM Committee D-30 on High Modulus Fibers and Their Composites was sponsor. C. E. Browning, Air Force Wright Aeronautical Laboratories, served as symposium chairman and has also edited this publication. The title of this volume differs slightly from that of the symposium.

Related ASTM Publications

Composite Materials: Testing and Design (Sixth Conference), STP 787 (1982), 04-787000-33

Damage in Composite Materials, STP 775 (1982), 04-775000-30

Short Fiber Reinforced Composite Materials, STP 772 (1982), 04-772000-30

Composites for Extreme Environments, STP 768 (1982), 04-768000-33

Joining of Composite Materials, STP 749 (1981), 04-749000-33

Test Methods and Design Allowables for Fibrous Composites, STP 734 (1981), 04-734000-33

Commercial Opportunities for Advanced Composites, STP 704 (1980), 04-704000-33

Nondestructive Evaluation and Flaw Criticality for Composite Materials, STP 696 (1979), 04-696000-33

Composite Materials: Testing and Design (Fifth Conference), STP 674 (1979), 04-674000-33

A Note of Appreciation to Reviewers

The quality of the papers that appear in this publication reflects not only the obvious efforts of the authors but also the unheralded, though essential, work of the reviewers. On behalf of ASTM we acknowledge with appreciation their dedication to high professional standards and their sacrifice of time and effort.

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Introduction

The Symposium on Producibility and Quality Assurance of Composite Materials, sponsored by ASTM Committee D-30 on High Modulus Fibers and Their Composites, was held in St. Louis, Missouri, on 20 October 1981. The objects of the symposium were to bring together active workers in composites technology and to provide a forum for presentation and discussion of the latest developments in composites quality assurance and processing, including applications to the aerospace, automotive, and related industries.

Composite materials have reached a level of maturity where they are in routine production for applications as critical as primary structural components in aircraft. In general, this has been the result of the many well-documented performance advantages of composite materials. As a consequence of this status, recent emphasis has been directed towards the areas of composite quality assurance and processing. Therefore this symposium was very important and timely. Many different aspects of the subject area were discussed. Topics ranged from the development of quality assurance techniques for specifying the composition and processing behavior of the materials to the modeling of their curing processes.

This volume provides the reader with an understanding of relevant methodologies, rationale, and experimental results, as well as a general understanding of current and future trends of research activities in this highly important area. It will be valuable to a broad range of interests—the materials and process engineers of industry, scientists and engineers of government and industry, and professors and students at universities.

Appreciation is expressed to J. F. Carpenter and T. T. Chiao for serving as session chairmen and to the many reviewers who contributed their valuable time.

C. E. Browning

Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio; symposium chairman and editor

T. A. Sewell[1]

Quality Assurance of Graphite/Epoxy by High-Performance Liquid Chromatography

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REFERENCE: Sewell, T. A., **"Quality Assurance of Graphite/Epoxy by High-Performance Liquid Chromatography,"** *Composite Materials: Quality Assurance and Processing, ASTM STP 797,* C. E. Browning, Ed., American Society for Testing and Materials, 1983, pp. 3–14.

ABSTRACT: Factors contributing to the reliability and reproducibility of high-performance composites include advanced resin matrixes with consistent purity and concentration of chemical constituents, as well as mix homogeneity and processing uniformity. Variation of these matrix parameters can affect manufacturing processibility and finished laminate quality. For these reasons, a wide variety of analytical tools have been evaluated for their capability of ensuring matrix reproducibility. In most cases, test development has been required to optimize and tailor the methodology for each new matrix system. In this way analytical information more precisely characterizes the matrix and monitors batch-to-batch consistency.

This paper covers work under U.S. Air Force Contract F33615-78-C-5177, "Chemical Composition and Processing Specifications for Air Force/Navy Advanced Composite Matrix Material." It discusses the development of high-performance liquid chromatography (HPLC) as a quality-assurance method of certifying resin matrix composition of Air Force/Navy graphite/epoxy AS/3501-6 advanced composite matrix material. A gradient-elution/binary-solvent separation technique was developed by using a Spectra Physics 8000 liquid chromatograph in reverse-phase mode.

Resin and derived prepreg from full-scale production lots having predefined concentration variations were investigated. Lot variations were verified quantitatively by using a standard production batch for baseline comparisons. Resin matrix ingredients were used as concentration standards for test calibrations. Test data are reported in weight percent for two types of epoxies and one curing agent (diaminodiphenyl sulfone).

Details concerning the evolution of method development are discussed. Data are included to demonstrate test capabilities for quantitative measurements of unreacted epoxies and diaminodiphenyl sulfone. Data are presented for test verification of intentional ingredient alterations and tracking capability for compositional changes due to ambient aging and short thermal advancements due to hot-melt fiber impregnation.

KEY WORDS: composites, resin matrix, liquid chromatography, quality certification tool

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Numerous analytical techniques have been exploited for characterizing complex epoxy resin matrixes found in advanced composite prepregs. Reverse-phase liquid chromatography has received considerable attention because of its capabilities for resolving resin matrixes by adsorption partioning and for providing quantitative information on selected unreacted epoxies and hardening agents.

Reverse-phase gradient elution is a chromatographic technique utilizing a stationary packed column which acts to delay the passage of sample components carried by a mobile phase which contains the sample. The mobile phase contains a polar and nonpolar solvent that differentially sweeps through the column. Detection is accomplished with an ultraviolet wavelength detector.

Under U.S. Air Force Contract F33615-78-C-5177, a reverse-phase liquid chromatographic test was investigated as a quality-certification tool for AS/3501-6 graphite/epoxy prepreg. Investigations focused on optimizing test conditions in order to enhance resolution of the resin matrix. The effects of solvent elution gradients, flow rate through the test column, and water purity on matrix resolution were investigated. Peak test sensitivity was achieved by using individual epoxies and hardener agents as test standards. In this way, optimized ultraviolet detector sensitivity was determined for each matrix ingredient. Results of these investigations showed capabilities for quantitative measurements on major portions of the resin matrix.

One test provided quantitative data on tetraglycidyl methylenedianiline (TGMDA), diaminodiphenyl sulfone (DDS), and a novalac-type epoxy. Together, these ingredients comprise more than 90% by weight of the resin matrix. The remaining portion contains boron trifluoride catalyst and carbonyl-containing epoxy, which were not detected by this technique.

Test verification was made by conducting chromatographic analyses on full-scale production batches having predefined matrix alterations. Intentional weight percent variations of TGMDA, DDS, and novalac resin were verified.

Unreacted amounts of TGMDA, DDS, and novalac resin were found to be lowered by resin mixing, fiber impregnation, and ambient aging for 20 and 40 day periods. These effects were realized by conducting tests on resin before and after fiber impregnation and after desiccated ambient exposure.

Experimental

A Spectra-Physics (Santa Clara, California) 8000 microprocessor-controlled high-pressure liquid chromatograph (HPLC), equipped with a dual channel Spectra-Physics 4000 data system and a Schoeffel (Westwood, New Jersey) Model 7700 variable-wavelength ultraviolet detector, was used in these analyses. Injection was accomplished by use of a pneumatically operated, microprocessor-controlled valve-injection system equipped with a 10-μL sample loop. A Whatman ODS-II-octadecylsilane column was used for resin separations. Ultraviolet-grade tetrahydrofuran and acetonitrile (Bardick and Jackson) and HPLC reagent-grade water (J. T. Baker Company) were used as chromatographic solvents.

Solutions of 3501-6 resin were prepared by dissolving 2.0 g of resin in 100 mL of ultraviolet-grade tetrahydrofuran (THF). For prepreg tests, 5.0 g of prepreg was washed with THF and volumetrically diluted to 100 mL. Ten-microliter sample solutions were loop-injected in all analyses. Quantitative data were obtained by injecting standard solutions of TGMDA, DDS, and novalac resin, and constructing calibration curves (integrator count versus standard concentration) for each component. Calibration charts were prepared by using known component concentrations that surrounded the anticipated concentration in the test sample. Phenyl laurate was added to test solutions as an internal standard.

Method Development

Early separations of 3501-6 using reverse-phase liquid chromatography were conducted at a 254-nm ultraviolet wavelength by using tetrahydrofuran (THF) and water (H_2O) as the binary solvent media. Gradient elution of solvents was programmed from 80 to 20% by volume H_2O. Figure 1 shows the matrix resolution for DDS and TGMDA. Note the baseline drift starting at 24 min elution time and continuing throughout the analysis as the concentration of THF is increased. Baseline drift was attributed to an increased concentration of THF, which contains impurities and oxidative products.

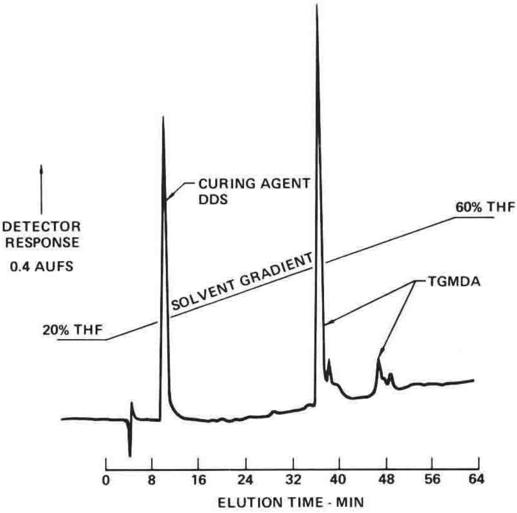

FIG. 1—*Early separation of 3501-6 resin.*

Development was initiated to improve test sensitivity for improved matrix resolution and reduced baseline drift. Solvent selection, water purity, gradient programming, optimizing flow rate, and ultraviolet wavelength selection were investigated.

Solvent Selection

A more polar solvent, acetonitrile (ACN), was tested as a substitute for THF to reduce baseline drift. Having polarity closer to water and less impurities (oxidative products) than THF, acetonitrile showed more stable baselines as concentrations were increased during gradient programming.

The effect of water purity on chromatographic separation was examined. Figure 2 illustrates blank analyses for three water samples. Baseline drift was measured for J. T. Baker water (fresh and after three days in a closed container) and from a Milli "Q" water filtration system. Drift ranged from 2 and 10 mm deviation from a flat baseline. Fresh J. T. Baker water was selected for later experiments because of its small baseline drift.

Gradient/Wavelength Selection

Using ACN and J. T. Baker water as the selected solvent media, gradient programming of solvent mixes played a key role for optimizing separation of the resin components. Since water acts as a polar solvent and ACN as a nonpolar (less polar) solvent, gradient programming for broad polarity changes was accomplished by slowly advancing the concentration of acetonitrile during the elution period. The mobile phase was programmed to move from polar mix (H_2O concentration > ACN concentration) to nonpolar mix (ACN concentration > H_2O concentration). The effect of initial solvent mix ratio on resolution is shown in Fig. 3. The top chromatogram shows the separation achieved using an initial mix of 55% by volume H_2O and 45% by volume ACN. Note the fused peaks occurring at the beginning of the separation. By

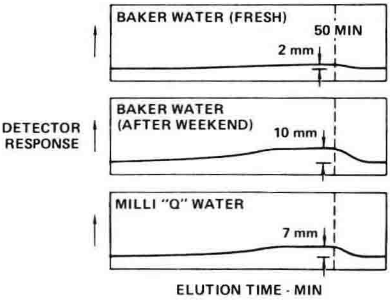

FIG. 2—*Effect of water purity on baseline drift.*

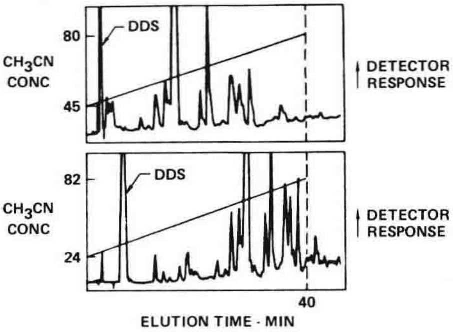

FIG. 3—*Effect of gradient on resin separation.*

adjusting the mix ratio for more polar mix having H_2O concentration >> ACN concentration, the elution of polar ingredients (for example, DDS) is enhanced.

Ultraviolet wavelengths were investigated for optimizing detector sensitivity for the maximum number of matrix ingredients. Early chromatographic tests were restricted to a 254-nm wavelength because ultraviolet detectors for liquid chromatographs were available only as fixed 254-nm wavelength detectors. When variable wavelength detectors were commercially available, tests were conducted to determine detector sensitivity to TGMDA, DDS, and the novalac resin at wavelengths surrounding 254 nm. Identical chromatographic tests were performed at 280, 254, and 230 nm. Results showed adequate sensitivity for TGMDA and DDS at 280, 254, and 230 nm (Fig. 4). Optimum sensitivity was 254 nm for TGMDA and 280 nm for DDS. The novalac resin was visible only at 230 nm. Test development was continued at 230 nm so that the three components could be measured from a single test.

Flow Rate

The effect of solvent flow rate through the stationary separatory column on peak resolution was investigated by using a gradient program of 75% by volume H_2O, 25% by volume ACN, programmed to 20% by volume H_2O, 80% by volume ACN in 40 min. This concentration was held constant for 25 min, and then the concentrations were returned to original conditions in 5 min. Identical gradient separations were made on 3501-6 resin by using flow rates preset at 1.3, 2.0, and 4.0 mL/min. Results showed that the 1.3 mL/min flow rate allowed optimum matrix separations. Higher flow rates at 2.0 and 4.0 mL/min caused column overloading and fused peak resolution. Figure 5 shows the separation obtained at 1.3 and 2.0 mL/min. Peak fusion at 2.0 mL/min flow rate introduces test inaccuracies due to integrator errors on poorly defined peaks.

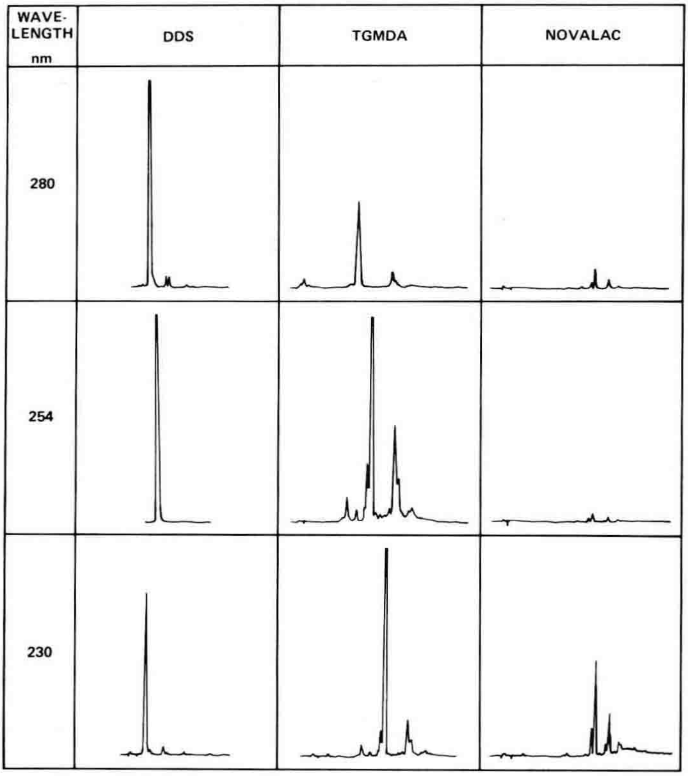

FIG. 4—*Chromatographs for TGMDA, DDS, and novalac resin at 280, 254, and 230 nm wavelengths.*

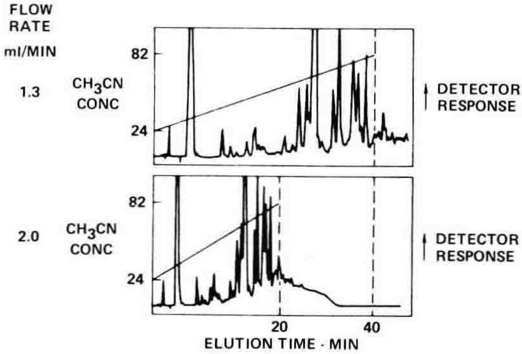

FIG. 5—*Effect of flow rate on resolution.*

Optimized Test

Developments for improved solvent selection, ultraviolet wavelength, improved water purity, gradient programming, and optimized solvent flow rate were combined under one test. Results show significant improvements for matrix resolution. Changing the ultraviolet wavelength settings from 254 to 230 nm included the bonus of ultraviolet detection of the novalac resin and reaction products formed by interaction occurring between DDS, TGMDA, and the novalac resin. Test parameters selected for further test verification are compared to earlier test conditions in Fig. 6. Figure 7 shows a comparison of resin separation for each set of test conditions. Note the increased number of peaks detected with adequate resolution for the DDS, TGMDA, and novalac resin, which allows peak area measurements without interference by broad peaks or unresolved shoulder peaks.

Altered Batch Tests

Five 3501-6 production batches with predefined percent-by-weight variations of TGMDA, DDS, and novalac resin were available for test verification. Samples of resin (before impregnation) and prepreg in the form of 305-mm (12-in.)-wide 127-μm (5-mil) tape were tested with the improved liquid chromatographic test.

Test results for TGMDA, DDS, and novalac resin are recorded as unreacted or "free" quantities. The remaining amounts of TGMDA, DDS,

TEST PARAMETERS	INITIAL CONDITIONS	IMPROVED CONDITIONS
MOBILE PHASE	THF/H_2O	ACN/H_2O
FLOW RATE (ml/MIN)	1.2	1.3
GRADIENT PROGRAM	20 → 60 Percent by Volume THF 80 → 40 Percent by Volume H_2O	25 → 80 Percent by Volume ACN(1) 75 → 20 Percent by Volume H_2O
TEST DURATION (MIN)	60	70
WAVELENGTH (nm)	254	230
COLUMN	WATERS MICROBONDAPAK C_{18} 30 cm LONG	WHATMAN PARTISIL ODS-II 21 cm LONG

3501-6 INGREDIENTS	DETECTION CAPABILITY	
TGMDA	✓	✓
DDS	✓	✓
NOVALAC		✓
COMBINED PRODUCTS		✓

(1) Gradient programming occurs during a 40 min time period. Then 80% ACN/20% H_2O mix is held constant for 25 min. Solvent concentrations are returned to 25% V/75% V in 5 min.

FIG. 6—*Improved test conditions.*